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INJECTION MOULDING VARIABLES AND THEIR INFLUENCE ON SOME PROPERTIES OF SEMI-CRYSTALLINE POLYMERS

by

MOGENS JENSEN

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy

of the Loughborough University of Technology, October 1980

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Mr U.M. HENIUS, The Technological Institute, Copenhagen

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SUMMARY

The present thesis is written according to the following sequence. First a literature review on injection moulding is presented, followed by an account of the influence from process variables on properties of mouldings. Then follows a description of the instruments developed in relation to the project and used to characterize properties of mouldings. Finally, a section gives an account of the following experimental work.

The effect of injection moulding variables on properties of 3 and 5 mm quadrant mouldings was studied. Specimens were moulded from polyethylene, polypropylene, polyoxymethylene and polyamide under a wide range of carefully controlled and reproducible moulding conditions to establish the effect of melt temperature and pressure in the nozzle, cavity pressure, mould temperature and injection rate.

Microscopy of microtomed sections cut parallel and transverse to flow at two positions revealed at least three distinct morphology regions, ranging from a non-spherulitic surface layer, followed by an intermediate layer characterized by spherulites oriented towards the surface to a core of non-oriented spherulites. In general, an increase in melt and mould temperature leads to a decrease in skin thickness and a more uniform microstructure in the core. Mould temperature had most influence on the surface layers, whereas melt temperature influenced the core most.

Density, determined with a gradient column, increased with melt temperature for polyethylene and polyoxymethylene, but decreased for polypropylene. Increasing mould temperature increased density for polypropylene, polyoxymethylene and polyamide. Density increased by annealing at temperatures above $T_g$. 
Thermal analysis on samples taken from layers in the axial direction of the moulding showed that melting point and crystallinity generally increased with the distance from the surface. The two endotherms found with polyethylene were investigated. It is proposed that they are associated with the temperature rise from crystallization of the melt last injected into the cavity.

Reversion after heating of layers microtomed at various distances from the surface of polyethylene mouldings showed high orientation in the vicinity of the gate. The orientation profile along the length of flow was corresponding to the assumed thickness of the solidified layer. Some influence from processing was found on the orientation profile in the axial direction.

Tensile strength, modulus of elasticity and flexural modulus were determined on samples from three positions of the specimens, whereas instrumented falling-weight tests were carried out on the whole plaque.

Weight, dimensions, and shrinkage were determined for all sets of moulding conditions.

Samples were stored up to three years for determination of post-shrinkage, which was found to be a function of mould temperature only. Post-shrinkage was found to correlate with changes of dimensions for specimens annealed with variation of time at constant temperature.

KEY-WORDS
Injection-moulding, morphology, density, shrinkage, mechanical properties, thermal analysis, semi-crystalline polymers, polyethylene, polypropylene, polyoxymethylene, polyamide.

471 pages, 35 tables, 120 figures, 270 + 18 + 29 references, 12 appendices.
Acknowledgements
This thesis is written as a synthesis of the research work I have been engaged in at the Department of Plastics Technology, The Technological Institute, Copenhagen during the period of 1974-78.

A part of the work has been published earlier in reports and articles, listed in a separate section following the list of references. They are about experimental work carried out with the combined efforts and ungrudging cooperation of several colleagues at the Technological Institute.

It is therefore only fair to admit, that the work presented in the thesis could not have been successfully completed without close cooperation and mutual inspiration, which is a pleasant, but also necessary feature in present day research and development work.

A thesis written-up by an individual is therefore not an obvious result of the team work also prevalent at the Technological Institute, and I should not hesitate to bring my most sincere thanks to all of my former colleagues.

I am also thankful to the authorities of the Technological Institute for granting me leave for a period of four months in 1977 for personal studies. The period was spent at the Institute of Polymer Technology, Loughborough University, and I would like to convey my thanks to Professor Birley and his collaborators for the warm and inspiring atmosphere which I met at the Institute.

My grateful thanks must also go on record for my tutor Mr. M.J. Stevens, whose integrity and dedication to research work has always been an example.

Thanks are also due to Mr. U.M. Henius and to Mr. T. Knudsen, Head of the Chemical and Plastics Department respectively, who have encouraged and supported the idea behind the work.
In particular I would like to thank my close colleagues Mr. S. Pedersen, Ms. A.-L. Dyhl, Mr. E. Jensen, Mr. K. Stubgaard, and Mr. B. Palfelt. Finally, I would like to thank Ms. L. Scheving, Ms. L. Scheving, Ms. E. Rühl, and Ms. Phyllis Larsen for help in preparing the typescript, and Mr. P. Laursen for the binding of the thesis.
Statement on work included in the thesis which has not been carried out by the author.

The work included in this thesis is a part of a continuing investigation of the injection moulding process. It is based on various projects where other workers have contributed with practical or theoretical work.

It has been attempted in the text as clear as possible to acknowledge the contribution of other people. In most cases, however, I have initiated the work, developed the procedure, carried out the first experiments and then supervised the person, who have done the routine work like measuring weight and shrinkage. The name of the persons involved are also stated in the acknowledgements.

When original work is included from other projects or when work in relation to the thesis has not been carried out by the author, the name of the responsible person is written in CAPITAL LETTERS, his contribution of work stated in a footnote, if necessary, and the relevant reference given. Permission to include the work has been obtained in all cases.

However, as an official disclaimer the following statement is made:

The DSC-instrument described in Chapter 5 has, apart from some minor modifications, been designed entirely by Mr. M. J. STEVENS of Loughborough University. The calibration with indium in the same chapter has been made by Mr. A. BOOTON of Loughborough University. Mr. S. PEDERSEN of the Technological Institute has done a part of the thermal analysis experiments as well as the electronic wiring and initial experiments with the falling weight impact equipment also described in Chapter 5. Ms. U. KNUDSEN has helped with the measurement of reversion after heating and Knoop hardness. Mr. E. JENSEN and Ms. A. L. DYHL have carried out a part of the measurements of weight and shrinkage. Ms. A. L. DYHL also assisted in microtoming and density measurements. Finally is the efforts of Mr. H. GUDMUNDSSON in obtaining the experimental data in Appendix D gratefully acknowledged.
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  9.1 Introduction
During work with my M.Sc. Thesis\(^1\), which was carried out at the Rubber and Plastics Research Association of Great Britain, Shawbury, I became intrigued with the variation found in injection moulded articles. A great deal of work had already been carried out at Shawbury about the variation found during production\(^2\). Also the general trend of the factors which influence the properties of mouldings had been established by various workers\(^3-5\). At the same time a considerable effort was made in the beginning of the 1970's to update and further develop the existing techniques for control systems for injection moulding machines\(^6-7\). The control systems called for a still better understanding of the processes going on in the mould cavity\(^8\). This understanding was facilitated by suitable sensing devices, which had become available\(^9-13\).

It was therefore natural when research in the injection moulding process was taken up at The Technological Institute, it was decided to study the background for the new control systems offered as well as the factors in the mould cavity, which affects the properties of the moulding. It was soon clear, however, that these two approaches could not be separated and despite the numerous investigations concerned with the influence from processing variables on the structure and end use properties of mouldings, it would be necessary to carry out an analysis where the same objective was pursued, but based on the monitoring with new instrumentation of a conventional injection moulding machine, which could be considered typical for the industry. This objective, therefore, is the aim of the project.

It has been carried out in the Plastics Department, which was founded as an independent department in 1968. The research was initiated mainly as a result of a new act of Parliament (Lov nr. 142 of 21 marts 1973 om Teknologisk Service), which provided a basis for a project oriented re-
search and development work. The work included in the thesis, therefore, is based on the following projects; "Styringssystem for sprøjtestøbemaskiner", a joint project with Mr. K. Stubgaard, where the first part was financed by Danmarks Teknisk-videnskabelige Forskningsråd. In its final report it also included work by Mr. H. Heron, IKI at the Danish Technical University.

Other grants comprise the following projects under the sole responsibility of the author; "Strukturundersøgelser af delkrystallinske termoplast", "Varmebehandling af delkrystallinske termoplast", "Spændingsrevnedannelser i termoplast", and "Fugtoptagelse i varmebehandlede polyamidemner". Some of the above mentioned projects have been followed by a group with members from industry and Institutes of Higher Education. Their advice, as well as the financial grants from The Technological Institute is greatly appreciated.
Injection moulding is a complex, multivariable process of great practical interest to the plastics industry. The development of the process has been based on the work of a multitude of people, who have investigated the influence from the processing variables on properties of mouldings. As a result of their work the investigators have proposed changes in the design of moulds and machines, which gradually have been adopted by the industry. Due to the complexity of the process with interaction of many variables, changes in design or improvements of equipment have then created a demand for or given rise to new investigations.

In this way, various workers have established the general trend of the factors which influence the properties of mouldings. There are still, however, few detailed considerations which take advantage of the additional information gained by the use of instrumentation of the mould and the injection moulding machine. Such instrumentation with additional thermocouples, pressure sensors and velocity transducers is useful in obtaining a better understanding of the effect from the rheological and thermal conditions in the injection mould and how they influence not only the change in properties with the processing variables, but also the variation of properties within a moulding. It also provides information necessary for a systematic analysis of the process aiming at improved control.

For the overall process, the objective of a strategy is to optimize the production of mouldings with a given quality.

In this relation three questions of particular importance claim attention 14):

(I) The processability (and reprocessability) of the polymer as such.

(II) The controllability of the processing.

(III) The influence of the processing on the ultimate properties of the product.
A study of the injection moulding process should be concerned with all three factors.

This study however, which may be considered as a part of a long-term project aiming at the formulation of a model for the control strategy for the injection moulding process, will mainly be concerned with the last two aspects.

Before the long-term aim is accomplished it was thought necessary to do the following preliminary work:

(I) Propose a control strategy for each of the process variables to be controlled. These strategies may be based on a combination of intuitive knowledge of the process, literature studies and the results of tests to determine the interactions between machine controls and process variables.

(II) Carry out a testing programme to obtain data which can be used to determine how the process variables are related to each other and to the machine settings and, at the same time, determine how they influence the properties of mouldings.

(III) Using the experimental data, develop the relationship between process variables and the final properties of mouldings.

In conclusion, the objective of the work which is reported here is to identify those variables which have the most profound influence on the properties of mouldings. Emphasis is laid not only on the processes which take place in the mould cavity, but the study also considers other factors in the process which are thought to influence the quality of mouldings.
1.1. FORMULATION OF THE PROBLEM

Of the dominant factors which influence the properties of mouldings, including the raw material, the shape of the moulding, the mould and machine and the conditions of processing, the last named may be the most difficult to predict and to control.

The term "processing conditions" comprises a number of regulated values which have to be set on the machine, e.g. barrel temperature, injection pressure, packing pressure, cooling time, mould temperature, as well as external factors such as temporary shut-downs, change of shift and machine operation. Some of these variables are contradictory in nature and some are more important than others. 15)

Among the variables that are of importance in determining the quality of mouldings are the pressure, specific volume and temperature of the polymer in the mould just before the mould is opened. In general, it is well to know the values of these quantities as a function of time after the mould has been filled.

In principle, the temperature distribution in the mould may be computed as a function of time when one knows the geometry of the mould, the temperature at which the polymer enters the mould and the mould temperature. 16) This may involve approximations, but a sufficiently accurate answer can be obtained in most cases, leaving the pressure and specific volume to be determined as a function of time. Fortunately, it is not necessary to measure both of these quantities, inasmuch as they are related through the pVT-equation of state, which can be represented in diagrams and which have become available for a number of amorphous and semi-crystalline polymers. 17)

Such diagrams may represent a long-term solution for the setting of processing conditions to achieve optimum results, particularly if used with computer control of the process. In practice, a rigorous theory based on the use of pVT-diagrams is very difficult to develop, because of the geometri-
cally complex shape of a mould and of the rheologically complex nature of the polymer being moulded.

In practice, production is increased through the reliability and reproducibility of the machine, utilization of the plant and by reducing reject rates. Quality of mouldings are generally characterized by criteria for strength, deformation properties, weight and dimensional stability and appearance. These factors are closely related to the mould geometry and polymer used. For a given mould geometry and polymer, the part qualities can be optimized by proper controlling of the process variables, since they are so intimately related.

Maximum quality is achieved in the completely isotropic state of the moulding. In this ideal case the properties depend only on the characteristics of the raw material, e.g. molecular weight, molecular weight distribution, polymer structure, degree of branching, desired crystallinity, etc.

In practice this ideal situation is only partly achieved as the polymer is influenced by the thermal and mechanical processes in the barrel and nozzle and, as a consequence, reaches the cavity in an anisotropic state.

This effect is enhanced during the mould filling and the cooling in the cavity by position and time-dependent processes. The variation of properties within a moulding may even be greater than the variation found between mouldings from widely different processing conditions. In production a compromise then has to be made between the optimizing of the quality and the cost of increasing moulding cycles.

After moulding, the physical state of the part is dependent on the:

- raw material properties
- molecular orientation
- internal stresses
- morphology.

A certain interaction exists between these parameters. Raw material properties, as described in data sheets, often form

+ As a result, properties measured in one direction are different from properties measured in any other direction.
the basis for the choice of a polymer. However, even when determined according to standard test methods, such properties are not always representative of the properties of mouldings. Several examples from practice have shown that the processing may have a more pronounced influence on mechanical and physical properties than structural parameters like molecular weight, polymer structure, etc. The influence from processing is due to changes in the structure and morphology of the polymer. In amorphous materials, molecular orientation and internal stresses are induced and in crystalizable materials the degree and pattern of crystalline phases, additionally, occur.

Molecular orientation arises from the stretching of the molecules during flow, the subsequent cooling and fixation of the stretched molecule in the moulding. The degree of orientation is dependent on various factors like processing conditions, viscosity of the melt, part design, type of gate, flow length, wall thickness and other factors influencing the flow of the melt. Molecular orientation is the main cause of anisotropy in the macroscopic physical properties and contributes to instability in dimensions or shape.

Internal stresses are residual thermal stresses which arise when a moulding is cooled inhomogeneously (e.g. from the surface inwards) and when the cooling, moreover, causes the material to stiffen. The inhomogeneity of the cooling is responsible for the thermal stresses; the temperature dependence of the elastic properties is necessary for converting these temporary thermal stresses (which only act during cooling) into residual stresses which persist when the cooling has been completed. Different kinds of internal stresses exist, e.g. frozen-in molecular orientation, physical aging stresses and cooling stresses. The residual stresses are active at room temperature and proportional to the deforming strain. They can be considered as a change in potential energy, which also influences the molecular and crystalline structure. In certain environments internal stresses will cause a polymer to fracture at stresses much lower than in the absence of the environments. This phenomenon, which is frequently encountered in practice, is referred to as environmental stress cracking (ESC).

+) There can also be stress from variation in inelastic strain across a flow profile.
The morphology of melt crystallized polymers is known to be related to the fabrication technique. In injection moulding polymers crystallize from a melt that has been exposed to flow, shear and temperature variations. For a given moulding, therefore, different properties for a polymer moulded under different conditions are due to a change in the morphology, which can be understood in terms of the interrelationships between crystallization kinetics, melt rheology and thermal environment.

In other words, when a given polymer is used, the molecular structure (the first order structure) is the same, and therefore the differences in physical properties under different moulding conditions are supposedly caused by the changes in the arrangements of molecular chains (the higher order - or superstructure). Based on these arguments, it is essential in a study of the influence from moulding variables on properties to clarify the effects of molecular structure and moulding conditions on physical properties via analyses of higher order morphology.

Such investigations have recently been conducted on the more common crystallizable materials (polypropylene, polyoxymethylene and polyamide). Clark found in a study of polyoxymethylene that at least three types of morphology occur: a skin of high molecular orientation, a less highly oriented intermediate "transcrystalline layer", and a spherulitic core.

The skin represents that portion of the melt crystallizing during the filling period. The transcrystalline and spherulitic regions result from crystallization under low melt stress with their relative volumes determined by the rate of heat transfer to the cavity wall.

Other workers have investigated the influence of processing variables on morphology and the complicating effects of crystallinity in determining the shrinkage of mouldings in semi-crystalline polymers and the maintenance of narrow tolerances for precision mouldings. In most studies, however, a qualitative model only for the origin of the skin-core morphology has been constructed, and only few studies link morphology and orientation with moulding conditions on the one hand and with resultant properties on the other.

+) Flow profile gives high elastic strain at wall and zero strain in centre.
It should be pointed out that during injection moulding the
development of morphology and orientation in semi-crystalline
polymers occurs in a manner quite different from that in
amorphous polymers. However, recent investigations\textsuperscript{27} have
shown that a limited amount of short range order exists in
most polymeric solids and that amorphous polymers also have
a certain molecular order in small domains in the solid state,
which may well explain some of the anomalous properties of
amorphous polymers.

In summary, a moulding of good quality is one with low orien-
tation, few residual stresses and homogeneity in structure
and morphology.

So far most experiments have been based on the setting of
the controls of the injection moulding machine. This ap-
proach, while convenient for simulation experiments\textsuperscript{14}, is
not suitable for analytical purposes.

With more reliable techniques for measuring and recording
the temperature of the polymer being injected, and the pres-
sure cycles at the nozzle and in the mould cavity a step
forward has been taken in order to bridge the gap between
material data, e.g. in the form of pVT-diagrams, and the re-
sultant properties of mouldings.

However, further progress along this line is dependent on
analyses of the process state variables in injection moul-
ding.

Simulation experiments, therefore, should be followed by
systematic processing experiments on a model machine (which
is a small, well-equipped production machine). Provided the
analysis is based on the process state variables as recorded
during a cycle, this gives data that is still closer to
practice, because they have been obtained under practically
equal, though carefully watched circumstances.

Time is very important in injection moulding and emphasis
must be placed on the length of time consumed by a single
moulding cycle. Along with the correct time sequence for a good moulding, the moulder must also have the proper temperature and pressure sequence.

Practice itself will afterwards supply the feedback information, which may be even more important. It will be clear that the practical knowledge of the processor is essential here. Mostly, however, this knowledge has no background in the research data available.
1.2. PROCEDURE FOR THE WORK

In this passage the general lines of approach for the project is given, whereas the detailed experimental planning is presented in a subsequent chapter.

The work is divided into three parts, a general literature review, the instrumentation of an injection moulding machine and the development of additional testing equipment and finally the experimental part with discussion of the results.

The first part is initiated in Chapter 2, which is an attempt to single out the principal elements in injection moulding in order to establish a framework for the project, as well as for further studies of the process.

This is followed by a summary of the influence from processing variables on part properties (Chapter 3). It is especially about the relation between those factors which determine the morphology and superstructure in mouldings and the resulting relationship between morphology and mechanical and dimensional properties.

The experimental planning is outlined in Chapter 4 based on the objectives formulated in Chapter 1. It is also a discussion of the choice of materials for investigation, the test specimen geometry and the moulds, the processing conditions and the experimental method used.

The second part of the project is described in Chapter 5 and the first sections of Chapter 6.

Chapter 5 is a description of the instruments used for characterization of properties, including a short description of the principles, upon which the instruments are based. Only instruments developed in relation to the project are described in detail.

The third, experimental part is initiated in Chapter 6. It describes the experimental equipment, characterisation of the polymers, processing conditions and the investigations and tests performed on the mouldings.
In Chapter 7 the procedure for evaluation and computation of the data is given, with emphasis on the relationship between machine settings and the effective processing variables measured in the mould.

This is followed by a presentation of the results (Chapter 8) and a discussion (Chapter 9) of the results.

Finally, the conclusions of the work is summarized in Chapter 10, and as the work also is supposed to provide a background for further investigations, Chapter 11 gives suggestions for this aim.
2.1 INTRODUCTION

The objective of this chapter is to form the background for the guidance of present and future research of the injection moulding process. It is based on a review of literature. As an introduction, a short summary of the history and development of the injection moulding sector is given. It then proceeds with a description of the principal elements in injection moulding, as well as those factors which must be taken into account in an analysis of the process. Also, the relevant methods for prediction of polymer processing properties are dealt with.

2.1.1. History and Development

The development of injection moulding is closely related to the development of synthetic materials, which has its origin in the search for substitutes for ivory and ebonite in the 1860's.

One substitute for this purpose ("Celluloid") was found in 1869 by Hyatt, who also designed a single-action moulding machine for the processing of the material.

The advance of injection moulding was almost entirely dictated by the availability of suitable materials for moulding. As there was no early alternative to cellulose nitrate, the advance was held up until some 25 years later, when cellulose acetate became available.

This material, however, was mainly processed by compression moulding, but in 1919 Eichengrün developed an injection moulding material based on ethyl cellulose. In the second half of the patent description the injection moulding process is clearly explained.

It is from those beginnings that injection moulding, as we know it today, really began.

The first hydraulic or pneumatic vertical injection moulding machine was brought on the market by "Gebrüder Eckert" in 1922-23.
A further innovation was the first automatic machine by "Eckert und Ziegler" from 1927. Automatic, electromechanical machines were designed by Gastrow 1932-33.

The first injection moulding machines were all piston machines. Virtually all are now replaced by the pre-plasticizing, reciprocating, single-screw injection moulding machine. It was developed by Beck in 1956.

The single-screw unit became established in the 1960's. These units are fundamentally unchanged in basic design concepts, but since that time there have been extensive reinforcements of injection moulding machines in order to adjust the technique to other processing requirements, or other materials.

The control of the injection moulding machine started with fixed logic systems based on mechanical timers, limit switches and relays being tripped in a preset sequence. Now solid state circuits and proximity switches using semi-conductor devices have almost entirely replaced solenoid-type relays, but the control system is, in principle, still based on the event type of control. The latest systems, however, aim at controlling the process rather than the event. For example, rate-of-fill, pressure, and temperature can be controlled by some sort of analog or analog-digital system.

These instruments operate in such a way that they control the injection phase as a function of the quantity or the speed and the packing and holding phase as a function of the pressure, starting out from either the hydraulic or the mould cavity pressure.

Microprocessor-based machine controllers may be used in either of the above-mentioned systems. Here, the conventional electronic system has been replaced by a freely-programmable micro-processor. Apart from improved and more easily realized process information, there are no advantages and changes for the operator. However, a microprocessor offers the best prerequisites for further expanding the control system in the areas of process, machine, sequence, and temperature control, production management, as well as system reliability and maintainability through diagnostic systems. Thus, it is a part of a fully operational system which may be linked to a computer for overall control.
During the next 5 - 10 years new control systems that will be made possible with a combination of sensors, high-power microprocessors and servo valves (incorporating themselves, a closed-loop pressure sensing system, and, preferably, mounted directly on the relevant cylinder) will increase the speed of measurement, reaction and control, resulting in ease of operation, greater reproducibility and repeatability of machine settings. However, even more important will be the simplicity of construction made possible by this form of control eliminating limit switches, associated wiring, solenoid valves, preset flow valves, hydraulic pipework, indicator lights, etc.

The improved systems call for a still better understanding of the process, especially what factors need to be controlled. One of the first requirements should be a further development in compilation of sets of data on pressure-volume-temperature functions and flow functions and their subsequent incorporation in total or part process models which describe, e.g., the filling and the pressure holding phase in terms of physically established laws.

If we look at everyday practice, however, we find that conventional techniques are used to a great extent and that new technologies in measurement and control are introduced only sporadically. There is still a considerable deviation from what is now theoretically feasible and actual practice. The process engineer is still searching for suitable numerical systems which reliably describe the relationship between quality and process variables.

2.1.2 The Extent of the Injection Moulding Sector

In terms of turn-over, injection moulding is considered to be the most important plastics conversion process.

In Denmark, approximately 250 firms out of about 600 processing companies of one type or another are working with injection moulding. In 1978 an estimated 25-30%, out of the total consumption of 500,000 t of plastics materials, was processed by injection moulding. The production value, however, was nearly 50% of the total of approximately six billion Dkr for the whole sector. The per capita consumption was 63.0 kg. The plastics processing firms employed between them some 15,000 people. The size of the firms
vary considerably with 80% employing less than a 100 people and often 5-10 people only. Few employ more than 500 people. The installed capacity in the injection moulding sector is estimated at 3500 - 4000 injection moulding machines in a range from a few grammes up to several kilogrammes shotweight. Due to the high growth rate of the sector\(^1\), the machine installations are quite new, as compared with other industrial sectors with more than half of the machines being less than 10 years old. In the period 1975-77 the investment per man for new plants was an average Dkr. 379.000.

2.1.3. Literature Review

The literature review was initiated by a study of various text-books, monographs and dissertations. Then, approximately 15-20 journals from the 1970's were searched and relevant references traced further back. This was supplemented by use of two abstracts systems, Kunststoff-Dokumentum and RAPRA-Abstracts. For a specific problem an on-line search was made in the computer based ESA-RECON system which is situated in Frascati in Italy. This could be carried out within the library of the Technological Institute, but frequent contacts were made with external libraries and documentation centres.

In the thesis an attempt has been made to use a coherent system of nomenclature and symbols. Therefore, in a few cases, terms or symbols are different from those found in the original papers. It should also be noted that the continental use of a comma as a decimal point has been followed throughout the thesis

\[\text{\(^{[+]\) 1974 - 78, True growth, \(^\dagger\)}} \]

<table>
<thead>
<tr>
<th></th>
<th>in value</th>
<th>in volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastics industry</td>
<td>124</td>
<td>104</td>
</tr>
<tr>
<td>General industry</td>
<td>110</td>
<td>130</td>
</tr>
</tbody>
</table>

\((\dagger) 1974 = 100\)
2.2. THE PRINCIPAL ELEMENTS IN INJECTION MOULDING

2.2.1. Introduction

In essence, the technique of injection moulding consists of heating a charge of thermoplastic material to a consistent state of fluidity and transferring it under pressure by enclosed channels into a closed space. There, it is cooled to produce a solid part with the greatest possible degree of homogeneity and, it is then physically ejected from the machine and the sequence repeated\(^{34}\). It is worth noting that the injection moulding process is a cyclic operation which lies somewhere between flow and batch production.

Spencer and Gilmore\(^{34-37}\) showed, in the first serious scientific studies of injection moulding, that the pressure-volume-temperature behaviour of polymer melts can be represented reasonably well by a modified van der Waal's equation of state:

\[
(p + \pi)(V - \omega) = \frac{RT}{M_u} \tag{2.1}
\]

where \(p\) is the applied pressure, \(V\) is the specific volume of the polymer, \(T\) is the absolute temperature, \(R\) is the "gas constant", which is dependent on the "interaction unit" of the polymer (\(M_u\)). The constants \(\pi\), \(\omega\), and \(M_u\) must be determined experimentally.

Spencer and Gilmore assumed a homogeneous, isotropic melt in the cavity. But each single volume element has its own thermal and rheological history as well as its own pVT-relation. Therefore, Equation (2.1) applies only at a point in the flow. It indicates, however, that any conditions that will affect the temperature and pressure will affect the specific volume. For a practical application it may be even more important that the material properties of polymers show a distinct time dependence, i.e., depending on the rate of change of state, they show different thermal behaviour, particularly in the transition range between melt and solid. Thus, the values of specific volume differ for low and high cooling rates.

The inherent complexities of the above-mentioned relationships make an analysis of the injection moulding process difficult. Initially it is, therefore, viewed as an input/output system. In this system the variables can be classified as the input vari-
ables, the process state variables and the output variables (Fig. 2.1).

Referring to Fig. 2.1., the process is subdivided into the three basic operations which are operated sequentially in injection moulding: melt production (plastication), injection, and melt solidification (packing and cooling). The fundamental variables associated with each process are pressure, temperature, distance, and time. Implicit with distance and time is velocity (ds/dt). As far as any of the basic operations are concerned, the output state variables of the previous step would be the input variables for the next step. For instance, the final state of the melt temperature is the output state variable from the plastication process, and it becomes an initial condition input for the following process which is injection.

In this way the multivariable nature of the process may be analyzed with a view to identifying some of the variables which can be considered separately in the hope that integration may take place later. It is clear, however, when correlations are derived between input and output variables, that detailed considerations of what happens in the operation may be neglected. But the diagram does indicate the important items, and perhaps suggests some of the complex interactions possible.

Input variables. There are two basic types of input variables affecting the process and causing changes in output:

(i) Controllable or deterministic variables (not necessarily absolutely measurable)

(ii) Uncontrollable or random variables - generally not measurable on-line.

Type (i) variables are largely those of groups 2 and 3 in Fig. 2.1. The group 3 variables which comprise article, mould, and machine design are all under the control of the mould designer or machine builder. Once a machine is operating these variables largely become fixed.

The group 2 variables are the machine variables which comprise two functions. Sequence control functions comprise the control of the injection moulding cycle. Parameter control functions are based on open or closed loop control of the various variables,
Fig. 2.1 The injection moulding process
e.g. barrel temperature, mould temperature etc., which affect process variables $P(x, y, z)$, $T(x, y, z)$, $\gamma(x, y, z)$, etc. Often machine variables only are controlled in the hope that this will result in the correct process state variables.

Type (ii) variables may be exemplified by variation in raw material properties. Small variations in rheological, thermal, and bulk properties are not normally under the operator's control but affect the processing characteristics and, hence, the process output. It is largely as a result of random changes in these that a control scheme is required.

It is apparent from the numerous articles written on the subject that the effects of these variables are greatly dependent upon the specific mould, machine, and raw material combination. Therefore, a break-down of the moulding cycle in terms of operating controls, while convenient for setting the controls of the machine, is not suitable for analytical purposes and a prediction of machine effects can only be made in the most general terms. The inter-relationship of variables is even more difficult to predict. It is unlikely that the study of machine variables will ever lead to a conclusive interpretation of the injection moulding process. It is rather by the direct measurement of conditions during moulding that machine variables can be analyzed, and more importantly, correlated with the final properties of the product.

**Process state variables.** These are polymer physical conditions as a function of time and position. For instance, the melt temperature in the mould is a variable dependent upon barrel temperature and cooling rate. Melt flow rate during injection is another example of a process state variable. The polymer physical conditions are extremely important because they are closely related to the properties of the mouldings.

**Output variables.** These are the physical and mechanical properties of the moulding. They depend upon the input and process state variables. Molecular orientation, morphology, surface finish, mechanical properties and dimensional accuracy are typical output variables affecting the quality of the final product.
The purpose of a functional analysis is to develop functional relationships between the process variables. To take the above general arguments further into detail, it is necessary next to look at particular subprocesses.

Initially, however, some important variables are defined (Fig. 2.2), and the moulding cycle analyzed (Table 2.1).
Pressure increase until pressure relief valve opens and a second pressure relief valve is actuated.

Fig. 2.2 Definitions of motions, pressures, and times during the injection moulding cycle (Partly according to DIN 24 450)
Table 2.1  The injection moulding cycle.

<table>
<thead>
<tr>
<th>Time</th>
<th>Operative component</th>
<th>Machine function</th>
<th>Effect on conditions in cavity and moulding</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_1$</td>
<td>Pressure control valve for injection pressure $(p_{inj})$ and flow control valve for injection speed $(v_{ss})$.</td>
<td>Screw forward motion starts after pressure build-up. Increased delivery (flow rate) from hydraulic oil pump. Setting of: higher/lower oil pressure, or more/less throttling of flow control valve results in higher/lower screw forward velocity.</td>
<td>Start of injection time $(t_{is})$ cycle time $(t_{cs})$. Flow front velocity of the melt or shear rate close to the surface, respectively, increases/decreases.</td>
</tr>
<tr>
<td>$t_2$</td>
<td>Screw moves forward</td>
<td>Melt flows through nozzle, sprue, runners, and gate into the cavity and reaches transducer close to the gate. Start of effective injection time $(t_{ie})$ cooling time $(t_{ke})$.</td>
<td></td>
</tr>
<tr>
<td>$t_3$</td>
<td>Screw strikes a micro-switch after travelling a preset distance $(l_3 \rightarrow l_2)$.</td>
<td>The generated signal is used to switch one solenoid-actuated pressure relief valve out of the circuit and another, set at the lower packing pressure $(p_{hp})$, into the circuit. Reduced delivery of oil pump. The position dependent switch-over $(l_3)$ can be set so that it corresponds to the volumetric filling of the cavity.</td>
<td>Termination of injection time $(t_{ie})$. Start of packing time $(t_{pe})$. Termination of effective injection time $(t_{ie}^{<em>})$. Start of effective packing time $(t_{pe}^{</em>})$. Thus, injection time $(t_{ie})$ is set by the injection pressure together with the throttling of the flow control valve. The increase of pressure before the volumetric filling of the cavity is a function of the geometry, viscosity, and rate of filling. The transition from a flat to a steep rise of pressure in the cavity indicates the volumetric filling of the cavity.</td>
</tr>
</tbody>
</table>
The signal to switch-over may come from a micro-switch activated by the screw, a timer, or a pressure transducer. It is also possible not to switch over to a lower pressure.

The effective injection time \( t_e \), and, depending on the conditions, the start of the packing time \( t_p \) together with the melt temperature \( T_m^\text{PPS} \) and the mould temperature \( T_f \) influences the molecular orientation in the melt as well as nucleation and the size of crystallites in semi-crystalline polymers.

The solidification process is a semi-static pressure situation, where the melt pressure \( p_m \) is proportional to the hydraulic pressure \( p_h \) but where the constant of proportionality \( C \) is time-dependent. Hence \( p_m = C(t) \cdot p_h \).

<table>
<thead>
<tr>
<th>( t_3 - t_5 )</th>
<th>Relief valve for the nozzle during packing time. Setting of the pressure ( p_n ) in the cavity.</th>
<th>The effective packing time ( t_e ) takes place with an isobaric change of the melt in the cavity. The static pressure ( p_s ) in the melt decreases along the length of flow (The constant ( C(t) ) decreases. Therefore, the pressure curve varies with the position in the cavity.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Setting of the pressure ( p_n ) in the cavity:</td>
<td>[ p_n = p_h \frac{D_1^2}{D_2^2} ]</td>
<td>The first packing phase ( p_e ) takes place with an isobaric change of the melt in the cavity. The static pressure ( p_s ) in the melt decreases along the length of flow (The constant ( C(t) ) decreases. Therefore, the pressure curve varies with the position in the cavity.</td>
</tr>
<tr>
<td>Where:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D_1 ) = diameter of the piston</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D_2 ) = diameter of the screw</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Termination of effective packing time \( t_e \) defined from the intersection of the tangents drawn to the pressure curve (Fig. 2.2). Sealing at the position of the pressure transducer close to the gate corresponds, subject to certain exceptions, to the sealing of the moulding.
From this event no further influence on the thermodynamic state of the melt in the cavity - and, hence, the mass of the moulding - from the machine variables.

Sealing time is dependent on:
- melt temperature
- mould temperature
- packing pressure (especially for semi-crystalline polymers)
- dimensions of the gate
- additives
- wall thickness of the moulding

The pressure gradient in the solidifying core depends on relaxation of the melt pressure equalization in the moulding.

The pressure (p) decreases during cooling and the isochoric contraction of the melt.

**t₄** - **t₇**

Time dependent switch-off of packing pressure (pₚ). Pressure drops in the hydraulic system.

Start of the set cooling time (tₛ). Start of plastication and metering time with rotating screw. Back pressure (pₛ) is set in the hydraulic cylinder by the throttling valve in the hydraulic line.

Termination of packing time (t₉). The weight of the moulding is directly related to the average temperature and pressure in the cavity at the time of sealing. If the sealing time (tₛ) is shorter than the packing time (t₉), the latter will not influence dimensions and weight of the moulding. If the packing time is shorter than the sealing time and the barrel pressure is lower than the cavity pressure, a "discharge" from the cavity can take place.
<table>
<thead>
<tr>
<th>$t_6$</th>
<th>Screw strikes a micro-switch after travelling a preset distance backwards ($l_1 \rightarrow l_3$)</th>
<th>Termination of screw rotation ($n_s$). Metering time ($t_{ds}$).</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_7$</td>
<td>Timer</td>
<td>Termination of set cooling time ($t_{ks}$).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mould opening and ejection of moulding.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Termination of effective cooling time ($t_{ke}$).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drop of remaining pressure in the cavity.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cooling continues in the moulding.</td>
</tr>
<tr>
<td>$t_8 - t_1$</td>
<td>Timer</td>
<td>Termination of mould opening and pause time ($t_{os}$).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Termination of cycle time ($t_c$) and start of new cycle.</td>
</tr>
</tbody>
</table>
2.2.2. The Plastication Process

During plastication a shot volume of the plastic compound is melted, mixed and displaced to the front of the screw for injection into the cavity.

For a given screw geometry the melt flow rate ($Q$) is only a function of barrel temperature ($T_b$), screw rotational velocity ($n_s$), screw back pressure ($p_d$) and disturbances, that could be caused by raw material property variations and/or the screw geometry variations due to wear\textsuperscript{38}.

Theoretical and experimental work on the plastication process in injection moulding is only rarely reported. Since the plastication process is quite complicated it would be sensible to divide a study into models, e.g., a melting model, a melt temperature model, and a pressure profile model\textsuperscript{47,48}. By applying the conservation laws of mass, momentum, and energy to appropriate regions along the screw channel, and by introducing physical property relationships and suitable engineering assumptions, each model becomes a well-determined mathematical formulation which is amenable to solution.

A simplified equation for continuous extrusion, based on several assumptions, for the melt flow rate ($Q$) can be verified from the text by Schenkel\textsuperscript{49}, Torner\textsuperscript{50} suggests to apply the equations for adiabatic screw plastication for extrusion by McKelvey\textsuperscript{51}. As these equations are based on a total balance of energy, and as the assumed high screw rotational velocity gives a nearly autogenous plastication useful approximations are to be expected.

The simplified equations for continuous extrusion have now been superseded by the work of Pearson\textsuperscript{64}, Tadmor\textsuperscript{267}, and Fenner\textsuperscript{273}, Nunn\textsuperscript{275}, who performed an experimental study of reciprocating-screw plastication, showed that a comprehensive analysis of the process involves coupling the separate phenomena of screw rotation, steady conduction, and injection stroking.

The decisive factors for the plastication process are, for a given plastication volume, the melt temperature ($T_m$), its consistency across the cross-section and along the cushion in front of the screw, as well as homogeneity of the plasticated volume.
The rise in melt temperature during plastification is caused by frictional or shear heating from mechanical work, and from conduction heat generated from the temperature of the barrel heaters. The temperature increase due to shear heating ($\Delta T_s$) for a given material is proportional to the diameter of the screw and the screw rotation velocity and inversely proportional to the channel depth. (See following section)

The temperature increase due to heat conduction ($\Delta T_c$) depends on:
- The temperature difference at the start of the heat transfer process.
- The position of a volume element in the barrel or screw channel, respectively.
- The thermal diffusivity.
- The time period
- The square of the thickness of the layer in the barrel or screw channel, respectively.

The thermal diffusivity of polymers is too low for conductive heat from the barrel to heat the polymer at an economic rate. Therefore, the work-to-heat conversion of the screw generally accounts for fifty to seventy-five percent of the heat required by the plastic. However, this form of energy is not readily controllable. To achieve temperature control, it is desirable to utilize the conductive heat from the barrel.

Melt temperature and/or pressure measured at one position are not entirely significant for melt quality. They represent system conditions but not material properties, which themselves depend in a rather complicated way on pressure and temperature and several other criteria. The general quality criterion is the melt homogeneity. It is represented by the real variations of state and properties in time and place. It is influenced by the longitudinal and radial temperature differences which are known to exist. Longitudinal differences may amount up to 9 °C and up to 30 °C for amorphous and semi-crystalline materials, respectively. Radial differences may be 0-3 °C and up to 15 °C, respectively.

The reasons for the radial and longitudinal temperature differences may be summarized as follows:

0 2 6
(i) The radial temperature differences are a result of local differences in velocity and shear rate for the melt in the screw, differences in heat dissipations at different positions, and the temperature gradient between screw and barrel.

(ii) In injection moulding plastication is a discontinuous process. When the screw rotation stops the plastic compound is further heated by conduction until screw rotation starts again. In this way melt, which reaches the nozzle has spent uneven periods in different sections of the cylinder, which are also heated to different temperatures.

(iii) In each cycle a thermal heating process takes place which, however, is interrupted before stationary conditions have been reached. With constant parameters \( (Q, T_m', T_b', D_1, D_2) \) this process approximates a quasi-stationary state, that is, the same variation is found from cycle to cycle.

(iv) The active screw length is continuously reduced during plastication. This influences the pressure build-up, throttling ratio and hence the heat dissipation. At the same time the position of the screw relative to the barrel changes.

(v) The torque on the screw generally varies during the screw rotation causing the energy input per volume unit to vary. A constant screw rotation is achieved only when the working pressure of the hydraulic motor is well below the system pressure. Otherwise an uncontrollable amount of oil is let-off when the pressure relief valve opens.

Apart from the influence of process variables and attempts to optimize the screw geometry several measures have been proposed in order to reduce the temperature differences, e.g., shear zones at the screw, mixing elements, torpedos etc.

Kohler investigated the thermal homogeneity of the melt and found, when using the standard deviation of the mean temperature as a measure of melt homogeneity, that an increasing back pressure reduced the output, increased melt temperature and decreased temperature differences. Switch-over to a lower back pres-
sure during plastication gave a better homogeneity than when a constant back pressure was used. A temperature profile on the barrel which increased from the hopper to the nozzle gave a less homogeneous melt than when all heating zones were set at the same temperature. When output was increased the average melt temperature decreased, while the temperature differences increased. Kloss and Müller found that the melt temperature decreased and the temperature differences increased with increasing screw rotational velocity.

During the following injection process the melt is subjected to considerable mechanical and thermal stresses. In the nozzle/runner system, in particular, it has been shown that the influence of shear heating and dissipation is of considerable significance with small diameters, low melt temperatures and high velocities, and give rise to pronounced temperature peaks. These, however, are very quickly compensated when the cavity filling process is terminated.

The main influence, however, on the temperature of the melt which reaches the cavity arises from injection pressure. By equalizing mechanical and thermal energy the following (isenthalpic) relation is valid for the adiabatic incompressible process, when the kinetic energy of the flowing melt is neglected:

\[ \Delta T = \frac{\Delta p}{\rho \cdot c_v} \]  

Equation (2.2) gives the temperature increase in the case where no heat is exchanged between runners and melt and without considering geometry, melt temperature, rate of injection, surface temperature, rheological properties etc. Also the density is temperature and pressure dependent and the specific heat capacity temperature dependent. The assumed adiabatic conditions are also a simplification. Therefore, temperature increases calculated after Equation (2.2) may be overestimated.

In theory the temperature profile can be calculated for circular channels from the equations of momentum and energy together with a relevant rheological power-law equation.
Increase in temperature due to shear heating in the barrel.

The increase in temperature from mechanical work is caused by external and internal friction on the material.

External friction acts at the surface of the material particles. The generated heat is then conducted into the interior of the particles.

Internal friction arises from deformation or compression of the particles as a reaction to the influence from shear forces. Shear deformation may take place in the solid, viscoelastic, or elasticoviscous state.

External friction, which is present mainly in the hopper zone, has only a limited consequence, because the surface of the particles soften, due to the heating and the external friction is then transformed into an internal friction. An exact analysis of external friction is quite complicated.

The increase in temperature is proportional to the power from the motor driving the screw.

\[ \Delta T_s \propto \frac{P}{G \cdot C} \quad \text{(K)} \]  \hspace{1cm} (2.3)

where

\[ \Delta T_s = \text{increase in temperature (K)} \]
\[ P = \text{power from the motor (W)} \]
\[ G = \text{mass from processed material (kg/s)} \]
\[ C = \text{average specific heat capacity (J/kg·K)} \]

The increase in temperature from shear heating during flow, e.g., in an extruder channel may be estimated from flow relations for the melt.

The energy transformed by shear heating per unit volume is given by:

\[ E = \tau_s \cdot \dot{\gamma} \quad \text{(W)} \]  \hspace{1cm} (2.4)

where

\[ \tau_s = \text{shear stress (N/m}^2) \]
\[ \dot{\gamma} = \text{shear rate (1/s)} \]

\( \tau_s \) depends on geometry and pressure conditions but is independent of the rheological properties of the melt.
The shear rate relation in a screw channel (melting zone only) takes the following form for a Newtonian fluid:

\[ \dot{\gamma} = \frac{\dot{y} \cdot D \cdot n}{H} \quad \text{(1/s)} \]  

where

- \( D \) = diameter of screw (m)
- \( n \) = screw rotational velocity (1/s)
- \( H \) = channel depth (m)

The temperature profile across the cross sectional flow area can be determined only when the flow front velocity profile is known.

For a Newtonian fluid the relation between shear rate and shear stress is given by:

\[ \dot{\gamma} = \frac{1}{\eta} \cdot \tau_s \quad \text{(1/s)} \]  

which, combined with equation (2.4) gives:

\[ E = \frac{1}{\eta} \cdot \tau_s^2 \quad \text{(W)} \]  

In this case, the temperature profile takes the form of a parabola corresponding to the flow front profile. It shows that shear heating is higher at the wall than at the center.

When \( \tau_s = \eta \cdot \dot{\gamma} \) is combined with (2.7), then the shear heating per unit volume per unit time is derived.

\[ E = \frac{1}{\eta} \cdot \tau_s^2 = \frac{1}{\eta} \cdot (n \cdot \dot{y})^2 = \eta \cdot \dot{y}^2 \quad \text{(W)} \]  

for a non-Newtonian fluid the apparent viscosity is used:

\[ \eta_s = f(\dot{\gamma}) \]

one of the main problems in the above treatment is to define accurately the shear for all types of deformation. It is also evident that only the temperature rise due to friction is computed in the above relations. The effects of compression on changes in entropy are not considered.

The total increase in temperature for a given period of time may be computed by multiplying the energy per unit volume with the volume of material processed in the corresponding time period.

\[ W_1 = E_1 = \eta_s \cdot \dot{y}^2 \cdot v \cdot t_u \quad \text{(J)} \]  

0 3 0
where
\( W \) = work (J)
\( E \) = energy (J)
\( v \) = volume of processed material (m\(^3\))
\( t_u \) = time period (s)

Energy transformed by shear heating may also be estimated from:
\[
e_2 = v \cdot \rho \cdot c \cdot \Delta T \quad (J) \quad (2.10)
\]
where
\( v \) = volume of processed material (m\(^3\))
\( \rho \) = density (kg/m\(^3\))
\( c \) = average specific heat capacity (J/kg\( \cdot \)K)
\( \Delta T \) = increase in temperature (K)

By equalizing equation (2.9) and (2.10)
\[
\Delta T_s = \frac{n_s \cdot \gamma^2 \cdot t_u}{c \cdot \rho} \quad (2.11)
\]

It should be noted that the specific heat capacity, density, and apparent viscosity depends on the temperature.

with equation (2.5)
\[
\Delta T_s = n_s \left( \frac{1}{H} \right)^2 \cdot n^2 \left( \frac{1}{c \cdot \rho} \right) \cdot t_u \quad (K) \quad (2.12)
\]
or
\[
\Delta T_s \propto \left( \frac{1}{H} \right)^2 \cdot D^2 \cdot n^2 \propto \left( \frac{D}{H} \right)^2 \cdot n^2 \quad (K) \quad (2.13)
\]
that is, the temperature increase is proportional to the diameter of the screw and the screw rotational velocity and inversely proportional to the channel depth.
Measurement of melt temperature

The problems involved in the measurement of the melt temperature have been discussed and listed by several authors \(^8\), \(^9\), \(^57\), \(^281\)-\(^284\), and a number of methods have been proposed, from shot purging through the nozzle into a PTFE-cup with a built-in thermocouple\(^{285}\), to the use of infrared optics\(^{58}\).

Thermocouples protruding into the melt can be placed upstream, downstream, flush with the barrel, perpendicular to the flow, or in a measuring device according to a design by van Leeuwen \(^9\), \(^286\).

However, thermocouple readings from a probe inserted into the melt have to be corrected because the mere insertion of the probe disturbs the steady state developed in the flow system and sets up a new steady state. The temperature recorded, therefore, differs from the true, undisturbed melt temperature and must be corrected.

The various factors which contribute to the total errors are\(^{283}\):

(i) heat conduction along the probe
(ii) heat convection from the probe
(iii) energy dissipation at the probe due to shear heating.

These are represented diagrammatically in Fig. 2.3.

Inertia is significant in practical moulding due to the short injection times, which are of the same order as the response time of a ruggedly designed thermoprobe. Also, a slow response thermoprobe may not indicate to the fullest extent the adiabatic heating during injection\(^{59}\).
Energy conducted either to or from the thermocouple tip

\( q_c \) energy convected from the probe

\( q_s \) energy created by shear heating at the surface of the probe

**FIGUR 2.3. Heat fluxes present in the thermocouple**

Generally, the errors which occur from conduction and shear heating are evaluated by balancing each against the energy convected from the surface and then calculating the total error by superposition. This procedure is considered acceptable when the errors are small.

**Inertia and heat conduction errors**

The error due to heat conduction along the thermocouple probe was investigated by van Leeuwen, Wiegand and Hulatt and Wilkinson.

The calculation of \( T_p \) is simplified, when the temperature across the probe is assumed to be uniform and when no heat is exchanged between the thermocouple tip and the wall of the probe. This assumption is fulfilled when the junction is small, in direct contact with the flowing melt, and highly insulated from the rest of the probe.

The simplified energy equation may then be written in the form.
\[ \rho \cdot c \cdot v \cdot \frac{\delta T}{\delta t} = \alpha \cdot A (T_m - T) \quad (2.14) \]

where
\( \rho = \) density of thermocouple construction material
\( c = \) specific heat capacity of thermocouple
\( v = \) volume of junction
\( \alpha = \) coefficient of heat transfer
\( A = \) area of heat transfer.

The actual recorded temperature of the probe (T) is defined by the previous temperature (T_1) and the local, true melt temperature (T_m).

\[ T = T_1 + (T_m - T_1) \cdot e^{-t/\tau} \quad (2.15) \]

where
\[ \tau = \frac{\rho \cdot c \cdot v}{\alpha \cdot A} \quad (2.16) \]

The time constant, (\( \tau \)), is small, when the specific heat capacity, c, as well as the density of the thermocouple construction material and the volume of the junction are small, or when the heat transfer coefficient and the area of heat transfer are large.

Geibel et al \(^{59}\) found a rate of time response of 1 sec. for a thermoprobe with a wall thickness \( s = 0.2 \) mm. Higher flow velocities, such as those found during injection, may shorten the rate of time response. However, this increases the shear heating at the surface of the probe.

The calculation of heat conduction error assumes steady state, a constant melt temperature across the cross-section, and a constant coefficient of heat transfer (\( \alpha \)), between melt and thermoprobe. The thermoprobe is simplified when considered as a circular thin walled tube (for the length between \( T_p \) and \( T_w \)), Fig. 2.4.
The simplified energy balance for a segment $dx$ in the axial direction of the probe may be written

$$\frac{dQ}{dx} = \frac{dQ}{dx} = \lambda \frac{d^2T}{dx^2} A \ dx = \alpha(T - T_m) \ U_x \ dx$$

When this equation is solved for the usual boundary condition, the heat conduction error $\Delta T_C$ is given by

$$\Delta T_C = \frac{1}{\cosh \left( \frac{x U}{\lambda A} \right)}$$

For a circular thermoprobe

$$A = \pi (R^2 - r^2)$$

When the wall thickness $s$ of the thermoprobe is small then

$$2R \approx R + r$$

$$s = R - r$$

Equation (2.17) may be rewritten
\[
\Delta T_c = \frac{1}{\cosh \sqrt{\frac{\alpha \cdot h^2}{\lambda \cdot s}}}
\]

Equation (2.18) shows, that the heat conduction error is small when the distances between probe and wall are large, the coefficient of heat transfer high, the thermal conductivity of the material of construction is low and the wall thickness of the probe is small.

Hulatt and Wilkinson \(^{283}\) state that results calculated from Equation (2.18) have been widely accepted as valid. But, in any case, the error is usually small and can be neglected. However, thermoprobes used for melt temperature recording in production have to be rugged enough to withstand the forces that occur. A rugged design has a relatively large mass and the heat conduction error cannot be ignored. Wiegand \(^{246}\) refers to investigations of PT 100 thermosensors with a high conductivity and found a \(\Delta T_c = 0\) to 0,6. Finding the exact temperature requires that the wall temperature, \(T_b\), to be measured. The corrected melt temperature is then given by

\[
T_m = \frac{T_p - (\Delta T_c \cdot T_b)}{1 - \Delta T_c}
\]

Energy is conducted from the junction along the thermocouple when the melt is hotter than the probe and therefore, the correction is positive. Conversely, if energy is conducted to the junction, the correction is negative.

The heat conduction error disappears, when \(T_p\) equals \(T_b\). Therefore, the use of double thermocouples and built-in heating elements is widely used in injection moulding to reduce heat transfer and conduction effects by making the housing temperature the same as the thermoprobe tip \(^{8}\).
Shear heating error

If the conduction along the thermocouple probe is neglected, the energy convected away from the probe must equal the energy dissipated at the surface of the probe by the shear heating effect.

Hulatt and Wilkinson [283] reconsidered the work of van Leeuwen [286] and proposed the following equation for calculation of the shear heating error:

\[ \Delta T_s = m \left[ \frac{2u}{r_w} \right] \frac{2r_1}{N_{Nu} \lambda_{melt}} \]  

Equation (2.20) shows that the correction to be deducted from the recorded polymer melt temperatures is a function of the orifice size through which the melt is flowing. In order to be able to evaluate the shear heating correction it is necessary to know the consistency index at the uncorrected temperature, as well as the other parameters which are necessary for the calculation of the conduction correction.

Radial and tangential temperature differences are known to exist within the flowing melt [53]. *

*) \( \dot{\gamma} \) as a function of radius for a circular pipe is given by

\[ \dot{\gamma} = \frac{\Delta P \cdot r}{\Delta l \cdot 2 \eta} \]

and viscous heating per unit volume is \( C_{\rho} / \rho \) \( dT = \tau \cdot \dot{\gamma} = \eta \cdot \dot{\gamma}^2 = r^2 \eta \).

Hence

\[ dT = \frac{\rho}{4 \eta \cdot C_{\rho}} \left( \frac{\Delta P}{\Delta l} \right)^2 r^2 \]

which is clearly a maximum when \( r \) is maximum, i.e., \( r = R \) at the wall.
The determination of an average melt temperature, i.e., a property of the melt en masse, as compared to a point value, necessitates that the position of the thermocouple in the duct, the relative weight of the thermocouple reading and the velocity profile of the flowing melt are taken into consideration.

Wiegand\textsuperscript{246} states that a mass average temperature, calculated by giving the same weight to all measurements across the duct, leads to an error of approximately 10$^\circ$C when compared to an average weighted in proportion to the velocity profile. He proposes the following formula:

$$T_m = \sum_{i=1}^{n} \frac{T_i}{A_i} \frac{A_i}{A_{\text{total}}} \frac{v_i(r)}{v_m}$$

(2.21)

where

- $A_i = 2\pi r \Delta r$ (for a circular tube)
- $A_{\text{total}} = \pi R^2$
- $v =$ velocity

When a single radial position of the thermoprobe is used he suggests a position between 1/3 to 1/2 from the wall, because this layer contributes with the greatest weight to the mass average temperature.

**Summary**

During plastication, only a few variables can be selected for control because such parameters as screw geometry, injection time, holding time and mould open-time frequently are fixed by other considerations, and cycle time reduction can only be achieved by reducing the available screw rotation time. However, a proper choice of plasticating variables can significantly improve melting and mixing without greatly increasing the melt temperature. The improved melting and mixing provides greater flexibility in mould filling, as a wider range of injection rates and injection pressures will fill a given mould.
2.2.3. The Injection Process

During the injection phase of the moulding cycle, the melt is forced through a nozzle into the mould, which includes the sprue, the runner and the gates connected to the cavities. Melt temperature and pressure in the mould during injection are important process variables and are closely related to the final quality of the moulded parts.

For a given mould geometry and nozzle size, the nozzle pressure of the melt \( p_n \) is a function of screw-forward velocity \( v_s \), melt temperature \( T_m \) and external disturbances such as back flow valve leakage. The nozzle pressure is proportional to the injection speed. This is because of the shear force created from the viscous melt pushing through the downstream passages of the cavity. The melt temperature is related to the melt viscosity that affects the nozzle pressure.

In attempting to develop a model of the injection process most analytical work is divided in two parts:

(i) The flow of the polymer melt in the nozzle assembly of the injection moulding machine, and the sprue, runner and gate system of the mould

(ii) The flow in the mould cavity itself.

The reason that the work has been broken up into two parts is that there are differences in the choice of suitable coordinate systems, in the appropriate simplifying assumptions, and consequently, in the solution techniques for the two analyses which make combining them into a single analysis inconvenient.

In the following section stress is laid on the melt flow into the mould cavity.

Cavity filling

The cavity filling may be divided into three stages\(^{61}\)

(i) A molten polymer flows from the narrow constriction at the gate into the cavity and usually spreads in an approximately radial manner.

(ii) After the corners are filled, there is a transition region in which the front changes from a circular shape to an almost flat profile.
The nearly flat front continues to move forward until the cavity is filled.

A rigorous analysis of cavity filling, without simplifying assumptions of doubtful validity is very difficult, if not impossible, to carry out for the following two primary reasons. One is the complicated form of rheological equations of state, and the other is the complex flow geometry encountered in many practical situations.

In the past, some serious attempts have been made to give a physical-analytical interpretation of the cavity filling. Starke has summarized the effects which must be considered in a mathematical treatment.

(i) Changes in cross-section of the mould geometry
(ii) Shear heating and its influence on viscosity
(iii) De-compression cooling and its influence on viscosity
(iv) Boundary cooling and its influence on viscosity
(v) Pressure changes and their influence on viscosity
(vi) Boundary cooling and its influence on the geometry of the fill volume
(vii) Compressibility
(viii) Thermal volume contraction

In principle all effects can be formulated mathematically and solved. The mathematical treatment, however, is complicated because two processes are superimposed; the non-steady flow of a non-Newtonian melt and the non-steady heat transfer. Also, digital computation is discouraging because of the core storage and execution time requirements, as well as the sophisticated programming required.

In principle, two components of flow may be found during cavity filling. The first is the shear flow, which in its simple form is found, e.g., with a melt flowing through a runner with a constant diameter. The second is the elongational flow, which is found e.g., in the middle layer of the radial spreading flow in a disc. With increasing shear rate, shear viscosity decreases. Elongational viscosity increases for low density polyethylene, but decreases for polypropylene with increasing shear rate. However, the two types of flow do not exist separately. True flow is actually a mixture, since even in shear flow at stress \( \tau \) there is a \( \tau^2/G \) elastic component.
The unsteady-state shear flow which exists in round runners during injection was investigated by Kohler. No experimental measurements of elongational flow in the shear rate range found in injection moulding have been recorded.

Even the treatment of polytropic, in-compressible flow-processes without boundary cooling in the case of a flow-channel with constant simple geometry is a complicated problem, and only an iterative solution is possible, at a considerable computational expense.

Therefore theoretical studies, analytical and experimental studies, technological tests as well as laboratory measurements and flow visualizations have been applied in order to understand the cavity filling process.

**Theoretical studies**

The aim of the theoretical approach is to predict velocity and temperature profiles during the cavity filling process. Such studies are based on equations derived from the three fundamental equations of continuity, momentum and energy and a flow equation.

Berger and Gogos have simulated the radial filling of a circular, center-gated disc, by treating the channel leading to the cavity and the cavity itself as one flow system under conditions of constant inlet pressure. In the numerical simulation of the filling they solved the fundamental equations using a power-law model. They concentrated on the detailed temperature and velocity profiles in an attempt to investigate the formation of the surface layer which freezes during the filling process. The theoretical prediction showed that the shape of both the velocity and the temperature profiles will be affected by the initial melt temperature and the injection pressure, because, they in turn affect the rheological properties. It was also found that the shear rate goes through a maximum somewhere near the wall.

They did not compare their predictions to any experiments. This study was extended by Wu, Huang and Gogos to include additional materials and to give more detailed temperature and velocity profiles.
Pearson has suggested a model for filling by radial flow in a geometrically simple, flat circular cavity of constant shallow depth, with an entry at the center. He assumed a linear pressure drop across the mould, and gives an outline of a computational procedure for a simulation and numerical solution scheme using a finite difference approximation.

Other authors found certain inconsistencies in the numerical method and disagree with his expression for evaluating the average temperature of the newly formed melt front.

Harry and Parrott proposed a model based on the filling of a rectangular cavity with a gate, which occupied the whole cross-section of the cavity, assuming a one-dimensional flow. They have attempted to account for the two controls, pressure and flow rate, of the injection moulding machine. Initially flow may be roughly equal to the maximum output rate of the pump, since the hot melt does not offer sufficient resistance to obtain the preset source pressure. When sufficient resistance is experienced, it is the maximum source pressure that controls the injection mould filling operation. (See Fig. 2.5 and 2.6).

In spite of the calculus complexity the agreement between experiment and prediction was not completely satisfactory. Some authors point to the constant pressure gradient as a severe assumption. Stevenson et al. also point out that a "pressure" transducer flush-mounted in a mould does not measure the pressure but rather a component of the stress which is a combination of the pressure and extra stress. The distinction between pressure and stress is important in determining the correct form of the equation of motion.

Kamal and Kenig simulated the filling, packing and cooling stages in a center-gated half-disc cavity. They used a generalized Newtonian fluid constitutive equation and a power law viscosity model, and suggested a numerical solution for radial flow. The use of a constant heat transfer coefficient for the thermal boundary condition at the melt-mould interface was examined by Hieber, who concluded that equating the melt temperature at the cavity wall to the initial mould temperature (or the temperature of the circulating heat-transfer fluid) is a simple and reasonably accurate thermal boundary condition for short fill times.
Fig. 2.5 Functional diagram of the hydraulic system for reciprocating screw injection unit

1. System pressure relief valve
2. Directional valve for injection cylinder and hydraulic motor
3. Pressure reducer for injection pressure
4. Throttle valve for screw forward velocity
5. Directional valve for stepped injection pressure
6. Relief valve for stepped injection pressure
7. Valve combination for back-pressure
8. Throttle valve for hydraulic motor
9. Directional valve for screw movement
(i) **Screw-forward velocity** is programmed to be a constant 30 mm/s. The curve shows that this velocity is maintained with good accuracy and reproducibility. Hydraulic pressure varies for the 20 shots due to fluctuations in viscosity and resistance to flow in the cavity.

(ii) Screw forward velocity is programmed to be 80 mm/s. The curves show that there is not sufficient pressure (max. 70 bar) to maintain this velocity. Fluctuations in viscosity and resistance to flow result in variations in the level of velocity. Hence, velocity is not constant but is determined by the flow geometry.

Machine: Netstal N 150 / 75 - 3 SyCap
Moulding: PMMA cover (Approx. 120 x 80 x 2 mm)
Process. con.: $T_m / T_f$: 225 °C / 60 °C

Curves are redrawn from oscilloscope for 20 mouldings

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Fig. 2.6 Hydraulic pressure and screw forward velocity (Ref. Stubgaard, Styresystemers effektivitet) (1979)
Kamal, Kuo and Doan\textsuperscript{68} extended the numerical model of Kamal and Kenig to study the behaviour in rectangular cavities in the injection, packing and cooling stages. Rothe\textsuperscript{69} simulated the flow of a fluid having a constitutive equation and calculated temperature, speed and pressure profiles for the intermittent filling process. Stevenson et al.\textsuperscript{66,70} simulated the filling of a center-gated disc cavity with ABS, and presented\textsuperscript{71} a graphical method based on dimensional analysis for estimating the injection pressure and clamp force. Bigg\textsuperscript{72} suggested the use of a numerical analysis and computer logic to simulate mould filling. Williams and Lord\textsuperscript{73} divided a model of the mould filling process into two parts: (a) the flow in straight and tapered, hot and cold walled circular flow channels (b) the flow in the cavity. A finite difference analysis for the temperature, velocity and pressure fields for each part is described. Thiene\textsuperscript{74} calculated the velocity, temperature, pressure, and fluidity fields as a function of time and position, together with the following individual values: flow front coordinates, mean velocity, mean temperature, mean fluidity, shear rate profile and the thickness of the solidified layer.

Analytical and experimental studies

The analytical and experimental studies are usually based on a less sophisticated mathematical approach by incorporation of greater simplification and additional assumptions in the differential equation system. The work of Barrie\textsuperscript{76-79} comprises the mould filling stage only and excludes any subsequent attempts to pressurize the melt in the filled cavity. The mould filling analysis is divided in two parts; (a) the flow in the delivery channels from the injection barrel (b) the flow in the cavity. Barrie also points to four distinct factors, which must be included in any quantitative description of flow behaviour of a non-Newtonian melt, namely: (a) the degree of non-Newtonian behaviour of the melt (b) the viscosity of the melt (c) the thermal and freezing-off properties of the melt (d) the geometry of the flow.
Barrie found that the presence of the nozzle, sprue, channels and gate between the reservoir and cavity causes a substantial pressure loss before the melt reaches the cavity and that this loss might exceed 50% of the pressure at the injection end. The complexity of these effects, coupled with swelling and other viscoelastic effects at the entrance to the cavity, makes it difficult to treat the cavity, nozzle, channel and gate as one system as, e.g., proposed by Berger and Gogos\textsuperscript{62}).

Barrie's work was supported by practical observation in the case of mouldings made from a foamable system. A section of the moulded part shows a constant solid skin section. However, in the non-isothermal situation a layer of frozen polymer appears in time, which reduces the effective plate separation. Its thickness $\Delta x$ can be approximately estimated assuming an infinite slab of melt at $T_1$ is in contact with a thermally conducting wall at $T_0$, provided that the "freeze off" temperature and thermal diffusivity are known. Alternatively he proposes a purely empirical expression where the thickness of material frozen off is proportional to the cube root of filling time; substituting the reduced separation into the expressions for the pressure components and adding them yields the pressure estimate.

Good agreement with the observed pressure was obtained only when the empirical estimate of $\Delta x$ was used. The results of Berger and Gogos\textsuperscript{62}) predict a layer of frozen polymer which increases in thickness as one follows it away from the disc entrance at any time. At the instant of fill the difference in pressure at the disc entrance for the isothermal and non-isothermal flows was only about 4.5%. Berger and Gogos confirm that such a slight modification of the isothermal momentum equation should result in good estimates. Furthermore, at high flow rates the time to fill the cavity will be unaffected by the cavity wall temperature, making the isothermally predicted fill times reasonable.

The implicit steady state assumption used in Barrie's work is the most misleading, since it implies that the entrance pressure has a unique value when the cavity is being filled at a constant flow rate. This is true at any instant but both change with time. To say that the cold cavity is being filled at a
constant flow rate during which time the pressure at the disc entrance is also constant, is inconsistent, since more pressure is required to keep a colder material flowing at a given rate than a hotter one.

Grinblat\textsuperscript{80-81}, on the basis of experiments, assumed that the melt flows into the cavity within a immobile envelope of cooled polymer.

Ballmann and Toor\textsuperscript{82} and Ballmann, Shusman and Toor\textsuperscript{83,84} treated the cavity filling process as a transient and non-isothermal flow of a non-Newtonian, power-law fluid. They were the first to use this approach in treating the axial filling of a rectangular cavity. Despite the excessive number of assumptions on the energy equation their results are useful and interesting.

Bauer\textsuperscript{85-86} reported experimental results on the filling of a rectangular, thin mould with low-density polyethylene. He also shows that the melt becomes distorted as it contacts the wall. The flow front velocity was derived from measurements with thermocouples built into the cavity. This gave for the investigated polymers a characteristic profile: a steep slope to a minimum, rise to a maximum, gradual decrease, more or less depending on the polymer used. The flow front velocity was calculated using the continuity equation and the velocity from the screw forward velocity, based on simplified assumptions like isothermal filling and incompressibility of the polymer. Depending on the polymer this gave a more or less reasonable agreement between calculated and experimental values.

Moroni, Ferrario and Casale\textsuperscript{87} calculated the melt flow rate in steady state conditions in a rectangular section using the Ostwald/de Waele power-law equation, and using an empirical correlation between the length of a spiral moulding and viscosity at high and constant shear stress. Maximum flow length in a mould was found by considering the effect of decreasing cavity height with time of melt flow. The filling rate was found to be a product of two terms. The first term contains the pressure gradient along the flow direction, which was considered constant up to the compression stage of the material and equal to the ratio of pressure to final flow length. The second term was a function of time. The maximum flow length was found under the boun-
dary condition that $z = 0$ at $t = 0$, $z = L$ at $t = t_c$ and substituting the differential pressure gradient with the constant value $(\frac{P}{L})$.

Bassow and Feliptschuk in an analytical and experimental investigation, similar to the work of Moroni et al., derived an equation for the maximum flow length in a cavity. Their work showed a fairly good agreement over long flow lengths (> 800 mm).

Trepte and Richter developed a differential equation for the mould filling. They also gave the, so far, most exact description of the melt condition in the reservoir by using the relationship between screw displacement, pressure and melt changes in the reservoir and derived from this basis an equation for the shot volume as a function of measurable pressure and displacement processes.

Starke has proposed a model for the cavity filling, based on a system of sub-models. For the development of the model only the following input data are assumed: geometric and thermal data for the mould, thermal and rheological data for the polymer, and the machine input-variables for the injection moulding machine. The principal item of the model is the geometrical-mechanical model of the cavity filling. It takes the following effects into account.

