Processing, structure and properties of plasticized PVC

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PROCESSING, STRUCTURE AND PROPERTIES OF PLASTICIZED PVC

by

SHIRISH V PATEL, BSc(Hons), MSc

A DOCTORAL THESIS

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology

1983

Supervisor: M Gilbert, PhD
Director: Professor A W Birley

Institute of Polymer Technology

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This thesis is dedicated to my parents
ACKNOWLEDGEMENTS

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My thanks are also due to Miss Pauline Daubney for assisting me with some of the graphs and to Mrs Janet Smith for her immaculate typing of the script.
ABSTRACT

The fusion and rheological behaviour of PVC compounds play a dominant role in the processing operations and in the development of physical properties in the processed material. These phenomena are governed by the complex morphological structure of PVC resin, compound composition and processing conditions which in turn affect the physical properties of the final product.

The fusion process of flexible PVC compounds was investigated by a combination of several techniques. Samples with varying states of fusion were prepared using shear and temperature as the processing variables in extrusion, Brabender Plastograph and compression moulding. The degree of fusion of processed compounds was characterized by rheology, thermal analysis, acetone test, optical microscopy, tensile strength and extrudate appearance.

The formulation of a PVC compound has a strong influence on the rheological properties of the melt. Hence several plasticizers were chosen from a wide activity range and compounded at three plasticizer concentrations of 30, 50 and 70 phr. These compounds were processed at five different temperatures (150-200°C) in a Banbury mixer. They were further processed in an extruder or on a two-roll mill followed by compression moulding.

In assessing the state of fusion a universal method was found which could define the fusion state adequately for a given PVC sample which had undergone any processing condition. Rheometer studies were found useful in assessing state of fusion of samples from specific formulation and processing conditions with processing temperature as the variable. Differential scanning calorimetry results showed that more understanding was needed to interpret the results. However, it proved to be a versatile method in determining the maximum temperature a sample would have reached, irrespective of its formulation or processing history.
High speed mixing data proved to be useful commercially since increased plasticizer concentration gave decreased blending times. Davenport extrusion pressure, tensile properties, morphology and extrudate surface texture showed significant differences between plasticizers. An identical trend for ease of smooth extrudate formation and its glossy texture was observed.
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CHAPTER 1
INTRODUCTION

1.1 General

Though polyvinyl chloride (PVC) has been in existence for a long time, far less is known about it than about the comparatively newer polyolefins. It is incomparably more difficult to process because of its low decomposition temperature. Many research workers say that chlorine begins splitting off just above 100°C.\textsuperscript{1-3} It shows the lowest activation energy for decomposition of all plastics, except for PVA.\textsuperscript{4}

It can be attributed to its low-material price - it is a typical recycling product of the chemical joint utilities - as well as to its excellent compatibility with bad low-molecular weight solvents, the so-called plasticizers, that PVC has nevertheless developed to become the greatest mass plastic at certain times.

Whilst the use of plasticizers is not confined solely to PVC technology, the interaction of PVC with plasticizers facilitates fusion and melt processing at lower temperatures, to yield softer and more flexible products, but the properties change progressively with plasticizer level, to give wide range of useful compositions.

1.2 Processing of PVC

The various possible ways of converting PVC to useful end-products have been reviewed and described fully as a whole and separately. Practically every kind of plastics processing can be applied to PVC in one form or another, and some PVC processing, e.g. paste processes, are not generally applicable to other polymers. The various different routes by means which PVC or copolymer and additives can be converted to finished products are illustrated.
diagrammatically in Figure 1. It will be understood that not every combination of polymer and additives can be put through every possible sequence of processing treatments.

The various processes may be broadly classified into three classes: (1) mixing, (2) compounding, and (3) shaping, but it is not suggested that any one is mutually exclusive of the others, and indeed much of modern processing involves all three in one step. In the present context 'mixing' is seen as any process in which the various components of a composition are blended together mechanically, or physically, any softening or agglomeration of polymer occurring being insufficient to produce a continuum of gelled polymer. 'Compounding' is seen as involving mixing on a molecular scale, usually within the formation of a continuous polymer matrix. Compounding is thus seen as a particular form of mixing, but, although the differentiation between 'mixing' and 'compounding' may be fundamentally artificial, it is nevertheless a useful convention in practice. 'Shaping' comprises generally those processes which produce the final product. Some of these, e.g. extrusion and moulding, involve some amount of

![Diagram of Processing of Plasticized PVC](image)

**FIGURE 1:** Processing of Plasticized PVC
compounding, whereas others, e.g. thermoforming, do not include this at all. The object of processing is presumed to be the production of the required shape with the composition employed in as homogeneous a state as possible. Whereas more than one process is involved in the conversion each one may contribute towards the homogeneity. The greater the contribution from one process the smaller will be that required from the others. Thus each process needs to be considered from the point of view of the effect it will have on the homogeneity of the final end-product.

1.3 Formulation Ingredients

It is essential that the formulation used to produce PVC products shall be such that the required properties are attained, which naturally has a prime influence on determining the formulation. It is also essential that the formulation is such that the composition is amenable to the processing required to convert the components to the required product form and this can have a profound influence on the nature of the individual components of a formulation.

1.3.1 Resin

The kind of raw-material production has a considerable influence on the workability. There are five distinct methods of the production of PVC powders, viz. (1) suspension (S); (2) bulk (B) or mass; (3) emulsion (E); (4) gas phase or partial pressure; (5) solution or diluent. As can be seen from Table 1 certain kinds of raw material production and certain molecular weights (K-values) are associated with the different processing procedures. This is particularly connected with the grain structure, i.e. with

- porosity
- the bulk weight
as well as the contents and the distribution of polymerization admixes and others.

The K-value (molecular weight) is dependent on the method of measurement and in the past different suppliers have used different solvents and different polymer concentrations. Thus care must be taken when comparing these K-values with those of other suppliers.

The requirements for acceptable processing behaviour are less restrictive on K-value than in the case of rigid compositions,

TABLE 1: Ranges of Application of PVC

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The requirements for acceptable processing behaviour are less restrictive on K-value than in the case of rigid compositions,
and so relatively high K-values are generally employed in flexible compositions, to optimise product properties. K-values are typically in the range 65-72, with the higher end of the range being employed where mechanical properties, particularly performance at elevated temperatures is required and lower K-values where the emphasis is on easy processing. In practice, K-values across this range can be very successfully employed in many of the same applications, by minor adjustments, of plasticizer level or other formulation variables.

An essential quality in any polymer for flexible applications is that it should absorb plasticizer readily, but homogeneously. The plasticizer absorption characteristics are reflected not only in the performance during dry blend manufacture, but also in the ease with which a homogeneous melt, free of dispersion faults, may be produced. A key requirement is that the polymer grains should possess a relatively high level of porosity. An increase in porosity produces an increase in the equilibrium uptake of plasticizer, at ambient temperature.

1.3.2 Plasticizers

A plasticizer is a material incorporated in a polymer to increase its workability and its flexibility or distensibility (elongation). Addition of the plasticizer may lower the melt viscosity, the temperature of the second-order transition or the elastic modulus of the plastic.

The expression "monomeric plasticizer" and "polymeric plasticizer" are commonly used to classify plasticizers. In fact monomeric plasticizers are not monomers in the accepted sense of being polymerisable compounds. The word "monomeric" was used as the opposite of "polymeric" to distinguish high and low molecular weight plasticizers. But polymeric plasticizers are indeed polymers (e.g. Hexaplas PPA-poly(propylene)adipate.)
The monomeric plasticizers are further classified as primary plasticizers and secondary plasticizers. The primary plasticizers are highly compatible with the resin while the secondary plasticizers are poor solvents at best. Thus the secondary plasticizers are used in conjunction with the primary plasticizers to confer special properties.

The properties desired in a plasticizer are numerous, and the following are the more important properties looked for to satisfy most general purpose plastics applications.

a) low volatility.
b) good softening action.
c) good compatibility with PVC
d) resistance to migration from the base material.
e) non-flammability.
f) good resistance to degradation by heat and light.
g) good electrical insulation properties.
h) freedom from odour and taste.
i) chemical inertness.
j) non-toxicity.
k) good colour.
l) resistance to extraction by solvents.
m) little change in viscosity with temperature.
n) low comparative cost.

There is no single plasticizer which possesses all these properties and for many applications not all of the properties are required. Plasticizers are chosen according to the requirements of the end usage. Nevertheless, good compatibility with the polymer material and low plasticizer volatility are the two main requirements of choosing a plasticizer.

Common phthalates and phosphates are the most popular plasticizers. They are used for general purposes particularly where good compatibility, good colour, low odour, good softness and good food
contact is required. High molecular weight phthalates such as diisodecyl phthalate (DIDP), ditridecyl phthalate (DTDP), dinonyl phthalate (DNP) are used where low volatility and low (but not very low) temperature applications are required. High solvating phthalates such as butylbenzyl phthalate (BBP) and dibutyl phthalate (DBP) are used where rapid fusion and good solvation in processing, good stain resistance and resistance to solvent extraction is required. Aromatic phosphates (e.g. trityl phosphate TTP, trisoyl phosphate TXP) are general purpose plasticizers and can be used for the following purposes: good compatibility, good tensile strength, high electrical resistivity, non-flammability, and high viscosity in pastes. But aliphatic phosphates are used for reasonable low-temperature properties and for high electrical resistivity. For many years the sebacates such as dibutyl sebacate (DBS) and dioctyl sebacate (DOS) were used where low temperature properties are required. Today they have been replaced by cheaper esters of similar effect in PVC derived from mixed acids produced by the petrochemical industry. The most important of these mixed acids are the AGS acids (a mixture of adipic, glutaric and succinic acids). These are esterified with octyl, nonyl and decyl alcohols to give plasticizers now generally referred to as nylonates but occasionally as sugludates. The sebacate, adipate and sugludate-type plasticizers can also be used to give compounds of high resilience. "Hexaplas" trimellitates (TATMS) are speciality plasticizers for PVC manufactured from alcohols in ICI range and from linear 7-9 and 8-10 alcohols. The low volatility and excellent low temperature performance properties enable them to be used to advantage in a number of applications e.g. high temperature cable, calendered and extruded film, and spread coating. Polymeric plasticizers such as polypropylene adipate (PPA) and polypropylene sebacate (PPS) have high molecular weight and are used for low volatility, for resistance to migration and extraction and high viscosity in pastes. Chlorinated paraffins, are used for cheapness and non-flammability but they should not be used where good electrical properties are important. Epoxidised oils and esters are
similar to polymeric plasticizers but should not be used where good colour is important.

1.3.3 **Stabilizers**

Stabilizers are added to PVC compositions to protect against degradation - to which this polymer is prone - under the influence of heat and mechanical shear in processing, and also to afford longer-term protection in service, mainly against the effects of heat, light and oxidation.

For most general applications where opacity and non-toxicity are not required, basic lead carbonate or tribasic lead sulphate may be selected, the latter where relatively high melt temperatures arise during processing. For maximum light stability, dibasic lead phosphite is usually recommended. Where maximum clarity is essential an organotin, or where the odour is acceptable, a thio-organotin stabilizer will generally be required, although the best combinations of epoxy compound with a barium/cadmium/zinc stabilizer can be very nearly as good. Where slightly inferior stability can be tolerated barium/cadmium or barium/cadmium/zinc stabilizers together with an epoxy compound and possibly an organic phosphite will generally suffice. Selection of stabilizers for 'non-toxic' applications depends on the nature of the application and on local regulations. In general for water-pipes, up to about 2 phr of tribasic lead sulphate can be safely used in unplasticized compositions.

1.3.4 **Miscellaneous Additives**

A PVC compound may also contain the following ingredients: lubricants, fillers, pigments, polymeric processing aids and impact modifiers. In plasticized PVC the main function of a lubricant is to prevent sticking of the compound to processing equipment. This is brought about by selecting a material of limited compatibility which will thus sweat out during processing to form a
film between the bulk of the compound and the metal surfaces of the processing equipment. Calcium stearate has been most commonly used with non-transparent compounds and stearic acid with transparent compounds. Fillers are commonly used to reduce cost, increase hardness, reduce tackiness, to improve electrical insulation properties and to improve the hot deformation resistance of cables. Blowing agents such as azodicarbonamide are frequently used in manufacture of cellular PVC. Antimony oxide is useful in improving fire retardance of plasticized PVC.

1.4 Aim of the Project

The overall object of this project for ICI was to investigate and establish relationships between plasticizer type and processing variables so that ICI can:

a) Participate more readily and effectively in customer problems;
b) Advise on the implications on reformulating to new plasticizer systems.

This was to be achieved by increasing the understanding of plasticized PVC. Hence, the aim was to describe the state of fusion of plasticized PVC compound and relate this to compound composition and processing variables.

The first stage of the project was to define and validate a method or methods of measuring the state of fusion of a compound, Figure 2. Here a fixed formulation containing 50 phr DIOP was to be mixed in a high speed mixer. The resulting dry blend was then to be compounded and processed. The effect of variables such as thermal history, shear history and process type employed on the state of fusion were to be studied. The degree of fusion of the samples was to be assessed by rheology, thermal analysis, acetone test, optical microscopy, tensile strength and extrudate appearance.
In the second stage the defined method (or methods) to assess the state of fusion was to be used to measure the effect of plasticizer type and concentration and processing parameters on the state of fusion, Figure 3. This second stage of the programme was divided into three sections to study how the variation of plasticizer affects dry blending, compounding, and the formation of the final article. The plasticizers DIOP, DPN, OPN, DINP, TATM, DTDP and BBP which cover some new plasticizers and other well used plasticizers which represents the extremes of processing characteristics from a wide activity range were to be studied at 30, 50 and 70 phr: Variations of plasticizer concentration were to allow comparisons to be made at equal softness and equal molar concentrations.

a) **Dry blending**

Plasticizers were to be assessed in dry blending efficiency by the time taken to achieve 120°C discharge temperature in the Fielder mixer. Changes in Tg were to be monitored by differential scanning calorimetry (DSC).

(Hot plasticizer absorption test was to be carried out if the Fielder results were insufficient).

b) **Compounding**

Using the dry blends, samples were to be prepared on a Banbury at 10°C intervals in the range 150-190°C and evaluated by:

1. Rheometer extrusion pressure.
2. Extrusion rate (at fixed die temperature and screw speed).
3. DSC.
4. Microscopy
5. Extrudate appearance

c) **Evaluation**

Compounded samples were to be evaluated by the tensile properties of the extrudates.
FIGURE 2: To Assess the State of Fusion of S-PPVC
Fusion - amount of continuous network formed on breakdown of powder grains (~ 100 μm) on processing.
Structurisation - effect of the surface texture of extrudates.

FIGURE 3: To Assess the Effect of Plasticizer on Fusion State
CHAPTER 2
LITERATURE SURVEY

2.1 Plasticization Theories

Three or perhaps four major theories have been proposed to account for the main effects produced by plasticizers. The gel theory and lubricity theory are the product of many workers in the first half of the century. They were developed almost concurrently and although they are in reality two separate theories used to explain plasticization, they are so intermingled in the thinking of researchers that the two are commonly employed to explain different parts of the total phenomenon of plasticization and the deformation of plasticized polymers.

2.1.1 The Lubricity Theory

The lubricity theory considers the resistance of a resin to deformation (its rigidity) to result from intermolecular friction. The plasticizer acts to facilitate movement of resin macromolecules over each other; it gives internal lubricity. As a polymer is flexed, the macromolecules must work back and forth over each other, and the plasticizer lubricates these internal glide planes. It is assumed that there is no bonding between macromolecules beyond that of surface irregularities and that there is at most very weak bonding between plasticizer molecules and/or between plasticizer and resin molecules much like the low interfacial energy between a solid and liquid lubricants.

Figure 4 illustrates the theory according to early workers such as Clark and Houwink.
A - POLYIOTER PLASTICIZER

FIGURE 4: The lubricity theory of plasticization. A-polymer-polymer bonds and plasticizer-plasticizer bonds are preferred over polymer-plasticizer bonds. B-polymer-plasticizer bonds are preferred.

Plasticizer molecules are in reality much larger than polymer repeating units in most cases, and there are fewer plasticizer molecules actually present.

2.1.2 The Gel Theory

The gel theory considers the rigidity of a resin to result from an internal, three-dimensional honeycomb structure. This gel is formed by more or less loose attachments which occur at intervals along the polymer chains. The dimensions of the cells in a stiff or brittle resin are small because the points of attachment are close together. Any attempt to deform the specimen cannot be readily accommodated by movement within the mass. Its limit of elasticity is low.

The plasticizer acts on a resin that has many points of attachment along the polymer chain by breaking the attachment at places and masking the centres of force (we need not define them yet as Van der Waals, London, Debye, hydrogen bonding, crystal, or primary valence forces) that have held these polymer chains together. The plasticizer masks these centres of force by selectively solvating the polymer chains at these points. This produces much the same result as if fewer points of attachment had been provided.
on the macromolecules in the first place. This potentially reduces the rigidity of the gel structure.

The free unattached plasticizer molecules appear particularly effective in swelling the gel and in facilitating movement of the polymer molecules, that is, increasing flexibility. In partially crystalline resins a plasticizer affects primarily the amorphous regions or the areas of crystal imperfection. If it has sufficient solvent power it may cause dissolution of some crystallites, but if a gel structure remains it probably does not permanently dissolve all of them, for plasticization requires limited swelling, not unlimited swelling or dissolving\textsuperscript{11,16-22}. Figure 5 represents unlimited and limited swelling of polymers as illustrated by early workers\textsuperscript{5}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Development of the gel theory of plasticization. A. The polymer-polymer bonds are all alike—type $a$. B. Two types of polymer-polymer bonds are present—types $a$ and $b$. C. One type of polymer-polymer bond exists, but the polymer chains are interlinked and cannot be completely separated. Adapted from Houwink\textsuperscript{16}.}
\end{figure}
2.1.3 The Free Volume Theory

Since a major function of a plasticizer is to lower the glass transition temperature, $T_g$, much of the application of the theory depends on an understanding of $T_g$.

The free volume or free space of a crystal, glass or liquid may be defined as the difference between the volume observed at absolute zero temperature and the volume measured for the real crystal, glass, or liquid at a given use temperature $^{23-25}$. This may be expressed by the equation

$$V_f = V_t - V^0$$

where $V_f$ is the free volume, $V_t$ is the specific volume ($\text{cm}^3 \text{g}^{-1}$) at temperature $t$, and $V^0$ is the specific volume at some reference point. Yet there are insurmountable difficulties in determining the volume at $0^0K$, and not all substances behave as we might predict as they approach absolute zero $^{16}$. The free volume concept therefore remains somewhat vague and confusingly defined in the literature because of these difficulties with the lower reference point $^{27}$.

In an ideal crystal at absolute zero we can imagine all atoms or molecules perfectly compact in a completed lattice. In a real lattice they are not this compact, supposedly as a result of non-harmonic vibrations and because of imperfections in the lattice structure, commonly called holes. In a liquid the number or volume of these holes has increased greatly. The free volume is therefore divided into two parts: (1) a continuous part that results from oscillations and that persists and increases slightly as the temperature is raised, and (2) a discontinuous part called holes, which increases greatly with temperature $^{23}$.

Figure 6 represents some of the basic concepts of free volume, relying heavily on earlier presentations $^{25,27,28}$. In a typical dilatometric experiment (Figure 6A), when a noncrystallizing liquid
of a rubber is cooled, its volume decreases slowly and more or less linearly with temperature (Curve a) until a temperature, or narrow temperature range, $T_g$, is reached at which the material becomes glassy. At this point the decrease in volume continues, but the amount of change per °K is smaller. The change that occurs, however, is almost instantaneous: Since no mass is removed the decrease must represent the decrease in space between the atoms and molecules. If the steeper, rubbery portion of Curve a is extrapolated linearly to absolute zero (Figure 6B), a specific volume, $V^0_L$, can be obtained, which is too small to represent the hypothetical volume of the pure material. If on the other hand

![Figure 6](https://example.com/figure6.png)

**Figure 6** Thermal expansion and free volume of a polymer or a noncrystallizing plasticizer. $V = \text{specific volume}$; $V^0_L = \text{specific volume at absolute zero for hypothetically pure and perfectly ordered material}$; $V^0_L$ and $V^0_L$ = specific volumes of the glass and liquid extrapolated to $0°K$; $T_g = \text{the observed glass transition temperature}$; $T^*_g = \text{the hypothetical glass transition temperature at infinite test time}$; $\alpha_0$, $\alpha_0$, $\alpha_2 = \text{coefficients of expansion of the pure, ordered material and of the real glass and liquid, respectively.}
the glassy portion of Curve a is extrapolated to absolute zero, a specific volume, $V_G^0$, can be obtained. This is too large to represent the hypothetical occupied volume, because at lower temperatures the molecules cannot move to adjust to an ideally compact position. Some "frozen-in" free volume persists. The hypothetical, real specific volume, $V_O^0$, lies below $V_G$. Such linear extrapolations assume the coefficients of expansion are constant, whereas they approach zero at 0°K, yet we may assume the value $V_O^0$ represents a true occupied volume which remains constant at all ordinary temperatures (Curve b, Figure 6B). The area between Curve a and b represents the free volume.

A small portion of this free volume originates from the nonharmonic oscillations of the atoms. This interstitial of oscillation free volume is shown between Curves b and c in Figure 6C. This accounts for much of the thermal expansion of the glass but not all. The frozen-in imperfections or holes, which are submolecular and molecular in size, account for the rest. The coefficient of expansion, $\alpha_o$, of the hypothetical flawless material cannot be measured but must be slightly less than the coefficient of expansion, $\alpha_G$, of the real glass. Above $T_g$ the glass becomes rubbery or fluid; the molecules have enough energy to move, bend, rotate. The Brownian motion of molecules or segments of molecules produces a greater amount of free volume-hole free volume.

Because an increase of hole free volume permits increased motion of polymer molecules, a study of plasticization is a study of ways to increase free volume. Free volume comes from three principal sources: (1) the motion of chain ends, (2) the motion of side chains, and (3) the motion of the main chain. These motions, and therefore the free volume of a resin may be increased by:

1. Increasing the number of end groups (lower the molecular weight).
2. Increasing the number or length of (proper) side chains. (Internal plasticization).

3. Increasing the chance for main chain movement by inclusion of segments of low steric hindrance and low intermolecular attraction (low polarity and H-bonding). (Internal plasticization).

4. Inclusion of a compatible compound of lower molecular weight that acts as though it does all of 1 through 3 above. (External plasticization).

5. Raising the temperature (Plastication).

2.1.4 Solvation-Desolvation Equilibrium

The action of a plasticizer on a resin having many points of attachment along the polymer chains appear to be to separate the chains, break the attachment, and mask the centres of force that have held these polymer chains together, perhaps by selectively solvating the polymer at these points. This produces much the same result as if fewer points for attachment had been provided on the macromolecules in the first place.

It seems probable that solvents and external plasticizers of different classes are attached to resin macromolecules by forces of different magnitudes and that none of them are bound permanently when they are attached. Instead there is a continuous exchange whereby one plasticizer molecule becomes attached to a given active group or force centre only to be dislodged and replaced by another. This results in a dynamic equilibrium between solvation and desolvation in which a certain fraction of the force centres on the polymer chains is masked by solvent or plasticizer under a given set of conditions such as plasticizer concentration, temperature, and pressure. This is the basic concept of the kinetic theory of Doolittle, or as he prefers to call it, the mechanistic theory of plasticization.
In crystalline resins, plasticization affects primarily the amorphous regions between crystallites or the areas of crystal imperfections. Yet even the crystal imperfections such as short chains, abnormal branching, and foreign components permit plastic deformation of the crystal itself thus plasticize it internally.

