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THE EFFECT OF CALCIUM CARBONATE FILLERS ON FUSION AND PROPERTIES OF RIGID PVC

by

AMANDA MAY PLASKETT

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University of Technology

SEPTEMBER 1989

Supervisor: M. Gilbert, Ph.D.

Institute of Polymer Technology and Materials Engineering

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Finally my thanks go to my parents for their constant encouragement and occasional financial assistance, and to Bill for the sacrifices he has made during the writing of this thesis.
ABSTRACT

Although the addition of fillers (both coated and uncoated) to PVC compounds is now commonplace, research into their role in the fusion process and subsequent end product properties is limited.

Thus five grades of natural calcium carbonate filler of varying particle size were incorporated into a simple rigid PVC pipe formulation by dry blending and then extrusion on a twin screw extruder.

Work was also carried out on the same fillers coated with both 1% by weight stearic acid and with a monolayer stearic acid covering. Further work involved the coating of one filler with a range of coating levels between 0.3% and 3% by weight stearic acid. In each instance a control formulation containing no filler was run.

Dry blends were compared using density measurements, ash analysis, electron and light microscopy techniques and torque rheometry tests, whilst solvent testing and thermal analysis of the pipe gave an indication of fusion level.

Analysis of the blends and pipe in this way showed up distinct filler effects on fusion behaviour with finer fillers greatly aiding fusion, while coarser particles hindered the process. The presence of a stearate coating on the filler modified fusion further, the observed behaviour depending on the relative amounts of calcium stearate coating and unreacted stearic acid, which act as internal or external lubricants respectively.

Tensile and impact properties of the processed pipe were measured. In agreement with previous studies tensile properties reached an optimum value with fusion level whilst impact properties passed through a maximum. Mechanical properties in this way were found to be directly related to fusion levels.

By using a range of coating levels on one filler an optimum coating level for fusion and mechanical properties was achieved.
LIST OF SYMBOLS

A  endothermic peak area
tensile specimen overall length
cross sectional area

B  time base setting
length of narrow section (tensile specimen)
endothermic peak area
brittle mode of failure

BD brittle/ductile mode of failure

C  tensile specimen width

ΔH_f  heat of fusion

ΔH_{max}  maximum heat of fusion

ΔP  entrance pressure loss in capillary rheometry

ΔP_{ENT}  pressure loss due to entrance effects

ΔP_{VISC}  viscous pressure loss

Δq_s  y axis sensitivity

d  particle diameter

D  capillary diameter
tensile specimen thickness
ductile mode of failure

DB ductile/brittle mode of failure

ε_B  elongation at break

E  cell calibration coefficient
percentage elongation

F  force

g  acceleration due to gravity

k  constant

l  displacement at break

l_0  initial gauge length

L  capillary length

m  sample mass

m  mass output rate
M  screw torque
M₀  background torque
n  fluid viscosity
n  viscous loss term
degree of polymerisation
screw speed
number of observations
phr  parts per hundred resin
q  specific energy consumption
ρ  density of particle
ρ₀  density of fluid
rpm  revolutions per minute
σₖ  stress at break
σᵧ  stress at yield
s, s.d  standard deviation
Sᵣ  recoverable shear strain
τ  shear stress
Tₑ  annealing temperature
T₉  glass transition temperature
V  terminal velocity
X  value of single observation
X̄  arithmetic mean
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1.1 Polyvinyl Chloride

Poly (vinylchloride) is produced from the polymerisation of the monomer vinylchloride, CH$_2$CHCl. It is a thermoplastic homopolymer, commonly abbreviated to PVC, with the repeat unit:

$$\left[ \begin{array}{c} CH_2 \\ CH \\ Cl \end{array} \right]_n$$

where 'n' denotes the degree of polymerisation.

Its first commercial opportunity came during World War II when, in plasticised form, it alleviated rubber shortages. Since then world-wide sales of PVC have expanded dramatically, and it is now one of the top five thermoplastics used commercially (along with high density polyethylene, low density polyethylene, polypropylene and polystyrene). Its popularity stems mainly from its versatility, this came from the necessity to incorporate additives into PVC to overcome its inherent processing problems. These additives now permit a vast range of compositions to be formulated, resulting in a broad and varied service life, as illustrated in Table 1.1.
### Table 1.1

Breakdown of the West European PVC Market by Application (1985)\(^{(126)}\)

<table>
<thead>
<tr>
<th>Processing/Application</th>
<th>Market Share (%)</th>
</tr>
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<tr>
<td><strong>Rigid PVC</strong></td>
<td></td>
</tr>
<tr>
<td>Hollow articles</td>
<td>8.3</td>
</tr>
<tr>
<td>Films</td>
<td>10.5</td>
</tr>
<tr>
<td>Pipes and fittings</td>
<td>23.9</td>
</tr>
<tr>
<td>Profiles</td>
<td>12.9</td>
</tr>
<tr>
<td>Blow mouldings</td>
<td>2.0</td>
</tr>
<tr>
<td>Records</td>
<td>1.9</td>
</tr>
<tr>
<td>Others</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
<tr>
<td><strong>Plasticized PVC</strong></td>
<td></td>
</tr>
<tr>
<td>Film and sheet</td>
<td>8.2</td>
</tr>
<tr>
<td>Floor covering</td>
<td>5.1</td>
</tr>
<tr>
<td>Tube and fittings</td>
<td>4.0</td>
</tr>
<tr>
<td>Wire and cable insulation</td>
<td>9.5</td>
</tr>
<tr>
<td>Different coatings</td>
<td>3.9</td>
</tr>
<tr>
<td>Other</td>
<td>7.8</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

### 1.2 Grain and Molecular Structure of Polyvinyl Chloride

The significant effect that grain and molecular structure can have on polymer melt rheology was first demonstrated by Berens and Folt\(^{(1)}\) in 1967. This has led to
much greater technical awareness of the importance of structure with respect to processing behaviour and end product properties, both of which will be discussed in later sections.

1.2.1 Morphology

The grain structure or morphology of a PVC polymer is developed during the polymerisation process; suspension polymerisation being the most widely used for commercial PVC, and throughout this project. The mechanism of suspension polymerisation has been widely reported in literature (2,3,4) and thus only a simple schematic representation put forward by Allsopp (3) shall be given here, Figure 1.1.

Figure 1.1
Schematic representation of the mechanism of VCM polymerisation
This uses nomenclature put forward by Gei1(5), and listed here by Allsopp(6), in Table 1.2, which was proposed in an attempt to obtain consistency in authors terminology.

**Table 1.2**

<table>
<thead>
<tr>
<th>Term</th>
<th>Approximate Size</th>
<th>Origin or Description</th>
<th>Previous Terminology (with References)</th>
</tr>
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<tbody>
<tr>
<td>Grain</td>
<td>50-250 µm</td>
<td>Visible constituent of free flowing powders, made up of more than a monomer droplet.</td>
<td>Granule (2) Cellulor grain (3)</td>
</tr>
<tr>
<td>Sub-grain</td>
<td>10-150 µm</td>
<td>Polymerised monomer droplet.</td>
<td>Sub granule (2) Undissel (3)</td>
</tr>
<tr>
<td>Aggregate</td>
<td>1-10</td>
<td>Formed during early stage of polymerization by coalescence of primary particles (1-2 µm). Grows with conversion to size shown.</td>
<td>Aggregate (2) Cluster (3) Micro globule (4)</td>
</tr>
<tr>
<td>Primary particle</td>
<td>0.6-0.8</td>
<td>Grows from domain. Formed at low conversion. Contains about 10^2 micro-domains. Only observed at low conversion (less than 2%) or after mechanical working. Term only used to describe 0.1 µm species; becomes primary particle as soon as growth starts.</td>
<td>Micronucleus primary particle (2) granule (3) micro-globule (4)</td>
</tr>
<tr>
<td>Domain</td>
<td>0.1-0.2</td>
<td>Primary particle nucleus. Contains about 10^5 micro-domains. Only observed at low conversion (less than 2%) or after mechanical working. Term only used to describe 0.1 µm species; becomes primary particle as soon as growth starts.</td>
<td>Primary nucleus (2) Granule (3)</td>
</tr>
<tr>
<td>Micro-domain</td>
<td>0.02</td>
<td>Smallest species so far identified. Aggregate of polymer chains - probably about 20 in number.</td>
<td>Basic particle (2) Particle (3)</td>
</tr>
</tbody>
</table>

Notes on Table 1

1. The domain is not a feature of PVC morphology in high conversion polymer samples since a growth of this species with conversion obliterates 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 µm primaries at low conversion.