(i) Non-Newtonian flow properties of the melt
(ii) Accommodation of the complicated geometry of the filling volume including the nozzle and runner system.
(iii) Decompression of the melt.

Starke then develops a system of transport equations for isothermal flow.

In preliminary models the conditions for the determination of the effective injection pressure, the conditions for achieving a homogeneous melt and the formulation of the flow properties of the melt were discussed.

Further correction of the calculations may be considered as additional models. They include:

(i) The thermally dependent geometrical changes of the filling volume due to freezing of the boundary layers.
(ii) The change of viscosity of the melt due to non-isothermal
flow, which is also influenced by decompression cooling, heat dissipation and heat transfer effects.

Cavity geometry, rheological constants and the specific volume used in the system of transport equations were iteratively included and the equations solved for a polytropic flowing, compressible non-Newtonian liquid. Not included were the effects of pressure on viscosity, the influence of cavity hydraulic friction on changes of flow directions, Diesel-effects in the cavity, possible elastic turbulences and entropyelastic deformations. These effects, however, should be incorporated as empirical correction factors, as the present state of affairs does not permit a quantitative analytical treatment.

The exploration for a given practical purpose of the derived velocity, pressure and temperature profiles is done in later phases (post-models).

Technological tests as well as laboratory measurements and flow visualization

Spencer and Gilmore\textsuperscript{35-39} made photographs of the flow patterns of polystyrene in a disc-shaped cavity.

Leibfried\textsuperscript{5} filmed flow in a specially designed mould with glass windows and incorporated a mirror for visualisation of the vertical and horizontal velocity profiles. He divided flow in three profiles (i) the flow front (ii) the moving melt behind the flow front (iii) transverse velocity profiles in and behind the flow front respectively.

Schmidt\textsuperscript{90} used a specially designed mould attached to a modified Instron capillary rheometer. In conjunction with this mould, a tracer technique has been developed to illustrate flow patterns so that the deformation and velocity of fluid elements in a mould cavity can be investigated and the extensional and shear flows analyzed, since the injection moulding process is not dominated by only one type of flow.

White and Dee\textsuperscript{60} in a similar set-up studied flow patterns of rheologically characterized low density polyethylene and polystyrene melts under various moulding conditions. However, the patterns presented by these authors are misleading because part of each tracer was left behind in the reservoir due to the large shear gradient near the reservoir wall.
Generally, melts being injected under high injection rates are in the unstable flow region and distorted extrudates are flowing into the mould (Confirmed by research with a mould with variable runner and gate geometry by the author of this thesis). However, the melt flow instability would not logically seem to be the cause of jetting. A major goal for injection moulding research could be the development of a criterion for jetting.

Sleeman and West investigated the types of flow occurring in the runner, gate and cavity of a cylindrical bar mould for polystyrene. The results show low bend pressure drops in the runner, suggesting a non-isothermal shear flow resulting in the absence of turbulence. The type of flow in the gate depends markedly on the mould temperature. The cavity fills by a jetting mechanism involving spiral formation unless the injection speed is low.

Summary

The filling phase in injection moulding can be described by the three fundamental equations together with a suitable flow equation. However, a solution of the equations is based on several assumptions and good agreement with experimental values are only obtained for simple geometries and long flow lengths.
2.2.4. The Solidification Process

After injection is completed, packing pressure control immediately follows the purpose of which is to allow more polymer into the mould, thus compensating for volumetric shrinkage during cooling. It is accompanied by a steep rise in pressure until it reaches its maximum value, where it is kept constant during the remainder of the holding time. The packing or compression stage is then defined from the time that there are no more empty spaces in the cavity and stops after the gate has solidified. During packing partial solidification of the melt takes place. A careful interlinking of control of the injection and packing stages is essential if optimal control is to be achieved.

Hydraulic pressure during packing \( (P_h) \), mould temperature \( (T_f) \) and holding time \( (t_p) \) are the important input variables during the packing process. Cavity pressure \( (P_c) \) and melt temperature \( (T_m) \) are process state variables.

Two factors compete with regard to pressure variation in the cavity during the packing stage. The first is the flow of the polymer into the mould which leads to an increase of pressure corresponding to a decrease of the specific volume of the polymer in the cavity. The second factor is the cooling of the polymer which continues during all stages of the injection moulding process. Cooling acts to reduce the pressure in the cavity.

Very little work is reported in the literature regarding a theoretical analysis of the packing stage. The main contribution is an attempt by Spencer and Gilmore\(^{37}\) to calculate the maximum pressure in the mould by means of an equation of state and an empirical relation for filling time.

The bulk of the other work deals with the thermodynamics of the packing stage, especially as it relates to shrinkage\(^{68}\), or the effect of screw-forward time on the discharge from the cavity which takes place with a premature retraction of the screw\(^{95}\).

The cooling stage, in principle, comprises the total period in which the melt is cooled by virtue of the lower temperature of the mould. Therefore, cooling and solidification also take place.
during injection and packing, the effect, however, being most pronounced for the outer layers of the moulding. As the amount of heat exchanged during injection is relatively small most analyses treat the cooling process as a separate process, starting either when the maximum packing pressure has been reached\(^9\), or when the gate has solidified and melt is no longer injected into the cavity\(^7\). In both cases the cooling stage ends when the moulding is ejected.

Effective control of the final solidification is most important if a good quality product is to be obtained. Also the time of cooling is important as this stage on average comprises 50 to 70% of the cycle time.

During solidification two situations exist side by side. The first is heat removal, the drawing away as rapidly as possible of the heat released to the cavity wall by the solidifying melt from the surface through the mould to the cooling channels. The second is heat transfer within the mould which can improve the quality of moulded parts by smoothing temperature profiles on the cavity surface and thus within the solidifying polymer.

An analysis, therefore, may be divided in two parts, where the first part is related to the moulding and the second part to the mould\(^9\).

The variables involved in a heat transfer analysis of the moulding are:

(i) The geometry and properties of the melt (thermal conductivity, viscosity and density)
(ii) The initial and final temperature of the plastic compound and the mean temperature of the cooling medium.
(iii) The overall heat transfer coefficient combining the basic elements of the materials involved, i.e., coolant and properties of the mould material and design.

The variables involved in a heat transfer analysis of the mould are:

(i) The amount of heat exchanged by convection, radiation and conduction.
(ii) The thermal conductivity of the mould material affects the heat transfer within the mould itself.
(iii) The heat transfer coefficient of any fluid is a function of the flow characteristics of the fluid itself.

(iv) The temperature difference between the coolant and the part to be cooled is also important.

A theoretical analysis of the cooling phase should comprise an unsteady-state transfer of heat under pressure in a melt that exhibits variable properties. Since the heat transfer is accompanied by phase transformations, the resulting non-linear partial equations, which describe the system, are not amenable to explicit analytical solutions*).

A number of workers 4, 97-102 treated the problem as a single-phase, variable property problem with varying sophistication in the mathematical solution. The theoretical basis for such calculations is based on a non-stationary temperature field described by a Fourier differential equation, which was solved by Faltin 103. It is derived from an energy balance on an infinitesimal, one-dimensional plane layer, where the solidification process is considered to take place in a liquid held between two plates at \( T_f \) and spaced apart a distance 2 \( h \). The moulded part is considered thermally symmetric around the centerline. The governing parabolic differential equation is expressed by 104):

\[
\frac{\partial^2 T}{\partial x^2} = a \frac{\partial T}{\partial t}
\]  

Equation (2.22) can only be solved analytically, based on the following boundary conditions:

(i) One-dimensional heat conduction is assumed.

(ii) No ambient losses due to radiation and convection.

(iii) Thermal diffusivity \( a \) is assumed constant (usually an "averaged effective value" 101) is used).

(iv) Latent heat of solidification neglected for semi-crystalline polymers (usually included in the specific heat capacity \( c_v \) of the melt).

*) In the classical manner, the solidification problem known as the Stefan-Neumann problem is solved as a two-phase heat-transfer problem with a moving boundary.
(v) No air gap between moulding and cavity surface.
(vi) Injection is considered instantaneous, that is at time $t = 0$ the temperature in the moulding should be equal to the melt temperature ($T_m$).
(vii) The temperature at the surface of the moulding should fall instantaneously to the mould temperature ($T_f$).
(viii) The mould temperature should remain constant during the whole cooling phase.
(ix) Resistance to heat transfer between the mould and the coolant is neglected.

Based on the above conditions the Fourier differential equation can be solved as shown in a following section on calculation of cooling time. The simplified solutions have lately been replaced by more sophisticated ones, usually based on numerical methods and taking more parameters into account.

Kenig and Kamal\textsuperscript{198} solved the unsteady-state conduction equation for a cylindrical mould filled with polyethylene and cooled under pressure. They introduced temperature and pressure dependent material parameters into the cooling algorithm, but assumed that thermal diffusivity was independent of pressure. Their analysis yielded information regarding the progression of the solidification front with time. Their predicted temperature profiles matched those measured by the instrumented mould within $\pm 5^\circ \text{F} (\pm 2.8^\circ \text{C})$ except at short times in the region near the cold wall. It was interesting that the time needed for the gate to solidify may be calculated by using their calculation for cylindrical mould solidification.

Broyer et al.\textsuperscript{105} adapted the flow analysis network method (FAN-method) to isothermal filling of a rectangular channel with a Newtonian fluid. They also calculated the amount of melt added during the packing stage and the final mean density of the moulding on basis of the degree of melt solidification inside the mould at the end of the packing stage, as well as the melt density as a function of temperature and pressure.

Siegert et al.\textsuperscript{94,106} formulated equations for calculation of pressure and temperature distribution during the packing stage with superimposed cooling. No experimental data was published.
Bassow et al.\textsuperscript{107} analyzed solidification of polyamide in a mould as a function of packing time. They assumed melt temperature in the core to be constant and a linear temperature profile in the not yet solidified layer. Correlation between calculated and experimental data was only fair.

Janeschitz-Kriegl\textsuperscript{108} described the interaction between mould filling and heat transfer in the form of a dynamic model for the growth of the solidifying layer.

Dietz\textsuperscript{109} analyzed the cooling of a crystallizing polymer under pressure taking the pressure drop into account and using a $pVT$ diagram to obtain material functions. Thermal conductivity and diffusivity of low density polyethylene were determined in earlier experiments\textsuperscript{110}. A numerical cooling model based on these material functions was established and predictions showed good agreement with experiments.

\textbf{Discussion of boundary conditions}

Analyses have shown that for the main part of injection mouldings the wall thicknesses determining cooling time may be considered as an infinitesimal, one-dimensional plane layer. Other cross-sections can be solved by the methods given by Tautz\textsuperscript{111}.

The ambient losses due to radiation and convection are important for the temperature stability of the mould. They can be estimated from a heat balance of the mould. It seems fair to assume, that they do not have a significant influence on the calculation of the cooling of the moulding.

The thermal diffusivity is not independent of pressure and temperature. However, values for thermal diffusivity are difficult to find in the literature. Often, values also differ between different sources. The pressure dependence of the thermal diffusivity is probably of less significance. At the same time there are quantities which vary with pressure. There are relatively few reports on experimental studies of the thermal conductivity of polymers under pressure. Generally, polymers with high compressibility favour high pressure response in conductivity. The effect of pressure on density can be estimated fairly accurately from $pVT$-
diagrams. The specific heat capacity as a function of temperature has been published for a limited number of polymers only. Such data can also be obtained from high accuracy pVT-diagrams.

The temperature dependence of the thermal diffusivity is quite distinct\(^{14}\) even for amorphous polymers. For highly crystalline polymers the temperature dependence cannot be neglected. For practical calculations of cooling times Wübken\(^{16}\) has introduced the concept of "averaged effective values". An effective value is a quantity assumed constant, which is used in simplified calculations on the condition that the same degree of cooling is achieved as if a temperature dependent thermal diffusivity is used. In theoretical work, the lack of published reliable data is probably the biggest source of error introduced in the calculations.

Despite the sensitivity of crystalline polymers to cooling conditions, an adequate analysis of crystalline polymer solidification in an injection mould has not been developed. Only a few studies have tried to predict the thermal history during cooling at any location within the material as well as the resulting crystalline structure. In order to resolve the position-dependent thermal and structural history, the analysis of transient heat transfer must incorporate the latent heat of crystallization and the crystallization kinetics of the polymer. The general procedure is to convert the latent heat of crystallization into an equivalent temperature change through specific heat and to ignore the kinetics of crystallization\(^{112}\). This method, however, does not predict accurate temperature profiles\(^{113}\).

Transient heat conduction with heat generation due to crystallization, assuming heat transfer principally in one direction and thermal conductivity to be constant, is expressed by the nonlinear, parabolic differential equation\(^{114}\)

\[
\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + \frac{Q}{\rho \cdot c_p}
\]

(2.23)

\(Q\) is the heat generation via polymer crystallization and is time and pressure dependent. The rate of heat generation \(Q\) is expressed by
\[ Q = \rho_c \Delta \bar{H}_c \frac{dx}{dt} \]  

(2.24)

where \( dx/dt \) is the change in crystallinity with time, \( \Delta \bar{H}_c \) and \( \rho_c \) the latent heat and density at 100% crystallinity respectively. The crystallinity is related to the volumetric growth of spherulites as follows

\[ x = x_w \left( \frac{V}{V_m} \right) \]  

(2.25)

where \( V \) is the time dependent spherulitic volume and \( V_m \) is the volume of a spherulite at impingement plus the inter-spherulitic volume associated with each spherulite.

Equation (2.23) is non-linear and is not readily amenable to an analytical solution. It can be solved using the Crank-Nicolson (115,116) finite difference technique.

Meyer (117) proposed for thick, semi-crystalline mouldings an empirical equation for the cooling time (\( t_k \)), but few details were available.

The assumption of contact between moulding and cavity is not fulfilled for mouldings with a high shrinkage (semi-crystalline polymers) and a thick wall thickness. Some polymers, e.g., polypropylene tend to sink rather than to void during cooling and may retract more from the wall. Wübken (116) states that the influence from a thick wall thickness to some extent is compensated as the air gap becomes of minor importance with longer holding times.

The melt temperature usually drops during injection. This effect is counteracted by the temperature increase due to shear with high pressure drops in the gate.

The assumption of an instantaneous temperature drop on the cavity surface is probably fulfilled at least for the outermost layers.

The mould cavity surface temperature is not constant but varies in a cycle. It is also subject to periodic variations during production, corresponding to the control characteristic of the mould tempering unit. An arithmetic mean of the two extreme values is a good approximation. Some workers (102) have compensated this influence in their calculations.
The neglect of resistance to heat transfer between the mould and the coolant is a fair assumption for steady-state conditions. The transfer is dependent on the interface heat transfer coefficients which, generally, are considerably higher between the metal and cooling water than between the polymer and metal because the water can be maintained in turbulent flow, increasing the heat transfer capability.

Calculation of cooling time

The cooling time is calculated from a given melt, mould and ejection temperature $^{97-102}$. The theoretical basis for such calculations is based on a non-stationary temperature field described by a Fourier differential equation. It is derived from an energy balance for an infinitesimal, one-dimensional plane layer (Fig. 2.7).

\[
\hat{q}_x = -\lambda \frac{\partial T}{\partial x} \quad \hat{q}_{x+dx} = \hat{q}_x + \frac{\partial \hat{q}_x}{\partial x} \, dx \quad \hat{q} = \rho \, c \, \frac{\partial T}{\partial t} \, dx
\]

Fig. 2.7 Temperature distribution in a moulding at ejection.

In Fig. 2.7

- $\hat{q}$ = Density of heat flow rate
- $T$ = Temperature
- $t$ = Time
- $x$ = Distance
- $\lambda$ = Thermal conductivity
- $\rho$ = Density
- $c$ = Specific heat capacity
- $s$ = Wall thickness.
The partial differential equation is derived from

\[ \frac{\partial q}{\partial x} = q \frac{\partial x}{\partial x} + \frac{\partial q}{\partial x} \]

\[ \frac{\partial T}{\partial t} = a \frac{\partial^2 T}{\partial x^2} \]  

(2.26)

with

\[ a = \frac{\lambda}{\rho c} = \text{thermal diffusivity} \]

Equation (2.26) can be solved analytically based on the boundary conditions given in the above section. Hence the following equation is derived\( ^{101} \):

\[ T - T_f = \frac{4}{\pi} \left( T_m - T_f \right) \sum_{n=0}^{\infty} \left\{ \frac{1}{(2n+1)} e^{-a(2n+1)^2 \pi^2 t / s^2} \sin \left( \frac{(2n+1)\pi}{s} x \right) \right\} \]

(2.27)

Equation (2.27) gives the temperature at any time and at any position in the moulding.

In the literature two criteria for ejection are given:

(i) The cooling front has advanced to the center of the plaque, that is, the maximum temperature \( T \) in the center has reached a temperature of dimensional stability.

(ii) The temperature of ejection \( T \) is taken as an average temperature across the moulding at the time of ejection.

One of the main problems is to define a "temperature of dimensional stability". In practice, the heat distortion temperature is often used which, however, is only a very rough guideline. Wübben\(^{16} \) suggests the empirical constant \( \Theta = (T - T_f) / (T_m - T_f) = 0.16. \)

Starke\(^{52} \) compared calculated and actual cooling times for a number of mouldings and found that the observed incongruity was not primarily dependent on the model used, but rather on production considerations (shape of article, injection moulding machine, etc.), uncertain material data and a criterion for ejection stability.

When the first criterion for ejection is used, that is the ejection temperature \( T_{E} \) is taken as the temperature in the center at the time of ejection, and equation (2.27) is simplified by considering the first term of the series only \( (n = 0) \) the following equation is derived:
$$T - T_f = \frac{4}{\pi} (T_m - T_f) e^{-\frac{a \pi^2 t}{s^2}} \sin \frac{\pi}{s} x$$

(2.28)

If this equation is solved with respect to time, the cooling time ($t_k$) becomes:

$$t_k = \frac{s^2}{\pi^2 - a} \ln \left( \frac{4}{\pi} \frac{T_m - T_f}{T_E - T_f} \right)$$

(2.29)

The first criterion of ejection is rarely achieved in a moulding with a thick wall (thickness: $s > 4$ mm), as the core in such mouldings may be plastic, even when the outer layers have solidified and cooled sufficient to eject the moulding. Therefore, it is more realistic to define the temperature of ejection ($T_E$) as an average temperature across the moulding at the time of ejection. If this definition is used the following equation for the cooling time ($t_k$) is derived:

$$t_k = \frac{s^2}{\pi^2 - a} \ln \left( \frac{8}{\pi} \frac{T_m - T_f}{T_E - T_f} \right)$$

(2.30)

Equations (2.29) and (2.30) become more exact with increasing cooling time, because the neglected terms of the Fourier series converge increasingly to zero. It has been shown\(^5\) that the error introduced is less than 1%.

The simplified equations (2.29) and (2.30) were solved and programmed for a calculator (Appendix G). The differential equation was also solved by numerical methods using two available programmes\(^5\). The two programmes were based on the Finite-Difference Method (FDM) and the Finite-Element-Method (FEM), respectively.

The finite difference programme (TFELD) was developed at the IKV Aachen\(^{118}\) and calculates also shrinkage and the distribution of internal stresses in a moulding with a simple geometry. Thermal properties are assumed constant and the programme is, in principle, only valid for amorphous materials. The finite element programme (FINEL) was developed at B & W, Copenhagen\(^{119}\) and calculates two or three dimensional thermal stresses. All material parameters including melting and solidifica-
tion can be described as a function of temperature. The calculated cooling curves for both programmes were in full agreement with published results for amorphous mouldings with simple geometries.

Cooling curves calculated after\textsuperscript{102} were also compared with the simplified programmes for a 2,5 mm ABS moulding. For cooling times of approximately 15 s the simplified programme predicted a cooling time approximately 1,5 s lower, even when an averaged mould temperature was used.

Wübken and Catic\textsuperscript{101} also integrated the differential equation (2.26) using a difference-method and found good correlation with the simplified equations (2.29) and (2.30) for longer cooling times. Equations (2.29) and (2.30) also show the relative influence from the variables. The influences from mould and ejection temperature on the cooling time are of the same order, melt temperature one order lower.

**Energy balance for the mould**

The requirement of the cooling system is to remove an amount of heat, in the cycle time, equal to that put in by the injection of polymer melt. The rate of heat removal depends on the rate at which heat transfers through the setting polymer to the polymer surface, the rate of transfer from the polymer to the metal of the mould, then through the metal and from the metal into the coolant. The transfers are dependent on the interface heat transfer coefficients, the surface areas involved and the various temperature differentials. Heat transfer within the mould depends on the thermal conductivity of the metal, its thickness and the temperature drop across it.

Although the importance of a constant cavity surface temperature is generally recognized, fairly little attention is given to the correct design of cooling channels and mould temperature controls. Here it must be noted that, in spite of the greatest accuracy of the coolant temperature, variation in the cycle time, melt temperature or ambient temperature will cause variation in the mould temperature.

Heat transfer within the mould was investigated by Craig and Miller\textsuperscript{120}, who compared computer-produced results based on a
finite element model using several relevant heat transfer equations with the results from a mould instrumented with surface and internal thermocouples. The results showed a fairly good agreement between computed and experimental values.

Such investigations are very useful for improving the energy balance of a given mould. A heat flow balance for the injection mould is also a prerequisite for calculation of cooling requirements and the lay-out of the cooling system \(^{16,100}\).

Summary

The solidification process is important in determining the morphology and final dimensions of the moulding. It also comprises a significant proportion of the cycle time. It is directly influenced by four of the five main variables. Especially for crystalline polymers it has been far less investigated as, e.g., the filling process. The results of the investigations, however, have provided more useful relationships than for other parts of the moulding process.
2.3. PREDICTION OF PROCESSING BEHAVIOUR FROM POLYMER PHYSICAL PROPERTIES

The physical properties that are important in injection moulding can be classified broadly as rheological, thermal, and bulk properties.

Rheological as well as thermal properties of polymer melts under processing conditions have been the subject of extensive research investigation. Numerous rheological equations and devices have been developed in an attempt to understand the flow behaviour of polymers. But few of the techniques of measurement simulate the rapidly varying conditions of shear rate and temperature experienced during injection moulding.

For the results of a test to be useful, the test must be well-defined and should give results which can be interpreted in a unique and concise manner. For the test to be well-defined, the details of the deformation which occurs in the melt should be known, although only direct control over the movement of the melt along the boundaries of the region in which the deformation occurs is possible. In order for the test to give results which can be interpreted in an unique, concise manner, the test results should allow the determination of a well-defined material function the definition of which depends neither on some arbitrary complexity in the deformation pattern nor on the assumption of a specific constitutive equation.

Rheological properties

The most popular methods for rheological characterization of fluids are those involving viscometric flows, which are measured by the use of capillary and rotational rheometers. Whisson found, in a comprehensive review of melt flow tests and their application to processing, that the complexities of developing suitable theoretical equations from apparent viscosity/shear rate/temperature data, which are applicable to practical conditions, have meant continued reliance on a single point test although the inadequacies are generally recognized.

Most material suppliers express the flow properties of their materials in the form of a melt flow index, or the length of flow in a spiral mould. The fundamental flow property, vis-
cosity, in the corrected form over the range of shear rates and temperatures is generally not readily available. Single point tests, such as a melt flow index, can serve to distinguish broad viscosity differences among polymers. These parameters can be grossly inadequate in ranking polymers correctly for injection moulding performance when subtle differences such as molecular weight distribution are introduced. In an attempt to derive more sophisticated data from melt index determinations, Menges et al. developed a programme for calculators to estimate a viscosity based on melt index determinations.

Empirical methods employing the injection moulding machine are widely used in conjunction with the actual production mould or an instrumented prototype. Alternatively, a mould having a defined flow path of a spiral is used in conjunction with an injection moulding machine to compare flow length or determine polymer viscosity under selected conditions of temperature and pressure.

With production moulds the minimum pressure/temperature method may be used. With this method the minimum pressure at a given temperature or the minimum temperature at a given pressure necessary just to fill the mould is determined. The minimum value is then increased with a fixed value for pressure or temperature. An inherent difficulty of this technique is that of judging a "full" moulding on which the minimum conditions are based.

The spiral moulding has been investigated by a number of workers. Holmes et al. made an engineering analysis of the test and found that the ultimate length of the spiral is a function of two groups of variables, one describing the process conditions, the other representative of the polymer's rheological and thermal properties. Weir et al. used an averaging technique for shear rate and temperature dependence of viscosity to determine a mouldability index (the index STV for shear-temperature-viscosity) to predict mouldability in the non-isothermal changing shear rate injection moulding process. This parameter was further correlated to spiral flow measurements, minimum cycle temperatures and moulding area diagram limits.

The superiority of the \( \alpha_{STV} \) value for predicting spiral flow
length was further evaluated for a number of ABS types by Mal-
pass 134) and for a number of different plastics by Deeley and Terenzi 135). However, Hagan et al. 136) point out that Weirs' treatment assumes a power law which most polymers do not completely obey and does not account for the change in shape of the flow curve as a function of temperature. Furthermore, the selection of low shear viscosity data limits the value of the theory.

Pezzin 137) checked experimentally the validity of the choice made by different researchers using styrene polymers and copo-
lymers. As a conclusion, the author proposed a correlation be-tween the spiral length and the melt viscosity at the same temperature and at a constant shear rate of 1500 s\(^{-1}\).

It appears from the above that spiral tests with a given mould or injection moulding machine do not give a concise characteri-
sation of the material, but more the complex relationship of material, mould, and machine.

**Thermal properties**

**PVT-data.** The work of Spencer and Gilmore 35-37) (Equation 2.1.) has been extended by researchers, who have proposed other forms of the pVT-relationships. Their equations differ from each other primarily in the number of material parameters (2 to 6) and the degree of accuracy which can be attained in the de-
scription. In a review of the practical application of pVT-
equations, Schenkel 138) states, that two parameters, generally, are insufficient for calculation of the specific volume in a broad temperature and pressure range, but that calculation six parameters are too strenuous, also when the so far achieved accuracy of the dilatometric methods are taken into consideration. The latter observation is emphasized by the difference in re-
sults when pVT-diagrams are recorded with instruments based on piston 139) or a bellows-technique 140) Generally, the latter me-
thod has provided results which are superior to the former me-
thod when compared with other determinations, e.g., density at room temperature 141).

By differentiating V in the equation with respect to p and T the relationships giving the compressibility and thermal ex-
pansion coefficients, in terms of the equation-of-state con-
stants, can be calculated. From measurements of these two
properties alone, however, it is not possible to evaluate
the equation-of-state constants.

The volumes calculated from the pVT-equation and, for that
matter, volume changes calculated from coefficients of expan-
sion and compressibility, assume that the polymer sample has
come to volume equilibrium at the given conditions.

According to Kosfeld\(^{142}\), the molecules are continuously try-
ing to improve their state of order with decreasing temperature. In
order to achieve the equilibrium state at each temperature, there is a certain amount of time passage necessary, which must be
less than that corresponding to the cooling rate. Amorphous
polymers reach their equilibrium degree of order above the
glass temperature \(T_g\) within the time of measurement. This
is not possible at temperatures below \(T_g\); the melt will then
pass over from a state of equilibrium to one of disequilibri-
um, i.e., to the frozen-in, or glassy state. This state is
distinguished, in general, by a greater heat content (enthal-
py). In this range there is a smaller coefficient of thermal
expansion compared to the molten state. In the glassy state
the molecules retain the state of order they have reached at
the glass temperature. At higher cooling rates the glass tem-
perature is shifted to higher values. Since at higher glass
temperatures a lower state of order prevails, a high cooling
rate causes a lower density or a greater specific volume than
do lower cooling rates (Fig. 2.8).

With semi-crystalline polymers, crystallization (and solidifi-
cation) take place below the temperature of crystallization
\(T_c\). As the cooling rate is increased, the crystallization
temperature decreases but quickly approaches a limiting value.
If the time available for crystal growing decreases, due to an
increased cooling rate, crystallization will be slowed down or
reduced. The reason may be found in the kinetics of the cry-
stallization processes. With an increased cooling rate the cry-
stallization passes over from thermal to athermal crystalliza-
tion. The more the athermal crystallization dominates the
more the optimal interrelationship between nucleation and cry-
Fig. 2.8 Temperature dependence of the specific volume of an amorphous and a semi-crystalline polymer at different cooling rates.
crystal growth is disturbed. This becomes evident in a shift of the crystallization temperature to lower values and in a growing increase of specific volume below this temperature.

Apart from the effects of cooling rates during the transition between melt and solid, specific volume below the glass transition temperature or the crystallization temperature is, furthermore, influenced by\(^{17}\):

(i) the pressure during cooling

(ii) the method of measurement (isobaric or isothermal)

(iii) the rate of change.

It appears that the use of pVT-diagrams for process analyses assumes a homogeneous isotropic melt in the cavity. However, in injection moulding the melt is subjected to a very complex system of shear stresses, pressure and severe cooling in the mould, and, as each single volume element has its own thermal - and rheological - history, each single volume element also has its own pVT-relation\(^{143}\) (Fig. 2.9). The dimensions of a freshly moulded piece most likely cannot be reliably computed from the cavity dimensions and the equilibrium pVT-relationships, assuming such a relationship were available for the solid polymer. The solution of additional equations involving rate relationships will be necessary. Even then the following limitations exist.

(i) pVT-data, which are recorded in a state of thermodynamic equilibrium can be used only for approximated estimations as nonstationary or inconstant temperature fields are present during mould filling and cooling.

(ii) Differences in the instantaneous and delayed increase or decrease in the specific volume arise from differences in the rate of temperature and pressure changes.

(iii) The temperature profiles in the moulding are replaced by an average melt temperature. The true melt temperature is one of the most difficult variables to measure.

(iv) The inhomogeneous pressure conditions in the cavity are replaced by an average cavity pressure. Pressure gradients in the unsolidified melt cause transport phenomena which may create internal stresses.
Fig. 2.9: Change in pVT relationships during injection moulding

- a) Amorphous polymer
- b) Crystalline polymer
However, pVT-diagrams remain valuable and important for characterization of physical properties which gradually become important also in process analyses.

**Thermal conductivity**, which in the solid state is a function of temperature, crystallinity and molecular orientation\(^{143}\), controls to a large extent the rate of heat transfer in molten and solid plastics. It is an important quantity in mathematical models of the injection moulding process.

**Thermal diffusivity**, controls the time dependent temperature distribution in the absence of heat generation within the material. In cooling time calculations it is the only thermal property needed.

**Specific heat** of a polymer is necessary for evaluating the heat and shear energy needed during plastication and also the heat to be removed for part cooling. A review on the subject of specific heat has been done by Collins et al.\(^{145}\).

Generally, considerations about the specific heat \((c_v)\) are made as a function of constant volume, although measurement of specific heat by DSC is made under constant pressure conditions. However, a thermodynamic correlation between \(c_p\) and \(c_v\) exists and can be calculated by means of pVT-data\(^{14}\).
2.4. SUMMARY AND CONCLUSIONS

In this chapter an attempt has been made to present a fairly complete review of the principal elements in injection moulding, as well as those factors which must be taken into account in an analysis of the process. This task was obviously too ambitious to be fulfilled satisfactorily.

The literature review has revealed a vast amount of papers from purely theoretical to purely empirical which deal with the injection moulding process. A large number of the papers deal with the influence of processing variables on properties of mouldings, which are summarized in the following chapter.

For practical purposes, the papers still show an unsatisfactory agreement between theories and experiments. To date, the wholly empirical approach has been, generally, more fruitful than a theoretical approach or a semi-empirical approach based on continuum mechanics through constitutive equations.

As an example, the geometry of a practical moulding is, generally, far too complex for the heat transfer equations and the boundary conditions to be applied to the complete moulding. Here, however, the finite-element technique may be a solution in dividing the irregular shape of the body into a mesh of simple shapes, often rectangles or triangles, and then the heat transfer equations can be applied to each of these simple shapes in turn.

In the control of the process, it is thought that process control can be achieved by controlling the subprocesses. However, not one discreet subprocess can be selected for control. Rather, more than one and perhaps all of the subprocesses will have to be under one form of control or another in order to accommodate the interdependency of the subprocesses. Some of the controls may only be supervisory, but these can serve as monitors of the process.

The problem of coordination of the different theories has not been dealt with explicitly. The main conclusion then of the review can be that, in principle, the theories for the
different processes, considered in isolation, are sufficiently developed at least for simple geometries of mouldings. However, for a process as complex as injection moulding one has to start with a simplified picture. By carrying out suitable experiments, one can learn, where ill-considered assumptions should be replaced by more suitable ones. As an example, while conditions of flow and solidification exist during most of the injection cycle the effect of solidification on flow during the filling stage may often be neglected. Similarly, flow effects may not be accounted for in computing solidification rates during the packing and cooling stages. Generally, the form of the model used applies to amorphous materials. However, for the flow of a semi-crystalline polymer into a cavity at high injection rates a higher injection pressure is to be expected when freezing is taken into account.

One other area which is not treated in detail is the application of general-purpose or minicomputers to control the injection moulding machine. Here again, suitable control algorithms (which depend on the existence of transfer functions) have yet to be developed, as the conclusions reached and described in the literature, have not been sufficient to derive anymore than a qualitative relationship between process variables.

The section on processing properties clearly revealed the importance of this data in understanding and predicting processing behaviour. Further work is needed to measure some of the processing properties more rapidly and more economically in order for an average processor to make the best use of them.

In conclusion, it still seems necessary to investigate the effect of process variables on the properties of mouldings. By treating the process as a number of discreet processes, whose inputs and outputs can be adequately and uniquely de-
fined, a number of control schemes for the individual processes become possible. Then, with an ever increasing sophistication in the computation of the theoretical work, a better understanding of fundamental polymer properties, and more uses of newer control systems for the injection moulding machine the gap between what is desirable and what is possible is closing.
CHAPTER 3. INFLUENCE FROM PROCESS STATE VARIABLES ON PROPERTIES OF MOULDINGS - A REVIEW OF LITERATURE

3.1. INTRODUCTION

The objective of this chapter is to describe those changes in the structure and morphology of the polymer which takes place during processing and which have a dominate influence on most mechanical and physical properties. It is initiated with a description of molecular orientation and residual stresses which have the main influence in amorphous materials. In crystallizable materials the degree and pattern of crystalline phases occur additionally. For quality mouldings dimensions and shrinkage are important concepts together with the mechanical properties. A qualitative description of the relationships between these factors should also be the outcome of the review.
3.2. ORIENTATION AND RESIDUAL STRESSES

The detailed character of orientation and residual stresses in amorphous polymers has been the subject of several papers (19,27,146-154). In contrast, orientation in semi-crystalline polymers has received less experimental attention (155-163).

During injection moulding complex deformation and flow processes take place due to the shear flow and thermal conditions within the mould cavity. As a result, the macroscopic properties of the mouldings are anisotropic and inhomogeneous within a moulding.

The anisotropy and inhomogeneity is a consequence of molecular orientation and residual stresses caused by deformation of the material in the molten or rubbery state and subsequent fixation of the desired shape by rapid cooling to below the glass transition temperature \( T_g \).

The forces causing the deformation are balanced against retardation and relaxation forces, \( R \), which may be considered as a change in free energy, \( F \), with the deformation. The change in free energy arising from an isothermal deformation along the \( x \)-axis is determined by the internal energy, \( U \), the temperature, \( T \), and, the entropy, \( S \), (Assuming the number of molecules, \( N_1 \), = constant).

\[
R = \left( -\frac{\partial F}{\partial x} \right)_T N_1 = \left( -\frac{\partial U}{\partial x} \right)_T N_1 - T \left( \frac{\partial S}{\partial x} \right)_T N_1
\]

The first term of the expression is the energy-elasticity, where the deformation is instantaneous and without losses. It is physically and thermo-mechanically reversible. The work performed against the interatomic forces is stored as potential energy.

The second term is the entropy-elasticity, where the deformation is time-dependent and causes a decrease in the entropy of...
the system. It is physically reversible and thermodynamically irreversible and associated with a transformation of energy. The forces arising from energy and entropy-elasticity may change relative to each other as a function of temperature. As an example, the explicit dependency on temperature of the entropy-elastic relaxation forces is very low at low temperatures, whereas they have a more dominating influence at higher temperatures.

Struik\textsuperscript{19) extended the considerations above and made a distinction between the three essentially different kinds of internal stress present in amorphous polymers. First, the deformation process results in a state of molecular orientation. Upon cooling this orientation is frozen in, together with the internal stresses with which the material reacted to the deformation process. This causes anisotropy in various physical properties as well as instability in dimensions or shape.

A second kind of internal stress results from the single fact that the polymer, when cooled to below $T_g$, is no longer in thermodynamic equilibrium. Its volume, entropy, etc., being too large, it slowly begins to approach the equilibrium state, a process which causes many properties of the material to change with time. This physical aging process can be considered to be caused by a hydrostatic internal stress which, by a process of bulk creep, produces a slow and gradual contraction of the material\textsuperscript{152}).

The third kind of internal stress results from the rapidity of the cooling to below $T_g$. Because the material is cooled from its surface inwards, rapid cooling is inherently inhomogeneous and accompanied by thermal stresses. As the elastic properties of the polymer change during cooling, part of these thermal stresses will persist when the cooling has been completed as residual, thermal or cooling stresses in the moulding.
The following review deals mainly with molecular orientation and residual stresses.

3.2.1. Orientation (Entropy - elasticity)

In connection with injection moulding, one of the great needs is to achieve a better understanding of orientational effects - how orientation arises and affects product properties.

An amorphous polymer is said to be molecularly oriented when the directions in the space of the chain segments are not distributed randomly. If they are distributed randomly, the material is said to be unoriented.

Molecular orientation should not be confused with mechanical strains or frozen-in deformations. Of course, orientation in polymers is generally the result of deformation, and frozen orientations are generally accompanied by frozen-in strains. However, the degree of orientation is not simply determined by the degree of deformation. This follows from the theory of rubber elasticity, which shows that for a certain degree of strain, the degree of molecular orientation increases with the cross linking density. This also applies to amorphous thermoplastics, which are not chemically cross-linked. Here, however, the role of the cross-links is played by the entanglements, and their effective density increases with decreasing temperature and increasing rate of deformation\(^{19}\).

Orientation of polymer molecules will usually occur when the normal random arrangements of molecular chains are perturbed by some imposed stress giving more molecular chains aligned in the direction of the resulting strain. Ideally, the molecular axis will be perfectly aligned in an extended conformation. However, such a state can only be attained if all of the bonds assume the trans-configuration, i.e., the state of least energy. It turns out, however, that the energy difference between the trans and gauche configurations (minimum to minimum) is very small so that all configurational states are thermally populated, at least to some extent\(^{164}\). Hence, both the direction
and extent of alignment will vary widely from molecule to molecule within the stressed volume. An orientation distribution function will, therefore, be required to describe such an alignment process even over small volumes where the overall average orientation is uniform.

Pronounced orientation will, in general, only be developed during processing of a thermoplastic above the glass transition temperature and will not normally be retained once the causative stress has been removed for times longer than the relaxation time for the material at that temperature. For crystalline materials considerable orientation may be retained below the crystallite melting temperature, or in some circumstances in the melt itself.

Orientation is introduced during the flow of the melt through nozzle, runners, gate and cavity by a deformation of the melt. This may occur in two ways

(i) Differences in velocity along flow lines, which create shear or extensional flow of the generally viscoelastic polymer melt (Primarily during the flow process in the filling stage)

(ii) Differences in velocity between adjacent layers, which may arise, e.g. between solidified and molten layers, and which create shear in the melt—("Creeping flow") Primarily during the packing- and cooling stage).

In amorphous polymers orientation is largely a result of the former and to a lesser extent by the latter.

The above mentioned forms of orientation are referred to as monoaxial orientation by Wiegand and Vetter. A classification of the type of orientation will usually be related to the type of strain causing the orientation, for example, we may have planar, uniaxial, biaxial, triaxial, radial or tangential orientation types, or combinations of these.
Biaxial orientation occurs as a result of the expansion flow on two or three dimensional spreading out of the flow front at the entrance of the mould cavity. If this expansion is frozen, there is also an arrangement of the molecular structure at right angles to the direction of flow and thus biaxial orientation of the material.

With semi-crystalline polymers crystallization results in essentially a mass of crystallites dispersed in an amorphous matrix. Chain alignment is controlled not only by the orientation stresses, but also by the crystallization forces. Generally, orientation can be created in two distinct ways. An isotropic polycrystalline polymer can be deformed below the melting point with extensive reorganization of the crystal morphology, or an oriented amorphous melt can undergo crystallization to yield an oriented crystalline polymer. Performance of an oriented semi-crystalline polymer depends upon orientation of the amorphous phase, as well as orientation of the crystallites. As with amorphous polymers orientation can be uniaxial, biaxial, etc.

As a consequence of the orientation, the molecules are no longer in their equilibrium state, that is, the state which they most probably would have attained without any outside influence. This effect decreases the entropy of the system, corresponding to a more orderly arrangement of the molecules.

The disorientation is temperature dependent. As long as the temperature is higher than the glass transition temperature ($T_g$), the intramolecular or micro-Brownian motions (movements of single sections or segments of a chain) and the intermolecular or macro-Brownian motions (movements of complete configurations in relation to each other) result in entropy-elastic forces, which cause a disorientation in amorphous polymers. The same happens in semi-crystalline polymers, with the exception that only molecules in the amorphous part may relax at a temperature between the crystallization temperature ($T_c$) and the glass transition temperature ($T_g$).
The disorientation can take place in two ways:

(i) Retardation: disorientation without external influences, e.g. free shrinkage in monoaxially stretched polymers at constant stress

(ii) Relaxation: disorientation at constant (external) deformation.

In the mould cavity, no free (uninhibited) shrinkage is possible for the orientated melt. The melt deformation, which originates during filling, remains extrinsically constant (relaxation)\textsuperscript{150}).

The disorientation is also time-dependent, as the rearrangement is governed by the height of the energy barriers. The rapidity of the rearrangement can be described by a relaxation time, which is the reciprocal of the rate constant for the internal rearrangement\textsuperscript{164}).

Mould filling is complete in approximately 0.8-1 s, while it can be shown using the theory of Bueche \textsuperscript{*)} that the maximum molecular relaxation time is approximately seven seconds at the melting temperature of polypropylene.

If the melt is cooled very rapidly (quenched) to a temperature below the glass transition temperature there is not enough time for the molecules in an amorphous polymer to attain their preferred conformation and, therefore, the term frozen-in orientations is used.

In principle, a disorientation is possible at a temperature below the glass transition temperature, provided there is a sufficient free volume. However, even for an amorphous polymer this is less than 2.5\% \textsuperscript{165)**}. Not until the free volume amounts to approximately 2.5\% of the total volume is the geometric hindrance for movements so small that chain segments in addi-

\textsuperscript{*)} Bueche F., J. Chem. Phys. 22 (1954) 1570-1576

\textsuperscript{**}) V = const. \approx 0.025 V_g, \quad V = \text{Volume below } T_g; \quad V_g = \text{Volume at } T_g
tion to rotation at single bonds also has space for oscillatory movements. As long as the free volume has not reached this minimum value, movements in chain segments are only possible by cooperative plate shifts \(^{165}\). In the solid state molecules are also influenced by the inter-molecular (van der Waal) forces. For practical purposes one may assume that hardly any disorientation takes place below the glass transition temperature.

In summary, orientation is introduced during injection moulding by the following sequence of events:

(i) Flow in the melt state under conditions of high stress causes the chains to orient in the flow direction. To effectively introduce strain the product of the strain rate times the relaxation time must be \(\gg 1\).

(ii) Part of the orientation will be lost due to relaxation processes while the temperature is higher than the glass transition temperature. The system tends to revert to its lowest energy state of maximum entropy.

(iii) The sample is cooled below its glass transition temperature, causing the relaxation time to dramatically increase thus preventing further relaxation. Residual orientation is then frozen-in indefinitely.

3.2.2. Residual stresses (Energy-elasticity)

Internal stresses are stresses in a moulding which is not subjected to an external force. They are, like stresses induced by an external force, stresses which act against a displacement of the axes and angles of the primary valence bonds, which
have disturbed the state of equilibrium in the molecular chain. A displacement of chain segments (against the secondary valence bonds) may also induce internal stresses. The primary valence bond energy is much higher (40 - 800 kJ/mol) than the secondary bonds (2 - 20 kJ/mol), depending on the type of atom, bond and distance between atoms 165).

The resulting strains are proportional to the stresses, which are active at room temperature. The work performed against the interatomic forces influences the molecular and crystalline structure and is stored as potential energy. The stresses are also termed energy-elastic stresses.

In a moulding, after removal from the mould, the stresses are in equilibrium, that is, compression stresses are balanced against tensile stresses and vice versa. If the stresses are not in equilibrium the moulding would warp.

The stresses develop from different sources during processing, but they are, generally, a result of a hindered relaxation. As the variables which determine the size of the internal stresses (Modulus of elasticity, coefficient of thermal expansion, etc.) are functions of the anisotropy, which change over a cross-section, it is clear that the stress profile over a cross-section can be very complicated. Also, widely different opinions are found in literature over the direction of the stresses (e.g. tensile or compressive stresses at the surface). A plausible assumption about the distribution of internal stresses in a moulding is that this distribution is equal to that of residual thermal stresses 166). However, other factors will also influence the distribution of stresses:

(i) Amorphous polymers
   a) Cooling stresses
      Stresses can be induced during cooling whenever there is a hindrance to thermal contraction, perhaps produced by a difference in cooling rates between the different layers. The mould temperature has a significant influence on those
stresses, which decrease with increasing mould temperature. Other processing parameters have less influence. The direction of the stresses is toward the compression on the surface at a depth of 0.05 mm only\(^+\) and tension in the core of the moulding\(147,151,169\). Also tension at the surface has been reported\(168\).

b) **Expansion stresses**

Stresses can be induced by the expansion of mouldings, which are ejected from the mould while they are under pressure. The level is usually proportional to the cavity pressure at ejection. The direction of such stresses is a subject for discussion in the literature and, compression as well as tensile stresses at the surface have been reported. In the latest publications, however, it is generally agreed that there are tensile stresses at a depth of 0.05 mm and compression at 0.7 - 1.0 mm, dependent on the rate of cooling.

c) **Flow-dependent or flow-induced stresses**

Stresses can be induced by a stretching of the melt at the flow front during the cavity filling. These are always tensile stresses, often with a maximum approximately 0.3 mm below the surface.

d) **Shrinkage stresses**

Stresses can be induced by anisotropy in shrinkage (or post-shrinkage in an anisotropic morphology). Anisotropy may develop due to the differences in orientation (molecular, pigments, reinforcements, etc.) between different positions of the moulding. Generally, shrinkage, due to anisotropy is higher along the molecules than transverse to them, whereas the coefficient of thermal expansion has a lower value along the molecule rather than transverse to it.

\(^+\) The distances mentioned here will, of course, vary with the thickness of the moulding, material, processing conditions, etc., and are only to be considered typical for, e.g., a 2 mm moulding emphasizing that the direction of the stresses may change within a short distance from the surface.
e) **Orientation stresses**  
Stress caused by frozen-in molecular orientation, which is not relieved with an annealing below the glass transition temperature.

(ii) **Semi-crystalline polymers**  
Stresses induced by differences in morphology, e.g., caused by differences in crystallinity due to differences in cooling rate, thermal contraction or relaxation. The internal stresses may also be stresses of a higher order, at certain positions (e.g., within a spherulite).

If the strain caused by the stresses is higher than a critical value, minor-cracks can develop. With tensile stresses at the surface the mouldings are more susceptible to environmental stress cracking. This effect is even more serious where biaxial stresses are involved. The fact that for most ductile materials there is a specific environment-stress combination which will cause embrittlement should be mentioned. This property can be monitored by measurement of the ductile behavior of the material (elongation at break, area under the stress-strain curve, biaxial impact, etc.). Tests are usually carried out by holding two of the embrittlement variables (time-temperature-stress) constant and varying the third. Environmental embrittlement can be more severe than environmental stress cracking and, as it does not result in a visible change in the material, it is more difficult to detect.

In summary:

(i) The development of internal stresses is strongly dependent on processing conditions.

(ii) The level and direction of stresses vary with position, as well as over the cross-section of the moulding.

(iii) Conflicting evidence is reported about the influence from processing on the direction of the stresses at the surface.
3.3. MORPHOLOGY AND CRYSTALLINITY

A polymer chain consists of a large number of structural units which are to some extent mobile with respect to each other. They can, therefore, arrange themselves in different ways and the number of different possible polymer structures is tremendous.

In classifying structures and in analyzing the relationships between structure, processing and physical properties, it is helpful to distinguish between a primary, secondary, and tertiary structure.\(^{174}\)

The primary structure refers to the kind of structural unit a chain consists of and to the sterical arrangement of neighbouring structural units (cis, trans, isotactic, etc.) The primary structure of a polymer chain means the same as its chemical constitution and configuration, or in other words - the nature of the repeating unit or units. The primary structure affects some characteristics directly, e.g. solubility and chemical behaviour. It affects most properties, however, only indirectly by influencing the degree of flexibility or mobility of the chain and, thus, the secondary structure.

The secondary structure relates to the arrangement of the polymer chain within the range of a single macromolecule, i.e., conformation or the type of aggregation state of an individual macromolecule.

A polymer chain can exist in a number of different shapes: as a completely extended chain, in the form of a random coil, or in the form of a periodically regular arrangement of chain segments. As an example, polyethylene crystallizes in the folded chain shape, polypropylene in a helical shape.

The tertiary structure, which is strongly influenced by the secondary structure, is concerned with the arrangement of the macromolecules to form more complex aggregates. A polymer crystal with folded chains is an example of a tertiary structure.
In a crystalline thermoplastic, crystals usually have the form of crystallites, that is microscopically smaller crystals without a definite geometrical form. In crystallites the dominant local structure can be relatively simple. Parallel polymer chains are packed together in a regular pattern. In some cases a crystallographic "unit cell" adequately specifies this structure. (Fig. 3.1.)

Structure on a somewhat larger scale is referred to as morphology. This term encompasses such structural features as crystallite size and shape and the relative arrangement of crystallites.

When a polymer is crystallized from the melt by cooling, the final density is always intermediate between the density of the amorphous state and the theoretical density of a perfect crystal, calculated from the unit cell dimensions. Therefore, the term semi-crystalline polymers is usually applied.

For those polymers that crystallize, the morphology has a strong influence on dimensions and mechanical properties. The development of morphology in turns depend on the processing conditions. In order to control the properties of mouldings it is important to examine crystallinity and determine the factors which control the extent of crystallinity.

3.3.1. Classification of structures

Crystallinity

The formation of stable crystalline regions in a polymer requires, firstly, that an organized closely packed arrangement of the chains in the three dimensions can be achieved and, secondly, that a favourable change in internal energy is obtained during the process.

This imposes restrictions as regards the type of chains which can be crystallized from the melt. Generally, they are characterized by 174)
Fig. 3.1 Schematic representation of morphology in injection mouldings (Polyethylene)
(i) Symmetrical chains which allow the regular close packing required for crystallite formation.

(ii) Chains possessing groups which encourage strong intermolecular attraction, thereby stabilizing the alignment.

In addition to the thermodynamic requirements, kinetic factors relating to the flexibility and mobility of a chain in the melt must also be considered. There are also factors in the injection moulding process which influence the crystallization process. Therefore, the main factors which determine morphology and crystallinity can be summarized as follows:

(i) The molecular (or primary) structure of the polymer.

Factors affecting crystallinity can be dealt with under the general headings; symmetry, intermolecular bonding, tacticity, branching and molar mass.

Generally, symmetrical linear chains, such as polyesters, polyamides and polyethylene, crystallize most readily. Secondary (intermolecular) bonding can lead to a stimulation of the crystallization process. The close packing achieved in e.g. polyethylene crystallites also allows the van der Waal's forces to act co-operatively and provide additional stability to the crystallite. If a chain possesses large groups, these will not only increase the rigidity but will also increase the difficulty of close packing to form a crystalline array. This latter problem can be overcome if the groups are arranged in a regular fashion along the chain. Isotactic polymers tend to form helices to accommodate the substituents in the most stable steric positions; these helices are regular forms capable of regular alignment. As an example, isotactic polypropylene will normally have a packing with four possible helices (back/front, left/right hand spiral) and where two of the forms are packed with alternation of the spirals. With injection moulding, however, a structure with a random choice of helices dominates at the surface. This reduces density and tensile strength.

+) The term "smectic" is often used for the quenched form of polypropylene without implying the structure of the material.
Polypropylene crystallized in contact with chrome plate, a common mould surface, forms a columnar structure perpendicular to the mould surface and this can lead to the formation of surface cracks which can cause mechanical failure by stress cracking.

Syndiotactic polymers are also sufficiently regular to crystallize, but not necessarily as a helix. If the chain is substantially branched, the packing efficiency deteriorates and the crystalline content is lowered. Molar mass has an influence on the melting point. Generally, the melting point increases with molar mass\textsuperscript{174}.

(ii) Cooling rate
A high cooling rate creates a finer structure and a lower degree of crystallinity. This causes a higher post shrinkage due to post crystallization.

(iii) The rheological history
Shearing the polymer or stressing it will tend to align the molecules and, thereby, induce crystallization. Therefore, layers in a moulding which have been exposed to shear will often show strongly deformed spherulites (transcrystallization), thermally stable structures and often a high degree of crystallinity.

(iv) The thermal history
The random order of molecules may not be reached in the melt under normal process conditions. Clusters of aligned molecules remain from the results of previous thermal treatment during polymerisation and pellet formation. When the granules are later processed the material may stay in the barrel for a time, which is not sufficient to neutralize crystallization states caused by previous heat cycles. These older crystalline sections influence recrystallization from the melt\textsuperscript{176}. 

039
Pressure and temperature conditions during processing

The pressure, volume, temperature relationship of a polymer can be followed in a pVT-diagram. A change in pressure or a pressure oscillation influences the temperature gradient and with that the rate of crystallization for the not yet solidified melt.

Nucleating agents

Crystallization may be initiated by homogeneous as well as heterogeneous nucleation. The latter is based on additives which regulate the crystallization. Other additives, impurities, pigments, cavity surfaces, etc. may also act as nucleating agents.

The factors (ii) to (v), and to some extent (vi) are influenced by the processing conditions. It is clear, therefore, that processing conditions have an influence on the crystallinity of mouldings.

Morphology

In crystalline polymers the morphological aspects of structure are complex and only partially understood. However, a number of distinct morphological units have been identified during the crystallization of polymers from the melt, which have helped to clarify the mechanism. Some of the ordered forms which have been identified are discussed in the following.

Single crystals. When a polymer is crystallized from the melt, imperfect polycrystalline aggregations are formed in association with a substantial amorphous content. This is a consequence of chain entanglement and the high viscosity of the melt combining to hinder the diffusion of chains into the ordered arrays necessary for crystallite formation.

If these restrictions to free movement are reduced and a polymer is allowed to crystallize from a dilute solution, it is possible to obtain well-defined single crystals. These crystals are usually made up of thin lamellae, often lozenge shaped, sometimes oval, about 10 to 20 nm thick, depending on the type...
of polymer, crystallization conditions etc. It is a characteristic feature of these lamellae that, while the molecular chains may be as long as 1000 nm, the direction of the chain axis is across the thickness of the platelet. This means that the chain must be folded many times to be accommodated in the crystal.

The crystals, thus formed, have a hollow pyramid shape, because of the requirement that the chain folding must involve a staggering of the chains if the most efficient packing is to be achieved. (Fig. 3.2)

![Diagram of lamellar crystal](image)

**Fig. 3.2** Idealized cross-section through a single crystal, showing folded chain structure and hollow pyramidal shape.

Lamellae crystallized from the melt are usually rectangular because the growth rate in the two directions of the plane of the lamella is different (Fig.3.2). In polyethylene, for example, the edges of the lamella are parallel with the axes of the unit cell. The c-axis (the direction along the chain) is then perpendicular to the plane of the lamella whereas the a- and b-axes are in the plane of the lamella. The lamellar chain-folded crystals have proven to be general both in crystallization from solution and from melt, and for all crystallizable polymers examined so far 177).
While opinions vary between kinetic and thermodynamic reasons for the constancy of fold distance, it is suggested that the fold structure allows the maximum amount of crystallization of the molecule at a length which produces a free energy minimum in the crystal.

One suggestion is that kinetic conditions control the initial crystallization, but that the crystals then improve in the degree of perfection through movements of defects (e.g. loops in the chain) with a simultaneous reduction in free surface energy, as they approach the perfection, which is required by the thermodynamic theory.

**Multilayer crystals** (Axialites or hedrites, twin crystals). The preceding discussion implies that the lamellae making up crystals and spherulites are independent. However, in fact some molecules pass from lamella to lamella in a single crystal and from crystallite to crystallite in spherulites. These "tie molecules" hold the structure together. Obviously, the number of tie molecules will affect the ease with which the crystallites separate under stress.

A proposal for the formation of stacks of parallel lamellae growing from the melt has been made by Reneker \(^{178}\).

![Schematic representation of folded - chain lamellae](image-url)

**Fig. 3.3** Schematic representation of folded - chain lamellae
Fig. 3.3 represents folded chain lamallae growing into the melt. At certain locations in the course of growth two (or more) lamallae will overlap. Reneker\textsuperscript{178} proposes that at these points, a single molecule may fold across adjacent lamella incorporating itself in two lamallae, thus forming a "tie molecule" between lamallae. The growth of these lamallae into the melt will produce a line of "tie-points" stitching the lamellae together.

Crystallites. As a rule, the crystalline polymer obtained from the melt is composed of stacks of parallel lamallae formed by diffusion of molecules, or sections of molecules, into close packed, ordered arrays which then crystallize. As discussed above, various portions of one chain may become incorporated in more than one crystallite during growth, thereby imposing a strain on the polymer which retards the process of crystallite formation. This will also introduce imperfections in the crystallites which continue growing until the strains imposed by the surrounding crystallites eventually stop further enlargements. Thus, a matrix of ordered regions with disordered interfacial areas is formed.

The first attempts to explain the crystalline structure of a polymer sample produced a model called the fringed-micelle structure. Here, the chains form short bundles wherein they are parallel over a short portion of their length. Within these parallel portions they give rise to a crystal lattice, but they sprout into an amorphous tangle at both ends producing a network of amorphous chains, with the crystallites acting as junction points. The whole structure was, thus, made up of crystalline regions embedded randomly in a continuous matrix\textsuperscript{177}).

This model was virtually discarded, in the light of research which had revealed features incompatible with this picture, and the theory was replaced with models, where a semi-crystalline sample was considered as a two-phase system, an ordered
and a disordered, where loops and kinks at the surface of the crystal, together with defects, contribute to an additional phase.

The non-perfect crystals were first investigated by measurements of the enthalpy of fusion of single crystals. It was found that a significant amorphous content is associated with each crystal. This must be on the surface and, it has been suggested that it arises from the disordered folding planes produced by the emergence and re-entry of a chain in the crystal. Three models to describe this have been suggested:

(i) Regular, with adjacent re-entry folds
(ii) Irregular, in which folding, though still adjacent, is made up of unequal lengths of chain
(iii) Switchboard, where the entry is random

By incorporation of these models into the fringed-micelle theory, this has been taken up again and revised. The concept has been further developed with a considerable amount of chain-folding, as is assumed with crystallization from the melt.

The overall picture of crystalline portions of linear macromolecules is, thus, that of lamellae with more or less para-crystalline defects and possible additional distortions and amorphous portions located between the lamellae. A typical microscopic structure model showing possible defects which could account for many of the observations is shown in Fig. 3.4.

The strength of a stack of lamellae varies in the direction of the three axes. In the direction of the c-axis the lamellae can easily be separated, as only inter-lamellar chains (e.g. A in Fig. 3.4) keep the material together in this direction. It is obvious that such chains are determining the force necessary to separate the lamellae in this direction. The lamellae themselves, however, are very strong in this direction due to the covalent bonds along the chain. In the direction of the a- and b-axes a deformation can take place either by an unfolding of the folded chains or by a displacement of the
lamellae relative to each other in the load direction. Both mechanisms are possible, but the latter alternative generally requires less energy. The strength along the a- and b-axes is much greater than along the c-axis.

The orientation of lamellae or stacks of lamellae relative to each other depends on the conditions of crystallization.

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Fig. 3.4 Schematic representation of possible defect structure in macromolecular crystals

(After Hosemann, Polymer 3 (1962) 153)
With stresses in the melt the chains are oriented with the c-axis in the direction of the stress vector and the lamellae are then growing perpendicular to the direction of the stress. However, when temperature gradients are present in the melt, the lamellae grow parallel to the gradients (Fig. 3.5).

Fig. 3.5 Simplified, schematic representation of orientation of the lamellae b-axes (I) and c-axes (II), respectively, parallel to a vector v.

Spherulites. The fringed-micelle theory was based on the concept of irregularly formed crystallites, and did not take the macro- or suprastructure into consideration. Examination of thin sections of semi-crystalline polymers reveals that the crystallites themselves are not arranged randomly, but form regular birefringent structures with circular symmetry. These structures are termed spherulites. Each spherulite grows radially from a nucleus formed either by density fluctuations which result in the initial chain ordering process (homogeneous nucleation), or from an impurity accidentally or intentionally added to the system (heterogeneous nucleation).
Fig. 3.6 Spherulite in polyoxymethylene, presumably showing a fibrous substructure.
Preparation: A 165°C hot solution of the polymer was solidified by pouring on a cover glass at 20°C. After evaporation of the solvent the film was melted on a hot bank at 190°C and then cooled rapidly on a cold metal plate.
Electron micrograph, 600 x, gold-plated, approx. 300 Å, angle of incidence of the beam 20°, Accelerator voltage 20 kV.

A study of the fine structure in the central region shows how the spherulitic growth starts from fibrous crystal units which spread outwards from the nucleus in bundles into the surrounding amorphous phase (Fig. 3.7). These units grow longitudinally but fan out forming sheaves gradually approximating spheres. At some intermediate stage in the development the spherulite often resembles a sheaf of grain. On the optical level, the spherical symmetry (except for the central region of the sheaf nucleus) is revealed by the Maltese-extinction-cross between crossed polaroids (Fig. 3.1). Although the fibrils are arranged radially, the molecular chains lie at right angles to the fibril axes. This has led to the suggestion that the fine structure is created from a series of lamellar crystals winding helically along the spherulite radius (Fig. 3.7).
Fig. 3.7 Schematic drawing of a polyethylene spherulite showing the orientation of the crystallographic axes 174, 182).

A system of concentric extinction rings can often be seen. They are known to arise from a periodic rotation of the optical index ellipsoid along a given radius, these variations being in phase around a given circumference, and corresponding to the periodic twisting of the crystal lamellae.

However, the details of the mode of twisting and stacking of the lamellae are unknown, and the origin of the twisting itself has so far defied all explanation. Also, the principles of space filling are not even qualitatively understood 182).

As the structure of the spherulite is not a single crystal, the sizes found vary generally between 5 and 100 μm.

The number, size, and fine structure depend on the temperature of crystallization, which determines the critical size of the nucleating centre. This means that large fibrous structures form near \( T_m \), whereas greater numbers of small spherulites grow at lower temperatures. When the nucleation density is high, the spherical symmetry tends to be lost as the spherulite edges impinge on their neighbours.
If it is assumed that the structure of spherulites is based on a mechanism with branching, growth may start in two ways. The start may be a heterogeneous, nucleated, complex crystal-center, where several crystalline substructures radiate in all directions. Growth may also proceed from a small crystal nucleus which develops into a fibril. Low branching and twisting then produces bundles of diverging and spreading fibrils which eventually fill out into the characteristic spherical structure (Fig. 3.8).

Fig. 3.8 Schematic representation of different types of nuclei

Spherulites with the apparent homogeneous center may occur in polymers where a dendrite acts as a nucleating agent. They are, however, more typical for non-polymeric materials. Spherulites are especially easily formed in melt with a relatively high viscosity, that is in a situation where the rate of diffusion is low and the relation between the constant of diffusion and crystal growth $D/G$ is small. Based on the above considerations, several of the general properties may be explained qualitatively;
(i) Generally, the spherulites grow under isothermal conditions with a constant radial rate of growth.

(ii) When the crystallization temperature is increased the spherulite texture generally becomes more coarse.

(iii) The morphology varies from system to system in the radial crystalline substructure. The birefringence observed in polarized light arises for two reasons.

(i) In the spherulite the polymer is arranged tangentially or radially. Tangential is the most common.

(ii) The polymer molecules normally have a higher refractive index along the chain than in other directions.

Spherulites are classified as positive when the refractive index of the polymer chain is greater in the radial direction, and negative when the greater refractive index is in the axial direction ($\Delta n = n_r - n_t$, where $n_r$ and $n_t$ are values of the radial and tangential refractive indices of the spherulites)

$184, 186$.

Different spherulites are observed with some polymers. In isotactic polypropylene different crystal modifications are found, although the molecular conformation is the same for all forms.

Monoclinic (α-form), weakly positive or negative spherulites are most common, but a hexagonal (β-form) is also found$^{179}$.

A metastable, trigonal form (γ-form) with a different packing of the chain develops when the melt is cooled rapidly and is subjected to high pressures. When heated above $60 \degree C$, the latter form changes to the monoclinic form. It is probably not found with normal processing conditions $^{185}$.

Padden and Keith $^{186}$ observed that the different types develop depending on the temperature of crystallization. They classified the two monoclinic forms and found that type I is weakly positive birefringent and type II weakly negative. Also γ-spherulites are found in two forms type III and IV, which, according to Padden and Keith are both mixed birefringent.
β-spherulites have a birefringence approximately three times higher than α-spherulites, and appear much brighter in polarized light \(^{185}\). Also, mixed types can be found \(^{187}\).

Generally, monoclinic spherulites are most common, but the cooling conditions determine the type of spherulites found. According to Wunderlich, type III spherulites are formed by rapid cooling down to 110 - 132 °C. Between 128 °C and 132 °C type IV spherulites are found occasionally. Type I was found when the temperature of crystallization was lower than 134 °C and type II when the temperature of crystallization was above 138 °C.\(^{179}\)

Dragaun et al. \(^{188}\) found that the shear rate is important for β-form crystallization. A critical average threshold value for the shear rate of approximately \(3 \times 10^2 \) s\(^{-1}\) has to be exceeded. The β-modification is mostly connected with type III spherulites and partly to row structures, and it is observed at processing conditions in oriented structures only.

Schöenefeld \(^{189}\) observed that the boundaries between the type I and type III spherulites, in cases where well defined spherulites are involved, are generally curved and concave toward the positive form indicating that the negative spherulites grow at a faster rate \(^{190}\).

The difference in birefringence arises from differences in the substructure of the spherulites. The fine structure of the monoclinic spherulites is quite complicated \(^{179}\). It is, however, generally agreed that the difference in birefringence for α-spherulites arises from different proportions of tangential and radial lamellae, which is dependent on the growth conditions.
Hexagonal spherulites are composed of radial lamellae only. However, type IV have periodic rotating lamellae, which result in characteristic ringed birefringence.

Apart from the difference in birefringence the different modifications also have different melting points. The monoclinic type I spherulite melts at 162 - 166 °C, the hexagonal type III spherulite at 144 - 148 °C [191]. However, when a type III spherulite has melted and the temperature is kept at 155 °C for approximately 5 min, it recrystallizes in a type I spherulite and remains in this modification even after cooling.

Spherulites may also show various other features such as zig-zag patterns and dendritic structures, a combination of the normal and dendritic, or normal and hedritic structures.

Transcrystallization (Epitaxy, palisades). The term epitaxy is used on an oriented growth of crystalline matter on a substrate of a different substance. Surfaces, which do not have an orienting influence on polymer nuclei, should not show epitaxy. However, if the surface (e.g. in a mould cavity) is wetted by the polymer, crystallization on such a surface is promoted by a fall in energy for the joining surfaces. It can in this way act as a heterogeneous nucleating agent (Fig. 3.9).

Fig. 3.9 Surface nucleation of polyoxymethylene (Ultraform) on a mould cavity surface (125x)
A further promotion of the tendency to nucleation on a surface arises from the fact that a sample cooled to the crystallization temperature usually is colder on the surface.

The geometrical structure of the polymer chain should cause the crystal growth to orientate on the chain axis parallel to the surface in order to achieve a maximum reduction in free energy during nucleation. The fastest direction of crystal growth should then be perpendicular to the surface.

The first description of epitaxy was given by Jenckel et al. In accordance with the corresponding crystal growth in metals, they proposed the term "transcrystallization". They found that the transcrystalline surface morphology is formed when the polymer is crystallized slowly near the melting point.

The morphology consists of densely packed columnar spherulites with their long axes perpendicular to the surface. Polyethylene and polypropylene samples with such a surface morphology show increased adhesion to moulding surfaces.

Transcrystallinity has been observed on several metal oxides. Fitchmun and Newman explored extensively the conditions for forming transcrystallinity from mould surfaces. To show that supercooling is not a prerequisite for transcrystallinity, crystallization on an embedded Mylar sheet was also studied.

Generally, the transcrystalline morphology is a result of heterogeneous nucleation at a surface. The density of nucleation sites at the surface is high and spherulite growth is perpendicular to the surface. The surface must have a nucleating efficiency equal to or greater than that of the other nuclei within the sample. In addition, the relative efficiency of the nucleating surface to that of the dispersed nuclei appears to increase as the crystallization temperature approaches the melting point.