2.1.5 Generalized Structures

A visual concept of plasticization of a resin is attempted in Figure 7. The base polymer is represented according to fringed micelle theory with small areas of order among general disorder of molecules. These compact macromolecules, micelles, may be ordered enough to be crystallites. For convenience we will designate them as "crystallites" without commitment regarding size or degree of order. These tend to make the resin rigid while the amorphous areas between tend to be more flexible.

If a small amount of plasticizer is incorporated into the mass, perhaps by heating and cooling, it brings with it slightly more free volume and gives more opportunity for movement of the macromolecules. Many resins tend to become more ordered and compact as existing "crystallites" grow or new "crystallites" form at the expense of the more fluid parts of the amorphous material. As there are few plasticizer molecules, they may be almost totally immobilized by attachment to the resin (bound plasticizer) by various forces. This tends to restrict the freedom of small portions of the polymer molecule - side chains and segments - so necessary for absorption of mechanical energy. Therefore it results in a more rigid resin with high tensile strength and modulus than the base polymer itself. This is anti-plasticization, which is also observed in resins as diverse as PMMA, polycarbonate and nylon 6,6 which vary from completely amorphous to highly crystalline. Horsley's study shows by X-ray diffraction that small amounts of DOP, up to 10 to 15%,
progressively increase in order which may be considered to include crystallites. Further increase up to 25% DOP resulted in a decrease in order. This increase and decrease in crystallinity paralleled exactly the increase and decrease in tensile strength and modulus, as well as the decrease and increase in impact strength.
2.2 Molecular Structure

2.2.1 Configurational and Conformational Isomerisms

PVC has a fundamental repeating unit -CH₂CHCl-. The chlorine atom can be disposed in three different ways with respect to the backbone giving rise to configurational isomers, see Figure 8. These three forms are termed as isotactic, syndiotactic and atactic. Two of these, the syndiotactic and isotactic arrangements, are regular, but the third, heterotactic, is random and irregular. A tactic polymer is defined as one in which

\[-\text{-CH}_2\text{-CH}-\text{CH}_2\text{-CH}-\text{CH}-\text{CH}_2\text{-}\]

\[\text{X X X X} \quad \text{ISOTACTIC} \quad \text{mmm}\]

\[-\text{-CH}_2\text{-CH}-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}\]

\[\text{X X} \quad \text{SYNDIOTACTIC} \quad \text{rrr}\]

\[-\text{-CH}_2\text{-CH}-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}\]

\[\text{X X} \quad \text{HETEROTACTIC} \quad \text{rrr}\]

FIGURE 8: The Three Types of Tactic Placements for PVC

there is an ordered structure with respect to at least one site of steric isomerism in each monomeric unit. A minimum of three monomer units, a triad, is required to define these three types of configurational isomers, but it is possible to describe their stereoregularity, and that of longer sequences, in terms of two types of diads, meso(m) with the substituents on the same side of the backbone and racemic (r) where they alternate. In this
notation the three triads become rr, mm and mr.

The overall syndiotacticty or isotacticty of a particular polymer is determined by energetic considerations. If one type of placement is very much favoured the polymer will be highly stereoregular. Conversely, if the enthalpy difference between the two types of placement is small the polymer will approximate to heterotactic. A material polymerized at +30°C and hence not greatly different from commercial polymers, was found to be 54% syndiotactic by Nakajima et al.61.

2.2.2 Chemical Defect Structures

There are several probable defect structures such as chain branching, unsaturation, labile chlorine, head to head units and tail to tail units and, on present evidence, they are all potential sites for the initiation of thermal and photochemical decomposition82,83. The result of various workers proved to be in substantial disagreement as to the amount of chain branching as they varied by almost an order of magnitude, between 2-18 branches per thousand carbon atoms134.

There can be several possible steric forms depending on the placement of successive monomer units. If we consider -CHCl as head and -CH₂ as tail in vinylchloride monomer (CH₂=CHCl), then placement of successive monomers can be shown as follows:

i) \(-\text{CH}_2\text{-CHCl}\text{-CHCl}\text{-CH}_2\)  Head to Head (defect)

ii) \(-\text{CH}_2\text{-CHCl}\text{-CH}_2\text{-CHCl}\)  Head to Tail (normal)

iii) \(-\text{CHCl}\text{-CH}_2\text{-CH}_2\text{-CHCl}\)  Tail to Tail (defect)

Koleske and Wartman suggested that 1.2 mole per cent of vinylchloride adds in the tail to tail fusion.135

2.2.3 Crystallinity

The way in which adjacent chains pack together, and so determine the presence of absence of three dimensional order, will be
a function of the configurational and conformational isomers present. In the case of n-paraffins, and polyethylene the planar zigzag structure permits optimum packing and this may also be true in some cases with vinyl polymers. However, the planar zigzag arrangement is the simplest possible form of a more general three dimensional arrangement, the regular helix, and it is not unreasonable to suppose that polymers whose chains follow other types of helical arrangements may be able to pack adequately and so have a reasonable degree of crystallinity. If the three-dimensional order occurs over a limited distance only the crystallite size will be small. If there is limited order along the chain some degree of lateral packing may be possible, in a fringed micelle type of structure.

Natta and Corradine performed X-ray measurement with oriented fibres of commercial PVC. Their work has shown that the unit cell is orthorhombic, with a-, b- and c-dimensions of 10.6, 5.4 and 5.1 Å respectively. The chains, two per unit cell, are planar syndiotactic and laterally ordered domains, almost 50 Å wide, but the order in c-direction, along the chains, is rather poor. This latter fact was attributed to imperfections in the syndiotactic arrangement of the chlorine atoms.

Crystallographic studies by several workers have provided confirmatory evidence for the presence of a phase intermediate between what is commonly accepted as wholly ordered and completely disordered in PVC. This phase structure appeared to constitute a mesophase (in between liquid and solid) and was considered to be nematic liquid crystals. In the nematic phase the molecules are oriented in parallel direction to give one degree of order. It is reasonably well established that a two-dimensional
nematic phase is present to an extent determined partially by the thermal and processing history of the sample. The conditions under which this may transform into crystalline material are not well understood. The observed crystallinity is greater than anticipated from the syndiotactic content and the lateral dimensions of the crystallites are comparatively small. These high crystallinity values than anticipated have been discussed in depth by Juijn\textsuperscript{88} and will be outlined here.

If it is assumed that only syndiotactic sequences are capable of crystallising and that a run of ten to twelve such units is required to establish a sufficient degree of c-axis order to permit crystallisation, then it is possible to predict the crystallinity from the probability of their occurrence, for a given syndiotacticity. This led to the conclusion that the crystallinity of commercial polymers should be no more than a few tenths of one percent, and even if sequences as short as six units are involved in the crystallisation process, as has been suggested by Gray and Gilbert\textsuperscript{89}, the crystallinity is still rather less than that found in practice. Juijn\textsuperscript{88} has suggested that this is indicative of the participation of some types of isotactic sequences in the crystallisation process; he has shown, using molecular models, that it is possible to construct an isotactic straight chain structure. He therefore argued that this structural unit is involved to a significant extent in the crystallization of PVC, thus accounting for the difference between the calculated and the observed values. This interesting hypothesis had not yet received experimental confirmation.

2.3 Morphology of S-PVC

Whereas other polymers may be concerned with molecular weight distribution, rate or level of crystallization, density, melt flow behaviour, etc., the success or otherwise of a PVC polymer depends
largely on its grain structure or morphology. The grain form depends exclusively on the polymerization process used. From a morphological viewpoint there are five distinct methods for the production of PVC powder, viz (1) suspension; (2) bulk or mass; (3) emulsion; (4) gas phase or partial pressure; (5) solution or diluent. Of these, suspension polymerization predominates commercially and will form the main body of discussion in this section.

In the technical literature the terminology used to describe the morphology of PVC is varied and very confusing. Since it is important to have a clear and unambiguous system of nomenclature this aspect of the subject will be covered in some detail here.

A review of the literature shows many important features of PVC morphology. Sections of PVC grains (150 μm) show the primary particles (1 μm) and agglomerates (3-10 μm) of the primary particles. Smaller, microdomain structure is revealed by small angle X-ray scattering as density fluctuations at about 0.01 μm spacing. Interpretation of wide angle X-ray scattering shows a crystallite structure at slightly smaller than 0.01 μm. It has been suggested that the microdomains are related to PVC crystallites.

Following the second symposium on PVC at Lyon Villeurbanne in 1976 a discussion of the terminology used to describe PVC morphology was summarised and published by Geil in an attempt to obtain consistency. Geil's terminology forms the basis of the system used here (Table 2).

Deriving from reports by several authors an idealised model of PVC grain, as shown in Figure 9, can be obtained.

Although the domain may be important in terms of the molecular ordering/crystallinity of PVC at low-conversion and hence it may exert a considerable influence on say, rheological properties, it is not a fundamentally important feature of morphological texture of high conversion polymer.
FIGURE 9: Model of PVC Grain Morphology

TABLE 2 PVC Nomenclature

<table>
<thead>
<tr>
<th>Term</th>
<th>Approximate size</th>
<th>Origin or description</th>
<th>Previous terminology (with references)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain</td>
<td>50-250</td>
<td>Visible constituents of free flowing powders, made up of more than 1 monomer droplet.</td>
<td>Granule(^{19}) Cellular grain(^{20})</td>
</tr>
<tr>
<td>Sub-grain</td>
<td>10-150</td>
<td>Polymerised monomer droplet.</td>
<td>Sub-granule(^{19}) Uncell(^{19})</td>
</tr>
<tr>
<td>Agglomerate</td>
<td>2-10</td>
<td>Formed during early stage of polymerisation by coalescence of primary particles (1-2 (\mu)m). Grows with conversion to size shown.</td>
<td>Aggregate(^{19}) Cubes(^{20}) Micro-globule(^{21})</td>
</tr>
<tr>
<td>Primary particle</td>
<td>0.6-0.8</td>
<td>Grows from domain. Formed at low conversion (less than 2(%)) by coalescence of micro-domain: grows with conversion to size shown.</td>
<td>Microgranule Primary particle(^{19}) Granule(^{20}) Micro-globule(^{21})</td>
</tr>
<tr>
<td>Domain</td>
<td>0.1-0.2</td>
<td>Primary particle nucleus. Contains about 10(^3) micro-domains. Only observed at low conversion (less than 2(%)) or after mechanical working. Term only used to describe 0.1 (\mu)m species, becomes primary particle as soon as growth starts.</td>
<td>Primary nucleus(^{19}) Granule(^{20})</td>
</tr>
<tr>
<td>Micro-domain</td>
<td>0.01-0.02</td>
<td>Smallest species so far identified. Aggregate of polymer chains- probably about 50 in number.</td>
<td>Basic particle Particle</td>
</tr>
</tbody>
</table>

Annotations:
1. The domain is not a feature of PVC morphology in high conversion polymer samples since a growth of this species with conversion obliterate all memory of it. It may only be 'regenerated' and observed after subsequent processing.
2. As soon as formation of the domain is complete and growth is registered it is preferable to call it a primary particle. Therefore, the term domain is often ignored in favour of primary particle even at the point of morphogenesis of the 0.2 \(\mu\)m-primary particle at low conversion.
3. The reason for a separate identity for the domain is that it may be shown in future to contain an unusual morphological or molecular feature e.g. higher level of crystallinity.
2.4 Processing of Plasticized PVC: Effects on

2.4.1 Morphology

Many attempts have been made by investigators to find the relationship between PVC morphology and its processing. It was shown that during processing, 150 μm PVC grains are broken down to 1 μm primary particles, which appear to be flow units at low melt temperatures. Berens and Folt found that at processing temperatures of 180°C and above, these particles began to agglomerate, with almost complete obliteration of particle identity by 200°C.

Singleton et al. studied the relationships between processing, morphology and properties for plasticized PVC. They concluded that 170°C was a unique temperature for PVC, above which there was a fusion and the formation of a nearly homogeneous melt.

Whereas it has been shown that a significant 'memory' of the original polymer grains can persist in the processing of rigid PVC compositions, this is much less true of plasticized PVC. Summers et al. developed a technique for the identification of primary particles by swelling samples of extrudate in acetone, shearing between glass slides and examining optically. They prepared compounds containing 0, 30, 60 and 90 phr of dioctyl phthalate (DOP) plasticizer, using the least rigorous compounding concordant with adequate dispersion. These compounds were then extruded on a small single-screw extruder, over a range of temperatures. Acetone swelling and microscopic examination of the extrudates showed unagglomerated particles in the samples corresponding to low extrusion temperatures, partially agglomerated particles in the intermediate samples and a continuous melt for the highest temperature extrudates. These particles were of the same size, allowing for the acetone swelling, as the primary particles identified in the original polymer granules. The same transition took place in all the compounds, regardless of
plasticizer level, except, of course, that the increasing plasticizer, the temperature for each morphological condition was lowered.

Singleton et al\textsuperscript{35} have described the use of freeze fracture-replication electron microscopy (EM) and small angle X-ray diffraction (SAXD) to observe an approximately 100 Å microdomain structure in DOP plasticized PVC. They showed that although the freeze fracture technique was not satisfactorily reproducible, the size of the domains or at least their spacing increased with plasticizer content, the distinctness of the microdomain (SAXD peak intensity) increased with milling temperature (up to ca. 165°C) and plasticizer content, and evidence for a domain (0.1 μm) structure could also be found in some electron micrographs.

Soni et al\textsuperscript{95} have also showed by EM that milled samples consist of microdomains of the order of 0.01-0.02 μm in diameter which are poorly plasticized and, in addition in many of the samples, an ca. 0.1-0.2 μm domain structure in which the microdomains are more closely packed than in the domain boundaries. On increasing the plasticizer level, in contrast to prior observations based on freeze fracture studies which indicated an increase in microdomain size\textsuperscript{35}, ion etching and staining indicated an increase in centre to centre distance with little change in size. This they suggested was due to the additional plasticizer primarily going into the regions surrounding the microdomains and was in agreement with their prior SAXS intensity results. They also showed that increasing milling time at a given temperature had little effect on the morphology whereas milling at 180°C resulted in an essentially homogeneous distribution.

The behaviour of rigid PVC on a Banbury mixer has been described by Allsopp\textsuperscript{78,96} who also identified two general mechanisms of grain modification during processing, comminution and densification. The Banbury mixer was characterized as being a high-shear method of compounding which favoured comminution. Some preliminary
studies by Bottrill\textsuperscript{97} and Stephenson showed that addition of plasticizer shifts the process away from comminution towards a combination of densification and comminution as anticipated.

It has been shown by Cogswell\textsuperscript{110} that neither the microdomain (0.01 \textmu m) nor the domain (0.1 \textmu m) structure is deformable of itself, but that the connective tissue between the domains is highly deformable in rigid formulations.

Bottrill and Stephenson\textsuperscript{97} examined Banbury mixed PPVC samples using EM. Surfaces for examination were prepared by both freeze fracturing and microtome techniques. Their results are tabulated in Table 3. They summarised their results as follows. At the lowest compounding temperatures the surfaces are incoherent and the primary particles are clearly visible. However there is already some indication that boundaries are becoming blurred. At higher magnification a smaller structure on the domain scale is visible. At the higher processing temperatures the surfaces are continuous, densification has taken place, and the primary structure is no longer detectable. However the domain feature remains visible, particularly for the softer compositions. The micrographs suggest that, at the highest temperatures, the domain scale feature is becoming less distinct. No marked effect of plasticizer level was distinguished apart from that on the domain.

There is no direct evidence on the morphology of the crystallites to this date. The addition of a plasticizer has been shown by wide angle X-ray scattering (WAXS) to have no noticeable effect on the crystal structure of PVC. However it causes small increases in crystallinity for concentrations of up to 20 pph of DOP in PVC. For concentrations above this value the crystallinity drops, but only down to 50\% of its original value at 60 pph of DOP\textsuperscript{98}. The annealing and melting of PVC crystallites have been studied by a number of workers using thermal analysis techniques\textsuperscript{89,99-102}. It is hard to relate the measured enthalpies to crystallinities, as estimates of the enthalpy of fusion of PVC crystals vary between
TABLE 3: Effect of Increasing Processing Severity on Texture of Banbury 'Dolly' from Electron Micrographs

<table>
<thead>
<tr>
<th></th>
<th>Measured Banbury Drop Temperature</th>
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<tr>
<td></td>
<td>71°DIOP**/30***</td>
</tr>
<tr>
<td>Primary Particle Domain</td>
<td>123°C Distinct (micro-tome)</td>
</tr>
<tr>
<td></td>
<td>163°C Not visible Indistinct</td>
</tr>
<tr>
<td></td>
<td>191°C Not visible Grainy at 0.1 μm scale Indistinct</td>
</tr>
<tr>
<td>71/DIOP/50</td>
<td>142°C Not visible V. Distinct</td>
</tr>
<tr>
<td>Primary Particle Domain</td>
<td>159°C Not visible Distinct</td>
</tr>
<tr>
<td></td>
<td>188°C Not visible Distinct</td>
</tr>
<tr>
<td>71/DIOP/80</td>
<td>124°C V. Distinct V. Distinct</td>
</tr>
<tr>
<td>Primary Particle Domain</td>
<td>151°C Becoming indistinct V. Distinct</td>
</tr>
<tr>
<td></td>
<td>178°C Not-visible V. Distinct</td>
</tr>
</tbody>
</table>

* K-value; ** diisooctylphthate; *** phr. plasticizer

2.7-11.3 kJ mole⁻¹ 103-104. It is not clear whether the material which melts over the relatively small temperature range after annealing is the vast majority of the crystallines in the material 102, or just secondary crystallites and mesomorphic material.

Brown et al 105 demonstrated by WAXS that most of the crystallinity of plasticized PVC was removed in the heating/quenching process. However in the case of highly plasticized materials, WAXS study showed some crystallinity although their DSC thermograms were equally smooth.

2.4.2 Rheology

The influence of compounding history on subsequent processing behaviour can be assessed by capillary rheometry 57,58,106,107, as well as other techniques. The majority of research in this field has been carried out in rigid PVC formulations.
Krzewki and Collins\textsuperscript{60} showed that capillary extrusion pressure profiles are significantly displaced by just minor alteration in the formulation, Figure 10. The samples tested were prepared in a Brabender Plasticorder using dry blends. They also showed that calcium stearate can facilitate or delay the fusion process of the compound. Increased calcium stearate levels in compounds with wax enhance the fusion process, Figure 11. Increased calcium stearate without wax decrease fusion at relatively low temperatures but accelerate fusion at higher temperatures.

The state of fusion of a PVC formulation is not solely determined by formulation and thermal history but also by time and process deployed. Gray\textsuperscript{106} has shown that the standard fusion curves are shifted merely by altering the mixing head of the Brabender. Terselius et al\textsuperscript{108} showed that roll milling rigid PVC gave higher fusion levels than that of Brabender processed samples.

Moore\textsuperscript{109} studied the influence of plasticizer concentration and type in relation to viscosity, melt modulus and thermal history using a capillary rheometer. The effect of plasticizer concentration on the extrusion pressure is shown in Figure 12. He showed that the threshold temperature is influenced by the plasticizer concentration, as summarised in the data in Table 5. He showed that increases in plasticizer concentration led to reductions in viscosity and modulus. Using BSS 40 composition, with DIOP as the plasticizer, Moore evaluated the effect of thermal history and different types of plasticizer system. The effect of thermal history on viscosity at 120°C is illustrated in Figure 13. The higher processing temperature has resulted in both a higher viscosity at a particular shear rate and a departure from a power-low relationship ($\tau = k \gamma^n$). To evaluate the effect of plasticizer type, Moore processed BSS 40 compositions to fully fused states. Viscosity and tensile melt modulus results at 120°C are summarised in Table 4. The results demonstrate that choice of plasticizer can have a pronounced effect on rheological
**FORMULATION NO.**

<table>
<thead>
<tr>
<th>PVC</th>
<th>2 phr</th>
<th>2 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin Stabiliser</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Paraffinic Wax</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>CaSt.</td>
<td>0.25-0.20</td>
<td>0.15-0.20</td>
</tr>
</tbody>
</table>

**FIG. 10** The standard (a) and normalized (b) fusion curves for two compounds.

**FIG. 11** The normalized fusion curves for compounds with wax.
Table 4. Viscosity and melt modulus for different types of plasticizer formulation that have been well processed.

<table>
<thead>
<tr>
<th>Type of plasticizer</th>
<th>Concentration</th>
<th>Newtonian viscosity (N/m²)</th>
<th>Tensile melt modulus (MN/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Used in BSS 40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>composition)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Di-octyl phthalate</td>
<td>57</td>
<td>5.2</td>
<td>7.1</td>
</tr>
<tr>
<td>Di-2ethylhexyl</td>
<td>52</td>
<td>5.7</td>
<td>9.3</td>
</tr>
<tr>
<td>phthalate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Di-alkyl phthalate</td>
<td>52</td>
<td>5.1</td>
<td>7.4</td>
</tr>
<tr>
<td>Di-tri-decyl phthalate</td>
<td>77</td>
<td>3.4</td>
<td>5.5</td>
</tr>
<tr>
<td>Di-decyl phthalate</td>
<td>60</td>
<td>3.9</td>
<td>6.1</td>
</tr>
<tr>
<td>Di-octyl adipate</td>
<td>50</td>
<td>3.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Phthalate of straight chain alcohol</td>
<td>51</td>
<td>4.9</td>
<td>6.4</td>
</tr>
<tr>
<td>Di-butyl phthalate</td>
<td>40</td>
<td>7.5</td>
<td>10.0</td>
</tr>
<tr>
<td>Epoxidized soya-beans oil</td>
<td>60</td>
<td>7.0</td>
<td>8.6</td>
</tr>
<tr>
<td>Alkyl sulphonate ester of phenol</td>
<td>55</td>
<td>6.0</td>
<td>10.8</td>
</tr>
<tr>
<td>DIOP/chlorinate paraffin</td>
<td>40:24</td>
<td>4.5</td>
<td>6.9</td>
</tr>
<tr>
<td>Mixed glycol adipate (alcohol-chain-stopped)</td>
<td>57</td>
<td>8.7</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Table 5. Threshold temperature as a function of plasticizer concentration.

<table>
<thead>
<tr>
<th>BSS</th>
<th>Plasticizer concentration (DIOP)</th>
<th>Threshold temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>25</td>
<td>135</td>
</tr>
<tr>
<td>24</td>
<td>40</td>
<td>130</td>
</tr>
<tr>
<td>40</td>
<td>55</td>
<td>128</td>
</tr>
<tr>
<td>67</td>
<td>75</td>
<td>118</td>
</tr>
</tbody>
</table>
properties; spreads of 2.5 fold for viscosity and 2.8 fold for melt modulus were noted. Thus he suggests the choice of plasticizer is considerably more critical than the effect of thermal history on melt properties. Nevertheless, once a particular plasticizer has been selected, the consequence of thermal history on melt properties will once again become relevant.

2.4.3 Structurization (Extrudate Surface Appearance)

The term melt fracture and sharkskin are used to refer to extrudates having distorted shapes. Structurization will be used as a synonymous term here for both melt fracture and sharkskin. The level of structurization of extrudates have long been used as a rough guide to the state of fusion. The greater the distortion of the extrudate the greater its fusion state.

There are two important categories by which the structurization is assessed:

1. Extrusion performed at temperatures below the region of previous compounding temperature. Here the samples are processed (120-220°C) to various states of fusion followed by extrusion at a fixed low temperature (ca 120-140).

2. Extrusion performed at a range of temperatures and shear, the samples being compounded below the extrusion temperature.