3. The reason for a separate identity for the domain is that it may be shown in future to contain an atypical morphological or molecular feature, eg higher level of crystallinity.

**List of PVC Nomenclature(6)**
It is thus clear that the growth of PVC takes place through a series of aggregation steps, finally creating a resin consisting of grains 20-250\,\mu m in size surrounded by protective colloidal skins. Each grain is formed from agglomerates (2-10\,\mu m) of primary particles (0.6-0.8\,\mu m) termed sub-grains. The primary particles are in turn made up of smaller structures namely the domains (0.2\,\mu m) and microdomains (0.02\,\mu m). This then gives us an idealised model of a PVC grain, shown in Figure 1.2, although in practice structural heterogeneity in suspension PVC resin is common\(^{(7,9)}\).

![Figure 1.2](image)

**Figure 1.2**

Model of PVC grain morphology\(^{(6)}\)

### 1.2.2 Molecular Structure and Crystallinity

The macro and microscopic morphology of PVC is thus now fairly well understood and characterised. However, the
submicroscopic morphology is still very much an area of research\(^\text{10-13}\), not least because of the problems of actually resolving the structures present. The main areas of interest include the domain and microdomain, and how these are related to crystallinity.

The ability of the PVC macromolecules to pack in an orderly crystalline array is determined by the regularity of the polymer chain. There is general agreement that it is only in the presence of short syndiotactic sequences (rather than isotactic or atactic) that the polymer is capable of crystallisation\(^\text{14,15}\). The first proof of the existence of crystallites was provided by Natta and Corradini\(^\text{16}\) based on studies using wide angle X-ray diffraction.

\[
\begin{align*}
\text{Cl} & \quad \text{CH} \quad \text{CH} \quad \text{CH} \\
\text{CH} & \quad \text{CH} \quad \text{CH} \quad \text{CH} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

Syndiotactic sequence

The degree of syndiotacticity correlates well with reported degrees of crystallinity\(^\text{14,17}\), which in conventional industrial PVC lies usually between 5\% and 10\%\(^\text{18}\). A model of the microdomain structure of PVC was created by Summers\(^\text{10}\), from PVC crystal sizes determined by Wenig\(^\text{18}\), which showed crystallites typically 100\% apart connected by tie molecules, Figure 1.3.
Due to the variation in size and perfection of these crystallites PVC exhibits a broad range of crystalline melting points, reportedly from 120-260°C. Each thermal cycle that the PVC experiences shifts this range towards higher temperatures, and in this regard working or reworking with PVC is like working with a new material each time.

1.3 **Formulation Ingredients**

Since the earliest development of polymers additives have been used to compound around problems rather than laboriously changing processing equipment or base polymer structure. Additives have been used to permit processing or
increase output rate on existing equipment, to enhance or overcome processing deficiencies, and to reduce cost.

PVC is unique in that to undergo processing (i.e. mixing, compounding and shaping) it must contain additives to overcome several problems including thermal degradation and high melt viscosity. A whole host of additives are now added to PVC, of which some of the most common are listed below:

- stabilisers
- lubricants
- plasticisers
- polymeric processing aids
- fillers
- pigments
- impact modifiers

The presence of these additives has meant that PVC can be processed into a wide variety of products.

To reduce the effect of additives on the parameters of interest only fillers, stabilisers and lubricants were used in this project. Thus only these three additives will be discussed in this introduction.

1.3.1 Fillers

For many years the use of unfilled PVC compounds was commonplace, until it was realised that reasonable quantities of filler could be incorporated into the blends whilst only slightly modifying certain properties such as hardness, rigidity, viscosity or colour. These filler additions resulted in substantial cost savings, and a wide variety have
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since been used in the compounding of PVC. These include ground whitings\(^{(19)}\), precipitated chalks, clays, calcined clays, ground silica, calcium silicates, carbon black, wood flour, asbestos, and a host of others.

In recent years standards of production of fillers have virtually equalled those of PVC themselves, and work\(^{(20)}\) has shown that by the correct selection of fillers not only can certain properties of the unfilled material be enhanced\(^{(21)}\), but considerable processing advantages can be achieved. For example ultrafine stearate coated calcium carbonate at loading 1-30 phr is increasing used as a processing aid rather than a filler, improving extrusion properties and impact performance\(^{(22)}\).

1.3.1.1 Calcium Carbonate Fillers

In 1957 Phillips and Youde\(^{(23)}\) compared the behaviour of a number of mineral fillers in PVC, and clearly showed that the calcium carbonate fillers possessed the most suitable characteristics for the great majority of PVC compounding applications. Its success is due, in part, to its following properties\(^{(25)}\):

- a. white in colour
- b. non-toxic
- c. odourless
- d. stable to 800°C (except in acids)
- e. has a low refractive index
f. soft, and therefore does not cause abrasion problems during processing

and

g. there is an unlimited supply of the raw material which can be ground to any number of reproducible grain size distributions

Due to these properties, and its compatibility with PVC, it accounts for the greatest proportion of filler used in PVC\(^{(24)}\) with its specific properties readily improved through surface coating.

Calcium carbonate fillers divide into two types:- natural and precipitated\(^{(25)}\). These are produced by grinding minerals, or by controlled precipitation from solutions of lime or calcium salts, respectively.

Second to silicon, calcium is the most abundant naturally occurring element, and is found mainly as calcium carbonate in chalk, limestone and marble. It is formed from the consolidation of deposits of minute marine organisms during the formation of the earth's crust, chalk deposits, limestone rocks and marble resulting from soft compression, hard compression and metamorphism respectively. These natural materials are termed whittings and are predominantly amorphous (although it has been stated that the ultimate particles of these materials are of micro-crystalline structure\(^{(19,27)}\)). They assume a cubic or blocky shape with a low aspect ratio thus acting as extenders rather than
reinforcing materials\textsuperscript{(28)}. Precipitated calcium carbonate has a much finer rhomboid or needle shaped crystalline form.

Before selection of a suitable calcium carbonate filler for PVC can be made, the significance of several parameters must be considered. These include size and surface area, colour and refractive index, and surface treatments\textsuperscript{(29)}. These parameters can ultimately affect colour, processing characteristics, and most importantly the physical and mechanical strength properties of the end product. Although most fillers are sold as fine white powders when dispersed in PVC, their colours can range through transparent to numerous shades and hues. This is due to naturally occurring contaminants, and differences in refractive index between the PVC resin and the filler. Gibson\textsuperscript{(20)} in 1966 wrote a paper dealing with the different types of calcium carbonate used for PVC, and other applications, and found that metallic impurities such as iron, copper and aluminium seriously affected the efficiency of the stabiliser system used. It has since been found that a low silica content is also beneficial, significantly reducing wear in the processing equipment\textsuperscript{(30)}.