Transcrystallinity may also form from surfaces other than mould surfaces. It may also be localized and grow at an internal surface within a polymer matrix.
It has also been pointed out by Judge and Stein \(^{196}\) that when the polymer crystallizes under molecular orientation at high elongation, the crystals grow with their c-axis parallel to the stretched direction forming bundle-like crystallites, but at low elongation there is a rather abrupt transition to a mode of growth in which the a-axis is aligned parallel to the stretching direction forming lamellae.

If the flow stops completely before solidification occurs one has no reason to expect any chain orientation because the specimen solidifies from a relaxed liquid phase. There is, however, a temperature gradient with the lowest temperature at the boundary between the polymer and the mould and the highest temperatures in the central parts of the liquid. The crystallization in such a temperature gradient results also in transcrystalline structures with the growth axis of the crystals, the b-axis in the case of polyethylene, the hydrogen bond in the case of polyamide, parallel to the gradient, i.e., perpendicular to the substrate. The orientation of the other two axes is at random in the plane perpendicular to the growth direction \(^{108, 197}\).

**Skin/core structure in injection mouldings**

In the moulding process, hot melt is forced under pressure into a mould cavity in which the walls are kept at a temperature below the melting point of the polymer. Crystallization takes place while the melt is subjected to a shearing force. It begins at the mould walls and proceeds into the interior. Therefore, different morphological structures are formed at the skin layer and the core of a moulding. These are, as a whole, called the skin/core structures and it is known that they influence various physical properties of a moulding.

Despite the facts that the skin/core structures have been known for a long time there have been relatively few papers dealing with the analysis of this structure, the moulding conditions and, further, the quantitative discussions on the

\(^{*)}\) In this section attempts at the theory of the texture and morphology of injection moulded specimens are summarized first, to be followed by a discussion of some initial, experimental results.
effects of this structure on the mechanical properties of the mouldings.

Clark \(^{20,21}\) envisaged three layers, regarding the change in form from the surface to the interior of injection moulded tensile bars, of a polyoxymethylene homopolymer. (Fig.3.10) He proposed that three effects influence the orientation of lamellae during crystallization: surface nucleation, temperature differentials, and induction time for crystallization. Clark attributed the three zones to three stages of crystallization corresponding to the filling, packing and cooling of the mould, respectively.

![Diagram of crystallization zones](image)

*Fig.3.10 Change in crystal orientation from surface to centre in injection moulding \(^{20}\).*

Other investigations have been carried out on injection-moulded specimens from semi-crystalline polymers such as polyethylene \(^{198-200}\), polypropylene \(^{22,23,25,201-202}\) \(^*)\), polyoxymethylene \(^{20,21,203-205}\), polyamides \(^{206}\), a copolymer of

\(^*)\) A paper on the texture and morphology of injection-moulded polypropylene has recently been published by Menges, Schmidt, Beyer, and Cordes. Gummi, Asbest + Kunststoffe, \(^{33}\) (1980)7, 469-476.
Zone 1 Surface zone
The surface or skin layer is developed immediately during the filling from a simultaneous influence from a shear induced crystallization and a high heat transfer through the cavity wall. The molten polymer molecules are quenched under a high shear rate near the cavity surface and the lamellae orient perpendicular to the cavity surface, because fibrils are formed in the initial stage of crystallization. The finely textured morphology is a result of a high density of nuclei. Also, a high growth rate for the nuclei is achieved with the supercooling, as the maximum for nuclei growth is at a lower temperature than the maximum for crystallite and spherulite growth. Mould temperature has a strong influence on this zone, which generally comprises a region extending for about 0.1 mm from the surface.

Zone 2 Intermediate zone
The morphology in this zone is developed after the filling of the cavity while the temperature gradient is still so high that the spherulites will be oriented towards the cavity surface directly under the skin layer (Fig. 3.11). However, the lamellae growing from the skin layer gradually lose their orientation since neither the temperature gradient nor the shear stress in this zone are as great as near the cavity surfaces, and the lamellae, thus, break down as they grow. The observed macrostructure has been related to the properties of the moulding.

Zone 3 Central zone
The central or core zone is characterized by non-oriented spherulites, the size of which is dependent on the polymer and the processing variables. When both shear stress and temperature

*) The experiments were carried out by the author as a supplement to the literature review.
Fig. 3.11 Spherulitic morphology in polyoxymethylene (Hostaform C 9010)
gradient have become relatively small new crystal nuclei are formed spontaneously and grow to the spheroidal stage.

It has been shown that zone III has a higher modulus of elasticity and a slightly higher tensile strength than zone I and II. Zone III is also much less ductile than zone I and less than zone II\(^2\). Hence, a broad zone III results in a rigid moulding and good dimensional stability.

The above observations were proven in an experiment, the results of which are shown in Fig. 3.12 and Table 3.1. The main variable was mould temperature which was varied at four levels. It appears from Fig. 3.12 that increasing the mould temperature results in a broader core zone at the expense of the intermediate zone.

When Fig. 3.12 is compared with Table 3.1 it appears that an increasing mould temperature results in mouldings with high tensile strength, low elongation at break, and a low post shrinkage. The lower elongation at break after annealing can be explained by the reduction of the amorphous layer between the crystallites after annealing.

In an attempt to measure the properties of the various zones the following experiment was conducted.

From the central part of tensile dumb bells, one as moulded and the other annealed at 140 °C/30 min and then cooled overnight, sections were cut in the oven specimens: (l=50mm,b=5mm,h=10mm), using a test bar milling machine. The edges of the specimens were carefully polished and bonded to a piece of metal, which was used for fixing in a microtome. From the surface and towards the center were cut 0,030 mm sections from the specimen. Every second section was tested in an Alwetron electronic tensile testing machine with a rate of deformation of 30 mm/min.
Fig. 3.12 Polyoxymethylene, effect of mould temperature on morphology
Table 3.1 Influence from mould temperature on weight, shrinkage, tensile strength and elongation at break for injection moulded polyoxymethylene tensile test bars.

<table>
<thead>
<tr>
<th>Mould temperature setting °C</th>
<th>40</th>
<th>65</th>
<th>90</th>
<th>115</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mould surface temperature °C</td>
<td>43</td>
<td>67</td>
<td>88</td>
<td>116</td>
</tr>
</tbody>
</table>

| Weight g | 14,68 | 14,25 | 13,81 | 13,52 |
| Shrinkage (24 h after moulding) % | 2,04 | 2,31 | 2,29 | 3,16 |
| Post shrinkage (140 °C / 30 min, cooled overnight in the oven) % | 0,76 | 0,41 | 0,76 | 0,06 |
| Tensile strength *) MN/m² | 54,6 | 56,4 | 57,8 | 57,4 |
| Tensile strength (140 °C / 30 min) MN/m² | 61,2 | 60,0 | 62,1 | 60,3 |
| Tensile elongation **) % | 46,6 | 14,2 | 17,9 | 13,4 |
| Tensile elongation (140 °C / 30 min) % | 20,0 | 10,7 | 15,1 | 9,2 |

*) \( n = 5 \)

**) Rate of elongation 50 mm/min

Material: Hoechst Hostaform C 901/0
Process.condition: Netstal/Sycap N 150/75
\( T_b : 185 - 195 - 210 - 215 °C \)
\( t_k : 25 \text{ s} \)
Fig. 3.13  Tensile strength and elongation at break as a function of distance from the surface.

The results for zone I and II (zone I: 0.29 mm, zone II: 1.76 mm) for the tensile bar, moulded at the rather low mould temperature of 43 °C, should only be taken as an indication of a trend. (Fig. 3.13) They indicate, however, that tensile strength for the two layers decrease after annealing and that elongation at break, especially for zone II, decreases drastically.
According to literature\textsuperscript{204}, a premature switch-off of holding pressure before the gate has solidified may influence the morphology. Firstly, the sudden drop in pressure or a pressure oscillation will cause the crystallization temperature to change. This influences the temperature gradient and, hence, the rate of crystallization for the not-yet-crystallized melt. A change in pressure of 70 bar will, as an example, change the temperature $1^\circ\text{C}$ for polyoxymethylene\textsuperscript{150}. The result is a discontinuity in the structure\textsuperscript{204}. When the pressure holding time is increased, the discontinuity moves towards the core of the moulding where it finally disappears. Secondly, when the pressure is relieved before the gate has frozen and the pressure in the cavity is higher than in the nozzle, the melt may flow out of the cavity which creates a row nucleation and a discontinuity in structure in zone II and III. There is some disagreement in literature about the importance of these discontinuities. Generally, they are not considered critical for the mechanical properties. However, it is agreed that they may act as "micro-voids", giving a high stress concentration and, hence, reduce elongation at break.

These assumptions are in good agreement with the results of an informative experiment where screw forward time was varied at six levels (Table 3.2).

The results show that when screw-forward time is increased, part weight and elongation at break also increase, but mould shrinkage decreases. Part weight is constant at a screw-forward time of more than 25 s, indicating that the gate has frozen. With a screw-forward time of 15 s voids were observed in the core of the mouldings. For these samples also, a very distinct discontinuity in the structure was observed in zone II. The appearance of such discontinuities may draw attention to a lower part weight, a higher shrinkage and lower mechanical properties than a moulding moulded with optimal conditions.
<table>
<thead>
<tr>
<th>Series</th>
<th>2</th>
<th>3</th>
<th>(4)</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screw forward time</td>
<td>s</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Mould temperature</td>
<td>°C</td>
<td>67</td>
<td>67,1</td>
<td>67,1</td>
<td>62</td>
<td>60</td>
</tr>
<tr>
<td>Weight</td>
<td>g</td>
<td>13,46</td>
<td>13,80</td>
<td>14,25</td>
<td>14,73</td>
<td>14,97</td>
</tr>
<tr>
<td>Shrinkage</td>
<td>%</td>
<td>3,13</td>
<td>2,68</td>
<td>2,31</td>
<td>2,04</td>
<td>1,89</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>MN/m²</td>
<td>55,7</td>
<td>55,9</td>
<td>56,4</td>
<td>55,8</td>
<td>57,5</td>
</tr>
<tr>
<td>Tensile elongation at break</td>
<td>%</td>
<td>26,1</td>
<td>24,8</td>
<td>14,2</td>
<td>37,8</td>
<td>37,7</td>
</tr>
</tbody>
</table>
They indicate that pressure should be maintained until the gate has frozen for polyoxymethylene. A change from injection pressure to holding pressure may have the same effect due to the pressure gradients in the hydraulic system of the injection moulding machine. (see Section 2.2.2).

Clark 20,21) found that the width of the skin (Region 1) of an injection-moulded tensile bar of a polyoxymethylene homopolymer was affected by melt temperature. As melt temperature was increased, the width of the skin decreased. He showed that the lamellae are aligned perpendicularly to the direction of flow, from the electron microscopy of the surface of the injection-molded polyoxymethylene bars and their small-angle X-ray scattering.

Kantz et al. 25) reported that an injection moulded homopolymer polypropylene tensile bar is composed of three distinct crystalline zones, namely, a highly oriented non-spherulitic skin, a row or shear-nucleated spherulitic intermediate layer, and a typically spherulitic core. The thickness of the oriented skin layer is a function of the polymer melt temperature and varies inversely with temperature. The thickness of the intermediate layer varies with injection pressure, but in a complex manner. They found that the crystallites are oriented biaxially in the flow direction. Tensile yield strength, impact strength and shrinkage increase with increasingly combined thicknesses of the two oriented outer layers.

Fitchmun and Mencik 22) found that the injection-moulded polypropylene is composed of fine layers from polarized light microscopy and confirmed that there existed oriented layers of at least three kinds on the surface of an injection moulded polypropylene product. On the extreme surface layer, no spherulite structure is noticed at all. But from the second layer, the spherulite structure is observed in the layers and the spherulite sizes become smaller gradually with the smallest around
the center of the third layer. After passing this point, they increase in size as the boundary between layer three and the core is approached.

By X-ray diffraction, Mencik and Pitchman \(^{23}\) examined the orientation patterns of each layer and found that the thickness of the fine layers varies depending on the moulding conditions. The third layer which is the oriented layer has the mixed orientation of the c-a* axes in the flow direction, and as the orientation mechanism, they propose that, first, the lath type crystallites with a*-axis orientation are formed, then they are unfolded by shear stress and the c-axis orientation components are formed. This view differs basically from that of Clark *), who carried out X-ray diffraction studies of polypropylene and assumed the a-axis oriented component to be formed by epitaxy on the c-axis oriented substrate.

Fujiyama et al. \(^{201,202}\) described the structure of skin-layer in injection moulded polypropylene as a two-phase structure. In the skin-section the c-axis is highly oriented parallel to the flow direction and consists of a shish-kebab structure imbedded in a row structure. The core section is of the spherulite structure. The thickness of the skin layer increased with decreasing the cylinder temperature, injection speed and MFI. It was almost unaffected by injection pressure and mould temperature.

Henke et al. \(^{210}\) found with polypropylene tensile specimens that varying the mould temperature affected the width of Region 2 (the intermediate zone) and strongly influenced the average size of the spherulites within the specimen.

Heise \(^{161}\) used wide- and small angle X-ray scattering of injection moulded beakers of HDPE, revealing uniaxial orientation

*) E.S.Clark: Paper presented at meeting of the American Physical Society. Dallas (1970) reported in \(^{201}\).
at the wall and biaxial orientation at the bottom of the beaker. The uniaxial orientation is characterized by a mean orientation of the crystallographic b-axis perpendicular to the injection direction and parallel to the beaker's wall. Biaxial orientation is composed of an orientation of the b-axis perpendicular to the injection direction and a sharp orientation of the c-axis parallel to the plane of the bottom. In some cases, biaxial orientation seems to be overlapped by a row orientation.

3.3.2. Nucleation, crystal growth and kinetics of crystallization

In injection moulding of a semi-crystalline polymer, crystallization normally takes place by cooling from the melt. The resulting morphology is characterized by lamellae of folded chains, with a spherulitic suprastructure. The degree of crystallinity depends on the structure of the polymer (side-groups, branches), processing conditions (shear, orientation) and cooling conditions (temperature across the moulding). The degree of crystallinity will influence properties of the mouldings. It is, therefore, important to know how processing conditions will influence the extent of crystallinity.

Glanvill (1982) states that between very slow cooling and quenching the degree of crystallinity varies 2-3 % in a low density polyethylene and up to 10 % in high density polyethylene. With polyamide extreme conditions can give variations of 40 - 50 %, although post-moulding crystallization increases the density from initially low levels of crystallization.

In a description of crystallization it is appropriate first to consider the normal crystal growth from a melt without disturbances, and then look at the conditions which influence crystallization.

Normal Growth

The creation of a three-dimensional ordered phase from a disordered state is a two-stage process.
As the temperature decreases during cooling, the volume available to the molecule also decreases and the polymer assumes an ordered conformation in which the chain bonds are in the rotational state of lowest energy. The influence of intra-molecular interactions among chains plays a dominant role. However, various other factors will tend to oppose crystallization; chain entanglements will hinder the diffusion of chains into suitable orientations and, if the temperature is above the melting temperature, thermal motions will be sufficient to disrupt the potential nuclei before significant growth can take place. As long as the potential nuclei are unstable and easily disrupted, they are called subcritical nuclei or embryos. When the ordered regions are stable and grow, they are called stable nuclei or small crystals\textsuperscript{179}.

The size of the stable nuclei is strongly dependent on temperature. With a high supercooling, even small nuclei are stable and able to form crystallites. Therefore, at high cooling rates (e.g. at the surface of the moulding) a higher number of nuclei and a finer morphology is to be expected. As the maximum of the rate of nuclei formation appears at a lower temperature than the maximum of nuclei growth rate, a lower rate of cooling (in the center of the moulding) causes relatively fewer and bigger spherulites.

Primary nucleation is called homogeneous nucleation, if no preformed nuclei or foreign surfaces are present. A foreign surface frequently reduces the nucleus size needed for crystal growth, since the creation of the interface between polymer crystal and substrate may be less hindered than the creation of the corresponding free polymer crystal surface. The resulting enhanced nucleation process is called heterogeneous nucleation.

In practice, nucleation is normally heterogeneous and is often caused by the addition of nucleating agents. The higher nuclei density, which is achieved in this way, means that the polymer
crystallizes at a higher temperature and, hence, achieves a higher degree of crystallinity, bigger crystallite sizes and a higher melting temperature, which generally improves properties but, possibly, also introduces more stress during processing\textsuperscript{213}. It may also be assumed that polymers with nucleating agents compared under the same conditions with polymers without nucleating agents will have a higher tendency to shrinkage and distortion\textsuperscript{214}. The differences in morphology between normal and nucleated specimens of isotactic polypropylene only arise from differences in conditions of crystallization and, not from the nucleating agent\textsuperscript{213}.

**Isothermal crystallization**

Two main factors influence the rate of crystallization at any given temperature: (i) the rate of nucleation; and (ii) the subsequent rate of growth of these nuclei to macroscopic dimensions.

When the temperature of crystallization is close to the melting temperature, nucleation is sporadic and only a few large spherulites will grow. At lower temperatures, nucleation is rapid and a larger number of small spherulites are formed. Therefore, a higher cooling rate causes a higher nuclei density and, generally, a finer texture. The higher the cooling rate, then the faster is the crystallization range passed, which means that the temperature of crystallization ($T_c$) is reached at a lower temperature. When the temperature drops faster, or less heat of crystallization is given out, a lower degree of crystallinity is obtained, which creates a higher specific volume and enhances the tendency to post-crystallization.

At inspection of the morphology of the grown crystals, either crystals of "all equal size", or of "varying sizes" are observed. The former indicates that all crystals started growing at the same time, which is called athermal nucleation; the latter indicates that new crystals started growing throughout the crystallization, which is termed thermal nucleation. While the
homogeneous nucleation is connected with thermal nucleation, the converse is not true. Heterogeneous nucleation may be either athermal or thermal. Since the number of heterogeneous nuclei is limited however, the thermal nucleation of heterogeneous origin must level off after all nuclei are exhausted. Any sample may contain more than one type of nuclei and a clean separation is not possible under practical conditions.

The growth of the spherulites may occur in one, two, or three dimensions and the rate of radial growth is taken to be linear at any temperature, that is, the volume of the spherulite increases with the cube of time. Likewise, the number of spherulites increases linearly with time.

Temperature and growth rate

As the temperature drops from $T_m$, the melt viscosity, which is a function of the molar mass, increases and the diffusion rate decreases, thereby giving the chains greater opportunity to rearrange themselves to form a nucleus. This means that there will exist an optimum temperature of nucleation, which depends largely on the interval $T_m$ to $T_g$, but also on the molar mass of the sample. The growth rate of crystalline areas also pass through a maximum in this range (Fig. 3.14).

![Fig. 3.14 Crystal growth and nucleation as a function of degree of undercooling in viscous liquid](image)
Close to $T_m$ the segmental motion is too great to allow many stable nuclei to form, while near $T_g$ the melt is so viscous that molecular motion is extremely slow. Measureable rates of crystallization, therefore, occur between $(T_m - 10 \, \text{K})$ and $(T_g + 30 \, \text{K})$ a range in which the thermal motion of the polymer chains is conducive to the formation of stable ordered regions.

**Growth - or crystallization rate**

The kinetic treatment of crystallization from the melt relies on the establishment of a relation between the density of the crystalline and melt phases and the time. This provides a measure of the overall crystallization rate. It is assumed that the spherulites grow from nuclei whose relative positions in the melt remain unaltered, and the analysis allows for the eventual impingement of the growing disc on one another. The final relation describing the process is known as the Avrami equation:

$$\frac{M_m}{M_0} = \exp(-kt^n)$$  \hspace{1cm} (3.1)

where $k$ is the rate constant, $M_m$ and $M_0$ are the masses of the melt at zero time and that left after time $t$. The exponent $n$ is the Avrami exponent and is an integer which can provide information on the geometric form of the growth.

The macroscopic advance of a crystal front is termed its linear growth rate. It can be observed directly by microscopy, or indirectly by noting the overall increase in crystalline content by dilatometry or similar methods. In principle, the two methods give the same result.

Development of crystallinity for a polymer is not instantaneous. The curve for the specific volume as a function of time at temperatures below the crystalline melting point shows that crystallization even for longer time periods cannot be considered as terminated.

As the time for a complete crystallization is difficult to determine it is common to define the rate of crystallization at
a given temperature as the inverse value of the time needed to attain one-half of the final crystallinity \( t_{1/2}^{-1} \).

The rate, defined in this way, is a characteristic function of temperature. When the temperature decreases, the rate increases, passes through a maximum, and then decreases, as the mobility of the chains decreases and crystallization is determined by diffusion.

Godowski \( ^{215} \) found empirically by analyzing half-times of crystallization for 23 macromolecules that the maximum crystallization rate is found at \( 0.82 T_m \) to \( 0.83 T_m \), regardless of the absolute level of \( T_m \).

For the polymers used in this study the maximum crystal growth rates are given in Table 3.3.

Table 3.3 Maximum crystal growth rates \( ^{179} \)

<table>
<thead>
<tr>
<th>Macromolecule</th>
<th>Growth rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>( 8.3 \times 10^4 )</td>
</tr>
<tr>
<td>Polyamide 6.6.</td>
<td>( 2.0 \times 10^4 )</td>
</tr>
<tr>
<td>Polyoxymethylene</td>
<td>( 6.7 \times 10^3 )</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>( 2.5 \times 10^3 )</td>
</tr>
<tr>
<td>Polypropylene, isotactic</td>
<td>( 3.3 \times 10^2 )</td>
</tr>
</tbody>
</table>

In practice, crystallization is also influenced by factors other than the temperature. As an example, an orientation of the chains may cause a premature crystallization or eventually solidification in the flowing melt at a temperature higher than normal for crystallization. This phenomenon also depends on the polymer. As an example, polypropylene copolymer is more sensitive to such conditions than polypropylene homopolymer, because the rate of crystallization is considerably higher for the former \( ^{212} \).

Additives like pigments may also influence the rate and temperature of crystallization. An increased melt temperature will tend to minimize such effects and, as crystallization is
time dependent, an increased flow rate may also reduce the influence\textsuperscript{212}. Also, lubricants may influence crystallization as the contribution of heat from internal friction is reduced.

The rheological and thermal history also influences crystallinity in the raw material (see Section 3.3.1.), as different polymerization methods lead to different degrees and types of crystallinity. When slurry or gas polymerisation is used, the polymer chains crystallize as they are formed. This is called nascent crystallization. It reduces the incidence of individual crystallite regions and leads to a uniform structure. On the other hand, solution polymerization gives a modified type of crystallization with structure determined by the chosen conditions. These conditions also control such parameters as molecular weight, molecular weight distribution and molecular structure.

Also, the extra thermal input and the extra shear history caused by granulation is significant. A raw material in powder form may result in better physical properties than granular raw material\textsuperscript{216}.

Post-crystallization
Apart from the crystallization, which takes place during moulding, this process also has a secondary stage which continues for days or months after moulding. During this secondary, or post-moulding crystallization, the thickness of the lamellae increase. At the same time the amorphous layers between the lamellae are reduced, resulting in an increased crystallinity. This causes changes in shape and dimensions, known as post-shrinkage.

Degree of crystallinity
The crystallinity concept in its simplest form assumes that macromolecules crystallize only partially. The semi-crystalline sample is thought to consist of two portions: a crystalline portion to be described by the ideal crystal structure; and an amorphous one, to be described by the ideal melt. The fraction of crystallinity, which is thought to be the single parameter which at least describes all structure-insensitive properties of the sample, is then given by:

\[
\frac{\text{Degree of crystallinity}}{2} = \frac{\text{Fraction of crystallinity}}{2}
\]
\[ m_c = \frac{((1/\rho) - (1/\rho_{a}))}{((1/\rho_{c}) - (1/\rho_{a}))} \]  \hspace{1cm} (3.2)

where

\[ m_c \text{ = the weight fraction crystallinity} \]

\[ \rho, \rho_{a}, \rho_{c} \text{ = total, amorphous and crystalline density.} \]

In a comparative determination of crystallinity it may be difficult to achieve identical results. This is due not only to experimental difficulties, but also because the determinations are based on different properties.

The most important methods for determination of crystallinity are determination of specific volume, thermal analysis, X-ray diffraction and infrared spectroscopy.

Summary

To summarize, crystallinity is a basic concept for semi-crystalline polymers and a crystallinity parameter based on the presence of ordered and disordered portions of the material is the first step toward characterization of the material.

In a description of crystallization the following sequence of events must be taken into consideration:

(i) Growth from a nucleus, as it is assumed in the classical description of primary crystallization

(ii) Spontaneous perfection of the original partly grown crystallites

(iii) Secondary crystallization of initially excluded or restrained material

(iv) Slow crystal perfection by processes, corresponding to those, which take place during long term annealing.
3.3.3. Morphology and mechanical properties

In a discussion of the relationship between crystallinity and properties it is important to realize that the degree of crystallinity alone is not sufficient for characterization, and, therefore, this concept must be compared with crystal structure, size and the number of spherulites and orientation. Some of these phenomena are in turn influenced by the conditions of processing. However, with this reservation, the degree of crystallinity alone is effective in determining the stiffness and yield point for most semicrystalline polymers. As crystallinity decreases, both stiffness and yield stress decrease. As a result of the latter change, the chance of brittle failure is reduced.

A decrease in spherulite size, usually accompanied by an increase in the number of spherulites, has a marked effect on some mechanical properties of polymers, but the direction of the effect may differ with the type of polymer. However, the trend of reported results indicates that if the spherulites are small and numerous the polymer tends to be stronger, stiffer, more transparent, and more resistant to impact failure. If the spherulites are large there tend to be built-in strains at the interfaces with the amorphous polymer which results in crazing or silvering. The large crystallites may fracture along the weak layers between crystallites and around spherulites. Also, micro voids will often accompany bigger spherulites.

Higher crystallinity with larger spherulites and crystallites yields a more brittle product than smaller spherulites and crystallites and lower crystallinity, unless the orientation is favourable and ample numbers of tie molecules are present.

Most semi-crystalline polymers can be rendered somewhat harder by decreasing the spherulite size. However, it is, as yet, uncertain whether the causal correlation may be with some other parameter, say crystallinity or lamellar geometry, which parameter in turn correlates with spherulite size.

4) This section is a summary of: M. Jensen:Strukturparameter indflydelse på mekaniske egenskaber (1978). Ref. C8.
The following Table 3.4. shows a summary of the effect of a decrease in spherulite size.

Table 3.4. Effect of a decrease in spherulite size on the mechanical properties of polymers (partly after Fred. W. Billmeyer, Textbook of Polymer Science, Interscience, New York (1962))

<table>
<thead>
<tr>
<th>Property</th>
<th>Polymer</th>
<th>PP</th>
<th>POM</th>
<th>PA 66</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact strength</td>
<td></td>
<td>Increased*)</td>
<td>Increased ***)</td>
<td>Increased 217)</td>
</tr>
<tr>
<td>Yield stress</td>
<td></td>
<td>Decreased</td>
<td>Decreased</td>
<td>Increased 217)</td>
</tr>
<tr>
<td>Ultimate elongation</td>
<td></td>
<td>Decreased</td>
<td>Increased 205)</td>
<td>Decreased 217)</td>
</tr>
</tbody>
</table>

*) No effect in ref. 218)

**) No effect except in thin films, also true for high density PE.

The effects of orientation on the physical properties of polymers are profound. They lie in the generally expected direction of increased tensile strength and stiffness with increasing orientation. As orientation is increased, anisotropy of the mechanical properties appears.

As with crystallinity, a determination of the degree of orientation in semi-crystalline polymers is complicated due to the complexity of the types of orientation which may be present, as well as to the conceptual problems associated with the present understanding of structure in an oriented sample.

3.3.4. Annealing

The term annealing implies, in a narrow sense, the imparting of a certain property by heat treatment without large-scale melting 179). In industry, annealing of plastics is used to improve the heat resistance and dimensional stability of amorphous and crystalline polymers when exposed to elevated temperatures. Furthermore, annealing frequently improves the impact strength and prevents crazing and cracking of excessively
stressed items. Amorphous, rigid polymers are mainly annealed for stress relief, while crystalline polymers show, in addition, changes in the nature of their crystalline state.

These changes are a result of heating to temperatures below the melting point which should lead to the growing of crystalline areas, perfection of crystals, and a change to more stable crystal structures.

A detailed description of the changes which take place during annealing has not yet been developed, for one reason, because the conditions of the crystal structure of the starting materials have not been analyzed in detail.

It is assumed, however, that the main effect is a change in concentration of defects and higher regularity in the crystallite surfaces. It is possible that the thicknesses of the folded chain lamellae increase. Some thermodynamic conditions, not yet defined, should probably also be included in a macroscopic description.

A simpler mechanism, which only creates a re-arrangement of parts of the molecule, without a coordinated displacement of the whole molecule has also been proposed. This process is shown in Fig. 3.15

Fig. 3.15 Schematic drawing of successive stages of the fold increase on annealing.
Relief of internal stresses

Stress relief in other than macromolecular crystals, has been connected with the motion of grain boundaries and dislocations and recrystallization.

A much more prominent effect in macromolecular crystals is caused, however, by internal stresses connected with changes in the macroconformation of amorphous macromolecules or the amorphous portion of a partially crystalline macromolecule. Such changes in macroconformation may be produced during solidification while the molecules are deformed by external forces, by non-uniform cooling, or through partial crystallization (see Section 3.2.2.). Internal stresses of this type can also be introduced subsequent to solidification by macroscopic deformation.

Annealing is expected in such samples by heating to a temperature where sufficient molecular motion is possible. This motion is on a several-chain-atom scale and involves fully amorphous molecules or the amorphous parts of partially crystalline molecules which are involved in amorphous defects or in disordered interfaces. The onset of sufficient molecular motion is usually indicated by the glass transition temperature. Often the glass transition temperature is observed between one-half and two-thirds the melting temperatures in degrees Kelvin. Annealing is, thus, possible much below the melting temperature.

The relaxation behaviour of semi-crystalline samples is mainly complicated by the effect of the crystalline parts of a molecule on its non-crystalline parts. Surface defects are frequently the location of internal stresses caused by the continuation of macromolecules from crystalline to amorphous regions. Depending upon the detailed structure, the mobility of sections of molecules adjacent to crystals is more or less restricted. A gross assessment can be obtained through the measurement of the glass transition temperature as a function of crystallinity \(^\text{179}\).
Recrystallization

Recrystallization is the term used to describe crystallization of a partially molten or dissolved material using the remaining crystalline parts as substrate.

Recrystallization may occur during annealing processes, which in addition to motion of defects or surface diffusion, also cause a partial melting and subsequent crystallization of the material.

Annealing investigations have been carried out for injection-moulded specimens from semi-crystalline polymers such as polyethylene\(^\text{219}\), polypropylene\(^\text{218,220}\), polyoxymethylene\(^\text{221}\), and polyamide\(^\text{222,223}\).

Summary

During annealing several processes may occur simultaneously. Typically a portion of a sample may melt on annealing, while other portions change crystal habit or increase their grain size mainly through changes in fold length. The latter process starts during heating to the annealing temperature. The defect concentration changes simultaneously with the changes in shape and macroconformation and internal stresses are removed. In time, recrystallization of initially molten material takes place, frequently complicated by molecular weight segregation and nucleation effects. Changes of crystal structure and chemical reactions may also occur under appropriate conditions.

As long as the various processes cannot be followed simultaneously, interpretation of annealing remains uncertain.

A major conclusion of the discussion of most macromolecular materials is that they are far from the equilibrium structure. Annealing helps these materials approach closer to equilibrium, but leaves them usually far from equilibrium.
3.4. WEIGHT, DIMENSIONS AND SHRINKAGE

Weight

Weight of the mouldings is the simplest and cheapest way, in terms of resources, to achieve a statement about the reproducibility of the process.

The relation between the weight of a moulding and its volume is given by

\[ V = \frac{m}{\rho} = m \cdot v \]  

(3.3.)

where

- \( V \) = Volume of moulding
- \( m \) = Mass of moulding
- \( \rho \) = Density
- \( v \) = Specific volume

The weight of polymer in the mould and, consequently, the constant mass line for the ideal process along which the pressure and temperature decrease, will be determined by the pressure and temperature at which the gate seals.

Dimensions and shrinkage

Volume shrinkage (\( S_v \)) is defined as the difference between the volume of the mould cavity and the volume of the moulding measured at normal conditions (23 °C/ 50 % r.h.)

\[ S_v = \frac{V_C - V_m}{V_C} \]  

(3.4.)

where \( V_C \) and \( V_m \) is the volume of the cavity and the moulding, respectively.

With isotropic shrinkage, the moulding would be geometrically similar to the mould and one could compensate for shrinkage by enlarging the mould by the proper factor for linear shrinkage (\( S \approx 1/3 S_v \)).

As a consequence of non-uniform cooling, shrinkage is, however, always non-uniform. As an example, density increases more ra-
pidly in thin sections than in thick ones. This tends to create a pressure differential that causes some of the polymer in the thick sections to flow into the thin.

Shrinkage is also anisotropic for thin, flat parts, especially where the thickness dimension is small compared to the length dimension.

In principle shrinkage may be estimated from $pV\text{-d}i\text{a}r\text{a}g\text{m}a\text{s}^{51}$, assuming an infinite slow cooling which, however, is never realized in practice (Section 2.3). It has, so far, not been possible to calculate the linear shrinkage for dimensions of complex mouldings with simple and, for practical purposes, relevant methods. For simple geometries Kurfess$^{224}$ has proposed a method for calculation of shrinkage from an approximated temperature distribution in the moulding during cooling, packing pressure, mould temperature, and wall thickness. More elaborate methods have been used by Targiel$^{118}$, who used a step-wise (layer model) approach, simple geometries and a high capacity computer and the following simplified assumptions:

(i) No loss in pressure transfer to the cavity before the sealing point (on the pressure curve)
(ii) Identical pressure conditions at all positions in the cavity
(iii) Complete instantaneous sealing of the gate at the end of the packing time
(iv) Relaxation of internal stresses follows an exponential power-law
(v) No deflection of the mould

In a theoretical work he simulated shrinkage of polystyrene as a function of packing time and found that the shrinkage in the thickness direction was much more influenced than the shrinkage in the length and width directions of the moulding. According to this work, the fact that thickness shrinkage differs from longitudinal and transversal shrinkage for flat mouldings is not a result of the mould separation during the injection phase of the moulding cycle.
Due to the complexity of the theoretical calculations numerous investigations have been carried out with the purpose of determining shrinkage as a function of processing conditions. Main variables are material, part geometry, mould design, moulding conditions, and moulding machine.

In summarizing, shrinkage generally increases with increasing wall thickness for amorphous, as well as for semi-crystalline polymers. Shrinkage increases with increasing distance from the gate and with decreasing gate area, due to the decreasing pressure gradient and the higher pressure loss.

Shrinkage (and dimensional variation) is smaller for mould dependent dimensions than for free dimensions (see e.g. SIS 161952 or DIN 16 901).

Shrinkage decreases with increasing cavity pressure and effective holding time. Shrinkage generally decreases with increasing melt temperature, because the pressure transfer from barrel to cavity is improved with a higher melt temperature. With fast freezing (small) gates the opposite trend may be found as the thermal contraction increases due to the higher temperature difference.

Shrinkage generally increases with increasing mould temperature. However, if the pressure transfer is considerably improved by the higher mould temperature the opposite effect is also possible. The latter depends on the design of and the freezing of the gate. Shrinkage is generally not dependent on the rate of injection for unreinforced plastics. Small gates, however, may have an influence on the cavity pressure curve. In this case, shrinkage decreases with the increasing rate of injection. An increase is also possible due to increased thermal shrinkage effects.

Recent investigations also point to the influence from processing on the deformation of the mould. This influence on dimensional stability, which is small for a well designed mould, can be calculated after Geyer.

The dimensional variation generally increases with increasing values for shrinkage.

+ G.Wübken, Zum Schwindungsverhalten thermoplastischer Spritzgussteile. Interner Bericht des Bayer, Leverkusen (1978)
3.5. SUMMARY AND CONCLUSIONS

In this chapter, an attempt has been made to present a review of the influences from process state variables on properties by treating the quality parameters separately. However, in injection moulding complex interactions are known to exist. For example, orientation and internal stresses are very difficult to separate and both are known to influence the crystallization morphology.

Entropy-elastic deformations are created mainly in amorphous injection mouldings. As a consequence, the birefringence, which can be seen in transparent mouldings using polarized light, mainly result (maybe up to 90-95%) from molecular orientation and not, as often presumed, from internal stresses\(^{146}\). Whether frozen-in energy-elastic deformations also develop during the gradual cooling of the melt and the resultant decrease of the molecular movements is dependent on the processing conditions.

The morphology of semi-crystalline mouldings is a result of the flow and cooling processes in the mould, where the temperature and pressure conditions have a dominant influence on the rate of nucleation and crystal growth. The macro, or supra-structure, is also influenced. The most characteristic feature are the spherulite. Their conditions of growth depend, among other things, on the properties of the polymer, molecular weight, degree of crystallization and, the nucleating agents. The melting and cooling conditions during processing influence not only their size but also the way they are arranged. In some cases, spherulitic crystallization may be suppressed.

Processing usually produces some degree of anisotropy (non-uniformity) in a moulding. The anisotropy may vary in position within the moulding, for example because of a variation in the rheological and thermal conditions. Additionally, there may be other structural variations within a moulding. There is accumulated evidence that such anisotropy is carried through to the mechanical properties of the moulding.
4.1. INTRODUCTION

The objective of this chapter is to discuss and select the variables which should be considered in the study and then on the basis of an evaluation, outline a plan for the work.

The general objective was formulated in Chapter 1. as; "to comprehend those variables which have the most profound influence on the properties of mouldings."

The results of the study aim at the production of semi-technical products in a range from 15 to 150 g made of semi-crystalline polymers. Typical examples are battery-boxes, cabinets, fittings, pumps, electrical- or automotive parts. The term "semi-technical" implies that anisotropy in mechanical properties should be within defined limits and that dimensions are important, but not so critical as, e.g., the dimensions of fast running gear-wheels. Usually, the products are produced in a competitive market with processing conditions which vary considerably between manufacturers of nearly identical parts.

Factors which should be considered in the experimental planning include the raw material, the geometry of the moulding, methods of control and recording of experimental variables, processing conditions, and test methods and properties of mouldings. The selection of variables should take into consideration the intended work as outlined in Chapter 1.:  

(i) Propose a control strategy for each of the process variables to be controlled.

(ii) To obtain data of the relationships between process variables, machine settings, and properties of mouldings.

(iii) Using the experimental data, develop the relationships between process variables and the final properties of mouldings.
The outcome of the work should be:

(i) An understanding of the influence from processing variables on properties of semi-crystalline mouldings.

(ii) A proposal for a control strategy for the process variables which should be controlled, as a background for evaluating process control systems.

(iii) A background for the formulation of a model for the injection moulding process.

(iv) Collection of data for the design of parts and moulds.
4.2. GENERAL PLANNING

The general plan for the long-term work can be divided into four phases:

1) Establishment of the basis for the project, review of literature, working out of specifications and procurement of equipment, selection and screening of the most important variables, exploratory experiments with calibration of equipment, investigation of the capability of the injection moulding machine and establishment of methods of characterization.

2) Experimental work with different materials and specimens under conditions of controlled variations.

3) A summary, conclusions and outline for further work on modelling of the injection moulding process.

4) Outline of the practical implications of the results in industry (testing of relevance, reliability and validity).
4.3. SELECTION OF VARIABLES

Materials

In accordance with the aim of the work, several commercially important materials should be used in the investigation. Therefore, high density polyethylene, polypropylene, polyoxymethylene, and polyamides have been selected for the first general stages. In later stages, polypropylene and polyoxymethylene will be chosen for detailed investigations, representing two typical but distinctly different materials with a relatively coarse morphology, thus, making them ideal for a general study.

All materials should be standard injection moulding grades. A polypropylene homopolymer should be chosen to avoid the complications suffered by the copolymer. Each material should carry the same lot number and should be characterized before use.

Moulding

The selection of the geometry of the moulding should take into consideration:

(i) the important variables

(ii) the subsequent tests.

Depending upon the intended application of the mouldings, a variety of properties might be of interest. However, mechanical properties, dimensional stability and shrinkage are important for practically all applications. Weight of mouldings are important in process analysis, e.g. for evaluation of the controllability of the process. Therefore, emphasis will be placed on evaluating the effect of moulding variables on these properties.

Generally, mechanical properties can be determined on most geometries. Hence, the selection of geometry should concentrate on a specimen ideal for evaluating shrinkage and dimensional distortion and stability. Therefore, the following requirements were formulated:
(i) Shrinkage should be free and not hindered by obstacles.
(ii) Shrinkage should be determined quickly and accurately on a simple geometry.
(iii) The specimen should allow measurement of differential shrinkage, which is generally not possible on, e.g., a disc-shaped specimen.
(iv) Shrinkage should be determined as a function of processing conditions and wall thickness.

Woebcken\textsuperscript{146} has pointed out that a quadrant specimen with \( r=100 \) mm fulfills most of the above considerations. By measuring the contour of a specimen, radial mould and post-shrinkage in the direction of flow can be determined. Differential shrinkage, that is the difference between radial and tangential shrinkage can be determined at a position corresponding to a circular arc of 100 mm. (see Fig. 5.2.) By changing the cavity insert, different wall thicknesses can be moulded.

The selection of the thickness of the specimen will influence the properties of the moulding, particularly at the centre. With a thick moulding, the cooling rate will be slow and the crystallinity high at the centre and largely independent of the mould temperature. Similarly, the narrowing of the flow path due to the frozen surface layer of material will be proportionately less with a thick moulding and, hence, the effect of mould temperature, melt temperature and injection pressure on the rate of injection and initial orientation will be less. At the same time, since surface conditions are practically unchanged, the differences in properties between the centre and surface of the moulding will be greater. On the other hand, with a very thin moulding it is important to keep both mould halves at the same temperature.

The product range in view for the experiments generally have a wall thickness of 2 to 6 mm. Therefore, a 3 mm wall thickness was selected as the principal moulding, supplemented with a 5 mm moulding primarily intended for the investigation of the variation in properties across a moulding.
The quadrant can be considered as fundamental geometry, typical for several parts with a spreading flow front which is drastically increased along the length of flow. This mechanism of filling creates a biaxial orientation in the mould. In order to create a specimen with monoaxial flow in the cavity, a fan-gated specimen with parallel sides was also made for comparative investigations of the two types of flow (see Fig. 6.3.)

A disadvantage with the chosen dimensions is the relatively low length/wall thickness ratio, which means that the cavity can be filled with a melt with a relatively high viscosity and, hence, possibly an unrealistically wide range of processing conditions.

Instrumentation of injection moulding machine

In the experimental work, the injection moulding variables are divided into (i) those variables, which should be monitored in order to secure stable conditions, and (ii) those parameters which are varied and used in a subsequent evaluation of the results.

One problem in stipulating processing conditions is to determine those variables which depend on the injection moulding machine and those variables which do not depend on the injection moulding machine. A second problem is to determine which of the many critical areas of the injection moulding process must be instrumented. Then means should be found for instrumenting these areas, many of which seem extreme conditions and are difficult areas in which to install instrumentation. Accompanying the instrumentation problem is to design and construct a system that can record and store data and, eventually, read back and analyze the data in an appropriate manner.

The selection of processing variables is discussed in the following paragraph. The environment of the mould was controlled by:
(i) Providing repeatable machine cycles (Fully automatic operating modes).
(ii) Measuring the temperature of the mould with thermocouples as close as possible to the cavity surface.
(iii) Measuring the melt temperature in the nozzle.
(iv) Measuring the rate of melt entering the mould by measurement of screw forward velocity.
(v) Measuring the pressure gradient from the hydraulic system over the nozzle to the cavity.
(vi) Measuring the temperature of the hydraulic oil.
(vii) Securing turbulent flow ($N_{Re} > 3500$) in the cooling channels.
(viii) Measuring the temperature, flow and pressure of the coolant before and after the mould.
(ix) When possible ensure that all machine settings are done by the same operator.
(x) Monitoring the ambient temperature and humidity.

Processing variables, chosen for variation, were (ii) to (v).

Due to the difficulty of choosing a position for measurement of mould separation during injection and the consideration that this variable is less important with a cavity placed in one mould half only, this variable was not included in the measuring system.

A prime consideration in choosing a system for recording the variables was that the system should be generally applicable, e.g. in a moulding shop. Therefore, all recordings were made using strip chart recorders and oscilloscopes. In the later stages, this system will be superseded with a system composed of a TV-screen for simultaneously monitoring of the main processing conditions and a cassette recorder for recording of data, which may later be evaluated together with other experimental input in a computerized system.
Processing conditions

The literature review has shown that melt and mould temperature, rate of filling, cavity pressure and effective packing time are important processing variables. Some of these variables are related, but none of them are directly controlled.

As no fundamental changes are expected in the design of injection moulding machines, there are reasons to believe that the main variables will remain important parameters in the future, no matter how much the method of control changes.

Of the five main variables, the effective packing time is dependent on the four other main variables and cannot be varied independently. For this reason, packing time was discarded as an experimental parameter.

Also, the rate of injection suffers from experimental difficulties. Firstly, it is dependent on the specific mould geometry, venting, surface conditions, etc., and the results, therefore, may not be generally applicable. Secondly, if it is defined as "equal to the screw-forward-velocity", it depends on the diameter of the screw. Thirdly, screw-forward-velocity is generally less interesting as a variable for a moulding with a constant geometry.

However, the level of the rate of filling should be defined. Here, a setting in the lower range (25 mm/s) was chosen to ensure that the screw-forward-velocity was not pressure controlled. (See Fig. 2.6) Also, as the variation in viscosity at high shear rates is greater than at lower rates, the higher injection speed tends to make the injection stroke more sensitive to variations in melt temperature, mould temperature, hydraulic valve actions and the many other variables that occur during the injection stroke.

Of the three remaining main variables, mould temperature was considered to be the prime experimental parameter, and was
varied with all materials. Melt temperature and cavity pressure were also varied with polypropylene and polycrylonitrile. They all vary with position and time during a cycle and, therefore, should be defined. Melt temperature was taken as the temperature of the melt in the center of the nozzle. Mould temperature was the average temperature of the mould 0.5 mm from the cavity surface. And, cavity pressure was the maximum pressure in a cycle measured 24 mm from the center of the gate. The total experimental array is given in Table 4.1.

Table 4.1. Experimental array

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PE</th>
<th>PP</th>
<th>POM</th>
<th>PA66</th>
<th>PA6</th>
<th>PA6F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt temperature</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mould temperature</td>
<td>(x)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Rate of filling</td>
<td>(x)</td>
<td>(x)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cavity pressure</td>
<td>(x)</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wall thickness</td>
<td>(x)</td>
<td>(x)</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(x) Supplementary experiments

Test methods and properties of mouldings

Mechanical properties, dimensional stability and shrinkage were considered to be the most important properties to be investigated.

Several mechanical properties could be of interest, however, falling weight impact, tensile properties and flexural modulus were chosen because in combination they give a fairly complete characterization of the moulding. They also, to some extent, depend on the variation found across the moulding.
In simplification, impact strength tends to depend on the surface properties, tensile strength tends to represent an average through the thickness, and flexural modulus depends to a large extent on the skin/core morphology.

The above properties are influenced by orientation and morphology. Therefore, the characterization of mechanical properties should be supplemented with observation of morphology by microscopy and characterization of crystallinity and orientation.

Post-crystallization processes usually are so slow that a predetermination at the product development stage is not possible. With a wide variation of the processing conditions, post-shrinkage may be even more difficult to predict and correlate with data obtained by annealing. Therefore, it was found appropriate to store samples under controlled conditions and measure the long-term post-shrinkage.
5.1 INTRODUCTION

This chapter describes the equipment for characterization of properties of mouldings, which have been developed as a part of the project.

The design of the mould, methods for recording of experimental variables, and apparatuses used for general characterizations are described in the following chapter.

The DSC-instrument was built according to a concept, kindly placed at our disposal by Mr. M.J. STEVENS at Loughborough University. It was thought that the apparatus was better than the commercially available ones for the intention of later investigations of thermal properties of polymers.

The falling-weight impact system was developed because a conventional falling-weight method used on polyethylene mouldings did not seem to discriminate between mouldings from widely different processing conditions.
5.2. DEFINITIONS AND MEASUREMENT OF DIMENSIONS

Shrinkage is defined as the difference in dimensions between the mould and the moulding (Fig. 5.1.)

Fig. 5.1. Changes in dimensions with time according to VDI-Richtlinie 2006

Shrinkage is not a constant value as the volume of mouldings is strongly dependent on temperature and pressure. For semicrystalline polymers especially, it is also dependent on time, due to long-term changes in the structure of mouldings. Such changes are related to the processing conditions and may be accelerated by annealing. Some hygroscopic polymers, e.g. polyamides, also increase in volume by absorption of matter from the environment.
It is, therefore, necessary to define when and at which conditions shrinkage is determined.

Mould or processing shrinkage \( (S_f) \) is defined according to DIN 16 901 as the difference in dimensions between the mould and the moulding both measured between 24 and 168 hours after moulding and after conditioning in a standard atmosphere \((23 \pm 2 \, ^\circ\text{C}/50 \pm 5\% \, \text{r.h.})\)

\[
S_f = \frac{L_f - L_m}{L_f} \times 100 \quad (\%) \quad (5.1.)
\]

For the quadrant the following applies: (Fig. 5.2.)

Radial mould shrinkage \( (S_r) \) is shrinkage in the direction of flow.

Tangential mould shrinkage \( (S_t) \) is shrinkage in the direction transverse to flow.

Differential shrinkage \( (\Delta S) \) is the difference between radial and tangential mould shrinkage.

Post shrinkage \( (S_p) \) is defined as "that, under defined conditions, generated difference in dimensions between the moulding cooled to 23 \( \pm \) 2 \(^\circ\text{C}\) and the same conditions for the moulding after storage at 23 \( \pm \) 2 \(^\circ\text{C}\) or annealed at a higher temperature."

Other dimensional changes are variations in the dimensions of the moulding, usually related to the fact that it is used in other environmental conditions than the standard atmosphere.

Sign – by convention, shrinkage is defined as, "positive and dilation (increase in volume or dimensions) negative."

Measurement – shrinkage of the quadrant is measured in a set-up, where the moulding is fastened in a fixed position by a spring-loaded lever (Fig. 5.2.). Two dial gauges record radial and differential shrinkage, respectively. The measuring point has a radius of \( R=1.5 \), which gives a penetration of approximately 4 \( \mu \text{m} \) according to Mekan 75617. Error of measurement is 6 \( \mu \text{m} \) at 6 mm and variation \( \pm 1 \mu \text{m} \) after DIN 878.

Anisotropy arise from different values for radial and tangential shrinkage. After demoulding, the specimen might change.
Fig. 5.2 Definition of shrinkage of quadrant specimen
its shape. A positive differential shrinkage (radial shrinkage larger than tangential shrinkage) causes an obtuse angle. A negative differential shrinkage (radial shrinkage smaller than tangential shrinkage) causes an acute angle (Fig. 5.2.).
Thermal Analysis is a joint designation of techniques for detecting the thermal effects accompanying physical or chemical changes in a sample as its temperature is varied through a region of transition or reaction, by means of programmed heating or cooling.\(^ {145}\)

Thermal Analysis was used for two purposes:

(i) Determination of the equilibrium (crystalline) melting temperature \(T_m\)

(ii) Determination of the fraction of crystallinity.

In this section the concept of differential scanning calorimetry is introduced, the apparatus used in the experiments described, together with the calibration procedure and the experimental method.

Introduction

In Differential Thermal Analysis (DTA) a sample and an inert reference material are heated at the same rate in identical cells and the temperature difference between the two is monitored by thermocouples placed in the centers of the sample and reference. Under steady-state conditions the "baseline" is a slowly varying function of temperature which reflects the gradual change in the overall thermal properties of the assembly. However, when a thermal event (recrystallization, a phase change, decomposition or any other chemical reaction) occurs the thermocouple output is perturbed because the sample temperature is less than (endothermic event) or greater than (exothermic event) steady-state conditions would suggest. The output signal is roughly proportional to the magnitude of the event.\(^ {235}\)

The basic differences between DTA and Differential Scanning Calorimetry (DSC) lie in the design of the heating system and the mode of operation of the instrument. In DSC, the sample and reference are heated separately by individually
controlled elements. The power to these heaters is adjusted continuously in response to any thermal effects in the sample, so as to maintain sample and reference at identical temperatures. The differential power required to achieve this condition is recorded as the ordinate on an x-y recorder, with the (programmed) temperature of the system as the abscissa.

In classical DTA, the sample forms a major part of the thermal conduction path. Since its thermal conductivity changes in a way that is generally unknown during a transition, the proportionality between temperature differences and energy changes is also unknown. This makes the conversion of peak areas to energies uncertain and relegates DTA to an essentially qualitative category. In contrast, in DSC the peak area is a true measure of the electrical energy input required to maintain the sample and reference temperatures equal, independent of the instrument's thermal constants or any changes in the thermal behaviour of the sample. The calibration constant relating DSC peak areas to calories is known and constant, permitting quantitative analysis.

It is, however, not difficult, with proper design and operating conditions, to make any DTA apparatus perform functions similar to those of DSC. This can be done by removing the thermocouples from the interior of the sample and reference, locating them close by, but external to these materials.

This eliminates the dependence of the thermal conductivity on changes in the sample, but the temperature dependence remains. This type of cell, which is used in commercial DSC cells for use with DTA equipment, is also known as Dynamic Differential Calorimetry (DDC). The apparatus used in the thermal analysis reported here was based on this principle of design. To make reliable calorimetric measurements with this design requires calibration with a standard having a transition temperature close to that of the unknown, and particular care must be taken that the thermal conductivity remains the same from one experiment to the next.
Apparatus

The instrument used in this work was built to a design by M.J. STEVENS of Loughborough University to fulfil a specific requirement arising from research on the thermal properties of polymers at high pressures. The equipment basically comprises a constantan disc which is heated around its outer edge. The starting and maximum temperatures can be preset and the rate of heating can be accurately controlled (The cooling rate can only be controlled up to the point where the natural cooling rate of the cell becomes slower than the programmed cooling rate). Two small aluminium pans are located on the disc at the same distance from the centre.

One pan contains the sample, and the other an inert material (aluminium foil) in order to balance the heat capacity of the system, thus providing a more straight baseline. Beneath each pan and welded to the disc is a chromel/alumel thermocouple. The thermocouple beneath the sample detects sample temperature and the chromel wires of the two thermocouples are utilised in forming a chromel/constantan - constantan/chromel thermocouple to detect the differential temperature between the reference and sample pan.

The sample temperature signal (x axis) is fed directly to the recorder, the differential temperature signal (ΔY axis) is fed into a 3000 gain amplifier.

All parts with the exception of the cell and the amplifier were purchased from approved suppliers.

The cell comprises an upper and lower body. The upper consists of the block and disc assemblies, lids and thermal shielding. The lower body virtually acts as a base and encloses the thermocouple and heater wire junctions. (Fig.5.3.)

*) Constantan is a degenerated trade name. Actually a material with the trade name "Ferry" (46 Ni/54 Cu) was used.
Temperature control

DSC - cell

Cold junction reference

Junction box (insulated)

Digital voltmeter

3000x amplifier

Constant voltage instrument

$x - y$ recorder

Fig. 5.3 DSC instrument
The block, lids and plates are machined from copper and are silver-plated to reduce the risk of oxidation and to improve the thermal resistance. Care was taken during the machining of the block and during the wrapping of the heater coils to ensure the symmetry of the block. The temperature of the block is monitored by the control thermocouple which is backed off by the cold-junction thermocouple and the resultant signal fed into the controller/programmer-equipment.

The block is mounted on PTFE pedestals well above the lower body to avoid heat transferance to and from the lower body during heating and cooling of the block at low pressures. The insulation around the block is made of aluminium foil folded in a random fashion in order to provide relatively small interconnected spaces to minimize the effects of convection, which was thought to be a major cause of instability in an earlier model when nitrogen pressure was increased beyond 35 bar. A 5-layer foil cylindrical shield with closed top is fitted over the block and finally a glass bell jar is fitted over the shield. The controller, programmer and thyristor unit were purchased (Eurotherm Indicating Solid State Temperature Controller Type 090, Eurotherm Set Point Ramp Generator Programmer Type 120 and Eurotherm Thyristor Units Type 031, respectively.)

The pressure vessel, which is not used in the work reported here, has a capacity of 0.013 m³ and is designed for working pressures up to 700 bar. Nitrogen bottles with an initial pressure of 175 bar are utilized in purging the vessel and building up initial pressure and then a pneumatic drive gas pump with an inlet pressure up to 140 bar completes the process.

A potentiometric recorder (W-W-1100) is used to record each run by plotting one axis against time, or, alternatively, a x-y recorder (Linseis, L-800) is used to record differential temperature against sample temperature. A 5,5 digit 0,004%
multimeter (Data Precision, model 3500) is included in the electronic circuit, connected to perform many varied tasks (Fig. 5.3).

The most important parameters for the instrument to be considered at the design stage were:

(i) To be capable of operating in a Nitrogen atmosphere from 1 bar to 700 bar pressure at temperatures up to approximately 300°C.

(ii) Repeatability of runs.

(iii) Sensitivity better than 0.05°C per cm (3 μV per cm). Resolution better than 0.002°C (0.1 μV).

(iv) Compatibility with existing control and read out equipment.

(v) Capable of disassembly for maintenance, repairs and modification.

With the actual cell the following data has been achieved

(i) Sensitivity ≥ 0.02°C/cm

(ii) Resolution ≥ 0.003°C

≥ 0.12 mW energy flux between sample and reference.

(iii) Reproducibility at calorimetric measurements ± 5%

(iv) Rate of heating: 0.8 – 100°C/min.

(v) Working pressure: 35 MPa (Measured at Loughborough University as our equipment does not include a pressure vessel).

Modification to improve performance are currently being adapted so the configuration as outlined here should not be regarded as final.

Testing of Apparatus

After the apparatus had been built some minor modifications were made. As an example, all wires were electrically shielded and the ice bath for the cold junction thermocouple was replaced by an electronic cold junction.
The constantan disc was then annealed in-situ 6 hours at 625°C in a N₂ atmosphere in a chamber built around the cell. The lower part of the cell was cooled with compressed air during the annealing.

For the initial experiments, a potentiometric recorder (Servoscribe RE 11.29) was used to record $T_{heating} = f(t)$ (Fig. 5.4). The corresponding voltage was read from a voltmeter (Solartron A 210) with 1 minute intervals. These values were then plotted on A3 millimeter paper and the line $T=f(t)$ drawn. In later experiments, a stop-watch was used to determine the time from when the "Hold" contact was switched-on until the maximum value was registered on the digital-voltmeter. The peak temperature was then read from the $T=f(t)$ diagram. The base line was tested with two empty pans for linearity. It was found that the base line was constant and reproducible (Fig. 5.4).

The programming unit was tested several times with and without a glass reference with sample temperature signal (x-axis) and differential temperature signal (± Y-axis) being recorded. The time from "Switch-on" until the illumination of the diode for "set-pt" disappeared was recorded and found to be consistent. It was later found that this period could drift approximately 3% for 20 min. runs over a period of 12 h.

The linearity of the recorder was checked for rising and falling voltage, using a constant voltage instrument (Eurotherm, Type 039).

Calibration

In using the equipment for measurement of change in enthalpy during melting it is necessary to calibrate the cell. This was done with two methods:

4) After consulting the Metallurgical Department at Loughborough University, it was later revealed that an annealing above 600°C may result in a partial and uneven crystallization of constantan. Instead, it was suggested to heat-up the cell a few times to a temperature a little higher than the usual working temperature for the cell.
Fig. 5.4. Base line and heating curve for DSC-instrument.
Conventional enthalpy calibration using a substance (Indium) with known heat of fusion and well defined melting and transition enthalpy.

Electrical calibration using a small heating element of own design capable of giving a constant energy flux between the element and the reference.

**Calibration with indium**

This procedure comprises the following steps.

(i) Determination of a calibration factor so that the enthalpy can be calculated from a given melting peak area.

(ii) Determination of the relation between the calibration factor and the energy flux between the sample and the reference. That is, how it depends on sample weight and rate of heating.

(iii) Determination of the relation between calibration factor and cell temperature.

(iv) Determination of the range where a given calibration factor can be assumed to be constant (linearity) and without influence from the cell temperature.

The calibration factor is determined by measuring the area under the fusion endotherm, which is proportional to the heats of reaction or transition \( \Delta H \) for the reaction or transition, which causes the peak. This is expressed by:

\[
\Delta H \cdot m = K \cdot A \\
\implies \Delta H = K \cdot \frac{A}{m}
\]

(5.2.)

where

- \( \Delta H \) = Heats of reaction or transition
- \( m \) = Mass of the reactive sample
- \( K \) = Calibration factor
- \( A \) = Area between the peak and the base line

K is dependent on the instrument and how the measurement is registered. If the sensitivity for \( \Delta T \) (°C/cm) and the chart speed setting is included, the following expression is ob-
served for the calibration factor \( K \) (in mcal/min °C)

\[
K = \frac{\Delta H \cdot m \cdot C}{A \cdot \Delta T_s}
\]

(5.3.)

where

\( \Delta H \) = Heat of transition (cal/g)

\( m \) = Mass of sample (mg)

\( C \) = Chart speed (cm/min)

\( A \) = Area under the peak (cm²)

\( \Delta T_s \) = Sensitivity for \( \Delta T \) (°C/cm)

Relevant data for calibrants must be checked with literature. For indium, however, the most commonly used of all calibrants, there are reservations about literature data\(^{145}\). Special care must be taken with old data, since not only have experimental techniques improved but the purity of materials now available may be orders of magnitude greater than those of only a few years ago.

As an example of a calibration (for the experiments described in Section 6.7.) the following example is given.

The heat of fusion of indium was used as standard, as recommended by the Du Pont Manual\(^{237}\) which quotes a melting point of approximately 155°C and heat of fusion as 6.79 cal/g (28.42 kJ/kg) from the American Institute of Physics Handbook. The CRC Handbook of Chemistry and Physics, 53rd edition p.B 17 and D56 gives a melting point 156.61°C, boiling point 2080°C, specific gravity 7.31, atomic weight 114.82 and heat of fusion 0.775 kcal/g.mol. This is equivalent to 6.75 cal/g (28.30 kJ/kg), which is in good agreement with the Du Pont value.

Another reference\(^{238}\) gives the melting point as 156.4°C and the heat of fusion as 6.79 cal/g (28.42 kJ/kg).

Du Pont recommend a mass of 1.5 mg, but in the calibration a bigger mass was used in order to improve the accuracy in weighing and to obtain a larger signal. There was no evidence
of an effect of mass on the calibration, and repeat runs showed negligible change due to oxidation of the sample (which was blanketed with nitrogen).

The rate of heating was set at 0.2025 mV/min, corresponding to 5.04 °C/min. when based on an average e.m.f. of chromel/alumel of 4.02 mV per 100 °C (mean 105-205°C). Other sources (Pyrotenax) gives the e.m.f. of chromel/alumel to 4.034 mV per 100 °C, which corresponds to 5.02 °C/min.

The result of the calibration is shown in Table 5.1. It should be noted that the calibration would change for a different heating rate.

Table 5.1. Calibration of DSC cell *)

<table>
<thead>
<tr>
<th>Run No</th>
<th>Sample No</th>
<th>Sample Weight g</th>
<th>Chart Speed mm/min</th>
<th>Scale mV/20 cm</th>
<th>Peak Area cm²</th>
<th>Equiv Area cm²</th>
<th>100 cm² ~ cal²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1</td>
<td>0.124</td>
<td>120</td>
<td>100</td>
<td>52.8</td>
<td>8.78</td>
<td>0.960</td>
<td></td>
</tr>
<tr>
<td>2 1</td>
<td>0.124</td>
<td>120</td>
<td>100</td>
<td>52.6</td>
<td>4.91</td>
<td>0.954</td>
<td></td>
</tr>
<tr>
<td>1 2</td>
<td>0.0069</td>
<td>120</td>
<td>50</td>
<td>59.1</td>
<td>15.35</td>
<td>0.974</td>
<td></td>
</tr>
<tr>
<td>2 2</td>
<td>0.0069</td>
<td>120</td>
<td>50</td>
<td>58.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 3</td>
<td>0.022</td>
<td>120</td>
<td>200</td>
<td>46.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 3</td>
<td>0.022</td>
<td>120</td>
<td>200</td>
<td>45.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) for 50 mV scale and chart speed 600 mm per hour
2) based on indium latent heat of fusion 6.79 cal/g.

(28.43 kJ/kg)

Calibration with heating element

In order to facilitate the calibration an electrical calibration was developed. This method is based on a small heating element capable of giving a constant energy flux between the element and the reference. C 10)

Preliminarily, the use of a conventional aluminium wire and the filament of an automobile bulb was tried as a heating

*) The calibration was done by A.BOOTON of Loughborough University
element. It was soon obvious, however, that this was not feasible due to the necessary small dimensions.

Therefore a semiconductor junction diode with a resistance of approximately $8 \, \Omega$ only was used. This also solved the problem of finding connecting wires, with a resistance considerably less than in the heating element and with a low thermal conductivity. The wires should also have a fair mechanical strength. To fulfil these requirements constantan wires were chosen.

The final assembly was embedded in epoxy in a conventional 6 mm aluminium pan (Fig. 5.5.).

![Diagram of heating element](image)

Fig. 5.5. Heating element for cell calibration

The actual calibration was carried out by running the cell at various temperatures and at the same time depositing a given amount of energy in the heating element while the corresponding voltage from the differential amplifier was registered on a recorder. Effect was registered using a milliamperemeter and a voltmeter.

The result of the calibration is given in a graph (Fig. 5.6.), which shows the relation between energy flux and amplifier
Fig. 5.6 Calibration of DSC cell
output. The time for recording of the graph was approximately three hours.

The graph shows that the relation between $\Delta T$ and $Q$ is not linear, and that it is dependent on the cell temperature. However, with an energy flux lower than 15mW, the relation can, with reasonable exactness, be assumed linear for all cell temperatures. For a higher energy flux a correction factor must be included.

The final calibration then simplifies to

$$\Delta H = 0,1 \int_{T_1}^{T_2} y \, dt \quad (mJ) \quad (5.4.)$$

where

$\ y = $ recorder deflection with sensitivity 5mV/cm

$\ t = $ time in sec.

A control measurement using indium as a reference gave a calculated melting enthalpy of 28,1 kJ/kg as compared to the stated reference value for the sample in question of 28,4 kJ/kg. The difference being approximately 1%, which is acceptable, taking into consideration that the calibration can be done under stationary conditions which are easy to control and reproduce.

Procedure for measurement of peak area

The variation of crystallinity across an injection moulded specimen can be used as an indication of the thermal and rheological conditions during solidification. Using thermal analysis for this purpose, however, creates some experimental problems.

Some of these problems can be attributed to the measurement of the peak area because semi-crystalline polymers have a broad melting interval, associated with a shift in baseline after melting due to a difference in heat capacity before and after melting.

A consequence of the gradual melting is that the baseline will shift in proportion to the part of the sample which has melted (Fig.5.7.).
Endotherm

Heating rate 7.0 °C/min
Sample weight 2 mg

Fig. 5.7 Melting endotherms for polyoxymethylene
It should be mentioned, also, that two identical samples of the same material, but with a different thermal history will not show the same melting characteristics.

This difference is clearly seen in Fig. 5.7, which also shows that the true baseline cannot be identical for the curve with the dotted line and the fully drawn line.

Therefore, an attempt was made to eliminate this problem by calculating the actual melting enthalpy in the following way:

First, the thermal analysis of the samples is carried out as indicated with the dotted line. The sample is then cooled in the cell at a constant, slow rate of cooling. After this slow cooling the sample will have a degree of crystallinity independent of the first thermal history. The thermal analysis is then repeated, starting from the same base line as in the first run. This gives the fully drawn curve. The area measurement can then be done on entirely closed areas, as indicated with the hatched areas of the figure and the degree of crystallinity measured on the basis of a difference between the two curves.

The proof that this additional work is well worth doing can be seen with polyoxymethylene, when compared with the density of samples taken from the same positions as used for thermal analysis (Fig. 5.8.a).

In the graph, mode I represents calculations based on the conventional method and mode II is the improved method based on closed curves. The same tendency can also be seen when comparing the relation between melting enthalpy and the distance from the surface (Fig. 5.8.b)

A similar result was achieved with polypropylene (Fig. 5.8.c). With polyethylene, however, a lesser agreement was found (Fig. 5.8.d). It is believed that this can be attributed to factors relating to a crystallization-melting-recrystallization process, which is more pronounced with polyethylene than with polyoxymethylene and polypropylene. Some observations to prove this hypothesis are described in Section 8.4.2.
Fig. 5.8 Density and melting enthalpy

**Density and melting enthalpy**

- **Polyoxymethylene**
- **Polyethylene**

---

Figures a, b, c, and d illustrate the density and melting enthalpy for Polyoxymethylene and Polyethylene. Each figure contains two graphs, one for calculation mode I and one for calculation mode II. The graphs show the relationship between density (in Mg/m³) and melting enthalpy (in J/kg).
Summary

An apparatus has been developed for thermal analysis of polymers. An electrical heating element reduces the time used for calibration. It was found that melting peak areas measured on the basis of closed curves eliminate problems arising from the drawing of a base line.
5.4. DESIGN OF EQUIPMENT FOR INSTRUMENTED FALLING WEIGHT IMPACT

Compared with a conventional falling weight impact test, an instrumentation of the test equipment results in a better reproducibility with fewer samples. Additional information is also obtained by the recording of an energy/time diagram which provides information about the ductility of the material and where the curve shape read-out aids analysis of the fracture.