Berens and Folt showed by extruding pellets of virgin PVC through a capillary die that increased extrusion temperature and shear rate led to increased structurization. They schematically represented the temperature and shear rate effect on structurization as shown in Figure 14. They concluded that the "scaly-to-smooth" transition regularly shifts to higher shear rates as temperature is increased, while the "smooth to rippled" boundary generally moves towards lower shear rates. The shear rate range for smooth extrusion thus narrows with increasing temperature.
They explain their results in terms of particle slippage and molecular deformation.

It has been observed that when plasticized samples are extruded, the extrudate acquires an ever increasing structurization with extrusion temperature until a transition temperature is reached where smooth extrudate begins to appear. Here the smooth extrudates from low temperature compounded samples are dull, while the smooth extrudates from high temperature compounded samples appear glossy. Rudin has shown that increasing the die length and decreasing the shear rate both led to decreased structurization. This effect has also been observed by Khanna. Khanna also found that addition of plasticizer caused a decrease in viscosity which was particularly marked at low shear rates. With 30% DIOP plasticized compounds he obtained improved smooth and glossy extrudates at extrusion temperatures of 150 and 170°C, but increase in plasticizer content to 50% showed no further improvement and impaired extrusion quality was observed at the higher extrusion temperatures. Shah and Rudin have shown that by incorporating certain polymeric additives the degree of structurization can be reduced.
Several researchers\textsuperscript{110,79,71} have shown that when PPVC is compounded at high temperature followed by low temperature shearing, a better extrudate quality is obtained.

2.4.4 Tensile Properties

The effect of increasing the process temperature is to increase fusion level, hence the tensile strength\textsuperscript{114} of plasticized PVC.

Ghersa\textsuperscript{114} showed, as shown in Figure 20, the effect of concentration of a liquid plasticizer such as DOP in suspension-type PVC. There is some critical concentration at which the tensile strength reaches a maximum, the elongation at break reaches a minimum, and the material becomes quite brittle. At a slightly higher concentration, the plasticization threshold, the tensile strength and elongation reach the original values. Beyond this the material becomes softer and tougher with lower tensile strength and higher elongation, as expected, by plasticization. With completely compatible liquid plasticizer, the tensile strength eventually drops to zero at the point where fusion no longer exists, and the PVC is simply in solution in the plasticizer. The elongation at break does not continue to increase indefinitely for at higher concentrations there are relatively few macromolecules and these tend to flow apart under a tensile stress. The antiplasticization range is broader or the plasticization threshold is higher for more polar and more globular-shaped molecules, especially with higher aromaticity, than with linear, more aliphatic and less polar plasticizers.

The effect of a number of phthalate and polyester plasticizers' concentration on British Standard Softness (BSS) is given in Figure 15\textsuperscript{115}.

Plasticization of PVC modifies not only flexibility and softness, but also all other mechanical properties. Thus tensile
Figure 15. Variation of British Standard Softness with concentration for a number of phthalate and polyester plasticisers. 

Figure 16. Variation of Ultimate Tensile Strength with concentration for various plasticisers. 

Figure 17. Variation of elongation at break with concentration for various plasticisers.
Figure 18 Variation of modulus at 100% extension with concentration for various plasticizers.

Figure 19 Variation of Ultimate Tensile Strength with British Standard Softness for various plasticizers.

Figure 20 Effect of concentration of plasticizers on mechanical properties of PVC. The solid curves approximate the behavior of common liquid plasticizers typified by DOP; data adapted from various sources (16-17). The broken curves indicate the type of behavior obtained by elastomeric plasticizers with adequate compatibility, illustrated here by polyurethane plasticizer (11-15).
strength and moduli decrease and elongation at break increases with increase in plasticizer content, the precise relationship depending on the particular plasticizer is compiled in Figures 16, 17 and 18. For any given plasticizer the actual values for each property are also dependent on the polymer used, particularly on its average molecular weight.

It is more meaningful to compare performance of plasticizers against BS softness\textsuperscript{116}. Figure 19 illustrates\textsuperscript{116} that similar plasticizers, the alkyl phthalate plasticizers, have the same tensile strength and softness. Markedly different plasticizers, such as aryl phosphates, however, show an appreciably different relationship.

2.5 Fusion Hypotheses

There are three major hypotheses that have been proposed to account for the main effects produced by PVC compounds. The crystallinity theory, entanglement theory and the particle breakdown theory are the products of many workers. They are used to explain fusion process, and are so intermingled in the thinking of researchers than the three are commonly employed to explain different parts of the total phenomenon of fusion.

2.5.1 Crystallinity Theory

The most common idea used in literature to explain the behaviour of PVC is that PVC crystallites, of a wide melting range and spaced at 0.01 \textmu m, act as crosslinks, in a three-dimensional network.

J Summers\textsuperscript{73} has used a model from X-ray diffraction and small-angle scattering data, swelling data, and processing data to explain fusion. The model of the average crystallite is illustrated in Figure 21. These crystallites, he suggests, are connected together by tie molecules and have a 100 \textmu A (0.01 \textmu m) spacing as
Fig 21. Average crystal size of PVC. Real crystals are probably not so uniformly structured.

Fig 22. The microdomain structure of PVC.

Fig 23. Primary particles in a low temperature melt (162°C) (not to scale).

Fig 24. Primary particles, partially melted and interacting, in a 177°C melt (not to scale).

Fig 25. Primary particles after cooling and recrystallization from a 177°C melt (not to scale).
shown in the model in Figure 22. This model explains the reason for the poor interaction of the primary particle flow units in the low temperature melt\textsuperscript{52,74,75}. Because the material within a primary particle is held together by a three dimensional network structure, it cannot interact with other primary particles, Figure 23. At a higher temperature as some of the crystallites melt (177°C) interaction between primary particles increases even though the primary particle is not completely destroyed\textsuperscript{52,75}, Figure 24. As this melt cools, recrystallization occurs linking the primary particles together by newly formed crystallites, Figure 25. These crystallites cause fibrils in acetone swollen/sheared samples\textsuperscript{62,75} and gives a much tougher product\textsuperscript{76}. This structure proposed in Figures 23 and 24 by Summers, can also explain the melt rheology data of Collins and Metzger\textsuperscript{77}. When they plotted log viscosity vs the inverse of temperature, the slope relates to the activation energy for flow. At low melt temperature the slope was low indicating a low activation energy that corresponds to the structure of Figure 23. Here one expects melt fracture at the primary particle boundary since primary particles flow independently of each other therefore giving the low activation energy. At high temperatures where enough melting occurs to give strong interactions between primary particles such as in Figure 24 or at higher temperatures with more melting, melt fracture will cease and therefore give a higher activation energy for flow.

2.5.2 Entanglement Theory

This theory is similar to that of Crystallinity Theory in that in the Crystallinity Theory it is proposed that the crystallites form the crosslink sites which impart the behaviour of PVC compounds while in the Entanglement Theory, the entanglements provide the character.

This theory will be dealt with to an extent to explain solvent test, Section 2.6.1 and extrudate surface texture,
Section 2.6.4. The hypothesis is being looked upon as follows. A PVC powder consists of primary particles often aggregated into agglomerates. The primary particles (0.1-1.0 μm) are derived from polymerization process. Following Berens and Folt $^{74,78,79}$, that the primary particles often maintain their identity throughout a processing operation. Each polymer particle itself represents a molecular entanglement network formed during polymerization and limited in extent by particle boundaries. Upon compounding at low temperatures a clear coherent mass can be formed, but the particle boundaries remain well defined. The bonding forces at the interfaces are only interactions between adjacent chain segments. Compounding at high temperatures results in increased interdiffusion of short-chain segments across particle boundaries. Entanglements of molecules remain concentrated within the particles and are weak at the boundaries.

2.5.3 Particle Breakdown Theory

Here both the Crystallinity Theory and Entanglement Theory have been used in conjunction with the way in which the PVC grain breaks down to explain the process of fusion. There are two hypotheses one by Krzewki and Collins $^{60}$ and the second by Allsopp $^{59,78}$ suggested to explain the process of fusion on breakdown of the PVC grain.

That proposed by Krzewki and Collins will be discussed first. They suggested the breakdown of coarse, porous resin particles and formation of finer structure are two steps involved in the processing of PVC compounds. The second step, defined by an increase in the melt elasticity, begins when the primary particle, which results from the breakdown of the original resin particles are compacted and the formation of molecular network across their boundaries commences. This stage of fusion process can also be looked upon as sintering or interdiffusion of particles. With further progression of interdiffusion the boundaries between particles disappear, the particles lose their identity, and a three-dimensional network of polymer chains is formed. The degree
of interpenetration of particles can be used as a measure of the extent or state of fusion achieved during the processing operation. The interparticle strength then becomes the main factor, determining the strength of the fused material.

Krzewki and Collins suggest the resin particles can be broken all the way down to domains or only to primary particles. The extent of breakdown is primarily dictated by the amount of thermomechanical energy introduced into the processed material.

If the microparticles are not broken down to domains at lower temperature, they begin to fuse internally. This increases the strength within primary particles and decreases the probability of their breakage at higher temperature. The weakest link which determines the overall strength of processed material then becomes the interface between primary particles.

A schematic illustration of the three patterns of fusion is shown in Figure 26. All three patterns of fusion can play a role in processing of PVC compounds. The relative ratio of the three mechanisms at a given position or time in processing equipment is determined by processing variables. The overall generalized picture of the fusion process is illustrated in Figure 27. The amount of energy input, in turn, is determined by a balance between compound composition, equipment parameters, and processing conditions.

Allsopp\textsuperscript{59,78} has described the mechanism of gelation with regards to the amount of temperature, shear and the pressure profile of each processing machine. He suggests the fusion of UPVC involves the compaction, densification, fusion and elongation of grains, the CDFE mechanism, with little if any comminution of the PVC grains taking place, Figure 28. He concludes that confusion had arisen since published work generally uses high shear/aggressive mixing equipment, e.g. Brabender, as the basis for mechanistic studies. In his work he confirms that a considerable degree of
FIGURE 26: A Schematic Illustration of the Three Patterns of Fusion

FIGURE 27: A Generalized Picture of the Fusion Process
comminution takes place in both the Brabender Plasticorder and the laboratory scale Banbury mixer but the mechanism operating on this specialised equipment cannot be transposed to extrusion.

Allsopp summarised the behaviour on different machines in Figure 29 and is related to temperature, pressure and shear profile of each machine. If conditions are such that pressure/shear is applied before densification is complete, i.e. Brabender, grain comminution results but in the less aggressive conditions in an extruder, grain densification is complete before shear forces can be applied. The importance of pressure on fusion mechanism is seen in Figure 29, where the large scale Banbury mixer and the
ICI modified Brabender behave in an intermediate manner. In each case the machine is operated under a lower pressure regime than normal and a partial changeover in mechanism from comminution to densification is recorded, markedly so in the case of the ICI modified Brabender. Use of the latter ensures that more relevant studies can be completed on the small scale since the mechanism is more typical of that in extruders.

2.6 Methods of Assessing the State of Fusion

2.6.1 Solvent Testing

Although commercial PVC is largely an amorphous polymer, X-ray and electron diffraction studies have indicated the presence of 5-15% crystallinity44,61-63. Natta and Corradini, in their study of oriented PVC fibres, reported that these crystalline regions possessed a low order of perfection along the main chain axis and were formed from syndiotactic sequences of polymer45.

As early as 1949 it was reported that crystalline PVC segments acted as crosslinks allowing the resin to accept large amounts of solvents46. The model assumed that the amorphous regions of the polymer were solvated while the crystalline domains were not. Direct observation of the network-like structure of plasticized PVC was gained by Bain47,48 and Davis49 using staining techniques.

Thus, since increased network by crystallites leads to increased fusion, see Section 2.4.1, and that acetone does not destroy the crystallites52, fusion state can be assessed using suitable solvents. Swelling in solvents is of no value in itself in determining the difference between fused and unfused polymer since both PVC polymer and fully fused PVC swell. If, however, we consider the mechanical effect such swelling would have on a PVC sample on mixed fusion state, we may deduce that where a fusion network exists, swelling will have little effect on the cohesion of the sample because of the restraining effect of the network. But where particles
which are not part of the molecular network exist and which are held together at best by sintering, it is reasonable to assume that sufficient swelling could dislodge them from their neighbours and cause some disintegration of the sample. The more of such particles there are, the more will be the disintegration; the fewer such particles, the less will be the disintegration. But when very few 'free' particles exist they will be protected from physical separation by the pressure of fused material. Thus it might be assumed that the effect of a suitable solvent on a poorly fused PVC could be dramatic, i.e. disintegration, but to use such an effect to attempt to distinguish fine differences between fairly well fused PVC samples might prove difficult.

At first, acetone was the most widely used solvent and this led to the introduction of standards in both Britain and the USA. In recent years methylene chloride has been suggested as an alternative solvent to acetone despite the fact that methylene chloride is toxic although it has the advantage of being less hygroscopic compared to acetone.

2.6.2 Microscopy

On processing under heat and shear, the PVC grain (unfused) morphology is gradually broken down until a stage is reached whereby the PVC structure is completely broken down to give a continuous matrix (fully fused). Thus a logical way to establish the state of fusion of PVC is to elucidate the stage at which the destruction of the PVC morphology has taken place. This is simply done by observing it with a microscope. The ideal instrument is the scanning electron microscope (SEM). The freeze fractured surface of the specimen is coated with metal, usually gold, prior to examination by the SEM.

The SEM method has limitations in that, for example, only a very small area of the specimen surface is examined. As a quality control instrument it is a non-starter and a much faster and easier technique is necessary.
Summers and Rabinovitch have demonstrated\textsuperscript{52} that swelling a PVC product in acetone and shearing between glass-slides reveals the morphology under optical microscopy that is consistent with that observed in fractured specimens by SEM.

Many other techniques have also been used e.g. X-ray diffraction, fluorescence microscopy, staining techniques, ion-etching, etc.

2.6.3 Capillary Rheometry

The pressure necessary to extrude a material through a capillary with diameter D and length L can be expressed as:

\[ \Delta P = \tau(2n + S_R) + \tau \cdot \frac{4L}{D} \]

where the first term is the capillary entrance pressure loss and the second term originates from the viscous dissipation during flow through a capillary\textsuperscript{53,54}.

The entrance pressure loss is a product of the wall shear stress \( \tau \) and a sum of two terms. The first term, \( n \), is the viscous loss and the second, \( S_R \), is the elastic term, also called recoverable shear strain.

For viscoelastic fluids, the total entrance-drop \( \Delta P_{ent} \) may be divided into two parts: the viscous entrance pressure-drop \( \Delta P_{vis} \) and the elastic pressure drop \( \Delta P_{ela} \):

\[ \Delta P_{ent} = \Delta P_{vis} + \Delta P_{ela} \]

The viscous entrance pressure drop is related to the viscous dissipation due to the converging flow prior to entering the capillary and to the development of the velocity profile near the entrance of the capillary.
The elastic entrance pressure drop is the pressure drop which may be converted into elastic energy, some of which is recoverable due to the elastic nature of the melt.

It has been observed in several polymer melts that the value of $\Delta P_{vis}$ is approximately 10% of the entire pressure-drop\textsuperscript{55,56}. This indicates that most of the entrance pressure-drop may be considered to be due to the melt elasticity, rather than to the melt viscosity.

Therefore for practical purposes, it can be assumed that:

$$\Delta P_{ent} = \Delta P_{ela}$$

and the variation in the entrance pressure loss can be attributed primarily to changes in the elasticity of the material under test\textsuperscript{45}. Since we are interested in measuring the elastic effect (molecular network), a very short capillary - very small L/D ratio (a "zero-length" die) - to give pressure drop nearly identical to the entrance pressure loss and can be obtained from a single measurement. Lamberty\textsuperscript{57} was able to demonstrate this for PVC and thus explained his own results and earlier results of Gonze\textsuperscript{58}.

In his earlier paper Gonze described a method of obtaining a numerical value for the "percentage fusion" of a PVC compound. Here they processed PVC to various temperatures and the pressure necessary to cause elastic deformation of the melt at the die entrance of these samples was measured to give a reference curve or standard curve, see Figure 30\textsuperscript{59}.

Once the reference curve is produced, it can be used to evaluate the degree of fusion of other samples of the same material made on the same equipment. Gonze identified the maximum value of the extrusion pressure reached ($P_{max}$) as representing full fusion and the lowest value ($P_{min}$) as minimum fusion. A sample of unknown state of fusion might give a value $P_{sample}$ and its state of fusion is
obtained from the expression:

\[
\% \text{ Fusion} = \frac{P_{\text{sample}} - P_{\text{min}}}{P_{\text{max}} - P_{\text{min}}} \times 100
\]

The morphological changes, in PVC grains, that take place on processing as shown in Figure 30, are exemplified in Section 2.5.3. The anomalous 'negative degree of fusion' reflects the breakdown of PVC grains and the very beginning of formation of a molecular network across the primary particle and domain boundaries.

2.6.4 Structurization

Further information can be gleaned from the extrudates obtained from the Capillary Rheometer. As we increase the state of fusion of a sample, we observe a transition of smooth (poorly fused) to scaliness (characterised by surface tearing varying in frequency, regularity and depth) to rippling (an irregular surface without tearing) and finally to the extreme amount to 'knotty' highly distorted appearance (highly fused) in that order. Thus the
extrudate state of distortion gives a means for giving an idea of the state to which a sample is fused.

The term melt fracture was first designated to these distorted shapes by Tordella\(^ {64}\). Sieglaff\(^ {65}\) has shown the presence of melt fracture in PVC at certain conditions, and a decrease of melt fracture from adding certain additives. Shah\(^ {66}\) has shown increases in the degree of melt fracture with decreases in the percentage of plasticizer in PVC. In his work, Shah has also shown that melt fracture is reduced when certain internal lubricants are added to PVC. Furthermore he showed that the onset of melt fracture was noticed as a change in the slope of a log-log plot of shear stress vs shear rate\(^ {67}\). Shah's results closely agree with the findings of Ballenger et al\(^ {68}\), which show that the onset of melt fracture is associated with the elastic properties of polymer melts.

The shearing action of processing tends to disentangle the polymer molecules which not only influence melt fracture but also die swell in extruded products\(^ {69}\). Rudin\(^ {70,71}\) found that fused PVC exhibited both of these unwanted phenomena. He considered this to be at least in part a relaxation process which could be approximated by one-parameter Maxwell decay relation:

\[
\frac{D}{D_0} = e^{-\frac{t}{\tau}} \tag{1}
\]

where \(D\) is the observed severity of extrudate distortion, \(D_0\) is the corresponding severity with a zero length capillary, \(\tau\) is a relaxation time characteristic of the polymer (and its history) and \(t\) is an average residence time in the capillary. The average residence time may be expressed on a volume transit basis as:

\[
t = \frac{\pi r^2 L}{Q} \tag{2}
\]
where \( r \) and \( L \) are the capillary radius and length and \( Q \) is the volumetric polymer flow rate. Since the apparent Newtonian shear rate of the polymer, \( \dot{\gamma} \), is:

\[
\dot{\gamma} = \frac{4Q}{\pi r^3}
\]  

(3)

\[
t = 4\left(\frac{\pi r^3}{4Q}\right)^\frac{L}{r^3} = \frac{4L}{r\dot{\gamma}}
\]  

(4)

Thus the Maxwell relation of Equation 1 is equivalent to:

\[
\frac{D}{D_0} = \exp\left(-\frac{4L}{r\dot{\gamma}}\right)
\]  

(5)

This last equation predicts that the extrudate will show less distortion when the relaxation time is shortened. This can be accomplished by increasing the extrusion temperature or by adding more plasticizer, since this permits the polymer molecules to adjust quickly to more favourable energetic positions. Rudin\textsuperscript{70,71} showed this to be true by extruding PVC plasticized with BBP at temperatures from 140\(^\circ\)C, where it gave severe melt fracture, to 160\(^\circ\)C, where it gave no melt fracture.

Equation 5 also predicts that decreasing the shear rate would decrease the distortion of the extrudate, and this is true after melt fracture has occurred and the extrudate is trying to heal the wound. Yet in the entangled polymer melt, shearing should reduce the entanglement and consequently the hot melt elasticity. This decreases the relaxation time \( \tau \), since an unentangled molecule can adjust to a relaxed position much faster than an entangled one. Given time, however, the molecules will revert to an entangled mass if the polymer molecules in the melt have sufficient mobility for segmental movement. At relatively low temperatures, shear should produce a disentangled polymer which would briefly have a much shorter relaxation time. If the same shear is applied at
higher temperatures there is less tendency to disentangle the polymer chains, and disentangled chains can quickly become entangled again. Rudin demonstrated that PVC plasticized with either BBP or with 6-10 phthalate which was milled at 160°C for 5 minutes and then 5 minutes at a lower temperature 140°C, would produce a smooth extrudate, while one which had been milled at 160°C for 10 minutes produced a rough extrudate. The disentangled molecules produced at 140°C remain disentangled long enough to pass the critical point in the extrusion where melt fracture otherwise would have occurred. In the disentangled state they could adjust to the demands of the extruder. He theorizes that polymeric flow aids act to stabilize the disentangled state of a sheared melt.70,71

2.6.5 Thermal Analysis

The most recent possibilities for measuring the state of fusion have been reported by Gilbert and Vyvoda.72 They used a Du Pont 990 Thermal Analyser fitted with DSC cell, an instrument which measures the heat necessary to raise a specimen of the test material through a selected range of temperature and displays the endothermic or exothermic effects encountered. Samples of rigid PVC compound were compression moulded at various temperatures and subsequently examined in the Analyser in which they were heated from room temperature to 240°C at 20°C min⁻¹. Figure 31 shows the DSC traces obtained which they interpreted as follows.

Three features were observed in the DSC traces. First, an endothermic baseline shift corresponding to the glass transition temperature of the polymer. In addition there were two endothermic peaks A and B. Peak B represents the melting of crystallites of various sizes and degrees of perfection. They showed that this peak decreased in size and shifted to a higher temperature as the processing temperature increased. The size decrease was attributed to melting of less perfect or smaller crystallites while the temperature shift was caused by annealing of unmelted crystallites. As processing temperature was increased endotherm A appeared and
increased in size. They observed similar results with samples from Brabender plastograph. Gilbert and Vyvoda plotted the size of A against processing temperature and noted the development of a steep rise in area at a similar temperature to the initial increase in extrusion pressure found in the fusion curve obtained by capillary rheometry. Thus they identified this technique as a potential method of assessing the state of fusion. In their analysis they suggested that the position of peak B provided information about the maximum temperature to which the polymer has been subjected. The area of A, they suggested, might be related to the degree of fusion. The nature of endotherm A is not yet fully understood but it is possible that it is due to the formation of imperfect ordered
regions which are produced as a continuous PVC network develops, and which subsequently melts on reheating.

Although the results are not fully understood it provides a potential method to assess the state of fusion. The method has the advantage in that it uses small samples.

2.7 Reprocessability

The process of molecular diffusion and network formation which is fusion seems unlikely to be reversible. This, perhaps surprisingly, proves not to be the case. Lamberty\textsuperscript{57} was able to show evidence of rheological changes in reprocessed PVC to support a theory of reversibility. This effect has been studied in greater detail by Portingell\textsuperscript{79}.

Portingell processed UPVC in Brabender Plasticorder to \(180^\circ C\) and then reprocessed it from room temperature to \(180^\circ C\) and to \(135^\circ C\). He extruded these samples through a low L/D ratio die on a Capillary Rheometer at \(130^\circ C\). The value of the entry pressure on the sample reprocessed to \(180^\circ C\) was the same order as he had measured before reprocessing. The value of the sample reprocessed to \(135^\circ C\) showed reduction in the measured entry pressure of 35 kN m\(^{-2}\). He explains this lowering state of fusion by the application of shear at lower temperatures as that the shearing forces have a 'combing out' effect on the molecular network. Such an effect is known in polyethylene processing can result in chain entanglement.