1.3.1.2 Filler Particle Size

Modern grinding procedures and current screening techniques permit producers to offer natural fillers which meet today’s high requirements of sizing. Two characteristics can be rated as the most important, and are
Introduction

well documented by Schlumpf (28, 31). These are:-

1. so called 'top cut', upper section of the filler distribution curve. This gives an indication of the coarsest particles in the mixture which in turn influence notched impact strength, as the coarsest particles are the greatest concentrators of stress, surface properties such as gloss, tear resistance and elongation at tear, and the wear in the processing machinery.

2. filler specific surface area expressed in $m^2/g$. This gives a picture of the possible surface of interaction between polymer molecules and filler. A large filler surface can be beneficial in producing many bonding sites for the polymer chains, thus giving good mechanical properties; but detrimental if there is insufficient shear force or too strong forces of attraction between filler particles to completely disperse the filler in the polymer matrix. The resultant agglomerates will then function as coarse particles. This problem is more common in precipitated calcium carbonates where surface areas of up to 2-3 times that of natural whitings can be produced.

Many authors (25, 32) have carried out work on the effect of filler particle size on mechanical properties. Martin (27) in 1965 studied moderately plasticised PVC compounds, and found that at a given calcium carbonate filler loading end product properties of tensile strength and elongation at break were dependent on the specific surface area and particle size distribution in such a way that better
properties resulted from using finer fillers. Gibson(20), the following year, stated that 'generally speaking, the finer the filler the less its effect in degrading the mechanical strength properties and, in the case of rigid materials, the greater its effect on the resulting reinforcement of impact strength'. Shaw and Diluciano(33) studied the effect of content of chalk between 0% and 5% and the effect of average particle size between 0.07 and 3.5 microns on mechanical properties of rigid PVC pipes. They found that an increase in the amount of chalk, in the range explored, had very little influence on impact strength, while an increase in particle size decreased impact strength. This they explained by the fact that the larger particle size calcium carbonates would cause larger discontinuities in the PVC matrix, allowing easier crack initiation and propagation. Bystedt et al.(34) in 1987 studied the effects of adding a fine calcium carbonate filler (average particle size 1 micron) and a coarser filler (3 microns) to rigid PVC in a range of levels from 1-5 phr. Results showed that the content of filler had an obvious effect on impact strength, with the finer filler giving a clearly positive effect, whilst the coarser grained filler showed a slightly negative one.

The increase in impact strength attributed to fine fillers may be due to the creation of stress concentrations which then transmit the impact energy to the PVC matrix by the formation of microcracks. These stress concentrations
would be generated upon cooling of the melt due to the clearly different expansion coefficients of PVC and filler. Another theory is based on the concept that the PVC molecules may slide off on the filler surface under the effect of impact, the absorbed energy being dissipated\(^{(25)}\).

Fine fillers were also found to be less abrasive to processing equipment\(^{(29)}\) causing fewer shear burning problems whilst giving a higher gloss end product than coarser grades.

Other authors looked at the effect of more highly filled (between 0-100 phr) PVC formulations on properties. Schlumpf et al.\(^{(35)}\) found tensile modulus to increase with increasing filler content (i.e. the filler became more rigid), whilst notched impact strength also distinctly increased until such filler levels were reached that optimum dispersion was no longer possible. Danylink\(^{(36)}\) agreed with these findings stating that both tensile and flexural modulus increased with filler levels. He also concluded that with increased filler levels there was a need for both stabiliser and processing-aid concentrations to be increased, coupled with an increase in external and a decrease in internal lubricants (as the screws became worn) to extrude compounds successfully.

From all these findings the most consistent was that finer fillers were more beneficial to rigid PVC formulations. However, this left the problem of their increased tendency to agglomerate. It was known that the mixing process was very important\(^{(35)}\), strongly influencing both the behaviour and
gelling of the blend. There was therefore a need for fillers to be capable of easy and rapid incorporation\(^{(20)}\) during compounding, not least as there was a tendency to use dry blend extrusion compounding processes rather than internal mixers of the Banbury type, which were more severe.

1.3.1.3 Filler Coating

With fine fillers therefore, either longer mixing times are required or, to go someway in overcoming the agglomeration problem, they are coated. The commonest coating agent is calcium stearate, and quantities of 1-3\% by weight are usual. Stearate coating not only improves dispersion of the filler, but also reduces moisture absorption, aids stabilisation and lowers processing abrasion\(^{(29)}\). Calcium stearate is known to promote fusion in PVC\(^{(33)}\), thus a coating of this on the filler may promote PVC adhesion to and around the calcium carbonate particle. The PVC around the particle will then be tougher and more resistant to crack initiation and propagation.

Thus to date, finely divided surface coated calcium carbonates with mean particle diameters of approximately 1 \(\mu\)m have proved to be the most successful with rigid PVC, improving both impact strength and rigidity. One main area of technical development for calcium carbonate fillers now is aimed at obtaining the optimum upper cut of the filler distribution curve.
1.3.2 Stabilisers

PVC degrades\(^{(37,38)}\) when exposed to heat or light, and the purpose of stabilisers is to prevent discolouration or thermal degradation during processing, as well as to give it an extended and more varied service life.

Thermal degradation takes place above approximately 120°C releasing hydrogen chloride, a toxic and corrosive gas, whilst forming polyene. Degraded products may contain voids formed from gaseous by-products, and have dramatically reduced mechanical and electrical performances. Whilst attack of the corrosive hydrogen chloride on both operators and machinery may hinder production. It is the presence of the polyene structure which causes the distinct colour changes from yellow through brown to black. To alleviate all these problems an ideal stabiliser should therefore be capable of performing many functions -

- removal of reactive chlorine
- absorption of hydrogen chloride
- reaction with polyene structure
- U.V. absorbance, thus screening out damaging ultraviolet light

Although no such stabiliser yet exists many available stabilisers, and stabilising systems, are highly effective; falling into the following groups:-

1. Lead salts or soaps
2. Metal soaps or salts
3. Organotin compounds
4. Organophosphites
5. Epoxy compounds

The last two (groups 4 and 5) are generally known as 'secondary stabilisers' as they are never used alone but always in conjunction with the metal based 'primary stabilisers' (groups 1 to 3).

The most commonly used stabilisers lie in group 1, in particular basic lead carbonate and tribasic lead sulphate. These have long dominated the market\(^{(39)}\) due primarily to their low cost and good long term heat stability. They are often used in conjunction with group 2 stabilisers which, because some are produced from long chain fatty acids, can also function as lubricants and/or plasticisers.

Relatively little work has been carried out on the effect of stabilisers on fusion, although Kulas and Thorshaug\(^{(40)}\) discovered a marked difference in the influence of tin and lead stabilisers on the rate of fusion in a single screw extruder. This they explained, in part, by the chemical structure of the particular stabiliser.

1.3.3 Lubricants

Lubricants are chemical compounds necessary for minimising the shearing and frictional forces created during processing. They allow greater ease of fabrication without
causing detrimental effects to the physical properties of the polymer.

High shear extrusion was developed in the mid '60's causing processing technology to leap forward, with output rates doubled or tripled from those of a single screw extruder. This produced an increase in both shear and frictional forces during processing, resulting in additional heating in the polymer melt. Thus problems of polymer decomposition, adherence to machine components and possible degradation were experienced. These changes led to the compounding ingredients being examined more closely, and it soon became clear that of all additives lubricants were the most crucial and least well understood. A great deal of work was then put into lubricating systems\(^{41-43}\) with one of the first workers, Jacobson\(^{44}\), concluding that lubricants should have a low solubility in PVC, be as polar as possible, and have a certain viscosity at the processing temperature. Lubricants are generally placed into either one of two categories :-

**Internal**

Internal lubricants are readily compatible with PVC and diffuse, and thus act, chiefly inside the molten polymer material by lowering the internal i.e. inter-particular and inter-molecular friction of the compound. This in turn reduces the melt viscosity of the polymer and the frictional heat build up.
External lubricants have little compatibility with PVC and act primarily at the interface between the resin and the equipment surface, reducing the friction and adhesion. They may also coat large aggregates of the polymer molecules reducing friction between agglomerates.