Principle

The test applies excess energy using a transducer to detect force/time characteristics of fracture. As velocity is considered constant with excess energy systems, time can be converted into displacement and hence a force/displacement diagram can be derived. The derivation of time to displacement is possible when the actual energy in the dart is so high as compared with the necessary energy to fracture that the velocity of the dart during penetration is almost unchanged ( > 5% according to DIN 53 753).

The total penetration energy \( E_b \) is equal to the integral of the force exerted on the specimen by the falling weight \( F \) and the displacement of the point of action \( s \)

\[
E_b = \int F \, ds \quad (5.5.)
\]

or

\[
E_b = \int Fv \, dt \quad (5.6.)
\]

where

\( v = \) Speed of the falling weight at the point of impact.

However, when the penetration energy comprises a substantial part of the kinetic energy of the falling weight the velocity will be reduced.

In this case the assumptions in Equation (5.5.) are no longer fulfilled and a correction for the reduction in velocity should
be introduced\textsuperscript{239}, and Equation (5.5.) becomes

\[ E_b' = A \cdot v_o (1 - \frac{v_o A}{4 E_{\text{max}}}) \]  

(5.7.)

where

- $E_b'$ = Energy absorbed on the specimen during impact
- $v_o$ = Velocity at the point of impact = $\sqrt{2gh}$
- $E_{\text{max}}$ = Maximum available energy = Wh
  where $W$=Weight of dart, $h$= drop height.

In the above relation, the weight of the dart and the height from which it is dropped is easily measured. Measurement of the impulse requires that the dart be instrumented in such a way that the force being exerted on the specimen during the short time duration of the impact process can be measured.

The actual force, as a function of time acting on the specimen, is measured with a transducer which transmits information to an oscilloscope. However, as it was not considered feasible to build the transducer directly into the tip of the dart, it was mounted instead inside the dart where only a fraction of the total weight is influencing it. Therefore, the test results should be corrected by:

\[ \text{Real force: } \frac{\text{Registered force} \times \text{total weight of dart}}{\text{Weight above transducer}}. \]

The position of the transducer inside the dart was also preferred because it was thought to give a faster resonant frequency response and a better resolution than at a position in the support plate.

In the experiments with polypropylene reported in Chapter 8 the force/time diagram was integrated to an arbitrarily chosen position of 5 ms on the time axis. This position on the curve corresponded approximately to the point where breaks occur and to a damaging force ($F_s$) exerted on the impact point of the sample in the direction of penetration approximately 10% less than the maximum force ($F_{\text{max}}$) (Fig. 5.9).
It has been shown in experiments using high-speed photography that the first cracks occur in materials when the damaging force is reduced by 10% of the maximum value*).

---

*) See e.g. Ronfalin. Instrumentierter Flachfalltest DSM Technical note 5/79.
takes place in the material between the dart and the mounting plate. It has been shown (see footnote op.cit.) that a flat dart also makes it possible to distinguish between (i) the impact yield strength at short load times and (ii) the toughness which is represented by a "constricting area" equal to \( \varepsilon F_{\max} - \varepsilon_s \), where \( \varepsilon_s \) equals the damaging deformation.

As only the first part of the curve is used in the further calculations, the disadvantage of the hemi-spherical form used in these experiments, where the total penetration energy also comprises the friction energy used between sample and dart from the first cracks to the termination of penetration, did not appear serious enough to change the design of the dart.

Finally, it should also be observed that the damaging energy alone does not give a unique description of the material, because two materials with a different ductility may have integrated force/deflection curves with approximately the same area. A complete characterization would require the establishment of a reference curve where \( E_b \) and \( F_{\max} \) are depicted as a function of wall thickness. When such a graph is established on compression moulded sheets it will provide a very useful tool for investigating the influence from processing.

Apparatus

The equipment consists of a support stand with a mounting plate for the test sample. Mounted on the support stand is a framework with two columns guiding the falling dart. A device for holding the falling dart by an electromagnet is fixed to the framework. This mechanism can be raised or lowered thereby adjusting the falling height.

The specimen is supported by a 54 mm i.d. ring attached to a machine-surfac ed iron support block mounted on the support stand, the height of which can also be adjusted (Fig. 5.10).
Fig. 5.10 Instrumented falling weight impact equipment
Initial tests showed that the test samples could simply be placed upon the mounting plate without being clamped.

The test involved a 25 mm diameter impactor with the tip formed as a cap of a sphere with \( h = 10 \) mm. The dart had a total mass of 3500 g. A drop height of 2000 mm was used. This gives a total energy of 68.7 J and a velocity before impact of 6.26 m/s.

The transducer, which is mounted inside the dart, transmits information to an oscilloscope connected to a measuring bridge, a variable power supply, a differential amplifier and a device to trigger the oscilloscope (Fig. 5.11).

![Diagram of instrumentation of falling weight equipment](image)

Fig. 5.11 Instrumentation of falling weight equipment

The transducer, which is based on the strain-gauge principle, consists of a brass bushing mounted with five strain gauges (Fig. 5.12).

![Diagram of transducer](image)

Fig. 5.12 Transducer, scale 1:1
The strain gauges form a part of a bridge (Fig. 5.13). They are coupled in series and have a total resistance of approximately 600 Ω. \( R_1 \) also consists of 5x100 Ω strain gauges in series in order to achieve temperature stability. \( R_2 \) and \( R_3 \) are 5 W resistors with a resistance of approximately 600 Ω.

For reasons of stability, it is necessary to use resistors of minimum 5 W. The two variable resistors are potentiometers which can be varied between 5 MΩ and 10 MΩ.

Fig. 5.13 Measuring bridge.

The power supply should be stabilized and variable between 10 and 20 volt d.c. The differential amplifier is the same as used for the thermal analysis apparatus (Section 5.3). The trigger device is an optical system working with a mirror and giving a negative slope by activation. It is adjusted so that the oscilloscope is triggered just before the dart touches the sample. The oscilloscope (Tektronix) has storage facilities.

Calibration is done by using a fixture in which the measuring cell is mounted. With a given bridge voltage, a given amplification, and sensitivity on the oscilloscope, the displacement is then registered in proportion to the acting force. With the cell in question a calibration factor of 0.062 mV per Newton per Volt bridge voltage was found.
The absorbed energy was calculated from Equation (5.7). A graph was drawn from the oscilloscope screen on a transparent material and the area determined by planimetry or by weighing. The absorbed energy was calculated by the combined use of a schema and a programmable calculator (Appendix G.).

Modifications to the design outlined here have been suggested. They could comprise measurement of the real velocity before impact by use of photo cells: Equipment for automatic data recording could also easily be incorporated.

Example

As an example, two sets of 3 mm quadrant specimens of polypropylene were tested. Each set consisted of five mouldings. The specimens were moulded with a melt temperature of 240 °C, cavity pressure 550 bar. Mould temperature was varied on four levels. The impact was on the center of the mouldings. The test was carried out at room temperature. Other conditions are described above. The following results were obtained (in J)

<table>
<thead>
<tr>
<th>Mould temperature (°C)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set I</td>
<td>2.16</td>
<td>2.18±0.020</td>
<td>2.13</td>
<td>2.11</td>
</tr>
<tr>
<td>Set II</td>
<td>2.17±0.058</td>
<td>2.19±0.027</td>
<td>2.18±0.018</td>
<td>2.13±0.057</td>
</tr>
</tbody>
</table>

Considering the difficulty in reproducing moulding conditions, (e.g. injection rate), the results show a satisfactory agreement between the two sets. The samples were stored and conditioned before testing. However, the time from moulding to testing was slightly shorter with set II. (In a similar experiment with polycarbonate, it was found that the damaging energy decreased with time from 67.5±0.4 to 65.4 to 59.9 J, immediately, 24 h, and 36 h after moulding respectively, indicating a relaxation of the samples and a more resilient material with time.)

A typical curve from a test on samples moulded with different melt temperature is shown in Fig. 5.14.
Generally, three modes of failure can be observed in a falling weight impact test: (i) Brittle failure; (ii) Crack failure; (iii) Puncture failure. These three modes, however, are principal types and in practice mixed failure modes are often found\(^{239}\).

In Fig. 5.14 both failures were brittle, but the failure curves of different types. A low melt temperature resulted in a higher maximum force and a more pronounced single peak. A high melt temperature resulted in a lower force and a double peak with a more controlled crack growth.

The double peak is thought to be the result of a bouncing of the dart. It was found also when the specimen was firmly clamped.

Fig. 5.14 Change in damaging energy with processing conditions (Curves redrawn from oscilloscope trace)
A possible explanation is that the trace represents two different types of energy; (i) energy being given up by the specimen in both a plastic and elastic manner, and (ii) energy being given up by the specimen in moving the dart upward.

The first peak then should arise when the dart penetrates into and deforms the specimen. The force should reach a maximum and then begin to decrease as the drawing process begins. When the drawing process has proceeded as far as possible and the deflection of the specimen has reached a maximum, the dart will change direction and begin to move until it loses contact with the specimen. All through this process, a force will be exerted on the dart. However, for a certain portion of the time, the dart will be moving down and for another portion it will be moving up. Therefore, a change in the sign of the velocity will have occurred, and the specimen may have absorbed all the energy available. However, this energy was not absorbed in a plastic manner; rather, it was absorbed in an elastic manner, and part of the energy absorbed by the specimen was given up in moving the dart upward. The difference between the maximum energy available and the energy required to move the dart upward is the amount of energy the specimen absorbed in a plastic manner 

It should be noted that for the experiments reported in Chapter 6 the force/time trace was integrated to an arbitrarily chosen position of 5 ms on the time axis, which to some extent compensates for the above effects.

Summary

A system has been developed whereby the energy absorbed during fracture in a falling-weight impact test can be measured for each specimen tested. Also, a more representative value of falling-weight impact strength can be determined in cases where there are mixed modes of failures.
6.1. INTRODUCTION

This chapter describes the characterization of processing properties of the polymers, the set-up for moulding of the specimens, computation of cooling curves and the characterization of the morphology and properties of the mouldings.

The experimental array, the polymers investigated, and the processing conditions are given in the following Table 6.1. Polystyrene mouldings were moulded only as a reference for characterization of orientation.
Table 6.1 Experimental array: Materials and Processing parameters (nominal values)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Supplier</th>
<th>Type</th>
<th>Density (g/cm³)</th>
<th>Melt index (g/10 min)</th>
<th>Specimen</th>
<th>Melt temp. (°C)</th>
<th>Cavity wall temp. (°C)</th>
<th>Cavity pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Hoechst</td>
<td>Hostyren N 3001</td>
<td>1.04</td>
<td>200/5 = 13</td>
<td>3 mm-1/4</td>
<td>180-210-240</td>
<td>35</td>
<td>80</td>
</tr>
<tr>
<td>PE</td>
<td>Hoechst</td>
<td>Hostalene GC VP 7260</td>
<td>0.958</td>
<td>190/2 = 7</td>
<td>3 mm-1/4</td>
<td>160-190-220</td>
<td>35</td>
<td>55</td>
</tr>
<tr>
<td>PP</td>
<td>Hoechst</td>
<td>Hostalene PNN 1060 (Homopolymer)</td>
<td>0.905</td>
<td>190/5 = 3, 230/2 = 1.5, 230/5 = 7</td>
<td>2 mm-mono, 3 mm-1/4, 5 mm-1/4</td>
<td>190-240-290, 240</td>
<td>40</td>
<td>20-55</td>
</tr>
<tr>
<td>POM</td>
<td>Hoechst</td>
<td>Hostaform C 9010 (Copolymer)</td>
<td>1.41</td>
<td>190/2 = 9</td>
<td>4 mm dumbbell 1 = 175 mm</td>
<td>210</td>
<td>40-65-90-115</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Hoechst</td>
<td>Hostaform C 9021 R</td>
<td>1.41</td>
<td>190/2 = 9</td>
<td>2 mm-mono, 3 mm-1/4, 5 mm-1/4</td>
<td>185-220, 220, 185</td>
<td>60-80-100-120, 60-80-100-120, 80-100-120</td>
<td>50, 50, 50</td>
</tr>
<tr>
<td>PA 66</td>
<td>BASF</td>
<td>Ultramid A 3 K</td>
<td>1.12-1.15</td>
<td>3 mm-1/4, 5 mm-1/4</td>
<td>285, 285</td>
<td>60-80-100-120</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>PA 6</td>
<td>Bayer</td>
<td>Durethhan BK 30 S</td>
<td>1.14</td>
<td>5 mm-1/4</td>
<td>255</td>
<td>60-80-100-120</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>PA 6 f</td>
<td>Bayer</td>
<td>Durethhan BKV 30 S</td>
<td>1.36</td>
<td>5 mm-1/4</td>
<td>280</td>
<td>80-100</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>
6.2. MATERIAL PROCESSING PROPERTIES

6.2.1. Melt Index

Melt index of polyethylene, polypropylene and poly(oxy)methylene was checked on a routine basis using a Davenport Melt Indexer. A standard (0,2096 cm) die, as well as a "small bore" capillary were used.

6.2.2. Crystalline Melting Point, Crystallization Temperature and Spherulite Growth Rate

The crystalline melting point, crystallization temperature and spherulite growth rate were determined, using a Reichert Thermopan microscope with a Mettler FP5 + FP 52 hot stage (at. IPT, Loughborough University).

The microscope was equipped with a 10x achromatic objective, a 12,5x Zeiss measuring ocular and a 10x photo ocular, respectively. The measuring eyepiece was calibrated from a graticule. Several determinations gave the result that 1 unit equals 0,098 mm. For illumination a 15W/220V Lux NT lamp was used. The analyzer and polarizer were set to complete extinction.

The Mettler hot stage consists of (a) a control unit (FP 5) which provides rapid temperature changes in either direction, and heating at five controlled rates. (0,2-1-3-10 °C/min); (b) a remote pushbutton unit for holding the stage temperature (in the range 30 - 300 °C) constant momentarily and for recording three selected temperatures for later digital display; and (c) the hot stage proper (FP 52) which was placed on the microscope stage. The temperature of the sample was measured with a built-in calibrated platinum resistance thermometer.

The precision of the melting point determination using the hot stage depends upon heating rate: At 10 °C/min, Tm can be estimated to be no better than ± 1 °C, whereas at 0,2 °C/min,
a precision of $\pm 0.1^\circ\text{C}$ can be reached. However, accuracy is difficult to specify, since the melting point of any specimen depends upon its previous thermal history\textsuperscript{145}).

For the determination of spherulite growth rate, two methods were used: (i) direct determination by observation in the measuring ocular and (ii) at the lowest temperatures and, hence, highest rates of crystallization using photographs taken at constant intervals with a KAM-ES camera unit using an Ilford HP 5 film exposed at 1600 ASA. The diameters of the spherulites were then measured on 13 x 18 cm prints.

The crystalline (optical) melting point was taken as the temperature at the disappearance of the last traces of birefringence after heating the sample, and the onset of crystallization as the point of its first reappearance upon cooling.

**Determination of the crystalline melting point. Polyethylene**

An approximately 2 mg specimen was cut with a scalpel and placed on a glass slide and covered with a cover slip. The slide with the specimen was placed in the hot-stage unit and heated rapidly to 165 $^\circ\text{C}$ ($T_m + 40^\circ\text{C}$). After melting, the cover slip was pressed onto the molten polymer to form an approximately 0.10 mm thin film. After melting, the specimen was kept a further 5 min. at 165 $^\circ\text{C}$, and then cooled rapidly to 95 $^\circ\text{C}$ ($T_m - 40^\circ\text{C}$). The average rate of cooling was 14.6 $^\circ\text{C}$/min. At the most rapid heating or cooling rate, the sample temperature lagged behind the indicated temperature, reaching it only when the control light glowed steadily. The specimen was kept at 95 $^\circ\text{C}$ for 1 min. and then heated with a rate of heating of 1 $^\circ\text{C}$/min. to 130 $^\circ\text{C}$, and then with 0.2 $^\circ\text{C}$/min. The temperature at which the sample started to melt was recorded as $T_A$. The temperature at which the light intensity was reduced to about 1/2 as $T_B$, and the temperature where the field became completely dark at $T_C$.  

\[179\]
This procedure was repeated in three successive experiments and the following results were obtained:

$T_A : 131,0 - 131,0 - 130,9 \degree C$

$T_B : 131,8 - 131,8 - 132,0 \degree C$

$T_C : 132,6 - 132,7 - 132,8 \degree C$

The crystalline melting range, and the crystalline melting point, respectively, were determined as:

$T_{A-C} = 131,0 - 132,7 \degree C$ and $T_m = 132,7 \pm 0,1 \degree C$

**Polypropylene**

The following procedure was followed. Melting at $210 \degree C$ for $5 \text{ min}$, then rapid cooling to $115\degree C$ with an average rate of cooling of $23,3 \degree C/\text{min}$. This temperature was kept for $1 \text{ min}$ with subsequent heating at $3 \degree C/\text{min}$ to $160 \degree C$, then $1 \degree C/\text{min}$ to $170 \degree C$ and then $0,2 \degree C/\text{min}$.

This procedure was repeated in three successive experiments and the following results obtained

$T_A : 164,1 - 162,3 - 163,7 \degree C$

$T_B : 170,0 - 169,6 - 169,4 \degree C$

$T_C : 171,2 - 170,1 - 170,2 \degree C$

The crystalline melting range, and the crystalline melting point, respectively, were determined as:

$T_{A-C} = 163,4 - 170,5 \degree C$ and $T_m = 170,5 \pm 0,6 \degree C$

**Polyoxymethylene**

The following procedure was followed, melting at $210 \degree C$ for $5 \text{ min}$, then rapid cooling to $115 \degree C$ with an average rate of cooling $23,7 \degree C/\text{min}$. This temperature was kept for $1 \text{ min}$ with subsequent heating at $3 \degree C/\text{min}$ to $160 \degree C$, then $1 \degree C/\text{min}$ to $165 \degree C$ and then $0,2 \degree C/\text{min}$.
This procedure was repeated in three successive experiments and the following results obtained:

\[
\begin{align*}
T_A & : 160.8 - 162.1 - 162.2 \, ^\circ C \\
T_B & : 166.0 - 166.3 - 166.4 \, ^\circ C \\
T_C & : 167.2 - 167.1 - 167.0 \, ^\circ C \\
\end{align*}
\]

The crystalline melting range, and the crystalline melting point, respectively, were determined as:

\[
T_{A-C} = 161.7 - 167.1 \, ^\circ C \text{ and } T_m = 167.1 \pm 0.1 \, ^\circ C
\]

**Polyamide 66**

With polyamide 66 one informative determination was made according to the following procedure, melting at 280 \, ^\circ C for 5 min, then rapid cooling to 150 \, ^\circ C, which was kept for 1 min, then heating at 10 \, ^\circ C/min.

The crystalline melting range, and the crystalline melting point, respectively, were determined as:

\[
T_{A-C} = 263.4 - 265.9 \, ^\circ C \text{ and } T_m = 265.9 \, ^\circ C
\]

**Polyamide 6**

The same procedure as for PA 66 was followed. The crystalline melting range, and the crystalline melting point, respectively, were determined as:

\[
T_{A-C} = 221.5 - 223.3 \, ^\circ C \text{ and } T_m = 223.3 \, ^\circ C
\]

**Determination of crystallization temperature**

**Polyethylene**

The crystallization range was determined by the melting of a sample placed on a glass slide and covered with a cover slip. Melting was completed at 175 \, ^\circ C, was kept holding for 5 min, after which the sample was cooled to 130 \, ^\circ C with an average rate of cooling of 22.5 \, ^\circ C/min, and then with a rate of cooling of 0.2 \, ^\circ C/min.
Following this procedure the first visible spherulites were observed at 125,8 °C and the crystallization was terminated at 124,8 °C.

With a new sample the same procedure was repeated except that the rate of cooling was 10 °C/min from 130 °C. At this determination crystallization was initiated at 118,5 °C and terminated at 114,8 °C.

**Polypropylene**

With polypropylene the sample was heated to 210 °C, which was kept for 5 min, after which the sample was cooled at 10 °C/min.

In two determinations crystallization was initiated at 121,9°C and terminated at 114,5 °C.

**Polyoxymethylene**

The same procedure as with polypropylene was followed. In four determinations crystallization was initiated at 149,3 °C and terminated at 141,8°C (Average values).

**Polyamide 66**

With polyamide the sample was heated to 280 °C which was kept for 5 min, after which the sample was cooled at 10 °C/min.

In one determination crystallization was initiated at 239,9 °C and terminated at 234,3 °C.

**Polyamide 6**

The same procedure as for polyamide 66 was followed. In one determination crystallization was initiated at 199,1°C and terminated at 191,9°C.

**Comparison of results with pVT-data from literature**

CHRISTOPH²⁴⁰) used a pVT-apparatus for determination of the crystallite melting and crystallization temperatures. He investigated a polyethylene (Hoechst GF 4760) of the same
range of density, but with a lower melt index, and the same polypropylene (Hoechst PPN 1060). The following results were obtained.

<table>
<thead>
<tr>
<th></th>
<th>CHRISTOPH</th>
<th>This investigation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PE</td>
<td>PP</td>
</tr>
<tr>
<td>$T_m$ (slow heating)</td>
<td>141</td>
<td>171</td>
</tr>
<tr>
<td>$T_c$ (slow isobaric cooling)</td>
<td>127</td>
<td>123</td>
</tr>
<tr>
<td>Density</td>
<td>0.953</td>
<td>0.958</td>
</tr>
<tr>
<td>MFI (190/2)</td>
<td>0.4</td>
<td>7</td>
</tr>
</tbody>
</table>

The comparison demonstrates the difference in the cooling rate between the two methods.

**Spherulite growth rate**

The spherulite growth rate was determined for polyethylene and polypropylene by melting a sample at 175 °C and 210 °C, respectively, for 5 min and then cooling with a constant rate of cooling of 10 °C/min to the temperature where the spherulite growth rate was determined. At selected time intervals the radius of chosen spherulites were measured using the micrometer eyepiece, which had been calibrated using a graticule. The experiment was repeated several times with new samples at the same temperature, as well as with several temperatures in the interval 122.5 - 135 °C.

**Polyethylene**

It was found with polyethylene that the spherulite growth rate at all temperatures could not be measured, as the average size of the spherulites was less than one graduation mark on the scale in the micrometer eyepiece (0.098 mm).

**Polypropylene**

The results with polypropylene are shown in Fig. 6.1., which shows the spherulite growth rate as a function of temperature.
Fig. 6.1 Sperulite growth rate vs. temperature of crystallization \((n = 3)\)
The relation was found to be linear, when the logarithm of the spherulite growth rate is drawn against temperature.

**Determination of morphology as a function of crystallization temperature.**

With the purpose of preparing samples with a known heat history and, therefore, different morphologies, which could be compared with the moulded specimens, crystallization experiments at different temperatures were carried out. The morphology of the samples prepared in this way depends on size and perfection of the crystalline regions. These in turn depend upon the rate of crystallization, which is a function of the degree of supercooling of the sample below its equilibrium melting point during the crystallization process. It is clear, however, that the influence from shear and other effects in actual mouldings cannot be observed in such carefully prepared samples.

**Polyethylene**

With polyethylene the starting temperature was 175 °C, which was kept for 5 min, then cooling at 10 °C/min to the isothermal crystallization temperature. With the two lowest temperatures the crystallization interval was passed before the equilibrium temperature was reached. At the highest temperature (130 °C) no nucleation was visible after 1 h, after which the experiment was interrupted.

The following results were obtained:

<table>
<thead>
<tr>
<th>Isothermal temperature (°C)</th>
<th>Crystallization initiated (°C)</th>
<th>Crystallization terminated (°C)</th>
<th>Time for total crystallization (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>119,2</td>
<td>115,3</td>
<td></td>
</tr>
<tr>
<td>115</td>
<td>120,2</td>
<td>116,4</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>120,0</td>
<td>120,0</td>
<td></td>
</tr>
<tr>
<td>122,5</td>
<td>122,5</td>
<td>122,5</td>
<td>321</td>
</tr>
<tr>
<td>125</td>
<td>125,0</td>
<td>125,0</td>
<td>~ 1080</td>
</tr>
<tr>
<td>127,5</td>
<td>127,5</td>
<td>127,5</td>
<td>~ 7200</td>
</tr>
<tr>
<td>130</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Polypropylene

With polypropylene the starting temperature was 210 °C, which was kept for 5 min, then cooling at 10 °C/min to the isothermal crystallization temperature. With the three lowest temperatures the crystallization interval was passed before the equilibrium temperature was reached.

The following results were obtained:

<table>
<thead>
<tr>
<th>Isothermal temperature</th>
<th>Crystallization initiated (°C)</th>
<th>Crystallization terminated (°C)</th>
<th>Time for total crystallization (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>121,9</td>
<td>112 - 115</td>
<td></td>
</tr>
<tr>
<td>115</td>
<td>121,9</td>
<td>115</td>
<td>330</td>
</tr>
<tr>
<td>120</td>
<td>122,2</td>
<td>120</td>
<td>342</td>
</tr>
<tr>
<td>122,5</td>
<td>122,5</td>
<td>122,5</td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>124</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>125</td>
<td>125</td>
<td>655</td>
</tr>
<tr>
<td>126</td>
<td>126</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>127,5</td>
<td>127,5</td>
<td>127,5</td>
<td>1200</td>
</tr>
<tr>
<td>128</td>
<td>128</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>130</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>132,5</td>
<td>132,5</td>
<td>132,5</td>
<td></td>
</tr>
<tr>
<td>135</td>
<td>135</td>
<td>135</td>
<td></td>
</tr>
</tbody>
</table>

Polyoxymethylene

With polyoxymethylene the starting temperature was 210 °C, which was kept for 5 min, then cooling at 10 °C/min to the isothermal crystallization temperature.

The following results were obtained:

<table>
<thead>
<tr>
<th>Isothermal temperature</th>
<th>Crystallization initiated (°C)</th>
<th>Crystallization terminated (°C)</th>
<th>Time for total crystallization (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>142,5</td>
<td>148,9</td>
<td>143,8</td>
<td></td>
</tr>
<tr>
<td>145</td>
<td>149</td>
<td>145</td>
<td>20</td>
</tr>
<tr>
<td>147,5</td>
<td>149</td>
<td>147,5</td>
<td>30</td>
</tr>
<tr>
<td>150</td>
<td>150</td>
<td>150</td>
<td>135</td>
</tr>
</tbody>
</table>
6.3. EXPERIMENTAL SET-UP FOR INJECTION MOULDING

This section describes the mould, the injection moulding machine with instrumentation and the experimental conditions for moulding.

6.3.1. Injection Moulding Machine

Specimens used in the experiments were moulded on an instrumented Stübbe injection moulding machine. In the preliminary and supplementary experiments, other machines, such as, firstly, a Netstal Sycap with closed loop controls were also used. These machines had the following data:

- **Stübbe S 150/235**
- Clamping force: 1715 kN
- Shot volume: 200 cm³
- Screw diameter: 50 mm

(For other screw dimensions see Fig. 6.2)

![Screw for Stübbe Injection Moulding Machine](image-url)
6.3.2. Injection Moulds

A quadrant specimen was chosen as the principal configuration of a test specimen for the experiments. For other mainly supplementary experiments specimens with configurations, as described in the following, were also used (Fig. 6.3).

Quadrant specimen: \( R = 100 \text{ mm} \); \( \theta = 90^\circ \); \( t = 3-4-5 \text{ mm} \)
- direct gating; sprue: \( l = 55 \text{ mm} \);
- \( D = 6 \text{ mm} \); \( d = 5 \text{ mm} \)

Rectangular specimen: \( 75 \times 50 \times 2 \text{ mm} \);
- direct gating through a \( 90^\circ \), 2 mm fan gate,
- sprue as the quadrant specimen.

Tensile dumb bell: \( 175 \times 10 \times 4 \text{ mm} \);
- film gate 6.4 · 1.5, land 0.8 mm

The quadrant and the rectangular specimen had the same mould base (D.M.E. Standard mould base) (Fig. 6.4). Also the tensile dumb bell mould could be used with different cavities. Both moulds were designed and constructed as a part of the project. A particularly rigid design was aimed at with the quadrant mould. The mould deflection was checked with appropriate stress calculations. It was found, as an example, that the mould cavity would only expand \( 1.2 \times 10^{-4} \text{ mm} \) in the longitudinal direction with a cavity pressure of 500 bar.

6.3.3. Instrumentation

The instrumentation of the Stühbe injection moulding machine and the quadrant injection mould is shown in Fig. 6.5.
Fig. 6.3 Test specimens
Fig. 6.4 Design of quadrant injection mould
Fig. 6.5 Instrumentation of injection moulding machine
The injection moulding machine was equipped with a specially designed extended nozzle incorporating a pressure transducer (Dynisco PT 435) for recording of the melt pressure and a heat-compensated thermosensor (Telemetric, Fe/Con. Thermocouple) for recording of the melt temperature. Behind the injection piston was placed a pressure transducer (Kistler 6011) for recording of the hydraulic pressure. A thermocouple for recording of the temperature of the hydraulic oil was placed in the hydraulic system. Also, fitted to the machine was a linear displacement transducer (BUHL LDT 100) for measurement of the position of the screw or, alternatively, its backward and forward velocity.

The mould was equipped with three force transducers (Brüel & Kjær, type 8200) built-in under the three injector pins in the centerline of the mould cavity. These transducers measured the pressure at 0, 24 and 74 mm from the center of the quadrant.

Four thermocouples (Ni-Cr/Ni-Al) were built in 0.5 mm below the surface of the cavity and were considered to give the best approximation of the cavity surface temperature. The thermocouples were placed with two in each part of the mould. In the fixed part they were positioned 24 and 50 mm from the center of the gate. In the moving part of the mould the thermocouples were positioned close to and far from the cooling channels, at 60 and 99.25 mm from the center, respectively.

The position of the thermocouples in the mould was not considered critical, due to the flat shape of the specimen and the good thermal conductivity of the mould material.

For other moulds the position will depend upon the shape of the article, but the following general rules can be given:

(i) The position should be close to that part of the specimen which is determining the cooling time.
(ii) The position should be between the cavity surface and the cooling channels, and not "behind" the cooling channels.
A position too close to the surface will show a high amplitude for the periodic change of the mould temperature with the moulding cycle.

(iii) A position close to a cooling channel will be highly influenced by changes in the flow and temperature of the cooling medium.

(iv) The position should not be too close to the gate (or heating elements) as long as ejection or cycle time are not influenced by these factors.

Mould surface temperature was also checked with a digital precision contact thermometer. An attempt was made to measure the temperature distribution over the cavity surface using thermography, but this method was abandoned due to problems arising from radiation from the shining mould surface. The experimental technique and the results obtained are described in Appendix C.

The temperature of the circulatory oil used as a coolant was measured with thermocouples in the inlet and outlet connections of the mould. Pressure and flow of the coolant were measured in a separate stand between the mould and the temperature control unit.

The temperature control unit (Regloplas, type 250 KL) has a heating capacity of 3.3 kW, the pump gives 8 l/min at approximately 5 bar. The cooling capacity is $1.4 \times 10^4$ kJ/h at 150 °C. Oil was used as the cooling medium. The mould was insulated from the injection moulding machine with 1 mm melamine sheets (Etronit) between the mould and the clamping plates.

The recording equipment used for registration of the variables is also shown in Fig. 6.5. It includes a six-channel uv-recorder (S.E.3006) for recording of pressures and screw velocity, a two-channel and a four-channel potentiometric recorder (Philips PM 8221 and PM 9833) for recording of temperatures and an oscilloscope (Tektronix) for recording of pressure and screw velocity.
Melt temperature was also checked by injecting the melt into a PTFE-cup with a built-in thermocouple connected to a digital temperature measuring instrument.

Not shown in Fig. 6.5, but fitted onto the machine, was a Hunkar 308-1 Adaptive Ram Programmer with servo-valve (Moog) for the programming of the injection speed. With this system the cavity pressure input is compared to the panel setting. The control insists that cavity pressure be reached when the screw is at a preset "cushion" position. The control adjusts the shot size to maintain the volumetric requirements of the cavity pressure/"cushion" relationship.

Finally, a pressure transducer with recording equipment (Maihak) for measurement of the hydraulic oil pressure as a function of screw position was fitted. Strain-gauges were fixed to all four tie-bars for measurements of extension during clamping. The whole set-up was carefully calibrated, tuned, adjusted and tested before experiments were conducted.

6.3.4. Experimental conditions

Before the moulding of the specimens used for characterization of the properties was initiated, a series of experiments were done in order to test and calibrate the equipment and to ensure the reproducibility of the moulding conditions. At the same time processing conditions for further experiments were established.

(i) The capability of the injection moulding process was investigated by moulding of a series of spiral mouldings, as this specimen was thought to be most sensitive to changing conditions. Usually 400 mouldings were made in a series and length and weight of the mouldings were recorded (Fig. 6.6). A general purpose crystal polystyrene moulding material (Hoechst N 4001 V) was selected for the initial stage of this work, as it was thought that an
Fig. 6.6 Variation in length and weight of a spiral moulding with start-up time (Polystyrene)
easily moulded amorphous material free of the added complications of crystallinity would simplify interpretation of results. During the experiments, voltage was recorded in a separate set-up. No influence from a change in environmental conditions (e.g. room temperature) or voltage variation during the day were found.

(ii) A screening of the most important processing parameters was carried out to determine which of the processing parameters had the most significant effect on spiral flow length (Appendix AA).

(iii) By decreasing the screw stroke, cavity fill-out patterns were obtained for each type of material with the rectangular and the quadrant specimen.

(iv) With each type of material a mould area diagram was made. This is a two-dimensional graph, which shows the lower limit of mouldability (short-short) and the upper limit (flash-point) as affected by processing temperatures and pressures (Fig. 6.7). While moulding may be carried out within the area set by these limits and thus the operating region established, one still has to define that region of the area that leads to the production of consistently acceptable parts.

(v) The time for sealing of the gate was established as the time where the shot weight became constant by increasing screw forward time. For each increment of the screw forward time, each sample consisted of ten mouldings taken when processing conditions were stable. The temperature-pressure plot around the sealing point for a number of screw-forward-times is shown in Fig. 6.8. The relationship between the various sealing points is approximately a linear variation of temperature with pressure. The position of the sealing line will depend largely upon the cavity wall temperature, polymer set-up temperature, and gate dimensions.
Fig. 6.7 Moulding area diagram (Polystyrene)
Fig. 6.8 Gate sealing diagram (Polypropylene)
(vi) For each material a set of standard conditions were determined, which is that combination of processing parameters giving a visually satisfactory moulding (subject to judgement), a reasonable cycle time with no backflow and, thus, permitting an automatic cycle.

The temperature and relative humidity of the room were recorded during the experimental periods. Whenever longer series were made, statistical $\bar{X} - R$ charts were used to monitor the process.

The above mentioned experiments have formed the basis for the experimental planning. However, as the specimens have not been subjected to detailed investigations, this section will not be elaborated upon further.

**Moulding of specimens for further experiments**

After the initial experiments had been evaluated two sets of specimens were moulded according to the following procedure:

**Moulding of polyethylene**

Quadrant specimens of high density polyethylene with a wall thickness of 3 mm were moulded by K. STUBGAARD and characterized in a statistically designed experiment. The main variables were cavity pressure, melt temperature, mould temperature and screw forward velocity.

The work formed a part of the project "Control Systems for Injection Moulding Machines" which also covered the reproduceability of the process and the interaction of machine variables and processing parameters. Characterization of mechanical properties was carried out on a part of the samples by H. HERON at the Danish Technical University. Another 30 specimens were taken from each of the series and used for further characterization in the present study.

The experimental design and a summary of the results of the testing of mechanical properties are reported in Appendix AB
Moulding of polystyrene, polyethylene, polypropylene, polyoxymethylene and polyamides

A one-variable-at-a-time experiment was carried out, with the experimental array given in Table 6.1. The main variables were material, mould geometry, melt temperature in the nozzle, cavity wall temperature measured 0.5 mm from the surface and cavity pressure measured 24 mm from the center of the gate.

During the adjustment of the injection moulding machine, one of the processing parameters was kept constant and the two others adjusted accordingly, by taking all readings from the recorders and using the following procedure:

The injection moulding machine was run for approximately two hours to reach stable temperature conditions. Then the melt temperature in the nozzle was adjusted until the temperature at the desired setting had a variation less than 1 °C. This was usually achieved within a period of 20 to 30 min. Kohler found that a temperature profile with all heating zones at the same level improved homogeneity more than a profile increasing towards the nozzle.

Therefore, a constant temperature profile was used, except for the hopper zone which was kept 30 °C lower.

The cavity wall temperature in the fixed mould part 24 mm from the gate and the melt temperature were adjusted simultaneously, with the melt temperature adjusted so that the average temperatures during a cycle were as close as possible to the desired temperatures. It was found that the wall temperature rises very rapidly during injection and falls relatively slowly as the melt cools and solidifies (Fig. 6.9). The variation during a cycle, as measured on the recorder, was typically in the order of 8 °C. With polypropylene as an example and at a nominal mould temperature of 40 °C, the temperature difference between the inlet and outlet of the coolant was approximately 0.2 °C. In the cycle the temperature varied 0.7 °C.
Fig. 6.9 Variation of cavity wall temperature with time (polystyrene)
With polyethylene only, a slightly different procedure was followed. In this experiment the temperature of the mould was set on the recorder at an average of 35 °C at the lowest melt temperature. This setting was also maintained during variation of the melt temperature. A higher melt temperature, however, causes a higher mould temperature, as can be seen from the following table which shows minimum and maximum values per cycle for the corresponding cylinder temperatures. Again, the mould temperature is measured 0.5 mm from the surface of the cavity.

<table>
<thead>
<tr>
<th>Cyl. temp. (°C)</th>
<th>160</th>
<th>190</th>
<th>220</th>
<th>250</th>
<th>280</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt temp. (°C)</td>
<td>159</td>
<td>196</td>
<td>218</td>
<td>249</td>
<td>289</td>
</tr>
<tr>
<td>Mould temp. min (°C)</td>
<td>30.1</td>
<td>32.5</td>
<td>33.9</td>
<td>34.8</td>
<td>35.6</td>
</tr>
</tbody>
</table>
| Mould temp. max (°C) | 39.7 | 42.4 | 44.1 | 44.5 | 46.9 )

*) The maximum value varied between 45.3 and 48.5 °C

The low viscosity at a barrel temperature of 280 °C caused problems during plastizising, as the screw occasionally rotated without bringing melt forward. In order to increase the time for plastizising the melt, the set cooling time was increased from 4 to 6 s at the expense of the set holding time, which was decreased from 40 to 38 s, so that the cycle time was kept constant at 50 s.

The series moulded at a cylinder temperature of 280 °C had a slightly larger variation in shot weight, with a standard deviation of 0.017 g as compared to 0.011 for the other series.

Screw rotational velocity was 50 rev/min = 0.131 m/s. Screw forward velocity was 0.025 m/s, corresponding to a volume flow of 49.1 cm³/s. A low back pressure (< 10 bar) was used to avoid too much frictional heat.

The maximum cavity pressure 24 mm from the gate was taken as the reference value. With polypropylene as an example, it was necessary to adjust the hydraulic pressure in a range from 25 bar to 49 bar in order to achieve a cavity pressure of 200 bar.
when the melt temperature was varied. With a cavity pressure of 550 bar, the hydraulic pressure was varied from 80 to 85 bar. The screw/hydraulic piston diameter ratio was 7.33.

There was no switch-over from injection to holding pressure, in order to avoid the influence from pressure oscillations (and related temperature variations) on the structure. To avoid back flow, the effective holding time was shorter than the set values for all the series.

The oscilloscope was used during the running-in to check the interaction between cavity pressure and screw-forward velocity. By using the storage facilities for storing of the pressure/velocity profiles for a set of mouldings, it was possible to monitor any deviation from the accepted pressure/velocity profile.

The proper condition for opening the mould was established on the pressure-time diagram and the weight/screw-forward curve (see Fig.6.8). Additionally, the moulding should be rigid enough to hold its shape, which means that the polymer temperature should drop to at least some value $T_s$. The mould was controlled at some lower temperature, and the moulding could not be cooled below this temperature while in the mould. On the pressure scale the residual cavity pressure $P_{res}$ should be less than some maximum value to avoid scoring or breaking the moulding when the mould is opened. Cooling time was 4 s for polyethylene, 8 s for other materials. Mould opening time was 2 s. A low backpressure was used during plastication.

After the machine was producing parts under "steady state" conditions for one-half to one hour, data was recorded from the transducers and samples were collected. Then the experimental variables were sequentially changed. In each instance, data and samples were collected.

*) In an actual moulding situation, a melt temperature change would result in an in-cavity pressure change unless the hydraulic oil pressure was corrected. Many effects, e.g., shrinkage, commonly attributed to melt temperature changes may actually be caused by the resulting pressure distribution change.
Cooling curves were calculated using Equations (2.18) and (2.19) (Section 2.2.5), which were solved for the processing variables used in this study. The equations were programmed for a TI-59 pocket calculator (Appendix G) and the results are depicted in Fig. 6.10 and 6.11. Due to the simplified assumptions, e.g., the neglected influence from the heat of crystallization, the curves cannot be considered as representative of the actual cooling conditions in the cavity. However, they do establish the relative influence from the processing parameters on the rate of cooling.

Material properties are based on "effective values". The cooling rate ($V_k$) may also be derived from Equation 2.19

$$V_k = \frac{1}{t} (T_m - \bar{T}_E)$$

It is clear from the definition of the "effective values" that they cannot be considered as invariable material properties, because they, in principle, change with processing conditions.
Fig. 6.10 Cooling curves, polyethylene

a) Demoulding: Average Temperature in center of moulding (T)
b) Demoulding: Maximum Temperature across moulding (T)
Fig. 6.11 Cooling curves, Polypropylene and Polyoxymethylene

Demoulding: Average temperature across moulding (T)
6.5. WEIGHT, DIMENSIONS, SHRINKAGE, ANNEALING

After moulding, the samples were cooled to room temperature and placed flat on a table over a period of 3-4 hours to avoid distortion. The sprue was cut-off in a set-up with an electric saw made specifically for this purpose so that the sectioning was done at the same position on all mouldings. Then the mouldings were stored in a polyethylene bag, which was sealed to prevent dimensional changes due to moisture absorption. With some 3 mm polyamide mouldings silicia gel was included in the bags for adsorption of the water vapour in the air. To evaluate this procedure, a sample was also kept in a desiccator during the period of evaluation. The bags were stored in a standard laboratory atmosphere inside a black cupboard.

Specimen weight and dimensional measurements were taken 24 hours after moulding and shrinkage determined. In both cases at least 30 and in most cases 100 consecutive mouldings from each set of conditions were measured, which was sufficient for a statistically large sampling (N >30).

Weight was measured using a Mettler H31 balance (\( \alpha =0.1 \) mg). Shrinkage was measured in a set-up with two micrometers, which had an error of measurement of 0.0006 mm (Section 5.2). Care was taken to minimize hand contact with the samples, as it was observed in one case that radial dimensions increased approximately 0.05 mm when the sample was held in the hand for 10-15 s.

A representative sample was enclosed in a polyethylene bag and stored for periods up to three years for determination of post shrinkage. After this period the specimens were measured again and the post shrinkage calculated.

Annealing was done in air using an oven (HERAEUS) with forced air-circulation. Annealing temperatures were selected within the interval given in DIN 53 497. A procedure corresponding to method B of the standard was followed. This implied that
the change of dimensions was measured after a geometrically adapted annealing time of 1/2, 1, 2, 4 and 8 hours. The specimens were allowed to cool to room temperature for a minimum of 24 hours before they were measured and then were placed again in the hot air oven.

Distribution curves for weight and dimensions were generated with each sample set. The curves were analyzed and the standard deviation (s) calculated.

With polyamide 66, an attempt was made to separate the opposing dimensional changes from the expansion changes caused by the physical presence of absorbed moisture and the contraction which accompanies post shrinkage. Using five samples for each experiment, the following investigations were conducted:

(i) Water absorption at two temperatures (60 °C and 90 °C) as a function-of-time with subsequent measurements of dimensions
(ii) Annealing at two temperatures (60 °C and 90 °C) as a function of time with subsequent measurement of dimensions
(iii) Water absorption for one surface exposed to water
(iv) Annealing at 140 °C as a function of time.
6.6. MORPHOLOGY

6.6.1. Optical microscopy

A sample was taken from each set of mouldings moulded by variation of the processing conditions. Two blocks, approximately 10 x 10 mm, were cut from two positions 24 mm and 74 mm from the center of the gate, respectively. These positions corresponded to the positions in the mould cavity where pressure and temperature were measured. Due to the pressure and temperature gradient in the mould which influences the morphological features, it was thought necessary to take samples from at least two positions along the path of flow.

Cutting was done using a Jung K-microtome, and the blocks were clamped directly in the vice. Sections were cut as well in the x-y as in the z-y plane, that is parallel and transverse to the direction of flow, respectively (Fig.6.17). Care was taken not to heat the samples during cutting.

With the K-microtome a choice can be made between different knives, and, after some trials, the following relationships of knives, thickness of the sections and polymer were established:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Knife</th>
<th>Thickness of Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>HK 2 + K 3</td>
<td>8 um</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>K 3</td>
<td>8 um</td>
</tr>
<tr>
<td>Polyoxymethylene</td>
<td>HK 2</td>
<td>8 um</td>
</tr>
<tr>
<td>Polyamide</td>
<td>HK 2</td>
<td>8 um</td>
</tr>
</tbody>
</table>

After the sections were microtomed, they were embedded in Canada-balsam on glass-slides and covered with a cover slip.

Observation of the mounted specimens was done through various microscopes (Leitz SM-Lux Pol, Zeiss Universal, and Reichert Zetopan). Generally, a 40, 100 and 400 x magnification was used. During observation the different structural layers were measured using the eyepiece in the microscope.

Photographs were taken using a Leitz 35 mm camera for each
Fig. 6.12 Positions and orientation of section for examination by microscope
microtomed section taken transverse to flow (z - y plane) at 40x magnification. For detailed investigations, photographs at 125x magnification were also taken. For black and white photographs an "Agfapan 25" (15 Din) film was used.
6.7. DENSITY AND CRYSTALLINITY

6.7.1. Density gradient column

Density was determined using a gradient column with a mixture of methanol and distilled water for polyethylene and polypropylene and a mixture of calcium iodide and distilled water for polyoxymethylene and polyamide.

Four samples, each 6 x 6 mm, were cut approximately 50 mm from the center of the gate from three mouldings, each determination being an average of 12. In nearly all cases the standard deviation of the 12 measurements was 0.0001 g/cm$^3$. For subsequent materials therefore, the determination were made on 8 samples taken from two mouldings. Generally, the density can be determined with an accuracy of $\pm$ 0.0005 g/cm$^3$.

Some polyamide mouldings had been stored in a normal laboratory atmosphere ($23^\circ$C/50% r.h.), and no attempt to dry them was tried. After a 10 day storage they had absorbed 1.5 - 1.7% water, which caused an increase in the density of 0.005 - 0.007 g/cm$^3$.

Also, after various techniques, e.g. immersion in paraffin according to ASTM, had been tried the effect of water absorption from the mixture in the column was neglected. These attempts, however, were discarded as the stability of the sample in the gradient column was achieved in less than 10 min, where it is assumed that water absorption is not significant at $23^\circ$C.

In the present work also a relative and not an absolute determination was aimed at. To a first approximation, density can replace crystallinity in the characterization of crystalline polymers. The degree of crystallinity is then calculated from:

\[
\frac{(V_a - V)}{(V_a - V_c)} \times 100 \% 
\]  

(6.2)

where

$V_a$ = Specific volume for amorphous fraction

$V_c$ = Specific volume for crystalline fraction

$V$ = Specific volume for sample
The specific volume for the sample is determined with the gradient column. The specific volume for the amorphous and crystalline fraction is found in standard reference books, e.g., 14).

6.7.2. Thermal Analysis

Thermal analysis was carried out on samples of polyethylene, polypropylene, polyoxymethylene and polyamide 66.

From the quadrant, a sample 6 x 6 mm was cut from the middle of the moulding with a center 50 mm from the center of the quadrant. By using a microtome, sections with thicknesses of 0.03 mm were then cut from the surface towards the middle of the 3 mm thick sample with a total of 50 sections being taken from each sample. For every 5 sections, corresponding to a layer of 0.150 mm, a 3 mg sample was taken. With polypropylene all five sections were used and with polyamide only three sections were used.

Generally, a sample between 2 and 10 mg is recommended for determination of crystallinity. Smaller samples (down to 0.1 mg can be used) giving, in most cases, a more distinct peak. Larger samples are used for materials with a low heat of fusion.

The mass of the sample was determined using an Oertling analytical balance as an average of, normally, 5 determinations, where the highest and lowest values were discarded. The accuracy was estimated to ± 0.00005 g. The balance was tared with the empty pan.
The variation of the mass of the pans was checked and found to be:
Top: $\overline{m} = 0.0105 \, g$, $s = 0.00030 \, g$, $n = 55$
Bottom: $\overline{m} = 0.0121 \, g$, $s = 0.00028 \, g$, $n = 53$

After weighing, the sample was placed in a pan. A top pan was placed bottom-up inside the pan, pressed down and firmly crimped with a tool of own design.

Care was taken not to touch the pans with the fingers, and that the pans had an undistorted bottom. To improve heat transfer, the pans were seated in the cell on a thin layer of a zinc-oxide filled silicone heat transfer compound. This also effectively "glued" the pans into position. An empty pan with a top was uses as a reference.

The rate of heating should be chosen between 1 and 20 °C/min. An increased rate of heating tends to give a broader peak and a shift to a higher peak value. Therefore, a rate of heating of 5 °C/min was chosen, which should also prevent a possible recrystallization during heating.

A normal atmosphere was used, as only a slight chemical change could be expected for the sample in the temperature range used.

In the choice of sensitivity for the recorder, an area under the fusion peak of more than 10 cm$^2$ was aimed at. For the $\Delta T$ measurements, the recorder was set to 50-20-10 mV/20 cm corresponding to 2.5-1-0.5 mV/cm

In the initial experiments heat of fusion was calculated by conventional methods using indium as a calibrant (see Section 5.3.). The area under the fusion endotherm was determined by drawing the enthalpic base line between the intercept on the heating curve representing constant heat capacity before and after melting. The peak area is then the area enclosed between the peak and the interpolated base line. This is an arbitrarily chosen procedure, where it is assumed...
that the phase change is terminated at the peak temperature, and that the thermal properties of the sample are changing discontinuously at the phase change, which should be the case with the melting of polymers.

As the trace registered by the instrument is obtained with a constant weight of the sample and a rate of heating proportional with the heat capacity \( C_p \) some influence arises which, however, is not a linear function of temperature. Assuming that the deviation is only approximately 1% of the \( C_p \) value at the melting maximum, it was considered acceptable to neglect the influence from \( C_p \) on the base line. As can be seen from the test runs with empty pans, the instrument had a good linearity in the temperature range used. In the case of polyamide, both peak areas were included in the measurements.

After the base line had been drawn, the curve cleaned of electronic noise, and shaded to set the curve off by the contrast, the peak area was determined using the macroscope of a Texture Analyzing System (Appendix D). The degree of accuracy was found to be approximately 0.7 %, when estimated from a 6 x 20 cm rectangular area drawn on the recording paper. Using this method measurement of area, approximately 75 curves were measured in less than two hours. The two hours also included the time for setting up of the instrument, programming and print out. In a later step it would be simple to include all the calculations in the computer programme.

The heat of fusion, or, as the heat of fusion in principle refers only to completely crystalline materials, then more correctly the difference in enthalpy before and after melting was calculated after:

\[
\Delta H = \int_{T_1}^{T_2} C_p \, dT = \int_{T_1}^{T_2} (k \Delta T/q) \, dT
\]

where

\[
T_1 \text{ and } T_2 = \text{Temperature before and after melting} \quad (T_1 < T_m < T_2)
\]
\[ k = \text{Heat transfer constant (from calibration curve)} \]
\[ C_p = \text{Heat capacity (for amorphous polymer)} \]
\[ q = \text{Rate of heating} \]

By dividing with \( m \) in Equation (6.3) it becomes the enthalpy per gram of polymer:
\[
\Delta H/m = k/g \cdot m \int_{T_1}^{T_2} \Delta T \, dT \tag{6.4}
\]

The degree of crystallinity (\( \alpha \)) is calculated after:
\[
\alpha = \frac{\Delta H_s}{\Delta H_\infty} \times 100 \% \tag{6.5}
\]

where
\[ \Delta H_s = \text{Difference in enthalpy for the sample} \]
\[ \Delta H_\infty = \text{Difference in enthalpy for the completely crystalline polymer} \]
\[ \Delta H_s, \text{ as well as } \Delta H_\infty \text{ depend on temperature, but by choosing } T_1 \text{ and } T_2 \text{ in the solid and liquid phase, respectively, this influence is to some extent compensated.} \]

The value for \( \Delta H_\infty \) was found in literature. In practice it is determined by extrapolation, since no polymer has been prepared in the complete crystalline form. (Crystallinities of about 95% have been attained for polyethylene, but this high value has never been approached in any other polymer). It is however, a major problem to find consistent and reliable values for the heat of fusion for 100% crystalline polymers. This is a consequence of the differences in the concept of crystallinity, methods of characterization and experimental techniques.

Heats of fusion are either measured directly from equilibrium crystals, extrapolated as a function of crystallinity (determined, for example, by dilatometry or x-ray diffraction), deduced from thermodynamic considerations of diluent melting point lowering, or are obtained from the increase of the melting temperature with pressure.
For highly accurate absolute determinations, it is also of importance if the heats of fusion are calculated in units of total chain atoms, at the same time taking the side chains into account. However, the experiments reported here are only intended to get results which relate reasonably well with the behaviour of the polymer during processing, and especially the variation found in a moulding. Such determinations can be made with a precision of 2-5%, when compared with values obtained by dilatometric techniques. For an absolute determination a precision of 10-12% may be obtained, considering the variation in the experimental parameters.

In the case of polyethylene an often quoted value for $\Delta H_m$ of 69,4 cal/g (290,56 J/g) was used. This value is an average from six references, using the same experimental technique with a standard deviation of ± 5,2%. For polypropylene, polyoxymethylene, and polyamide a reference from Wunderlich was used (Table 6.2).

Table 6.2 Specific enthalpy of fusion of crystalline polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molar weight per structural unit (J/g)</th>
<th>Heat of fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reference 179 p 388</td>
<td>Reference 242 div.p p 91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14 237 241</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>28,05</td>
<td>293,1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280,6 267,4-299,5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>290,6 292,9</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>42,08</td>
<td>209,3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>209 209,1-259</td>
</tr>
<tr>
<td></td>
<td></td>
<td>164,9</td>
</tr>
<tr>
<td>Polyoxymethylene</td>
<td>44,05</td>
<td>175,8 *)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>181-192 161,2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>196,6</td>
</tr>
<tr>
<td>Polyamide 66</td>
<td>226,32</td>
<td>188,4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>196,2-203,7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>255,0</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>113,16</td>
<td>188,4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>192,6-207,7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>229,8</td>
</tr>
</tbody>
</table>

*) Copolymer (trioxane/2% ethylene oxide)

As is understandable, the various methods of determination may lead to somewhat different figures for the same polymer. The data in table 6.2, therefore, cannot be compared directly without further proof of the methods of characterization. It appears, however, that the accurate measurement of crystallinity in polymers by calorimetric techniques depends upon having a reliable source for the heat of fusion of 100% crystalline materials.
6.8. ORIENTATION AND RESIDUAL STRESSES

Orientation was measured by reversion after the heating of 20 x 20 mm samples cut from 3 mm polystyrene and polyethylene mouldings and on microtomed sections cut from across the mouldings of polyethylene.

Knoop hardness was measured on polyethylene mouldings. (Sect. 6.9.5)

6.8.1. Reversion of 20 x 20 mm samples of polystyrene and polyethylene

For each of the two materials five specimens 20 x 20 mm were cut from the centre of the mouldings from each of the five levels of melt temperature. The length ($L_0$), width ($B_0$) and thickness ($T_0$) of the specimens were measured using a micrometer (Fig. 6.13).

Before cutting, the polystyrene mouldings had been stress-relieved in a closed press at 80 °C/1 h with no pressure except the weight of the platens. After stress-relieving, the mouldings were cooled in still air between sheets of asbestos that had been heated in an oven.

A specimen holder was made to the dimensions of Fig. 3 of DIN 16 770 ISO/DIS 2557, except that a 0.5 mm aluminium sheet was used to carry the specimens. The opening of the specimen holder was covered with an asbestos sheet. The specimen holder was placed in a hot-air oven. The temperature was measured by thermocouples in the specimen holder and continuously recorded on a pen-recorder. The temperature difference between the top and the bottom was found to be less than 0.5 °C and the total variation less than ± 1 °C from the set temperature.

The specimens were placed on a paste of 25% (by weight) of talc and 75% silicone oil (viscosity $500 \text{ cS} \sim 5 \times 10^{-4} \text{ m}^2/\text{s}$).

The optimum conditions for reversion had been established in an earlier experiment at 130 °C/1 h for polystyrene and 150 °C/1 h for polyethylene.
Fig. 6.13 Position of specimens for reversion
The specimens were removed on the sheet from the holder for heating, and then allowed to cool in still air between two asbestos sheets, which had been heated to the same temperature in the oven. The sheets were spaced to prevent the upper one from resting on the specimen when cold. After cooling to room temperature, length \((L_{r})\) and width \((B_{r})\) were measured at the edge and at the middle of the specimen using a micrometer.

The measurements were used to calculate the reversion \((R_{\|})\) and \((R_{\perp})\) at the surface and the middle of the sample and the revised and compensated reversion \((R_{\|}^*)\) and \((R_{\perp}^*)\) (Equation (19) and (20), Appendix E) at the surface and the middle of the sample, respectively. The calculation was done using a computer (RC 1006, 32 K) with the programme enclosed in Appendix G.

6.8.2. Reversion of microtomed sections of polyethylene

A specimen 6 x 6 mm was cut, using a rotating saw with a double blade, from one moulding from each series moulded with the variation of cavity pressure, melt temperature, mould temperature and screw forward velocity. The centerline of the sample coincided with the centerline of the moulding, and the center of the sample was placed on a position 50 mm from the center of the moulding. A whole strip was cut for one moulding with the "central" moulding conditions and was then sectioned into 13 pieces approximately 6 mm, the thickness of the saw blade being 1 mm approximately. (Fig. 6.13) After sawing the sample was cleared of burrs.

Before clamping the 3 mm thick sample in the microtome it was necessary to fix the sample onto a fastener. This was done with some difficulty and, therefore, the following methods were investigated.

- Use of freezing equipment for the microtome
- Bonding with an epoxy adhesive (Araldit Rapid) without pre-treatment of the sample
- Bonding with a cyanoacrylate adhesive (Loctite I.S.-04 E) without pretreatment of the sample
- Bonding with a cyanoacrylate adhesive with a pretreatment of chromtrioxide
- Bonding with a cyanoacrylate adhesive with a pretreatment of chromic acid.
- Bonding with an epoxy adhesive (Micro-Measurement M-Bond AE - 10/15) and a pretreatment recommended for gluing of strain-gauges to plastics.

None of the methods proved superior, but, in general, the following procedure gave the best result

(i) Pretreatment with chromic acid (8 weight percent potassium dichromate, 12 weight percent water and 80 weight percent concentrated sulphuric acid)
(ii) Bonding with an epoxy adhesive (Araldit Rapid)
(iii) After bonding the samples were kept under a light pressure overnight at 35 °C.

The samples were then measured parallel to flow (l_o) and transverse to flow (b_o). Measurement was done before cutting in order to avoid distortion by the microtome. The sections were cut to a thickness of 30 μm, with approximately 50 sections from each sample, using a K 1 knife (β=15°). The sections were cut from the ejector side of the plaque. The thickness of the sample was measured before and after cutting so that an average thickness for the sections could be calculated. This calculated average was very close to 30 μm

Each microtomed section was placed in a drop of silicone oil on a cover-glass. Another drop of oil was put on the section before a second cover-glass was put on top of the section. Care was taken to ensure that the cover-glass did not rest directly on the section, and that the cover-glass could move with a slight tilt of the assembly.
During the heat treatment, the assembly with the microtomed sections were placed in the specimen holder (see Section 6.8.1.) on an aluminium sheet powdered with talc. The reversion was done at 170/30 min. and was found to give the best reproducible results in preliminary experiments with variations of time and temperature. Paschke used similar conditions with 1 mm thick samples of polyethylene, whereas Fleissner and Paschke used 170 °C/30 s for 0.03 mm samples dipped in silicone oil. Probably the optimum time is controlled by heat transfer through the assembly-glass, oil and sample.

The temperature of the specimen holder was recorded during the test. During a continuous period of three weeks, the temperature varied between 166.1 and 171.6 °C. During experiments, however, the temperature was within 170 ± 1 °C.

After reversion the length ($l_r$) and width ($b_r$) was measured using a profile projector (Nikon, model 6 c) (Fig. 6.14).

Fig. 6.14 Reversion of microtomed sections

The measurements were used to calculate the reversion ($R_{||}$) and ($R_{\perp}$) and the revised and compensated reversion ($R_{||}$*) and ($R_{\perp}$*) . (See Appendix E)
6.9. MECHANICAL PROPERTIES

6.9.1. Tensile strength

Testing of tensile properties was carried out on polyethylene, polypropylene and polyoxymethylene on dumb bell specimens cut from three positions on the moulding, one parallel to flow (Pos.a) and two transverse to flow (Pos.b) near the gate, and (Pos.c) opposite the gate, respectively. (Fig.6.15) For each determination five carefully prepared specimens were used for polyethylene and, for polypropylene and polyoxymethylene three specimens were used. The specimens were cut using a KARL FRANK test specimen milling machine. Testing was carried out using a JJ tensile testing machine. The rate of cross-head movement was 100 mm/min with polyethylene and polypropylene, 12.5 mm/min with polyoxymethylene.

6.9.2. Tensile impact strength

Tensile impact strength was tested on similar specimens of polyethylene mouldings and cut from the same positions as for tensile strength. For each determination ten specimens were used. Testing was carried out using a Zwick model 5101 pendulum tensile impact testing machine following the procedure in DIN 53 448. Results were corrected for incremental energy contributed by the cross-head using the equation developed in Appendix F.

In order to evaluate the necessity of grinding and polishing of the specimens after milling, five extra sets of specimens were cut from the position parallel to flow and prepared. The results showed that the polished samples had an average standard deviation of 2.7% of tensile impact strength, as compared to 5.3% for the non-polished. No difference was found on elongation at break. As a result, further experiments were carried out using polished samples.
Fig. 6.15 Position of samples for testing of mechanical properties
Notched tensile impact strength

Notched tensile impact strength of polyethylene mouldings was determined following the guidelines in DIN 53 448 on samples taken from the same position in the direction of flow as used for tensile strength.

6.9.3. Falling weight impact

A falling weight test was used on complete mouldings of polyethylene following the guidelines in BS 2782 method 306 B. The carriage of the dart was fitted to take weights so that a specified series of increments of energy could be obtained. The dart was 55.5 mm long, with a base diameter of 23.1 mm, 10° cone and R=6mm at the tip. In the initial experiments, the dart was released from a height of 610 ± 2mm. The mouldings were placed on the support, so that the dart hit at the center of the moulding. Ten samples were used for each increment and the weight at 50% fracture recorded. Readings from a graphical plot of the results were then recorded as the impact strength.

The combination of a low height and a heavy weight did not seem to discriminate between the series. Therefore, an additional test was carried out using a height of 2000 ± 2 mm and a weight which was varied from 1,350 kg to 1,590 kg.

However, this change only gave a marginal improvement. As a consequence, it was decided to build an instrumented falling weight impact apparatus, described in Chapter 5. This instrument was used in subsequent tests of polypropylene, using the experimental conditions reported in Chapter 5.

6.9.4. Flexural modulus

The flexural modulus or modulus of elasticity in bending for polyethylene was determined in a four-point bending test according to DIN 53 457, with the modification that the distance between the supporting points was reduced from 110 mm to 85 mm.
The test was carried out in a Zwick compression testing machine. The rate of deformation was 5 mm/min. The specimens were cut transverse to flow, with the centerline approximately 74 mm from the center of the quadrant. The width of the specimens was 10 mm, and the length approximately 125 mm. Three specimens were used for each determination.

The load deflection curve was drawn and the flexural modulus calculated from the initial (straight) part of the curve using the following equation:

$$E = \frac{L_A \times L_B^2}{16 \times I} \cdot m$$

(6.6)

where

- $L_A$ = Horizontal distance between upper and lower supporting points
- $L_B$ = Length of cantilever
- $m$ = Relation between force increment and strain increment
- $I$ = Moment of inertia: $bh^3/12$ where $b =$ specimen width
  $h =$ specimen thickness

For polypropylene and polyamide the flexural modulus was determined on specimens cut parallel to flow in a three-point bending test according to DIN 53 457 with the modification that the distance between the supporting points were reduced from 110 mm to 75 mm. The supports had a diameter of 10 mm. The test was carried out using a JJ tensile testing machine, type T 5002. The rate of deformation was 5 mm/min. The width of the specimen was 10 mm, and the length approximately 90 mm. The flexural modulus was calculated after:

$$E_B = \frac{L_A \times L_B \cdot \Delta F}{16 \cdot I \cdot \Delta f}$$

(6.7)

6.9.5. Knoop-hardness

The test method is described in ASTM C 730 and ASTM D 1474. The instrument used was a Leitz Durimet Miniload Hardness Tester.
The Knoop Hardness Number (KHN) was computed as follows:

\[ \text{KHN} = \frac{P}{A_p} = \frac{P}{d^2 \cdot C_p} \]  \hspace{1cm} (6.8)

where

- \( P \) = Load (N)
- \( A_p \) = Projected area of indentation (mm²)
- \( d \) = Length of the long diagonal of the indentation (mm)
- \( C_p = \frac{1}{2} (\cot \frac{A}{2} \times \tan \frac{B}{2}) \)
  - where \( A \) = included longitudinal edge angle
  - \( B \) = included transverse edge angle

The indenter had a:

- Longitudinal angle \( A = 172^\circ 35' \)
- Transverse angle \( B = 130^\circ 11' \)
  - which gives \( C_p = 0.06979 \)

The rate of indenter motion prior to contact with the specimen was adjusted to 10s for the full movement. Another 10s (contact time) elapsed before reading. Load was 100 g (50g was tried, but did not improve the reproducibility). Readings were taken with a 10 x filar micrometer eyepiece which, with a further 10x magnification in the instrument, gave a total magnification of 100x.

Hardness was measured on polyethylene in the direction of flow as well as transverse to flow on a position 50 mm from the center of the quadrant. Six indentations, in two rows of three 1 mm apart and 0.2 mm between indentations, were made for each determination. On one moulding 15 x 3 measurements were made along and transverse to flow with a 6 mm distance between each point of determination. All measurements were determined from two readings. Measurements were done on the ejection side.

The Knoop Hardness Number (KHN) was calculated from Equation (6.8) with \( C_p = 0.06979 \); \( p = 0.1 \) kgf = 9.807 N; \( d \) = average of 6 measurements of the long diagonal of the indentation (mm).
7.1. INTRODUCTION

In this chapter the results from the recording of processing conditions are tabulated and evaluated. It also comprises an evaluation of the techniques used for measurement and recording of process variables.
7.2. MEASUREMENT AND RECORDING OF PROCESS VARIABLES

7.2.1. Measurement

Melt temperature. (T_m) An accurate measurement of melt temperature in the cavity is very important to the analysis of the injection moulding process. Yet experimental determination of the temperature distribution (or even the bulk temperature) within the cavity is a rather difficult task, because:

(i) the temperature field is highly transient in nature during rapid filling, (ii) the temperature gradient is very steep between the molten polymer material and the cold wall, and (iii) shear heating resulting from rapid filling of a cavity often makes the temperature profile more complex in shape. In addition, the technique must seek to minimize any disturbance to the flow which may be caused by the temperature measuring device.

In the experiments reported here, it was decided that instead of trying to measure melt temperature in the cavity to measure the temperature in the nozzle, using a heat-compensated thermoprobe. The additional increase in temperature due to the pressure drop across the sprue may then be estimated from Equation 2.7. With h.d.PE, PP and POM, respectively, temperature increases of 4.5, 4.3 and 3.6 °C/100 bar pressure differences have been reported. With the fairly large sprue used, this corresponds to bulk temperature increases of 2-3 °C.

A measurement with a non-heat compensated thermoprobe showed that the melt temperature in the nozzle varied with injection pressure (Fig.7.1). Each injection resulted in a rise of temperature, an effect of increased frictional heat, polymer melt shear, and compression.
Fig. 7.1. Effect of injection pressure on melt temperature (Polystyrene)

The temperature of the melt, injected into a PTFE-cup and measured by stirring it with a thermocouple probe, was found to agree well with the measurement in the nozzle at a range from 220 to 240 °C. A lesser agreement was found at lower temperatures, where the thermal inhomogeneity of the injected melt also increased.