Using scanning electron microscopy he showed that the sample processed to \(180^\circ C\) showed no evidence of a true primary structure. However the sample reprocessed to \(135^\circ C\) showed some evidence of primary particles. He gives no explanation of this phenomenon.

Further, evidence of reversibility can also be drawn from Rudin\textsuperscript{70,71} and Khanna's\textsuperscript{69} work. They processed samples to high temperatures followed by reprocessing them to low temperature from
room temperature. The samples processed at high temperatures gave very rough extrudates but the reprocessed samples gave smooth extrudates at low extrusion temperatures as did the low temperature processed samples. P Benjamin agrees (private communication) that a new structure is created when a well fused material is sheared at low temperatures.
CHAPTER 3

3.1 Assessment of Fusion Characteristics

3.1.1 Processing

3.1.1 Materials

A 'Corvic' S71/102 PVC, fully characterized by ICI, was used. The batch information is given below:

<table>
<thead>
<tr>
<th>'Corvic' S71/102</th>
<th>Batch 542/359</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-value</td>
<td>72.1</td>
</tr>
<tr>
<td>Packing Density</td>
<td>541 g l⁻¹</td>
</tr>
<tr>
<td>Sieve Analysis</td>
<td></td>
</tr>
<tr>
<td>retained on BS 60 mesh</td>
<td>0%</td>
</tr>
<tr>
<td>72 mesh</td>
<td>0%</td>
</tr>
<tr>
<td>100 mesh</td>
<td>24.5%</td>
</tr>
<tr>
<td>150 mesh</td>
<td>42.9%</td>
</tr>
<tr>
<td>200 mesh</td>
<td>29.3%</td>
</tr>
<tr>
<td>passing 200 mesh</td>
<td>3.3%</td>
</tr>
</tbody>
</table>

The K-value 71 was calculated from relative viscosity data obtained by method ISO-R174. A simple formulation was chosen by ICI (Cleveland UK) for this project as shown below:

<table>
<thead>
<tr>
<th></th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC Corvic 571/102</td>
<td>100</td>
</tr>
<tr>
<td>DIOP (plasticizer)</td>
<td>50</td>
</tr>
<tr>
<td>LC 68 (Cd/Ba stabilizer)</td>
<td>2</td>
</tr>
<tr>
<td>Calcium Stearate</td>
<td>0.5</td>
</tr>
</tbody>
</table>

For details on DIOP (Diisooctylphthalate) see Section 3.2.1.1.
3.1.1.2 Dry Blending

A laboratory scale high speed & T K Fielder mixer was used to mix the above ingredients. A schematic diagram of such a mixer is shown in Figure 32. The ingredients to be mixed are placed in the upper high speed mixing chamber which can be preheated to the desired temperature, usually by the circulation of hot heat exchange oil or steam. The rotors at the base of the chamber, which are often of complex design were sigmoidal in shape in our case, are caused to rotate at speeds of up to 4000 rpm. The powder is thrown out by the centrifugal action of the rotor and rises up the walls of the mixing chamber, to return down the central zone, creating a fluid like movement with a vortex. This ensures that all the ingredients at some stage will come into contact with the hot chamber walls and pass through the shear gaps between the blades and the wall. The chamber also consists of a large baffle to ensure contact of all parts of the mix enhancing thorough mixing. Iron/constantan thermocouples protrude through the baffle and the chamber wall. The thermocouples are connected to Servoscribe chart recorders which continuously record the temperature as milli-volts. Once the required temperature is attained the mix can be discharged automatically or manually into the large cooling mixing chamber. The cooling mixer has a large blade and capacity to that of the mixing chamber. The blade rotates at lower speeds and the chamber is cooled by a coolant like water. Thus the cooling mixer is designed to give minimal frictional heating.

The solids and the liquid ingredients were pre-mixed separately in buckets before adding to the mixing chamber. To have minimal processing effects on the blend the ingredients of the formulation were all added to the mixing chamber before blending and mixing was commenced. The solid pre-mix was added first, followed by the liquid pre-mix. To obtain as close a reproducible blend as possible, the jacket steam temperature was set at 80°C to give a constant blank baffle temperature (the temperature of the baffle before mixing commenced) of 72°C and a constant blank jacket temperature (temperature
of the mixing chamber wall before mixing commenced) of 70°C for each mix carried out. Three batches of these runs were mixed together in the cooler to minimize mix to mix variation. A rotor speed of 1000 rpm was used to mix and the mix was discharged when the baffle temperature reached 120°C. The discharged mix was cooled by mixing for one minute in the cooling chamber with the rotor-speed at 2000 rpm.

3.1.1.3 Mixing in Brabender Plastograph

The dry blends from the T K Fielder were mixed in a Brabender plastograph, whose construction and operation have been described in literature\(^1\)\(^2\)\(^3\)\(^4\), according to ASTM\(^5\)\(^4\). The plastograph is a laboratory version of a Banbury mixer and is equipped to measure the torque generated on the mixing rotors. The rotors rotate at a 3:2 ratio and are of rather irregular geometry. The Brabender is an unsteady-state operating device where the energy of the
stirring blades is transmitted to viscous shear energy of the melt which, in turn, appears as an increase in internal energy and temperature of the system. A schematic diagram of the mixing head is given below:

![Schematic Diagram of Brabender Plastograph Mixing Head]

FIGURE 33: Schematic Diagram of Brabender Plastograph Mixing Head

Figure 34 shows a typical plastograph for the evaluation of a dry blend of a rigid PVC. The powder after compressing and heating phase (a) in contact with the walls of the mixer and the rotors, begins to soften. Due to the external heating and to the energy supplied by the rotor movement, the particles begin to fuse from the outside inwards. An increase of the friction coefficient and consequently of the stress registered by the plastograph (segment b-c) results. At the same time the temperature of the mass increases.

The material increases in viscosity to a peak at time (c) indicated as apparent fusion time (B). The slope of the time-temperature curve is greatest in the fusion interval.

After (c) the viscosity of the mass tends to decrease as a result of terminal increase of temperature and of the increasing...
homogenization of the material. Therefore when the temperature is stabilized (d) it is possible to determine the equilibrium torque at the temperature indicated by the compound thermocouple. The difference, $T_{eo}$, between this temperature and that imposed on the jacket at fusion is a useful indication of the frictional heat development at that particular shear rate.

A preload weight of 2 kg, charge of 37 g, rotor speed of 30-200 rpm, and a jacket temperature of 120-200°C were used. The Goodrich type-chute inserts method given in the standard 124 was used. With the mixer running the sample was poured into the mixer allowing ½ min after which the mixer was shut off. The sample was allowed to heat up for a total of 3 min, including loading time. At the end of the heat-up time the mixer was started and mixing carried out for a further 12 minutes before removing the sample.
3.1.1.4 Extrusion

A large amount of literature is available on various aspects of extrusion. PVC dry blend from the Fielder was flood fed into the hopper of a Bone-Craven single-screw extruder. The material was extruded with varying screw speeds between 10-90 rpm with die temperatures set between 110-180°C. The five barrel temperatures were set at descending intervals of 50°C from the die temperature. Extrudate strips were obtained using a slot die of dimension 50 x 3 mm without any haul-off. The extrudate was allowed to cool in air. The first extrudate was obtained after running the extruder for half an hour to attain equilibrium. After which, on changing the processing conditions and maintaining it, at least a five minute run was allowed before taking samples. Samples were cut at one minute intervals to give output rate. The voltage was also recorded at each condition of extrusion.

3.1.1.5 Compressing Moulding

A constant blank weight of 110g of the dry blend was used to mould sheets at various temperatures 110-200°C using a mould of dimensions 232 x 155 x 2.2 mm. The following moulding conditions were used:

<table>
<thead>
<tr>
<th>Moulding temperature</th>
<th>&lt;170°C (steam heated press)</th>
<th>&gt;170°C (electrical heated press)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moulding pressure</td>
<td>25 tons</td>
<td></td>
</tr>
<tr>
<td>Preheating time</td>
<td>15 mins</td>
<td></td>
</tr>
<tr>
<td>Moulding time</td>
<td>15 mins</td>
<td></td>
</tr>
<tr>
<td>Cooling time</td>
<td>15 mins</td>
<td></td>
</tr>
</tbody>
</table>
3.1.2 Analysis for Fusion Characteristics

3.1.2.1 Capillary Rheometry

A Davenport capillary rheometer was used for studying the flow properties. The basic principle of a capillary rheometer is that a sample is heated to a specified temperature in a barrel. The sample is then forced out through a precisely dimensioned extrusion die using a plunger. Details of the instrument are found in reference 126.

A sensitive temperature measurement and control circuit ensures that the selected test temperature is accurately held and when the test sample has reached the desired test temperature, measured using a thermocouple and Comark, the sample is extruded through the die at a predetermined shear rate, by means of a power driven piston, the forward speed of which can be accurately controlled.

As the material is forced out through the die, the pressure needed to do this (generated by the constant speed piston) is continuously measured by a pressure transducer, whose sensing head is inserted into the side of the barrel and placed so as to be as close as is practically possible.

The pressure developed is displayed continuously on a chart recorder in millivolts. From the piston speed and the developed pressure corresponding thereto, SHEAR RATE and SHEAR STRESS, respectively, can be calculated.

The viscosity is described in terms of shear stress ($\tau$) versus shear rate ($\dot{\gamma}$) where

$$\tau = \frac{P r}{2 l}$$

'P' is flow pressure, 'r' is die radius, 'l' is die length.
\[
\gamma_N = \frac{4Q}{2\pi r^3}
\]

\(\gamma_N\) is Newtonian shear rate, \(Q\) is volumetric flow rate.

The moulded samples, Banbury mixes and the extruded strips were extruded through a low length/diameter (L/D) ratio die (a zero-length die) of diameter 0.2 cm at a barrel temperature of 120°C at a piston speed of 2 cm min\(^{-1}\) having a shear rate of 121 sec\(^{-1}\). The barrel was preheated for 15 minutes and then another 30 minutes with the sample before extruding. Measurements were carried out in duplicate.

3.1.2.2 **Differential Scanning Calorimetry (DSC)**

The DSC system easily and rapidly measures both the temperatures and the heat changes associated with transitions in materials. The measurement provides both qualitative and quantitative data about the physical and chemical change of the material involving either an endothermic (heat absorption) or exothermic (heat evolution) process.

The DSC-cell is the measuring unit, Figure 35. It uses a constantan disc as the primary heat transfer element, which is enclosed in a silver heating block with a silver lid. The sample of interest and an inert reference are placed in pans which sit on raised platforms on the disc. Heat is transferred through the disc into the sample and reference via the sample pans. The differential heat flow of the sample and the reference is monitored by the junction of the constantan disc and a chromel wafer. This thermocouple junction under the sample platform is used to measure sample temperature. An alumel wire welded to the reference platform is a dummy for thermal balance. Purge gas can be admitted to the sample chamber through an orifice in the block wall on the left between the two raised platforms. The purge gas enters the cell, and is preheated by circulation through the block before entering the sample chamber at block temperature.
The peak area under the DSC curve is used to calculate heat of fusion $\Delta H_f$ by substitution into the equation:

$$\Delta H_f = \frac{A}{m} (60 \times E \times \Delta_{QS})$$

where:

- $A$ = Peak area in cm$^{-2}$
- $m$ = Sample mass in g
- $E$ = Cell calibration coefficient in mW/mV
  
  \[ E = 0.1937 \]

- $\Delta_{QS}$ = Y-axis range setting in mV/cm
- $\Delta H_f$ = Heat of fusion in J/kg.

DSC traces of the Brabender, extrusion strips and compression moulding samples were obtained using a Du Pont 990 Thermal Analyser fitted with a DSC cell. Samples of 10-15 mg weight were heated from
ambient temperature to 230°C at 10°C per minute. The cell was
purged with nitrogen at 70 cm³ per minute.

3.1.2.3 Acetone Test

Small pieces of accurately weighed samples of compression
mouldings, extrusion strips and Brabender mixes were placed in
sealed containers with excess analytical grade acetone at ambient
conditions for two days. The samples were removed and thoroughly
washed with fresh acetone and the samples allowed to dry for a
further few days. The samples were reweighed to establish their
weight loss.

3.1.2.4 Optical Microscopy

Morphology studies by Summers⁵² showed that swelling of PVC
samples in acetone and shearing between glass slides reveals a
morphology in the optical microscope consistent with that observed
by low temperature fracturing and observation in the scanning
electron microscope.

Hence small samples of compression mouldings, extrusion strips,
and Brabender mixes were allowed to swell in acetone for two weeks
after which small portions of samples were sheared between glass
slides and observed using a common light microscope, except a dark
field was used to give better contrast for the opaque samples. The
instrument factors were kept constant for valid comparisons.

3.1.2.5 Tensile Testing

The stress-strain properties of the compression moulded speci­
mens and extruded strips were determined using an Instron Universal
Testing Machine at ambient conditions. The tensile test specimen
profile was according to BS 2782¹²⁸, shown overleaf.

The ultimate tensile stress (σₚ) of the specimen can be defined
as:

$$
σₚ = \frac{F}{A}
$$
Dimensions are in millimetres.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Minimum/Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>Overall length, 115/80.5</td>
</tr>
<tr>
<td>B</td>
<td>Width at ends, 25 ± 1</td>
</tr>
<tr>
<td>C</td>
<td>Length of narrow parallel portion, 33 ± 2</td>
</tr>
<tr>
<td>D</td>
<td>Width of narrow parallel portion, 6 + 0.4, -0</td>
</tr>
<tr>
<td>E</td>
<td>Small radius, 14 + 1</td>
</tr>
<tr>
<td>F</td>
<td>Large radius, 25 ± 2</td>
</tr>
<tr>
<td>G</td>
<td>Distance between reference lines, 25 ± 1</td>
</tr>
<tr>
<td>H</td>
<td>Initial distance between grips, 80 ± 5</td>
</tr>
<tr>
<td>I</td>
<td>Thickness, minimum 1, maximum 3, preferred 2</td>
</tr>
</tbody>
</table>

In any one specimen, the thickness of the narrow parallel portion shall nowhere deviate by more than 2% from the mean.

Method 320A. Test piece

FIGURE 36: Tensile test piece profile

where: F is the force at break (in N)
A is the initial mean cross-sectional area (in m²)

and the ultimate tensile strain is defined as:

\[ \gamma_b = \frac{l - l_0}{l_0} \times 100 \]

where: \( l \) is the final length between reference lines
\( l_0 \) is the initial length between reference lines.

The elongation at break (\( E_p \)) of the specimen can be expressed by the following equation

\[ E_p = \frac{l - l_0}{l_0} \times 100 \]

The secant modulus (\( E_m \)) can be defined as:

\[ E_m = \frac{F}{A} \]

where \( F \) is at a specified elongation, 100% in this case.
Test specimens were prepared from compression mouldings and the extruded strips. The extruded strips being uneven were profiled to smoothness using silicone "sandpaper", with water running over the paper to avoid frictional heating while rubbing the samples against the paper. The stress-strain curves were plotted automatically by an X-Y plotter. The test was carried out at low constant cross-head separation rate of 1 cm min⁻¹ and an average measured from three samples was taken as the result.

3.1.2.6 Extrudate Appearance

Extrudate appearance from capillary rheometers have long been used to give a guide to the level of fusion state. Hence the surface texture of the extrudates obtained from Davenport Capillary Rheometer, see Section 3.1.2.1, was observed visually.

3.2 Effect of Plasticizer on Fusion and Processing

3.2.1 Processing for Sample Preparation

3.2.1.1 Materials

The formulation used was the same as that given in Section 3.1.1.1:

<table>
<thead>
<tr>
<th>Material</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>100</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>30, 50, 70</td>
</tr>
<tr>
<td>Cd/Ba stabilizer</td>
<td>2</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Except seven different plasticizers each at three different concentrations were used. The structural formulae for these plasticizers is given below with hydrogens attached to carbon being omitted for clarity.
1. Diisooctylphthalate, DIOP
   \[ \text{C}_{24}\text{H}_{38}\text{O}_4 \]
   \[
   \begin{array}{c}
   \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\
   \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C}
   \end{array}
   \]

2. Diisononyl phthalate, DINP
   \[ \text{C}_{26}\text{H}_{42}\text{O}_4 \]
   \[
   \begin{array}{c}
   \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\
   \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C}
   \end{array}
   \]

3. Ditridecylphthalate, DTDP
   \[ \text{C}_{34}\text{H}_{58}\text{O}_4 \]
   An ester of very highly branched, mixed 13-carbon alcohols, e.g.
   \[
   \begin{array}{c}
   \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\
   \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C}
   \end{array}
   \]
   etc...

4. Butylbenzylphthalate, BBP
   \[ \text{C}_{19}\text{H}_{20}\text{O}_4 \]
   \[
   \begin{array}{c}
   \text{C} - \text{O} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C}
   \end{array}
   \]
5. **Trialthanol trimellitate, TATM** ca. \( C_{33}H_{54}O_6 \)
An ester of mixed, almost completely linear, 7 and 9 carbon alcohols, e.g.

\[
\begin{align*}
\text{C-O-C-C-C-C-C-C-C-C-C} \\
\text{C-C-C-C-C-C-C-C-O-C} \\
\text{C-O-C-C-C-C-C-C-C-C-C-C}
\end{align*}
\]

6. **DPN - 50:50 mixture of DIDP and isodecyl nylonate.**

7. **OPN - 50:50 mixture of DIOP and isooctyl nylonate.**

**Diisodecyl phthalate, DIDP** \( C_{28}H_{46}O_4 \)
An ester of 10 carbon, usually very highly branched oxo alcohol, e.g.

\[
\begin{align*}
\text{O} \\
\text{C-C-C-C-C-C-C-C-C-C} \\
\text{C-O-C-C-C-C-C-C-C-C-C-C}
\end{align*}
\]

**Isodecyl nylonate, IDN** ca. \( C_{25}H_{98}O_4 \)
A mixed acid (adipic, glutaric and succinic) ester of isodecyl

\[
\begin{align*}
\text{O} \\
\text{C-C-C-C-C-C-C-C-C-C-C-C-C} \\
\text{C-C-C-C-C-C-C-C-C-C-C-C}
\end{align*}
\]

**Isooctyl nylonate, ON** ca. \( C_{23}H_{40}O_4 \)
A mixed acid (adipic, glutaric and succinic) ester of isooctyl.

\[
\begin{align*}
\text{O} \\
\text{C-C-C-C-C-C-C-C-C-C-C-C-C} \\
\text{C-C-C-C-C-C-C-C-C-C-C-C}
\end{align*}
\]

See Appendix 2 for plasticizer efficiency in terms of British Standard softness. Density and viscosity (data supplied by ICI) data with respect to temperature is also given in the appendix.
3.2.1.2 Dry Blending

Seven plasticizers at concentrations of 30, 50 and 70 phr with the formulation given in 3.2.1.1 were dry blended in the TK Fielder mixer. (see Section 3.1.1.2 for details). The conditions used for dry blending were:

- Jacket temperature ($T_J$) 90°C
- Constant blank blade temperature ($T_{B}^{B}$) 75°C
- Constant blank jacket temperature ($T_{J}^{B}$) 81°C
- Discharge temperature ($T_D$) 120°C
- Rotor speed 1500 rpm
- PVC charge weight 1.5 kg

3.2.1.3 Banbury Mixing

A constant charge weight of 1.8 kg PVC dry blend from the Fielder was mixed in an internal mixer (Banbury Farrel Corp) with its rotors at maximum speed. The mixes were dropped at different temperatures between 150 and 200°C and the 'dolly' temperature was measured by a thermal probe. Each dolly was then immediately 'masson' cut whilst still hot.

3.2.1.4 Milling

About 120g of the 'masson' cut samples of the Banbury 'dolly' was milled on a two roll mill at 140°C for a few minutes. Only samples with Banbury dump temperature of 160 ± 3°C at the three levels of plasticizer concentration, 30, 50 and 70 phr were milled. The milling was continued until all the 'bumpy' nature of the chip on the milled sheets was removed to give smooth sheets.

3.2.1.5 Compression Moulding

Approximately 90g of each milled sheet was compression moulded at 170°C for 15 minutes at 20 tons pressure. The mould was water cooled for 10 mins before removing the sample. Tensile test pieces
were cut from the moulding sheets in the direction of milling. The mould was of dimensions 200 x 150 x 2.2 mm.

3.2.1.6 Extrusion

The masson cut samples from the dolly from the Banbury were extruded through a small Betol extruder using a PVC screw (L/D = 20:1). Preliminary extrusion studies were carried out using a strip and a lace die. To extrude strips a slot die of 50 x 3 mm was used while to extrude lace a die of radius 7 mm was used. The extrudates were allowed to cool in air and extruded without any haul off. A screw speed of 40 rpm was used and the barrels were set at 50°C less than the die temperature. The melt pressure generated along the screw and at the die (see Figure 37(a) below), the amperage and output were measured.

FIGURE 37(a): Pressure Transducer and die positions on the Betol extruder

Further extrusion experiments were carried out using the following die configurations.
FIGURE 37(b): Lace die configuration

The extrusion was performed without any haul-off to avoid tension in the lace and was allowed to cool in the air. A screw speed of 40 rpm with a temperature profile from the die along the barrel of 145:140:140:140. The melt pressure ($P_m$) and melt temperature ($T_m$) were measured at the die positions shown. At equilibrium extrusion conditions the amperage was recorded and at one minute intervals, extrudate was obtained to give output rate.

3.2.2 Analysis for Fusion Characteristics

3.2.2.1 Capillary Rheometry

For details of Davenport Rheometer and the conditions used see Section 3.1.2.1. The masson cut samples obtained from the Banbury mixes were tested for their extrusion pressure through a zero-length die at 120°C with piston speed of 2 cm min$^{-1}$.

3.2.2.2 Differential Scanning Calorimetry (DSC)

For instrument and experimental condition details see Section 3.1.2.2. Heats of fusion for all the samples from Banbury were measured.
3.2.2.3 **Optical Microscopy**

Samples from the Banbury mixes were swelled in acetone and sheared between glass slides to reveal its morphology under the optical microscope. For details of experiment see Section 3.1.2.4.

3.2.2.4 **Tensile Testing**

For experimental conditions and procedure see Section 3.1.2.5. Dumb bell test pieces were cut in the direction of milling from the compression mouldings. An average of three results was taken.

3.2.2.5 **Extrudate Appearance**

The surface texture of the lace-extrudates obtained from the Betol extruder was observed (see Section 3.2.1.6). Some extrudates were selected so as to give extrudates with an increasing roughness in surface texture. These samples were designated on an arbitrary scale ranging from 0 (smoothest extrudate) to 10 (the roughest extrudate). The rest of the extrudates were assessed with respect to this set of extrudates so as to give some measure of surface texture.

3.2.3 **Analysis for Plasticizer Properties**

3.2.3.1 **Hot Plasticizer Absorption Test (HPA)**

Here a fixed mass of polymer is mixed with an excess of plasticizer at 75°C, and the amount of plasticizer absorbed is determined after 10 minutes. This method was supplied by ICI.

For each plasticizer to be tested, two test tubes were charged with 20 ± 2 cm³ plasticizer. Similarly two such tubes were charged with 5 ± 0.1g of polymer. Each tube was accommodated with a thermometer reading from minus 10 to 110°C. These tubes were placed in a water bath at 75.0°C. When the samples of plasticizer and polymer reached 75°C and 73°C respectively, the plasticizer was poured onto the polymer and stirred immediately with a thermometer until all the polymer was wetted and moved freely. Stirring was continued...
at intervals of 2 minutes. This was carried out for each plasticizer. After 10 minutes the tube of each mix was removed from the hot water bath and placed in a mixture of ice and water. Stirring was carried out until the temperature of the polymer plasticizer fell below 20°C.