As a result of these properties internal lubricants were thought to have a slightly positive effect, if any, on the fusion rate of PVC compounds; whilst excessive external lubrication could result in melt slippage, poor surface finish and a reduction in fusion by surrounding particles with a lubricating layer\(^{(45,46)}\). Lubricants used include:-

- fatty alcohols
- fatty acid esters (butyl stearate)
- fatty acids (stearic acid)
- fatty acid soaps (calcium or barium stearate)
- fatty amines
- waxes and hydrocarbons (paraffin)

In recent years several authors\(^{(47,51-54,57)}\) have extensively studied the effects of lubricants in formulations. Marshall\(^{(42)}\) by light transmission and haze, King\(^{(47)}\) by their effects on the glass transition temperature and Andrews\(^{(45,46)}\) on their effects in a Brabender Plastograph. Hartitz\(^{(48)}\) used a Brabender and a fluidity
test described by Jacobson(44), and Bower(49) looked at their effects on impact strength after processing in the Brabender. Rabinovitch et al.(50) developed a theoretical mechanism to explain how lubrication works. The theory centres on the fact that the chemical structure of all lubricants fall into three groups(55):-

1. straight chain hydrocarbons (paraffin waxes, hydrocarbon waxes)
2. straight chain hydrocarbons with polar end groups (fatty acids, fatty acid esters)
3. molecules having a polar centre with long chain carbons on each side (metal stearates)

PVC polymer chains are somewhat polar molecules and are thus not only attracted to themselves but to the polar metal surfaces of processing equipment. Thus when lubricants which contain polar groups, such as calcium stearate with its highly polar CaOOC- group are added they not only adhere to the PVC, but preferentially wet the metal surfaces, separating the PVC particles from the metal with their long hydrocarbon chains. Straight chain hydrocarbons, such as paraffin wax, will not wet the metal surface and as such are relatively ineffective as sole lubricants. However, in conjunction with polar lubricants they help to produce a thicker separating lubricating layer providing a better system than either lubricant alone. This is shown clearly in Figure 1.4.
The efficiency of the lubricating system will, however, change during specific stages in processing and this will in turn affect fusion, and thus the productivity and efficiency of an operation. The fusion mechanism for rigid PVC in a twin screw extruder will be discussed in a later section, but it basically involves a series of particular changes from larger to smaller particles followed by fusion and elongation. The rate at which this process proceeds is influenced by lubrication. Incompatible lubricants such as hydrocarbon waxes are very effective in promoting slippage in the early heat absorption stage, thus delaying fusion, but
have low melting points and thus become ineffective during the higher temperature fusion stage. Compatible lubricants, such as calcium stearate, form a viscous melt on the hot metal surfaces promoting sticking, without impairing inter-grain friction, and therefore faster fusion. These continue to be effective at high temperatures due to their polar groups.

If fusion is delayed until late in the barrel complete dispersion of stabilisers will be hindered and degradation of polymer chains at particle centres may take place\(^{(56)}\). These chains may then be a source of further degradation and colour change due to weathering. Delayed fusion may also leave unfused material in the end product, affecting mechanical properties. Therefore choice of lubricant affects not only processing procedure, but also product properties.

1.4 Processing of Polyvinyl Chloride\(^{(58-60)}\)

1.4.1 Dry Blending

Dry blending\(^{(37,38,61,62)}\) is a technique involving the mixing of all the ingredients in a single operation to produce a completely dry free-flowing powder. It was developed in the early 1940's, but not found to be commercially viable until improvements in resin and extruders had taken place. Problems arose during processing because the powder had to be conveyed, compacted, fused and melt mixed in one process, which was more than had been asked of extruders previously. High speed internal mixers are now the
commonest and most widely used method of compounding rigid PVC, not least because they create high bulk density blends with low heat histories - meaning processing can be performed at higher temperatures resulting in superior end product properties.

High speed mixers usually contain two chambers, the first disperses the ingredients by use of a vertical rotor arrangement. The centrifugal action of the high speed rotor results in the formation of a vortex in the powder which ensures that it all, at some stage, comes into contact with the hot chamber wall and passes through the shear gap between the blades and wall. The shear energy produced by the blades imparts further heat to the powder, whilst the shear action produces both dispersive and distributive mixing of the ingredients with the PVC powder. This action not only ensures dispersion of the additives but may also cause some of the PVC grains to break down with liquid and low melting point additives being adsorbed onto the grains. The temperature of the blend is usually controlled by a heating or cooling jacket to 120°C, after which it is discharged to the cooling stage. This second chamber has a much larger surface to volume ratio facilitating rapid cooling, which is essential with heat sensitive PVC, and improves its storage life. A large slow rotating blade destroys agglomerates.

The characteristics of the dry blend will effect its processing behaviour, and these can be changed by altering
the mixing temperature, speed of rotation of the blades and mixing time, all of which are independent. Studies have shown that altering these parameters affects particle shape, and thus bulk density and flow characteristics \((56, 63-65, 119)\). These in turn influence fusion and output rate, particularly in the case of twin screw extruders. Dispersion of additives over the polymer can also play a critical part in a particular blends extrusion performance\((120)\). Optimum distribution of the additives is only assured if the mixing temperature exceeds the melting temperature of one of the additives\((66)\). Well dispersed or preferably adsorbed stabilisers are essential to stop degradation which will occur if unprotected polymer regions exist.

Schlumpf\((35)\) has suggested that when fillers are present initial mixing should take place between these and the polymer, making use of the increased friction to break open the PVC grains before the other ingredients are added.

**1.4.2 Principles of Twin Screw Extrusion**

This discussion will concentrate on intermeshing counter-rotating twin screw extruders, although comparisons may be made with other types\((38, 67-70)\).

Two main characteristics typify all intermeshing twin screw extruders, and these are - a positive conveying (pumping) action, and effective mixing\((121)\).

In intermeshing twin screw extruders separate chambers are formed along the length of the screws between adjacent
flights and the surrounding barrel on the outside, and sealed by the flights of the opposite screw at the point of intermeshing. This means that once the twin screw picks up the PVC powder at the feed throat it is moved forward along the barrel regardless of its condition, pressure, or feed rate, giving it a positive conveying action. (In a single screw machine no such action exists as a continuous helix chamber or channel runs the entire length of the screw. Thus, the forward travel of the material depends entirely upon the friction developed between the PVC and the screw and barrel.)

Positive conveyance in the twin screw affords the following processing benefits:

- very narrow residence time distribution, all particles having spent approximately the same time travelling through the barrel
- better control of the barrel venting operation and of compression and decompression zones, as all the material passes through each zone at the same rate
- self cleaning action, screws clean each other at the intermeshing point preventing material hang-ups and facilitating colour changes and purging
- surge-free melt discharge, as melt travel is little affected by pressure or viscosity
- a more homogeneous product because the particles have all been exposed to the same degree of heat and work.
Mixing is encouraged by opening up the clearance between screws and barrel and between the screws themselves, thus promoting interchange of material between screws. Additional mixing occurs at the points where the screws intermesh since it is here that the material encounters highest shear rates. Thus with counter-rotating screws the material is forced or milled between the screws at these points, not only creating high shear rates but transferring the material from one screw to another. The material passes through these high shear zones once per screw revolution, imparting excellent mixing. (In single screw machines mixing depends mainly upon back pressure and the resulting back flow in the metering section.)

Twin screw machines also have a much larger surface area of contact between the polymer and the screws and barrel than a single screw machine. This greatly improves the thermal transfer, minimising the amount of energy which has to be supplied mechanically via the screws. Twin screw machines can therefore be run at low screw speeds. Figure 1.5 shows the arrangement of screws and direction of rotation in a counter-rotating intermeshing twin screw extruder.