During experiments the melt temperature in the nozzle showed a maximum variation of 3-4 °C over a period of 8 to 10 hours. Short stops (1-3 min) did not affect the variation. During sampling the temperature varied ± 1 °C.

Generally, a variation of the bulk temperature of less than ± 5 °C is considered sufficient. Heating cylinders can be controlled to approximately ± 3 °C with on-off control and to
nearly ± 0,5 °C with SCR control\textsuperscript{246}). This degree of control, however, does not insure that the melt temperature is controlled accurately.

It was found that melt temperature did not vary with screw-back pressure, which is probably valid, as long as the additional work on the melt is compensated for by a smaller amount of heat from the heaters.

The mechanical stability of the thermoprobe presented no difficulties. As the measurement is superior to the conventional measurement of the barrel temperature, it is considered safe to also install this type of thermoprobe for control purposes on production injection moulding machines.

**Cavity surface temperature** ($T_f$) is also a variable which is not measured directly. However, the measurement at four positions 0,5 mm below the surface was found to be a good approximation due to the thermal conductivity of the steel.

The cavity surface temperature varies in each cycle (Fig.6.9). Superimposed on this variation are oscillations from the control-characteristics of the mould tempering unit, which increased the total variation with 1 to 2 °C. To avoid this interference the temperature in some experiments was shifted to a value slightly higher than the nominal.

Other analyses have shown that the weight constancy of mouldings can be increased by a factor of 2 to 4 for a given temperature control system, if the temperature of the coolant and the cavity surface show at least a permissible deviation of less than ± 2 °C \textsuperscript{13}). It would seem appropriate to establish a closed-loop control circuit by using the input from the thermocouple to control the temperature of the coolant, as this can be achieved without any practical problems in actual production.

In the experiments it was found that the temperature 0,5 mm from the surface changed immediately even after a short stop.
It stabilized again, however, after 8 - 10 shots.

Filling time \( (t_f) \) was defined as the time interval from when the screw started its forward movement until the end of the dynamic filling phase.

Measurement of screw-forward velocity or the screw position as a function of time presented no problems. It is suggested that the information derived from the kinetics of the injection screw could be utilized, e.g. to deduce when mould packing and, hence, optimum pressure switchover occurs. It is clear that the transducer senses an average of the factors influencing the filling of the cavity. However, other control features, e.g. pressure relief, close of nozzle shut-off valve and initiation of plastication, could be established for minimum additional effort.

Pressure was measured fundamentally at three different positions (Fig. 7.2)

Pressure in the hydraulic system \( (p_{hyd}) \) is easy to measure and provides, together with the screw-forward-velocity, valuable information during the filling phase. However, during packing and cooling this variable does not relate to the process and may only be used to monitor the function of the hydraulic system.

Pressure in the nozzle \( (p_n) \) is more difficult to measure due to the more severe conditions in the nozzle. It was found that changes in the hydraulic pressure were duplicated in the nozzle melt pressure. The relation between nozzle pressure and cavity pressure ceased once the melt had packed the cavity and started to cool. Changes in screw-rotational-velocity and back pressure had minimal or no effect on nozzle melt pressure. Increase of cushion caused a slight increase of pressure.

Cavity pressure \( (p_c) \) was measured at the sprue and at two positions in the cavity. It was found that the position closest to the gate provided the best information about the conditions in the cavity. Cavity pressure reacted to changes in the machine variables invest-
**Fig. 7.2** Variation in pressure and screw-forward-velocity with time. (PE 02.03)
igated, melt temperature, screw-forward-velocity and mould temperature. It also changed with cavity thickness.

Fig. 7.2 shows that the variation of the cavity pressure with time may be divided into three consecutive stages: a dynamic filling phase, a transition phase, and a quasistatic pressure phase. The three phases correspond in a good approximation to the filling, packing, and cooling stages of the moulding cycle. The dynamic filling phase is primarily of importance to the development of orientation, crystallization, surface properties, and mechanical properties. It starts as the melt enters into the cavity and continues until the cavity is full. During this stage, the pressure build-up is small. It was found that the screw-forward-velocity is highest during the first part, then slows down as the melt enters the cavity from the sprue. It then increases and becomes constant just before the cavity is volumetrically full. (Fig. 7.2)

The transition phase starts when the cavity is full and continues until the maximum cavity pressure has been achieved. It is characterized by an increasing pressure and a substantial drop in the screw-forward-velocity. The maximum pressure was taken as a reference value. Compared with data sheet values a comparatively low pressure was applied. However, such values usually refer to the hydraulic system, which means that pressure losses in the barrel (10-20 %) and the sprue (5-10 %) should be added for comparison. The simple geometry, large gate, and thick moulding require a comparatively low pressure. The pressure relief valve could only be varied in steps. Therefore, the reference pressure (24 mm from the gate) is not in all experiments identical with the intended nominal pressure.

The quasistatic pressure phase starts at the maximum cavity pressure and ends at a cavity pressure almost identical to atmospheric values at which the moulding may be safely ejected.
The quasistatic pressure phase primarily influences weight, dimensions, relaxation, and crystallization in the core.

The effective packing time \( t_{pe} \), which correlates with the time to seal the gate, was taken as the intersection of the tangents to the maximum pressure and the decay for the pressure curve.

Gate sealing depends upon the interaction between the process parameters; melt temperature, mould temperature and filling rate. It is known that the gate does not start to freeze until the main volume of the material has flowed into the cavity and that faster filling allows freezing to commence earlier. Other considerations, especially relating to the thermal characteristics of the polymers, may significantly influence gate sealing times. When the packing time is increased more melt is packed into the cavity. To equate the effective packing time with gate sealing represents a simplification which, especially with thicker mouldings, should be corrected when a more exact analysis of the flow process is required.

With some combinations of material and processing conditions an abnormal bulge was observed just before the pressure decay (Fig. 7.3). In effect, it increases the effective packing time. Some tentative suggestions can be made as to its origin.

(i) The bulge was not observed with amorphous materials using the same mould. With polystyrene, however, the thermal diffusivity is, with \( 8 \times 10^{-4} \text{ cm}^2/\text{s} \), approximately 130% of the thermal diffusivity of polyethylene. At similar boundary conditions this difference causes a faster cooling of polystyrene. With semi-crystalline materials the pressure is nearly constant until the temperature of crystallization is reached in the cavity. Due to the lower viscosity, the pressure transfer is improved just before the sprue solidifies, which happens just as the internal pressure in the cavity is relieved. After sealing of the gate the pressure decays faster with a semi-crystalline material, due to the higher volume contraction during crystallization. With the fast crystallizing PA 6 the bulge disappeared with increasing mould temperature.
a) **Polystyrene** \( (p_{c_{\text{max.}}} = 350 \text{ bar}) \)

- \( T_m = 230 \degree \text{C} \)
- \( T_f = 50 \degree \text{C} \)
- \( s = 3 \text{ mm} \)

b) **Polyethylene** \( (p_{c_{\text{max.}}} = 500 \text{ bar}) \)

- \( T_m = 170 \degree \text{C} \)
- \( T_f = 50 \degree \text{C} \)
- \( s = 3 \text{ mm} \)

- \( T_m = 270 \degree \text{C} \)
- \( T_f = 70 \degree \text{C} \)
- \( s = 3 \text{ mm} \)

c) **Polypropylene** \( (p_{c_{\text{max.}}} = 550 \text{ bar}) \)

- \( T_m = 192 \degree \text{C} \)
- \( T_f = 25 \degree \text{C} \)
- \( s = 3 \text{ mm} \)

- \( T_m = 283 \degree \text{C} \)
- \( T_f = 25 \degree \text{C} \)
- \( s = 3 \text{ mm} \)

d) **Polypropylene** \( (p_{c_{\text{max.}}} = 550 \text{ bar}) \)

- \( T_m = 241 \degree \text{C} \)
- \( T_f = 40 \degree \text{C} \)
- \( s = 2 \text{ mm} \)

- \( T_m = 239 \degree \text{C} \)
- \( T_f = 40 \degree \text{C} \)
- \( s = 5 \text{ mm} \)

---

**Fig. 7.3 Cavity pressure curves**
With polyethylene, the bulge was most pronounced at low melt temperatures. With polypropylene, which is more inclined to supercooling, it also was found at higher melt temperatures and at higher hydraulic pressures.

If the gate has solidified the pressure could rise due to the latent heat of crystallization. The time at which the bulge occurs corresponds, approximately, to the plateau in cooling curves and in pVT-diagrams. However, the bulge was more pronounced with a 2 mm than a 5 mm specimen of polyoxymethylene using the same sprue. It must be assumed that the latter releases more latent heat.

(ii) The bulge was not found at the position 74 mm from the gate. This could indicate that the mould is deformed during the moulding cycle, and that the pressure rise is a reaction to the deflection when the outer parts of the moulding have solidified. It was found that with a 3 mm polypropylene specimen the thickness of the moulding 24 mm from the center was approximately 0.10 mm higher than 74 mm from the center.

7.2.2. Recording

In the recording of the process cycle, a problem occurs in the packing and cooling phase where the registrations of cavity pressure and temperature take up a much longer portion of the moulding cycle than the registrations of the filling and the dynamic pressure loss rates. Ideally, the first variables should be recorded as a function of time, whereas the two last mentioned variables should be recorded as a function of screw-position.

With respect to equipment for registration, it was found during the experiments that the potentiometric recorders used for registration of temperatures presented no experimental difficulties. On the other hand, the uv-recorder, which was used to record pressure and screw-forward-velocity, was quite difficult to operate.

2 3 7
due, among other things, to the light sensitivity of the paper. For the same reason, the instrument would also be difficult to use permanently in a moulding shop. Such difficulties were not found with the oscilloscope, where the process variables could be recorded as a function of time (y-t function), or as a function of screw position (x-y function). The storage facilities of the oscilloscope were convenient to check the reproducibility of the process during test runs where the variables were continuously recorded.

For future experiments the recording instruments are replaced with a system where temperature and cycle time parameters for the last five shots are displayed on a console with an integral visual display unit and input keyboard. Pressure and velocity parameters are displayed on an oscilloscope. At the same time, recorded values are stored on a magnetic tape cassette recorder for later evaluation utilizing a central computer system.
7.3. RESULTS

Polyethylene

In this experiment processing conditions were established at a nominal melt temperature of 160 °C. Melt temperature was then varied at five levels while other conditions remained at their initial settings. The effect of temperature on pressure and screw-forward-velocity is demonstrated in Fig.7.4. Characteristic values measured from the pressure curves are shown in Table 7.1.*)

The table shows that filling time was reduced by approximately 30% with an increase in melt temperature, which is an effect of the temperature dependence of viscosity. Likewise, packing time measured 24 mm from center was doubled, cavity pressure increased 16% and the dynamic pressure loss halved. The longer the filling time the higher was the dynamic pressure loss.

The effective packing time increased linearly with melt temperature, but with a steeper slope close to the gate (Fig.7.5). This is the consequence of a higher heat content in the last injected melt.

The higher cavity pressure with increasing melt temperature is primarily a function of an improved pressure transfer with the lower viscosity melt. The pressure curves also showed that the hydraulic pressure (approximately 50% of the line pressure) was sufficient to achieve the intended rate of filling and cavity pressure. The dynamic pressure loss decreased substantially with increasing melt temperature. Other investigations5) have shown that, especially with a thin wall thickness, there is a strong correlation between molecular orientation and the dynamic pressure loss.

The dynamic pressure 74 mm from the gate was less dependent on melt temperature. This may be explained with the drastic decrease in the velocity of the melt front with flow length due

*) The curves were redrawn on transparent paper, 1 mm representing approximately 10 bar.
Fig. 7.4 Polyethylene - Effect of melt temperature on pressure and screw-forward-velocity
Table 7.1. Polyethylene - Experimental sequence and variation in processing conditions for 3 mm quadrant (PE 02.1-5)

<table>
<thead>
<tr>
<th>Nominal melt temperature (°C)</th>
<th>160</th>
<th>190</th>
<th>220</th>
<th>250</th>
<th>280</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex.no</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt; (°C)</td>
<td>159</td>
<td>196</td>
<td>218</td>
<td>249</td>
<td>289</td>
</tr>
<tr>
<td>T&lt;sub&gt;f&lt;/sub&gt; (°C)</td>
<td>30 - 40</td>
<td>33 - 42</td>
<td>34 - 44</td>
<td>35 - 45</td>
<td>36 - 47</td>
</tr>
<tr>
<td>t&lt;sub&gt;f&lt;/sub&gt; (s)</td>
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<td>1.85</td>
<td>1.80</td>
<td>1.70</td>
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<td>t&lt;sub&gt;p24&lt;/sub&gt; (s)</td>
<td>12.7</td>
<td>16.7</td>
<td>18.6</td>
<td>22.0</td>
<td>25.6</td>
</tr>
<tr>
<td>t&lt;sub&gt;p74&lt;/sub&gt; (s)</td>
<td>8.2</td>
<td>10.7</td>
<td>12.1</td>
<td>13.8</td>
<td>15.8</td>
</tr>
<tr>
<td>P&lt;sub&gt;hyd&lt;/sub&gt; (bar)</td>
<td>62.0</td>
<td>60.0</td>
<td>58.0</td>
<td>59.5</td>
<td>60.0</td>
</tr>
<tr>
<td>P&lt;sub&gt;dyn 24&lt;/sub&gt; (bar)</td>
<td>110</td>
<td>100</td>
<td>90</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>P&lt;sub&gt;dyn 74&lt;/sub&gt; (bar)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>P&lt;sub&gt;c 24&lt;/sub&gt; (bar)</td>
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<td>530</td>
<td>550</td>
<td>580</td>
</tr>
<tr>
<td>P&lt;sub&gt;c 74&lt;/sub&gt; (bar)</td>
<td>460</td>
<td>490</td>
<td>500</td>
<td>520</td>
<td>540</td>
</tr>
</tbody>
</table>

1 kp/cm² = 1 bar.
Fig. 7.5 Polyethylene and Polypropylene - Effect of melt temperature on effective packing time
to the biaxial filling together with the solidifying of the skin before the melt reaches the second transducer. Compared with amorphous materials, the dynamic pressure loss is influenced less by a change in melt temperature because viscosity is less dependent on temperature.

Screw-forward-velocity first increased, then decreased as the melt passed the sprue and reached the cavity and then became constant just before the cavity was volumetrically full. With a low melt temperature the intended velocity was achieved only during the first part of the stroke. At this temperature an oscillation in velocity, possibly a slip-stick effect, was observed.

Polypropylene

In this experiment processing conditions were adjusted so that changes in one parameter were compensated for before sampling. This established the actual values as close as possible to the intended nominal values. In Fig.7.6 a set of curves typical of the changes in cavity pressure with hydraulic pressure and mould temperature is shown. The total set of pressure curves are tabulated in Table 7.2.

Table 7.2 shows that filling time decreased substantially with melt temperature at a low cavity pressure. At a high cavity pressure filling time is only reduced when melt temperature was varied from 190 to 240 °C. Generally, filling time also decreased with increasing mould temperature due to a decreasing frozen layer, thereby increasing the cross-sectional flow area. At the highest melt temperature filling time is affected very little by cavity pressure. This is attributed to two opposing factors. At a low pressure a stronger cooling of the melt is expected, whereas at a high pressure a delayed build-up of pressure may be expected.

The effect of melt temperature on effective packing time is more pronounced \(^1\) than with polyethylene (Fig.7.5). Generally, an increase in melt temperature also increased the time needed to reach atmospheric pressure, because the slope of the pressure decay became less steep.

\(^1\) with polypropylene
Fig. 7.6 Polypropylene - Effect of hydraulic pressure and mould temperature on cavity pressure


$T_m = 190 \, ^\circ\text{C}$

---

*Fig 7.6 Polypropylene - Effect of hydraulic pressure and mould temperature on cavity pressure (PP 05, 17-24)*
**Table 7.2 Polypropylene - Experimental sequence and variation in processing conditions for 3 mm quadrant (PP 05.1-24)**

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
<th>200 Cavity pressure (bar)</th>
<th>550 Cavity pressure (bar)</th>
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<td>Mould temperature (°C)</td>
</tr>
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<td></td>
<td>20</td>
<td>40</td>
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<td>37 - 43</td>
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<tr>
<td></td>
<td>10,0</td>
<td>10,0</td>
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</table>

*) No measurement due to a bulge on the pressure curve
The effective packing time also increased with mould temperature, but the slope of the pressure decay did not change. The decreasing trend for gate sealing time with increasing cavity pressure is typical for semi-crystalline materials, because solidification takes place at a higher temperature (with polypropylene the temperature of crystallization increases 2.5 °C/100 bar \(^\text{150}\)).

The low filling rate with the low cavity pressure caused an earlier solidification than filling at the high cavity pressure. Therefore, hydraulic pressure had to be adjusted comparatively more at low pressure when melt temperature was varied.

**Polyoxymethylene**

With polyoxymethylene the experimental procedure described for polypropylene was followed.

The effect of a change in mould temperature on pressure curves is shown in Fig.7.7. The tabulated values are shown in Table 7.3.

In addition to the observations with polypropylene, the following observations were made:

Table 7.3 shows that filling time decreased when mould temperature increased. The time to seal the gate increased with a time-factor of 1.5 with an increase in mould temperature from 60 to 120 °C (indirectly showing the economic considerations needed to mould this material at higher mould temperatures, e.g. to achieve a better dimensional stability) (Fig.7.8).

![Fig.7.8. Polyoxymethylene. Relative time to seal the gate.](image-url)
Fig. 7.7 Polyoxymethylene - Effect of mould temperature on cavity pressure (POM 10.1 - 4)
Table 7.3 Polyoxymethylene - Experimental sequence and variation in processing conditions for 3 mm quadrant (POM 10.1-4)

<table>
<thead>
<tr>
<th>Mould temperature (°C)</th>
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<td>Tf (°C)</td>
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<td>67</td>
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<td>Pc24 (bar)</td>
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<td>490</td>
</tr>
<tr>
<td>Pc74 (bar)</td>
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</tbody>
</table>
The pressure drop from the nozzle to the cavity decreased substantially with increasing mould temperature. The dynamic pressure drop decreased with increasing mould temperature. The difference in dynamic and static pressure between the two positions of measurement did not depend on mould temperature. It may be assumed that the change in mould temperature did not affect viscosity with the wall thickness employed.

Polyamide

The two non-reinforced polyamides showed, in contrast to the three other materials, an increasing filling time with increasing mould temperature. The dynamic pressure loss first decreased and then increased with polyamide 6. At a low mould temperature a pressure oscillation during injection was duplicated in the cavity pressure curve. These features are caused by the cooling of the tip of the nozzle when it makes contact with the mould during the cooling phase and is enhanced by the fast crystallization of the nucleated grades. The nucleation also explains the small difference in pressure between the two positions, where the effective packing time varied very little with position (Fig. 7.4 and 7.5). The glass-reinforcement of polyamide 6 also acted as a nucleant and reduced the effective packing time by a factor of 2. The glass-reinforcement also caused a slightly higher loss of pressure in the cavity.

+)(The temperature of crystallization was determined to approximately 240 °C in Section 6.2.2.)
Table 7.4 Polyamide 66 - Experimental sequence and variation in processing conditions for 5 mm quadrant (PA 66 01.1 - 4)

<table>
<thead>
<tr>
<th>Ex.no</th>
<th>Mould temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>T_m (°C)</td>
</tr>
<tr>
<td></td>
<td>T_f (°C)</td>
</tr>
<tr>
<td></td>
<td>t_f (s)</td>
</tr>
<tr>
<td></td>
<td>t_p24 (s)</td>
</tr>
<tr>
<td></td>
<td>t_p74 (s)</td>
</tr>
<tr>
<td></td>
<td>P_hyd (bar)</td>
</tr>
<tr>
<td></td>
<td>P_dyn24 (bar)</td>
</tr>
<tr>
<td></td>
<td>P_c24 (bar)</td>
</tr>
<tr>
<td></td>
<td>P_c74 (bar)</td>
</tr>
</tbody>
</table>
Table 7.5 Polyamide 6 and 6f. - Experimental sequence and variation in processing conditions for 5 mm
quadrant (PA 6.01.1-4) and (PA 6f 00.1-2)

<table>
<thead>
<tr>
<th>Ex. no</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>80</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_m (°C)</td>
<td>256</td>
<td>255</td>
<td>255</td>
<td>254</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td>T_f (°C)</td>
<td>65 - 69</td>
<td>77 - 82</td>
<td>96 - 103</td>
<td>116 - 121</td>
<td>80 - 85</td>
<td>118 - 120</td>
</tr>
<tr>
<td>t_f (S)</td>
<td>1,75</td>
<td>1,70</td>
<td>1,80</td>
<td>2,0</td>
<td>2,9</td>
<td>2,65</td>
</tr>
<tr>
<td>t_p24 (S)</td>
<td>29,6</td>
<td>29,6</td>
<td>30,0</td>
<td>30,4</td>
<td>18,8</td>
<td>14,3</td>
</tr>
<tr>
<td>t_p74 (S)</td>
<td>25,7</td>
<td>26,8</td>
<td>28,6</td>
<td>31,1</td>
<td>18,9</td>
<td>14,4</td>
</tr>
<tr>
<td>P_hyd (bar)</td>
<td>69,5</td>
<td>68,5</td>
<td>69,5</td>
<td>68,5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P_dyn24 (bar)</td>
<td>15</td>
<td>12,5</td>
<td>18,0</td>
<td>18,0</td>
<td>42,5</td>
<td>42,5</td>
</tr>
<tr>
<td>P_dyn74 (bar)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17,5</td>
<td>15,0</td>
</tr>
<tr>
<td>P_c24 (bar)</td>
<td>500</td>
<td>495</td>
<td>500</td>
<td>493</td>
<td>498</td>
<td>493</td>
</tr>
<tr>
<td>P_c74 (bar)</td>
<td>475</td>
<td>483</td>
<td>478</td>
<td>473</td>
<td>455</td>
<td>450</td>
</tr>
</tbody>
</table>
The optimum control of the injection moulding process is done in the mould cavity, since it is here that the combination of all the parameters is most directly apparent. For this purpose, a process analysis must be carried out in order to obtain guidelines for reliable process control.

Some initial results from this type of investigation have been presented showing the kind of information which may be derived with an instrumented injection moulding machine.

The materials investigated reacted similar to a change in processing conditions, apart from polyamide where the low melt viscosity caused a lower pressure loss and where a premature freezing of the gate influenced the results. However, some variations were found between the materials. For example, an increase in melt temperature had more of an influence on the effective packing time of polypropylene than for polyethylene.

Filling time and dynamic pressure loss decreased with increasing melt and mould temperatures. During the filling phase the influence of the melt temperature was appreciably greater than that of the mould temperature, the latter dominating in the packing phase. A lower mould temperature during filling leads to longer filling times due to a thicker frozen layer on the cavity wall (narrowing of the channel), which also increases the shear stress on the melt.

With polypropylene the pressure drop across the cavity ($\Delta p_c$) decreased substantially with melt temperatures. However, with polyethylene no effect was found. This may be understood as differences in tendencies towards supercooling between the two polyolefines. Some influence on the pressure drop was also found from the cooling rate (differences in melt and mould temperature) with polypropylene. The hydraulic pressure required to fill the mould decreased with increasing melt and mould temperatures.

In summary, the shape of the pressure curve in the cavity is suitable for evaluation and control of the process. It provides information about filling, packing and solidification. It may be considered as a cumulative quantity influenced by the decisive moulding variables.
CHAPTER 8. RESULTS

8.1. INTRODUCTION

This chapter presents the results of the characterization of properties, together with an analysis of the influence from processing variables.
8.2. WEIGHT, DIMENSIONS, SHRINKAGE, ANNEALING

Polyethylene

By variation of barrel temperature at five levels, one-hundred 3 mm quadrant specimens were moulded and then weighed and measured 24 h after moulding (Table 8.1).

The results show that a higher melt temperature results in a higher weight, because the gate solidifies later, thereby increasing the effective holding time (see Fig. 7.4). This effect compensates the greater specific volume of the melt at the higher temperature.

An increasing melt temperature also increases thickness. Radial shrinkage decreases with increasing melt temperature due to the slower cooling. The higher melt temperature will also increase pressure transfer and with the increased holding time will tend to decrease shrinkage by injecting more material and, possibly, by inhibiting relaxation of orientation. Differential shrinkage increases with melt temperature, but decreases slightly at the highest melt temperature.

Polyethylene specimens were also moulded in a statistically designed experiment (Appendix A), with variations of cavity pressure, melt temperature, cavity wall temperature and screw-forward-velocity at three levels.

A sample of ten specimens were enclosed in a polyethylene bag and stored for 36 months at 23 °C and 50% r.h. After this period the specimens were again measured and the post-shrinkage calculated. The results are shown in Table 8.2.

An analysis of variance showed that cavity pressure, melt temperature and cavity wall temperature had a very highly significant influence on the radial and differential shrinkage. Screw-forward-velocity had no effect on these properties.

+ The following terminology is used for probability levels: 5% and less (significant); 1% and less (highly significant); 0.1% and less (very highly significant).
Table 8.1. Effect of melt temperature on weight, thickness and shrinkage of 3 mm polyethylene mouldings

<table>
<thead>
<tr>
<th>Test no</th>
<th>PE 02.1</th>
<th>PE 02.2</th>
<th>PE 02.3</th>
<th>PE 02.4</th>
<th>PE 02.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder temperature °C</td>
<td>160</td>
<td>190</td>
<td>220</td>
<td>250</td>
<td>280</td>
</tr>
<tr>
<td>Melt temperature °C</td>
<td>159</td>
<td>196</td>
<td>218</td>
<td>249</td>
<td>289</td>
</tr>
<tr>
<td>Weight, ((\bar{x})) g</td>
<td>21,19</td>
<td>21,26</td>
<td>21,27</td>
<td>21,32</td>
<td>21,38&lt;sup&gt;1)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Weight, (s) g</td>
<td>0,009</td>
<td>0,012</td>
<td>0,010</td>
<td>0,011</td>
<td>0,017</td>
</tr>
<tr>
<td>Thickness, ((\bar{x})) mm</td>
<td>3,03</td>
<td>3,05</td>
<td>3,05</td>
<td>3,06</td>
<td>3,07&lt;sup&gt;2)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Thickness, (s) mm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0,001</td>
</tr>
<tr>
<td>Shrinkage, radial, ((\bar{x})) %</td>
<td>1,66</td>
<td>1,65</td>
<td>1,53</td>
<td>1,49</td>
<td>1,46&lt;sup&gt;3)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Shrinkage, radial, (s) %</td>
<td>0,006</td>
<td>0,011</td>
<td>0,004</td>
<td>0,006</td>
<td>0,076</td>
</tr>
<tr>
<td>Shrinkage, differential, ((\bar{x})) %</td>
<td>0,03</td>
<td>0,23</td>
<td>0,25</td>
<td>0,21</td>
<td>0,22&lt;sup&gt;4)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Shrinkage, differential, (s) %</td>
<td>0,005</td>
<td>0,008</td>
<td>0,007</td>
<td>0,006</td>
<td>0,022</td>
</tr>
</tbody>
</table>

n = 100
1) \(\bar{x}_1 = 21,32\) (=\(\bar{x}_4\)), n = 74
2) n = 90
3) n = 88
4) n = 88
Table 8.2  Radial mould shrinkage ($S_r$), radial post-shrinkage ($S_{rp}$), after 36 months storage differential shrinkage ($\Delta S$) and differential post-shrinkage ($\Delta S_{p}$) after 36 months storage (in percentages) for 3 mm quadrant specimens of polyethylene by variation of cavity pressure, melt temperature, mould temperature and screw-forward-velocity*)

<table>
<thead>
<tr>
<th>Mould temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0) = 30</td>
</tr>
<tr>
<td>(1) = 50</td>
</tr>
<tr>
<td>(2) = 70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Melt temperature ($^\circ$C)</th>
<th>Melt temperature ($^\circ$C)</th>
<th>Melt temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0) = 170</td>
<td>(1) = 220</td>
<td>(2) = 270</td>
</tr>
<tr>
<td>(0) = 170</td>
<td>(1) = 220</td>
<td>(2) = 270</td>
</tr>
<tr>
<td>(0) = 170</td>
<td>(1) = 220</td>
<td>(2) = 270</td>
</tr>
</tbody>
</table>

| Screw-forward-velocity: (0) = 9 mm/s, (1) = 18 mm/s, (2) = 36 mm/s |

*) In the experimental design the first digit indicates cavity pressure, the second melt temperature, the third mould temperature and the fourth screw forward velocity.

Example: 1102 indicates (1) cavity pressure = 350 bar, (1) melt temperature 220°C, (0) mould temperature 30°C, (2) screw-forward-velocity 36 mm/s.
Radial and differential shrinkage decrease with increasing cavity pressure. An increasing melt temperature causes a decreasing radial shrinkage, whereas differential shrinkage first increases and then decreases. An increasing cavity wall temperature increases the radial and differential shrinkage.

The analysis of variance showed that cavity wall temperature had a highly significant influence on the radial post-shrinkage. No influence was found from the three other variables. None of the four variables had a significant influence on the post-differential shrinkage.

The dimensional variation, defined as the standard deviation of the shrinkage measurements, was dependent on the experimental variables only at the highest melt temperature, where a slightly higher variation was found.

**Polypropylene**

Weight, dimensions and shrinkage of 3 mm polypropylene specimens were determined following the same procedure as for polyethylene, except that the sample for determination of post shrinkage was stored for only 24 months. Additionally, experiments were carried out to determine dimensions as a function of annealing time at a constant temperature.

The influence of the variables was analyzed with a three-sided analysis of variance, assuming no three-factor interaction (This assumption can only be checked graphically for n = 1).

A very highly significant two-factor interaction was found between melt temperature and cavity pressure for weight, radial shrinkage and differential shrinkage. It was assumed, therefore, that these factors had an effect, after which the main effects were tested. (It may be assumed that main effects, with a significant F-value of a higher order, generally approximately 10 times higher, are dominate over the two factor interactions).
All variables were then found to have a very highly significant influence on weight. Melt temperature and cavity pressure had a very highly significant influence, and cavity wall temperature had a significant influence on radial shrinkage. Melt temperature and cavity pressure had a very highly and a highly significant influence, respectively, on differential shrinkage. Cavity wall temperature had a very highly significant influence on radial post-shrinkage. All variables showed two factor interaction with differential post-shrinkage. Melt temperature and cavity wall temperature were found to have a very highly significant influence on differential post-shrinkage.

The influence from cavity pressure, melt temperature and cavity wall temperature on volume, weight and shrinkage are shown in Figs. 8.1 to 8.3.

The results show that by increasing the cavity pressure and the melt temperature, weight, thickness (not shown in the graphs) and volume increase. This effect is probably the result of simply packing more material into the constant-volume cavity. The compressibility of the melt increases with melt temperature, which may explain the increase in thickness with melt temperature. Also, the effective holding time increases with temperature. The time to seal the gate increased >15 s, between the two extremes of the melt temperature, as measured from the pressure curves (see, also, the shot weight/screw-forward time graph for polypropylene, Fig.6.8). This effect more than compensates for the increase of the specific volume with temperature.

Firstly, weight increases with pressure, because the higher pressure creates a faster filling (Fig. 7.6). Secondly, it is, also, possible that an increasing pressure may create a remelting of already solidified material, by an adiabatic compression which makes an additional filling possible.

Weight decreased with increasing mould temperature. This illogical trend is probably the effect of several interacting factors. Thickness decreases with increasing cavity wall temperature as a result of the tendency for polypropylene to sink rather than void. Radial shrinkage increases with mould temper-
Fig. 8.1. Polypropylene—Effect from processing on volume.
Fig. 8.2. Polypropylene—Effect from processing on weight

Cavity wall temperature (°C)

Weight (g)

Pc  Tm
1 196 bar / 192 °C
2 196 °C / 242 °C
3 196 °C / 282 °C
4 539 °C / 192 °C
5 539 °C / 241 °C
6 539 °C / 283 °C
Fig. 8.3. Polypropylene-Effect from processing on shrinkage.
ature and, as the volume decreases proportionately more than the density increases (Section 8.4), this effect contributes to the decreasing weight with increasing mould temperature.

When this observation is compared with the influence from mould temperature on dimensions, it appears that a direct relation between weight and dimension of a moulding is not always found because the two properties depend on different phases of the cavity pressure variation during the cycle. Therefore, although the weight of the specimens are useful for determining the reproducibility of the process, it does not necessarily correlate with other properties \(^2^{49}\). Generally, weight stabilizes in ten cycles and dimensions stabilize in fifty cycles.

It was found that radial shrinkage increased with cavity wall temperature. An increasing cavity pressure results in a decreasing radial shrinkage. Two factors may have a dominating influence. Firstly, the specific volume decreases with increasing pressure. This, also, means that the specific volume has a low value, as the volume contraction is initiated after the gate has frozen. The difference between the specific volume, at this point, and at demoulding is smaller, resulting in lesser shrinkage. Secondly, the crystallization temperature increases with increasing pressure, which may increase the rate of crystallization. Radial shrinkage, also, decreases with increasing melt temperature. This could be a result of the low cavity pressure, where this effect is most pronounced and the inter-related low rate of filling. Brydson\(^2^{50}\) states that this, perhaps surprising, relation has been observed with polypropylene, polyamides and polyoxymethylene. He explains that just above the melting temperature the molecules are still in a somewhat ordered state in regions previously occupied by a spherulite and do not have to move very much in order to take up a crystalline form. Thus, such ordered regions form nuclei so that when the melt cools rapid crystallization occurs. At higher temperatures there is more disorder and so the amount of crystallization occurring is rather less. This observation is in good agreement
with the measurement of density, which also decreases with increasing melt temperature. (see Section 8.4) Differential shrinkage changes from a negative value (shrinkage transverse to flow is larger than shrinkage parallel to flow (see Fig.5.2) to a positive value with increasing melt temperature. The differential shrinkage is negligible at a melt temperature of 240°C indicating that a low varpage would be obtained at this temperature. Except for a slight decreasing tendency, the differential shrinkage is affected only a little by the cavity wall temperature and is only affected by the cavity pressure at the lowest melt temperature.

The radial post-shrinkage after a storage of 24 months was found not to depend on cavity pressure, an observation which is in agreement with other investigations\(^228,230\), as long as the holding time is longer than the time for sealing the gate. Radial post-shrinkage showed a slightly decreasing tendency with increasing melt temperature, and a somewhat higher decreasing tendency with increasing cavity wall temperature (Table 8.3).

The sum of mould shrinkage and post shrinkage is more or less constant at the lowest mould temperatures for a given combination of cavity pressure and melt temperature.

Dimensional- and weight variation decreased with increasing melt temperature, but did not depend on the two other variables. A slight increase in dimensional variation after storage was observed (\(s: 0,125 \rightarrow 0,170\) mm for dimensions).

**Annealing**

The result of the annealing at 120 °C is given in Table 8.4 and 8.5. The tables show that when annealing time is increased the post radial shrinkage increases also, but that the effect is decreasing with time.

It is also shown that the highest shrinkage after annealing occur for the specimens moulded with a low melt temperature.
Table 8.3  Radial mould shrinkage ($S_r$), radial post-shrinkage ($S_{rp}$) after 24 months storage, differential shrinkage ($\Delta S$) and differential post-shrinkage ($\Delta S_{rp}$) after 24 months storage (in percentages) for 3 mm quadrant specimens of polypropylene by variation of cavity pressure, melt temperature and mould temperature.

<table>
<thead>
<tr>
<th>Cavity pressure (bar)</th>
<th>200</th>
<th>550</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mould temperature (°C)</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Melt temperature (°C)</td>
<td>190</td>
<td>240</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_r$ = 1.88</td>
<td>1.88</td>
<td>1.95</td>
<td>1.96</td>
<td>1.27</td>
<td>1.28</td>
<td>1.32</td>
<td>1.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_{rp}$ = 0.22</td>
<td>0.19</td>
<td>0.17</td>
<td>0.14</td>
<td>0.22</td>
<td>0.18</td>
<td>0.17</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta S$ = -0.39</td>
<td>-0.43</td>
<td>-0.45</td>
<td>-0.42</td>
<td>-0.30</td>
<td>-0.31</td>
<td>-0.31</td>
<td>-0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta S_{rp}$ = -0.12</td>
<td>-0.08</td>
<td>-0.08</td>
<td>-0.06</td>
<td>-0.06</td>
<td>-0.04</td>
<td>-0.04</td>
<td>-0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 8.4  Radial post shrinkage ($S_{rpa}$) (in percentages) after annealing at 120 °C as a function of annealing time for 3 mm quadrant specimens of polypropylene by variation of cavity pressure, melt temperature and mould temperature

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,5 h</td>
<td>0,80</td>
<td>0,75</td>
<td>0,65</td>
<td>0,47</td>
<td>0,69</td>
<td>0,65</td>
<td>0,58</td>
<td>0,50</td>
</tr>
<tr>
<td>1 h</td>
<td>0,80</td>
<td>0,76</td>
<td>0,66</td>
<td>0,48</td>
<td>0,69</td>
<td>0,66</td>
<td>0,60</td>
<td>0,53</td>
</tr>
<tr>
<td>2 h</td>
<td>0,81</td>
<td>0,77</td>
<td>0,66</td>
<td>0,50</td>
<td>0,70</td>
<td>0,67</td>
<td>0,61</td>
<td>0,53</td>
</tr>
<tr>
<td>4 h</td>
<td>0,86</td>
<td>0,80</td>
<td>0,69</td>
<td>0,53</td>
<td>0,73</td>
<td>0,70</td>
<td>0,63</td>
<td>0,55</td>
</tr>
<tr>
<td>8 h</td>
<td>0,87</td>
<td>0,80</td>
<td>0,69</td>
<td>0,55</td>
<td>0,73</td>
<td>0,71</td>
<td>0,64</td>
<td>0,56</td>
</tr>
<tr>
<td>24 h</td>
<td>0,89</td>
<td>0,82</td>
<td>0,71</td>
<td>0,57</td>
<td>0,76</td>
<td>0,73</td>
<td>0,66</td>
<td>0,59</td>
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<tr>
<td>48 h</td>
<td>0,84</td>
<td>0,82</td>
<td>0,71</td>
<td>0,58</td>
<td>0,77</td>
<td>0,75</td>
<td>0,66</td>
<td>0,61</td>
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</table>

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
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<th>40</th>
<th>60</th>
<th>80</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
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<tbody>
<tr>
<td>0,52</td>
<td>0,49</td>
<td>0,43</td>
<td>0,36</td>
<td>0,44</td>
<td>0,37</td>
<td>0,39</td>
<td>0,35</td>
<td></td>
</tr>
<tr>
<td>0,54</td>
<td>0,51</td>
<td>0,45</td>
<td>0,37</td>
<td>0,46</td>
<td>0,40</td>
<td>0,40</td>
<td>0,37</td>
<td></td>
</tr>
<tr>
<td>0,56</td>
<td>0,54</td>
<td>0,48</td>
<td>0,40</td>
<td>0,48</td>
<td>0,42</td>
<td>0,42</td>
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</tr>
<tr>
<td>0,59</td>
<td>0,56</td>
<td>0,50</td>
<td>0,42</td>
<td>0,50</td>
<td>0,44</td>
<td>0,44</td>
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</tr>
<tr>
<td>0,61</td>
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<td>0,52</td>
<td>0,43</td>
<td>0,54</td>
<td>0,47</td>
<td>0,46</td>
<td>0,44</td>
<td></td>
</tr>
<tr>
<td>0,64</td>
<td>0,62</td>
<td>0,55</td>
<td>0,47</td>
<td>0,56</td>
<td>0,52</td>
<td>0,49</td>
<td>0,47</td>
<td></td>
</tr>
<tr>
<td>0,64</td>
<td>0,62</td>
<td>0,56</td>
<td>0,49</td>
<td>0,56</td>
<td>0,52</td>
<td>0,51</td>
<td>0,48</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,38</td>
<td>0,39</td>
<td>0,37</td>
<td>0,27</td>
<td>0,36</td>
<td>0,36</td>
<td>0,34</td>
<td>0,26</td>
<td></td>
</tr>
<tr>
<td>0,40</td>
<td>0,42</td>
<td>0,40</td>
<td>0,30</td>
<td>0,39</td>
<td>0,38</td>
<td>0,37</td>
<td>0,30</td>
<td></td>
</tr>
<tr>
<td>0,42</td>
<td>0,45</td>
<td>0,43</td>
<td>0,34</td>
<td>0,42</td>
<td>0,41</td>
<td>0,40</td>
<td>0,32</td>
<td></td>
</tr>
<tr>
<td>0,43</td>
<td>0,47</td>
<td>0,45</td>
<td>0,34</td>
<td>0,44</td>
<td>0,42</td>
<td>0,41</td>
<td>0,32</td>
<td></td>
</tr>
<tr>
<td>0,48</td>
<td>0,50</td>
<td>0,48</td>
<td>0,40</td>
<td>0,47</td>
<td>0,46</td>
<td>0,46</td>
<td>0,48</td>
<td></td>
</tr>
<tr>
<td>0,53</td>
<td>0,55</td>
<td>0,53</td>
<td>0,44</td>
<td>0,51</td>
<td>0,51</td>
<td>0,49</td>
<td>0,43</td>
<td></td>
</tr>
<tr>
<td>0,53</td>
<td>0,55</td>
<td>0,53</td>
<td>0,45</td>
<td>0,52</td>
<td>0,52</td>
<td>0,51</td>
<td>0,43</td>
<td></td>
</tr>
</tbody>
</table>
Table 8.5  Differential shrinkage ($S_{pa}$) (in percentage) after annealing at 120°C as a function of annealing time for 3 mm quadrant specimens of polypropylene by variation of cavity pressure, melt temperature and mould temperature

<table>
<thead>
<tr>
<th>Cavity pressure (bar)</th>
<th>Melt temperature (°C)</th>
<th>Mould temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>200</td>
<td>0.5 h</td>
<td>-0.51</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
<td>-0.50</td>
</tr>
<tr>
<td>190</td>
<td>2 h</td>
<td>-0.49</td>
</tr>
<tr>
<td></td>
<td>8 h</td>
<td>-0.47</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>-0.45</td>
</tr>
<tr>
<td></td>
<td>48 h</td>
<td>-0.41</td>
</tr>
<tr>
<td>550</td>
<td>0.03</td>
<td>-0.05</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>-0.05</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>-0.06</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>-0.06</td>
</tr>
<tr>
<td></td>
<td>-0.05</td>
<td>-0.06</td>
</tr>
<tr>
<td>240</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>0.18</td>
<td>0.17</td>
</tr>
<tr>
<td>290</td>
<td>0.18</td>
<td>0.17</td>
</tr>
</tbody>
</table>
These specimens, also, had the highest mould shrinkage and the highest shrinkage after 24 months storage. This trend was not found with the mould temperature, as an increasing mould temperature results in an increasing mould shrinkage, with a decreasing post shrinkage after storage as well as after annealing. An increasing cavity pressure caused a decreasing mould shrinkage as well as a decreasing radial shrinkage after annealing.

The influence of melt temperature on shrinkage cannot be explained in terms of crystallinity, as density decreased with increasing melt temperature.

The highest differential shrinkage after annealing was found for specimens moulded at the lowest values for processing conditions. Such specimens will have a high tendency to warpage.

Weight after annealing

After annealing the specimens were weighed and the weight compared with the weight 24 h after moulding. In this way, a small but measurable change in weight was found. (Table 8.6) It is assumed that this change arises from an evaporation of low molecular additives. The highest change, approximately 0.2%, was found for specimens moulded at the lowest melt temperature. It is possible that the lower density obtained at higher melt temperatures promotes the diffusion of the additives. The additives in question are probably antioxidants or stabilizers added to improve processing stability. The solubility of such additives in polypropylene is limited due to the low polarity of the polymer. The "desorption", however, is strongly temperature dependent. Degradation of the polymer is facilitated by the presence of atmospheric oxygen. It is known that polypropylene is extremely susceptible to thermo-oxidative degradation. However, the screw injection moulding machine, by its more efficient plastication and expulsion of air from the feed material, notably reduces the tendency to oxidation.
Table 8.6 Change in weight (g) after an annealing for 15.5 hours at 120°C for 3 mm quadrant specimens of polypropylene by variation of cavity pressure, melt temperature and mould temperature

<table>
<thead>
<tr>
<th>Cavity pressure (bar)</th>
<th>200</th>
<th>550</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mould temperature (°C)</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Melt temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>240</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>290</td>
<td>0</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Beyer\textsuperscript{251} found by annealing of polypropylene (Hoechst PPN 1060) the following sequence of events:

(i) Post-crystallization, reduction of internal stresses
(ii) Diffusion of additives,
(iii) Oxidative degradation.

It has been stated in other publications\textsuperscript{221} that a predominant part of the volatile matter consists of water. This assumption does not agree with the influence found with melt temperature, as one would expect water to evaporate also at a melt temperature of 190°C.

Ginger\textsuperscript{216} has shown that the thermal stability of polypropylene homopolymer decreases drastically when the temperature of the barrel is raised from 270°C to 290°C, resulting in chain scission, reduction in molecular weight and melt viscosity. Melt flow index increased from approximately 8 to 10 g/10 min with a residence time in the barrel of 6 min.

In summary, the results indicate that the additives evaporate if the melt temperature is high during processing, or if the specimens are heated to a lower temperature but for a longer period of time. Several runs of thermal analysis of polypropylene at a normal atmosphere above the melting temperature clearly showed a deterioration peak between the endotherm melting peak and the final exotherm degradation.

\textbf{Polyoxymethylene}

Weight, dimensions and shrinkage of 3 and 5 mm quadrant mouldings of polyoxymethylene were determined, as described for polypropylene. In addition, 2 mm specimens with monoaxial flow were moulded with variations of melt temperature and cavity wall temperature.

The influence of cavity wall temperature on weight for 3 and 5 mm specimens and the influence from melt and cavity wall temperature for 2 mm specimens is shown in Fig. 8.4.
Fig. 8.4. Polyoxymethylene—Effect from processing on weight.
The graph shows that by increasing the melt temperature increases in the weight of the 2 mm specimens result. Weight decreases almost linearly with cavity wall temperature for all thicknesses. It was also found but not shown in the graphs that melt temperature had no influence on thickness, which decreased with an increase in cavity wall temperature.

The influence from cavity wall temperature on shrinkage of 3 and 5 mm specimens is shown in Table 8.7 and 8.8. With increasing cavity wall temperature radial shrinkage increases but post shrinkage after 24 month storage as well as after an annealing at 140 °C decreases for 3 mm specimens.

The sum of mould-shrinkage and post-shrinkage is nearly constant for 3 mm specimens. It is assumed, in part based on observations with the 2 mm rectangular specimen, that this observation is only valid when other processing variables, e.g. melt temperature, are at their optimum setting.

Differential shrinkage decreases, whereas post differential shrinkage after storage increases with increasing cavity wall temperature. After annealing of 3 mm specimens, differential shrinkage changes from a negative value to a positive value. The absolute value for the differential shrinkage is highest at the lowest cavity wall temperature.

Cavity wall temperature does not affect weight variation appreciably, although part weight does decrease rapidly with increasing mould temperature. Despite the greater absolute magnitude of shrinkage, higher melt and mould temperatures do not increase dimensional variation. Dimensional variation decreases with annealing times up to 2 h and then increases.
Table 8.7. Radial mould shrinkage \( (S_r) \), differential shrinkage \( (\Delta S) \), radial post shrinkage \( (S_{rp}) \), differential post shrinkage \( (\Delta S_{pa}) \) after 24 month storage and radial post shrinkage \( (S_{rp}) \), differential post-shrinkage \( (\Delta S_{pa}) \) after annealing at \( 140^\circ C \) (in percentages) as a function of annealing time for 3 mm quadrant specimens of polyoxymethylene by variation of mould temperature.

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
<th>Mould temperature (°C)</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mould shrinkage ( (S_r) )</td>
<td>1,59</td>
<td>1,65</td>
<td>1,81</td>
<td>2,05</td>
<td></td>
</tr>
<tr>
<td>( (\Delta S) )</td>
<td>0,17</td>
<td>0,16</td>
<td>0,15</td>
<td>0,11</td>
<td></td>
</tr>
<tr>
<td>Post shrinkage ( (S_{rp}) )</td>
<td>0,07</td>
<td>0,06</td>
<td>0,03</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( 23^\circ C/24 ) months ( (\Delta S_{pa}) )</td>
<td>0</td>
<td>0,02</td>
<td>0,01</td>
<td>0,03</td>
<td></td>
</tr>
<tr>
<td>Post shrinkage ( (S_{rp}) )</td>
<td>0,71</td>
<td>0,67</td>
<td>0,48</td>
<td>0,27</td>
<td></td>
</tr>
<tr>
<td>( 140^\circ C/0,5 ) h ( (\Delta S_{pa}) )</td>
<td>-0,04</td>
<td>-0,03</td>
<td>0</td>
<td>0,02</td>
<td></td>
</tr>
<tr>
<td>Post shrinkage ( (S_{rp}) )</td>
<td>0,76</td>
<td>0,69</td>
<td>0,50</td>
<td>0,30</td>
<td></td>
</tr>
<tr>
<td>( 140^\circ C/1 ) h ( (\Delta S_{pa}) )</td>
<td>-0,04</td>
<td>-0,02</td>
<td>0</td>
<td>0,02</td>
<td></td>
</tr>
<tr>
<td>Post shrinkage ( (S_{rp}) )</td>
<td>0,82</td>
<td>0,74</td>
<td>0,58</td>
<td>0,36</td>
<td></td>
</tr>
<tr>
<td>( 140^\circ C/2 ) h ( (\Delta S_{pa}) )</td>
<td>-0,03</td>
<td>-0,02</td>
<td>-0,01</td>
<td>0,03</td>
<td></td>
</tr>
<tr>
<td>Post shrinkage ( (S_{rp}) )</td>
<td>0,83</td>
<td>0,76</td>
<td>0,60</td>
<td>0,39</td>
<td></td>
</tr>
<tr>
<td>( 140^\circ C/4 ) h ( (\Delta S_{pa}) )</td>
<td>-0,04</td>
<td>-0,02</td>
<td>-0,01</td>
<td>0,01</td>
<td></td>
</tr>
<tr>
<td>Post shrinkage ( (S_{rp}) )</td>
<td>0,87</td>
<td>0,82</td>
<td>0,64</td>
<td>0,45</td>
<td></td>
</tr>
<tr>
<td>( 140^\circ C/8 ) h ( (\Delta S_{pa}) )</td>
<td>-0,04</td>
<td>-0,02</td>
<td>-0,01</td>
<td>0,02</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.8. Radial mould shrinkage \( (S_r) \), differential shrinkage \( (\Delta S) \), radial post-shrinkage \( (S_{rp}) \), differential post-shrinkage \( (\Delta S_{pa}) \) after 24 months storage (in percentages) for 5 mm quadrant specimens of polyoxymethylene by variation of mould temperature.

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
<th>Mould temperature (°C)</th>
<th>80</th>
<th>100</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>185</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mould shrinkage ( (S_r) )</td>
<td>2,22</td>
<td>2,34</td>
<td>2,59</td>
<td></td>
</tr>
<tr>
<td>( (\Delta S) )</td>
<td>0,06</td>
<td>0,03</td>
<td>0,03</td>
<td></td>
</tr>
<tr>
<td>Post shrinkage ( (S_{rp}) )</td>
<td>0,05</td>
<td>0,04</td>
<td>0,04</td>
<td></td>
</tr>
<tr>
<td>( 23^\circ C/24 ) months ( (\Delta S_{pa}) )</td>
<td>0,01</td>
<td>0,01</td>
<td>0,02</td>
<td></td>
</tr>
<tr>
<td>Post shrinkage ( (S_{rp}) )</td>
<td>0,30</td>
<td>0,19</td>
<td>0,10</td>
<td></td>
</tr>
<tr>
<td>( 140^\circ C/0,5 ) h ( (\Delta S_{pa}) )</td>
<td>0,03</td>
<td>0,02</td>
<td>0,03</td>
<td></td>
</tr>
</tbody>
</table>
Polyamide

Weight, dimensions and shrinkage of 3 and 5 mm quadrant mouldings of polyamide were determined for specimens moulded with variation of mould temperatures (Fig. 8.5). The polyamides used were PA 66, PA 6 and PA 6f with 30% glass.

The graph shows that an increasing cavity wall temperature decreases weight (and thickness) for all types.

Radial shrinkage increases with cavity wall temperature. For PA 66 and PA 6 cavity wall temperature had no effect on differential shrinkage, but caused a slightly decreasing differential shrinkage for PA 6f. Dimensional variation did not depend on cavity wall temperature. Samples of the mouldings were stored for 24 months at normal conditions. During the storage the specimens absorbed moisture, which caused a negative shrinkage ( expansion) ( Table 8.9 ).

With polyamide 66, the negative post-shrinkage is 0.21% in the direction of flow and independent of cavity wall temperature. By weighing, it was found that the water content in the specimens corresponded to approximately 0.91%. The specimens were then annealed at 120°C/24 h. These conditions were chosen in order to dry out the specimens with the relatively thick wall thickness. After cooling 24 h in a desiccator with silica gel, the specimens were again measured and post shrinkage calculated.

As expected, the results show that water absorption and post shrinkage parallel to flow is highest for polyamide 6. Water absorption did not depend on cavity wall temperature, but post shrinkage decreases with increasing cavity wall temperature.

In comparing the moisture content for the three polyamide grades it was found that glass reinforcement does reduce the rate of moisture pick-up substantially. The glass-filled polyamide, also, showed the lowest post-shrinkage and the best dimensional stability of the three grades.
Fig. 8.5. Polyamide-Effect from processing on weight, shrinkage and density.
Table 8.9  
Radial mould shrinkage ($S_r$), differential shrinkage ($\Delta S$), radial post-shrinkage ($S_{rp}$), differential post-shrinkage ($\Delta S_{p}$) after 24 months storage, and radial post-shrinkage ($S_{rpa}$), differential post-shrinkage ($\Delta S_{pa}$) after annealing at 120°C/24 h (in percentages) for 5 mm quadrant specimens of polyamide 66, 6 and 6f by variation of mould temperature.

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
<th>Mould temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>285/255/280</td>
<td>60  80  100  120</td>
</tr>
</tbody>
</table>

**Polyamide 66**
- Mould shrinkage ($S_r$): 1.77, 1.92, 1.94, 2.08
- Shrinkage ($\Delta S$): 0.25, 0.23, 0.26, 0.24
- Post-shrinkage ($S_{rp}$) 23°C/24 months ($\Delta S_{p}$):
  - 60°C: -0.21, -0.22, -0.22, -0.22
  - 80°C: -0.21, -0.22, -0.22, -0.22
  - 100°C: -0.21, -0.22, -0.22, -0.22
  - 120°C: -0.21, -0.22, -0.22, -0.22
- Post-shrinkage ($S_{rpa}$) 120°C/24 h ($\Delta S_{pa}$):
  - 60°C: 0.32, 0.21, 0.14, 0.05
  - 80°C: 0.32, 0.21, 0.14, 0.05
  - 100°C: 0.32, 0.21, 0.14, 0.05
  - 120°C: 0.32, 0.21, 0.14, 0.05

**Polyamide 6**
- Mould shrinkage ($S_r$): 1.00, 1.08, 1.18, 1.31
- Shrinkage ($\Delta S$): 0.22, 0.22, 0.23, 0.23
- Post-shrinkage ($S_{rp}$) 23°C/24 months ($\Delta S_{p}$):
  - 60°C: -0.33, -0.35, -0.34, -0.35
  - 80°C: -0.33, -0.35, -0.34, -0.35
  - 100°C: -0.33, -0.35, -0.34, -0.35
  - 120°C: -0.33, -0.35, -0.34, -0.35
- Post-shrinkage ($S_{rpa}$) 120°C/24 h ($\Delta S_{pa}$):
  - 60°C: 0.39, 0.28, 0.20, 0.11
  - 80°C: 0.39, 0.28, 0.20, 0.11
  - 100°C: 0.39, 0.28, 0.20, 0.11
  - 120°C: 0.39, 0.28, 0.20, 0.11

**Polyamide 6f**
- Mould shrinkage ($S_r$): 0.41, 0.43
- Shrinkage ($\Delta S$): 0.01, -0.06
- Post-shrinkage ($S_{rp}$) 23°C/24 months ($\Delta S_{p}$):
  - 60°C: -0.17, -0.18
  - 80°C: -0.17, -0.18
  - 100°C: -0.17, -0.18
  - 120°C: -0.17, -0.18
- Post-shrinkage ($S_{rpa}$) 120°C/24 h ($\Delta S_{pa}$):
  - 60°C: 0.03, 0.01
  - 80°C: 0.03, 0.01
  - 100°C: 0.03, 0.01
  - 120°C: 0.03, 0.01
The opposing dimensional changes, from post-crystallization to absorption of moisture, were further investigated with 3 mm PA 66 specimens (Table 8.10).*

The table shows that mould shrinkage increases with increasing cavity wall temperature. When compared with Table 8.9 it also shows that radial shrinkage decreases and differential shrinkage increases with decreasing wall thickness.

Radial shrinkage after annealing decreases with increasing cavity wall temperature. Dilation of the mouldings increases with increasing cavity wall temperature. This unfamiliar dependence, i.e. the higher the mould temperature the higher the negative shrinkage after conditioning, contradicts the results shown with long-term storage of the 5 mm specimens. Generally, absorbed moisture acts as a plasticizer in the amorphous and less perfect crystalline regions. Therefore, mouldings with a lower crystallinity, which may be expected with a lower mould temperature, absorb more moisture. Moisture may also relieve internal stresses, thereby increasing dimensions.

By weighing it was found that water absorption in percentages of the weight, as expected, decreases with increasing mould temperature:

* In part carried out by Mr. S. Pedersen

<table>
<thead>
<tr>
<th>Conditioning</th>
<th>Mould temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td>60 °C / 115 h</td>
<td>7,20</td>
</tr>
<tr>
<td>90 °C / 15 h</td>
<td>6,56</td>
</tr>
</tbody>
</table>
Table 8.10  Radial mould shrinkage ($S_r$), differential shrinkage ($\Delta S$), radial post-shrinkage ($S_{rpa}$), differential post-shrinkage ($\Delta S_{pa}$) after annealing and conditioning (in percentages) for 3 mm quadrant specimens of polyamide 66 by variation of mould temperature (PA 66.02.1-4)

<table>
<thead>
<tr>
<th>Melt temperature ($^\circ$C)</th>
<th>285</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex.no</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Weight (g)</td>
<td>25,29</td>
<td>25,18</td>
<td>25,11</td>
<td>25,05</td>
<td></td>
</tr>
<tr>
<td>Mould shrinkage ($S_r$)</td>
<td>1,13</td>
<td>1,34</td>
<td>1,51</td>
<td>1,64</td>
<td></td>
</tr>
<tr>
<td>Differential shrinkage ($\Delta S$)</td>
<td>0,67</td>
<td>0,70</td>
<td>0,61</td>
<td>0,55</td>
<td></td>
</tr>
<tr>
<td>Post-shrinkage</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 °C/115 h ($S_{rpa}$)</td>
<td>0,29</td>
<td>0,15</td>
<td>0,04</td>
<td>0,03</td>
<td></td>
</tr>
<tr>
<td>($\Delta S_{pa}$)</td>
<td>0</td>
<td>0,01</td>
<td>-0,02</td>
<td>-0,01</td>
<td></td>
</tr>
<tr>
<td>90 °C/15 h ($S_{rpa}$)</td>
<td>0,47</td>
<td>0,29</td>
<td>0,20</td>
<td>0,08</td>
<td></td>
</tr>
<tr>
<td>($\Delta S_{pa}$)</td>
<td>0,04</td>
<td>0</td>
<td>0,08</td>
<td>-0,01</td>
<td></td>
</tr>
<tr>
<td>140°C/15 h ($S_{rpa}$)</td>
<td>0,70</td>
<td>0,46</td>
<td>0,37</td>
<td>0,26</td>
<td></td>
</tr>
<tr>
<td>($\Delta S_{pa}$)</td>
<td>0,06</td>
<td>0,08</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Conditioning*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 °C/115 h ($S_{pc}$)</td>
<td>-1,72</td>
<td>-1,77</td>
<td>-1,80</td>
<td>-1,89</td>
<td></td>
</tr>
<tr>
<td>($\Delta S_{pc}$)</td>
<td>-0,35</td>
<td>-0,33</td>
<td>-0,31</td>
<td>-0,31</td>
<td></td>
</tr>
<tr>
<td>90 °C/15 h ($S_{pc}$)</td>
<td>-1,52</td>
<td>-1,54</td>
<td>-1,57</td>
<td>-1,72</td>
<td></td>
</tr>
<tr>
<td>($\Delta S_{pc}$)</td>
<td>-0,31</td>
<td>-0,25</td>
<td>-0,24</td>
<td>-0,34</td>
<td></td>
</tr>
</tbody>
</table>

*) Corrected for shrinkage due to annealing effects.
It seems, therefore, that the observed relation is an "experimental artifact" arising from insufficient time to reach equilibrium ($8.5 \pm 0.5\%$). The substantial change in differential shrinkage at the lower mould temperatures also tends to reduce radial expansion. It is known that the transition temperature is strongly influenced by the polymer's water content and falls from 70-80 °C for a dry polyamide to 15 °C for a material containing about 4% moisture. It is to be expected that a higher post-shrinkage takes place during conditioning when the temperature is above $T_g$ than in the dry atmosphere in a hot air oven.

The above relations also show that water absorption increases with water temperature. Absorption generally depends upon coefficients of diffusion, thickness, time and temperature. The coefficient of absorption increases exponentially with temperature, which explains the faster pick-up.

Water absorption in 90 μm sections cut after exposing one surface of the moulding at 60 °C/24 h is shown in Fig. 8.6.

![Fig. 8.6. Water absorption as a function of distance from surface](image-url)
It demonstrates a slight tendency to a faster moisture pick-up with a higher mould temperature. It, also, shows the disabsorption which has taken place on the saturated surface after removal from the water.

**Summary**

From the recorded results the following conclusions can be drawn on the effect of increasing moulding variables.

Weight increased with melt temperature for PE, PP and POM, increased with cavity pressure for PE and PP, and decreased with mould temperature for all materials.

Thickness increased with melt temperature and cavity pressure for PE and PP, but decreased with mould temperature for all materials.

Radial shrinkage decreased with melt temperature and cavity pressure for PE and PP, but increased with mould temperature for all materials, and wall thickness for PP and POM.

Differential shrinkage increased with melt temperature and decreased with cavity pressure for PE and PP. It increased with mould temperature for PE, but decreased for PP, POM and PA6f.

Radial post shrinkage decreased with mould temperature for PE, PP and POM. Radial shrinkage decreased as a result of annealing, differential shrinkage increased with melt temperature, cavity pressure and mould temperature for PP. A similar influence was found with mould temperature for POM, PA 66, PA 6 and PA6f.

Worthy of note is the opposing effect of melt and mould temperature for PE and PP.
8.3. MORPHOLOGY

8.3.1. Introduction

In a general study of the morphology of injection moulded specimens, it should be emphasized that although the influence from processing can, to some extent, be quantified most observa-

vations must be considered descriptive and based on given as-

sumptions and relationships. The following factors should be taken into account:

(i) Rheological history
(ii) Thermal environment
(iii) Polymer specific, crystallization kinetic entities

Chapter 3 described how the rheological and thermal conditions in the mould affects the morphology of an in-

jection moulded specimen, and how, by changing the processing conditions, especially the mould and melt temperatures, the morphology may be affected.

In most semi-crystalline, commercial polymers, nucleating agents are also widely employed to reduce moulding cycles and alter specimen performance. Generally, these agents are miner-

ral particles (e.g. in the case of polyamides), and are used in small quantities. The particles provide sites for crystal growth as the polymer cools. The result is small uniform crystals throughout the moulding. Unnucleated, the crystal growth is random, resulting in areas of large crystals and in amorphous regions. Variations in temperature across the cavity surface will affect the non-nucleated material far more than the nucleated.

All of the above mentioned factors vary with position in the cavity. Therefore, a characterization requires the morphology to be examined in different planes and, at least, at two diffe-

rent positions (Fig.6.12). For the over-all description of the morphology the three-zone designation by Clark\textsuperscript{20} is used in the following sections. It was found, however, that several separate layers of macrophases made up each zone.
8.3.2. Polyethylene

The main variable with polyethylene was barrel temperature and the resulting morphology in the z-y plane at Pos.A is shown in Fig.8.7 and the graphical presentation in Fig.8.8. The microscopical information for polyethylene is less informative, due to its higher rate of crystallization, when compared with polyoxymethylene. However, as was the case in the initial experiments with polyoxymethylene, three distinct layers could be observed (Fig.8.9.a). A closer examination also reveals that the grey value of the photo varies from the surface in towards the center, due to a variation in birefringence through the different layers. In semi-crystalline polymers, birefringence varies depending on the shape of the crystallites, as well as the orientation of the molecular chain. Therefore, the stratified variation in birefringence indicates a variation of these factors. This is particularly noticeable in the core zone, which is made up of an alternating fine and coarse spherulitic morphology (Fig.8.8).

Zone I, when investigated at a higher magnification was found to be composed of a surface skin and a transcristalline layer. In general, no morphological features were visible in the skin (Fig.8.9.a). The width of the skin was constant (20-30 µm) with melt temperatures from 210 - 270 °C. At the lowest and highest melt temperature the skin was approximately 10 µm. The constancy of the width in the normal processing range may be a result of two opposing effects during filling, where the heat evolved due to shear is balanced against the transport of heat due to cooling. The width of the transcristalline layer decreased with increasing melt temperature. Also, the conditions of growth for spherulites resulted in less hindered spherulites with increasing melt temperature.
Fig. 8.7 Polyethylene - Effect of melt temperature on morphology (Pos. A, z-y plane, 40x)
Fig. 8.8 Polyethylene - Schematic representation of morphology
Fig. 8.9 Polyethylene - Effect of processing on morphology (125x)

- a) Skin- and intermediate zone
- b) Core zone showing spherulites with distinct ring structure
- c) Flow lines in moulding (40x)
Although the skin appears featureless, it may be assumed that this layer is highly oriented based on the following considerations (Fig. 8.10, where Fig. 8.10 a has been redrawn after a concept by Woebcken\textsuperscript{146}) Fig.8.10 b visualizes the development in crystallinity with time).

Considering only the temperature and shear stress gradients, that portion of polymer in contact with the cold cavity walls cools more rapidly and experiences higher shear than the polymer in the interior of the mould. The shear stress at the wall disentangles and orients the previously coiled molecules in the direction of flow while the rapid temperature decline causes the viscosity of this oriented layer to increase. Thus, the orientation of these molecules is preserved. Just how thick the oriented skin layer becomes under the imposed conditions in the cavity is expected to depend chiefly on the thermal conductivity, thermomolecular weight parameters, molecular configuration, and chain segment mobility\textsuperscript{25}. These characteristics govern the molecular relaxation times, crystallizability, and the sensitivity of melt viscosity to shear rate or shear stress.

Fig. 8.10 b shows that the front which moves through the cavity has a rounded shape that is more blunt than the velocity profile behind the front. This leads to the rapidly moving, monoaxially oriented, melt in the middle of the narrow section and causes it to move forward to the front and then, as it is bi-axially oriented, causes it to flow out to the cavity walls. This is the so-called, "fountain effect" first recognized by Ballmann et al.\textsuperscript{82-84}. The skin of the moving front is cooled to a viscoelastic state during filling, due to the difference in temperature between the hot melt and the much cooler air in the cavity. According to this model, the orientation on the moulded part surface comes from extensional orientation on the melt front, and not from the shear flow at the wall.
a) Flow induced deformation and twisting by filling of a quadrant moulding (after Woebcken)

b) Development of surface crystallinity

$$t_1 = t_2$$
At the time \( t_1 \) the transverse flow component is depicted by the velocity profile in the upper half of Fig. 8.10 b. The direction of flow and the difference in velocity between different volume elements is shown by the three parallel vectors. The direction of growth for a crystallite formed under the influence from the transverse flow phenomena is also depicted. At the time \( t_2 \) the flow front has arrived at a new position. It is apparent that crystallites in a layer adjacent to the cavity wall are now elongated against the direction of flow. In polyethylene, the lamellae have the fastest growth rate along the \( a \)-axis (see Fig. 3.2). Therefore, crystallites in the skin are preferentially oriented with the \( c \)-axis along the direction of flow and the \( a \)-axis perpendicular to the surface. This is also the direction of the steepest temperature gradient. The number of nuclei formed is, according to Price \(^{252} \), higher the lower the melt temperature. At the high cooling rate at the surface and the corresponding short time for crystallization, the spherulites develop only to a very small size, mainly as a result of an athermal nucleus formation. The fine morphology also falls below the resolving power of a normal, optical microscope.

For specimens moulded with a melt temperature of 196 °C and higher the surface skin is followed by an intermediate layer with a width of approximately 175 µm at \( T_m = 196 \) °C decreasing to approximately 100 µm at \( T_m = 289 \) °C.