The contents of each tube were poured into a filter crucible (porosity 1 i.e. nominal 100 μm) fitted to a Buchner Flask under vacuum. The residue was washed out of the tube into the crucible with 3 to 4 aliquots of the plasticizer at room temperature. Filtration was continued at full pump rate for 15 minutes. The amount of plasticizer absorbed was recorded as an average of two results.

3.2.3.2 Polymer-Plasticizer Interaction Parameter (x)

The simplest method for determining x values for plasticizers is through measurement of the melting point of the resin in the presence of the plasticizer. This melting point will be lower than that of the pure resin. This method was conveniently adapted to a microtechnique by Anagnostopoulos, Coran and Gamrath \textsuperscript{103,130,131} in which a particle of resin immersed in a droplet of plasticizer is melted on a microscope hot-stage.

Flory's equation:

\[
\frac{1}{T_m} - \frac{1}{T^0_m} = \left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_1}\right)(x - \sqrt{v_1})
\]

was adapted by Anagnostopoulos, Coran and Gamrath for use with PVC by introduction of an extrapolated melting point for pure PVC \((T_m^0 = 174^0C)\) and an average value for the heat of fusion per "mole" of repeating unit \((\Delta H_u = 659 \text{ cal})\) to give the equation:

\[
\frac{1}{T_m} = 0.002236 + 0.1345 (v_1 - x \sqrt{v_1})
\]
where \( V_I \) is the molar volume of the plasticizer and \( \nu_I \) is the volume fraction of the plasticizer. Since at complete melting on the microscope the particle is severely swollen, they found they could make a final assumption that \( \nu_I = 1 \) which leads to the very simple equation:

\[
\frac{1}{t_m} = 0.002226 + 0.1351 \left( \frac{1 - \chi}{V_I} \right)
\]

This relationship permits the determination of \( \chi \) for a plasticizer from a single determination of the depressed melting point, \( t_m \).

The equipment consisted of a conventional light transmission microscope equipped with a Mettler FPS temperature regulator and a Mettler FP52 hot stage. A drop of plasticizer to be tested was placed on a microscope slide and a few grains of PVC sprinkled on the surface and thoroughly mixed, and then covered with a glass slide ensuring enough plasticizer to occupy the space between slide and cover glass. An almost spherical particle was chosen and observed on heating at 20°C per minute. The changes that took place as the temperature rose were observed under magnification with strong through illumination. Photographs were taken at the start of the experiment and from the point when the particle started to swell and pass through a gel-to-sol transition.

### 3.2.3.3 Plasticizer Viscosity

A Brookfield Synchro-Lectric Viscometer (Model RVT) was used to obtain the viscosity of the plasticizers. Here a spindle consisting of a flat circular disc attached nearer to one end of a rod is rotated in the plasticizer and the resistance of rotation is measured. Using Brookfield 'factor-finder' and reading the resistance from the dial and knowing the spindle size the viscosity was calculated. A spindle of size 3 was used at a rotation speed of 100 rpm and the resistance read from the dial after allowing rotation of the spindle for one minute.
3.2.3.4 Analysis of Plasticization of Dry Blend by DSC

For details of instrument and procedure see Section 3.1.2.2. DSC traces were run for dry blends obtained at various blending times from the start to discharge point of DTDP at concentrations of 30, 50 and 70 phr. The dry blends were compressed in the aluminium pans to avoid movement of the PVC grains.

3.2.3.5 Thermo-Mechanical Analysis (TMA)

This is a technique for measuring changes in the mechanical properties of a material. Perkin-Elmer TMA 56 was used as a penetrometer to measure the extent of penetration of a probe under known loading. This technique is important in the study of softening points, glass transition temperatures and phase changes. A schematic diagram of the Perkin-Elmer TMA 56 is given below with a typical TMA trace.

---

**FIGURE 38:** Schematic diagram of TMA 56 and a TMA trace
A 40g weight on the probe, which had 1 mm diameter shaft with a hemispherical shaped tip, was used. The samples were cooled to -160°C using liquid nitrogen, then the glass probe was lowered to rest on the sample. Flat disc shaped samples of approximately 5 mm in diameter and 1.25 mm thick were used. The samples were heated radiantly at 10°C per minute. The expansion-compression behaviour was recorded and from the trace the glass transition temperature was obtained. Compression mouldings at 170°C of the samples obtained by milling at 140°C of Banbury compounds dumped at about 160°C were analysed for their glass transition temperatures (Tg's) (see Section 3.2.1.5).

3.2.4 Particle Size Distribution Analysis

The method used to determine the particle size distribution was image formation i.e. optical microscopy. The optical method involves a Zeiss TG23 Particle Size Analyser. Photomicrographs were prepared from a representative sample of the blend to be analysed using an ordinary optical microscope. The diameter of each particle was measured from the micrograph by adjusting the area of the iris of the Zeiss to coincide with the area of the particle. On pressing a foot pedal, the particle size was recorded automatically on one of the 48 channels, each corresponding to small particle size range. At the same time a pin-hole is made automatically on the photomicrograph of particle to act as a marker to avoid remeasuring it. At least 1000 particles were analysed for each sample. Since the size of each individual particle is measured, it is absolutely essential that sufficient number of particles be measured or observed if the picture given by the sample size is to be representative of the whole.

Dry blends containing DIOP, TATM and DTDP at concentrations of 30, 50 and 70 phr after 13 minutes of dry blending and also samples containing TATM and DTDP which had reached a discharge temperature of 120°C were assessed for particle size distribution.
3.3 Reprocessability

3.3.1 Processing

The Banbury samples, containing DIOP, were extruded through a slot die of 50 x 3 mm to give extrudate strips which were cooled in air without any haul off. A screw speed of 40 rpm and a temperature profile from the die along the barrel of 140:140:140:130:120°C were used.

3.3.2 Analysis

Tensile, DSC, optical microscopy and capillary rheology tests, see Section 3.2.2 for details, were carried out on the extruded strips.
CHAPTER 4
RESULTS AND DISCUSSION: ASSESSMENT OF
FUSION CHARACTERISTICS

4.1 Processing for Sample Preparation

4.1.1 Brabender Plastograph Mixing

The dry blend of PPVC (BSS = 32.5) was compounded in a Brabender Plastograph. The effect of rotor speed and the jacket temperature on the mix history, due to shear heating and external heating is shown in Figures 39 and 40 respectively, as examples. We observe that at any given shear rate and jacket temperature we have an initial sharp rise in stock temperature after which it comes into a steady-state.

![Diagram showing shear effect and external heating effect on stock temperature](image)

**FIGURE 41:** Effect of (a) shear and (b) external heating on the thermal history of PVC blend on processing in Brabender Plastograph

**KEY:**
- \( T_0/\degree{C} \) blank temperature (temperature of the mixing chamber before addition of PVC blend to it)
- \( T_e/\degree{C} \) dump temperature (the equilibrium temperature attained by the mix in chamber before being dropped)
- \( T_j/\degree{C} \) jacket temperature of Brabender Plastograph
FIGURE 39: Effect of shear rate on the thermo-mechanical heat history of S-PVC blend
**FIG. 40 EFFECT OF JACKET TEMPERATURE OF BRABENDER ON THE HEAT HISTORY OF S-PVC BLEND**
N/rpm  rotor speed of Brabender plastograph
T_s/°C  stock temperature (temperature of the mix)

1+4   increasing quantity
T_{eo}/°C  thermomechanical temperature rise on compounding

The effect of shear rate and jacket temperature on the thermal profile of the mix can be represented schematically as shown in Figure 41. We find that for any given T_J, increase in shear level leads to an increase in T_e and T_{eo}. The same could be said for a fixed N with increased T_J except we have a decrease in T_{eo}. These relationships are exemplified in Figure 42.

A mathematical relationship between N, T_J and T_{eo} can be ascertained as follows. Extrapolation of all the straight lines in Figure 42 results in a close intersection point at T_e = 216.3°C with T_J = 260.0°C. Thus a relationship of the form:

\[(T_e - 216.3) = k(T_J - 260)\]  \(k = \text{constant}\)  \(1\)

can be obtained. A plot of the gradient \(k\) of these lines versus their respective rotor speeds provides yet another linear relationship, Figure 43, given by:

\[k = 0.66 - 0.00146N\]  \(2\)

Hence, substituting the \(k\) in equation (1) we obtain:

\[(T_e - 216.3) = (0.66 - 0.00146N)(T_J - 260)\]  \(3\)

which shows how \(T_e\) is governed by \(N\) and \(T_J\). Figure 42 also shows a plot of \(T_J\) versus \(T_o\), where the value of \(T_o\) is independent of \(N\) and depends only on \(T_J\) and is given by the relationship:

\[T_o = 0.7547 T_J + 20.48\]  \(4\)
Figure 42 - Thermomechanical history undergone by S-PVC blend in Brabender Plastograph with respect to jacket temperature and rotor speed.
Figure 43 - Plot of gradient versus Brabender rotor speed.
The thermomechanical temperature rise on compounding can be given by:

\[ T_{eo} = T_e - T_0 \]  \quad (5)

Now by substituting \( T_e \) and \( T_0 \) of equation (5) by \( T_e \) and \( T_0 \) from equations (3) and (4) respectively, we obtain:

\[ T_{eo} = (0.66 - 0.00146N)(T_J - 260) - 0.7547T_J + 236.8 \]  \quad (6)

Thus from this equation we can evaluate the steady-state thermomechanical temperature rise associated with \( N \) and \( T_J \). Although we have an increase in \( T_{eo} \), hence the total energy, with increased shear rate we do not have linear increments. The increment of \( T_{eo} \) becomes less with increased shear rate. With increased \( T_J \) we have a decrease in \( T_{eo} \), again the effect is not linear. This decrement of \( T_{eo} \) increases with \( T_J \).

An approximate shear rate, \( \dot{\gamma} \), can be obtained by using equation (7) to give results as shown in Table 6:

\[ \dot{\gamma}_{ideal} = \frac{3s}{h} = \frac{2\pi rN}{60} \cdot \frac{3}{10h} \]  \quad (7)

\( s = \) speed (ms\(^{-1}\)); \( h = \) gap between shearing notch and chamber wall (m); \( r = \) radius of chamber (m); \( 3 = \) number of notches on rotor.

<table>
<thead>
<tr>
<th>N/rpm</th>
<th>( \dot{\gamma}/sec^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>194</td>
</tr>
<tr>
<td>87.5</td>
<td>339</td>
</tr>
<tr>
<td>122</td>
<td>473</td>
</tr>
<tr>
<td>150</td>
<td>581</td>
</tr>
<tr>
<td>193</td>
<td>748</td>
</tr>
</tbody>
</table>

**TABLE 6: Brabender Shear Rate - rpm Relationship**

The effect of dump temperature and shear rate on the equilibrium torque, \( \tau \), is shown in Figure 44. The \( \tau \) can be expressed by:
FIGURE 44: Equilibrium torque variation with rotor speed of Brabender and dump temperature of the mix
\[ \tau = A n \gamma \quad \text{A - area of shearing notch (m}^2\text{)} \quad (8) \]
\[ n \text{ - viscosity (Ns m}^{-2}\text{)} \]

An increase in dump temperature leads to a decrease in torque and the viscosity as expected, \((n \propto \frac{1}{T_e})\). Also from the graph we can see that an increase in shear rate leads to an increase in torque at any given temperature.

Figure 45 shows a plot of \(\log \tau \) versus \(\frac{1}{T_e}\), described by a modified Arrhenius-type equation:

\[ \tau = A e^{B/T_e} \quad \text{or} \]
\[ \log \tau = \frac{B}{T_e} + \log A \quad (9) \]

where \(A\) is a constant and \(B\) is proportional to the flow activation energy. Three distinct linear portions 1, 2, and 3 can be observed with shear rates up to 339 s\(^{-1}\) after which we only have two linear segments simply because low dump temperature is not attained with high shear rates under the conditions used. These segments are described by the respective straight line equations, namely:

\[ \log \tau_1 = \frac{B_1}{T_e} + \log A_1 \quad (10) \]
\[ \log \tau_2 = \frac{B_2}{T_e} + \log A_2 \quad (11) \]
\[ \log \tau_3 = \frac{B_3}{T_e} + \log A_3 \quad (12) \]

whereby the intersection points between the straight lines of segments 1-2 and 2-3 are designated as \(T_1\) and \(T_2\) respectively.
FIGURE 45: Relationship between shear rate, equilibrium torque, and dump temperature (Te) of PPVC
The values of the transition temperatures (designated by the symbol $T_1$ and $T_2$), together with the parameters of the equations 10-12, for the various shear rates used, are given in Table 7:

<table>
<thead>
<tr>
<th>$\dot{\gamma}$/s$^{-1}$</th>
<th>$T_1$/°C</th>
<th>$T_2$/°C</th>
<th>$\tau_1$/Nm</th>
<th>$\tau_2$/Nm</th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$B_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>194</td>
<td>152.5</td>
<td>177.2</td>
<td>5.62</td>
<td>1.53</td>
<td>2.43</td>
<td>4.50</td>
<td>14.71</td>
</tr>
<tr>
<td>339</td>
<td>152.5</td>
<td>177.2</td>
<td>5.62</td>
<td>1.53</td>
<td>2.43</td>
<td>4.50</td>
<td>14.71</td>
</tr>
<tr>
<td>473</td>
<td>-</td>
<td>177.9</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>4.59</td>
</tr>
<tr>
<td>581</td>
<td>-</td>
<td>181.3</td>
<td>-</td>
<td>1.36</td>
<td>-</td>
<td>4.59</td>
<td>20.18</td>
</tr>
<tr>
<td>748</td>
<td>-</td>
<td>184.5</td>
<td>-</td>
<td>1.36</td>
<td>-</td>
<td>5.31</td>
<td>36.11</td>
</tr>
</tbody>
</table>

TABLE 7: Effect of Shear Rate on the Parameters of Modified Arrhenius Equation

The variations of slope values $B_i$ indicate changes of melt flow activation energies and moreover three regions of flow behaviour can be distinguished. The interaction points, $T_1$ and $T_2$, can be considered as critical transition temperatures between major structural transformations of PVC. The effect of increasing shear rate is to shift $T_2$ to slightly higher values and increase the value of activation energy required to cause flow.

The lower transition $T_1$, occurs at a higher torque while the higher transition, $T_2$, occurs at a lower torque. Shear rate has very little effect on the torque of the higher transition. It should be remembered that these torque values represent the equilibrium values of the compound that has undergone the maximum state of fusion under the conditions used (see Section 3.1.1.3). With increase in shear rate we need an increase in temperature to cause the second structural transformation of PVC. This is interesting in that we would have expected the second transition to take place at a lower temperature by increasing the shear rate. A replot of
Figure 45 using the 'B'-onset temperature as a measure of processing temperature (see Sections 4.2.2.2 and 5.3.2.2) instead of the equilibrium dump temperature reveals, as shown in Figure 46, that the same trend is obtained with increased difference in $T_2$ values. This suggests that the effect of shear on the second transition temperature is a real one.

The melt flow behaviour could be explained in the following manner. In the first region ($T < T_1$), the structure transformation is very slow. Here we have comminution of the more friable PVC grains and the development, from the remnants of these, of agglomerates. Here at low melt temperature we have melt fracture at the primary particle boundary since primary particles flow independently of each other therefore we need low activation energy to cause flow. As we approach $T_1$ the number of grains broken down and the number of agglomerates increases. When we reach $T_1$ we have advanced densification and no free powder exists in the sample. In the second region we have our major structure transformation of the primary particles. Here at these high temperatures enough melting occurs to give strong interactions between primary particles giving a higher activation energy for flow. With increased shear we have increased fusion of the primary particles giving increased flow activation energy. By the time we reach $T_2$ all memory of both grains and primary particle structure has been lost. In the third region, above $T_2$, where the structure transformation has terminated the PPVC behaves as a real molten polymer.

4.1.2 Extrusion

Two points on the nature of the extrudate obtained from dry blends should be noted. Firstly, as we go to conditions of very low processing temperatures with increasing screw speed, we find the extrudate to have a high level of unfused PPVC dry blend pockets within the fused extrudate strips. Secondly, at high temperatures and high screw speeds the fused material is embedded with hydrogen chloride bubbles derived from chemical degradation.
FIGURE 46: Relationship between shear rate, equilibrium torque and 'B'-onset temperature ($T_B$) of PPVC
Figure 47 shows the variation of output (Q) with screw speed (N) and die temperature. A linear relationship is obtained with output rate and die temperature. Increase in screw speed shows an increase in output rate. These results are readily explained by the familiar output equation \(^{32}\):

\[
Q = k'N - \frac{k''}{\eta} \left( \frac{\delta P}{\delta z} \right) \tag{13}
\]

where \(k'\) and \(k''\) = constants

\(\left( \frac{\delta P}{\delta z} \right)\) = axial pressure gradient along screw

\(\eta\) = viscosity

\(N\) = screw speed.

Since viscosity is inversely proportional to temperature, a rise in temperature decreases viscosity and hence the output. On the other hand, increasing screw speed increases output.

The output gradient drop with increased die temperature increases with the screw speed. Also we observe an increase in output rate at ca. 1780°C, this is due to the chemical degradation of PPVC.

The extrusion die temperature shall be used synonymous to dump temperature in the rest of the chapters for convenience of plotting various results on single graphs.

4.2 Analysis of Fusion Characteristics

4.2.1 Capillary Rheometry

The effect of processing equipment, thermal history and shear history on the fusion characteristics is given in Figure 48. Typical standard S-shaped curves are obtained. The minimum in these plots may be considered a threshold for good gelation. Pressure rises quite steeply through the temperatures to give a maximum in the region 180-200°C. The material state corresponding to this maximum can be described as highly processed.
Figure 47 - Variation of output with screw speed and die temperature of Bone and Craven extruder.
FIGURE 48 - SHOWS THE EFFECT OF DUMP TEMPERATURE, SHEAR AND THE TYPE OF PROCESS USED TO PROCESS PVC BLEND ON THE EXTRUSION PRESSURE IN A DAVENPORT RHEOMETER.
Variation in the standard fusion curves due to the processing equipment used is clearly borne out. The compression moulded and extruded samples exert the same maximum and minimum Capillary Rheometer extrusion pressure. However these curves only coincide by a shift factor of ca 15°C. Brabender Plastograph samples on the other hand show different maxima and minima. This suggests that the samples in Brabender Plastograph experience a different structure transformation to that in extrusion and compression moulding.

It should be noted that the samples processed by these different methods experience different levels of shear. The shear experienced in compression moulding is very low and is only due to the compression pressure. Samples in extrusion experience a moderate level of shear and in Brabender they undergo a very high level of shear. The effect on increasing the shearing power of the processing equipment is seen to increase the fusion state of the sample.

As we increase the shear level using the Brabender Plastograph, we increase the fusion state of the sample. The melt extrusion pressure rate drops rapidly with increased shear rate. The slope of the linear portion of the S-curve of the Brabender samples is tending towards zero and the curve itself is becoming linear with increased shear, however the maximum melt pressure remains constant.

The effect of shear on the fusion state of the extrudates is not significant, Figure 49. The melt pressure of samples processed at various screw speeds are thus represented as bars in Figure 40 and the standard S-curve presented by the shaded S-band. Since the process of fusion is a dynamic process, so the parameter time is also an important parameter. During extrusion, as we increase the screw speed we increase the throughput hence the residence time of the material at the extrusion temperature decreases. Thus it could be that as we increase shear we increase the fusion but at the same time the residence time is decreased leading to decreased
FIGURE 49: Shows the effect of screw speed at various extrusion temperatures on capillary rheometry extrusion pressure.

FIGURE 50: Compounding time effects fusion level.
fusion, hence the parameters shear and time work antagonistically to each other in promoting fusion. So to see if this was the case the processing time was decreased from twelve minutes to three minutes for samples mixed at 150 rpm in Brabender. It should be noted that the residence time of extrusion cannot be altered at a given screw speed. The results obtained are shown in Figure 50. We can indeed say that decreasing the residence time decreases the fusion level of a sample.

With the Brabender samples we find that the dump temperature 150°C (the initiation of high fusion state) and 180°C (maximum fusion level) correspond to the flow transition temperatures T₁ and T₂ (see Section 4.1.1, Figure 44) respectively. The S-curve can also be divided into three different zones (< 150°C, 150 to 180°C and >180°C) of structure-transformations.

The rheological method is useful in assessing the state of fusion of samples from specific formulation and processing conditions with processing temperature as the variable. The standard S-curve cannot be used to assess the state of fusion of a sample from a different piece of processing equipment or a sample of different formulation.

4.2.2 Differential Scanning Calorimetry

A typical DSC trace obtained is given schematically in Figure 51. The results obtained are similar to those obtained by Gilbert and Vyvoda for unplasticized PVC. The interpretation of the DSC trace is given in Section 2.6.5 and will not be reiterated here for sake of brevity. However with the plasticized samples the Tg (glass transition temperature) was observed at ca. -17 ± 5°C and another peak Ta at 42 ± 2°C corresponding to the ageing of the material, a secondary crystallinity. The glass transition is situated below zero degree meaning that storage in freezer or at room temperature is for this material equivalent to annealing it above the Tg. On heating the sample from room temperature to 800°C
FIGURE 51: A typical DSC trace of plasticized PVC and virgin PVC followed by quenching in liquid nitrogen and rerunning a DSC trace we find that the T\text{a} peak no longer appears. This confirms that T\text{a} is a peak due to ageing.

Generally speaking, it was observed that there was more of the secondary crystallite formation (A-endotherm) than the loss of primary crystallites (B-endotherm) as the processing temperature was increased. This does not necessarily mean that we have an overall increase in crystallinity with increased processing temperature. Ansari\textsuperscript{138} measured the energy of the two endotherm peaks A and B of rigid PVC samples processed from 160°C to 220°C. He showed that there was a drop in B-energy with an increase in A-energy as the processing temperature was increased. However his results show that the sum of A and B energy drop in value followed by an increase as the processing temperature was increased. But his X-ray results showed a gradual drop in overall crystallinity as the processing temperature was increased.
4.2.2.1 'A'-Endotherm Energy

The effect of shear rate and the dump temperature on the 'A'-endothermic energy for extruded samples is given in three dimensions in Figure 52. Two distinct features, a maximum and a minimum of endothermic energy at a given dump temperature, can be observed (indicated by dotted lines). At high shear rates we find the isotherm curves are tending to give a second maximum which is less well defined because of the restricted screw speed range used. At low screw speeds, the magnitude of the maximum at lower dump temperature is lower than that at higher dump temperature. As we increase the dump temperature, the maximum at lower shear rates increases to that of the second maximum at higher shear rates.

At any given shear rate an increase in dump temperature leads to an increase in endothermic energy. Also at any particular low dump temperature, application of increased shear rate leads to an increase in endothermic energy. However at high dump temperatures, increase in shear rate leads to a decrease in the endothermic energy.

A plot of dump temperature versus the 'A'-endothermic energy for the extruded samples is shown in Figure 53. We observe that there is no apparent effect of shear rate on the endothermic energy except at very high shear rate. The effect of compression mould temperature on endothermic energy is also shown. The compression moulded and extruded samples show close similarities in their endothermic energies.