Higher output rates are continually being pursued with new designs working with fuller screw flights, increased torques and earlier plastification(71). Larger volume die heads, as shown in Figure 1.6, give longer residence times in which to equalise temperatures and reduce shear(72).
Figure 1.5
Arrangement of screws in a counter-rotating intermeshing twin screw extruder (108)

Figure 1.6
New larger volume die design for high output pipe lines (71, 72)
1.5 **Fusion of Polyvinyl Chloride**

The fusion of PVC can be described as the process by which boundaries between grains are removed to produce a continuous homogeneous molecular structure.

1.5.1 **Fusion Mechanisms**

The earliest experimental evidence for the existence of rheological flow units consisting of many molecules acting as a single body came from Mooney and Wolstenholme\(^{(73)}\). It was not, however, until the work of Berens and Folt\(^{(1,74,75)}\) in the 1960's, on extrudates of emulsion polymerised PVC from a constant load capillary rheometer, that the presence of supermolecular flow units within PVC were established. Broadening their study they looked at suspension polymerised PVC, and here found that the primary particles acted as the melt flow units surviving extrusion temperatures of the order of 180°C; increasing extrusion temperatures caused increasing die swell suggesting a trend away from particle slippage and towards molecular deformation. From their results they postulated that particle size, shape and extent of fusion between particles would have a major effect on melt rheology. Collins and Krier\(^{(76)}\) studied thoroughly the melt rheology (as a function of shear rate) of a typical stabilised PVC dry blend, and found two distinct flow activation energies in the range of temperatures from 160 - 230°C. Where particle flow predominated, in the low temperature range, a corresponding low activation energy existed. However, at higher
temperatures where molecular flow became more important a higher activation energy was seen. This suggested the possibility of a transition from particulate to molecular flow.

This hypothesis helped to explain many of the processing properties of PVC which were contrary to other thermoplastics. These included the observed decrease in apparent viscosity with particulate flow, and the observed increase in viscosity of virgin material subjected to work or higher temperature history. It also explained the dramatic changes in mechanical behaviour which took place in the vicinity of 190 - 200°C, and why under constant shear rate post extrusion die swell increased with increasing temperature.

The particular nature of PVC melt flows, and that the final melt is strongly dependent on its thermomechanical history is now rarely disputed. However, the morphological character during processing is, with observed mechanisms fitting into two main groups. The first supported by Benjamin(77) and Menges et al.(78), amongst others(4,79-82), suggests that the transition from powder to melt involves commination of the PVC grains; whereas the second, proposed by Allsopp(66) suggests that particle breakdown plays a minor role.

The first mechanism basically proposes that the resin grains are broken down into primary particles which are then compacted and sintered, with interdiffusion between primary
particles and microdomains taking place. The boundaries between particles thus disappear and a three dimensional network is formed, the degree of interpenetration of the particles being the main factor which determines the strength of the end product material.

Both Benjamin\(^{(77)}\) and Portingell\(^{(62)}\) put forward similar models whereby particle grains were initially broken down to give primary particles. The addition of shear and heat then compressed and broke down these particles further, and melted the crystallites increasing the mobility of the molecular chains. Diffusion of chains across boundaries then took place (depending on shear and temperature) finally forming a continuous molecular network of entanglements, with crystallites reforming on cooling. Menges et al.\(^{(78)}\) found a similar situation with the material passing through four stages of plasticisation with increasing temperature. He found powder grains to be the units of flow up to 160°C, these then broke open, depending on shear rate, and primary particles became the units of flow, which in turn melted above 190°C.

Krzewki and Collins\(^{(82)}\), and Sieglaff\(^{(81)}\), further suggested that shear was an important component in the breakdown of the original grains, and proposed three possible routes depending on temperature, pressure and shear conditions, Figure 1.7.
The second mechanism introduced a totally different process involving the compaction, densification, fusion and elongation of the grains - the CDFE mechanism. It proposed that the material is heated and compressed, the mechanism then involves the elimination of free space between the PVC resin grains. This is followed by elimination of free space between the primary particle agglomerates and finally between the primary particles themselves. Interparticle fusion
initiates as the melt temperature increases, and finally as the amount of shear stress increases the primary particles undergo an elongation in the direction of applied shear.) In this process Allsopp (66) saw little, if any, comminution of the PVC grains taking place. He argued that authors working on high shear aggressive mixing equipment (of which most supporting the first mechanism were), such as the Brabender Plastograph and the laboratory scale Banbury mixer, could not compare their results to the mechanism operating in low shear twin screw extruders. He found quite high fusion at the ends of the screws, with both grain boundaries and shear still very much in evidence. As the material advanced through the adaptor and head region towards the die elongation gradually encompassed all the grains, but it was only as the material left the die that most grain memory was removed. He proposed that the behaviour of different machines was related to the temperature, pressure and shear profile of that machine. If pressure/shear is applied before densification is complete (as in Brabender Plastograph) grain comminution results; but in less aggressive conditions grain densification is complete before shear forces can be applied.

Allsopp's (66) CDFE model has since been supported by many authors (56, 87). Marshall et al. (83) found the presence of the original grain structure, albeit deformed, in the final extrudate; whilst Gilbert et al. (84) confirmed that in twin screw extrusion the main route for fusion was through the deformation of grains by low shear. They also extended
Allsopp's\textsuperscript{(66)} theory by postulating a melting and recrystallisation process, leading to a network formation of molecules linked by small or imperfect crystallites formed during the cooling that follows extrusion, Figure 1.8.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.8.png}
\caption{Fusion mechanism\textsuperscript{(85)}}
\end{figure}

Covas et al.\textsuperscript{(85)} also confirmed the CDFE mechanism with the grains initially being compacted aiding heat transfer as their initial porosity is eliminated. The grains near the barrel wall are eventually subjected to shear and elongation and break open, and a melt is progressively formed.

A third mechanism proposed by Summers\textsuperscript{(86)} places more emphasis on the molecular interdiffusion process. He assumes that primary particles are the units of flow, and that for a
given combination of processing temperature and shear rate the level of fusion is determined by the state of interdiffusion of molecules across the primary particles, Figure 1.9.

(a) Primary particles in a low temperature melt

(b) Primary particles in a higher temperature melt

(c) Primary particles after cooling and recrystallisation

Figure 1.9

Schematic illustration of the molecular diffusion fusion mechanism(86)
It seems therefore a common idea that a final three dimensional recrystalline network results from processing\(^{(88)}\); whilst observations of highly elongated particles\(^{(89)}\), and the known fact that particle memory is preserved, lend strong support for the CDFE mechanism in twin screw extruders.

1.6 Assessment of Fusion Level

It is clear that the level of fusion has a profound effect on the properties of rigid PVC, and therefore several tests have been developed to quantify this value, all of which are well documented in literature\(^{(90)}\). Thus for the purpose of this introduction, only tests relevant to this project shall be reviewed.

1.6.1 Solvent Testing

Immersion of processed PVC in a fairly compatible solvent (e.g. acetone or methylene chloride) will cause swelling due to absorption or diffusion of the solvent. Where a fusion network exists the solvent will have little effect on the cohesion of the sample. However, in unfused areas sufficient swelling will dislodge particles and cause disintegration\(^{(62)}\). This test will therefore successfully identify poorly fused products, but difficulties arise in distinguishing between materials with a greater than 70% fusion level, as particles become protected from physical separation by the presence of unfused material.
Although not suitable for accurate measurement of fusion levels the method is useful in giving a general impression of fusion and, due to its simplicity, has become a common quality control test for PVC pipe.