At 400 x magnification it was found that spherulites in this layer were free growing. It was also observed, from sections cut in the x-y plane, that these structures did not run strictly parallel to the surface, but along lines with a slightly decreasing distance from the surface with increasing distance from the gate. The strong birefringence is also an evidence of shear as is the observation that some microtomed sections had a tendency to delamination, probably from relaxation after cutting.
Spherulites developed in this layer are formed under the influence of a high shear stress and a steep temperature gradient during mould filling. The considerable shear not only creates molecular orientation but also a high nucleus density when the shear rate has passed a critical value, which is dependent on the melt viscosity. The retention of relatively high orientation in the intermediate layer can be understood from the standpoint that molecular relaxation processes involving the large molecules are slower than the rate of injection of polymer into the mould \(^{25}\). Along the stream-lines, row nucleated structures develop with a direction of growth perpendicular to the surface and against the temperature gradient.

Insulation by the skin may have caused a temporary retention of heat due to shear, heat from later injected melt, as well as heat evolved during crystallization, creating a temperature favourable for free spherulitic growth.

**Zone II** (Intermediate zone) decreases with increasing melt temperature. The morphology is generally fine and changes gradually towards the core zone. This effect was most visible at a melt temperature of 159 °C where the size of the spherulites increased towards the center of the moulding. The maximum rate of nuclei formation is, according to Hoffmann and Weeks \(^{253}\), at a lower temperature than the maximum for spherulite growth. The closer the melt is to the center of the moulding the more the thermal nucleation dominates. Fewer nuclei develop, but these grow to larger spherulites.

**Zone III** (Core zone), which starts approximately 500 to 600 μm from the surface, can be divided into layers where a coarse morphology alternates with a less coarse one. It is assumed that these differences arise during the filling of the cavity, with melt flowing in different layers.
Specimens moulded at a melt temperature of 159 °C are characterized by a homogeneous morphology, with spherulites gradually increasing in size towards the center. With a melt temperature of 196 and 218 °C malformed spherulites are frequently observed. At higher melt temperatures the spherulites become more perfect and increase in size with melt temperature, and the number of symmetrical spherulites with a pronounced ring structure increase (Fig. 8.9.b). Such spherulites are usually found with a slow cooling. However, it has also been shown by Geil187) that such rings do not appear when the crystallization takes place slowly and perfectly enough, and with so many nuclei present that only a sheaflike structure develops.

As in zone II, the bigger spherulites found with increasing melt temperature are a result of fewer embryos present at the higher temperature, which, with the faster cooling at the higher melt temperature, also results in fewer athermal nuclei. Nucleation occurs in an essentially quiescent state with the formation of few nuclei which, however, grow to large spherulites. Generally, spherulites in zone III had the same appearance in all planes.

Flow lines, corresponding to the flow situation at the end of the filling process, were clearly apparent in all sections. For sections cut from the edge of the moulding the flow lines corresponded to the contours of a short-shot moulding (Fig. 8.9.c).

At 600 x magnification it was observed that the flow lines were composed of spherulites which grow perpendicular to the lines. Schönefeld and Wintergerst 189) found that flow lines in polyethylene mouldings did not disappear with an annealing just below the melt temperature. They assumed that they consisted of particularly stable structures.

In zone II and III where a fine texture often alternates with a coarse one, such layers may be visualized as consisting of up to 200 μm broad flow lines. The layers may be formed after the volumetric filling of the cavity where the pressure gra-
dient from the gate to the vent end causes a creeping flow, or a small transport of material in the not yet solidified core. Also, the number and size of spherulites varied, indicating that the rate of cooling does not decrease continually from the surface towards the center. This is an effect from the complex thermal environment, where heat from the last injected melt, frictional heat, and the latent heat of crystallization influence the formation of crystallites.

8.3.3. Polypropylene

Polypropylene compared with polyethylene is characterized by a lower rate of crystallization, which causes a more distinct influence from processing on morphology. This makes the material ideal for studying the influence from processing and may explain why the polymer has been investigated in so much research work. However, the result of different investigations are often contradictory, because a rather narrow interval for the processing conditions have been chosen. In this investigation a broad range was chosen. This had the effect that despite the carefully monitored moulding conditions some features not normally associated with a moulding of good quality were also observed.

Zone I consisted of a 1 - 40 μm surface skin where no morphological features were observed with up to 800 x magnification (Fig. 8.11 to 8.17). With parallel extinction of polarization colour, it was found that this skin was highly oriented. Other workers using x-ray diffraction found the skin highly crystalline and possessing fiber texture. It was found that the width of the surface skin did not depend on wall thickness, flow length, mould and melt temperature or cavity pressure. In some cases the surface skin was well-defined, but in other cases a more diffuse transition was observed. This difference did not seem to correlate with the processing variables. In some cases, especially with high mould and melt temperatures, the surface skin had a torn appearance as if
Fig. 8.11 Polypropylene - Effect of mould temperature on morphology of 3 mm quadrants ($p_c = 19.6$ MPa, $T_m = 191-192$ °C)
Fig. 8.12 Polypropylene - Effect of mould temperature on morphology of 3 mm quadrants
($P_c = 53.6$ MPa, $T_m = 191-192$ °C)
Fig. 8.13 Polypropylene - Effect of mould temperature on morphology of 3 mm quadrants
($p_c = 19.6$ MPa, $T_m = 241-243$ °C)
Fig. 8.14 Polypropylene - Effect of mould temperature on morphology of 3 mm quadrants 
($P_c = 53.6$ MPa, $T_m = 237-243 ^\circ C$)
Fig. 8.15 Polypropylene - Effect of mould temperature on morphology of 3 mm quadrants
($p_c = 19.6$ MPa, $T_m = 282-283$ °C)
Fig. 8.16 Polypropylene - Effect of mould temperature on morphology of 3 mm quadrants
\(p_c = 53.9\, \text{MPa}, T_m = 282-283\, ^\circ\text{C}\)
Fig. 8.17 Polypropylene - Effect of thickness on morphology of 2 (PP 08.1) and 5 (PP 06.1) mm quadrants.

**PP 08.1 A**
- $T_f = 40 \, ^\circ C$
- $P_c = 45.5 \, MPa$
- $T_m = 241 \, ^\circ C$

**PP 08.1 B**
- $T_f = 40 \, ^\circ C$
- $P_c = 53.9 \, MPa$
- $T_m = 239 \, ^\circ C$

**PP 06.1 A**
- $T_f = 40 \, ^\circ C$
- $P_c = 53.9 \, MPa$
- $T_m = 239 \, ^\circ C$

**PP 06.1 B**
- $T_f = 40 \, ^\circ C$
- $P_c = 53.9 \, MPa$
- $T_m = 239 \, ^\circ C$
the surface had moved into the interior. Portions of the skin have apparently moved and extended into the interior to act as a nucleus with a bright, hemispherical, tooth morphology. At the highest mould temperatures and the highest cavity pressure the surface skin was followed by a narrow layer with rod-shaped spherulites with their main axis oriented perpendicular to the surface and with some tendency to transcrystallization. No proper ring structure was observed in these spherulites.

Fitchman and Newman \(^{194}\) have shown that it is the cavity surface which is the most important variable for development of surface morphology in polypropylene. With compression moulding of polypropylene against surfaces of oxidized aluminium and copper they produced a spherulitic surface. Moulding against Mylar (PETP) or Teflon (PTFE) caused a transcrystalline morphology, which probably could be traced back to a heterogeneous nucleation induced at the cavity surface.

They also showed, in contradiction to the general conception in literature, that the surface energy at the cavity surface and the temperature gradient over the melt are not the prime factors for development of transcrystallinity in polypropylene.

Nucleation generally takes place through the moulding at random. In the special case where nucleation is initiated at the surface, the spherulitic growth centres are pressed together and forced to continue growth towards the center of the moulding.

Zone II is the intermediate zone following the surface zone. Its boundary with the surface zone is fairly easy to determine, whereas this layer is less discrete and changes more gradually towards the core. The widths of zone I and II decrease with increasing flow length, mould and melt temperature (Fig.8.18). With fixed processing conditions, there is a slight tendency to an increasing zone II with increasing wall thickness.

(Example: Pos.A, s=2 mm: 0,31 mm, s=3 mm: 0,35 mm, s=5 mm: 0,36 mm).
Fig. 8.18 Polypropylene – Effect of mould temperature on the width of zone I and II
At the lowest melt temperature (190 °C), increasing cavity pressure causes a narrowing of zone II. At the medium melt temperature (240 °C), an increasing cavity pressure causes a slightly decreasing width of zone II at the position (A) near the gate at a mould temperature up to 40 °C. At a higher mould temperature no influence was found. Opposite the gate (Pos. B) an increasing cavity pressure results in a broader zone II for all mould temperatures. At the highest melt temperature (290 °C), an increasing cavity pressure causes a broader zone II at both positions. It is characteristic that cavity pressure has comparatively more influence on the width of zone II close to the gate (Pos. A) than it has opposite the gate (Pos. B).

Generally, the temperature of crystallization increases with pressure and this increases the temperature gradient, resulting in an increasing rate of cooling of the melt and a broader zone II, as found with a high melt temperature. Cooling of the melt may also improve under pressure, due to the better contact between melt and cavity surface. However, the time of contact may decrease with a faster cooling, enhanced by the tendency of polypropylene to sink from the cavity surface.

The effect of pressure at the low melt temperature arises mainly from the very long filling time at 200 bar (6.5 s at $T_f = 40$ °C, Table 7.2 a), where the slowly injected melt acts as an insulated runner, in effect, causing two discrete phases or morphological layers in the cross section of the moulding.

At a melt temperature of 240 °C, zone II is still fairly broad, whereas it decreases to a narrow layer close to the surface at the melt temperature of 290 °C. The morphology becomes more coarse toward the center and the spherulites increase in size. This effect was most pronounced at higher melt temperatures, where the coarse morphology was found also in zone I.
The boundary layer between zone II and III, especially at low mould temperature, was characterized by flow lines, often with a tendency to transcristallization. Also, deformed spherulites were identified in the flow lines. The morphology in the flow lines arises at random, as a result of a change from heterogeneous nucleation to nucleation induced by shear. The boundary layer may represent the cooling situation at the time when the cavity is completely filled.

In those cases where a gradual change in the core was observed, which was the case especially at the highest melt temperatures, a slight change in the orientation of the axis perpendicular to the surface with a more random orientation was found.

This change was followed by an increase in the size of the spherulites, a consequence of the slower cooling which creates few, but correspondingly larger spherulites.

Samples moulded at a medium melt and mould temperature and a low cavity pressure (Fig. 8.13) showed a transition zone between zone II and III which was subdivided into layers, where the size of the spherulites in each layer increased gradually towards the center of the moulding, and as a general trend also increased in each individual layer. Together with the abrupt change in size between the layers, an alternation of spherulites grown in rows with spherulites with a more random orientation was also observed.

From this observation it may be concluded that layers with equal size of spherulites develop at the same rate of cooling. The rate of cooling does not decrease continuously from the surface towards the center of the moulding, because filling and packing takes place simultaneously with cooling.
Zone III comprises the last injected and last cooled part of the moulding. This region showed, for specimens moulded at the lowest melt temperature (190 °C), an unexpectedly large variation in morphology, with distinct transcry stallization. Specimens moulded with a high cavity pressure and mould temperatures up to 40 °C also showed separation in the morphology at the position near the gate (Fig. 8.19a).

Specimens moulded at a lower cavity pressure were less drastically influenced, apart from a distinct transcry stallization (Fig. 8.19b). However, with these specimens it was characteristic that, especially at the lowest mould temperature, several different types of spherulites were observed (Fig. 8.19b). The typical were large (up to 50 μm), bright, and often negative (β-type) birefringent spherulites with a radial fibrous structure.

At Pos. A, large spherulites (> 50 μm) were found with three combinations of processing conditions:

(i) Low melt temperature/low mould temperature/low cavity pressure
(ii) Medium melt temperature/high mould temperature/high cavity pressure
(iii) High melt temperature/low mould temperature/high cavity pressure

It was found that the bright spherulites of type III, according to Padden and Keith 186), had a concave boundary, whereas spherulites classified as type I, by Padden and Keith, had surfaces which were plane, convex or concave. A possible explanation of this phenomenon is that the surface shape depends on the growth rate of the spherulites. Two spherulites growing at the same rate meet along a plane surface, whereas two spherulites growing with different rates will have a curved boundary - convex with slow growing and concave with fast growing. From this concept, hexagonal spherulites should grow faster than monoclinic. 218).
Fig. 8.19 Polypropylene - Morphology as a function of processing conditions (125x)

a) Fracture in morphology  
b) Transcrystallization  
c) Hexagonal spherulites

Fig. 8.19 Polypropylene - Morphology as a function of processing conditions (125x)
Type III spherulites are formed by rapid cooling, according to Wunderlich (179). However, it has also been observed that the β-modification, which is mostly connected with type III spherulites and partly to row structures, is enhanced with high mould temperatures (254). Also, the shear rate is important for β-form crystallization (188).

Generally, increasing melt and mould temperatures cause fewer bright hexagonal spherulites. Pressure increases the temperature of crystallization. In relation to the rate of crystallization, this corresponds to a decrease of the mould temperature. The higher pressure also compensates the volumetric contraction and, consequently, shrinkage. Pressure also tends to minimize the air gap between cavity wall and moulding, which improves heat transfer and increases cooling.

At the lowest melt temperature, which is only 20 °C above the optical melting point (see Section 6.2.2), the memory of the previous crystalline order has not been cancelled out. Crystallites still present in the melt are partially re-established and act as centers for further crystal growth. An insufficient mixing may also be expected with the fairly deep screw combined with a low shot weight, when compared with the plasticizing capacity of the injection moulding machine. That hexagonal spherulites also develop at higher melt temperatures and high pressures can be explained by the higher shear. Primary nuclei tend to line up along flow lines. The increase in crystallization rate under orientation is, thus, mainly attributed to an increasing number of primary nuclei, creating bunched rows of negatively birefringent spherulites (211, 254-255).

The size of the spherulites also influences the critical deformation \(^+\) of the samples.

\(^+\) The theory of critical deformation developed by Menges is based on a critical limit of strain, defined as the deformation, where the first failure of the sample is visible to the naked eye. With translucent semi-crystalline polymers such failure is characterized by a milky appearance, for amorphous polymers as crazes.
As shown by Menges and Horn\textsuperscript{256}, negative birefrigent spherulites are the first regions where the critical deformation is exceeded. The finer the spherulitic morphology, the higher is the critical deformation.

With increasing mould temperature, the distinct transcristallization at the lowest melt temperature decreases, but dark flow lines are still visible against a finely textured background, indicating orientation in the melt. Filling time is also decreasing with increasing pressure (see Fig. 7.6), which increases shear and, hence, a nucleation induced earlier during the moulding cycle.

The distinct flow lines tended to disappear opposite the gate (Pos. B) with increasing mould temperature. Cooling time also had an influence as mouldings slowly cooled over several hours in the mould did not show flow lines on either of the two positions.

8.3.4. Polyoxymethylene

With polyoxymethylene, a first order quartz filter was inserted in the path of rays in the microscope and used to discriminate between positively and negatively birefrigent spherulites. It may be assumed that the birefrigence observed is due only to orientation, as microtomed sections below 30\,\mu m have no internal stresses\textsuperscript{150}.

In contrast to the experiments reported in Chapter 3, the different zones were less clearly identifiable, probably due to a heterogeneous nucleation of the polymer. (Fig. 8.20 - 8.23)

No investigations were found in the literature review which describe the structure of polyoxymethylene spherulites. In this investigation, only one type of spherulites was found.
Fig. 8.20 Polyoxymethylene - Effect of mould temperature on morphology of 2 mm rectangular mouldings
($P_c = 45,5$ MPa, $T_m = 185-186^\circ C$)
Fig. 8.21 Polyoxymethylene - Effect of mould temperature on morphology of 2 mm rectangular mouldings
($P_c = 45,5$ MPa, $T_m = 221-222\, ^\circ\text{C}$)
Fig. 8.22 Polyoxymethylene - Effect of mould temperature on morphology of 3 mm quadrants
($p_c = 45.5$ MPa, $T_m = 220$ °C)
Fig. 8.23 Polyoxymethylene – Effect of mould temperature on morphology of 5 mm quadrants
($p_c = 45.5$ MPa, $T_m = 185^\circ$C)
When compared with the other polymers investigated it was observed that a positive or mixed birefringence was shown. Zone I was determined as the layer where the birefringence was distinctly different from the rest of the sample. It was initiated with a surface skin where no suprastructure was observed with up to 800 x magnification, except at the most favourable crystallization conditions, that is a high melt and mould temperature where a few radiating spherulites oriented perpendicular to the surface were observed.

The surface skin, which was approximately 20 \( \mu \text{m} \) wide, was found to be independent of mould temperature, wall thickness, flow length, and flow direction (x-y vs z-y plane).

The surface skin was followed by a region with small spherulites, restrained during growth by impingement on other spherulites and with their axes oriented towards the surface. The width of this layer was approximately 100 \( \mu \text{m} \), relatively constant at mould temperatures of 80 and 100\( ^\circ \)C but with a greater variation at the lowest and highest mould temperatures. The layer was generally 20 \( \mu \text{m} \) broader at position A than at position B. The layer also varied with wall thickness and was smallest at a wall thickness of 3 mm. Sections cut parallel to flow (x-y plane) showed a greater variation than sections cut transverse to flow (z-y plane).

Zone II was divided in two layers. In the immediate vicinity of zone I was found a region with small spherulites (zone II a), close to zone I oriented with the axis perpendicular to the surface but with a more random orientation further from the surface. This layer had a width approximately 100 - 150 \( \mu \text{m} \) but decreasing slightly with increasing mould temperature. However, at the lowest mould temperature it was found to be narrower than at a mould temperature of 80\( ^\circ \)C.
Zone II a was followed by a region (zone II b) approximately 150 - 250 μm wide with a marked coarse spherulitic structure and with the axes of the spherulites oriented towards the surface. This layer also decreased with increasing mould temperature. Melt temperature, which was varied for 2 mm mouldings, was found to have the same influence as mould temperature on the size of zone II.

The centres of the spherulites in the first part of zone II a and in the whole of zone II b, generally follow flow lines at a slightly decreasing distance from the surface with increasing flow length.*)

The deflected spherulites were followed by layers of a fine texture. The transition between the two layers represents the position of the front of crystallization when the cavity was completely filled and the shear stress due to flow dropped to zero.

Zone II was followed by a transition region which at a mould temperature of 60°C showed the same features as zone II, as regions with smaller unoriented spherulites changed to layers with a more coarse morphology. This region became more homogeneous with increasing mould temperature.

The transition region points to temperature variations in the melt which together with the variation in shear may cause internal stresses. Temperature gradients and stresses in the melt

*) During the cavity filling shear stresses develop in the melt. Close to the surface they run antiparallel to the direction of flow. When the front of solidification progresses from the surface towards the center the spherulites develop increasingly parallel to the stresses. This effect was observed in zone II where the axes of the spherulites were no longer strictly perpendicular to the surface but were deflected against the direction of flow.
also influence orientation of the chains in the amorphous phase, which also depend on crystal growth and deformation of the crystallites. The mechanical properties depend to some extent on the "tie-molecules" in the amorphous phase. Generally, the orientation of the "tie-molecules" increase strength in the direction of orientation. This orientation cannot be observed directly in an optical microscope. Generally, the amorphous chains follow the orientation of the crystallites.

The quite marked subdivision of zone II and the transition region was less pronounced for sections cut further away from the gate (Pos.B). Mouldings with a 5 mm wall thickness also had a less marked division in zones. Generally, zone II had the same thickness as zone II with 2 mm mouldings when the section was cut from position A (Fig.8.23).

Flow lines with coarse spherulites were observed approximately 0.6 mm from the surface of 5 mm mouldings. Generally, mould temperature was found to have the same influence on 5 mm mouldings as on 2 and 3 mm mouldings, where zone II decreased with increasing mould temperature.

Zone III was characterized by fairly big spherulites with a random orientation for all three wall thicknesses. The growth of the spherulites was terminated by merging with other growing spherulites. At a high melt temperature and a low mould temperature, up to 50 μm big spherulites were found in zone III of 2 mm mouldings (Fig.8.20 and 8.21).

Closer to the gate some orientation of the spherulites was found in a transition region between zone II and III. At the center of the mouldings a line was observed which, despite the otherwise random orientation of the spherulites, forms a boundary between spherulites oriented towards the two cavity surfaces.
8.3.5. Polyamide

Compared with the polyolefines and with polyoxymethylene the morphology of the investigated polyamides (PA 66, PA6 and PA 6f) revealed less information. This is a consequence of the grades chosen for investigation, which were fast crystallizing.

**Polyamide 66**

Zone I had a surface skin \( 10 \) - \( 50 \ \mu\text{m} \) wide which was found on all specimens investigated. It was found to be independent of cavity wall temperature (Fig. 8. 24). For specimens moulded with a mould temperature of \( 60^\circ\text{C} \) the surface skin was followed by a region with spherulites increasing slightly in size towards the center of the specimen but without a distinct zone division.

Zone II was not particularly developed but could be observed at higher mould temperatures. It had a width between \( 70 \) and \( 150 \ \mu\text{m} \) and decreased slightly with increasing mould temperature.

Zone III was found to be independent of mould temperature, as no variation in spherulite size or spherulite orientation was observed.

**Polyamide 6**

Zone I showed a surface skin comparatively wider than found with other polymers investigated. It had a width of approximately \( 27 \ \mu\text{m} \) at a mould temperature of \( 60^\circ\text{C} \) and \( 31 \ \mu\text{m} \) with a mould temperature of \( 80^\circ\text{C} \), but then rapidly decreasing with mould temperature, so that it was just identifiable at a mould temperature of \( 120^\circ\text{C} \) (Fig. 8. 25).

An intermediate zone II was not observed, but in a region approximately \( 0,3 \ \text{mm} \) from the surface strong flow lines were observed together with deformed spherulites, which at the highest mould temperature developed to microcrazes visible at \( 10 \times \) magnification. No explanation was found for the crazes. They could have developed due to volume contraction during the cooling phase.
Fig. 8.24 Polyamide 66 - Effect of mould temperature on morphology of 5 mm quadrants
($P_c = 45.5$ MPa, $T_m = 284-287$ °C)
Fig. 8.25 Polyamide 6 - Effect of mould temperature on morphology of 5 mm quadrants
($P_c = 45.5$ MPa, $T_m = 254-256$ °C)
Polyamide 6f
This glass-reinforced material was investigated as a reference for the other polymers but a detailed analysis was not carried out. However, the investigation did reveal that the orientation of the glass fibres was influenced by the processing variables. Approximately 1.6 mm from the surface the fibres are oriented in the direction of flow. The width of this layer is comparatively constant with the length of flow at a mould temperature of 80°C. At higher mould temperatures (e.g. 120°C) the width increased from approximately 1.3 to 1.5 mm from pos A to pos B. The layer was symmetrical around the center line. In the core fibres were also oriented transverse to flow (Fig. 8.26).

These observations indicate an anisotropy due to the fibre orientation. A trial was made to characterize the orientation by milling off a layer from both sides of the surface until the remaining layer had a thickness of approximately 0.1 mm. This layer was then investigated with x-rays (radiography). However, in all cases the size of the fibres were less than the grain size of the film and, therefore, could not reveal the image. Other methods, e.g. SEM, were not tried because such investigations were considered outside the scope of this project.

8.3.6. Summary
In summation, the following influence from processing on morphology was found when the cross section was divided into three zones:

Zone I consisted of a surface skin without any morphology features because it had been quenched to a temperature where the size of the crystallites falls below the resolving power of a microscope.
Fig. 8.26 Polyamide 6f - Effect of mould temperature on morphology of 5 mm quadrants
($P_c = 45.5$ MPa, $T_m = 280^\circ$C)
The surface skin was followed by a region with small spherulites with their axis oriented towards the surface. With polyethylene and polypropylene, row nucleated spherulites were present. This layer, generally, was independent of the processing variables but decreases in size with increasing distance from the gate.

Zone II generally showed a fine morphology, and may be visualized as a transition zone with a gradual increase in the size of the spherulites. It decreased with increasing mould and melt temperatures. In some cases flow lines were visible. In the layer close to zone I the spherulites were oriented perpendicular to the surface.

Zone III was characterized by spherulites with a random orientation. With polypropylene, the size of the spherulites was constant except for some combinations of processing conditions which caused large, negatively birefringent spherulites.
8.4. DENSITY AND CRYSTALLINITY

8.4.1. Density

Polyethylene

Density was determined as a function of melt temperature and as a function of distance from the gate (Fig. 8.27). Density increased with melt temperature, except for the highest melt temperature. The higher density with increasing melt temperature is a result of the slower cooling and, hence, improved conditions for crystallization.

Density decreased with increasing distance from the gate, which may be the result of two effects. Firstly, prior cooling may reduce the time that the polymer is within this temperature range for rapid crystallization. Additionally, the mould has been heated less because less material has passed. Secondly, during crystallization the absolute pressure is highest close to the gate. Opposite the gate, therefore, there is a greater tendency to supercooling and a shorter time for primary crystallization, which also reduces the density. Higher pressure in the gate region also increases density.

Polypropylene

The influence from melt temperature, cavity wall temperature and cavity pressure on density can be seen in Fig. 8.28. The graph shows that by increasing the melt temperature and the cavity pressure there is a decrease in density. An increase in mould temperature has the opposite effect.

Fujiyama attributed a decreasing density with increasing cylinder temperature to a decrease in the width of the skin layer which, according to Fujiyama, was assumed to have a higher density. However, in this investigation density (and melting enthalpy) was found to increase with distance from the surface (see Fig. 5.8, and the following section).
Fig. 8.27 Polyethylene  a) Effect of melt temperature on density and b) density profile

a) $T_f=35^\circ\text{C}; P_C=55 \text{ MPa}; \nu=25 \text{ mm/s}$

b) $T_m=220^\circ\text{C}; T_f=50^\circ\text{C}; P_C=34.3 \text{ MPa}; \nu=18 \text{ mm/s}$
Fig. 8.28 Polypropylene - Effect of processing variables on density

<table>
<thead>
<tr>
<th>Point</th>
<th>PC (bar)</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>196</td>
<td>192</td>
</tr>
<tr>
<td>2</td>
<td>196</td>
<td>242</td>
</tr>
<tr>
<td>3</td>
<td>196</td>
<td>282</td>
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<tr>
<td>4</td>
<td>539</td>
<td>192</td>
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<tr>
<td>5</td>
<td>539</td>
<td>241</td>
</tr>
<tr>
<td>6</td>
<td>539</td>
<td>283</td>
</tr>
</tbody>
</table>
Compared with polypropylene however, polyethylene has a much higher rate of crystallization (see Table 3.3). Polyethylene is also less susceptible to supercooling than polypropylene (see Section 6.2).

Also, at a high melt temperature a highly disordered melt is present, whereas some molecular order may be present in melts which have not been heated much above the crystalline melting point. Such regions of order would provide sites for an athermal nucleation causing a high density of nuclei and a high overall density.

At a higher melt temperature, thermal nucleation dominates over the athermal nucleation, with new crystallites starting to grow throughout the crystallization period. It can also be seen from Fig. 6.11 and the slope of the density curve, (Fig. 8.28) that the higher the cooling rate, that is the higher the difference between melt and mould temperature, the faster the crystallization region is passed. This suppresses the temperature of crystallization to a lower value and fewer molecules will crystallize. The temperature also decreases faster as less heat of crystallization is evolved. The molecules will have less time to arrange themselves causing a low degree of crystallinity and hence, a low density.

It should be noted that, although the polymer used was a commercial grade and probably heterogeneously nucleated, this form of nucleation may be either thermal or athermal. However, since the number of heterogeneous nuclei is limited the thermal nucleation of heterogeneous origin must level off after all nuclei are exhausted.

For a given melt temperature and cavity pressure, density increased with increasing mould temperature, a consequence of the slower cooling rate which enhances crystallization.

Density decreased with increasing cavity pressure, contrary to the fact that pressure promotes crystallinity and density.
As can be seen from the pressure curves, however (Fig. 7.6), the rate of pressure build-up, which may be used as a measure of the filling rate, is a dependent variable which increases with pressure and mould temperature. The time for filling is reduced when the cavity pressure is increased from 20 to 54 MPa (Table 7.2).

The time to seal the gate increases only slightly with pressure for a given melt temperature. An increasing pressure, however, tends to promote contact between the solidified layer and the cavity surface, hence promoting supercooling, which, as explained above, tends to decrease density (Fig. 7.5).

The variation of density across the moulding was investigated by taking the eight 6 x 6 mm samples at 41 positions (Fig. 8.29). It shows that density decreases with the distance from the gate, as explained with polyethylene. The graph also demonstrates how the solidifying front moves from the periphery of the moulding, where a low density is found because the melt is cooled by two cavity surfaces, toward the gate, where pressure and temperature is higher, hence improving conditions for crystallization.

Density after annealing at 120 °C/186.5 h is also shown in Fig. 8.29. It shows that the lower the original density, the higher is the effect of annealing.

Since the extremities of the moulding have a lower initial density than the centre, these will have a faster rate of post-moulding crystallization. This in turn leads to increased shrinkage relative to the centre and, hence, induces warpage in the component.
Fig. 8.29 Polypropylene - Variation in density (pp 05.12)

120°C/186°F H
Density after annealing at
Density before annealing

Scale 2:1
**Polyoxymethylene**

The influence on density from melt temperature, cavity wall temperature and thickness is shown in Fig. 8.30.

The graph shows that an increased melt temperature increased density for 2 mm mouldings. Density increased with cavity wall temperature for all thicknesses due to the slower cooling and higher crystallinity. Mouldings with 5 mm thicknesses moulded at 185 °C had a higher density than 3 mm mouldings moulded at 220 °C. Provided that the same relation holds as with 2 mm mouldings, it is clear that wall thickness has a greater influence on density than does melt temperature.

**Polyamide**

With polyamide 66 and 6 density increased linearly with cavity wall temperature (Fig.8.31)

8.4.2. Thermal Analysis

Qualitative interpretation

Typical melting curves for the four polymers investigated with thermal analysis are shown in Fig.8.32

![Fig. 8.32 Typical melting curves](image-url)
Fig. 8.30 Polyoxymethylene - Effect of processing variables on density
Fig. 8.31 Polyamide - Effect of cavity wall temperature on density
The shape of the DSC trace is determined, in general, by two competing processes, melting of the sample according to type, size, and perfection of the crystallites and reorganization of the sample as it is heated up in the scan. The relative importance of these processes in a particular instance will depend on the reorganization rate in relation to the DSC scan rate.

Fig. 8.32 shows that the melting behaviour is different for the four polymers. As an example, the broad diffuse peak with polypropylene reflects the progressive melting of smaller crystallites, which first melt because of their higher specific surface energy. Also, the less thermally stable crystallites melt during the initial heating.

The peak value, "the equilibrium melting point" ($T_m$), represents the temperature where all thermal effects are balanced. It is the temperature closest to the temperature at which the bigger and more stable crystallites have also melted.

The rate of phase change amorphous/crystalline can be deduced from the slope of the low temperature side of the curve. The steep slope with polyethylene is a result of a fast change and the less steep slope with polypropylene indicates a slow melting of the crystalline structure. A sharp peak is typical of a highly crystalline and probably oriented sample (see e.g. Fig. 8.33).

The double peak found with polyamide indicates a more complex morphology. The two peaks may be attributed to differences in crystallite modifications, where the first peak is the melting point for the $\beta$ or parallel form of crystal ($T_m \approx 246 \degree C$) and the second peak is then the melting point of the $\alpha$ or the anti-parallel form of the crystal ($T_m \approx 254 \degree C$).

It has also been proposed that the two peaks are a result of the melting of two distributions of crystallites of different size and/or degree of perfectness. The formation of the crystallites

*) Polyamide 66 may crystallize in triclinic (a), monoclinic (b) and a (pseudo)hexagonal (y) form. (Ref: C.W. Bunn and E.V. Garner, Proc. Royal Soc. (London) 189A (1947) 39)
melting at a higher temperature has also been explained by a melting-recrystallization process which takes place at the lower temperatures during scanning. It has also been suggested that the first endotherm peak is a result of a disorientation of extended chains or similar structures followed by a normal melting.

It should be noted that by cooling the sample the rate of crystallization can be followed, thereby observing the influence from e.g. nucleating agents on crystallization, which is important in determining cycle time in injection moulding.

Quantitative interpretation

A quantitative interpretation of the melting behaviour of a given polymer presents some experimental difficulties. As an example, are the peak area and the equilibrium melting temperature dependent on the rate of heat change, due to the lag in temperature between sample and block. If the exact melting temperature is to be determined, it can only be done by heating small samples (~1 mg) at different heating rates and extrapolating them to zero.

The differences in molecular configuration also make it impossible to compare the melting curves of different polymers.

Therefore, the following presentation should only be considered semi-quantitative.

Polyethylene

The heating curves for polyethylene, as a function of distance from the surface, are shown in Fig.8.33 for a typical charge of 3 mg of sample heated at 5.5°C/min.

The equilibrium melting temperature varies across the section, but with a tendency to increasing values with increasing distance from the surface. The melting temperature gener-
Fig. 8.33 Polyethylene - Melting curves as a function of distance from the surface (PE 03.1)
ally increases with increasing lamellae thickness, which increase is caused by a higher temperature of crystallization. It is, therefore, surprising that the melting temperature is high at the surface, where the surface layer is quenched on contact with the cavity surface.

This layer, however, crystallizes under a high shear as explained in Section 8.3. This may, in some cases, result in an odd morphological structure called "shish-kebab". It consists of a thin extended chain fibril (about a dozen molecules in diameter) with ordinary crystal lamellae growing perpendicular from the fibril. The shish-kebab modification has a high melting temperature 179). With higher rates of heating the barely discernible shoulder, which can be seen on some melting curves, develops into a characteristic double peak (Fig. 8.34). The first peak has a maximum at 129 °C, the second partly merging peak has its maximum at 133 °C.

The difference in melting enthalpy between the two modifications was measured to 19.0 kJ/kg, corresponding to a difference of approximately 11.6 %. Between very slow cooling and shock cooling crystallinity can vary up to 10 % in high density polyethylene 212)*. Such differences in crystallinity are not revealed in a thermal analysis carried out with low rates of heating, where the double peaks are not separated.

*) The variation in crystallinity between a slow and a fast cooled sample was later, kindly, investigated by Messrs. T. Leffers and O. Toft Sørensen at the Research Establishment, Risø. Using a Philips PW 1130 -90-96 diffractometer and Cu-Kα radiation they examined a slow and a fast cooled compression moulded high density polyethylene sample. The interplanar spacings, d-values, for strongest reflection were for both samples: 4.15 - 3.74 - 2.98 - 2.48 Å. None of the samples showed preferred crystal orientation (texture). The X-ray crystallinity was calculated as the ratio of the integrated crystalline scattering to the total amorphous and crystalline scattering. The degree of crystallinity between 15 ° and 28 ° intersections on the 2θ axis was determined to 69 and 60 % for the slow and fast cooled samples, respectively. The author acknowledges the assistance by Messrs. Leffers and Toft Sørensen.
Fig. 8.34 Polyethylene - Melting peak

Heating rate 15 °C/min
Sample weight 3.5mg
Holden in a study of the effects of thermal history on polyethylene found that double peaks in melting curves of linear polyethylene are a property of the polymer resin rather than of any interfacial nucleation sites. Pope observed that the lower melting peak is generally found to increase in size and move up the temperature scale with increased annealing time. This behaviour can be explained by the crystals becoming more stable so that they melt at higher temperatures and, therefore, recrystallize less readily. Another type of low melting peak moves to lower temperatures and eventually disappears with increased annealing time. These peaks have been attributed to the formation of imperfect crystals during cooling from a semi-molten state.

Other factors are also known to influence the complex situation during melting in a DSC-cell. As a consequence, the nature of the melting curve should be examined critically. Initial experiments with other polymers ruled out the possibility of instrument interference. The shape of the melting curve suggests the possible explanation that the low-melting crystallites undergo rapid recrystallization to produce the minimum before the high melting peak. If this were the case, the peak temperature could be expected to show a strong dependence on the heating rate. Although the resolution of the two features was somewhat reduced when the heating rate decreased the experiments did not support this hypothesis.

This phenomenon of two melting peaks has also been explained by particular thermally stable structures with a high temperature melting peak at 133 °C, resulting from high shear during mould filling.

In this investigation it was found that the high shear creating transcrystallization appeared just under the surface
skin of the moulding (Section 8.3.2). Consequently, the double peak should also be most pronounced in this layer of the moulding. However, the results showed a decreasing trend for the high temperature peak with increasing distance from the surface (Fig. 8.35). The high temperature peak nearly disappears towards the center of the moulding. At a further distance from the surface and within a brief region between 750 and 900 µm the temperature of the principal peak shifts and merges with the high temperature peak at 133 °C (Fig. 8.36).

A tentative explanation of the conditions which cause structures resulting in a double peak may be that the melt first injected into the cavity has crystallized during a fast cooling resulting in a morphology with a maximum at 129 °C. This layer is then annealed by the latent heat of crystallization from the melt injected during the later stages of the packing phase, which is released as the interface progresses from the surface toward the center of the moulding.

This assumption has been tried by annealing in the cell of samples from a section with crystallites predominantly with a peak maximum at 129 °C. Annealing was carried out with temperatures between 124,7 and 127,4 °C (Fig. 8.37). The results show that annealing changed the melting curves in such a way that the peak maximum changed quite abruptly from 129 °C to 133 °C, but, with an indication of a shoulder at the point where the double peak was observed in earlier experiments.

When the sample is annealed at higher temperatures, the surviving crystallites are more and more uniform and the discrepancy between the peaks vanish. A possible explanation for the fact that it has not been possible to separate the
Heating rate 17 °C/min

Polyethylene 3mg

Fig. 8.35 Polyethylene - Variation in melting peak with distance from the surface
Fig. 8.36 Polyethylene - Variation in melting peak with distance from the surface

Polyethylene 3 mg

Heating rate 17 °C/min
Fig. 8.37 Polyethylene - Influence of thermal conditioning on melting peak temperature

Exposure temperature:
- 124.7 °C
- 125.9 °C
- 126.7 °C
- 127.4 °C
peaks is that the experiments were done at normal pressure and not the elevated pressure in the cavity, which is of the order of 500 bar.

Generally, crystallization following homogeneous nucleation with high cooling takes place very rapidly. Holden states that on the basis of calculations from published data, the latent heat released by the adiabatic crystallization of supercooled polyethylene is sufficient to heat the sample 50 - 80 °C. Thus, experiments carried out by quenching or under nominally isothermal conditions with large supercooling will produce crystallites in a very rapidly rising local temperature environment. Also, at demoulding the centre of the moulding is likely to be hotter than the surface. At demoulding the heat sink represented by the mould is removed, the heat flux decreases and, hence, the temperature gradient through thickness. This will also cause an increase in surface temperature, although remelting may also occur. (With polypropylene mouldings moulded at $T_m = 240$ °C and $T_f = 40$ °C, the rise in temperature at the surface after ejection was measured to approximately 8 °C by stacking the mouldings directly after demoulding and using a flat, fast responding, thermocouple connected to a recorder).

Based on the results and the above discussion it is reasonable to conclude that shear is not the primary factor for creating the structures which cause a double peak in the melting curves. Rather, the peak is characteristic of the sample. When it is observable at the position in question it is brought about by the occurrence of two types of crystallization processes, where the low temperature peak is the result of a fast cooling from the melt and that the high temperature peak is the result of a slow cooling, in part caused by annealing from the latent heat of crystallization from the last injected melt.

The results show the strong influence of thermal history on the crystalline morphology.

+) Kanig found, that 2nd generation thin lamallae (t ~ 25 nm, melting point 124,6 °C) develop between the original lamallae (t ~ 70 nm, melting point 133,0 °C) when high density polyethylene samples are rapidly cooled from 130 °C. It was also shown that the thickness of the lamellae as well as the thickness of the interzonal (amorphous) regions increased in size after annealing. (Ref: G. Kanig; Neue Elektronennikroskopische Untersuchungen, Vortrag an der ETH, Zürich, 31 mai 1979)
Polypropylene

Heating curves for polypropylene as a function of distance from the surface, are shown in Fig. 8.38. Compared with polyethylene, the curves show a higher variation in peak temperature, and that melting occurs over a much broader temperature interval, corresponding to a broader distribution of crystallites. *)

The mean peak value for the 10 curves was determined to 164,2 ± 2,5 °C. The average degree of crystallinity was 40,0 ± 4,2% (Based on $\Delta H_\text{m} = 209.3$ kJ/kg).

Polyoxymethylene

Heating curves for polyoxymethylene (Hostaform C 9021 R) as a function of distance from the surface, are shown in Fig. 8.39. The peak temperature as a function of distance from the surface, is plotted in Fig. 8.40, where each determination is an average of three samples. Both graphs show the familiar dependence, i.e. the higher the crystallization temperature the higher the melting temperature.

The mean peak value for the 3 x 10 curves was found to 163,3 ± 2,0 °C. The average degree of crystallinity was found

*) The variation in texture and crystallinity between samples taken at the center (I) and periphery (II) of a polypropylene quadrant (PP 05.12) was investigated by X-ray diffraction, as described with polyethylene. Each sample was examined at the skin (a) and core (b). The samples had the surface parallel to the surface of the quadrant. The results showed that all diagrams were different with respect to relative intensities. Generally, a bigger difference was found between center and periphery than between skin and core. Texture also varied between the samples. However, all samples showed that the crystallographic [010] direction (perpendicular to the plane with the d-value 5.31 Å) had a trend to orientation perpendicular to the radius of the quadrant with the strongest reflexion at $d = 5.31$ Å in all samples.

An informative determination of the X-ray crystallinity, which should be interpreted with care due to the texture, gave the following results with intersection at 10° and 27° at the 2θ axis Ia:62%, Ib:62%, IIA: 53%, IIB:51%.

The author acknowledges the assistance by Messrs. Leffers and Toft Sørensen.
Fig. 8.38 Polypropylene - Melting curves as a function of distance from the surface (PP 05.12)
Fig. 8.39 Polyoxymethylene - Melting curves as a function of distance from the surface (POM 10.1)
Fig. 8.40 Poyloxymethylene - Equilibrium melting temperature as a function of distance from the surface, average of three determinations (POM 10.1)
to 44 ± 10.5% (based on ΔH_\text{fus} = 175.8 kJ/kg). The large deviation in the degree of crystallinity arises from the difference in crystallinity between the surface (31%) and the core (55%).

Wilski\textsuperscript{259} measured the specific volumes of various commercial polyoxymethylene types (Homopolymers "Delrin" and co-polymers "Hostaform"). By calculating the crystalline fraction from the specific volumes of the amorphous phases a crystallinity in the range 56 - 59% was obtained for "Hostaform" specimens slowly crystallized from the melt. These figures correspond approximately to the crystallinity found in the core.

For the slower crystallizing polyoxymethylene (Hostaform C 9010), which was moulded in the shape of a 4.2 mm thick tensile bar, melting temperature as a function of distance from the surface is shown in Fig. 8.41 for four different mould temperatures. Contrary to the former polymer, the melting temperature decreases with distance from the surface. Also, the peak value (and crystallinity) was less dependent on the distance from the surface. This may be understood partly as a consequence of the flow situation in the much longer cavity and partly as an effect of the lower heterogeneous nucleation. Other investigations\textsuperscript{260} showed melting enthalpy (in a range of 110 - 130 J/g) to be independent of wall thickness and mould temperature for a "Hostaform" C 27 021 with enhanced flow properties. However, only wall thicknesses lower than 1 mm were investigated. A melting enthalpy gradient with distance from the gate was not observed\textsuperscript{260}.

With "Hostaform" C 9010, also, the highest crystallinity was found at the surface with the two highest mould temperatures. Annealing increased crystallinity at an average of 24% for the four samples taken at the surface. When these results are compared with the microscopical observations, it appears that the polymer, which showed the highest variation in morphology, (Hostaform C9010) had the lowest average variation in melting temperature and crystallinity.
Fig. 8.41 Polyoxymethylene - Equilibrium melting temperature as a function of distance from the surface.
Polyamide 66

With this polymer the melting temperature was found to 254.1 ± 2°C.

Comparison of the equilibrium melting temperature with the optical melting point.

When the melting point is defined as the temperature at which the last detectible traces of birefringence disappear (Section 6.2.2), a comparison with the equilibrium melting temperature showed a good correlation between the layers taken from the core of polyethylene and polyoxymethylene mouldings. With polypropylene a somewhat higher difference was found and a poorer correlation was obtained with polyamide. However, the melting temperature, when measured with thermal analysis, is in the bulk of the sample and not from the highest melting material, as in hot-stage microscopy.

8.4.3. Summary

Density

From the results the following conclusions can be drawn on the effect of increasing moulding variables.

Density increased with melt temperature for polyethylene and polyoxymethylene, but decreased for polypropylene. Density increased with mould temperature for polypropylene, polyoxymethylene, polyamide 66 and 6. Density decreased with cavity pressure for polypropylene, due to the effect of the slower filling with decreasing pressure.

Thermal analysis

Thermal analysis was applied to investigate the variation in crystallinity across the moulding. Generally, the equilibrium melting temperature showed an increasing trend with increasing distance from the gate.
The double peak found with polyethylene melting curves was investigated. Impressing a variety of thermal histories on the sample in the cell showed that the temperature rise associated with annealing influences the subsequent melting curve. An estimate of the degree of crystallinity was made, and showed that crystallinity increases with distance from the surface. However these results should be interpreted with care because factors, e.g., the contribution in enthalpy from the surface of the crystallites, which is significant with poorly crystallized samples with a low melting enthalpy and small crystallites, was not taken into account.
8.5 ORIENTATION

For the determination of the orientation pattern and magnitude in injection mouldings, various techniques are available. As an example, X-ray diffractometry is commonly used to investigate the orientation of crystal axes in semi-crystalline polymers. In the experiments reported here, the much simpler and correspondingly, less exact technique of measuring recoverable strain was applied. With semi-crystalline polymers, this technique is mainly an indication of recovery in the amorphous or inter-zonal regions, and the interpretation only partially quantitative as long as the complex reorganization taking place during the heat treatment is not taken into account.

Crystallization of semi-crystalline polymers results essentially in a mass of crystallites dispersed in an amorphous matrix. Chain alignment is controlled not only by the orientation stresses but also by the crystallization forces. If an oriented semi-crystalline specimen is heated above the crystalline melting point, relaxation forces become active and the sample recovers. This is an effect of the entropy-elastic forces, which are active as soon as the fixation by the crystalline regions is allowed to elapse. The result is then an integral evidence of orientation across the specimen influenced by the inhibited recovery as well as the relaxation processes.

The integral recovery is, especially with thicker mouldings, only a partial assertion of frozen-in orientations, as different sections may show orientation in different directions. It is even possible that thermally induced reversible changes in different sections are opposing each other.

It is, therefore, of interest to assess the orientation distribution across the specimen, which requires a sectioning of the moulding. Such investigations have been carried out on amorphous as well as semi-crystalline polymers\textsuperscript{148,155}. It is clear,
however, that in the latter case some of the above mentioned influences on the recovery cannot be neglected in the interpretation of the results.

Initially, non-sectioned specimens from an amorphous (Polystyrene) and a semi-crystalline (Polyethylene) polymer were investigated. In the following investigation of the microtomed sections it was assumed that the orientation profile was approximately symmetrical. Specimens were, therefore, only sectioned to the centerline of the moulding.

Reversion of 20 x 20 mm specimens

The 20 x 20 mm polystyrene samples after reversion and the integral coloured fringe patterns (isochromatics - whose order represents the magnitude of the principal stress difference in that plane) as a function of melt temperature are shown in Fig. 8.42. It should be noted for the interpretation of Fig. 8.42, that proportionality between birefringence and orientation only exists for low orientations.

Fig. 8.42 Recoverable strain and birefrigence in polystyrene injection mouldings.
In Fig. 8.42 the general pattern of birefringence is mainly an effect of entropy-elastic strains, as it may be assumed that the contribution from energy-elasticity amounts to less than 10% of the birefringence. It is clear from Fig. 8.42 that orientation decreases with increasing melt temperature. It can also be seen that a high orientation is found in the gate area. The contour of the 20 x 20 mm polyethylene samples after reversion is shown in Fig. 8.43. Reversion against melt temperature is plotted in Fig. 8.44 for polystyrene and Fig. 8.45 for polyethylene.

The results show that reversion for polystyrene is much higher than for polyethylene. The variation for 5 samples is also depicted and indicates a much better reproducibility with amorphous materials. The revised and compensated reversion (Fig. 8.44 and 8.45, b) show, especially for the extreme processing conditions, that the influence from the bi-axial orientation cannot be dispensed with, affirming the relevance of compensating this influence.

Fig. 8.44 shows that higher melt temperatures result in lower longitudinal and transverse orientation at the surface for polystyrene. This can be understood in terms of a decrease in relaxation time with temperature. With polyethylene, longitudinal orientation first increases and then decreases with increasing melt temperature. Transverse orientation at the surface is also less pronounced than with polystyrene (Fig. 8.45).

Orientation in the middle of the specimen is largely unaffected by melt temperatures above 210°C and is considerably lower than at the surface for polystyrene. This can be explained by the poor heat transport properties of polystyrene. One expects that the temperature in the interior of the sample will be greater than Tg for amorphous polymers and Tc for crystalline polymers for a relatively longer time, irrespective
Fig. 8.43 Polyethylene - Contour of 20 x 20 mm specimens after reversion as a function of melt temperature.
Fig. 8.44 Polystyrene - Reversion of 20 x 20 mm samples as a function of melt temperature
Fig. 8.45 Polyethylene - Reversion of 20 x 20 mm samples as a function of melt temperature
of the melt temperature. This will lead to considerable relaxations and small orientations at all melt temperatures. Thus, the orientation in the interior of the sample will generally be less than that at the surface. The comparatively higher orientations with polyethylene are then presumably determined, mainly by the crystallization forces in the interior of the sample after the shear stresses have dropped to zero.

Transverse orientations are much smaller than longitudinal orientations, because the transverse ones can only occur during secondary flow in the cavity while the longitudinal ones can occur both during flow through the sprue and runner system and during secondary flow in the cavity (see also Fig. 8.10, Section 8.3.2). Some transverse orientations may also be developed through the build-up of normal stresses during primary flow through the sprue and runner system.

In conclusion, it should also be mentioned that a statistically designed experiment (Appendix A B) showed that longitudinal orientation was very highly significantly influenced by melt and mould temperature and significantly influenced by cavity pressure. Transverse orientation was very highly significantly influenced by melt temperature and significantly influenced by mould temperature and cavity pressure. No influence was found from screw forward velocity.

Reversion of microtomed sections

In this section an attempt has been made to analyze the effect of various injection moulding processing parameters on the orientation profile of polyethylene mouldings. From each specimen 50 6 x 6 x 0.03 mm sections were cut (Fig. 6.13). On one moulding the orientation profile was also investigated as a function of distance from the gate (Fig. 8.46)
Fig. 8.46 Principle of determination of orientation profile

Fig. 8.47 shows the longitudinal orientation profile as a function of distance from the gate and surface. The graph shows that the level of orientation decreases with increasing distance from the gate. This is presumably due to the fact that the primary orientation from the passage of the sprue relaxes during flow in the cavity at a faster rate than when new orientations are introduced from cavity flow. Transverse orientations (which are not shown in the graph) are approximately constant at a larger distance from the gate, while longitudinal orientation decreases.

The position of maximum orientation moved away from the interior of the moulding with increasing distance from the gate, an effect arising from two different processes. When the hot melt contacts the much colder cavity wall, a wedge-shaped layer is formed from solidified melt, and this increases in thickness.
Fig. 8.47 Polyethylene - Longitudinal orientation of 6 x 6 x 0.03 mm samples as a function of distance from the gate and surface (PE 03.1)
from the end of the cavity towards the gate. As the solidifying front is moving from the periphery of the moulding towards the gate, this region is also exposed for a longer time to the shear, which causes a higher absolute orientation. Secondly, due to the quadrant shape of the moulding, elongational flow increases with flow length causing an increasing biaxial orientation (Fig. 8.48).

Also, in some profiles, which are not shown in the graph, a negative orientation was observed, which may be interpreted as an orientation perpendicular to the plane.

Fig. 8.48 Texture, as determined with X-ray diffractometry in a 1 mm polyethylene moulding262
(The arrows indicate the average orientation of the polyethylene crystallographic axes. At the gate, preferred crystal orientation with extension of chains (c-axis) in the direction of flow was observed. The middle of the quadrant dominates a biaxial orientation of the c- and b-axes, due to the transverse flow of the melt)
The average reversion of microtomed sections, taken from the center of the moulding was investigated in an experimental design with variations of cavity pressure, melt temperature, mould temperature and screw-forward-velocity (Table 8.11). The statistical analysis showed, however, that none of the parameters had a significant influence on the average orientation.

It may be argued that, since orientation exist as a gradient, a particular moulded part cannot be said to be oriented x amount or cannot be more oriented than another. A given value cannot describe the orientation of a moulded part. This complexity has a special significance when one tries to relate moulding conditions, orientation, and part quality. There were, however, distinct differences between most of the orientation profiles. With the experimental design, where two variables were varied simultaneously, it is difficult to assess which variable causes the differences. Therefore, only a few typical examples from observation of the 27 curves are shown in Fig. 8.49. (To smooth out irregularities in the curves it was initially tried to calculate a moving average for the 50 data sets.)

a) A low cavity pressure and a low mould temperature tend to give a high orientation at the surface and less orientation in the interior.

b) A high cavity pressure, a low mould temperature, and a high melt temperature tend to create an orientation profile with several maxima.

c) A medium pressure with a high mould and melt temperature tend to give an orientation profile with no distinct maxima.

Summary

Determination of the orientation pattern and magnitude is important in order to explain anisotropy in injection mouldings. However, the results have shown that there is no easy way to establish the relationship between injection moulding variables and molecular orientation in semi-crystalline polymers.
Table 8.11 Average reversion of microtomed sections parallel ($R_p$) and transverse to flow ($R_t$) by variation of cavity pressure, melt temperature, mould temperature and screw forward velocity.

<table>
<thead>
<tr>
<th>Mould temperature ($^\circ$C)</th>
<th>Melt temperature ($^\circ$C)</th>
<th>Melt temperature ($^\circ$C)</th>
<th>Melt temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0) = 30</td>
<td>(1) = 50</td>
<td>(2) = 70</td>
</tr>
<tr>
<td></td>
<td>(0)=170</td>
<td>(1)=220</td>
<td>(2)=270</td>
</tr>
<tr>
<td>Cavity pressure (bar)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0) = 30</td>
<td>(1) = 50</td>
<td>(2) = 70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0002</td>
<td>0101</td>
<td>0200</td>
</tr>
<tr>
<td></td>
<td>0,85</td>
<td>0,79</td>
<td>0,76</td>
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<td>1,03</td>
<td>0,97</td>
<td>0,95</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1102</td>
<td>1201</td>
</tr>
<tr>
<td></td>
<td>0,84</td>
<td>0,82</td>
<td>0,78</td>
</tr>
<tr>
<td></td>
<td>1,01</td>
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<td>2100</td>
<td>2202</td>
</tr>
<tr>
<td></td>
<td>0,88</td>
<td>0,80</td>
<td>0,76</td>
</tr>
<tr>
<td></td>
<td>1,02</td>
<td>0,96</td>
<td>0,96</td>
</tr>
</tbody>
</table>
Fig. 8.49 Polyethylene - Orientation profiles across 3 mm mouldings.
With the technique used, it must be assumed that recovery measurements are primarily representative for orientations in the amorphous regions. The details of the forces which are active between the oriented crystallites are only partially qualitatively understood. They are known, however, to influence recovery from thermally induced changes in the structure.

The results obtained show that orientations generally decrease with increasing melt temperature and, to a lesser extent, with increasing mould temperature and cavity pressure. The maximum orientation along the flow length was presumed to correlate with the thickness of the solidified layer, which is decreasing with increasing flow length.

It should be noted that the orientation profiles will be dependent on wall thickness, which was not varied in these experiments.
8.6. MECHANICAL PROPERTIES

8.6.1. Tensile strength

Polyethylene

Tensile strength for the three sets of specimens as a function of melt temperature is shown in Fig. 8.50. The graph shows that the tensile strength parallel to flow decreases when the melt temperature increases. Tensile strength transverse to flow is more or less constant with increasing melt temperature, but with a difference in the slope of two curves, as an increasing melt temperature gives a slightly decreasing tensile strength opposite the gate. A higher melt temperature also decreases anisotropy, defined as the ratio of tensile strength transverse to flow to tensile strength parallel to flow. The average standard deviation ($\bar{S}$) parallel to flow was 2.6 MN/m$^2$. Transverse to flow 0.6 and 0.4 MN/m$^2$, respectively ($n=5$).

Modulus of elasticity was taken at the linear section of the stress-strain diagram.

Polypropylene

Tensile stress at yield, tensile strength, elongation and modulus of elasticity as a function of cavity pressure, melt temperature and cavity wall temperature are shown in Table 8.12 to 8.15.

The influence from the processing variables was analyzed with a three-sided analysis of variance. As tensile strength and modulus of elasticity showed no two- or three factor interaction, a pooled estimate of variance ($s_m^2$) with the degrees of freedom ($f_m^2$) was used for the variance ($\sigma^2$) 248.

The average standard deviations on the determinations were: tensile yield stress 0.26 MPa, tensile strength 0.42 MPa, elongation 20 % of the individual values, and modulus of elasticity 88 MPa ($n=5$).
Fig. 8.50 Polyethylene - Effect of melt temperature on properties (PE 03.1)
Table 8.12 Tensile yield stress (MPa) parallel and transverse to flow of polypropylene quadrants by variation of cavity pressure, melt temperature and mould temperature.

<table>
<thead>
<tr>
<th>Cavity pressure (bar)</th>
<th>Mould temperature (°C)</th>
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<th>550</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mould temperature (°C)</td>
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<td>40</td>
</tr>
<tr>
<td>Melt temperature (°C)</td>
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<td></td>
</tr>
<tr>
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<td>pos a 29,2</td>
<td>28,9</td>
<td>27,9</td>
</tr>
<tr>
<td></td>
<td>pos b -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>pos c 19,4</td>
<td>19,7</td>
<td>20,8</td>
</tr>
<tr>
<td>240</td>
<td>pos a 24,6</td>
<td>25,1</td>
<td>24,8</td>
</tr>
<tr>
<td></td>
<td>pos b 18,9</td>
<td>18,9</td>
<td>19,6</td>
</tr>
<tr>
<td></td>
<td>pos c 18,4</td>
<td>18,6</td>
<td>19,2</td>
</tr>
<tr>
<td>290</td>
<td>pos a 18,5</td>
<td>18,7</td>
<td>19,1</td>
</tr>
<tr>
<td></td>
<td>pos b 17,2</td>
<td>17,8</td>
<td>17,7</td>
</tr>
<tr>
<td></td>
<td>pos c 17,8</td>
<td>17,7</td>
<td>18,2</td>
</tr>
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</table>
Tab. 8.13 Tensile strength (MPa) parallel and transverse to flow of polypropylene quadrants by variation of cavity pressure, melt temperature and mould temperature

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>20</th>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td>550</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>41,9</td>
<td>43,5</td>
<td>42,1</td>
<td></td>
<td>41,5</td>
<td>41,2</td>
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<td>42,8</td>
</tr>
<tr>
<td>pos b 39,9</td>
<td>40,2</td>
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<td></td>
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<td>40,5</td>
</tr>
<tr>
<td>pos c 36,3</td>
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<td>36,9</td>
<td>36,2</td>
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<td>pos a 37,6</td>
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<td>37,7</td>
<td>37,7</td>
<td>38,0</td>
<td>40,3</td>
<td></td>
</tr>
<tr>
<td>pos b 38,8</td>
<td>36,1</td>
<td>37,6</td>
<td>39,7</td>
<td>36,4</td>
<td>36,7</td>
<td>36,5</td>
<td>40,0</td>
<td></td>
</tr>
<tr>
<td>pos c 34,7</td>
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<td>35,7</td>
<td>37,5</td>
<td>32,8</td>
<td>33,4</td>
<td>35,0</td>
<td>38,1</td>
<td></td>
</tr>
<tr>
<td>pos a 33,7</td>
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<td>35,8</td>
<td>36,1</td>
<td>33,5</td>
<td>35,3</td>
<td>34,6</td>
<td>37,0</td>
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<tr>
<td>pos b 33,0</td>
<td>34,5</td>
<td>35,7</td>
<td>36,7</td>
<td>33,2</td>
<td>36,2</td>
<td>34,7</td>
<td>36,5</td>
<td></td>
</tr>
<tr>
<td>pos c 33,8</td>
<td>34,0</td>
<td>35,0</td>
<td>36,5</td>
<td>32,3</td>
<td>36,1</td>
<td>34,1</td>
<td>36,7</td>
<td></td>
</tr>
</tbody>
</table>
Tab. 8.14 Unit elongation of 20 mm (%) parallel and transverse to flow of polypropylene quadrants by variation of cavity pressure, melt temperature and mould temperature.

<table>
<thead>
<tr>
<th>Cavity pressure (bar)</th>
<th>200 Mould temperature (°C)</th>
<th>550 Mould temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt temperature (°C)</td>
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<td>20 40 60 80</td>
</tr>
<tr>
<td>190</td>
<td>pos a 75 77 57 50</td>
<td>pos a 78 63 53 50</td>
</tr>
<tr>
<td></td>
<td>pos b 21 22 20 26</td>
<td>pos b 28 46 50 30</td>
</tr>
<tr>
<td></td>
<td>pos c 363 210 190 55</td>
<td>pos c 728 407 262 78</td>
</tr>
<tr>
<td>240</td>
<td>pos a 542 480 390 177</td>
<td>pos a 472 490 535 222</td>
</tr>
<tr>
<td></td>
<td>pos b 125 412 88 25</td>
<td>pos b 368 537 317 63</td>
</tr>
<tr>
<td></td>
<td>pos c 427 723 382 267</td>
<td>pos c 842 788 463 273</td>
</tr>
<tr>
<td>290</td>
<td>pos a 530 523 340 55</td>
<td>pos a 567 592 447 77</td>
</tr>
<tr>
<td></td>
<td>pos b 495 397 147 45</td>
<td>pos b 535 278 298 155</td>
</tr>
<tr>
<td></td>
<td>pos c 455 387 260 90</td>
<td>pos c 477 333 388 110</td>
</tr>
</tbody>
</table>
Tab. 8.15  Modulus of elasticity (MPa) parallel and transverse to flow of polypropylene quadrants by variation of cavity pressure, melt temperature and mould temperature

<table>
<thead>
<tr>
<th>Cavity pressure (bar)</th>
<th>Mould temperature (°C)</th>
<th>Mould temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Melt temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>pos a 606</td>
<td>868</td>
</tr>
<tr>
<td></td>
<td>pos b 562</td>
<td>610</td>
</tr>
<tr>
<td></td>
<td>pos c 644</td>
<td>510</td>
</tr>
<tr>
<td>240</td>
<td>pos a 551</td>
<td>723</td>
</tr>
<tr>
<td></td>
<td>pos b 513</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>pos c 479</td>
<td>590</td>
</tr>
<tr>
<td>299</td>
<td>pos a 532</td>
<td>528</td>
</tr>
<tr>
<td></td>
<td>pos b 551</td>
<td>864</td>
</tr>
<tr>
<td></td>
<td>pos c 593</td>
<td>543</td>
</tr>
</tbody>
</table>
The analysis showed that melt temperature had a very highly significant influence (see foot-note, p.294) on tensile strength at all three positions. Mould temperature had a highly significant influence on specimens taken parallel to flow (a) and transverse to flow close to the gate (b), and a very highly significant influence far from the gate (c). No influence was found from cavity pressure.

Melt temperature had a highly significant influence on modulus of elasticity parallel to flow, whereas no influence was found at the other positions or with the two other variables. Melt and mould temperature showed a very highly and a highly significant interaction on unit elongation parallel to flow (a) and transverse to flow, close to the gate (b), respectively. Cavity pressure had no influence parallel to flow, whereas, some influence was found transverse to flow at the gate (b). (Probability level could not be tested due to the two-factor interaction). No two or three factor interaction was found transverse to flow opposite the gate, where melt- and mould temperature was found to have a highly significant influence on unit elongation.

An increasing melt temperature decreases tensile stress at yield, tensile strength, and modulus of elasticity. Isotropy between pos. b and c improves with melt temperature. With increasing melt temperature, tensile strength decreases (and falling weight impact) with increasing unit elongation. The decrease in tensile strength and modulus with melt temperature and the increase with mould temperature are often related to decreased skin thickness and, therefore, decreased orientation at high temperatures. However, it is also important to consider the influence of crystal perfection. Increasing the mould temperature has little effect on orientation but improves crystal perfection throughout the sample which, in turn, improves tensile strength and modulus.

The interaction between melt and mould temperature (at position a and b) caused a substantial elongation at low mould
temperatures but a less pronounced influence with a high mould temperature, where the molecules presumably have a longer time for relaxation. This also explains that no interaction was found opposite the gate. The increase of unit elongation with cavity pressure is an effect of shear stress in the melt, which increases with pressure. It can be expected that specimens moulded at high pressures will, in principle, contain a larger amount of oriented lamellae (extended chain structures), which may result in an increase in the elongation to rupture. Also, transverse orientation can occur only during secondary flow in the cavity. Specimens taken close to the gate are exposed for a longer time to the shear, which cause a higher absolute orientation than opposite the gate.

An increasing mould temperature causes a decreasing yield stress parallel to flow, but an increasing yield stress transverse to flow, hence isotropy improves with increasing mould temperature. Tensile strength increases on all positions with increasing mould temperature, presumably due to the higher density. Strength increases not only with tie-molecules but also with inter-molecular forces.

Modulus of elasticity decreases with increasing melt temperature. A (not significant) increase with increasing mould temperature was observed. Transverse to flow the modulus of elasticity increases at the lowest cavity pressure, whereas the modulus of elasticity showed a slightly decreasing trend with increasing mould temperature at the highest cavity pressure. However, those influences were not significant.

It is perhaps surprising that cavity pressure did not have a significant influence on the tested properties as pressure and rate of filling were related in these experiments. Generally, one would expect a faster filling to increase the time for relaxation and, hence, increase isotropy.
Polyoxymethylene

Tensile strength, elongation and modulus of elasticity as a function of cavity wall temperature is shown in Table 8.16. The mechanical properties were also determined parallel to flow on mouldings annealed at 140 °C/30 min.

Tensile strength and modulus of elasticity are only influenced a little by the cavity wall temperature, and very little anisotropy was found.

Annealing improves tensile strength and modulus of elasticity for all mould temperatures. The average standard deviation on the determinations were: Tensile strength 1.0 MPa, elongation 0.06, and modulus of elasticity 45 MPa.

8.6.2. Tensile impact strength

Polyethylene

Tensile impact strength for the three sets of specimens, as a function of melt temperature, is shown in Fig. 8.51. Tensile impact strength parallel and transverse to flow (Pos. c) as a function of cavity wall temperature and screw forward velocity, is shown in Table 8.17.

The results (Fig. 8.51) show that tensile impact strength parallel to flow first decreases drastically with melt temperature and then increases. Tensile impact strength transverse to flow increases slightly with melt temperature and then decreases from a melt temperature of approximately 220 °C. A high tensile impact strength parallel to flow corresponds to a low value transverse to flow. The two curves for tensile impact strength transverse to flow show a more uniform slope than the curves for tensile strength. Elongation at break (not shown in the graph) decreases to a melt temperature of 196 °C and then increases. Except for the lowest temperature at the position near the gate, elongation at break transverse to flow decreases with increasing melt temperature. A low value near the gate and transverse to flow corresponds to a high value parallel to flow and vice versa. The average standard
Tab. 8.16 Tensile strength (MPa), unit elongation of 20 mm (%) and modulus of elasticity (MPa) parallel and transverse to flow of polyoxymethylene quadrants by variation of mould temperature.