The effect of shear rate and dump temperature on the endothermic energy of Brabender samples is given in three dimensions in Figure 54. The Brabender shows much more erratic results as compared to extrusion or compression moulding. Two maxima and a minimum of endothermic energy can be identified. The two maxima and the minimum increase in value with increased shear rate.
Figure 52- Enthalpy corresponding to PVC processed at various screw speeds and dump temperatures in a single-screw Bone and Craven extruder.
Figure 53 - Enthalpy corresponding to PVC processed at various dump temperatures by compression moulding and extrusion.
Figure 54 - Enthalpy corresponding to PVC processed at various rotor speed and dump temperatures in a Erabender Plastograph
At high shear levels the maximum at lower dump temperature is higher than that at higher dump temperature. However at lower shear rates the maximum at lower dump temperature is lower than that at higher dump temperature.

We observe that at any given dump temperature an increase in the shear rate leads to an increase in the endothermic energy. However at any given low shear rate an increase in dump temperature gives higher endothermic energies. With a given high shear rate, increase in dump temperature gives lower endothermic energies.

The effect of shear rate ($\gamma$) and the dump temperature ($T_D$) on the endothermic energy ($\Delta H$), for the three processes studied, can be summarised in the following Table 8. We find that with both Brabender and extruder, high levels of shear accompanied by high temperature leads to a decline in the endothermic energy.

<table>
<thead>
<tr>
<th>Constant Parameter</th>
<th>Compression Moulding</th>
<th>Extrusion</th>
<th>Brabender Plastograph</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>$T_D \rightarrow \Delta H^+$</td>
<td>$T_D \rightarrow \Delta H^+$</td>
<td>low $T_D$, $T_D \rightarrow \Delta H^+$</td>
</tr>
<tr>
<td>$T_D$</td>
<td>$-$</td>
<td>$T_D \rightarrow \Delta H^+$</td>
<td>high $T_D$, $T_D \rightarrow \Delta H^+$</td>
</tr>
<tr>
<td></td>
<td>low $T_D$, $\gamma \rightarrow \Delta H^+$</td>
<td>$\gamma \rightarrow \Delta H^+$</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 8: Comparison of the effects of shear and dump temperature on endothermic energy of compression mouldings, extrusion and Brabender samples

It could be that under these conditions we have a reduction in the number of nucleation sites. When high shear is applied in conjunction with high temperature, the recrystallized secondary crystals drop in its amount but it is difficult to say what effect shear has on its own.
4.2.2.2 'B'-Endothermic Peak

Figure 55 shows the effect of shear, processing temperature and processing equipment on the 'B'-endothermic peak temperature. Several distinctive trends can be ascertained from the results. We have linear relationships for all the three processes. The Brabender samples have the highest B-endotherm values followed by the extruded samples with the compression moulded samples having the least value, this is in accordance with the amount of shear applied in the processing equipment. Samples extruded at different screw speeds (10-90 rpm) at a given die temperature show no variation in the B-endothermic peak temperature except due to experimental variation which is represented by the use of bars on the graph. Unlike the extrusion the Brabender shows an increase in B-value with increased rotor speed at any given dump temperature. The slope of the linear relationships is increasing with rotor speed and the lines are tending to converge at ca. 140°C dump temperature.

The onset temperature of the B-endothermic peak corresponds to processing temperature of this compound, as is shown to be so by more convincing results in Section 5.3.2.2. This B-endothermic peak temperature was also shown to be the processing temperature of the material in rigid formulations by Gilbert et al.\textsuperscript{136} recently. However we note that the high levels of shear encountered in Brabender deviates the B-onset temperature to high values from the processing temperature on increased shear. The compression moulded samples show closer resemblance of B-onset temperature to the processing temperature.

4.2.3 Acetone Test

Figure 56 shows the effect of shear, processing temperature and processing equipment on the fusion level of PPVC determined by the acetone test. The compression moulded samples, having undergone minimal processing shear, require higher processing temperature compared with extrusion and Brabender mixing to give a significant level of
Figure 55- The effect of shear and dump temperature on the B-endotherm peak with various processes.
Figure 56- Effect of shear, dump temperature and type of process on the fusion level of samples determined by acetone test.
acetone stability. Extrudates on the other hand having undergone higher shear level to compression moulding require much lower processing temperatures for acetone stability. However the Brabender with its very high shear levels gives samples which are very stable to acetone even when the samples are processed at temperatures as low as 130°C.

The Brabender samples having undergone high shear show no effect of shear on the acetone test and are represented by the shaded area in the figure. With extrusion there is a clear indication of shear effect on the acetone test. Increase in screw speed leads to a sample which is more resistant to disintegration when swollen in acetone.

On processing above 150°C we find that the material remains completely intact and the effect of neither shear nor processing equipment is seen by this test. The maximum level of PPVC retained is ca. 70%, the 30% less is attributed to plasticizer diffusion into the acetone media. With this method to distinguish fine differences between fairly well fused PVC's proves to be difficult.

4.2.4 Optical Microscopy

Plate 1 shows the effect of compression mould temperature on the PPVC morphology. The degree of fusion, particularly of particles and the grains, is clearly evident. Having applied only compression shear the PVC grains have remained completely intact, although they have swollen ca. 2-3 times. With moulding temperatures up to 130°C we have unfused complete PVC grains with high level of internal structure of primary particles imparting dark texture on the grains. Between 130-140°C we observe a sharp transition in that the 140°C sample shows a distinct fused grain boundary and the internal structure is beginning to become translucent in nature due to plasticizer absorption. With increased moulding temperature there is a progressive loss of the fine structure. Between 150-160°C we find that the PVC grains are becoming fused to give larger structures. On going from
PLATE 1: Optical photomicrographs of compression mouldings (c) showing the effect of mould temperature on fusion level
160°C to 170°C most of the internal structure seems to have disappeared although the larger formed structure is not fully fused and the grain boundaries are still visible. Further increase of mould temperature above 180°C has increased fusion of the grains to give a continuous melt which becomes very difficult to shear between the glass slides. On reaching 200°C we have complete loss of grain boundary memory and of primary particles but with good additive distribution in the sample.

Plate 2 shows the effect of extrusion temperature on the morphology of PPVC extruded at 50 rpm. Unlike the compression moulded samples, the high shear in the extruder has completely broken down the PVC grain into individual primary particles at temperatures as low as 110°C. On increasing the extrusion temperature from 140 to 150°C we have agglomeration of the primary particles. The fine structure of the primary particles is still evident. There are small areas of fused boundary of these agglomerated structures. A major structural transformation takes place as we go from 150 to 160°C, there is complete loss of primary boundary memory although fine structure is still visible. The primary particles have fused to give large structures with well defined boundaries. By the time we reach 180°C the PPVC gets very uniform with good additive distribution. The effect of increasing the screw speed is to shift the structural transformations to lower processing temperatures.

The Brabender samples give photomicrographs like those samples obtained at high temperature by extrusion (160-200°C) and compression moulding (180-200°C) as shown in Plates 1 and 2 and not repeated here. Neither the effect of shear nor of processing temperature was observed since highly fused samples were attained from the Brabender Plastograph.

Superficially the microscopy test for particulate structure appears to be the most reliable since it depends on a physical phenomenon.
PLATE 2: Optical photomicrographs of extruded strips showing the effect of extrusion temperature on fusion level (extruded at 50 rpm)
4.2.5 **Tensile Properties**

The effect of processing temperature on the ultimate tensile strength and elongation at break for extruded and compression moulded samples is given in Figures 57 and 58. A typical 'S'-shaped curve is obtained, the maximum tensile strength and elongation at break is approached asymptotically. Thus the curves could be used to give numerical fusion values as for the Capillary Rheometry results. The extruded strips show higher tensile strength and elongation properties to compression moulded sheets having undergone higher shear history. Both the extruded and moulded samples show the same maximum but different minimum in tensile and elongation properties. However a shift factor of 15-20°C superimposes the two curves in both tensile and elongation results. There is no apparent effect of screw speed on the tensile and elongation properties and results are represented as a range by use of bars on the figures. This method has the disadvantage in that it requires a large amount of sample and of specified dimension.

4.2.6 **Structurization**

Structurization is believed to go hand in hand with fusion in that both are governed by formulation, shear, temperature and pressure. While fusion is believed to be the amount of continuous network formed on breakdown of powder grains (approximately 150 μm in diameter) on processing, structurization is the effect on the surface texture of the extrudate affected by structural variation on the grain scale (150 μm), quite apart from the effects of molecular structure.

Plates 3, 4, and 5 show the effect on the surface texture of the extrudate from the Davenport Rheometer due to different shear and thermal history undergone by PPVC in compression moulding, single-screw extrusion and Brabender mixing. For all the three processes we have a transition of smooth to scaliness (characterised by surface tearing varying in frequency, regularity and depth) to
Figure 57 - Ultimate tensile strength obtained with varied dump temperature on extrusion and compression moulding.
Figure 58 - Percentage elongation attained with varied dump temperature on extrusion and compression moulding.
PLATE 3: Effect of mould temperature on structurization

rippling (an irregular elastic recovery occurs throughout the extrudate without surface tearing) and finally to the extreme amounting to 'knotty' highly distorted appearance in that order with increased dump temperature and shear.

With the compression moulded samples we have very regular shape, depth and interval of surface tearing up to moulding temperature of 130°C. This surface tearing increases with decrease in moulding temperature below 140°C. This effect is not seen with the other two processes and can be explained as follows. At low moulding temperatures the PVC grains are only held together by sintering forces generated during compression. During extrusion the compression stresses are relieved by surface tearing. At slightly higher temperatures, 130-140°C, the outer surface layer
PLATE 4: Effect of screw speed and die temperature of an extruder on structurization of extrudates obtained on extrusion in Davenport Rheometer
PLATE 5: Effect of Brabender rotor speed and dump temperature on structurization of extrudates obtained on extrusion in Davenport Rheometer
of the PVC grains are more fused resisting the induced compressive stresses giving better extrudates. This phenomenon is due to die exit effects and is known as Sharkskin.

4.3 Discussion

As expected, processing conditions significantly affect fusion with the greater influence being that of temperature rather than process or shear rate. This is a consequence of the effect of increased shear at higher extrusion screw speeds (i.e. an increase in fusion level), being partially offset by the reduction in residence time resulting in less heat input. The ultimate level of fusion is not greatly affected by the process or the shear rate although they clearly influence the rate of fusion attainment.

The amount of secondary crystallinity is increased both with increase in processing temperature and shear rate. However very high shear with high temperature has a detrimental effect on the amount of secondary crystallites.

Increased fusion with shear, temperature and processing time leads to increased amount of secondary crystallites, hence the number of three dimensional crosslink sites. This increased molecular network reduces the amount of particles and/or grains held together at best by sintering. Thus with increased fusion level we have decreased disintegration of samples when placed in acetone. As soon as some interparticle fusion is obtained the acetone test becomes invalid in distinguishing fine differences between these fairly well fused PPVC's.

With increased secondary crystallinity we have an increase in the degree of inhomogeneity of the PPVC matrix. These crosslink sites impart PPVC with built-in stresses. The built-in stresses are relieved during extrusion by rupturing the extrudate. Thus with increased fusion state we have increased structurization.
The methods used to characterize fusion do not provide us with a universal method in analysing a sample from a different process. We need to provide a standard for each processing condition. However analysing the results of DSC and Capillary Rheometer in combination we find a unique relationship.

Plots of dump temperature versus extrusion pressure, endothermic energy, ultimate tensile strength (or elongation at break), give Figures 48, 52, 54 and 58, all show S-shaped curves. With the endothermic energy plots we do not obtain a maximum and the relationship deviates from an S-shaped curve with high shear rates. This is very evident in extrusion of 90 rpm and even more so with the Brabender where very high shear rates are encountered. All the S-shaped curves are shifted by some temperature factor and even then we find that the maxima and the minima do not coincide although the linear portion of the curves does. The displacement of these curves for the various process equipment and shear levels can be explained as follows. With equipment generating low shear level as in compression moulding and extrusion, the temperature is the major factor governing the measured property for the given formulation. However with equipment generating high shear levels as in the Brabender Plastograph, shear becomes a strong influence on the property of the compound. Thus a plot of temperature or shear rate against compound property is inappropriate as temperature and shear rate have a synergistic effect on the properties of the compound. Thus it would be better to plot some factor other than temperature and shear against the property of a compound which would give us a master curve for all the processing equipment irrespective of the amount of shear or heat applied.

Plots of endothermic fusion energy of samples processed at various temperatures and shear rates, versus extrusion pressure, Figure 59, and ultimate tensile strength, Figure 60, show yet other S-shaped curves. However, these curves have some unique features. For one we do not have a maximum and a minimum but an upper and a
FIGURE 59: Relationship between secondary crystallinity and extrusion pressure of PVC
FIGURE 60: Relationship between secondary crystallinity and ultimate tensile strength (UTS) of PPVC
lower limiting value. We find that these values are the same for all the three types of processing equipment regardless of temperature and shear encountered by the samples. With increase in endothermic energy we have an increase in both extrusion pressure and tensile strength. With 4.5 - 5 Jg\(^{-1}\) of PVC the UTS and extrusion pressure begin to level off and reach a limit with further increase in the endothermic energy. Hence further increase in the endothermic energy does not affect the tensile properties or extrusion pressure once the limiting value is achieved.

Replotting Figures 59 and 60 gives us master curves, Figures 61 and 62 in respect of extrusion pressure and ultimate tensile strength. It is interesting to note that the limiting values of the ultimate tensile strength is half that of extrusion pressure. There is some scatter of results but it is in concordance with the fact that only a small portion of the sample is tested for the endothermic energy and that large numbers of samples are considered in the plots.

This result has an important implication in that now we have a technique whereby we could assess the fusion level, tensile strength or extrusion pressure of a sample, using the master curve, irrespective of its thermomechanical history or the processing equipment used. A master curve could be easily obtained using compression moulded samples at various temperatures. To have a more accurate master curve several runs of DSC to measure the endothermic fusion energy would be advisable.

Once the master curve is obtained it could be used as a quality control for which only small samples are needed, ca. 10 mg. It also implies samples through the cross-section of a complex structure could be analysed for fusion state. There is a further implication in that we could assess the tensile strength of a small piece of sample without actually doing a tensile test experiment on it.

A possible mechanism of fusion is given overleaf in Figure 63.
% FUSION = \left( \frac{P - P_{\text{min}}}{P_{\text{lim}} - P_{\text{min}}} \right) \times 100

FIGURE 61: Master curve to assess the state of fusion of PPVC using extrusion pressure and heat of fusion.
FIGURE 62: Master curve to assess the state of fusion of PPVC using ultimate tensile strength (UTS) and heat of fusion.

\[
\% \text{ FUSION} = \left( \frac{\text{UTS} - \text{UTS}_{\text{min}}}{\text{UTS}_{\text{lim}} - \text{UTS}_{\text{min}}} \right) \times 100
\]
The mechanism is in accordance with that proposed by Krzewski and Collins\(^6\) and by Allsopp\(^5,7\). However some additional features in the mechanism are proposed with respect to the results obtained. During the initial stages of fusion we have internally fusing primary particles. This is followed by interparticle fusion of the primaries irrespective of them being within a grain boundary or as...
separate individual entities. With further processing a state of three dimensional network is obtained with hardly any primary particles remaining unfused. Further increase in network has no apparent effect on the tensile strength or Capillary Rheometer extrusion pressure. The three dimensional network is a result of secondary crystallites acting as tie points.
CHAPTER 5
RESULTS AND DISCUSSION: EFFECT OF PLASTICIZER TYPE ON FUSION AND PROCESSING

5.1 Plasticizer Properties

5.1.1 Hot Plasticizer Absorption Test (HPA)

The amount of plasticizer that could be absorbed by virgin PVC after 10 minutes at 70°C was determined. The results obtained are given in Table 9 below.

<table>
<thead>
<tr>
<th>Plasticizer Type</th>
<th>% Plasticizer Absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPN</td>
<td>54</td>
</tr>
<tr>
<td>TATM</td>
<td>58</td>
</tr>
<tr>
<td>DINP</td>
<td>61</td>
</tr>
<tr>
<td>DTDP</td>
<td>66</td>
</tr>
<tr>
<td>DIOP</td>
<td>66</td>
</tr>
<tr>
<td>OPN</td>
<td>69</td>
</tr>
<tr>
<td>BBP</td>
<td>203 x</td>
</tr>
</tbody>
</table>

**TABLE 9:** Percentage Plasticizer Absorbed at 75°C by PVC

As can be seen from the results, it is difficult to use HPA test to assess these plasticizers since there is no significant difference in the amount of plasticizer absorbed except for BBP. BBP is different in that it is imbibed three times as much as the other plasticizers by the PVC resin.

5.1.2 Polymer-Plasticizer Interaction Parameter (x)

On heating the PVC grains in various plasticizers an increase in the grain size was observed, see Plate 6 as an example. The increase in size is due to imbibition of plasticizer which causes the particle to lose its dark appearance and become translucent.
PLATE 6: Photomicrographs showing the effect of heating a single PVC particle in OPN
As heating continued, the particle swelled more and more, but maintained its form identity, retaining its distinct outlines and contours. Then a temperature was reached where the particle began to lose its distinguishable form; within a degree or so the particle changed from a seemingly firm gel with distinct contours to a smooth edged drop. This apparent gel-to-sol transformation was recorded as the depressed melting temperature, $T_m$. The molar volume of each plasticizer was calculated from their density values at gel-to-sol transformation temperature. Assuming isotropic swelling of the particles and that they are spherical, their swelled volume was calculated. The $x$-values and other parameters of the plasticizer are given in Table 10 below.

<table>
<thead>
<tr>
<th>Plasticizer Type</th>
<th>Molar Mass</th>
<th>Density (g cm$^{-3}$) at $T_m$</th>
<th>Molar Volume $V_1$/cm$^3$</th>
<th>$T_m/°C$</th>
<th>$x$</th>
<th>Swell Initiation Temperature ca/°C</th>
<th>% Swell by Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBP</td>
<td>312</td>
<td>1.0561</td>
<td>295.4</td>
<td>97-98</td>
<td>-0.03</td>
<td>30</td>
<td>430</td>
</tr>
<tr>
<td>DIOP</td>
<td>390</td>
<td>0.9251</td>
<td>421.6</td>
<td>113-114</td>
<td>-0.13</td>
<td>95</td>
<td>1076</td>
</tr>
<tr>
<td>OPN</td>
<td>372</td>
<td>0.8861</td>
<td>419.8</td>
<td>117-118</td>
<td>-0.04</td>
<td>100</td>
<td>446</td>
</tr>
<tr>
<td>DINP</td>
<td>418</td>
<td>0.8986</td>
<td>429.6</td>
<td>120-121</td>
<td>0.00</td>
<td>115</td>
<td>726</td>
</tr>
<tr>
<td>TATM</td>
<td>530</td>
<td>0.9219</td>
<td>574.9</td>
<td>126-127</td>
<td>-0.18</td>
<td>124</td>
<td>497</td>
</tr>
<tr>
<td>DPN</td>
<td>427</td>
<td>0.8630</td>
<td>494.8</td>
<td>133-134</td>
<td>0.14</td>
<td>126</td>
<td>1028</td>
</tr>
<tr>
<td>DTDP</td>
<td>530</td>
<td>0.8685</td>
<td>610.2</td>
<td>146-147</td>
<td>0.29</td>
<td>140</td>
<td>896</td>
</tr>
</tbody>
</table>

TABLE 10: Various parameters of plasticizers

The interaction parameter $x$ is a useful measure of the solvent power. Poor solvents have values of $x$ close to 0.5 while an improvement in solvent power lowers $x$. The results clearly show significant differences in plasticizer properties unlike the HPA test results. The HPA test was performed at 75°C. As the results indicate, this
is far too low a temperature for the plasticizers, except BBP, to be absorbed by the resin to significant level to show differences between plasticizers.

The swell initiation temperature indicates the temperature when the PVC resin first begins to increase in size on plasticizer absorption. The plasticizers follow the same order of swell initiation temperature as \( T_m \). This trend is also followed by the interaction parameter except that of BBP and TATM.

5.1.3 Plasticizer Viscosity

The viscosity of the various plasticizers obtained at ambient temperature is given in Table 11 below. The results show large differences in viscosity of plasticizers, however at high temperatures ca. 120°C their viscosities are almost the same (see Appendix 2).

<table>
<thead>
<tr>
<th>Plasticizer Type</th>
<th>Viscosity/cps</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPN</td>
<td>46</td>
</tr>
<tr>
<td>DPN</td>
<td>72</td>
</tr>
<tr>
<td>BBP</td>
<td>84</td>
</tr>
<tr>
<td>DIOP</td>
<td>96</td>
</tr>
<tr>
<td>DINP</td>
<td>173</td>
</tr>
<tr>
<td>TATM</td>
<td>279</td>
</tr>
<tr>
<td>ÖTDP</td>
<td>376</td>
</tr>
</tbody>
</table>

TABLE 11: Viscosity of Plasticizers

5.1.4 Thermo-Mechanical Analysis (TMA)

Banbury compounds dumped at ca 160°C were milled on a two roll mill at 140°C. These milled sheets were compression moulded at 170°C, see Section 3.2.1.5, and their Tg determined by TMA. The effect of plasticizer type, with respect to its concentration,
number of moles of plasticizer per kilogram of PVC and PPVC's British Standard Softness (BSS) on the Tg is given in Figure 64.

The effect of plasticizer amount and the BS Softness of PPVC on Tg is more or less linear for most plasticizers. The effect of BBP is different to other plasticizers, it has much less effect in lowering the Tg of PVC. A plot of BSS versus Tg, Figure 64(c), shows that at high BSS, the Tg is not affected by the type of plasticizer.

5.2 Processing for Sample Preparation

5.2.1 Dry Blending

5.2.1.1 Discharge Time

The effect of plasticizer concentration and type on the thermal history of the blend at the baffle is given in Figures 65 and 66 respectively. Each curve is a representation of 4 to 6 curves with good reproducibility having blend time differences between them of only ±1½ minute. On addition (A) of the blending ingredients and starting the rotor blade (Rs) we observe a steep fall in the blank baffle temperature (Tg₀) followed by a sharp increment in the temperature which steadies off with time. The initial drop in temperature is seen to increase with increase in plasticizer amount. This is simply because the extra plasticizer removes more heat from the baffle at the start of the mixing process.

Figure 67 shows the thermal profile of 30 phr DPM for several runs at the jacket. The jacket temperature never reaches the discharge temperature of 120°C obtained at the baffle. The rise in jacket temperature from its initial blank temperature is due to the heat generated from the high shearing forces and rotating blades. Thus heat is lost to the jacket of the mixer due to heat differential. The reason for the poor reproducibility of the thermal profile at the jacket is due to the sticky behaviour of the mix. During mixing the blend adheres to the walls of the mixing chamber which in
FIGURE 64: Effect of (a) plasticizer concentration, (b) number of plasticizer molecules per kg of PVC and (c) British Standard Softness on the glass transition temperature (Tg) of PPVC
FIGURE 65: Variation of thermal profile at the baffle of the Fielder for various plasticizer concentrations
FIGURE 66: Effect of plasticizer type on the thermal profile at the baffle of the Fielder mixer.
FIGURE 67: Reproducibility thermal profiles at the jacket of the Fielder for 30 phr DPN mix
time flakes off. The mix sticks again and the whole procedure repeats with time. Thus differential heat points are generated on the mixing chamber wall. This is why we have the jagged thermal profile at the jacket. Hence, the thermal profiles at the jacket for the various plasticizers have not been shown here having poor reproducibility.