1.6.2 **Microscopy Methods**

A variety of optical methods may be used to assess the state of fusion. Common light microscopy allows a resolution down to around 0.5μm, and therefore permits fusion to be examined at both the grain and primary particle levels of morphology. To increase the magnification and examine the morphology of microdomains scanning electron microscopy is popular despite its limitations in that specimen preparation is difficult, and only a limited area of specimen can be observed. These techniques alone, however, are incapable of permitting a detailed assessment of fusion level.

For a more precise study of fusion a technique known as differential interference contrast (DIC) may be employed\(^{(84, 91)}\). This works on the basis that total fusion would imply uniform density and hence refractive index (assuming constant section thickness). Thus the magnitude and extent of fluctuations in the refractive index of a sample would indicate the degree of fusion. Interpretation of the resultant images can be complicated if additives are present of similar particle size to primary particles. This problem is unimportant if comparisons are kept to different samples of the same compound.
A further microscopical technique developed by Summers and Rabinovitch (92) makes use of the effect of acetone on PVC. Small samples of processed material are immersed in acetone for a period of time and then sheared between a microscope slide and coverslip and examined under a light microscope. The sensitivity of this technique has since been improved using transmitted light dark field microscopy (84). Image contrast and visibility of particles is controlled by the refractive index difference between the swollen polymer and the acetone. The degree of fusion, particular of primary particles, is clearly visible.

1.6.3 Thermal Analysis

The existence of several characteristic peaks obtainable through Differential Scanning Calorimetry (DSC) of PVC has been known for some time (96), and investigated by several authors (97-102). A typical trace is shown in Figure 1.10.

The first endothermal peak occurs below the glass transition temperature ($T_g$), and has been attributed to enthalpy relaxation. The size and position of this peak can be altered by quenching and annealing the sample, such that with increasing time and temperature of annealing (below $T_g$) the endotherm increases in magnitude and shifts to a higher temperature. If the annealing temperature ($T_e$) approaches $T_g$ the endotherm is superimposed on the $T_g$ step and appears as a 'T$_g$ overshoot,' (98). There are three other obvious features
Figure 1.10
Schematic DSC trace of PVC over the temperature range 20-240°C

in the trace. An endothermic baseline shift corresponding to the glass transition temperature of the polymer at 70-80°C. A broad peak 'B', between 100-230°C, which represents the melting of crystallites of various sizes and degrees of perfection. This peak decreases in size and shifts to higher temperatures as the processing temperature increases, producing an endotherm 'A', which appears and increases in size. The endotherm 'B' is present in unprocessed PVC. The onset of degradation, 'D', depends on the stabiliser system used.

Many authors\cite{97,100,122} have studied the effects of annealing both below\cite{98} and above $T_g$. Gilbert and Vyvoda\cite{102} carried out thermal analysis on components processed in a Brabender Plastograph, a twin screw extruder,
or compression moulded over a range of temperatures. The results they obtained were similar to those obtained by Illers (97) and Otha (100) who had studied annealing PVC above $T_g$. They found that during processing $T_g$ remained the same, but the size and position of endotherms 'A' and 'B' changed which they explained in the following way. At any given processing temperature lower melting crystallites melt while higher melting crystallites are annealed (improving their state of order) so that their melting temperature increases. If the processing temperature is taken above approximately 160°C there is enough melted material present to recrystallise on cooling. Thus on subsequent heating in a DSC cell two endotherms appear ('A' and 'B'), 'A' relating to the original melted material, and 'B' to the annealed material. Figure 1.11 and 1.12.
Figure 1.11
DSC thermograms of compression moulded samples at various temperatures \(^{(100)}\)

Figure 1.12
DSC of a suspension PVC sample cooled at \(20^\circ\text{C/min}\) from \(240^\circ\text{C}\) and annealed for 5 min. at the indicated temperatures \(^{(97)}\)
Gilbert and Vyvoda (102) also found that the endothermal energy corresponding to the 'A' endotherm varied with processing temperature in the same fashion as the entrance pressure loss in capillary rheometry, and if plotted against processing temperature produced a similar S-shaped curve. Based on these findings thermal analysis became a method of evaluating PVC fusion level.

These authors also showed that the onset of the 'B' endotherm gave an accurate measure of the actual processing temperature experienced by the material, as shown in Figure 1.13.

![Figure 1.13](image)

'B' onset temperature versus extrusion temperature (84)

Advantages of this method include the small size of the necessary sample which allows for several measurements along a thick section, but can also create problems in obtaining a representative measurement.
1.7 Fusion Characteristics

The use of rheological methods to assess the degree of fusion of PVC was first developed by Gonze(93) and Lamberty(94), and later reported by several authors. Both capillary and Brabender torque rheometry(133) are now widely used techniques capable of quantifying the process of fusion and the effects of additives on fusion(42,45,46,52).

1.7.1 Capillary Rheometry

The rheological measurement of the elastic pressure in a short capillary (small length/diameter ratio) at low temperature can provide a measurable fusion level. For a capillary with diameter D and length L the entrance pressure loss, $\Delta P$, can be expressed as:

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

where

- $\tau$ - shear stress at capillary wall
- $n$ - viscous loss term
- $S_R$ - recoverable shear strain

This equation can be simplified to:

$$\Delta P = \Delta P_{ENT} + \Delta P_{VISC}$$

where $\Delta P_{ENT}$ - pressure loss due to entrance effects
$\Delta P_{VISC}$ - viscous pressure loss
Thus if a die with a low L/D is used the second term in the equation \( \Delta P_{\text{VISC}} \) becomes insignificant and pressure loss due to entrance \( \Delta P_{\text{ENT}} \) effects predominate.

The pressure loss due to entrance effects can itself be divided into two parts:

\[
\Delta P_{\text{ENT}} = \Delta P_{\text{ent}} + \Delta P_{\text{visc}}
\]

where

\( \Delta P_{\text{visc}} \) - viscous entrance pressure drop
\( \Delta P_{\text{ent}} \) - elastic entrance pressure drop

Han(125) has shown that the viscous component is only 10% of the total pressure drop and so for practical purposes the variations in entrance pressure loss can be attributed primarily to the changes in the elasticity of the material under test.

As the pressure loss does not give an absolute value of fusion a standard fusion curve must be produced from which percentage fusion results can be calculated in the following manner:

\[
\% \text{ fusion} = \frac{P - P_{\text{MIN}}}{P_{\text{MAX}} - P_{\text{MIN}}} \times 100
\]

where

\( P \) - pressure required to extrude sample
\( P_{\text{MIN}} \) - minimum pressure corresponding to least fused sample
\( P_{\text{MAX}} \) - maximum pressure corresponding to most fused sample
A typical standard fusion curve of capillary pressure versus processing temperature is shown in Figure 1.14. It has a distinctive 'S' shape which indicates the grains breaking down followed by the gradual formation of a molecular network.

![Capillary fusion curve](image)

Figure 1.14
Capillary fusion curve

1.7.2 **Brabender Torque Rheometry**

The Brabender is a heated bench internal mixer which subjects the sample to a dynamic test under conditions similar to that found in production equipment (it should be noted that the shear experienced in a Brabender is higher than that in a twin screw extruder). The PVC compound is
placed in the mixing chamber as a dry powder blend, and the combined influence of temperature and shear, and other less apparent factors such as internal friction and slip, are measured and recorded over a period of time. The most usual mode of operation is to maintain a constant mixing chamber temperature and constant weight of blend, thus obtaining typical curves plotting torque against time for each material. The curves are an indication of the viscosity of the material being tested. A typical trace is shown in Figure 1.15.

Figure 1.15
Illustration of a typical Brabender trace
Initially the material is compacted in the mixing chamber causing high internal torques which rapidly decrease as the grains are compacted. This compaction torque level continues as frictional and transferred heat is generated, until the material temperature reaches a point where fusion begins. The time between the two maxima is known as the 'total fusion time' and is useful in forecasting the likely processing behaviour of different formulations. The torque then drops as the PVC becomes a melt, eventually levelling off until degradation begins.