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
<th>Mould temperature (°C)</th>
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<th>80</th>
<th>100</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tensile strength</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pos.a</td>
<td>64,8</td>
<td>66,5</td>
<td>65,8</td>
<td>66,1</td>
<td></td>
</tr>
<tr>
<td>Pos.b</td>
<td>63,9</td>
<td>66,6</td>
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<td>64,4</td>
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</tr>
<tr>
<td>Pos.c</td>
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<td>66,8</td>
<td>67,1</td>
<td>65,0</td>
<td></td>
</tr>
<tr>
<td>Pos.a,ann. 140°C/30 min</td>
<td>71,6</td>
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<td>71,2</td>
<td></td>
</tr>
<tr>
<td><strong>Unit elongation</strong></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pos.a</td>
<td>0,52</td>
<td>0,46</td>
<td>0,40</td>
<td>0,45</td>
<td></td>
</tr>
<tr>
<td>Pos.b</td>
<td>0,28</td>
<td>0,37</td>
<td>0,25</td>
<td>0,32</td>
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<tr>
<td>Pos.c</td>
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<td>0,37</td>
<td>0,45</td>
<td></td>
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<tr>
<td>Pos.a,ann. 140°C/30 min</td>
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<td>0,57</td>
<td>0,43</td>
<td>0,53</td>
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<td>Pos.a</td>
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<td>1542</td>
<td>1534</td>
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<tr>
<td>Pos.b</td>
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<td>1600</td>
<td>1546</td>
<td>1533</td>
<td></td>
</tr>
<tr>
<td>Pos.a,ann. 140°C/30 min</td>
<td>1695</td>
<td>1707</td>
<td>1767</td>
<td>1742</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 8.51 Polyethylene - Effect of melt temperature on tensile-impact strength
Table 8.17 Tensile-impact strength (kJ/m²) parallel and transverse to flow of polyethylene quadrants by variation of cavity pressure, melt temperature, mould temperature and screw-forward-velocity

<table>
<thead>
<tr>
<th>Mould temperature (°C)</th>
<th>Melt temperature (°C) (0)=170</th>
<th>Melt temperature (°C) (1)=220</th>
<th>Melt temperature (°C) (2)=270</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0)=30</td>
<td>0002 0101 0200</td>
<td>0011 0110 0212</td>
<td>0020 0122 0221</td>
</tr>
<tr>
<td>(1)=50</td>
<td>313 327 285</td>
<td>310 268 280</td>
<td>250 252 243</td>
</tr>
<tr>
<td>(2)=70</td>
<td>259 261 243</td>
<td>247 242 232</td>
<td>230 235 226</td>
</tr>
<tr>
<td>(0)=200</td>
<td>1000 1102 1201</td>
<td>1012 1111 1210</td>
<td>1021 1120 1222</td>
</tr>
<tr>
<td>(1)=350</td>
<td>300 308 303</td>
<td>304 278 278</td>
<td>254 246 263</td>
</tr>
<tr>
<td>(2)=500</td>
<td>239 248 250</td>
<td>253 243 237</td>
<td>227 236 218</td>
</tr>
<tr>
<td>(0)=500</td>
<td>2001 2100 2202</td>
<td>2010 2112 2211</td>
<td>2022 2121 2220</td>
</tr>
<tr>
<td>(1)=750</td>
<td>290 323 309</td>
<td>306 283 282</td>
<td>245 259 263</td>
</tr>
<tr>
<td>(2)=1000</td>
<td>239 257 250</td>
<td>248 252 244</td>
<td>232 245 229</td>
</tr>
</tbody>
</table>

Legend: see Table 8.2
deviation for tensile impact strength was 3.3 kJ/m² parallel to flow, and 2.6 and 5.9 kJ/m² for position b and c, respectively. Elongation, 5.0, 3.9, and 4.1 for position a, b, and c, respectively (n=10).

In the statistically designed experiment (Table 8.17) it was found that cavity wall temperature had a very highly significant influence on tensile impact strength parallel and transverse to flow. Melt temperature had a significant influence on tensile impact strength transverse to flow.

Notched tensile impact strength

The notched tensile impact strength for polyethylene parallel to flow increased with increasing melt temperature, but with a slight decrease at the highest melt temperature. (Fig. 8.50).

Falling weight impact

Polyethylene

Falling weight impact strength increased with increasing melt temperature (Fig. 8.50). A marked difference in the level of energy causing fracture was found when the drop height was changed from 610 to 2000 mm, and the weight changed accordingly. The fracture pattern did not show orientation cracks, but only a crack along the edge of the indentation mark, indicating that the failure by impact could be considered a material failure not dependent on orientation. The cracks along the indentation were for all specimens, except those moulded at 196 °C, in the flow direction. For articles moulded at 196 °C the cracks were transverse to flow. It seems that these specimens have abnormalities creating a fracture transverse to flow and, hence, indicating a "structural anisotropy", depending on melt temperature. The results support the observation from tensile impact strength, which was very low parallel to flow and high transverse to flow for specimens moulded at 196 °C.
Polypropylene

Falling weight impact strength for polypropylene was measured using the instrumented test equipment described in Section 5.4. The results of the test are shown in Table 8.18. A typical set of traces for one set of mouldings is shown in Fig. 8.53.

The results were analyzed with a three-sided analysis of variance and showed a highly significant influence on the impact strength from melt temperature. No influence, or logical trend was found with cavity pressure and mould temperature.

All force-deflection graphs showed a step-wise progress of the trace. This was attributed to an initial overshoot - or oscillation - effected by the relatively rigid design of the set-up. A premature damage of the moulding did not seem to cause the stepped trace.

With polypropylene, where the influence from melt temperature was opposite that found with polyethylene, cracks were generally transverse to flow (Fig. 8.52), indicating the biaxial orientation of the melt.

Fig. 8.52 Polyethylene - Crack propagation in quadrant

The decrease in impact strength with melt temperature may be explained by a decreasing orientation with higher melt temperatures.
Table 8.18: Absorbed energy (J) after 5 ms influence from force for 3 mm polypropylene quadrant mouldings by variation of cavity pressure melt temperature and mould temperature.

<table>
<thead>
<tr>
<th>Melt temperature (°C)</th>
<th>200 Mould temperature (°C)</th>
<th>200</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>500 Mould temperature (°C)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>2.15</td>
<td>2.11</td>
<td>2.19</td>
<td>2.19</td>
<td>2.16</td>
<td>1.84</td>
<td>2.04</td>
<td>2.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>2.18</td>
<td>1.90</td>
<td>2.10</td>
<td>2.18</td>
<td>2.17</td>
<td>2.19</td>
<td>2.18</td>
<td>2.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>290</td>
<td>1.70</td>
<td>1.86</td>
<td>1.92</td>
<td>1.66</td>
<td>2.00</td>
<td>2.01</td>
<td>1.88</td>
<td>1.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 8.53 Polypropylene - Reproducibility of falling weight impact test (n=5)
This assumption was further investigated using samples moulded at two different melt and mould temperatures, 190 - 240 °C and 20 - 40 °C, respectively, and with an extremely fast injection of 250 mm/s as screw forward velocity by using an accumulator. The results clearly showed a decreasing falling weight impact strength with faster injection. As for example, impact energy decreased from 2,18 to 1,95 J at a melt/mould temperature of 240/40 °C, although the wall thickness increased from 3,06 to 3,13 mm due to increased mould separation during injection. However, other factors should also be taken into account, as the fast injection presumably caused additional movements of the melt in the core and hence increased internal stresses.

8.6.3 Flexural modulus

Polyethylene

The flexural modulus transverse to flow showed a high value with a low melt temperature. With increasing melt temperature the modulus first increases and then decreases to a lower value at the highest melt temperature (Fig.8.50). The average standard deviation was 69 MPa.

Polypropylene

The flexural modulus parallel to flow is strongly dependent on melt temperature (Fig.8.54). An increasing melt temperature decreases the flexural modulus due to less orientation at the higher melt temperature. Cavity pressure has only little influence. At the highest melt temperature the flexural modulus increases with increasing mould temperature. The average standard deviation was 57 MPa.

Polyamide

The flexural modulus parallel to flow was determined on 3 mm specimens before and after being conditioned at 60 °C/24 h. The results are shown in the following Table 8.19
Fig. 8.54 Polypropylene - Effect of processing variables on flexural modulus
Table 8.19 Flexural modulus of polyamide (MPa) by variation of mould temperature

<table>
<thead>
<tr>
<th></th>
<th>Mould temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Dry samples</td>
<td>2624</td>
</tr>
<tr>
<td>Conditioned</td>
<td>631</td>
</tr>
</tbody>
</table>

The results show that the flexural modulus increases with mould temperature. The flexural modulus decreases to about a fourth of the original value for the conditioned samples, due to the plasticizing effect of the absorbed moisture. The average standard deviation was 70 MPa and 16 MPa for the dry and the conditioned samples, respectively.

8.6.4. Knoop hardness

Knoop hardness for polyethylene mouldings by variation of cavity pressure, melt temperature, mould temperature and screw forward velocity is shown in Table 8.20. Knoop hardness as a function of distance from the gate is shown in Fig. 8.50. It was found that Knoop hardness parallel and transverse to flow was very highly significantly influenced by mould temperature and increased with increasing mould temperature, a consequence of increased crystallinity in the surface layer of the moulding. Knoop hardness transverse to flow was highly significantly influenced by melt temperature and increased with increasing melt temperature.

Knoop hardness parallel to flow was higher than transverse to flow indicating a higher surface orientation in the direction of flow. Surface hardness varied only a little in relation to the distance from the gate. The highest hardness was found close to the gate. Anisotropy decreased with increasing melt temperature, but increased with increasing mould temperature.
Table 8.20  Knoop-hardness (N/mm\(^2\)) parallel and transverse to flow of polyethylene quadrants by variation of cavity pressure, melt temperature, mould temperature and screw forward velocity.

<table>
<thead>
<tr>
<th>Cavity pressure (bar)</th>
<th>Mould temperature (°C)</th>
<th>Melt temperature (°C)</th>
<th>Melt temperature (°C)</th>
<th>Melt temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0) = 30</td>
<td>(1) = 50</td>
<td>(2) = 70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0) =170</td>
<td>(1) =220</td>
<td>(2) =270</td>
<td>(0) =170</td>
</tr>
<tr>
<td></td>
<td>(0) =100</td>
<td>(1) =165</td>
<td>(2) =200</td>
<td>(0) =100</td>
</tr>
<tr>
<td></td>
<td>0002</td>
<td>0101</td>
<td>0200</td>
<td>0011</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>653</td>
<td>662</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>1260</td>
<td>607</td>
<td>633</td>
<td>625</td>
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<tr>
<td></td>
<td>1300</td>
<td>655</td>
<td>659</td>
<td>652</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>600</td>
<td>606</td>
<td>592</td>
</tr>
<tr>
<td></td>
<td>2001</td>
<td>2100</td>
<td>2202</td>
<td>2010</td>
</tr>
<tr>
<td></td>
<td>658</td>
<td>699</td>
<td>656</td>
<td>629</td>
</tr>
<tr>
<td></td>
<td>614</td>
<td>623</td>
<td>628</td>
<td>618</td>
</tr>
<tr>
<td></td>
<td>2022</td>
<td>2121</td>
<td>2220</td>
<td>2022</td>
</tr>
</tbody>
</table>
8.6.5 Summary

Polyethylene

The results show that there is no unique relation between a change of barrel temperature and the mechanical properties determined in this experiment. As an example, a change in barrel temperature does not cause the same trend for properties, e.g. tensile strength, determined at two separate positions on the moulding.

It is assumed that this difference is a consequence of a change in the filling of the mould with a change in melt temperature. Therefore, with complex flow situations, which are known to exist in the quadrant moulding due to its biaxial flow pattern, properties determined at one position are not sufficient for an unambiguous characterization of the relation between process variables and mechanical properties. As the quadrant is representative for several mouldings with this pattern of filling, the results point to an essential problem in the testing of such articles.

The more general trend of the results confirm that the ductility for high density polyethylene increases with an increasing melt temperature, as can be seen from notched impact and tensile impact strength parallel to flow. It could be expected that a decreasing orientation would cause a decreasing notched impact strength, but it is assumed that other factors than orientation influence the results. It is possible that the non-oriented molecules in the amorphous phase are more entangled at the higher melt temperature and, therefore, absorb more of the impact energy.

The flexural modulus shows some agreement with orientation. It is to be expected that a high degree of orientation along the specimen and a proportionately low degree transverse to flow will give a high value for the modulus, as can be seen at the lowest melt temperature. However, the orientation profile across the specimen as well as the degree of crystallinity and its variation will also influence the results.
A high value for the flexural modulus is obtained at the melt temperature which gives the highest degree of crystallinity, notched impact strength, and falling weight impact strength, but these relations correlate poorly at other melt temperatures. As explained above, the filling pattern of the mould probably changes with the melt temperature, which explains the (presumed) high orientation transverse to flow at a melt temperature between 196 and 220 °C.

The low degree of orientation parallel to flow at a melt temperature between 196 and 220 °C may explain the drop in tensile impact strength parallel to flow and the observation that the fracture lines for falling weight impact at this melt temperature run transverse to flow.

**Polypropylene**

Characteristic of the results is the opposing effect of melt and mould temperature for tensile strength, elongation and flexural modulus. It was to be expected that both variables would have the same influence on the mechanical properties. But, as with weight and density, both variables influence the properties in the opposite way.

**Polyoxymethylene**

In contrast to polyethylene and polypropylene little anisotropy was found for tensile strength and modulus of elasticity.

**Polyamide**

The effect of moisture on the flexural modulus was clearly demonstrated.
CHAPTER 9. DISCUSSION.

9.1 INTRODUCTION.

This chapter contains some topics of an analysis of the injection moulding process. It attempts to cross-correlate the information derived from the observations of process variables, weight, dimensions, morphological characteristics, and physical property parameters.

The main problem in this investigation was to find and measure the most informative variables. Furthermore, the contents of that information for these variables had to be determined to give a general ranking in order of importance of the investigated variables.
9.2 CORRELATION BETWEEN PROCESS VARIABLES AND PROPERTIES OF MOULDINGS.

Output variables comprise physical and mechanical properties of the moulding. They may be divided into two basic types:

(i) Properties which can be measured and characterized by non-destructive testing, either directly in the mould before each new cycle, or during injection in the following cycle.

(ii) Properties characterized by a usually time-consuming destructive testing that is difficult to integrate on-line.

Type (i) properties comprise weight, dimensions, and shrinkage. They are the only properties which may form the basis for a product adaptive control system. Type (ii) properties comprise molecular orientation, morphology, surface finish, and mechanical properties. They are characterized, together with type (i) properties during the optimization of the mould.

The realization of any sort of process control based on type (ii) properties relies on the possibility of acquiring on-line data representing article quality.

A specification for the adaptive feed-back process element in Fig. 2.1 should establish the relationship between output variables and process state variables, as well as giving guidance to strategies for adjusting the input control variables. This is essentially a relationship between quantities which are directly measurable or controllable and those which are consequential.

Results shown in the previous chapters have demonstrated that certain properties are directly related to each of the three phases; plastication, injection, and solidification. Review of literature showed that theories based on simplified assumptions have been developed for each of the
three stages. Although they ignore interactions, they provide results in reasonable agreement with experimental measurements in cases of simple geometries. In industrial practice with arbitrary shapes of the cavity and multigate filling it is necessary to include empirical correction factors based upon measurements taken from operating machinery. A general solution applicable to all combinations of materials and design is, at the present time, difficult to establish.

Therefore, the results reported here do not pretend to represent a general control strategy or to form a scientific basis from which a general control strategy can be drawn. They may supplement existing theories, however, but they apply only to the materials and mould configurations which were used.
9.2.1 Plastication

Melt flow rate \( (Q) \) is for a given screw geometry a function of barrel temperature \( (T_b(x)) \), screw rotational velocity \( (n_s) \), screw back pressure \( (p_d) \) and disturbances caused by variation in composition and batch-to-batch of the material.

Fig. 9.1 shows a section of a barrel with the screw depicted as a shaft. It rotates during metering time \( (t_d) \) with a rotational velocity \( (n_s) \), but does not rotate during injection, packing, and cooling time.

![Diagram of plasticating unit](image)

Fig. 9.1. Model of a section of a plasticating unit for heat flow balance.

The melt flows between shaft and barrel with the average axial velocity \( \bar{V}_{ax} \), when the screw rotates. Assuming constant material properties and assuming that other forms of energy conversion of the melt are small (e.g. kinetic energy, the effect of pressure, etc.) compared to the change in internal energy, then the following energy balance may be set up:
\[ \dot{Q}_C + \dot{Q}_L + \dot{Q}_D + \dot{Q}_F = \frac{m_c \cdot c_p}{t_b} (T_n - T_h) \]  
(9.1)

where

- \( \dot{Q}_C \) = Heat convection
- \( \dot{Q}_L \) = Heat conduction
- \( \dot{Q}_D \) = Heat dissipation
- \( \dot{Q}_F \) = Frictional heat

\( m_c \) = Mass in screw channel

\( t_b \) = Time for material in barrel

\( T_n \) = Terminal temperature = \( T_n \) for the total system

\( T_h \) = Initial temperature \( \hat{=} \) hopper temperature (20°C)

Assuming stationary conditions and \( D \gg h \), and neglecting heat exchanged with the screw, the exchange of thermal energy may be written

\[ \dot{Q}_C = \alpha \cdot A_b \left( T_b (x) - T_m (x) \right) \cdot \frac{t_p}{t_c} \]  
(9.2)

and

\[ \dot{Q}_L = \frac{\lambda}{D} \cdot A_b \left( T_b (x) - T_m (x) \right) \cdot \frac{t_c - t_p}{t_c} \]  
(9.3)

where
\[ \alpha = \text{Coefficient of heat transfer} \]
\[ A = \text{Surface area of barrel in contact with the melt} \]
\[ T_b(x) = \text{Barrel temperature as a function of } x \]
\[ T_m(x) = \text{Melt temperature as a function of } x \]
\[ t_{pl} = \text{Plasticating time (screw rotation time)} \]
\[ \lambda = \text{Thermal conductivity} \]
\[ \delta = \text{Layer, where temperature gradient is considered constant} \]
\[ \text{(An approximate determination of } \delta \text{ is given by Elbe}^{48}) \]

\[ Q_D = n \cdot \gamma^2 \cdot h_A \cdot u \cdot L_s \cdot \frac{t_{pl}}{t_c} \quad (9.4) \]

where
\[ u = \text{Internal periphery of barrel} \]
\[ L_s = \text{Length of screw in contact with melt} \]

\[ Q_F = \mu \cdot p_{a+b} \cdot u \cdot L_f \cdot \frac{D}{2} \cdot n_s \cdot \frac{t_{pl}}{t_c} \quad (9.5) \]

where
\[ \mu = \text{Coefficient of friction} \]
\[ L_f = \text{Length of screw in contact with solid resin} \]

indices
\[ s = \text{melt section} \]
\[ f = \text{solid section} \]

Combining Equation 9.1 with Equations 9.2, 9.3, 9.4, and 9.5 it can be shown that \( T_m(x), \sigma, L_s, L_f \) and \( P_b \) are not determined.
Constant material properties as well as a simplified representation of the screw are generally assumed. Also, the equation does not describe the conditions at the interface between solid and melt.

Therefore, Equation 9.1 represents a qualitative relationship between input variables and melt temperature. A quantitative relationship would require studying the effect of other plasticating parameters. Information on local temperature conditions can be obtained only through a melting analysis and is not available experimentally.

In this study only $T_b(x)$ was varied. A relation between the input variables $T_b(x)$, $n_s$, and $p_d$ and the process variables $T_m(t)$ and $V_f$ was not established.

A series of experiments, in order to assure the reproducibility of the moulding conditions, were carried out before the main experiments (Section 6.3.4).

Screening of the most important variables in a statistically designed experiment using a spiral mould showed a strong coupling between the individual heating zones of the barrel (Appendix AA). Exploratory experiments showed that the heating zone next to the nozzle was best suited for melt temperature control due to its relatively good time-constant, as well as its coefficient of transfer (Equation 9.3). If the signal from the melt temperature thermoprobe was logged sequentially, it could be used to provide feedback for a melt temperature control system.

It was found that melt temperature did not vary with screw-back-pressure because the addition of friction and heat was compensated for by a smaller amount of heat from the barrel.

A measurement with a non-heat compensated thermoprobe showed that the melt temperature in the nozzle varied with injection pressure. Each injection resulted in a rise of temperature, an effect of increased frictional heat, polymer melt shear, and compression.
Changes in screw rotational velocity and back pressure had no effect on nozzle melt pressure. An increase of the cushion caused a slight increase in pressure.

The results showed that hydraulic pressure was reproduced in the nozzle. No inconsistencies were found between hydraulic pressure and nozzle pressure which could point to the latter as being superior for process control during injection and packing.

Characterization of morphology showed that the processing temperature range for the semi-crystalline polymers was narrower than had been expected. Only specimens of polypropylene moulded at 240°C had a morphology where the outermost layers were not influenced by the mould temperature (Section 8.3.3.).

It was considered that as the cycle time was long and as the barrel tended to be oversized then the residence time of the resin in the barrel should be sufficient for complete melting.

However, at the lowest melt temperature the memory of the previous crystalline order had not been cancelled out. Crystallities present in the melt were partially re-established in the cavity and acted as centers for further crystal growth. A high melt temperature increased the temperature-time history of the resin and caused an evaporation of low molecular additives. Thus, in minimizing the temperature-time history, the plasticating conditions as well as the screw geometry became increasingly important in establishing acceptable morphological properties.

As only $T_b(x)$ was varied in the main experiments, the results do not justify any comments on the effect of other plasticating variables on output variables.
9.2.2. Injection

Flow front profile as a function of time and position is the significant process state variable during injection. For a given mould temperature \( (T_f) \) and melt temperature \( (T_m) \), the controlling variable is screw-forward-velocity \( (v_s) \), or hydraulic pressure \( (P_h(t)) \) which is an alternative variable dependent on \( (v_s) \).

In cases of simple geometries (e.g., a center-gated circular disc or quadrant) theoretical studies may predict velocity and temperature profiles during cavity filling when considered as a one-dimensional radial flow process. In such cases, the melt front is known a priori. In industrial practice, with arbitrary shapes of the cavity, the melt front becomes a moving free surface and the computation should be extended to a two-dimensional case.\(^{290}\)

In the one-dimensional case it is assumed that the polymer melt, at a temperature \( T_m \), enters the cavity, whose walls are kept at a temperature \( T_f \), through a circular tube with a large \( L/D \) ratio, and that flow continues in a spreading radial flow pattern until the advancing front hits the center boundary of the wall. Such predictions are derived from the three fundamental equations of continuity, momentum, and energy and a flow equation.\(^{61}\)

The model equations are based upon some rather severe approximations, especially (i) the neglect of normal-stress and memory effects associated with fluid elasticity; (ii) the neglect of the "fountain" region in the vicinity of the advancing melt front, together with its effect upon the temperature field; and (iii) the neglect of thermal convection in the gap-wise direction.

The assumption of neglecting elastic (or memory) effects is an imposed one because of the absence of any realistic
and efficient model. To neglect the gap-wise convection is probably not justified on any order-of-magnitude basis. Neglect of the effects of inertia is justified because of a small Reynolds' Constant \( N_{Re} < 10^{-2} \), whereas neglect of streamwise \((X - \text{axis})\) conduction is related to a large Peclet number \( N_{Pe} > 10^2 \).

The above assumptions were not verified in this work. Recent one-dimensional-flow simulations have involved all of the above approximations and have still provided results in reasonable agreement with experimental pressure measurements.

Complex deformation and flow processes take place within the mould cavity during injection (Section 3.2). The forces causing the deformation are balanced against retardation and relaxation forces, \( R \), which may be considered as a change in free energy, \( F \), with the deformation.

The change in free energy arising from an isothermal deformation along the \( X \)-axis is determined by the internal energy, \( U \), the temperature, \( T \), and, the entropy, \( S \), (assuming the number of molecules, \( N_i \) = constant).

\[
R = \left( \frac{\partial F}{\partial X} \right)_{T, N_i} = \left( \frac{\partial U}{\partial X} \right)_{T, N_i} - T \left( \frac{\partial S}{\partial X} \right)_{T, N_i}
\]

The first term of the expression is the energy - elasticity, where the deformation is instantaneous and without losses. The second term is the entropy - elasticity, when the deformation is time-dependent and causes a decrease in the entropy of the system.

A generalized velocity \( (v) \), shear rate \( (\gamma) \) and temperature profile \( (T) \) is shown in Fig. 9.2. The shape of both the velocity and the temperature profiles will be affected by the initial melt temperature \( T_m \) and the
Velocity profile in the melt
Solidified surface layer
Flow lines behind flow front
High viscosity skin

Initial square element becomes:

At A:
- \( x \) High shear.
- Elastic strain of \( o-x \).

At B:
- \( x \) No shear.
- Small strain, or
- \( o-x \) unstrained.

Considered:
- Elasticoviscous flow.
- High frozen strain near boundary where wall shear rates are high causing high shear strain energy.

Fig. 9.2 Filling of quadrant moulding (See also Fig. 8.10)
injection pressure \( (P_n) \), because they, in turn, affect the rheological properties.

A fairly simple and, correspondingly, less exact technique of measuring recoverable strain was applied on 20 x 20mm samples cut from 3mm polystyrene and polyethylene mouldings and on 0.03mm thick microtomed sections cut from across the mouldings of polyethylene (Section 6.8 and 8.5). Surface orientation was measured using the Knoop hardness test on polyethylene mouldings (Section 6.9.5 and 8.6.4). Thermal analysis was applied to investigate the variations in melting temperature and crystallinity across the moulding (Section 6.7.2 and 8.4.2).

With semi-crystalline polymers recovery tests are mainly indicative of recovery in the amorphous or inter-zonal regions, and the interpretation is only partially quantitative. The details of the forces which are active between the oriented crystallites are only partially qualitatively understood. They are known, however, to influence recovery from thermally induced changes in the structure (Section 8.5).

The results of the reversion of microtomed sections showed that the level of orientation decreases with increasing distance from the gate.

When the hot melt contacts with the much colder cavity wall a wedge-shaped layer is formed from solidified melt, increasing in thickness from the end of the cavity towards the gate over about two-thirds of the total length.62) Firstly, as the solidification front is moving from the periphery of the moulding towards the gate, this region is also exposed for a longer time to the shear, causing a higher absolute orientation. Secondly, due to the quadrant shape of the moulding, elongational flow increases with flow length, causing an increasing bi-axial orientation. Close to the entrance a steady flow situation is
established during the relatively short filling period, whereas over the longer part of the mould wall an unsteady situation prevails until the mould is filled. The primary orientation from the passage of the sprue relaxes during flow in the cavity at a faster rate than new orientations are introduced from cavity flow during packing. Transverse orientations were approximately constant at some distance from the gate, while longitudinal orientations decreased.

The results showed that orientations generally decreased with increasing melt temperature and to a lesser extent with increasing mould temperature and cavity pressure. The maximum orientation along the flow length was presumed to correlate with the thickness of the solidified layer, which was decreasing with increasing flow length.

According to the proposed model, (Section 8.3.2), the orientations on the surface of the moulding arise from extensional orientations on the melt front, not from shear flow at the wall.

Screw forward velocity \( (v_s) \) was not varied in this experiment because it was found in preliminary and parallel experiments that this variable did not have a significant influence on weight, dimensions, and mechanical properties of polystyrene and polyethylene (Appendix AB). Screw-forward-velocity influenced molecular orientation parallel to flow, as well as surface quality of the quadrant moulding. Other investigations, however, have shown that orientation, morphology, and mechanical properties correlate with the flow-front-velocity, which is related to the screw-forward-velocity by the geometry of the moulding.

The geometry of the quadrant moulding cause a decrease in flow-front-velocity with increasing flow length. Additionally, the mould cross-section was large so that velocities,
shear rates, elastic strains, etc., were low. A high-powered injection moulding machine was used for the experiments. However, a constant screw forward velocity was not achieved with low melt temperatures. The screw forward velocity was highest during the first part of the stroke. It then decreased and became constant just before the cavity was volumetrically full.

It was found with polyethylene that Knoop hardness parallel and transverse-to-flow was very highly significantly influenced by mould temperature and increased with increasing mould temperature, a consequence of increased crystallinity in the surface layer of the moulding. Knoop hardness transverse to flow was highly significantly influenced by melt temperature. Hardness increased with increasing melt temperature.

Anisotropy measured with Knoop hardness decreased with increasing melt temperature, but increased with increasing mould temperature. Filling time was reduced by approximately 30% with the increase in melt temperature.

It was observed that the cavity wall temperature rises very rapidly during injection and falls relatively slowly as the melt cools and solidifies.

Control of the cavity wall temperature is important, because variation of this variable cannot be compensated for by changing other variables without a significant influence on weight and dimensions. It would seem appropriate to establish a closed-loop control circuit by using the input from the thermocouple(s) to control the temperature of the coolant.

By examination of the equation for flow of a non-Newtonian polymer along a tube, as a close analogy to mould filling, it was found that the dynamic pressure drop,

\[ \Delta p = f \ (T, \eta, \text{geometry, mass flow rate}) \]
As mass flow rate is proportional to velocity, velocity is a controlling variable, and $\Delta p$ is a controlled variable. The experiments proved that the dynamic pressure loss in the cavity was affected by melt temperature and injection pressure.

The pressure drop between the reservoir and cavity decreased substantially with increasing mould temperature. The losses, however, were much lower than predicted by Barrie\textsuperscript{76-79}.

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9.2.3 Solidification.

Hydraulic pressure during packing \((p_h(t))\), mould temperature \((T_f)\), and holding time \((t_p)\) are the significant input variables during solidification. Melt temperature \((T_m(t))\), and cavity pressure \((p_c(t))\) are process state variables. Solidification time \((t_s)\) and moulding properties are output variables.

During solidification the relation between cavity pressure \((p_c(t))\) and hydraulic pressure \((p_h(t))\) ceases once the gate has sealed. This is primarily a function of melt temperature \((T_m(t))\), and flow, and temperature of the circulating heat transfer fluid in the mould, which controls the cavity surface temperature \((T_f(t))\).

Theoretical work, as a basis for solidification models, have been described in various stages of development (Chapter 2). A main problem is a neglect of the variable material properties during solidification.

In order to resolve the position-dependent thermal and structural history for highly crystalline polymers, the temperature dependence of the thermal diffusivity cannot be neglected (Section 8.4.2). An analysis of transient heat transfer must also incorporate the latent heat of crystallization, as well as the crystallization kinetics of the polymer.

The general procedure is to convert the latent heat of crystallization into an equivalent temperature change through specific heat and ignore the kinetics of crystallization\(^{112}\). This method, however, does not predict accurate temperature profiles\(^ {113}\).

It is in this relation noteworthy that the effective packing time \((t_{pe})\) for polypropylene exceeded the effective packing time for polyethylene, even though the total latent heat generated in polypropylene is less (Table 7.1 and 7.2). However, more cooling time is required for polypropylene because the kinetics of crystallization are significantly slower.

Several attempts have been made to calculate sealing time\(^ {97,112}\). It correlates with the effective packing time \((t_{pe})\), and is primarily a function of pressure and temperature conditions during cooling. However, an adequate analysis has not yet been developed.
In the experiments reported here, the gate is not clearly defined by the geometry of the moulding. It may be assumed that the moulding freezes at the intersection between disc and sprue. This assumption is in agreement with recent investigations of procedures for experimental determination of gate sealing, where it is concluded that the results represent the progressive solidification of the moulding and not the gate sealing, as such.

The conception of "solidification" should then be defined in the present context:

It only means that the flow of the polymer is retarded so much at the distance δ (t, z) that the heat convection in the flow direction does not any longer play a significant role at that distance from the cavity wall.

In this investigation, gate sealing was taken as the intersection of two tangents to the cavity pressure curve. This method represents a simplification and would require a correction in a more exact analysis of solidification, especially with thicker mouldings and, correspondingly, thicker gates. The bulge on the pressure curve, most distinctly observed with polyethylene, tended to increase the gate sealing time (Section 7.2.1). This effect, however, was also neglected.

Wübken showed that experimentally determined packing times correlated with cooling times, calculated after Equation (2.31), when a sprue gate was employed. In this investigation the effective packing time 24mm from the center, as well as a value extrapolated to zero from the two positions of pressure measurements were compared with cooling times calculated after Equation (2.31). With high melt temperatures shorter cooling times were predicted than were experimentally achieved. With low melt temperatures longer cooling times were predicted than were achieved. The latter may be an effect of the relatively low melting temper-
tures resulting in shorter induction periods and a more rapid crystallization.

A fixed mass of melt is contained in the cavity after gate sealing and the moulding is cooled further isochorically \((V=\text{const.})\). This condition should provide a suitable condition for correlation of those properties of the moulding which are controlled primarily by the pVT characteristics of the material.

This approach was investigated, using pVT data for the particular grade of polypropylene (Replotted in Fig. 9.3 from\(^240\)).

These data were compared with density at room temperature, weight, radial shrinkage, and volumetric shrinkage. The latter was calculated from shrinkage and thickness measurements. Only results from specimens moulded with the highest cavity pressure were used in order to avoid the interference from the slow filling at the lowest cavity pressure.

The temperature at the time of sealing was calculated from Equation (2.31) and Fig. 6.11, using an extrapolated value for the effective packing time for estimation of the degree of cooling. This value was taken as an average of readings from the pressure curves 24 and 74 mm from the center, respectively. This position corresponds to the locality where density and thickness were measured.

The principles of calculating shrinkage based on pVT data is shown in Fig. 9.4.

![Fig. 9.4 Determination of specific volume (Principle)\(^{264}\)](image)

\(^{+}\) The two sets of curves show for the same polymer two different principles for recording pVT-diagrams.
Fig. 9.3. Polypropylene - pVT diagram (Hostalen PPN 1060)
The most significant source of error in the calculation is the estimation of the average temperature at the time of pressure decay (This temperature should not be confused with the temperature at ejection).

The results in Table 9.1 show that the average temperature at the time of pressure decay in the moulding decreases with increasing melt temperature and increases with increasing mould temperature. More material (Up to 4%) is introduced into the cavity at higher melt temperatures, thus necessitating longer cooling times. With low melt temperatures earlier crystallization takes place with higher rates of crystallization, hence decreasing the cooling time. The heat characteristics should also play a major role, as e.g., the thermal conductivity of polypropylene changes over a phase change.

The calculated values for density show that density decreases with increasing melt temperature, which is plausible, but opposite to the experimentally determined values. The results also show the illogical trend that density decreases with increasing mould temperature.

It is of interest that experimentally determined density shows a good correlation with shrinkage. This is clear because a higher density in the final moulding must infer a greater volumetric contraction for a fixed mass of melt.

A positive correlation was found between calculated density and weight (Coefficients of regression: 0.9866, 0.9232, and 0.9949, respectively, for the three melt temperatures).

This is the assumed relation for estimation of shrinkage from pVT diagrams. However, the experiments showed that an increase of melt temperature increased weight, but decreased radial shrinkage and density. An increase of mould temperature increased density and weight (strongly).
<table>
<thead>
<tr>
<th>PP</th>
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<td>12.3</td>
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<td>0.9031</td>
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<td>101.4</td>
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<td>20.17</td>
<td>1.32</td>
<td>3.06</td>
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<td>108.1</td>
<td>0.8913</td>
<td>0.9052</td>
<td>20.07</td>
<td>1.38</td>
<td>3.21</td>
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<td>05-09</td>
<td>237 - 25.5 - 550</td>
<td>21.2</td>
<td>63.3</td>
<td>0.9081</td>
<td>0.9024</td>
<td>20.70</td>
<td>0.86</td>
<td>1.81</td>
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<td>05-12</td>
<td>241 - 39.5 - 550</td>
<td>22.1</td>
<td>73.3</td>
<td>0.9046</td>
<td>0.9029</td>
<td>20.69</td>
<td>0.92</td>
<td>1.90</td>
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<tr>
<td>05-13</td>
<td>242 - 60.0 - 550</td>
<td>25.0</td>
<td>84.8</td>
<td>0.9007</td>
<td>0.9033</td>
<td>20.64</td>
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<td>05-16</td>
<td>243 - 80.5 - 550</td>
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<td>0.8971</td>
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<td>0.9097</td>
<td>0.9009</td>
<td>20.89</td>
<td>0.53</td>
<td>0.86</td>
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<td>0.9065</td>
<td>0.9013</td>
<td>20.87</td>
<td>0.53</td>
<td>0.86</td>
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<tr>
<td>05-04</td>
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<td>0.9025</td>
<td>20.85</td>
<td>0.57</td>
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<td>1.19</td>
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</table>
It was concluded in Section 8.2, as well as in other work\textsuperscript{249} that weight and shrinkage are not necessarily related. Furthermore, density measurements across the quadrant (Fig. 8.29, Section 8.4.1) proved that weight does not give any information about the distribution of material in the cavity, although it is an integral measure for the filling of a mould.

In summary, the results have shown that a simple calculation of shrinkage from pVT data is not possible. Naturally, a general conclusion would require a more specific and detailed investigation, where the characteristics of solidification of semi-crystalline polymers should be closely examined. This conclusion is in agreement with the work of Bolli\textsuperscript{143}, Kurfess\textsuperscript{224}, and Geyer\textsuperscript{233}, who use pVT diagrams for principal, and to some extent mathematically formulated considerations of shrinkage predictions, but, however, reject an exact calculation, especially with semi-crystalline polymers.

The variation across the geometry found with density measurements calls for a finite element approach. Woebcken and Kniesburger\textsuperscript{225}, and Neuhäusl and Brummer\textsuperscript{231, 265} have published general data on shrinkage, but comprehensive data on important semi-crystalline polymers, taking processing into account, are rarely found. Therefore, shrinkage tables as presented in Chapter 8 may be used as a guide for mouldings of similar flat shapes. Their particular value should be an indication of carefully specified production conditions, including that for the mould cavity pressure. For other geometries of mouldings the data is only applicable when all boundary conditions are carefully evaluated.

As an alternative, dimensions and shrinkage may be measured in the mould before the moulding is ejected. This has the advantage that the moulding is fastened in
a fixed position during the measurement, which may be done with a mechanical transducer built into the mould. The specific shrinkage of the moulding should be considered (Temperature gradient, mould related shrinkage, coefficient of thermal expansion). The measurement would increase the cycle time by 1 to 2 s, which is acceptable for the semi-technical articles considered in this study. (See Section 4.1). The set-up is essentially identical to the arrangement depicted in Fig. 5.2, except that a transducer with a pneumatic retraction of the measuring point must be used. The measuring point should be pressed against the moulding with a force of 0.64N, according to Mekan 75617. Maximum resolution 0.1 μm, reproducibility of the measurement < 10 μm.

The ejector movement is delayed during measurement when the mould has opened. The two measuring points move forward during this interval. The set-up is calibrated, as shown in Fig. 5.2. The measuring sequence may be repeated before the moulding is ejected for calculation of averages and variations. The result of the measurement is used as an input for the process control system (Fig. 2.1).

Weight of the moulding can be measured using an electronic weigh balance mounted in the discharge chute. Referring to Section 6.5, a balance is suggested with a low range up to 1.2 N and a high range up to 12 N. Sensitivity, ± 5 · 10^{-5} N and ± 5 · 10^{-4} N, reading accuracy 1 · 10^{-5} N and 1 · 10^{-4} N.

Two phases are used for the determination. Weighing is done after ejection and during injection in the following cycle. Then, the moulding is blown-off by compressed air. For control, a second weighing may take place to make sure that the moulding has been removed from the balance. The result is used as an input for the process control system, as well as for the control of compressed air and calibration of the balance.
Mechanical properties represent ultimate properties, however, a prediction of the influence from processing on mechanical properties from basic material data may be even more difficult than a prediction of density and shrinkage. The bi-axial filling of the quadrant adds further complications to the interpretation of the results.

Generally, process optimization is rarely based on mechanical strength, and mechanical strength is usually not a critical factor in the design of technical components because the design is done with regard to stiffness. Also, dimensional variation may be more important than mechanical properties. A correlation between dimensions and stiffness, or mechanical properties, was not demonstrated in this experiment. It is also clear that mechanical properties are difficult and time consuming to characterize.

The results with polypropylene indicated that moulding conditions can have a significant influence on the degree of anisotropy.

In particular, the material injected at lower temperatures showed a greater degree of anisotropy than that injected at a higher temperature. Pressure and the, correspondingly, slower rate of injection did not have a significant influence on anisotropy. This has implications in commercial injection moulding practice where temperatures tend to be kept low, and pressure high in order to reduce cycle time. Shrinkage was strongly dependent on melt temperature, whereas shrinkage after two years storage did not seem to be dependent on melt temperature.

The thicknesses of the skin and intermediate layer were strongly dependent on melt temperature (Fig. 8.18). A positive correlation was found between flexural modulus and the thicknesses of the two outermost layers, although the correlation showed a large scatter at low melt temperatures (Fig. 9.5). It was not possible to explain density
Fig. 9.5 Polypropylene - Density and flexural modulus as a function of the width of zone I and II
in terms of a skin/core ratio. Density and melting enthalpy increased with distance from the surface, whereas the melting point varied across the specimen.

The yield stress parallel, as well as transverse to flow increased with decreasing barrel temperature. For other polymers, e.g. for polystyrene, the yield-stress transverse to flow is weakened when the yield stress parallel-to-flow is strengthened by molecular orientation.

Fujiyama et al.\textsuperscript{200, 201} ascribe such tendencies for orientation-crystallized polypropylene to a "woven structure". However, the fact that the yield-strength parallel to flow is higher suggests that the woven structure is mainly composed of the warp, and that the weft component is small\textsuperscript{266}.

In general, polypropylene crystallizes under high shear stress on injection moulding, and it has been concluded that the skin layer is composed of, or contains, the so-called "shish-kebab" structure, parallel to the flow direction and imbedded in a row structure\textsuperscript{200}. However, orientation experiments with all their disadvantages with polyethylene did not show that orientation was concentrated specifically to the outermost layers (Fig. 8.49). Also, a relation between yield stress and thickness of the outermost layers was not found.

It may be summarily concluded that, although certain properties like skin thickness and flexural modulus, or skin thickness and shrinkage did seem to correlate, an exact correlation between moulding variables, structure and final properties could not be demonstrated. Based on this conclusion, an alternative approach in order to establish such a relationship is suggested in Chapter 11.
In this study a rather broad range of experimental conditions have been investigated. The results have shown that melt and mould temperature and injection pressure in injection moulding exert profound influences on morphology. Furthermore, that other properties such as Knoop hardness and flexural modulus are also related to the morphology and to the kind and degree of preferred orientation in the skin of the mouldings. Although the structure-property correlations presented are limited in scope, it is evident that such correlations can be found in relatively large, bulk-crystallized specimens.

Two logical implications of this work are (i) that one should know the morphologic state of the polymer to assure that mechanical test data are meaningful, and (ii) that a detailed knowledge of the structure may permit fabrication of injection-moulded articles having tailored mechanical properties.

In light of the results, the questions that arise are whether the work can contribute to a specification for the adaptive feedback process model element in Fig. 2.1 and, if then, to which extent it is possible to give guidance to strategies for adjusting the input control variables, based on a ranking of the most sensitive variables.

The answer to the first question is that only some of the main variables have been investigated. However, the work covers a wider range of semi-crystalline polymers and mechanical tests than are usually reported.

One of the important conclusions is that the polymers reacted differently to a change of process variables. Secondly, statistical analysis of the results showed very highly significantly interactions between process variables.
In process control one attempts to control the processing via machine parameters by taking into account disturbance variables like environmental conditions, raw material and wear. Some properties (melt index, crystalline melting point, crystallization temperature, and spherulite growth rate) were characterized (Section 6.2), and raw material variation was investigated by screening samples taken from commercial shipments (Appendix B). The results, however, were not integrated into the study.

Therefore, the study did not include important questions like;

Is it possible from a pressure measurement in the mould to analyze whether a viscosity change has resulted from a temperature change or a batch variation?

The decision is only made possible by means of an additional temperature measurement in the nozzle. If, furthermore, the mould temperature is to be included in the control loop by means of a signal from thermocouples in the mould, it is also necessary to measure the material temperature in the nozzle.

Both measurements must be used in such a way that if the material temperature changes it is not the mould temperature but only the cylinder heating and nozzle heating that are re-adjusted, otherwise cause and effect in the regulating system would be inverted.

Viewed in this way, it will be necessary to measure not only the pressure variation, but also the material temperature in the nozzle. Yet, conventional moulding machines do not sense melt temperature. It seems reasonable, therefore to suggest:

(i) Provision should be made for melt temperature indicating devices. The measurement should be used for incorporation in a closed-loop control system.

(ii) Mould temperature should be measured and incorporated in the control system.
In Chapter 8 it was concluded that the effect of temperature on some properties is relatively insignificant compared to that of pressure. This only applies, providing that all other parameters are kept constant or adjusted. A raised melt temperature can, in fact, indirectly affect, e.g., processing shrinkage, by changing the mould cavity pressure. It should be noted that other properties, e.g., the flexural modulus for polypropylene, were shown to be strongly dependent on melt temperature. However, it may be concluded that variation in melt temperature can, for certain properties, be compensated for by a closed loop control of the cavity pressure.

It is not possible, as with melt temperature, to compensate for variations in mould temperature by varying the cavity pressure. A constant cavity pressure (that is the cavity pressure is kept constant, and not as usual the hydraulic pressure) will tend to increase the effect of a change in mould temperature.

If the measured pressure in the cavity deviates while the melt temperature in the nozzle is constant, it can still not be decided unambiguously whether this is due to a material batch variation or to, e.g., the check ring allowing a greater amount of material to pass. This decision can be made only by an additional measurement of the flow-front-velocity. Since continuous measurement of the flow-front-velocity is complicated if the mould geometry is complicated, this measurement can be assimilated by measuring a mean flow-front-velocity, which can be done by measuring the time required to travel a defined distance. This time measurement can be carried out at very little expense by using the response times of, for example, the pressure transducer and the thermocouples in the mould. The average flow-front-velocity is also related to the dynamic pressure loss through the temperature and viscosity of the melt and the geometry of the sprue, runner, and cavity system. The dynamic pressure loss per unit length is easy to monitor with two pressure transducers at a known distance. (Due to heat transfer the pressure losses $\Delta p_1$ and $\Delta p_2$ will be different functions of velocity.)
Thus, it is possible to decide unambiguously from the three measured variables of the melt temperature in the nozzle \((T_m)\), the cavity pressure \((p_c)\) and the cavity wall temperature \((T_f)\) which of the disturbance variables mentioned is involved. A logical procedure is, first to examine the melt temperature in the nozzle \((T_m)\), then the time measurement \((t_{ie})\), then the cavity wall temperature \((T_f)\), and, finally, the pressure variation in the cavity \((p_c(t))\). (Fig. 9.6)

This discussion has centered on how to establish the cause of a deviation from the required output variables. It should then be discussed how possible measures should be executed.

If the melt temperature in the nozzle varies, due to changed environmental conditions, the set point of the temperature controller \((T_b(x))\) or the screw-back-pressure \((p_d)\) can be adjusted. Regulating the back pressure would be preferred, since the results are very rapid and effective. A temperature adjustment by means of a shear device could also be feasible.

A change in the mean flow-front-velocity can logically be compensated for by correcting the set value of the screw forward velocity. However, on standard injection moulding machines, the screw-forward-velocity may be limited by the available pressure or available quantity of oil. Disturbances which are not compensated for by controlling the screw forward velocity may then be regulated by changing the barrel temperature \((T_b(x))\).

If, when all the parameters hitherto mentioned have been regulated to constant values, there is still a difference in the pressure profile in the cavity, it can then only be attributed to a material batch variation. This can then be compensated for by a correction of the set points of the temperature controllers or of the back pressure, in which case a change in material temperature may be tolerated, but the viscosity remains constant.

If all individual variables were to be kept constant, and no disturbances other than the disturbance variables were to occur, regulating the pressure curve would no longer be necessary,
Fig. 9.6 Regulating sequence
since it would then, in any case, remain constant; the properties of the mouldings would also remain virtually constant.

The strategy for influencing the process, by measuring the interfering parameter and employing the regulating techniques indicated here, is intended to show a way whereby a regulating system could be used to counteract disturbance variables in a physically logical manner without considering the emperical corrections which have resulted from the study.

In Fig. 9.7 the results obtained have been incorporated in a similar strategy of decision-making applicable for the combination of material mould/machine used in the study. It is based on a standard injection moulding machine with additional equipment in the first stage of elaboration. It has, however, revealed information not achievable without the additional monitoring devices.
Input:
1) Material property data
2) Mould/Machine geometry specifications
3) Quality objective reference

Symbols: ↑ = increase
↓ = decrease

Fig. 9.7a Regulating sequence for 3 mm quadrant mould
Fig. 9.7b Regulating sequence for 3 mm quadrant mould
Fig. 9.7d Regulating sequence for 3 mm quadrant mould
Fig. 9.7e Regulating sequence for 3 mm quadrant mould
CHAPTER 10. CONCLUSIONS

During the last few years injection moulding has been studied, both from the mathematical simulation and the structuring-morphology points of view.

The work described here attaches importance to the latter areas of study. It is concerned with an investigation of injection moulding variables and their influence on some properties of semi-crystalline polymers.

The results of the work (Table 10.1) should contribute to a specification of the process model shown in Fig. 2.1. Developing a process control strategy for this purpose, in order to achieve a given quality objective reference, involves the choice of what to control, as well as how to control the variables, singly or in combination.

The effect of injection moulding variables \((T_m, T_f, V_s, P_c)\) on properties of 3 mm and 5 mm quadrant mouldings from HDPE, PP, POM and PA was studied.

A variety of techniques were employed to study the output variables; surface finish, mechanical properties, dimensions, shrinkage, morphology, residual stresses, and orientation.

A tentative control strategy in the form of a block diagram is depicted in Fig. 9.7. However, it is very difficult, on the basis of the results, to give a general ranking in order of importance of the investigated variables as to their effects on specific output properties.

One reason is that there is not always a unique relation between a change of a variable and the resultant property. This was illustrated by the influence of melt temperature on mechanical properties.

The results also showed that the polymers reacted differently to a change of process variables. As an example, density increased with an increase in melt temperature for HDPE and POM, but decreased for PP.
### Table 10.1. SUMMARY OF EFFECTS OF INCREASING MOULDING VARIABLES ON PROPERTIES

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<thead>
<tr>
<th>Variable</th>
<th>HDPE</th>
<th>PP</th>
<th>POM</th>
<th>PA66 - PA6 - PA6f</th>
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<td>***↑</td>
<td>***↑</td>
<td>***↑</td>
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<td>Radial shrinkage</td>
<td>***↑</td>
<td>***↑</td>
<td>***↑</td>
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</tr>
<tr>
<td>Differential shrinkage</td>
<td>***↑</td>
<td>***↑</td>
<td>***↑</td>
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<tr>
<td>Radial post</td>
<td>***↑</td>
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<tr>
<td>Radial post (after short-time annealing)</td>
<td>***↑</td>
<td>***↑</td>
<td>***↑</td>
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<tr>
<td>Morphology</td>
<td>core skin</td>
<td>core skin</td>
<td>core skin</td>
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<tr>
<td>Density</td>
<td>*↑</td>
<td>***↑</td>
<td>***↑</td>
<td>***↑</td>
</tr>
<tr>
<td>Knoop-hardness</td>
<td>***↑</td>
<td>***↑</td>
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<tr>
<td>Orientation</td>
<td>***↑</td>
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<tr>
<td>Falling weight impact</td>
<td>***↑</td>
<td>***↑</td>
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<tr>
<td>Tensile strength</td>
<td>***↑</td>
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<td>Tensile impact</td>
<td>***↑</td>
<td>***↑</td>
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<td>***↑</td>
</tr>
<tr>
<td>Flex. modulus, bend.</td>
<td>**↑</td>
<td>**↑</td>
<td>**↑</td>
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<tr>
<td>E-modulus</td>
<td>**↑</td>
<td>**↑</td>
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</tr>
</tbody>
</table>
It was to be expected, that melt and mould temperature would influence tensile strength, elongation, and flexural modulus in the same way. In fact they were found to have the opposite influence.

With PP a very highly significant interaction on elongation at fracture parallel and transverse to flow was found. However, not only properties but also process variables interact. As an example, a very highly significant two-factor interaction was found between melt temperature and cavity pressure for weight, radial shrinkage and differential (radial minus tangential) shrinkage.

Therefore, other combinations of material, mould/machine, and quality objectives may result in a strategy of decision-making which is different from the one depicted in Fig. 9.7.

Plastication

Barrel temperature \( (T_b(x)) \), screw rotational velocity \( (n_s) \), and screw-back-pressure \( (p_d) \) are the significant input variables during melt production. Melt temperature - and its homogeneity - is the controlled variable. Disturbances result from variations in resin properties and environment.

The plastication phase was not investigated in particular. However, it was found that melt temperature did not depend on back pressure. Melt temperature in the nozzle varied with injection pressure. A statistically designed experiment using a spiral mould showed that the heating zone next to the nozzle heating zone was best suited for melt temperature control.

A high shot/plasticizing ratio caused brittleness of polypropylene at high melt temperatures. A low melt temperature influenced morphological features strongly.

Injection

Flow front profile, as a function of time and position, is the significant process state variable during injection. Screw-
forward-velocity \((v_s)\) or hydraulic pressure \((P_h)\) may be controlled but not both independently. Output variables are: melt maximum temperature \((T_m)\), injection time \((t_i)\) and melt elastic strain profile.

The pressure drop between the reservoir and cavity decreased substantially with increasing mould temperatures. Changes in mould temperature did not otherwise influence cavity filling. The dynamic pressure loss in the cavity was affected by melt temperature and injection pressure.

Screw-forward-velocity did not have a significant influence on weight, dimensions, and mechanical properties of HDPE (and PS), which is a consequence of the geometry of the quadrant moulding.

Packing and cooling

Hydraulic pressure during packing \((P_h(t))\), mould temperature \((T_f)\), and holding time \((t_p)\) are the significant input variables during solidification. Melt temperature \((T_m(t))\) and cavity pressure \((P_c(t))\) are process state variables. Solidification time \((t_s)\) and moulding properties are output variables.

It was found that variation of mould temperature cannot be compensated for by changing other variables without a significant influence on weight and dimensions. An integrated control scheme should include mould temperature control, which is not the case in practice.

The effect of melt temperature on most properties was relatively insignificant compared to that of pressure. The properties in question were determined to a higher degree by the melt-temperature-depending pressure profile during solidification rather than by the melt temperature, as such. Variations in melt temperature can, for certain properties, be compensated for by a closed loop control of the cavity pressure, provided that the gate is still open. Gate freezing during solidification depends on the cooling rate and the polymer. As an example, a \(10 \, ^\circ C\) increase in melt temperature increased the effective
packing time by 0.5 s for PE, but by 3.2 s for PP.

For the conditions of this work increase of melt temperature was found to increase weight (strongly for HDPE and PP). Thickness (strongly for HDPE), and differential shrinkage (strongly for HDPE and PP). Radial shrinkage decreased strongly for HDPE and PP). Density increased for HDPE and POM, but decreased for PP.

Mechanical properties were investigated for HDPE and to a more limited extent for PP and POM. Increase of melt temperature correlated strongly with an increase of tensile strength parallel to flow for PP. Falling weight impact strength increased (strongly for HDPE) and decreased for PP.

Increase of mould temperature was found to increase density and radial shrinkage (strongly for HDPE and PP), thickness (strongly for HDPE) and radial post shrinkage. However, differential shrinkage decreased for PP, POM and PA while it was increasing strongly for HDPE, possibly reflecting a fundamental difference in the modes or rates of crystallization and relaxation for the latter polymer. Increase of mould temperature correlated with an increase of tensile strength and a strong decrease of impact strengths for HDPE associated with an increase of radial orientation; tensile strength of PP also increased strongly, but the effect with POM was small.

Cavity pressure was varied for HDPE and PP only. Increase of cavity pressure was found to increase weight (strongly for HDPE and PP), thickness (strongly for HDPE) and falling weight impact strength. Radial shrinkage decreased strongly for HDPE and PP and differential shrinkage decreased strongly for HDPE with increasing cavity pressure.

Microscopy of microtomed sections cut parallel and transverse to flow at two positions revealed at least three distinct morphological zones. Several separate layers of macrophases made up each zone. An increase in melt and mould temperatures caused a decrease in skin thickness and more uniform morphological features in the core. Mould temperature influenced the surface layers, whereas melt temperature influenced the core. Shear stresses develop in the melt during cavity filling. Close to
the surface they run antiparallel to the direction of flow. When the front of solidification progresses from the surface towards the center, spherulites develop increasingly parallel to the stress. This effect was observed in the intermediate layer, where the axes of the spherulites were no longer strictly perpendicular to the surface, but were deflected against the direction of flow.

An orientation profile was obtained by measuring reversion of microtomed sections of HDPE at elevated temperatures. A wedge-shaped profile was found in the radial direction with the maximum moving away from the interior with increasing distance from the gate.

Thermal analysis on samples taken from layers in the axial direction of the moulding showed, that melting point and crystallinity increased with the distance from the surface. The two endotherms found with polyethylene were associated with the temperature rise from crystallization of the melt, last injected into the cavity. It shows that an analysis of transient heat transfer should incorporate the latent heat of crystallization and the crystallization kinetics of the polymer.

PVT-data for the grade of polypropylene used were compared with density at room temperature, weight, radial shrinkage, and volumetric shrinkage, but a relationship for prediction of shrinkage from the data could not be proved.

Although a correlation between skin thickness and flexural modulus, or skin thickness and shrinkage was found, it was not possible to establish a general correlation between moulding variables, morphological features, and final properties. An alternative approach for this purpose was suggested for further work.
CHAPTER 11. SUGGESTIONS FOR FURTHER WORK

This thesis is only a first step to a better understanding of the injection moulding of semi-crystalline polymers. The broad review of literature was an attempt to give a fairly complete view of the complex relationships between machine, mould, material and processing variables. The experimental part then, should prepare the ground for an evaluation of the influence from injection moulding variables in subsequent more specific research work. Therefore, it is possible to formulate problems which still have to be resolved as a natural extension to the work reported here.

The results obtained from the test programme for empirically determining the relationship between processing variables and the final properties of mouldings have confirmed that it appears impossible, or not yet possible, to make an exact correlation between injection moulding variables and the investigated properties.

Therefore it is conceivable that the way of presenting the problems should be divided into two independent tasks.

(i) Deduce a correlation between process state variables one the one side and texture and macromorphology on the other side.

(ii) Deduce a correlation between crystallization conditions, and micromorphology on the one side and mechanical properties and shrinkage on the other side.

To achieve the first aim the following areas should be investigated:
- Derivation of a quantitative relationship between the process variables, where the coordination of the different sub-processes should be taken into account. Such work could be further extended to comprise the development of control algorithms for an overall computer control of the process.
Derivation of relationships between process variables and the resulting structure and morphology.

As an example, a simulation which will predict the thermal history during cooling at any location within the material as well as the resulting crystalline structure is desirable. Such an analysis of transient heat transfer must incorporate the latent heat of crystallization and the crystallization kinetics of the polymer in order to resolve the position-dependent thermal and structural history. Verification of crystallization kinetics by simulating (high pressure) DSC cooling curves for the polymer as well as observing volume changes as a function of pressure, temperature and time (pVT-relationships) could be a useful extension. An examination of the morphology of the samples crystallized in the DSC, in particular the size of the spherulites, should be matched by the simulation.

Also, as an example, morphology in crystalline polymers as a result of injection moulding will be better understood when the effect of the flow field on the crystallization kinetics is also taken into account. Such studies could be carried out by analyzing the morphology of samples crystallized during flow in a capillary rheometer. The development of surface stresses as well as the complex problem of internal stresses in semi-crystalline mouldings is an additional subject of great practical interest.

To achieve the second aim the following areas should be investigated.

- Development of methods for further characterization of texture and morphology at different locations within the moulding.

As an example, x-ray diffraction, hot-stage microscopy and scanning electron microscopy could be applied to such investigations.
Derivation of a correlation between morphologically well defined samples and changes in deformation and fracture properties.

In subsequent phases it should then be possible to combine conclusions to elucidate the relationships between crystallization conditions, microstructure and mechanical properties.

It is evident, however, that each of the above subjects within themselves present extensive areas for study.
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**Nomenclature**

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 6</td>
<td>Polyamide 6 (Polycaprolactam)</td>
</tr>
<tr>
<td>PA 6f</td>
<td>Polyamide 6, reinforced</td>
</tr>
<tr>
<td>PA 66</td>
<td>Polyamide 66 (Poly (hexamethylene adipamide)</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>POM</td>
<td>Polyoxymethylene</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
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**Prefix**

<table>
<thead>
<tr>
<th>Prefix</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ</td>
<td>difference, differential</td>
</tr>
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**Subindices**

<table>
<thead>
<tr>
<th>Subindices</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>max.</td>
<td>maximum</td>
</tr>
<tr>
<td>min.</td>
<td>minimum</td>
</tr>
<tr>
<td>s</td>
<td>used as second or higher subscript to indicate a value set on the injection moulding machine (e.g. ( t_s ) = set injection time)</td>
</tr>
<tr>
<td>e</td>
<td>effective value (related to a quantity measured on the pressure curve)</td>
</tr>
</tbody>
</table>

**Dimension**

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>length of arc</td>
</tr>
<tr>
<td>( b_0 )</td>
<td>width before recovery</td>
</tr>
<tr>
<td>( b_r )</td>
<td>width after recovery</td>
</tr>
<tr>
<td>( D_h )</td>
<td>screw diameter</td>
</tr>
<tr>
<td>( h )</td>
<td>height</td>
</tr>
<tr>
<td>( l )</td>
<td>length before recovery</td>
</tr>
<tr>
<td>( l_0 )</td>
<td>length after recovery</td>
</tr>
<tr>
<td>( lr )</td>
<td>deflection</td>
</tr>
<tr>
<td>( Ls )</td>
<td>mould dimension</td>
</tr>
<tr>
<td>( L_m )</td>
<td>moulding dimension</td>
</tr>
<tr>
<td>( R_l, R_{ll} )</td>
<td>radius</td>
</tr>
<tr>
<td>( R_{l1}, R_l )</td>
<td>reversion parallel to flow</td>
</tr>
<tr>
<td>( R_{l1}, R_{l1} )</td>
<td>reversion transverse to flow</td>
</tr>
<tr>
<td>( R_{l1} )</td>
<td>revised and compensated reversion parallel to flow</td>
</tr>
<tr>
<td>( R_{l1} )</td>
<td>revised and compensated reversion transverse to flow</td>
</tr>
<tr>
<td>( R_{l1} )</td>
<td>wall thickness</td>
</tr>
<tr>
<td>( s_f )</td>
<td>mould deflection</td>
</tr>
<tr>
<td>( s_{mf} )</td>
<td>displacement of screw during injection</td>
</tr>
<tr>
<td>( s_{me} )</td>
<td>displacement of screw during metering</td>
</tr>
<tr>
<td>( s_{mp} )</td>
<td>displacement of screw during packing</td>
</tr>
<tr>
<td>( s_s )</td>
<td>screw movement</td>
</tr>
<tr>
<td>( S, (S_f) )</td>
<td>mould or processing shrinkage</td>
</tr>
<tr>
<td>( \Delta S )</td>
<td>differential shrinkage</td>
</tr>
<tr>
<td>( S_p )</td>
<td>post moulding shrinkage</td>
</tr>
<tr>
<td>( \Delta S_p )</td>
<td>differential post moulding shrinkage</td>
</tr>
<tr>
<td>( S_f )</td>
<td>radial mould shrinkage</td>
</tr>
<tr>
<td>( S_{fa} )</td>
<td>radial shrinkage after annealing</td>
</tr>
<tr>
<td>( S_{pa} )</td>
<td>differential shrinkage after annealing</td>
</tr>
<tr>
<td>( S_{spa} )</td>
<td>radial shrinkage after annealing</td>
</tr>
<tr>
<td>( S_{pc} )</td>
<td>differential shrinkage after conditioning</td>
</tr>
<tr>
<td>( S_{t} )</td>
<td>tangential mould shrinkage</td>
</tr>
<tr>
<td>( t )</td>
<td>thickness</td>
</tr>
<tr>
<td>e</td>
<td>damaging deformation</td>
</tr>
</tbody>
</table>
Pressure

- $P_{\text{abs.}}$ (pressure measured with respect to zero pressure)
- $P_{\text{amb}}$ (atmospheric pressure)
- $P_b$, $P_d$ (back pressure measured in the nozzle)
- $P_c$ (cavity pressure)
- $P_{\text{dyn}}$ (dynamic pressure loss)
- $P_{\text{ex}}$ (pressure in excess of atmospheric pressure "gauge pressure")

Hydraulic pressure

- $P_h$, $P_{\text{hyd}}$ (hydraulic pressure during injection)
- $P_{\text{hm}}$ (hydraulic pressure during metering)
- $P_{\text{hp}}$ (hydraulic pressure during packing)
- $P_i$ (injection pressure)
- $P_m$, $P_n$ (melt pressure measured in the nozzle)
- $P_p$ (packing pressure)

Time (lower case "t")

- $t_0$ (mould open time)
- $t_c$ (cycle time)
- $t_{fi}$ (mould filling time ("volumetric filling time")
- $t_i$ (injection time)
- $t_k$ (cooling time)
- $t_{m'}$, $t_d$ (packing time (screw forward time))
- $t_{pl}$ (plastication time (screw rotation time))
- $t_s$ (sealing time)

Temperature (higher case "T")

- $T$ (average temperature in moulding at ejection)
- $T_{\text{m}}$ (maximum temperature in moulding at ejection)
- $T_a$ (ambient (room) temperature)
- $T_b$ (barrel temperature)
- $T_{\text{cr}}$ (crystallization temperature)
- $T_m$ (mould temperature)
- $T_g$ (glass transition temperature)
- $T_k$ (coolant temperature)
- $T_m$ (melt temperature, melting point)

Velocity

- $v_s$ (screw forward velocity)
- $v_i$ (injection rate)

Rotational velocity

- $n_s$ (screw rotational velocity)

Weight

- $G_m$ (weight of moulding)
- $G_s$ (shot weight)
Volume

\( v \)  
specific volume

\( v_a \)  
specific volume for amorphous fraction

\( v_c \)  
specific volume for crystalline fraction

\( v_c \)  
cavity volume

\( v_m \)  
cushion volume

\( v_m \)  
volume of moulding

\( v_s \)  
shot volume

Symbols of quantities

\( a \)  
thermal diffusivity

\( c \)  
specific heat capacity

\( \Delta H \)  
enthalpy sample

\( \Delta H_c \)  
enthalpy for completely crystalline polymer

\( \lambda \)  
thermal conductivity

\( \rho \)  
density

Mathematical

\( A \)  
area

\( R \)  
range

\( s \)  
standard deviation

\( x \)  
arithmetic mean

Other symbols

\( E_p \)  
penetration energy

\( E_p \)  
flexural modulus

\( E_d \)  
damaging energy

\( F \)  
force

\( F_s \)  
damaging force

\( K \)  
calibration constant

\( KHN \)  
Knoop Hardness Number

\( R \)  
Reynolds number

\( d \)  
rate of heating

\( Q \)  
melt flow rate

\( v \)  
heat flow

\( v_s \)  
cooling rate
<table>
<thead>
<tr>
<th>Appendix O</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conclusions</strong>†)</td>
<td></td>
</tr>
<tr>
<td>This study, carried out as a preliminary to subsequent investigations of more specific areas of the injection moulding process, has indicated that:</td>
<td></td>
</tr>
<tr>
<td>Moulding procedure</td>
<td>Carefully controlled moulding conditions with monitoring of pressure and temperature of the melt at the nozzle, screw movement, temperature of the mould, and cavity pressure give a direct, continuous and synchronised record of conditions and changes occurring in the material itself at the instrumented zones.</td>
</tr>
<tr>
<td>Industrial application</td>
<td>The monitoring facility can also be used for establishment of optimum processing conditions, assessment of machine performance, and as a basis for development of product and process control methods.</td>
</tr>
<tr>
<td>Monitoring of melt temperature</td>
<td>As pointed out in the literature review, absolute temperature measurements cannot yet be made with accuracy. However, melt temperature measurements in the nozzle provide an important aid for reproducing conditions of plastication and pressure transfer from the hydraulics to the nozzle.</td>
</tr>
</tbody>
</table>

†) This Chapter was submitted as "Conclusions" before later revisions.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screw movement</td>
<td>Screw forward velocity is, in principle, a machine variable. It is interacting with the hydraulic pressure. It was also found that a constant velocity was not achieved with low melt temperatures.</td>
</tr>
<tr>
<td>Mould temperature</td>
<td>Mould temperature is strongly influencing the cooling phase. Variations in mould temperature are the cause of differences in crystallinity and morphology with semi-crystalline polymers as well as weight and dimensional variation.</td>
</tr>
<tr>
<td>Monitoring of mould</td>
<td>Thermo-couples were built-in 0.5 mm below the cavity surface, and were used to reproduce cavity wall temperatures. Monitoring and control of the mould temperature improves reproducibility and is a prerequisite for close tolerances. An improved control is important because variation in mould temperature cannot be compensated by changing other parameters without a significant influence on weight and dimensions.</td>
</tr>
<tr>
<td>temperature</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>Pressure was monitored in the hydraulic system, in the nozzle, and in the cavity.</td>
</tr>
<tr>
<td>Nozzle pressure</td>
<td>The results showed that hydraulic pressure was duplicated in the nozzle. No inconsistencies were found between hydraulic pressure and nozzle pressure which could point to the latter as superior for process control.</td>
</tr>
</tbody>
</table>
Cavity pressure

Cavity pressure has, when compared with melt- and mould temperature, a strong influence on weight and dimensions of mouldings. Different sections of the pressure profile can be related to different physical property parameters.

Effect of melt temperature on cavity pressure

Changes in melt temperature influenced the dynamic pressure loss during filling as well as the maximum pressure, the latter being adjusted by changing the setting of the hydraulic pressure. Melt temperature influenced the effective packing time and caused a shift of the pressure decay curve. Melt temperature influenced the pressure gradient along the length of flow in the cavity.

Effect of mould temperature on cavity pressure

Changes in mould temperature influenced the pressure decay curve, but did not influence the filling phase.