From Figure 66 we can see that all the plasticizers irrespective of concentration, show two transitions, one at 81 ±1°C and the other at ca. 105°C. The first transition at 81°C is associated with the increased internal friction of PVC at its softening point (~80°C). The second transition is well marked with DTDP blends. To investigate the cause of the second transition in temperature rise, mixing was carried out for PVC and calcium stearate, PVC and Cd/Ba stabilizer and of virgin PVC itself. All the three showed only a single transition at 81°C, the second transition at ca. 105°C was not observed. Thus the second transition is associated with the type of plasticizer and is not due to calcium stearate, stabilizer or PVC.

Figure 68 shows the effect of concentration and number of moles of plasticizer on the blending time. Irrespective of the plasticizer type we have a drop in mixing time with increase in plasticizer concentration. This is unusual in that one would have expected increase in blending times with increase in the amount of plasticizer added. This is because with increased plasticizer we need increased time for absorption by the resin and longer time for heat transfer from the jacket to take place. The difference in blending times for the various plasticizers becomes less pronounced at higher concentrations. The mixing time is the same (ca. 21 mins) for all the plasticizers when 1.4-1.5 moles of plasticizer per kilogram of PVC resin is used. However when lower and higher moles of plasticizer are used the difference in mixing time for the various plasticizers increases.
FIGURE 68: Plasticizer concentration and number of moles of plasticizer effects on blend discharge time ($t_d$)
There are several factors which determine the flow behaviour in the mixer which determine the frictional heat that is generated during mixing, hence the mixing time and the thermal profile. Some of the more important parameters which govern the frictional heating are:

a) particle size - the smaller the mean particle size the greater the difficulty of maintaining flow. Thus the larger the particles the greater the frictional heating.

b) particle size distribution - presence of very fine particles may cause the powder not to flow but when only small amounts of fines are present the flow is improved. The fines now act as flow aid - lubricating the passage of one particle over another.

c) particle shape - spheres and near spheres always flow more easily than other shapes since spheres roll over more easily. The more angular the particle shape the greater the particles interlock and can only move relative to one another if the interlock is broken. Thus, the more the angular particle the more frictional heat generated.

d) resilience of the particles - if the coefficient of restitution of the particles is high, little energy will be lost when particles collide. Thus softer materials should give out more heat on particle collisions.

e) surface roughness - the greater the roughness of the particles the greater the frictional heating.

f) intra-particle shear - the softer the particle the greater the internal shear heating.

g) electrostatic effects - electrostatic charges are built up during mixing causing interparticulate attractions resulting in the agglomeration of powders, lowering frictional heating.
h) *differential heat transfer coefficient* - better the heat transfer capability of the plasticizer, the quicker the jacket temperature (81ºC) is attained by the baffle. Once this is achieved, the extra frictional heat is lost to the jacket. This is enhanced for mixes of higher heat transfer coefficients.

i) *plasticizer activity* - the higher the activity of the plasticizer the earlier frictional heating commences.

Low plasticizer concentration blends showed higher static charge having higher tendency to stick on the mixing chamber wall. This is one of the reasons why low plasticizer concentration requires longer mixing times. Different plasticizers swell PVC resin at different temperatures and to different levels not following the activity trend.

The effect of plasticizer type on the blending time is most pronounced at low concentration and has very little effect at higher levels. The effect of plasticizer type on the mixing time does not seem to follow the order of any of their properties e.g. activity, viscosity etc since several factors govern blending time, as seen above, each to a different extent depending on plasticizer type.

With increased plasticizer concentration we have increase in particle size, decrease in resilience, decrease in electrostatic charge and increased intra-particle shear all leading to decreased blending times.

Particle size distribution and plasticizer efficiency studies were carried out to have a better understanding of factors affecting blending time.
5.2.1.2 Particle Size Distribution

From Figure 65 we can see that the thermal profiles diverge after about 13 minutes of mixing so this might be the point where the effects of differences in plasticizers begin. So to investigate the effect of plasticizer type on the mixing time, dry blends containing TATM, DTDP and DIOP after 13 minutes of mixing were assessed for their particle size distribution, Figure 69. DTDP and TATM were chosen to account for their well marked 105°C transition, while DIOP with a less pronounced 105°C transition was chosen to see if there were major differences between plasticizers having well marked 105°C transition and those with less well defined 105°C transition. With increased plasticizer addition there is an increase in the size of the particles. This is much more marked with TATM plasticizer. DIOP shows a mean particle size of 100 μm while DTDP shows 120 μm. TATM shows a varied mean particle size depending on the plasticizer concentration. DIOP and DTDP shows a narrow range of particle size distribution while TATM shows a broad distribution.

Further particle size distribution analysis for TATM and DTDP at various concentrations after being mixed to the discharge temperature of 120°C showed distributions of the form shown in Figure 70. There is little difference in distribution on varying the concentration of DTDP or TATM except with 30 phr TATM. Both DTDP and TATM show a mean particle size of 120 μm. TATM shows a bimodal particle size distribution and the distribution has narrowed down from that obtained after 13 minutes of mixing. Also the difference in TATM concentration has become less apparent. With DTDP we have the same type of particle size distribution except we have agglomerated particles of 220 μm and also comminuted particles of 20 μm.

It is difficult to make generalisations on the effect different plasticizers have on the particle size distribution but we can say that increased plasticizer level increases the particle size which is more so with some plasticizers.
Figure 65 Variation of particle size distribution due to plasticiser concentration and type after thirteen minutes of dry blending.
FIGURE 70: Variation of particle size distribution of TATM and DTDP blends after thirteen minutes (A) of mixing and after discharging at 120°C (B)
5.2.1.3 Plasticization Efficiency

The homogeneity of the distribution of the plasticizer during dry blending, taking DTDP as an example, was studied by differential scanning calorimetry (DSC). Dry blends at two minute intervals from the start to the end of mixing were examined, at three plasticizer concentrations. All the samples showed the presence of two transitions, Figure 71; the lower transition resulting from the plasticized regions was seen at a temperature determined by the amount of plasticizer, and was lower with higher plasticizer concentration. The blending time had no effect on the position of either transition. The lower transition is the glass transition temperature of the dry blend. The transition at the higher temperature was found to occur at 54°C. The upper transition temperature was unaffected by the concentration of the plasticizer or the blending time. The ratio of lower transition to higher transition peak is seen to increase with increase in plasticizer concentration. The lower transition peak is found to be sharper with increase in plasticizer concentration.

When the DTDP sample was heated to 80°C followed by quenching in liquid nitrogen and the DSC trace rerun, it was found that the upper transition no longer persisted. This conclusively proves that the upper transition is due to ageing. The ageing endotherm is due to melting of the secondary crystallites. These crystallites are annealed on storage at room temperature since the Tg of PPVC is below room temperature.

The results indicate that the dry blend achieves a state of plasticization at very early stages of blending which does not change to any significant extent on further blending to discharge point.
After heating to 80°C followed by quenching in liquid nitrogen

FIGURE 71: Lowering of the glass transition temperature of DTDP dry blends with increased plasticizer concentration
5.2.2 Extrusion

Strips were extruded at 140°C for preliminary investigations, the results obtained are given in Table 12 below:

<table>
<thead>
<tr>
<th>Banbury Dump Temperature °C</th>
<th>DIOP phr</th>
<th>Output kg hr⁻¹</th>
<th>Ultimate Tensile Strength (UTS) MNm⁻²</th>
<th>Standard Deviation</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>145→200</td>
<td>30</td>
<td>2.76</td>
<td>24.8</td>
<td>0.8</td>
<td>70</td>
</tr>
<tr>
<td>145→200</td>
<td>50</td>
<td>2.63</td>
<td>12.0</td>
<td>0.7</td>
<td>95</td>
</tr>
<tr>
<td>145→200</td>
<td>70</td>
<td>2.39</td>
<td>7.8</td>
<td>0.5</td>
<td>96</td>
</tr>
</tbody>
</table>

TABLE 12: Banbury Dump Temperature Effect on Output and Tensile Strength of Extrusion Strips

Banbury dump temperature has no effect on UTS or output, although we have a definite decrease in output rate with increase in plasticizer concentration as expected. In tensile properties we observe a decrease in tensile strength with an increase in elongation at break as the level of plasticizer is increased. It should be noted that when the samples were processed at temperatures below their compounding temperature the output and the tensile properties were unaffected by the dump temperature of the sample.

To see if the extrusion temperature was too low to manifest the effects of sample compounding temperature the experiment was carried out at 155°C, Table 13.

<table>
<thead>
<tr>
<th>Banbury Dump Temperature °C</th>
<th>DIOP phr</th>
<th>Output kg hr⁻¹</th>
<th>UTS MNm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>144</td>
<td>50</td>
<td>2.70</td>
<td>12.4</td>
</tr>
<tr>
<td>191</td>
<td>50</td>
<td>2.65</td>
<td>12.9</td>
</tr>
</tbody>
</table>

TABLE 13: Effect of Increased Extrusion Temperature on Output and UTS of Extrusion Strips
Here again we have little if any difference in output and UTS with dump temperature of the sample. Further increase in extrusion temperature to observe the dump temperature effects on extrusion would mean that we would be processing at a higher temperature than that of compounding erasing the sample thermal history. A much less active plasticizer DTDP was used to remove the possibility of DIOP's inherent properties which might be giving the results that were obtained. Further a lace die was also used as 155°C to give more accurate output results as given in Tables 14 and 15 below.

<table>
<thead>
<tr>
<th>Die</th>
<th>DTDP phr</th>
<th>Dump Temperature °C</th>
<th>Pressure/psi</th>
<th>Amperage A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strip</td>
<td>50</td>
<td>146</td>
<td>0</td>
<td>1330</td>
</tr>
<tr>
<td>Strip</td>
<td>50</td>
<td>190</td>
<td>0</td>
<td>1830</td>
</tr>
<tr>
<td>Lace</td>
<td>30</td>
<td>149</td>
<td>270</td>
<td>2810</td>
</tr>
<tr>
<td>Lace</td>
<td>30</td>
<td>199</td>
<td>330</td>
<td>3120</td>
</tr>
</tbody>
</table>

TABLE 14: Pressure Profile Along the Extruder

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>DTDP phr</th>
<th>Dump Temperature °C</th>
<th>UTS MNm⁻²</th>
<th>Standard Deviation</th>
<th>Output kg.hr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dumbell</td>
<td>50</td>
<td>146</td>
<td>15.8</td>
<td>0.8</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>190</td>
<td>13.4</td>
<td>1.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Lace</td>
<td>30</td>
<td>149</td>
<td>26.8</td>
<td>0.4</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>199</td>
<td>27.4</td>
<td>1.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

TABLE 15: Tensile Strength and Output Rate of Strip and Lace Extrudates

The low pressure profile generated, Table 14, provides an ideal situation to give poor back flow of the melt, hence little work done on the material, thus the effects of the drop temperature from the Banbury should be retained. The thermal history of the sample
seems to have no difference on the power intake when using a slot die or a lace die. However the dump temperature does seem to have some effect on the output rate when using a lace die although no significant UTS differences are seen.

Further studies on output measurements were carried out using a smaller lace die of 2 mm diameter with an extrudate melt temperature of 134 ±10°C. The output results are given in Figure 72 to show the effects of dump temperature and plasticizer concentration, while Figure 73 shows the effect of dump temperature and plasticizer type at three concentration levels. Figure 74 shows the power needed to extrude the samples.

Generally speaking we can say that increase in plasticizer concentration leads to a decrease in output rate and the power consumed. An increase in plasticizer concentration gives a less viscous material hence less work to be done to extrude it. The low viscosity increases the back flow causing a drop in output rate.

The effect of plasticizer type on the output rate is small if any, except for DTDP and DIOP for reasons explained in the next paragraph. The difference in output rate due to plasticizer type, Figure 73, becomes more pronounced at lower plasticizer levels. This could be due to larger viscosity differences at lower plasticizer levels than at higher levels, where there are excess plasticizer molecules in the compounds.

Extrusion of PPVC just after two weeks from the time of compounding shows outputs of about 35g min⁻¹. However samples stored for three months show output of about 48g min⁻¹. This is why the DTDP and DIOP had higher output rates than the other plasticizers. To see if the storage time factor was the actual cause of output differences 70 phr DINP sample was extruded after 3 months of storage. The results, Figure 72(h), indeed show a
FIGURE 72: Variation of extrusion output rate ($Q$) with sample compounding temperature ($T_e$), plasticizer concentration and ageing of PPVC.  
A - extruded after two weeks of compounding 
B - extruded after three months of compounding
FIGURE 73: Effect of plasticizer type on the extrusion output rate.
A - extruded after two weeks of compounding
B - extruded after three months of compounding
FIGURE 74: Effect of plasticizer type and concentration on the power consumption by the extruder to extrude the PPVC compounds.
rise in output on storage with good reproducibility and the shape of the curve is maintained.

Generally speaking there is a drop in output rate with increase in dump temperature. The output rate of PPVC follows the general form shown schematically in Figure 75. The trend is not a simple one and can be divided into three sections. Initially there is a sharp drop in output (a) followed by an upsurge (b), and then there is a gradual drop in the output (c). This could be explained as follows. In region (a) increase in dump temperature leads to an increase in agglomeration of the primary particles. This is seen with all the plasticizers under investigation and the extrudates obtained are all smooth due to poor elasticity. As soon as some degree of elasticity is attained the output increases (b). Here the primary particles are completely agglomerated into large structures which themselves are becoming fused as the dump temperature is increased, increasing the elastic nature of the compound. Then as soon as a significant level of elasticity is achieved there is a drop in output with increased dump temperature (c). In this region there is no sign of large structure boundaries remaining. For structurization and morphology results see Sections 5.3.5 and 5.3.3.
5.3 Analysis of Fusion Characteristics

5.3.1 Capillary Rheometry (CR)

Figure 76 shows the effect of Banbury dump temperature and plasticizer concentration on the capillary rheometer extrusion pressure for the various plasticizers. At any plasticizer concentration we observe an increase in pressure with dump temperature to a point of attaining a maximum value as expected.

The effect of increased concentration of plasticizer is to decrease the capillary rheometry extrusion pressure. This is as expected and is due to the decreased viscosity of the PPVC with increased plasticizer content. The small plasticizer molecules ease the movement of the polymer chains by pushing them further apart, hence the decreased viscous nature with increase in the number of plasticizer molecules. Thus the compounds of lower plasticizer concentration being more elastic in nature generate higher extrusion pressure. We have a large drop in extrusion pressure as we increase the plasticizer concentration from 30 to 50 phr. Further increase from 50 to 70 phr leads to a much smaller decrease in extrusion pressure. Thus decrease in fusion level with increase in plasticizer concentration is not a linear relationship.

Figure 77 shows the effect of plasticizer type on the fusion characteristics at three levels of plasticizer concentration. The effectiveness of the plasticizer in lubricating the polymer molecules governs the extrusion pressure, as well as the fusion level. We observe a general tendency of increased fusion level with increase in activity of the plasticizer at any given plasticizer concentration, with BBP acting slightly out of the trend. The trend is borne out more clearly when we plot the results at a given BSS value, 20 in this case as given in Figure 78. Decrease in plasticizer activity decreases the number of plasticizer molecules bound to the polymer increasing the softness of the compound to give lower pressures.
FIGURE 76: Standard 'S'-curves for various plasticizers of various concentration
FIGURE 77(a): Fusion curves for various plasticizers at a concentration of 30 phr.
FIGURE 77(b) and 77(c): Fusion curves for various plasticizers at a concentration of 50 and 70 phr.
FIGURE 78: Fusion curves for various plasticizers at 20 BSS
5.3.2 Differential Scanning Calorimetry (DSC)

5.3.2.1 'A'-Endotherm Energy

Figure 79 shows the variation of 'A'-endothermic energy with compounding temperature for the various plasticizers. Unlike the Davenport Rheometer extrusion pressure which is due to semi-macro-changes, the 'A'-endothermic energy is due to microscopic changes in the polymer. The energy values correspond to the melting of the secondary crystallites of various degrees of perfection and size. It can be seen that with highly fused plasticized PVC we obtain approximately half the amount of secondary crystallinity to that of highly fused rigid PVC ($\Delta H = 12.5 \text{ Jg}^{-1}$). There is an increase in the level of secondary crystallinity with increase in processing temperature irrespective of plasticizer type or concentration except for 70 parts BBP samples which show a drop in the level of secondary crystallinity with processing temperature.

On increasing the concentration of a plasticizer there is increased difficulty in compounding the dry blend to high temperatures due to increased difficulty in applying shear heat. Hence the lower gains in maximum secondary crystallinity. However no specific trend of the effect of plasticizer concentration on the endothermic energy is observed.

We find that the endothermic energy versus dump temperature plots for various plasticizer types fall in a narrow band for 30 and 50 parts. However at high plasticizer concentration of 70 parts considerable deviation from this trend is observed. Generally speaking we find that the very active plasticizers give higher quantity of secondary crystallinity at any given concentration. DTDP being the least active of the plasticizer being studied shows the lowest level of secondary crystallinity. The above two observations can be explained as follows. Reduction in secondary crystallinity with increase in plasticizer concentration and with reduced plasticizer activity may be due to the accompanied reduction in
FIGURE 79: Variation of secondary crystallinity with processing temperature for various plasticizers
nucleation sites for the formation of secondary crystallites. With increased plasticizer activity we have increased dissolution of the primary crystallites freeing the polymer chains leading to increased secondary-crystallite formation.

5.3.2.2 'B'-Endothermic Peak Temperature

Figure 80 shows the effect of plasticizer type, its concentration and compounding temperature on the 'B'-endothermic peak temperature. A regression analysis of over hundred samples shows a linear relationship which is very close to a linear relationship with slope of one where the 'B'-endothermic peak temperature is equal to the dump temperature. We find that most of the scatter of results is due to 'B'-endothermic peak temperature values at lower temperature being towards higher dump temperature than expected. This scatter of results can be accounted for by (1) large number of samples are being looked at; (2) when the PPVC dry blend is mixed in the Banbury the 'dolly' obtained does not attain a uniform temperature and this is very apparent visually at lower dump temperature compared to high dump temperature; (3) the dump temperature of the dolly recorded is one which is the highest of the sample; (4) only a very small portion (~0.001%) of a very large sample (i.e. ~20 mg tested out of ~1.8 kg) is tested.

Thus the 'B'-endothermic onset temperature corresponds to the maximum temperature that PPVC had undergone. Hence DSC can be used to provide us with an 'internal' method of monitoring the maximum processing temperature that the polymer had undergone whatever the process or formulation that had been used. Since only small portions of samples are needed for this test we can find local heating in complex structures.

When a compound is reprocessed at a temperature lower than that of its compounding temperature we find that the 'B'-endotherm peak is not affected and still shows the maximum heat treatment it had undergone (see Section 5.4).
FIGURE 80: Shows 'B'-onset temperature is a measure of processing temperature
5.3.3 Optical Microscopy

All the seven plasticizers, at three different concentration levels and five processing temperatures (150-200°C) were looked at using a dark field optical microscope, after swelling the samples in excess acetone for at least two weeks, followed by shearing between glass slides. A dark field was used to impart sharp contrast to the translucent samples. With this acetone swelling technique, the sample being observed under the microscope was flooded with acetone at all times. This condition caused two problems: (a) poor depth of focus because the acetone layer maintains the sample at different depths; (b) under strong illumination the acetone depleted rapidly due to evaporation causing movement of the smaller samples. The latter problem was overcome by photographing at fast speeds.

Plate 7 shows the effect of Banbury dump temperature on the state of fusion of PVC plasticized by 50 phr OPN. We observe from the micrographs that even at 157°C the OPN plasticized PVC is unfused and the PVC grains have broken down to individual primary particles. The primary particles are larger than 1 μm as expected since they have been swollen by both plasticizer and acetone. By the time we reach 162°C we find the primary particle boundary is lost and the majority of the primary particles have become fused into larger structures. However we can still see the fine structure of the primary particles. The structural transformation imparts the material some elastic character. A further increment in processing temperature to 176°C gives us a much more fused and plasticized structure, the finer structure of the primary particles has become less apparent and a much more translucent structure is obtained. By the time we reach a processing temperature of 182°C the sample becomes completely translucent and very well fused. The sample is not torn easily and stretches when sheared between the glass slides. The sample behaves in a very rubbery manner at this processing stage. This trend of increased
PLATE 7: Effect of processing temperature on the morphology of PVC plasticized with 50 parts OPN
fusion level and plasticization with processing temperature is observed with all the plasticizers investigated. A further example of the effect of processing temperature on fusion is given in Section 5.4.

Observing the effect of plasticizer concentration, using DINP as an example (processed at approximately 180°C; see Plate 8) we find a similar trend to that observed with temperature. However with these highly processed samples as an example the difference is smaller but is there nevertheless. With 70 parts plasticizer we have a very fused translucent structure. With a lower concentration the samples are not as translucent and finer structure is apparent. Thus we find that there is an increase in the fusion level and plasticization with increased plasticizer concentration. However, this does not necessarily mean that properties increase in value with increase in plasticizer concentration. On the contrary we have a reverse effect as it can be observed from the micrographs that increased plasticizer level gives increased ease of tearing of the sample under shear between glass slides.

Plate 9 shows the effect of plasticizer type on the level of fusion when the sample is processed at about 160°C with 50 parts plasticizer. We have increased state of fusion with increase in the interaction parameter of the plasticizer. That is with very active plasticizers like BBP, DIOP and TATM we have well fused samples with the finer structure of the primary particles still evident. With the less active plasticizers like DTDP and DPN, the PVC grains have broken down to unfused primary particles. With intermediary plasticizers like DINP and OPN we have some well defined fused primaries and some individual presence of primaries, both structures showing well defined finer primary structure.

Thus we find that increase in processing temperature, plasticizer concentration and activity of the plasticizer all lead to increased fusion level and plasticization. Also, we can say that increased fusion level does not mean we have improved physical
PLATE 8: Effect of DINP concentration on the morphology of PVC
PLATE 9: Effect of plasticizer type on the morphology of PVC plasticized with 50 parts plasticizer and processed at 160 ±3°C
properties as was seen when looking at the effect of plasticizer concentration.

5.3.4 Tensile Properties

Figures 81, 82 and 83 show the effect of plasticizer type and concentration on the ultimate tensile strength (UTS), 100% modulus (E) and elongation at break respectively. The UTS curves are superimposeable except for BBP. There is a gradual drop in UTS and E with increase in plasticizer concentration while at the same time we have an increase in elongation which tends to level off at high plasticizer concentration. The same sequence of plasticizer type is followed in ultimate tensile strength and modulus while a reverse sequence is followed by elongation property.

Figures 84 and 85 show the effect of BSS and the number of moles of plasticizer per kilogram of PVC on the ultimate tensile strength. Similar results are again observed with Figure 84 showing superimposeable curves. However the effect of plasticizer type on UTS at a given mole concentration is quite different to that at a given BSS or at a given phr concentration. To obtain a given tensile property i.e. UTS, E or elongation at break, using different plasticizer type we require significant differences in the amount of plasticizer whether it is quoted in terms of BSS, phr or number of moles.

The various trends observed could be explained in terms of glass transition temperature (Tg). The plasticizer molecules tend to reduce the attraction between chains increasing the free volume and aiding internal molecule movement. This depresses the Tg of the polymer. The extent to which the plasticizer is able to lower the Tg of the sample should thus be reflected in its tensile properties.