It is generally found with different blends that as torque levels increase fusion times decrease. This can be explained simply by considering the effects of lubricants, although other additives may have a similar effect. As lubricant efficiency decreases, slippage is reduced which gives a rise in torque. This then generates more frictional heat which in turn reduces fusion time. Conversely, excessive lubrication by the same path reduces torque, thus generating less frictional heat, and increasing fusion time.

Several authors have reported using the Brabender Plastograph with mixing chambers which were programmed at a steadily increasing temperature. From this one can obtain a trace of the whole spectrum of behaviour of the mix as it is influenced by heat and shear. Faulkner(143) continued this work with microscopic techniques to examine the state of the compound at various stages of mastication. From this he developed a model of particle breakdown as fusion proceeds in
the Brabender. The use of the Brabender torque rheometer in this way is rare\(^{(95)}\), as temperature programmable devices for the mixing head are required along with much longer cycle times.

1.8 Mechanical Properties of Polyvinyl Chloride

1.8.1 Influence of Processing Conditions/Fusion on Properties

The fusion process occurring during the extrusion of rigid PVC pipe determines the morphological structure of the end product, and therefore, in turn, affects the short and long term properties of the pipe\(^{(118)}\). There are three basic properties by which the quality of the product can be characterised, these are:

1. stiffness - resistance to elastic deformation under applied stress
2. strength - resistance to plastic deformation and failure under applied stress
3. ductility - the amount of energy that can be absorbed before failure occurs

The relationship between these properties and the fusion level has long been an area for debate. Benjamin\(^{(77)}\) conjectured that at low fusion levels all these properties would be poor, however, as the fusion level increases stiffness and strength would increase whilst ductility would
reach an optimum level, and on further fusion would deteriorate, Figure 1.16.

![Graph showing the influence of gelation level on physical properties of uPVC pipe](image)

**Figure 1.16**

Influence of the gelation level on the basic properties of uPVC pipe (77)

To assess these mechanical properties a series of tests have been developed from which, in particular, stiffness can be determined from elastic modulus; strength from such properties as tensile yield strength and resistance to internal water pressure; and ductility from elongation to
break, resistance to impact, tensile impact energy, and resistance to crack formation. For the purposes of this study two tests were investigated - tensile testing and impact testing.

1.8.2 Tensile Testing

Tensile yield stress is normally clearly defined and is a consistent reproducible property of the material, at any given loading rate or temperature. Views on the dependence of yield parameters on processing conditions, and therefore fusion are, however, varied.

Observations made by Pezzin et al., for rigid PVC sheets milled at different temperatures, and Uitenham and Geil, for rigid PVC specimens from the walls of pipes extruded at different temperatures, indicated that both yield parameters (yield stress and yield strain) were independent of fusion level. Terselius and Jansson found similar insensitivity for test specimens cut from PVC pipes extruded at varying mass temperatures to yield parameters, over a wide range of drawing rates and temperatures. They concluded that since an increase in fusion level is associated with an increase in strength and coherence of the entanglement network, yielding must involve molecular rearrangements between entanglements and network junctions. This then limited the size of possible flow units at yield to the size of entanglement spacings.
Gilbert and Ansari (105), on the other hand, studying compression moulded samples found yield stress to increase with processing temperature, levelling off at higher temperatures. Benjamin (77) found tensile yield strength to show a gradual increase with increasing fusion level, reaching a maximum between 68% and 90% fusion and thereafter remaining constant.

Covas (124) studied the tensile properties of pipe specimens at various temperatures (from room temperature to 150°C) and test speeds. He found yield parameters to be insensitive to variations in the degree of gelation with yield strain increasing with increasing test temperature, and yield stress with increasing crosshead speed. From this he conjectured that yield must be related to the molecular relaxation process, as it was independent of both the relative coherence of the entanglement network and the number of crystalline junctions.

The reports on post yield deformation are more consistent, with several authors seeing a very clear effect of processing on stress and strain at break (79, 104, 106). Berens and Folt (75), Pezzin et al. (103), Chartoff (9), and Uitenham and Geil (79) all experienced ultimate strain increasing with processing temperature. Terselius (104) suggested this may be due to the increased ability of the material to cold draw with increased fusion. This he owed to the development of a load-bearing network of entanglements.
and crystallites. Berndtsen(111), however, found a maximum in the ultimate strain at a certain processing temperature.

Benjamin(77) studied the effect of fusion on elongation to break and discovered an optimum value at 44% fusion after which it decreased. Menges et al.(78) observed a similar maximum at a processing temperature of 185°C, this corresponded to the highest temperature which could be attained without causing destruction to the primary particle structure, which took place around 190°C.

In post-yield parameter studies Covas(124) found both elongation and stress at break to be sensitive to variations in fusion level. For test temperatures below $T_g$ both parameters reached a maximum for fusion levels between 65% and 85% corresponding to processing temperatures in the range 193-203°C. This observation, he believed, was due to the primary particle structure being progressively destroyed in this temperature range disappearing above 205°C. The maximums observed can thus be attributed to the existence of a network morphology. For test temperatures above $T_g$ Covas observed a continuous increase in elongation and stress at break with increasing fusion level. He found stress-strain curves to be superimposable, the only difference being the point where rupture occurred. For test temperatures around $T_g$ (approximately 90°C) the test specimens exhibited their highest elongation to break values, this supported work by Terselius(104). Covas explained this by the fact that for test temperatures above $T_g$ low melting primary crystallites
begin to be destroyed, creating easier disentanglement and resulting in a decrease in elongation at break. This crystalline melting will increase with higher temperature.

Similarly at elevated test temperatures (100±10°C) Terselius (104) found elongation at break to be very sensitive to fusion level in a linear manner, thus supporting proposals for the tensile test at 100°C as a potential alternative method for assessing fusion levels of rigid PVC pipe.

1.8.3 Instrumented Falling Weight Impact Testing

Traditional test methods such as Charpy and Izod have long been carried out on standard specimens machined from the product to be tested. This has several disadvantages not only in that machining the specimens from the pipe wall can influence the test result strongly, but also that the influence of the original pipe dimensions and the effects of extrusion can be diminished considerably.

Using an Instrumented Falling Weight Test (IFWT) evaluations can be made on actual pipe samples so that all the factors influencing quality are included (117,144). The impact strength of a material is a complex mechanical property reflecting the absorption of impact energy during different processes preceding break of the specimen. These processes include viscoelastic deformation, yielding, voiding, crazing and finally formation and propagation of true cracks leading to break. Using IFWT one test can give all the information about absorbed elastic energy, the energy
to failure, deformation and maximum force during the test. This test method requires therefore only a few samples to give a complete picture of the pipe material. Figure 1.17 shows a typical force-distance curve obtained.

![Typical force-distance curve](image)

**Figure 1.17**

Typical force-distance curve

At the first contact of the impactor with the pipe the sample shows an elastic deformation. The resultant gradient in the force-distance curve indicates the resistance of the sample to elastic deformation, and is a parameter representing stiffness. At a given moment this elastic deformation will change to a plastic deformation, the absorbed energy up to this point gives a value of the strength of the material. During plastic deformation a maximum in the force development will be reached, the force...
will then diminish until the sample fails. The total deformation and energy to failure gives an indication of the ductility of the material; whilst the maximum force, which is the highest force level that has acted on the sample during the test, is a parameter for the strength.

Failure of the sample can take place anywhere in this process depending on the quality of the pipe, with certain failure modes defined below, Figures 1.18 - 1.20.

**Figure 1.18**

Brittle failure - takes place after elastic deformation only
Figure 1.19
Failure takes place within the plastic deformation zone. Brittle-ductile when failure occurs before the maximum force has been reached, ductile-brittle when the maximum force level has been exceeded.