Control of cavity pressure

A closed-loop control of the cavity pressure during filling is not possible as the pressure is determined by the resistance to flow in the cavity. Also the necessary fast response time of the hydraulic system makes a direct control difficult. Cavity pressure may then be used either to change the packing pressure or it lends itself to direct control during cooling.
A switch-over to a lower packing pressure generated from a signal from the cavity pressure is per definition not a closed-loop control. However, as the pressure transducer signal is less influenced by external disturbances, it may be assumed, that it improves in some cases reproducibility of the conditions in the cavity.

The results have shown that cavity pressure during packing and cooling is of dominating influence on physical properties. However, the pressure curve during cooling is an integral value of several interplaying variables (melt temperature, mould temperature, hydraulic pressure and raw material properties).

Therefore, a closed-loop control of the pressure curve should take these factors into consideration according to a predetermined algorithm or moulding strategy. This type of control technology presents a very complex system if it should be generally applicable.

The results have indicated that there is not always a unique relation between a change of processing variables and the resultant properties of the moulding.

As the experiments were carried out with an article, which is fairly easy to mould, the results of characterization provide information about processing under ideal conditions.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen weight</td>
<td>Weight of the mouldings was found to provide a good indication of the reproducibility of the process. Specimen weight did not correlate with dimensions of the mouldings because the two properties depend on different phases of the cavity pressure variation during the moulding cycle. Weight increased with increasing melt temperature for PE, PP, and POM, it increased with cavity pressure for PE and PP, and decreased with mould temperature for all materials.</td>
</tr>
<tr>
<td>Thickness</td>
<td>Thickness increased with increasing melt temperature and cavity pressure for PE and PP, and decreased with increasing mould temperature for all materials.</td>
</tr>
<tr>
<td>Radial shrinkage</td>
<td>Radial shrinkage decreased with increasing melt temperature and cavity pressure for PE and PP, and increased with increasing mould temperature for all materials, and with increasing wall thickness for PP and POM.</td>
</tr>
<tr>
<td>Differential shrinkage</td>
<td>Differential shrinkage increased with increasing melt temperature and decreased with cavity pressure for PE and PP. It increased with increasing mould temperature for PE, but decreased for PP, POM and PA 6f.</td>
</tr>
<tr>
<td>Radial post shrinkage</td>
<td>Radial post shrinkage decreased with increasing mould temperature for PE, PP and POM.</td>
</tr>
</tbody>
</table>
Short-time annealing

Shrinkage after short-time annealing was in all cases substantially higher than post shrinkage after long-term storage at normal conditions. Short-time annealing decreased radial shrinkage.

Differential shrinkage increased with melt temperature, cavity pressure and mould temperature for PP. The same trend was found with mould temperature for POM, PA66, PA 6 and PA 6f.

Microscopical investigations

Using a microtome, thin sections were taken parallel and transverse to flow at two positions on the mouldings.

Rate of crystallization

Examination of the microtomed sections showed wide differences in morphology between specimens made from different materials. This could be traced back to differences in rates of crystallization as determined by using a hot-stage microscope. With polypropylene it was found that the logarithmic rate of spherulite growth was linear as a function of the temperature of crystallization.

Morphology

It is difficult to generalize as to the influence from processing on morphology. This is partly a consequence of the complex crystallization conditions in the cavity. But also other factors, like the type of nucleating agent, its compatibility with the polymer and its distributions after moulding, which were not included in the investigations, could influence the results.
Three-zone structure

However, by using a polarized-light microscope three distinct zones could be identified in mouldings with the materials investigated.

Surface zone

The outermost zone was subdivided into a skin and a surface layer. The skin appeared amorphous, or non-spherulitic because a resolution of the supposed fine crystalline structure was not possible with the light microscope.

The surface zone has developed during injection under the simultaneous influence from a shear induced crystallization and a fast heat transfer through the cavity wall.

The width of the skin did not depend on the processing variables, whereas some influence from processing was found in the following layer.

Intermediate zone

The second or intermediate zone was characterized by spherulites oriented toward the cavity surface, usually unrestricted growing, but often shear or row nucleated. In some cases also malformed spherulites were found.

It is assumed that the morphology in this zone develops during the cavity filling. Shear creates not only an orientation of the melt but also a high nuclei density. A common factor appears to be that nucleation lines usually lie parallel to the streamlines of flow. Subsequent growth of the crystallites occurs by epitaxial
transverse lamellar growth from the line nuclei, perpendicular to the surface and against the direction of the temperature gradient.

With polypropylene, this zone may often be subdivided in layers where the size of spherulites generally increases towards the core within each layer and as a general trend towards the core. At the same time, the spherulites change from growing in rows to spherulites with a more random orientation. It may be concluded that the rate of cooling does not decrease linearly from the surface towards the core. This may be explained as an effect of the simultaneous filling and cooling (crystallization) process.

The intermediate zone decreases with increasing length of flow, mould- and melt temperature.

The core was found to consist of non-oriented spherulites, the size of which was dependent on the polymer and the processing conditions. The core was in some cases subdivided in layers where a coarse morphology alternated with a less coarse one.

Among the process variables mould and melt temperature were found to have most influence on the morphology. Generally, the size of spherulites increased with both variables. Mould temperature had most influence on the surface layer, whereas melt temperature would influence the core most.
The morphology in the core, generally, became more coarse with increasing melt temperature. At a higher melt temperature fewer embryos are present, which, during cooling in the melt cause fewer athermal nuclei, which grow to bigger spherulites due to the slower cooling. Also the rate of cooling is reduced at higher melt temperatures. Therefore crystallization takes place at a lower rate of nucleation and a relatively higher rate of nuclei growth, which causes fewer, but more coarse spherulites.

Density

Density was determined using a gradient column on samples taken from the whole plaque along flow length and from selected positions from specimens moulded with various combinations of the processing variables.

Density increased with an increasing melt temperature for PE and POM, but decreased for PP. An increase in mould temperature produced an increase in density for PP, POM, and PA. Density decreased with increasing cavity pressure for PP, and decreased with increasing flow length for PE and PP. Density increased after annealing of PP and POM.

Thermal analysis

The degree of crystallinity and the melting temperature was determined using differential scanning calorimetry on samples taken from one position of the plaque and with various distances from the surface.
Melting curves for polyethylene

Generally the degree of crystallinity and the melting temperature increased with distance from the surface, but some variation was found, which was assigned to the variation in shear during mould filling and released latent heat of crystallization.

The double peaks found in the melting curves of PE were examined in detail. It is suggested that they mainly result from a melting-recrystallization phenomenon caused by the heat of crystallization from the melt last injected into the cavity.

Orientation

Reversion after annealing was measured for polyethylene. Reversion decreased with increasing melt temperature. Reversion profiles were obtained across the specimen. No logical trend was found on the average reversion of microtomed sections.

Mechanical properties

Tensile yield strength, tensile strength, elongation, modulus of elasticity and flexural modulus were measured at one position parallel to flow and two positions transverse to flow. Falling weight was carried out on the whole plaque. Mouldings had the lowest strength in a perpendicular direction to the flow of the melt in the cavity. With decreasing degree of orientation of the structure caused by increased temperature of the melt, isotropy of the mouldings increased moderately.
It was found that mechanical properties were not so uniquely related to the processing conditions as were weight and dimensions.

### Tensile properties

Tensile strength parallel to flow decreased with increasing melt temperature for PE and PP. Also modulus of elasticity decreased with increasing melt temperature for PP. Tensile strength increased with increasing mould temperature, but no effect was found from cavity pressure with PP.

### Falling weight impact

Falling weight impact decreased with increasing melt temperature for PP.

### Flexural modulus

Flexural modulus decreased with increasing melt temperature.

### Knoop-hardness

Knoop-hardness parallel and transverse to flow increased with increasing melt temperature.

### Falling-weight impact equipment

A minor part of the project which describes falling-weight tests should be presented as being of the greater practical importance not only for design but also for quality control purposes. With the presented procedure it should be easier to establish a satisfactory criterion of failure.

### Variation in properties

The considerable variability in properties found on selected positions over the moulding point to a subject of study which has been included in few investigations of physical property parameters of injection moulded specimens.
General conclusion

The study has resulted in a better understanding of the influence from processing variables on properties of semi-crystalline mouldings and hence provided a tool for optimizing the process.

The study has shown that it is necessary to include the combined effects of pressure, temperature and time during processing in any discussion of the effects of processing conditions on the structure and properties of injection mouldings.
Appendix AA

Isolation of injection moulding variables

The objective of the experiment was to determine the injection moulding variables which have the most significant influence on spiral mould flow length.

The experimental technique is describes by Kendrick\(^1\). The method which is based on a random balance technique is largely dependent on the assumption that the results obtained from a sample, drawn randomly from a population are applicable to that population.

The working procedure as described by Kendall is:

1. Define the requirements of the investigation and establish that the parameter (P) to be optimized can be measured in quantitative terms.

2. Establish all factors which impart variability to the process under investigation.

3. Specify a low, medium and high value for each of the variables defined in (2). A realistic range of values should be chosen to ensure a definite change in the measured parameter.

4. For each test sequence randomly allocate to Low (L), Medium (M), or High (H) values to each of the variables. A table of random numbers can be used for this purpose.

5. Complete each test sequence with the variables set at their randomly allocated levels and measure and tabulate the values obtained for the parameter (P). Care must be taken at this stage to ensure that the process under investigation is stabilized for each test sequence before results are taken.

\(^1\) C. Kendrick

Quality Control and Management

Plastics (1967) September, 1081-1084
6. Plot a graph for each variable with suitably chosen Low (L), Medium (M) and High (H) points on the abscissa, against which the measured values of parameter (P) are recorded. The arithmetic mean of the L, M and H values is calculated and the trend line drawn.

In the actual case it was thought that the spiral flow length could be a parameter representative of the mould filling. It can be argued that e.g. packing time probably is less significant with a long spiral length. The selection of machine variables is also a critical feature of the programme. Here the operating region diagram may define the boundary conditions.

**Experimental**

The injection moulding machine used in this experiment had the following data:

- **Netstal Neomat**: 150/173-3
- **Clamping force**: 735 kN
- **Shot volume**: ~120 cm³

The injection mould had a cavity for a spiral moulding with direct gating. The cross section of the trapezoidal channel was, \( a = 4.78 \text{ mm}, \ b = 5.96 \text{ mm}, \ h = 3.60 \text{ mm}, \ A = 19.3 \text{ mm}^2, \) pitch = 12 mm.

The flow length of the spiral could be read from points engraved in the cavity. The distance from the center to the points had been established using a Ferranti 3-coordinate measuring machine.

The moulding material was polystyrene (Hoechst N 4001 V).

The experimental processing conditions with the Low, Medium and High values are shown in the following table.
L, M, H values for processing variables (spiral mould)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Nozzle temperature (°C)</td>
<td>L 190</td>
</tr>
<tr>
<td></td>
<td>M 220</td>
</tr>
<tr>
<td></td>
<td>H 250</td>
</tr>
<tr>
<td>2. Heating zone 1 (front) (°C)</td>
<td>L 190</td>
</tr>
<tr>
<td></td>
<td>M 220</td>
</tr>
<tr>
<td></td>
<td>H 250</td>
</tr>
<tr>
<td>3. Heating zone 2 (middle) (°C)</td>
<td>L 180</td>
</tr>
<tr>
<td></td>
<td>M 210</td>
</tr>
<tr>
<td></td>
<td>H 240</td>
</tr>
<tr>
<td>4. Heating zone 3 (rear) (°C)</td>
<td>L 175</td>
</tr>
<tr>
<td></td>
<td>M 205</td>
</tr>
<tr>
<td></td>
<td>H 235</td>
</tr>
<tr>
<td>5. Mould temperature (°C)</td>
<td>L 10</td>
</tr>
<tr>
<td></td>
<td>M 20</td>
</tr>
<tr>
<td></td>
<td>H 30</td>
</tr>
<tr>
<td>6. Injection pressure (bar)</td>
<td>L 300</td>
</tr>
<tr>
<td></td>
<td>M 400</td>
</tr>
<tr>
<td></td>
<td>H 600</td>
</tr>
<tr>
<td>7. Injection velocity valve setting (4,0)</td>
<td>L (4,0)</td>
</tr>
<tr>
<td></td>
<td>M (4,8)</td>
</tr>
<tr>
<td></td>
<td>H (5,6)</td>
</tr>
<tr>
<td>8. Injection time (S)</td>
<td>L 2</td>
</tr>
<tr>
<td></td>
<td>M 4</td>
</tr>
<tr>
<td></td>
<td>H 6</td>
</tr>
<tr>
<td>9. Packing time (S)</td>
<td>L 0</td>
</tr>
<tr>
<td></td>
<td>M 4</td>
</tr>
<tr>
<td></td>
<td>H 8</td>
</tr>
<tr>
<td>10. Cooling time (S)</td>
<td>L 20</td>
</tr>
<tr>
<td></td>
<td>M 14</td>
</tr>
<tr>
<td></td>
<td>H 8</td>
</tr>
</tbody>
</table>

The random balance lay-out is shown in table A-1.

Results

For each test sequence an average of the length of ten mouldings has been calculated and the results presented in column $\bar{x}$ in the random balance lay-out. The maximum and minimum length was 791 and 153 mm respectively. For each of the variables the L, M and H value was plotted in a graph, the average calculated and the trend line drawn (fig. A1-A2).

According to Kendrick (op.cit.) those variables having a horizontal trend line may be regarded as having little effect on the measured parameter. Variables producing sloping trend lines have a significant effect on a degree which can be judged from both the slope of the line and the amount of scatter in the plotted test results. Thus the steeper the slope of the line and the smaller the scatter the more significant the variable.
<table>
<thead>
<tr>
<th>Test no</th>
<th>Parameter</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M H M M M M M H L L</td>
<td>499</td>
</tr>
<tr>
<td>2</td>
<td>H H L M L M L M L</td>
<td>555</td>
</tr>
<tr>
<td>3</td>
<td>L M H M M M H M M</td>
<td>289</td>
</tr>
<tr>
<td>4</td>
<td>M L H M M M L H L</td>
<td>449</td>
</tr>
<tr>
<td>5</td>
<td>H L H M L H L M M</td>
<td>763</td>
</tr>
<tr>
<td>6</td>
<td>L M L L H M L L H</td>
<td>266</td>
</tr>
<tr>
<td>7</td>
<td>L L H M L H M M L</td>
<td>505</td>
</tr>
<tr>
<td>8</td>
<td>L L H L L L M L M</td>
<td>173</td>
</tr>
<tr>
<td>9</td>
<td>H M M L H M M L L</td>
<td>556</td>
</tr>
<tr>
<td>10</td>
<td>H L M L L H H M L</td>
<td>710</td>
</tr>
<tr>
<td>11</td>
<td>L L H H H M L H M</td>
<td>298</td>
</tr>
<tr>
<td>12</td>
<td>M L L L H M L L H</td>
<td>375</td>
</tr>
<tr>
<td>13</td>
<td>L M M L L L L L H</td>
<td>153</td>
</tr>
<tr>
<td>14</td>
<td>M L L M L H M L H</td>
<td>572</td>
</tr>
<tr>
<td>15</td>
<td>L M M M H H M M M</td>
<td>434</td>
</tr>
<tr>
<td>16</td>
<td>L H L M M M M L L</td>
<td>427</td>
</tr>
<tr>
<td>17</td>
<td>H L M M M M H M M</td>
<td>566</td>
</tr>
<tr>
<td>18</td>
<td>H L L L H L L H L</td>
<td>395</td>
</tr>
<tr>
<td>19</td>
<td>L H L H H L L M H</td>
<td>202</td>
</tr>
<tr>
<td>20</td>
<td>M M L M H H H M M</td>
<td>627</td>
</tr>
<tr>
<td>21</td>
<td>H H L M L H M H H L</td>
<td>758</td>
</tr>
<tr>
<td>22</td>
<td>H M H H L M H L M</td>
<td>453</td>
</tr>
<tr>
<td>23</td>
<td>H M M H L H L M L</td>
<td>724</td>
</tr>
<tr>
<td>24</td>
<td>H M M H H H H H M M</td>
<td>791</td>
</tr>
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<td>25</td>
<td>M M M M M H H H H M</td>
<td>704</td>
</tr>
<tr>
<td>26</td>
<td>L H L H M L H H M M</td>
<td>203</td>
</tr>
<tr>
<td>27</td>
<td>M H M L M L H H M H</td>
<td>213</td>
</tr>
<tr>
<td>28</td>
<td>M H H L M L L H H</td>
<td>291</td>
</tr>
<tr>
<td>29</td>
<td>M H H L M L L H H</td>
<td>303</td>
</tr>
<tr>
<td>30</td>
<td>M H H H M L L L H H</td>
<td>290</td>
</tr>
</tbody>
</table>
Fig. AA-1 Effect of nozzle temperature on spiral flow length
Fig. AA-2 Effect of selected injection moulding variables on spiral flow length
Following these rules the likely significant variables in this particular exercise are nozzle temperature, rear zone temperature, mould temperature, injection pressure and injection speed.

There were some experimental difficulties in obtaining a water temperature lower than 13°C. Also two adjacent heating zones with a maximum difference in setting (e.g. nozzle temperature 250°C and heating zone 1 180°C) resulted in a 5 to 20°C higher temperature of the zone with the lowest setting.

Concluding remarks

Although the flow in a spiral mould cannot be compared to the flow in a fixed volume cavity, the exercise has proved the importance of certain parameters. It also draws attention to the various temperature zones of the cylinder.

It seems appropriate to investigate further the influence of the cylinder temperature profile with a variance analysis experiment.
Appendix AB

Experimental design for moulding of polyethylene

In the examination of the influence from the processing parameters it is desirable to isolate one variable and change it systematically while keeping all other factors constant and observing the effects. Unfortunately there is often an interaction between the various parameters.

Therefore a statistically designed experiment was conducted to establish the relationship between the moulding variables and the physical properties of the mouldings.

The experimental design, which is a part of a joint project with Mr. K. STUBGAARD on control systems for injection moulding machines, was based on a 1/3 fraction of a $3^4$ full factorial experimental design. The four moulding parameters and their selected coded levels, indicated with 0-1-2, which symbolizes low, middle and high level for the factor in question were:

- $P_c = \text{Maximum cavity pressure} = (0 = 200 \text{ bar, } 1 = 350 \text{ bar, } 2 = 500 \text{ bar})$
- $T_m = \text{Melt temperature} = (0 = 170 \text{ °C, } 1 = 220 \text{ °C, } 2 = 270 \text{ °C})$
- $T_f = \text{Mould temperature} = (0 = 30 \text{ °C, } 1 = 50 \text{ °C, } 2 = 70 \text{ °C})$
- $v_s = \text{Screw forward velocity} = (0 = 9 \text{ mm/s, } 1 = 18 \text{ mm/s, } 2 = 36 \text{ mm/s})$

The complete experiment is composed of a total of 27 sets of moulding conditions. Experimental design, numeration, and the experimental conditions are shown in Table AB-1. The principle in Table AB-1 is that the levels of the fourth factor have been coded in the diagonals of the diagram for the complete $3^3$ structure (3 factors at three levels). Determination of the main effect of the individual factors and possible interaction between variables are analyzed by means of a variance analysis.
### Table AB-1 Experimental design

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_f)</td>
<td>(T_m)</td>
<td>(T_m)</td>
<td>(T_m)</td>
<td>(T_m)</td>
<td>(T_m)</td>
<td>(T_m)</td>
<td>(T_m)</td>
<td>(T_m)</td>
<td>(T_m)</td>
</tr>
<tr>
<td>0</td>
<td>0002</td>
<td>0101</td>
<td>0200</td>
<td>0011</td>
<td>0110</td>
<td>0212</td>
<td>0020</td>
<td>0122</td>
<td>0221</td>
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<tr>
<td>1</td>
<td>1000</td>
<td>1102</td>
<td>1201</td>
<td>1012</td>
<td>1111</td>
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<td>1120</td>
<td>1222</td>
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<td>2</td>
<td>2001</td>
<td>2100</td>
<td>2202</td>
<td>2010</td>
<td>2112</td>
<td>2211</td>
<td>2022</td>
<td>2121</td>
<td>2220</td>
</tr>
</tbody>
</table>

In the experimental design the first digit indicates cavity pressure, the second melt temperature, the third mould temperature and the fourth screw forward velocity.

A consequence of using the partial structure instead of the complete structure is:

(i) The analysis of variance does not give the possibility of determining the interaction between the fourth factor and the remaining factors.

(ii) It is not possible to determine interactions of a higher order, that is three-factor interactions or four-factor interactions.

It should be noted, that the result of the analysis of variance makes it possible to check if the assumptions, that is, that the above interactions do not exist, are fulfilled.

The advantages of using a statistically designed experiment are:

(i) The influence from each factor (variable) is determined with greater certainty as the design allows a better utilization of the results (all experimental results are used for determination of the influence from each factor).

(ii) The experimental design allows the determination of possible interactions between the factors (variables). An interaction between two factors exists when the effect of one
factor varies with changes in the level of the other factor.

In summary the experimental design when analyzed by regression analysis provide the following information:
- main effects of variables
- relative significance of variables
- interaction between variables
- determination of correlation between variables and the physical properties of the mouldings
- estimate of experimental error.

The following Table AB-2 shows a summary of the results obtained in the project "Styring af sprøjtestøbprocessen (xxx", "xx", "x" indicate respective levels of significance, "-" indicate that no influence has been found. *)

*) Kaj Stubgaard: Styring af sprøjtestøbprocessen. Teknologisk Institut (1976)
Table AB-2 Influence from processing on properties

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>Tₘ</th>
<th>Tₖ</th>
<th>Vₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
<td>-</td>
</tr>
<tr>
<td>Radial shrinkage</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
<td>-</td>
</tr>
<tr>
<td>Different shrinkage</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
<td>-</td>
</tr>
<tr>
<td>Thickness</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
<td>-</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>X</td>
<td>XXX</td>
<td>-</td>
</tr>
<tr>
<td>Reversion, 20x20 mm</td>
<td></td>
<td>x</td>
<td>XXX</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td>X</td>
<td>XXX</td>
<td>X</td>
</tr>
<tr>
<td>Reversion 0.03 mm</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Knoop-hardness</td>
<td></td>
<td>-</td>
<td>-</td>
<td>XXX</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>xx</td>
<td>XXX</td>
</tr>
<tr>
<td>Tensile strength</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Tensile-impact</td>
<td></td>
<td>-</td>
<td>-</td>
<td>XXX</td>
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<td></td>
<td></td>
<td>-</td>
<td>x</td>
<td>XXX</td>
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<td>Impact-bending</td>
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<td>xx</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td>XXX</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>Falling-weight</td>
<td></td>
<td>XX</td>
<td>XXX</td>
<td>XXX</td>
</tr>
</tbody>
</table>

AB-4
Appendix B

Raw material variation

Raw material variation is a disturbance which is known to influence processing, but only little information has been published on the variation found between different batches.

Therefore a small programme was initiated with the purpose of screening samples taken from delivery of 4 shipments of polyethylene and 11 shipments of polypropylene (3 different grades) covering a period of approximately 3 months, and a total quantity of approximately 500 tonnes delivered in lots of 30 and 50 tonnes from two raw material suppliers.

The samples were characterized by melt index (2,16 - 5,0 - 21,6 kp load) and GPC using tri-chlorobenzene as a solvent.

The following results were obtained (Table B-1)

Table B-1. Melt index and GPC of PE and PP

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melt index (g/10 min)</th>
<th>GPC ((R))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nr</td>
<td>2,16</td>
<td>5,0</td>
</tr>
<tr>
<td>10</td>
<td>15,80</td>
<td>46,0</td>
</tr>
<tr>
<td>11</td>
<td>15,90</td>
<td>46,0</td>
</tr>
<tr>
<td>14</td>
<td>15,40</td>
<td>45,0</td>
</tr>
<tr>
<td>15</td>
<td>17,00</td>
<td>52,0</td>
</tr>
</tbody>
</table>

**Polypropylene**

(Hoechst Hostalen 1270)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melt index (g/10 min)</th>
<th>GPC ((R))</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2,00</td>
<td>10,1</td>
</tr>
<tr>
<td>12</td>
<td>2,10</td>
<td>10,6</td>
</tr>
<tr>
<td>13</td>
<td>2,50</td>
<td>12,6</td>
</tr>
</tbody>
</table>

*) Using a chromatograph (Waters) at the Pharmaceutical High School, where the assistance of Mr. V. Handloos is greatly appreciated.
(Montedison T 30 G)

<table>
<thead>
<tr>
<th></th>
<th>An</th>
<th>Aw</th>
<th>Mn</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.05</td>
<td>5.0</td>
<td>120</td>
<td>2925</td>
</tr>
<tr>
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<td>5</td>
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<td>6</td>
<td>1.03</td>
<td>4.8</td>
<td>122</td>
<td>2120</td>
</tr>
</tbody>
</table>

(Montedison T 30 S)

<table>
<thead>
<tr>
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<th>An</th>
<th>Aw</th>
<th>Mn</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
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<td>4.8</td>
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</tr>
<tr>
<td>8</td>
<td>1.15</td>
<td>5.2</td>
<td>118</td>
<td>2121</td>
</tr>
</tbody>
</table>

A_n = number average length  
A_w = weight average length  
A_w/A_n = ratio of polydispersity.

Caution is required in interpreting the results, as no calibration curve was established and the data not corrected for calculation of molecular weight. For a relative work, however, where relative values for each grade are of interest, the data provide a primary interpretation in terms of molecular-size distribution (which is not necessarily equivalent with molecular weight distribution) with other samples a larger variation may also be found.

It is apparent, however, that a variation does exist as seen from the ratio of polydispersity. It is also clear, that an increasing load on the melt indexes tend to give a better discrimination between the samples. No clear correlation between the two methods was found. From actual production of the articles (syringes) processing of the polymer with most variation (Hostalen 1210) tended to make an adjustment of the temperature of the needle of the hot-runner necessary. However, more work is needed to elucidate these problems.
Appendix C

Measurement of the Mould Cavity Surface Temperature using Thermography

The mould surface temperature is of dominating influence on the surface condition as well as the skin layer of injection moulded articles. These properties are influenced not only by the level of temperature and its variation during a cycle, but also by the temperature distribution across the mould surface.

It is therefore of interest to measure the temperature distribution and to see if it correlates with the variation of surface properties.

If a measure of the temperature distribution is desired, and not just a single point reading, an instrument capable of scanning the surface must be used. This is possible using a technique termed thermography where infrared heat radiation emitted from body surfaces can be measured and recorded.

The instrument used in this work was the AGA Model 750 Thermovision™. It consists of a detector or camera unit and the image display units (televisionscreens).

The essential part of the camera is an infrared detector which, when cooled by nitrogen at minus 196°C, can register and monitor temperature differences down to 0,2°C in the range -30°C to +2000°C.

As the unit scans across the object the intensity from the black body radiation is measured. As the object heats up, this intensity increases in a well defined manner*).

*) Planck's Radiation Law:

\[ I = K \cdot f^5/ [\exp (Df/T)-1] \]

where \( f \) is frequency, \( T \) is temperature and \( K \) and \( D \) are constants.
With appropriate circuitry the changing intensity signal is converted to changing brightness of a line on a black and white television screen. In this manner a black and white thermal image is created on the monitor.

The instrument can be calibrated so that the lowest temperature level corresponds to a black image. Then a temperature range $\Delta T = T_2 - T_1$ can be selected so that $T_2$ corresponds to the highest temperature.

On the display all points of the object with a temperature equal to or higher than $T_2$ appear white. Points with a temperature equal to or lower than $T_1$ will appear black. Temperatures between $T_1$ and $T_2$ are represented by a grey value scale, which is also visible on the display.

The instrument can also be adjusted so that all points with equal temperature (isotherms) appear white. Subtle differences in temperature may be difficult to observe in a black and white image, so a colour display is also available. In this mode the range of temperatures are broken up into ten equal increments. Each interval is assigned a particular colour and as the device scans the object, these different colours are displayed as different colours. The span of the isotherms can be selected. Usually $1/10$ of the temperature span is chosen.

Compared with other temperature measuring equipment the thermography method has the following advantage:

i) It can measure instantaneously across the surface of an object.

ii) The object is not influenced by the measurement.

As a disadvantage a measurement of true temperature when an object (e.g. a mould surface) differs significantly from the black body ideal involves calibration at an accurately measured temperature together with some calculation. A program-
able pocket calculator facilitate this work. Relative temperatures across an object are accurate without this calibration.

A more serious hindrance was found when measurements were carried out with the injection mould fitted in the injection moulding machine, as it was found that this was not possible, due to stray reflections from the surroundings, especially from the hotter part of the machine.

Therefore only static measurements are recorded in the following experiment.

**Experimental**

1) By way of introduction the surface temperature of the injection mould for tensile dumb bells were measured in a static arrangement with one half of the mould placed on a table, but connected with the mould tempering unit (Churchill Captain using water as cooling medium at a pressure ~7 bar). The temperature was set at 65°C on the tempering unit. As a reference the surface temperature was also measured with a contact thermometer with digital reading (Therm-Serie 3220) with compensation for heat transfer through the sensor for contact measurement.

The result of the thermography measurement can be seen in fig. C-1a. It shows how the different isotherms represented by different colours are placed around the cooling channels. In order to increase the intensity of the radiation, and with that the contrast, the mould has, in this case, been sprayed with a coat of black paint. Fig. C-1b shows the corresponding measurement with the contact thermometer.
Fig. c. a) Thermograph of mould for tensile dumb bell  
b) Mould temperatures measured with contact thermometer
2) The main experiment was also done in a static arrangement with the quadrant mould with a cavity thickness of 5 mm and with variation of the mould temperature on six levels 20-40-60-80-100-120°C.

The temperature of the mould cavity was measured with thermocouples 0,5 mm under the surface cavity and in a distance of 60 and 99,3 mm from the center of the quadrant. The temperature on these positions were recorded on a potentiometric recorder. The mould tempering unit was set so that the recorded temperature as far as possible corresponded with the nominal temperature. When stable conditions were achieved the mould surface temperature was measured with contact thermometer (on the positions corresponding to Fig. 6.13 in sect. 6.8.1) and by taken colourphotographs of the image display.

Table C-1 shows the result for measuring points corresponding to the position of the thermocouples. The table shows that in order to achieve a mould temperature of a given level it is necessary to set the mould tempering unit on a temperature higher than the nominal level. That is, if the mould temperature should be 120°C it is, under the given condition (static arrangement), and with the tempering unit in question, necessary to set the tempering unit at approximately 136°C.

The table also shows, at a temperature higher than room temperature (22°C), a good agreement with the temperature registered with recorder and the temperature measured with contact thermometer. Generally the temperature is lower on the surface than 0,5 mm below the surface, due to heat loss by radiation to the surroundings.

Apart from the highest temperature there is a good agreement between the measurement with the contact thermometer and the measurement with thermography on the position 60 mm
Table C-1
Measurement of the Mould Cavity Surface Temperature of a 100 mm Quadrant Mould using Thermography

<table>
<thead>
<tr>
<th>Tempering unit Temperature Nominal (°C)</th>
<th>Set 1) (°C)</th>
<th>Recorder Measured temperature 2) Center (°C)</th>
<th>Periphery (°C)</th>
<th>Contact thermometer Measured temperature 3) Center (°C)</th>
<th>Periphery (°C)</th>
<th>Thermography Measured temperature 4) Center (°C)</th>
<th>Periphery (°C)</th>
<th>Coefficient of emissivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20</td>
<td>20,2</td>
<td>20,7</td>
<td>22,2</td>
<td>22,3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>42</td>
<td>39,0</td>
<td>39,1</td>
<td>38,2</td>
<td>38,3</td>
<td>38,1</td>
<td>42,1</td>
<td>0,10</td>
</tr>
<tr>
<td>60</td>
<td>72</td>
<td>59,9</td>
<td>59,6</td>
<td>59,5</td>
<td>59,4</td>
<td>59,0</td>
<td>66,5</td>
<td>0,10</td>
</tr>
<tr>
<td>80</td>
<td>92</td>
<td>80,1</td>
<td>79,9</td>
<td>79,0</td>
<td>78,4</td>
<td>77,8</td>
<td>89,1</td>
<td>0,12</td>
</tr>
<tr>
<td>100</td>
<td>113</td>
<td>99,9</td>
<td>99,5</td>
<td>99,3</td>
<td>99,6</td>
<td>100,9</td>
<td>104,7</td>
<td>0,13</td>
</tr>
<tr>
<td>120</td>
<td>136</td>
<td>120,8</td>
<td>120,4</td>
<td>120,7</td>
<td>121,0</td>
<td>116,7</td>
<td>122,2</td>
<td>0,14</td>
</tr>
</tbody>
</table>

Accuracy of reading: 1) ±2°C  2) ±0,3°C  3) ±0,3°C  4) ±1,5°C

Room temperature: 22°C
from the center, whereas there is less agreement on the position 99.3 mm from the center. It is assumed that on the last-mentioned position occur reflections from the merging surfaces in the mould cavity, which influence the reflection and hence the measurement. This circumstance illustrates the practical problems in using the equipment.

Finally, the last column in the table shows, as expected, that the coefficient of emissivity increases with temperature.

The corresponding calculation for other positions was not done. However, as can be seen from the combined photograph (fig. C-2, b) the thermography measurement gave an excellent qualitative image of the temperature variation across the mould surface. For mould temperatures up to approximately 100°C this variation was approximately 3-5°C, for higher temperatures up to approximately 80°C.

Conclusion

Temperature measurement with thermography has the advantage that an instantaneous image of the temperature variation across the mould surface can be obtained.

The physical arrangement made it difficult to view the mould when fitted in the injection moulding machine. Difficulties with stray reflections, especially from the heaters were noted.

Measurement of true temperature involves calibration from a reference together with some calculation.

Under static conditions with the mould halves placed on a table correspondently reliable results could be achieved by using a contact thermometer.

For a continuous registration of the mould temperature the built-in thermocouples connected to a recorder appears to be the best solution.
a) Temperature source used as a reference

Position of thermocouples

Quadrant r = 100 mm

Fig. C-2a) Thermograph of quadrant mould $T_n = 40^\circ C$

b) Change in temperature distribution with temperature ($T_n = 20-120^\circ C$)

C-8
Appendix D

Determination of Morphology with Quantitative Image Analysis

Quantitative Image Analysis of injection moulded specimens can provide information about the morphology in quantitative terms. Such information may form the basis for an optimization of the morphology, e.g. through a statistically designed experiment which comprises the proper processing variables.

The theoretical basis of the latest developments of the technique, the Leitz Texture Analyzing System (T.A.S.)\(^1\) is the mathematical morphology developed by Matheron\(^2\) and Serra\(^3\). It has been used mainly within the field of metallurgy. In principle, the methodology is also applicable to other branches of materials science. For polymers, however, references have only been found for investigations of plastic foams.\(^1\)

Apparatus

The Leitz-T.A.S. was introduced to the market in 1974. Its principal components are shown in Fig. D.1. It is composed of a macro- or a microscope (Leitz Orthoplan) a closed circuit television system with a camera (Bosch), an operator screen and a (5x) larger external monitoring screen, a control desk with a data processing unit (Leitz), a computer (Hewlett Packard 9830 A), and an output A4 thermo-printer. Further tech-

---

2) G. Matheron, Elements pour une théorie des milieux parcux Masson (1967)
Technical data are given in 1). A detailed description of the apparatus is given in Reference R2.

---

![Texture Analyzing System with block-diagram.](image)

**Fig. D.1 Texture Analyzing System with block-diagram.**

The image from the object to be investigated is taken up by the macro- or microscope and projected onto the lightsensitive layers of the television tube and scanned line-by-line. Image features are selected by their grey value and different brightnesses are transformed into electrical signals for quantitative processing. The image features selected for measurement are discriminated brightly on the television monitor screen together with the corresponding grey-value interval of a grey scale. Electronic devices offer the additional advantage that a disturbingly inhomogeneous background in the specimen can be
removed. Also the spatial relationships (contact areas, topographical relations of several non-adjacent components to one another) of more than two different components can be analyzed by use of two electronic discriminators.

The counting principle applied can be described as follows: The pattern of lines, the raster, which scan the fluorescent screen in the television receiver consist of 400,000 - 500,000 points distributed evenly over the picture field. Fig. D.2 shows some particles from a picture in the field of lines on the television screen.

![Fig. D.2 Principle of counting](image)

It is assumed that these particles have the same grey value in relation to its surroundings. A counting pulse is then produced at every point of intersection between a line and the contour of a particle. An analysis consists in counting the number of intersections within the areas. Based on this counting various parameters can be calculated.

The apparatus is also equipped with a two-dimensional analysis function where a hexagonal scanning element is used to generate image data. This is used with complex connected image features occurring, for instance in plastic materials. As it is often necessary to have an exact reference for the measurements the object area can be covered in part or completely with measuring fields (masks) of various forms and sizes with known dimensions. The form of the mask can vary from rectangular to square and circular or it can be reduced to a single line.
The resolving power of the apparatus is determined by the macro- or microscope.

**Experimental**

The experimental work was divided in three phases

(i) Initial investigation using the elements; area, chords and particle size distribution

(ii) Investigation of specimens moulded with variation of processing conditions

(iii) Development of the analytical procedure using covariance analysis.

The initial investigation was carried out on a 20 μm microtomed section cut from a tensile test bar of polyoxymethylene (Delrin 500)\(^4\) (Fig. D.3).

Various functions of the equipment were tried by scanning in steps of 20 μm (1. step 1.5 μm relative) with a band width of 15 μm over a total of 450 μm of the section from the surface towards the center.

For the following functions a print-out was made:

1. Area of a particular grey value in a 15 μm wide band
2. Number of particles in a 15 μm wide band
3. Total number of chords in a 15 μm wide band
4. Number of chords longer than 1.5 μm in a 15 μm wide band
5. Number of chords longer than a given size (from 1.5 μm to 15 μm) in a 15 μm wide band.

The results for functions 1-4 are shown in Fig. D.4.

Investigation of specimens moulded with variation of processing conditions was carried out on 10 μm microtomed sections from tensile bars of polyoxymethylene (Hoechst C 9010) moulded with variation of mould temperature and screw forward time (see Table

\(^4\) The microtomed section was supplied from Du Pont de Nemours Geneve by the courtesy of Mrs. E. Böhme.
Fig. D-3 Microtomed section of polyoxymethylene
Fig. D-4 Morphology characterized by image analysis.
Only results from the variation of mould temperature are presented here.

The following functions of the apparatus were used:

1. Area of a particular grey value
2. Vertical projection
3. Number of chords
4. Two-dimensional particle size distribution according to the minimum inscribed circle diameter.

Contrary to the first investigation a band was not used as a measuring field. Instead a mask system with the following dimensions was chosen (Fig. D.5.)

![Mask system for measurement of POM morphology.](image)

With this form of measuring field each result is an average of three determinations.

The results for the first function used - area (in percent) of a particular grey value - have been drawn in the graphs, based on the print-out from the computer (Fig. D.6 to D.9).

In the graphs the dotted lines represent the extension of zone I, II and III, respectively, as determined with a stage micrometer using on optical microscope. It can be seen, that there is a reasonably agreement between the two methods.

Development of the analytical procedure using covariance analysis was initiated with the purpose of quantifying the morphology directly, e.g. as a description of shape size and distribution of spherulites as a function of distance from the surface of the moulding.
Due to the complexity of the problem, e.g. the fact that few isolated image figures are found in the texture, this work has mainly consisted in a review of published work on related cases mainly from metallurgy. However, it was soon clear from the studies that only the analytical methods which can be performed with the Leitz - T.A.S. apparatus, using two-dimensional structuring elements offers a possibility for solution, at least at the time of writing.

Therefore an outline of the theory of covariance analysis, which is a branch of mathematical morphology is given.

In principle this measurement is carried out with the aid of a scanning element which contains two test points the distance of which from each other can be freely chosen. The measured value is the frequency at which both points (at a given distance) are situated in the selected components.

Results

The result of the initial investigation (Fig. D.4) shows the same general trend. In an area up to approximately $50 \mu m$ the surface layer is so finely textured that it appears homogeneous. In the following layer the apparatus can resolve particle structures corresponding to the spherulites present in this layer. This means that the counted number of particles increases. The number of chords in this layer first increases and then decreases corresponding to the increasing particle size.

In the microscopical observation it was found that zone I could be divided in two regions reaching approximately $110 \mu m$ and $180 \mu m$ from the surface respectively. This gives a fairly good agreement with the quantitative analysis, where it was found that the intermediate zone II starts approximately $200 \mu m$ from the surface corresponding to the steep rise of the curve. Zone II terminates at approximately $525 \mu m$. The curve also reveals large variations in the texture which also was clear from the microscopical observation.
The covariance and the variogram function

The covariogram and a similar function known as the variogram have provided an efficient way of analyzing metallographic structures, e.g. inclusions in steel\(^5\) or different structures mixed with each other.

The definition and the mathematical derivation is described in detail in ref. 5.

This function was tried directly on the above mentioned microtomed samples with 16x incident light and the following raster mask:

Size of raster points: \(a = 0.6098 \, \mu m\)
\[\begin{align*}
    x &= 370 \, \mu m \\
    y &= 50 \, \mu m
\end{align*}\]

The results, which were only exploratory were printed out in the form of tables, which were redrawn. In principle, the pattern shown with the other function were found. A further refinement of the technique as described in ref. 5 should allow calculation of the apparent size of spherulites in a particular plane.

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Appendix E

Calculation of two-dimensional monoaxial orientation based on reversion of biaxial oriented specimens

A monoaxial orientation in a specimen will after heating to a temperature above $T_g$ change to an isotropic state, which will cause a change of dimension in three directions. In the direction of orientation the specimen will decrease its dimensions, but dimensions in the two other directions will increase. The volume, however, will remain constant, assuming that the reversion will not lead to a change in density.

Hence

$$l_o \cdot b_o \cdot t_o = l_r \cdot b_r \cdot t_r$$  \hspace{1cm} (1)

Where

$l, b, t =$ length, width and thickness of the specimen and the subscript "o" indicate the dimension before recovery and "r" is the dimension after recovery.

A biaxial orientation in a specimen can be considered as composed of a monoaxial orientation in two directions perpendicular to each other superimposed to form the biaxial orientation.

The change in dimensions which can be measured after a heat treatment can form the basis for an estimation of orientation in a specimen.

Wiegand and Vetter\(^1\) have elaborated on this concept and proposed that a measurement of orientation should be based on strain instead of reversion. Therefore a brief outline of this concept will be made in the following.

Based on statistical thermodynamics Wiegand and Vetter have developed the following equation for the force acting on a single molecule

\(^1\) H. Wiegand und H. Vetter, Molekulare Orientierung in Spritzgussteilen als Folge der Verarbeitung

I : Kunststoffe, \textit{56} (1966) H. 11, 761-769

II : Kunststoffe, \textit{57} (1967) H. 4, 276-284
\[ F = k \cdot T \cdot h/z \cdot a^2 \]  

(2)

where

\begin{align*}
  k & = \text{constant} \\
  T & = \text{thermodynamic temperature} \\
  a & = \text{length of molecule with } z \text{ free elements} \\
  h & = \text{distance between ends of molecule}
\end{align*}

Provided this equation can be applied to the molecular conformation, then the deformation will be proportional to the force, and using the principle of superposition the two-dimensional strain can be calculated from the uniaxial strain in the two directions.

Consider a three-dimensional volume element with the sides \( a, b \) and \( c \). A force \( F_{ii} \) acting in one direction strains the dimension \( a \) to \( \varepsilon_{ii} a \) and contracts the dimension \( b \) with \( \gamma \varepsilon_{ii} b \). The lateral force \( F_{ij} \) strains \( b \) to \( \varepsilon_{ij} b \) and \( a \) contract with \( \gamma \varepsilon_{ij} a \) (where \( \gamma \) is Poisson's ratio).
If the two forces are acting simultaneously then the two uniaxial strains can be added

\[ \varepsilon_n = \bar{\varepsilon}_n - \gamma \bar{\varepsilon}_\perp \] (3)

\[ \varepsilon_\perp = \bar{\varepsilon}_\perp - \gamma \bar{\varepsilon}_n \] (4)

Hence the strain by uniaxial acting forces

\[ \bar{\varepsilon}_n = \varepsilon_n + \gamma \varepsilon_\perp / (1 - \gamma^2) \] (5)

\[ \bar{\varepsilon}_\perp = \varepsilon_\perp + \gamma \varepsilon_n / (1 - \gamma^2) \] (6)

Hence the ratio of lateral strain to the longitudinal strain \( \tilde{\gamma} \) as a function of \( \bar{\varepsilon} \) for deformations with constant volume is given by

\[ \tilde{\gamma} = 1 \sqrt{\frac{1}{1 + \bar{\varepsilon}}} / \bar{\varepsilon} \] (7)

For small deformations \( \gamma \) is of the order of 0.5. Orientation in injection moulded specimens, however, causes a high deformation, which means that the calculation of reversion should be based on a variable ratio of lateral strain to longitudinal strain using equation (7).

Calculations with a variable ratio can be based on equation (3) and (4), which can be written:

\[ \varepsilon_n = \bar{\varepsilon}_n - \bar{\gamma}_\perp \bar{\varepsilon}_\perp \] (8)

\[ \varepsilon_\perp = \bar{\varepsilon}_\perp - \bar{\gamma}_n \bar{\varepsilon}_n \] (9)

and hence the strain by an uniaxial acting force:

\[ \bar{\varepsilon}_n = \varepsilon_n + \bar{\gamma}_\perp \varepsilon_\perp / (1 - \bar{\gamma}_\perp \bar{\gamma}_n) \] (10)

\[ \bar{\varepsilon}_\perp = \varepsilon_\perp + \bar{\gamma}_n \varepsilon_n / (1 - \bar{\gamma}_\perp \bar{\gamma}_n) \] (11)

By using equation (10) and (11) the uniaxial reversion \( \bar{R}_\perp \) and \( \bar{R}_n \) can be calculated from the dimensions measured on the sample \( \bar{R}_\perp \) and \( \bar{R}_n \) using a simultaneous approximation,
provided the reversion values are converted to strain values as given by

\[ \varepsilon = \frac{R}{(1-R)} \]  \hspace{1cm} (12)

This relation can be plotted in a graph.

For high reversion values the strain increases more than proportional. As an example a reversion of 80% corresponds to a strain of 400%. Therefore it seems quite appropriate to characterise orientation by strain values.

The calculations, however, are still based on several assumptions, not all of which have been investigated. For semi-crystalline polymers, where the problems associated with orientation are even more complex than for amorphous polymers, the substitution of the variable Poisson's ratio, with a constant ratio (of 0.5) seems justified. The reversion is generally also smaller for semi-crystalline materials and the relation between biaxial orientation and mechanical properties complex.

Therefore the experimental work reported in section 8.7 will be based on the following simplified concept using a constant Poisson's ratio.
Calculation of two-dimensional monoaxial orientation based on reversion of biaxial oriented specimens using constant Poisson ratio

Reversion tests, taking the biaxial orientation into account, have been reported by Wübken\(^2\) and by Heron et al\(^3\).

Fleissner and Paschke\(^4\) have investigated reversion of microtomed high density polyethylene, but did not compensate for biaxial orientation.

Therefore, before the work on reversion of semi-crystalline microtomed sections was started, reversion tests on 20 x 20 x 3 mm samples from an amorphous (PS) and a semi-crystalline (PE) polymer were carried out.

The analytical part and the equation used are basically those developed by Wübken, based on the following assumptions:

(i) the volumes of the specimens are the same before and after the heat treatment (eq. 1)

(ii) the dilation (expansion) in the length and thickness direction after reversion caused by transverse orientation is of the same order

2) Gottfried Wübken
   Einfluss Der Verarbeitungsbedingungen Auf Die Innere Struktur Thermoplastischer Spritzgussteile Unter Besonderer Berücksichtigung Der Abkühlverhältnisse
   Dissertation RW TH Aachen (1974)

3) H. Heron, S. Pedersen and L.L. Chapoy
   Linear viscoelastic theory and the understanding of orientation, recoverable strain and mechanical properties resulting from thermoplastic processing

4) M. Fleissner und E. Paschke
   Orientierungszustände und mechanische Eigenschaften von dünnwandigen Spritzgussteilen aus Niederdruck-Polyäthylen
   Kunststoffe 61 (1971) H. 3, 195-203
\[ \frac{1}{I_{0}} = \frac{t_{r}}{t_{o}} \]  
(13)

and

\[ \frac{b_{r}}{b_{o}} = \frac{t_{r}}{t_{o}} \]  
(14)

Combining equation (1), (13) and (14) shows that a transverse orientation (subscript \( \perp \)) causing a reversion in the transverse direction leads to a dilation in the longitudinal direction (subscript \( \parallel \)) of

\[ \Delta l = (l_{r} - l_{o})_{\perp} = 1 \left( 1 - \sqrt{\frac{b_{r}}{b_{o}}} \right)_{\perp} \]  
(15)

This shows that a biaxial orientation increases the longitudinal reversion with the value \( \Delta l_{\perp} \) arising from the transverse orientation. Assuming the measured values can be superimposed then

\[ \Delta l_{\parallel} = \Delta l_{r} + \Delta l_{\perp} \]  
(16)

and hence based on equation (1), (13), (14), (15) and (16) the corrected reversion ratio

\[ \frac{\frac{1}{l_{r}}}{\frac{1}{l_{o}}} = \frac{1}{1 + \sqrt{\frac{b_{r}}{b_{o}}} \left( \frac{1}{l_{o}} \right)} \]  
(17)

and

\[ \frac{b_{r}}{b_{o}} = \frac{1}{1 + \sqrt{\frac{b_{r}}{b_{o}}} \left( \frac{1}{l_{o}} \right)} \]  
(18)

As the ratio under the square root is unknown the calculation must be carried out by simultaneous approximation (iterative calculation) where the ratio in the first approximation is substituted by the measured values.

The equations (17) and (18) in this form correspond to the work of Wiegand and Vetter, but are very much simpler as they are based on length and width ratios, and not strain-values and a variable Poisson ratio.
If, instead of the corrected dimensional ratios, the reversion values are sought - which in the experimental work have been termed - revised and compensated reversion, then they can be found from

\[
R_n^* = 1 - \left( \frac{\text{r}}{\text{i_0}} \right)_n
\]

(19)

\[
R_\perp^* = 1 - \left( \frac{\text{b_r}}{\text{b_o}} \right)_\perp
\]

(20)

which is the uniaxial reversion in two directions based on biaxial oriented specimens.
Appendix F

Determination of correction factor for incremental energy contributed by the crosshead

The calculation is based on the appendix to DIN 53 448.

If the calculation of correction factor is based on the theory of an inelastic impact the following formula for the corrected impact is used:

\[ W_{zn}' = W_s - \frac{(W_0 - W_s) m_q}{m_p} \]

If the calculation is based on the theory of an elastic impact the following formula for the corrected impact is used:

\[ W_{zn}'' = \left( W_s - W_q \right) \frac{W_0}{W_0 - W_q} \]

where

- \( W_0 \) Energy of pendulum
- \( W_s \) Energy recorded on the dial (Scale reading)
- \( W_q \) Experimentally determined "elastic energy" for crosshead (at full falling height of pendulum)
- \( m_p \) Reduced mass of pendulum
- \( m_q \) Mass of crosshead

As the actual impact will be somewhere between the two extremes - inelastic and elastic impact - the arithmetic mean has been used for the determination of the following correction curve:

\[ W_{zn} = \frac{W_{zn}' + W_{zn}''}{2} \]

The curve shows the corrected energy for an impact energy of 75 kpcm and a 60 g crosshead.
Fig. F-2 Correction factor for impact energy for 75 kpcm pendulum and 60 g crosshead
Appendix GA

Computer programme for calculation of two-dimensional mono-
axial orientation based on reversion of biaxial oriented
specimens

PROGRAM: FOLIE.FR

HOUSEKEEPING
REAL L(3,5), B(3,5), S(3), LK(100), LB(100)
INTEGER IBL(100), ITIME(3), IDAY(3), NR(3)
DIMENSION TEST(7), TEXT(70)
RBLK = -9.0
SLRLK = -8.0
SLRBK = -7.0
ISIDE = 1

OVERSKRIFTER-FØRSTE GANG
WRITE(10,1000)
PAUSE - TEND FOR "$PTP", STRIKE ANY KEY
CALL OPEN (1, "$PTP", B)

INDLESNING AF DATA - FØRSTE GANG
READ(9,2000) KA, TEST, TEXT
IF(KA.NE.11)GO TO 5
WRITE(12,1001,ISIDE
WRITE(12,1002)
WRITE(12,1004)
GO TO 2

INDLESNING AF EMNEIDENTIFIKATION
READ(9,2000,END=20), KA, TEST, TEXT
IF(KA.NE.11)GO TO 5

OVERSKRIFTER
WRITE(12,1003) ISIDE
WRITE(12,1002)
WRITE(12,1004)
WRITE(12,1005)TEST, TEXT
WRITE(12,1004)
WRITE(12,1006)
WRITE(12,1007)
WRITE(12,1004)

NULSTILLINGER
INR = 1
DO 7 I=1,100
LK(I) = 0
LB(I) = 0
7 CONTINUE
IANT = 0
IBLK = 0
IGANG = 1
SUMB = 0
SUML = 0

GA-1
C  
INDLÆSNING OG TEST
3 READ(9,2001,END=5)KA,NR(1),L(1,1),L(1,2),B(1,1),B(1,2)
  IF(KA.EQ.12)GO TO 4
  IF(KA.EQ.13)GO TO 18
  IF(KA.EQ.0)GO TO 4
  GO TO 5
4 IF(L(1,2).EQ.0.AND.B(1,2).EQ.0)GO TO 1
  IF(L(1,2).EQ.0.OR.B(1,2).EQ.0)GO TO 6
  IF(L(1,1).EQ.0)L(1,1)= LS
  IF(B(1,1).EQ.0)B(1,1)= BS
  GO TO 21
C  
FEJLÆRDELSEL
5 STOP-FEJL I K.A.
6 WRITE(10,1012)NR(1),TEST
  LK(INR) = RBLK
  LB(INR) = RBLK
  INR = INR + 1
  GO TO 3
C  
BEREKNING AF X(1,3)
21 L(1,3) = (L(1,1)-L(1,2))*100/L(1,1)
  B(1,3) = (B(1,1)-B(1,2))*100/B(1,1)
C  
BEREKNING AF X(1,4) VED ITERATION
  TESTL = L(1,2)/L(1,1)
  TESTB = B(1,2)/B(1,1)
  9 TRYL = (1/(1+(1/(L(1,2)/L(1,1)))-SQRT(TESLT)))
  TRYB = (1/(1+(1/(B(1,2)/B(1,1)))-SQRT(TESBT)))
  DIML = DIM(TRYL,TRYL)
  DIMB = DIM(TRYB,TRYB)
  IF(DIML.LE.0.005.AND.DIMB.LE.0.005)GO TO 10
  TESTL = TRYL
  TESTB = TRYB
  GO TO 9
10 L(1,4) = TRYL
  B(1,4) = TRYB
C  
BEREKNING AF X(1,5)
  L(1,5) = 1-L(1,4)
  B(1,5) = 1-B(1,4)
C  
SUMMATIONER AF X(1,5)
  SUML = SUML + L(1,5)
  SUMB = SUMB + B(1,5)
C  
BEREKNING AF "S(1)"
  S(1) = 1/((L(1,2)/L(1,1))-(B(1,2)/B(1,1)))
C  
TEST PÅ FØRSTE GENNEMLØB A.H.T. MAX.-VÆRDIER
  IF(IGANG.NE.1)GO TO 13
  DO 11 I=2,3
    DO 12 J=1,5
      L(I,J) = L(I,J)
      B(I,J) = B(I,J)
    12 CONTINUE
  S(I) = S(1)
  NR(I) = NR(1)
11 CONTINUE
13 IGANG = 2
TEST PÅ STØRSTE R(L)

IF (L(1,4) .LE. L(2,4)) GO TO 15
DO 14 J=1,5
L(2,J) = L(1,J)
B(2,J) = B(1,J)
14 CONTINUE
NR(2) = NR(1)
S(2) = S(1)

TEST PÅ STØRSTE R(B)

15 IF (B(1,4) .LE. B(3,4)) GO TO 17
DO 16 J=1,5
L(3,J) = L(1,J)
B(3,J) = B(1,J)
16 CONTINUE
NR(3) = NR(1)
S(3) = S(1)
17 CONTINUE

UDSKRIFT AF EMNERESULTAT

WRITE(12,1008) NR(1), L(1,1), L(1,2), B(1,1), B(1,2), L(1,3), B(1,3)
#L(1,4), B(1,4), L(1,5), B(1,5), S(1)
LS = L(1,1)
BS = B(1,1)
LK(INR) = L(1,4)
LB(INR) = B(1,4)
INR = INR + 1
IANT = IANT + 1
GO TO 3

MANGLENDE EMNER - REGISTRERING

1 IBLK = IBLK + 1
IBL(IBLK) = NR(1)
LK(INR) = RBLK
LB(INR) = RBLK
INR = INR + 1
GO TO 3

AFSLUTNINGSRUTINER

18 SUML = SUML / IANT
SUMB = SUMB / IANT

UDSKRIFT AF PAPER-TAPE

WRITE (1,1015) TEST
INR = INR - 1
DO 22 I=1,INR
WRITE(1,1016)LK(I)
22 CONTINUE
WRITE(1,1016) SLRLK
DO 23 I=1,INR
WRITE(1,1016)LB(I)
23 CONTINUE
WRITE(1,1016) SLRBK

UDSKRIFT AF MAX.-VÆRDIER

DO 19 I=2,3
IF (I.EQ.2) WRITE(12,1009)
IF (I.EQ.3) WRITE(12,1010)
WRITE(12,1008) NR(I), L(I,1), L(I,2), B(I,1), B(I,2), L(I,3), B(I,3),
#L(I,4), B(I,4), L(I,5), B(I,5), S(I)
19 CONTINUE
UDSKRIFT AF SNIT-VÆRDIER
WRITE(12,1011)SUML,SUMB
ISIDE = ISIDE + 1

UDSKRIFT AF MANGLENDE EMNER
IF(IBLK.EQ.O)GO TO 8
WRITE(12,1013)
WRITE(12,1014)(IBL(I),I=1,IBLK)
GO TO 8
20 CONTINUE
CALL CLOSE(1,B)
STOP. END OF JOB

FORMATS

1000 FORMAT(1X,"SKRUMPNINGSFORSØG AF FOLIE")
1001 FORMAT(1X,T120,"SIDE",14)
1002 FORMAT(1X,T16,"T.I. - SKRUMPNINGSFORSØG AF PLASTFOLIE", ",<016>"
1003 FORMAT(1H1,T120,"SIDE ",14)
1004 FORMAT(1X)
1005 FORMAT(1X,T33,"FORSØGSNR.: ",7A1,5X,70A1)
1006 FORMAT(1X,T13,2("L",4X),2("B",4X),2("S",4X),3("R",4X) 
#"R",3X,"S/S", "<016>")
8X,
#"BK",6X,"S",3X,"O")
1008 FORMAT(1X,T15,T11,11(3X,F7.2))
1009 FORMAT(1X/1X,T15,"MAKSIMALVERDI AF R(L):.")
1010 FORMAT(1X/1X,T15,"MAKSIMALVERDI AF R(B):")
1011 FORMAT(1X/1X,T15,"SNIT AF R(L-KORR): ",F7.2,10X, 
#"SNIT AF R(B-KORR): ",F7.2)
1013 FORMAT(1X/1X,T15,"FØLGENDE EMNER MANGLER DER DATA FOR:"
1014 FORMAT(1X,T15,30(13," "))
1015 FORMAT(1X,T15,7A1)
1016 FORMAT(1X,F5.2)
2000 FORMAT(1X,T2,7A1,70A1)
2001 FORMAT(1X,T2,3X,T14,4F5.2)
END
Appendix GB

Computer programme for calculation of moving average

C       PROGRAM: PLAST. FR
C       HOUSEKEEPING
      REAL B(14), L(14)
      DIMENSION TEXT(70), TEST(7), ITIME(3), IDAY(3)
C       OVERSKRIFTER
      WRITE(10,1000)
      WRITE(12,1007)
C       GRUPPE-OVERSKRIFTER
      4 READ(9,2000,END=5)KA,TEST, TEXT
      IF(KA.NE.11)GO TO 6
      J=0
      WRITE(12,1001)TEST, TEXT
      WRITE(12,1005)
      WRITE(12,1006)
C       NUL-STILLING AF AKKUMULATORER
      DO 12 I=8,12
      L(I)=0
      B(I)=0
      12 CONTINUE
C       SLØJFEN FOR FORSØGSEMNER
      DO 1 I=1, 1000
      READ(9,2001,END=7)KA, NR,L(1), B(1), L(2), L(3), B(2), B(3)
      IF(KA.NE.12. AND. KA.NE.13) GO TO 6
      IF(KA.EQ.13)GO TO 11
C       SLØJFEN FOR BEREGNING AF 'K' (I=1) OG 'M' (I=2) VAERDIER
      DO 10 I=1, 2
      GO TO (21, 22) I
      10 CONTINUE
C       BEREGNING AF INPUT VEDR. 'K'-VAERDIER
      21 L(4) = L(1)/L(2)
      B(4) = B(1)/B(2)
      L(14) = L(4)
      B(14) = B(4)
      GO TO 23
C       BEREGNING AF INPUT VEDR. 'M'-VAERDIER
      22 L(4) = L(1)/L(3)
      B(4) = B(1)/B(3)
      L(14) = L(4)
      B(14) = B(4)
      GO TO 23
C       SLØJFEN FOR BEREGNING AF VAERDIER - UDEN AUTOMATISK
C       UDGANG I SLØJFEN - RESULTATAFHAENGIG
C       UDGANGSKRITERIUM
      23 CONTINUE
      B(6) = B(4) + 1.0 - SORT(1. 0/L(14))
      L(6) = L(4) + 1.0 - SORT(1.0/B(6))
      L(13) = DIM(L(6), L(14))
      B(13) = DIM(B(6), B(14))
C       UDGANGSKRITERIUM
      IF (B(13). LE. 0. 005. AND. L(13). LE. 0. 005) GO TO 24
      GO TO 23
      24 GO TO (25, 26) I
C       'K'-VAERDIER
      25 L(5) = L(6)
      B(5) = B(6)
      GO TO 10

GB-1
C 'M'-VAERDIER
26 L(7) = L(6)
   B(7) = B(6)
10 CONTINUE
C
   UDSKRIFT AF EMNE-RESULTAT
   WRITE(12,1002) NR,L(1),B(1),L(2),L(3),B(2),B(3)
*   L(5),L(7),B(5),B(7)
C
   ADDITIONER
   L(8) = L(8) + L(5)
   L(9) = L(9) + L(6)
   B(8) = B(8) + B(5)
   B(9) = B(9) + B(7)
   L(10) = L(10) + L(1)
   L(11) = L(11) + L(2)
   L(12) = L(12) + L(3)
   B(10) = B(10) + B(1)
   B(11) = B(11) + B(2)
   B(12) = B(12) + B(3)
J = J + 1
1 CONTINUE
BEREGNING AF GENNEMSNITSVAERDIER
11 CONTINUE
   DO 3 I=8,12
   L(I) = L(I)/J
   B(I) = B(I)/J
3 CONTINUE
C
   UDSKRIFT AF GENNEMSNITSVAERDIER
   WRITE(12,1003) L(10),B(10),L(11),L(12),B(11),B(12)
*   L(8),L(9),B(8),B(9)
   CALL TIDSP(12,6)
   WRITE(12,1004)
   GO TO 4

6 STOP - FEJL I KORTART
7 STOP - END-OF-FILE
5 STOP - END-OF-JOB
1000 FORMAT(1X,"PLASTFORSØG / KRYMPNING")
1001 FORMAT(1X//1X,T8,"T.I. - SKRUMPINGSFORSØG"/
   *1X,T8,"HOVEDORIENTERINGSFAKTORER FOR: "/
   *1X,T8,5X,"L = HOVEDORIENTERING / B = TVÆRORIENTERING"/
   *1X,T8,"FORSØG NR: ",7A1//1X,T8,70A1//1X)
1002 FORMAT(1X//1X,T8,14,2X,10FS.2)
1003 FORMAT(1X//1X,T8,86("-")//1X,T8,SNIT: ",10FS.2//1X,T8,86("-
   1004 FORMAT(1H1)
1007 FORMAT(1X)
2000 FORMAT(1X,I2,7A1,70A1)
2001 FORMAT(1X,I2,3X,I4,6F5.2)
END


**USER INSTRUCTIONS • BENUTZER INSTRUKTIONEN • MODE D'EMPLOI**

<table>
<thead>
<tr>
<th><strong>Beregning af køletid:</strong></th>
<th><strong>PROCEDURE</strong></th>
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<th><strong>PRESS</strong></th>
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<td>4 Emnets godstykke</td>
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<td>5 Materialets middeltemperatur-ledningsevne</td>
<td>$a , (\text{cm}^2/\text{s})$</td>
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<td>6 Beregn køletid</td>
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<td>7 De til denne køletid svarer se afformingstemperaturer kan beregnes som følgende:</td>
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<td>8 Beregn maximaltemperatur ved afforming</td>
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<td>Ønskes afformingstemperaturer beregnet udfra en køletid indføres trinene 1c, 2, 3, 4, 5 + enten 7 eller 8</td>
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**USER DEFINED KEYS • PROGRAMMA-ADRESSTASTEN • TOUCHES UTILISATEUR**

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**1977 Texas Instruments**
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| 6   | 76   | 76   | R/S |       |        | if, flg    | 0        | 87          | if
| 2   | 42   | 42   | STO |       |        |            | 22       | INV         |
| 10  | 10   | 42   | STO |       |        |            | 3         | (           |
| 9   | 91   | 91   | R/S |       |        |            | 32       | x ≥ t       |
| 1   | 76   | 76   | R/S |       |        |             | 65       | X           |
| 12  | 12   | 76   | R/S |       |        |             | 43       | RCL         |
| 42  | STO  | 42   | STO |       |        |             | 0        | O           |
| 11  | 11   | 61   | GTO |       |        |             | 54       | )           |
| 86  | St. flg | 24 | CE |       |        |             | 61       | GTO         |
| 0   | 0    | 76   | Lbl1|       |        |             | 22       | INV         |
| 2   | 76   | 23   | lnx |       |        |             | 53       | (           |
| 13  | 13   | 65   | x   |       |        |             | 32       | x ≥ t       |
| 1   | 12   | 53   | (   |       |        |             | 65       | X           |
| 2   | 22   | 43   | RCL |       |        |             | 53       | (           |
| 86  | ST. flg | 15 | 15 |       |        |             | 54       | )           |
| 0   | 0    | 89   | π   |       |        |             | 61       | GTO         |
| 91  | R/S  | 54   | (   |       |        |             | 13       | STO         |
| 76  | Lbl1 | 54   | (   |       |        |             | 76       | Lbl1        |
| 14  | D    | 33   | X²  |       |        |             | 33       | X           |
| 42  | STO  | 55   | (/  |       |        |             | 53       | (           |
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| 91  | R/S  | 16   | 16 |       |        |             | 61       | GTO         |
| 76  | Lbl1 | 54   | (   |       |        |             | 76       | Lbl1        |
| 19  | D'   | 34   | X   |       |        |             | 76       | Lbl1        |
| 65  | x    | 87   | if, flg |     |        |             | 22       | INV         |
| 93  | .    | 33   | X   |       |        |             | 33       | X           |
| 40  | 1    | 33   | X   |       |        |             | 33       | X           |
| 55  | ./   | 53   | (   |       |        |             | 53       | (           |
| 85  | 14   | 43   | RCL |       |        |             | 43       | RCL         |
| 75  | .    | 12   | 12 |       |        |             | 43       | RCL         |
| 40  | 55   | 25   | CLR |       |        |             | 43       | RCL         |
| 12  | 12   | 76   | Lbl1|       |        |             | 76       | Lbl1        |
| 0   | 0    | 91   | R/S |       |        |             | 91       | R/S         |
| 75  | .    | 64   | +   |       |        |             | 64       | +           |
| 85  | .    | 53   | (   |       |        |             | 53       | (           |
| 42  | STO  | 43   | RCL |       |        |             | 43       | RCL         |
| 15  | 15   | 25   | CLR |       |        |             | 25       | CLR         |

**Kodekombinationen**

| 62 | K | 72 | 63 | 73 | 84 | 92 |

**Texas Instruments**

GC-2
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**MERGED CODES**

KOMBINATIONS-KODES
TOUCHE COMBINERED

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**Texas Instruments**

GC-3
This programme calculates the absorbed energy ($E_b$) in an instrumented falling dart test from the following inputs: (a) falling weight; (b) weight above transducer; (c) falling height ($d$) 4,43 * $c$; (e) bridge voltage; (f) sensitivity osc.; (g) $f/K$-$e$; (h) sweeptime; (i) "area weight" of curve; (j) area weight 5,5 dev; (k) impulse $A = (g \times h \times 25 \times h \times a / j \times b) \times 10^{-3}$; absorbed energy $E_b = h \times d$ ($l = (d \times k) / 4 \times c \times a \times 9,8$). Note: STO K in 9. With repetitions RST go to 17 R/S. Ref. M. Jensen et al.; Spændingsrevedannelser i Termoplast, København (1978)
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**Texas Instruments**

GD-2