The effect of plasticizer type in lowering the Tg is different when the amount of plasticizer is quoted in different terms, see
Figure 81 shows the effect of plasticiser concentration and type on the ultimate tensile strength.
Figure 82 shows the effect of plasticiser concentration and type on the 100% modulus.
Figure 83 shows the effect of plasticiser concentration and type on the elongation at break.
FIGURE 84: Effect of plasticizer type and the number of moles of plasticizer on the ultimate tensile strength (UTS)
FIGURE 85: Variation of UTS of PPVC with plasticizer type and the BSS of PPVC
Figure 64. Similarly we can observe from graphs 81, 84 and 85 that the effect of plasticizer type on the UTS is different when the amount of plasticizer is quoted in different terms. However, the effect of plasticizer type on Tg and UTS is the same, generally speaking, when considering the amount of plasticizer in the same terms. That is to say that the effect of plasticizer type expressed in phr has the same effect on Tg and UTS. The same could be said when plasticizer type is expressed in BSS or moles per kilogram PVC.

5.3.5 Structurization

To analyse structurization quantitatively lace extrudates representing from very smooth to ever increasingly rough surface texture to extremely rough extrudates were chosen. These extrudates were designated with arbitrary units of 0 representing smooth extrudates with increasing value with roughness to 10 having extremely rough surface texture. The rest of the lace extrudates were evaluated with respect to this scale to give Figures 86 and 87 showing the level of structurization depending on the Banbury dump temperature and plasticizer concentration and type.

We have an increase in structurization with increase in Banbury dump temperature. At low plasticizer concentrations we observe a gradual increase in structurization with increase in dump temperature. However at higher plasticizer levels we have a sharper increase in structurization with dump temperature. DIOP concentration variations shows little effect on structurization. OPN and DINP show an increase in structurization level with plasticizer content but BBP shows the reverse effect. The rest of the four plasticizers, DTDP, DPN, TATM and DIOP, show a drop in the level of structurization as we increase the plasticizer content from 30 to 50 phr and further increase from 50 to 70 leads to increased structurization. This result could be explained if we consider for a given dump temperature increase in plasticizer
FIGURE 86: Effect of processing temperature and plasticizer concentration on the level of structurization of the extrudates
FIGURE 87: Effect of plasticizer type on the level of structurization of the extrudates
concentration gives decreased structurization to a minimum point after which further increase in plasticizer level increases structurization. This minimum would depend on the type of plasticizer. A possible explanation for this is as follows. Increasing plasticizer concentration lowers the Tg of PPVC making it softer and hence easier to extrude it giving lower levels of structurization until a minimum is reached. Further increase in plasticizer leads to increased structurization once the minimum is attained. This could be due to the increased number of free plasticizer molecules imparting phase inhomogeneity to PPVC causing irregular recovery of internal constraints of the sample during extrusion.

Using dump temperature at which structurization first starts to appear to classify the type of plasticizer, we can put the plasticizers in the following order irrespective of their concentrations:

\[ \text{BBP} < \text{DIOP} < \text{OPN} = \text{DINP} < \text{TATM} < \text{DPN} < \text{DTDP} \]

increased compounding temperature required for structurization initiation

This trend follows exactly the same trend as initiation of swell of PVC resin when placed in these plasticizers, see Section 5.1.2.

With 30 parts of plasticizer we do not obtain any glossy extrudates whatever the dump temperature or plasticizer type used. Also, DTDP shows no glossy extrudates at all even at high plasticizer concentration. A trend is observed in ease of glossy extrudate formation with the type of plasticizer as follows:

\[ \text{DTDP} < \text{DPN} < \text{TATM} = \text{OPN} < \text{DINP} = \text{DIOP} < \text{BBP} \]

increasing glossy extrudate at high plasticizer level (≥ 50 phr)
Unlike BBP which exhibits glossy extrudates of low level structurization over the whole compounding temperature range, the rest of the six plasticizers show glossy extrudates with high structurization only. They do not show glossy forms at high temperatures with low structurization. The above trend follows well with that of gel-to-sol transformation temperature ($T_m$, Section 5.1.2). Thus with plasticizers which solvate the PVC resin at low temperature (e.g. BBP, $T_m = 97-98^\circ C$) give more glossy samples while those which solvate at higher temperatures (e.g. DTDP, $T_m = 146-147^\circ C$), give less glossy extrudates. Putting the above two trends together we see that the higher the gel-to-sol transformation temperature of the plasticizer, the less the extrudates are glossy and lower the dump temperature for structurization initiation.

To see whether gloss and dull appearance of the extrudate was a surface or bulk effect samples of DINP were placed in a liquid of refractive index 1.54 (same as PVC). The gloss and dull appearance could no longer be differentiated in the liquid implying the phenomenon is due to surface effects. Thus scanning electron micrographs were obtained, see Plate 10, of DINP samples coated with gold followed by carbon. Comparing dull and glossy extrudates (70 DINP/166°C and 30 DINP/192°C) with identical structurization we observe from the micrographs that the glossy extrudate has very much more smoother surface. The glossy extrudate shows almost a uniform distribution of domain (0.2 μm) structures with almost no primary particles (1-1.5 μm). The dull extrudate on the other hand shows heavily convoluted surface with less distinct domain structures which seem to be fused to some extent. Could the differences be an artifact of the dump temperature? Comparison of micrographs of extrudates 70 DINP/167°C, with structurization level 8, and 30 DINP/166°C, with structurization level 4, we find it is not the case. We find extrudate 30 DINP/166°C has close resemblance to 30 DINP/192°C except that 30 DINP/166°C shows many more primary particles with many more distinctive domain structures.
PLATE 10: E.M. photomicrographs showing the effect of surface microstructure on the glossyness of the extrudates
5.4 Reprocessability

Manifestations of Banbury compound temperature were not borne out when the compounds were extruded at a processing temperature below that at which the sample was compounded, Section 5.2.2. This led to the question, is the process of fusion reversible? To answer this analysis of the fusion characteristics of the extruded lace at 134°C using the sample containing 30 phr DIOP as an example, was carried out using capillary rheometry (CR), DSC, optical microscopy and structurization techniques.

Table 16 shows the effect of reprocessing samples at a temperature below that of compounding on the capillary rheometer extrusion pressure and the 'A'-endothermic energy. The values for the entry pressures and the endothermic energy for all the samples

<table>
<thead>
<tr>
<th>Banbury Dump Temperature °C</th>
<th>CR Extrusion Pressure (After Banbury Mixing) MNm⁻²</th>
<th>'A'-endothermic Energy ΔH Jg⁻¹ of PVC</th>
<th>CR Extrusion Pressure (After reprocessing at 134°C) MNm⁻²</th>
<th>'A'-endothermic Energy ΔH Jg⁻¹ of PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>134</td>
<td>20.1*</td>
<td>0.90*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>154</td>
<td>26.4</td>
<td>1.98</td>
<td>20.8</td>
<td>0.89</td>
</tr>
<tr>
<td>162</td>
<td>30.8</td>
<td>2.56</td>
<td>19.6</td>
<td>1.08</td>
</tr>
<tr>
<td>177</td>
<td>42.8</td>
<td>3.41</td>
<td>20.4</td>
<td>1.07</td>
</tr>
<tr>
<td>188</td>
<td>48.4</td>
<td>4.70</td>
<td>21.2</td>
<td>1.18</td>
</tr>
<tr>
<td>195</td>
<td>46.8</td>
<td>6.30</td>
<td>20.8</td>
<td>1.29</td>
</tr>
</tbody>
</table>

*Estimated by extrapolation of curves

TABLE 16: Effect of Reprocessing on Extrusion Pressure and Secondary Crystallinity

compounded had reduced, to the values of the sample that would be compounded at 134°C, on reprocessing at 134°C. An explanation might be that the highly deformable connective tissue, the secondary crystalline cross-link sites, are broken down at various points under the high shearing forces.
The DSC traces also reveal that the 'B'-onset temperature corresponding to the maximum processing temperature the sample had undergone, is unaffected by reprocessing at a temperature well below its compounding temperature; see Figure 89 below.

![Figure 89: Effect of Reprocessing on 'B'-onset Temperature](image)

This implies that high shearing forces have no effect on the annealed more larger and perfect crystallites, which gives the 'B'-onset temperature on melting.

The extrudates from the Capillary Rheometer of the reprocessed samples show a much smoother surface texture, the same as that expected for a sample compounded at 1340C in Banbury. Thus we find a great improvement in structurization on reprocessing at a temperature lower than that of compounding at the expense of fusion state, Plate 11.

Studies of the structure of processed and reprocessed samples by swelling in acetone followed by shearing between glass slides and observing under a dark field optical microscope gave perhaps,
PLATE 11: Photomicrographs showing the effect of reprocessing 30 phr DIOP sample at a temperature below that of its compounding on structurization (R-reprocessed at 134°C, B.C. - Banbury compound)
the most surprising results. Plate 12 shows the anticipated destruction of the particulate structure to give a well fused sample as the compounding temperature is increased. The seemingly agglomerated structures in the photographs are in fact individual particles of <5 \mu m and have agglomerated while the acetone is evaporating rapidly under the intense heat from the microscope light bulb while photographing. However on reprocessing we observe that the fused structure is completely broken down to a structure of the order of <5 \mu m. The reprocessed structure resembles very closely that of the sample compounded at 1540C which has barely started to fuse to any significant extent. It is difficult to imagine that the primary particles have somehow retained their identity through the original processing to 1950C (where they are certainly not visible) and have reappeared on subsequent reprocessing to 1340C. A more likely explanation would be that a new structure is created, by applying high shearing forces, of the order of primaries.

Another sign of reversibility was seen, Section 5.2.2, when Banbury compounds dropped at temperatures between 150-200oC were extruded at 1340C and showed no difference in tensile properties of the extruded strips.

Evidence of reversibility can also be drawn from Rudin\textsuperscript{70,71} and Khanna's\textsuperscript{69} work. On reprocessing samples at lower temperatures they obtained smoother extrudates. Recent work by Portingell\textsuperscript{79} showed CR extrusion pressure drop and some evidence of particulate structure of 1 \mu m size when highly fused samples were reprocessed at a lower temperature. P Benjamin agrees (private communication) that a new structure is created rather than the PVC reverting to its initial morphology.
PLATE 12: Photomicrographs showing the effect of reprocessing 30 phr DIOP sample at a temperature below that its compounding on the morphology of PVC.
5.5 Discussion

The variation of activity of the plasticizers could be explained in terms of molecular weight and polarity as follows. The effect of molecular weight of the plasticizers on the \( \chi \)-value is given in Figure 88 below. This is the same trend as observed by Doty and Zable\(^{139} \) with a homologous series of dialkyl phthalates. With increased length of the hydrocarbon chain in the dialkyl phthalate homologous series we have increased steric hindrance of the carbonyl functional group. This minimizes the accessibility of the carbonyl group for interaction with the polymer, hence the lower activity with increased molecular weight. The curve of

FIGURE 88: Variation of \( \chi \) with Molecular Weight of Plasticizers

Doty and Zable\(^{139} \) with a homologous series of dialkyl phthalates. With increased length of the hydrocarbon chain in the dialkyl phthalate homologous series we have increased steric hindrance of the carbonyl functional group. This minimizes the accessibility of the carbonyl group for interaction with the polymer, hence the lower activity with increased molecular weight. The curve of
Figure 88 has a minimum at diisooctylphthalate showing it to be the most compatible of the dialkyl phthalates. The upsweep of the curve to the left is surprising. Intuition would say BBP should be the most compatible one of the series. However the extra bulky benzene ring buries the carbonyl functional group giving low plasticizer-polymer interaction. This is seen to be so by the fact that BBP exudes much more than the dialkyl phthalates, Table 16.140.

<table>
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<th>Plasticizer</th>
<th>Volatility % lost after 1 day</th>
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<td>DIOP</td>
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<td>0.8</td>
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<tr>
<td>TATM</td>
<td>0.4</td>
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</table>

TABLE 16: Percentage volatility of plasticizer at 87°C over activated carbon.

The nylonates having no benzene ring are less polar than the dialkyl phthalates giving slightly higher $\chi$-values than from the curve of Figure 88. The trimellitate, on the other hand, has an extra polar carbonyl group on each TATM molecule. Thus TATM has a very low $\chi$-value.

The negative values for very compatible plasticizers are thought to arise from the fact that the actual molecules are polar and therefore do not approach the polymer molecules randomly but with preset, directional forces operating. Also it should be noted that the interaction parameter is specific for that particular plasticizer with that particular resin.

Although BBP is absorbed more rapidly and to a greater extent than the other plasticizers, it does not seem to have the same ability in lowering the Tg. The choice of plasticizer shows a smaller
effect than the concentration of the plasticizer in lowering the Tg.

The effect of increased plasticizer concentration is to decrease the CR extrusion pressure. Similar results have also been obtained by Moore\textsuperscript{109}. As the results demonstrate, the choice of plasticizer could have a pronounced effect on the rheological properties of the melt, also in agreement with Moore\textsuperscript{109}. In fact, the choice of plasticizer appears to be more critical in this respect than the effect of thermal history. It has been shown additionally that increased activity of plasticizer leads to increased ultimate fusion level when the results are looked at a given BSS. This is in concordant with the very reasonable expectation, that more active plasticizers will more easily facilitate the fusion process.

Generally speaking it was observed that increased processing temperature, increased plasticizer activity and decreased plasticizer concentration led to increased amount of recrystallization. This is as expected since increased processing temperature increases the amount of melted material to cause recrystallization on cooling. Decreased plasticizer activity and increased plasticizer concentration increases the number of unbound plasticizer molecules to the PVC matrix. These molecules either reduce the recrystallization sites and/or solvate the recrystallized crystallites.

The B-onset temperature was found to correspond to the maximum processing temperature the material had undergone. A recent publication by Gilbert\textsuperscript{136} showed this was the case for rigid PVC. However reprocessability results also show that when a sample is reprocessed at a lower temperature the B-onset temperature still corresponds to the maximum temperature it had undergone previously. This suggests that the larger and more perfect annealed crystallites which melt to give the B-endothrm, are unaffected by shear, while the less perfect crystallites of various sizes, which melt to give the A-endothrm, are destroyed under the application of shear.
Morphology studies as suggested by Summers\textsuperscript{52} involving swelling PVC samples in acetone and shearing between glass slides proved to be useful. However by using dark field microscopy the contrast of the specimen was greatly enhanced. However with this method when we are looking at PVC grains the finer structure which is dark is not defined under the dark field of view. Thus dark and bright field optical microscopy can be used in a complementary fashion.

Whereas it has been shown that a significant 'memory' of the original polymer granules can persist in the processing of rigid PVC compositions, this is much less true for plasticized PVC. Like the CR extrusion pressure, morphology reveals that there is increased ultimate fusion level with plasticizer activity. Although higher plasticizer concentration samples show better fusion with respect to lower concentration, the low plasticizer concentration samples are very rubbery and not easily sheared between glass slides. The higher concentration samples on the other hand can be very easily sheared and torn when sheared between glass slides. The behaviour of fusion under high shear in a Banbury reveals similar results to that obtained by Allsopp\textsuperscript{59} using a rigid PVC formulation with the exception that fusion occurs at a lower processing temperature for plasticized PVC.

The tensile test results resemble those obtained by B P Chemicals Ltd\textsuperscript{115} and ICI Ltd\textsuperscript{116}. The results follow closely the ability of the plasticizers in lowering the Tg of the compound. The lower the Tg the lower the ultimate tensile strength.

Broadly speaking, it was found that increased plasticizer activity leads to increased ease of structurization and glossy extrudate formation. The effect of increased structurization with temperature is well known\textsuperscript{52,69,71,91,111,112}. The difference between glossy and dull extrudate formation was found to be due to extrudate surface microstructures. This has also been observed in polyethylene by Tordella\textsuperscript{137}. 


\textsuperscript{137}
We have seen in the previous chapter that a plot of A-endothermic energy versus the CR extrusion pressure provided us with a master curve to assess fusion of a sample irrespective of its thermomechanical history or the processing equipment used. Similar curves can be obtained by changing the formulation by changing the plasticizer type and concentration. Figure 89 shows the effect of plasticizer concentration on the master curve. We find that the limiting values are different with different concentrations of plasticizer. Changing the type of plasticizer at a given concentration showed signs of differing limits. Since incomplete master curves were obtained to show the effect of plasticizer type on the limiting values they are not presented here.

FIGURE 89: Effect of Plasticizer Concentration on the Master Curve
There is increased fusion with secondary crystallinity. However, at a given amount of secondary crystallinity increase in plasticizer concentration decreases the extrusion pressure. This does not mean we have decreased fusion with increase in plasticizer, on the contrary we have increased fusion. We have earlier attainment of fusion with increased plasticizer concentration. The fact that we do not have a constant CR extrusion pressure for a given quantity of secondary crystallites indicates that secondary crystallinity is not the sole factor affecting extrusion pressure.

Since different master curves are obtained for different formulations it means we can only use the master curve for the same formulation as that used to obtain the master curve. However, the same shape of the master curve for different formulations, indicates that the shape of the curve is a real one and that is not inherent of the formulation used in the previous chapter.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS
FOR FUTURE WORK.

6.1 Assessment of Fusion Characteristics

Several conclusions can be drawn from Chapter 4:

- A mathematical relationship can be obtained relating jacket temperature, rotor speed, dump temperature and the thermomechanical temperature rise during mixing in Brabender Plastograph.

- The Brabender Plastograph can be used to study the flow properties hence the structural transformations of particulate PPVC during the process of fusion.

- Drop in extrusion temperature and increased screw speeds lead to increased throughput.

- The rheological method is good in assessing fusion state of a sample having a standard curve derived from samples of the same formulation and processing conditions with temperature being the only variable.

- Increased shear leads to an increased fusion state, however the effect of increased shear at higher screw speeds during extrusion is partially offset by the reduction in residence time resulting in less heat input.

- The ultimate level of fusion is not greatly affected by the process or processing conditions, although they clearly influence the rate of fusion attainment.

- Secondary crystallinity is increased with temperature and shear.
• the acetone test is useful in assessing fine differences in poorly fused samples.

• microscopy tests for particulate structure appear to be the most reliable since they depend on a physical phenomenon.

• when a sample is extruded at a temperature below its compounding temperature the effect of compounding shear level and temperature is to increase structurization.

• a master fusion curve can be obtained using a combination of extrusion pressure and secondary crystallinity which could be used to assess the state of fusion of a sample irrespective of its thermomechanical history or the equipment used to process it. The master curve can also be obtained using tensile strength rather than extrusion pressure measurements. Simple temperature range compression moulded samples would suffice to give the master fusion curve.

6.2 Effect of Plasticizer on Fusion and Processing

Some of the more important conclusions that can be drawn from Chapter 5 are:

• there is a drop in blending time with increased plasticizer concentration. Several interrelating factors govern the frictional heat generation in a Fielder Mixer.

• two distinct upsurges in temperature during blending are obtained, one due to Tg of PVC and the other due to plasticizer type.

• ultimate plasticization is attained at very early stages of mixing, further mixing does not alter the Tg of the dry blend.

• a characteristic particle size distribution is obtained for each plasticizer dry blend.
• extrusion processing at a temperature below that of compounding obliterates the effect of increased tensile strength with increased compounding temperature.

• ageing of PPVC causes an increase in extrusion output. A unique relationship exists between output rate and compounding temperature for PPVC when extrusion is carried out at low temperatures.

• increased plasticizer level leads to decreased capillary rheometry extrusion pressure.

• at a given BSS we have an increase in the state of fusion with increased plasticizer interaction parameter.

• generally speaking we have an increase in secondary crystallinity with increase in the plasticizer interaction parameter.

• the DSC was found to be an "internal" method of determining the maximum processing temperature PPVC had undergone irrespective of the thermomechanical history, or formulation used.

• increased ability of plasticizer to lower Tg of PPVC leads to decreased ultimate tensile strength.

• when samples are extruded at a temperature below their compounding temperature the effect of compounding temperature is to increase structurization.

• generally speaking, increased plasticizer activity gives increasingly fused samples which give increased structurization. Increased plasticizer concentration leads to increased ease of structurization.

• higher plasticizer concentration compounds give glossy extrudates. The difference between glossy and dull extrudates is due to the microstructure on the surface of the extrudates.
micrographs reveal that we have increased fusion with processing temperature and plasticizer activity. The effect of increase in plasticizer concentration is to reduce the temperature in attaining its ultimate fusion level.

BBP was found to behave inconsistently with respect to its activity, while TATM proved to be more active than anticipated.

different formulations require different master fusion curves. The ultimate fusion level attained is lower with increased plasticizer concentration.

reprocessing a sample at a temperature below its compounding temperature lowers the state of fusion of the sample to a level which is the same as that of a sample compounded at the same temperature as that of reprocessing. We find both the extrusion pressure and the amount of secondary crystallinity falls on reprocessing. The level of structurization also falls, that is improved extrudate quality is observed on reprocessing. The micrographs reveal great similarity of the particulate structure of low temperature processed sample to the reprocessed highly fused sample. The most likely explanation being creation of new structures under the high shearing forces when highly fused samples are reprocessed at low temperatures.

6.3 Recommendations for Future Work

Since a combination of rheological and DSC techniques have provided a method to assess the state of fusion of a sample of unknown thermomechanical history, it would be appropriate to see if it can also be applied to other formulations of both rigid and plasticized PVC. This method uses secondary crystallinity in assessing the state of fusion. Thus more understanding of how the overall crystallinity, the A-endotherm energy and the B-endotherm
energy vary with various parameters is needed to have a better understanding of the fusion process. This for example could be done by using an overstabilised formulation which would give a more defined B-endotherm peak enabling more accurate measurement of B-energy. Investigations should be carried out from the stage of virgin PVC through every stage of processing.

Dry blending is the initial stage of processing PVC. Thus it would be interesting to see if blending variables [rotor speed, jacket temperature, blending time, type of blender (TK Fielder, Henschel, Papenmeir) and rate of plasticizer addition] has an effect on the final product properties. Using a continuously recording ammeter, the time taken for the upsurge in power intake to take place by the blender at the dry point of the blend could be used to assess different plasticizers.

Using Banbury compounds of various plasticizer formulations to assess the state of fusion by means of master curves proved difficult since incomplete master curves were obtained. Thus it would be better to assess plasticizer type by obtaining master curves with compression moulded samples.

Lace extrudates were used to assess structurization. With lace extrudates it is difficult to see fine differences in structurization. Using a slotdie to give strips would remove this problem.

Ageing of PPVC gave increased output rate. It would be interesting to see if ageing causes the sample to melt at a position further along the extrusion screw length. This could simply be done by looking at the melt front of PPVC in the screw flight, by removing the screw from the extruder, of aged and unaged samples.
REFERENCES


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51. ASTM D2152-67.


124. ASTM: D2538-79.


130. Anagnostopoulos, C E, Coran, A Y, and Gamrath, Mod. Plast., 43(2) 141, 1965.


### APPENDIX 1

#### SYMBOLS USED

<table>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$\sigma$</td>
<td>shear stress</td>
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<tr>
<td>$\gamma$</td>
<td>shear strain</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>shear rate</td>
</tr>
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<td>$P$</td>
<td>pressure</td>
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<td>$t$</td>
<td>time</td>
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<tr>
<td>$N$</td>
<td>rotor/screw speed</td>
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<tr>
<td>$\Delta H_f$</td>
<td>heat of fusion</td>
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<tr>
<td>$\chi$</td>
<td>polymer-plasticizer interaction parameter</td>
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<td>UTS</td>
<td>ultimate tensile strength</td>
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<td>$T_B$</td>
<td>'B'-onset temperature</td>
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Conversion Units:

\[ P \quad 1 \text{ MNm}^{-2} = 1 \text{ MPa} = 145 \text{ psi} \]
\[ \Delta H_f \quad 1 \text{J} = 0.239 \text{ cal} \]
\[ \eta \quad 1 \text{ Nsm}^{-2} = 10 \text{ poise} = 0.1 \text{ cp.} \]
\[ \tau \quad 1 \text{ Nm} = 10^2 \text{ m-g} \]
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Effect of plasticizer concentration on British Standard Softness