Figure 1.20
Ductile puncture - when maximum stress and strain capacities have been exceeded before failure occurs, this is a true ductile failure.
The effects of processing on the impact strength of PVC has been extensively studied, although comparing results proves difficult due to the variety of types of test and the preparation of specimens. It is generally agreed that impact strength improves with increasing fusion, but disagreements arise over the possible existence of a maximum.

An increase of tensile impact strength with extrusion temperature of both notched and unnotched samples was reported by Berens and Folt\(^{(75)}\) and Gonze\(^{(93)}\); of Charpy unnotched impact strength with extrusion temperature by Berndtsen\(^{(111)}\); of Izod notched impact strength with rolling mill temperature by Rabinovitch et al.\(^{(109)}\); and of falling weight impact strength with extrusion temperature by Lamberty\(^{(94)}\), Rabinovitch et al.\(^{(109)}\) and Summers et al.\(^{(110)}\). A decrease in notched impact strength with rolling mill temperature was observed by Gross et al.\(^{(116)}\).

In recent years, however, a distinct maximum in impact strength has been observed by many authors\(^{(78,106)}\). Bystedt\(^{(114,115)}\) has frequently observed a maximum in falling weight impact strengths of extruded PVC pipes at moderate fusion levels, adjusted by the amount of lubricant in the compound. Benjamin\(^{(77)}\) also observed a maximum of a similar kind in tensile impact strength at moderate fusion levels (extrusion temperatures).

More recently work by Covas\(^{(124)}\) on Izod tested notched extruded specimens has shown a maximum in impact strength in the fusion level range 60-70%. Covas concluded that as the
impact strength is defined by the ductility of the specimen the results obtained should be qualitatively similar to those observed in tensile testing for elongation at break. He thus attributed the maximum in impact strength to the existence of a network morphology with residual primary particles, the disappearance of these causing a drop in impact strength.

Summers et al. (110) observed a loss in dropped dart impact strength at high extrusion temperatures. However, because the loss was accompanied by an increased surface roughness of the high temperature extruded strip, and since the impact strength was regained after 'press polishing' of these strips, he assumed the loss in impact strength to be due to lubrication failure and melt fracture. Terselius et al. (113) checked this roughness effect and machined off the somewhat rougher inside surface of their pipe specimens. This they found did increase the impact strength, possibly due to a thickness effect. However, a distinct maximum was still obtained at 190°C mass temperature. They could detect no thermal degradation of the pipes, and concluded that the most efficient resistance to crack initiation is found in pipes of moderate fusion level, which they attributed to the existence of an 'interparticular coherent entanglement network' enhancing post-yield deformation.

1.9 Project Objectives

Over a number of years a great deal of work has been carried out at the Institute of Polymer Technology and
Materials Engineering in the area of structure/property/process relationships for PVC compounds. The work has resulted in a large number of characterisation techniques being established to examine both the structure and the properties.

This work seeks to investigate the particular influence of calcium carbonate filler, its particle size and distribution and coating on the processing behaviour and subsequent properties of rigid PVC. The research programme was therefore carried out in three parallel studies:

1a. Initially to incorporate 15 phr of various calcium carbonate fillers into a base composition, similar to that used for general pipes and fittings, and to monitor the dry blend using appropriate techniques,

1b. to extrude the filled blends at a standard extrusion temperature and monitor their fusion behaviour during processing,

1c. to evaluate the mechanical properties of the final pipe extrudate, particularly the impact performance and the ultimate tensile strength.

2. The coating of fillers with lubricants is commonly undertaken and it is known that the coating significantly affects the processing of PVC compounds. A study of the effect of level of coating on processing characteristics and subsequent properties was therefore undertaken.
3. Further studies examined one filler more closely looking at the effects of a wide range of stearic coatings on processing and end product properties, in a similar way as before.

Any inter-relationships between processing, structure and properties, and the effect on these by the incorporation of fillers and coatings were analysed.
EXPERIMENTAL TECHNIQUES

2.1 Materials

2.1.1 Polyvinyl Chloride

A commercial grade suspension PVC homopolymer supplied by ICI plc, was used throughout this study. This particular resin is ideal for the extrusion of profiles, especially those of a rigid nature. The technical reference for the grade is CORVIC S68/173 and its specifications are given in Table 2.1.

Table 2.1

<table>
<thead>
<tr>
<th>Typical properties of Corvic S68/173</th>
</tr>
</thead>
<tbody>
<tr>
<td>'K' Value (0.5% in cyclohexanone)</td>
</tr>
<tr>
<td>Viscosity No. (ISO Method R174:1974)</td>
</tr>
<tr>
<td>Apparent Density (g/ml)</td>
</tr>
<tr>
<td>Packing Density (g/ml)</td>
</tr>
<tr>
<td>Volatile Content (wt%)</td>
</tr>
<tr>
<td>Passing 250μm (wt%)</td>
</tr>
<tr>
<td>Passing 75μm (wt%)</td>
</tr>
</tbody>
</table>
2.1.2 Calcium Carbonate Fillers

The choice of fillers and coating levels used in this study has been dealt with in detail in Chapter 3, suffice to say that five natural calcium carbonate fillers were chosen with varying particle sizes. These were incorporated into the formulation in three series, either:

1. uncoated
2. coated with 1% stearic acid by weight
3. coated with a constant monolayer fraction of stearic acid

One of the grades (with technical reference Polcarb) was also coated with stearic acid over a range of 3% to 0.3%.

2.1.3 Other Additives

Other additives used include tribasic lead sulphate (TBLS), a stabiliser; normal lead stearate (NLS), a stabiliser and external lubricant; calcium stearate, an internal lubricant; and a hard wax (Sasolwaks H1), an external lubricant. Technical data on these additives are presented in Table 2.2.
Experimental 62

Table 2.2

<table>
<thead>
<tr>
<th>Additive</th>
<th>Form/colour</th>
<th>Specific gravity</th>
<th>Melting point °C</th>
<th>Lead content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tribasic lead sulphate</td>
<td>Powder</td>
<td>6.3</td>
<td>-</td>
<td>83.4</td>
</tr>
<tr>
<td>3PbO·PbSO₄·H₂O</td>
<td>white</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Normal lead stearate</td>
<td>Powder</td>
<td>1.4</td>
<td>104</td>
<td>28</td>
</tr>
<tr>
<td>Pb(C₁₇H₃₅CO₂)₂</td>
<td>white</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>Powder</td>
<td>1.05</td>
<td>121</td>
<td>-</td>
</tr>
<tr>
<td>Ca(C₁₇H₃₅CO₂)₂</td>
<td>white</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sasolwaks HI</td>
<td>Powder</td>
<td>0.94</td>
<td>94.5</td>
<td>-</td>
</tr>
</tbody>
</table>

TBLS, NLS and calcium stearate were supplied by Akzo Chemicals (UK) Limited\(^{(128)}\), Sasolwaks HI by Dussek Cambell Limited\(^{(129)}\).

2.2 Sample Preparation

2.2.1 Formulation

In order to limit the number of parameters affecting the fusion and to see more clearly filler effects,
the same simple formulation was used throughout this study regardless of filler type or coating level. This formulation is shown in Table 2.3.

Table 2.3

<table>
<thead>
<tr>
<th>Formulation</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corvic S68/173</td>
<td>100</td>
</tr>
<tr>
<td>TBLS</td>
<td>2.0</td>
</tr>
<tr>
<td>NLS</td>
<td>1.2</td>
</tr>
<tr>
<td>Calcium Stearate</td>
<td>0.4</td>
</tr>
<tr>
<td>Sasolwaks H1</td>
<td>0.1</td>
</tr>
<tr>
<td>Filler</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Each filler was dry blended into this formulation at each coating level giving three full ranges and one Polcarb range. With each range a standard formulation containing no filler was prepared. The blends were referred to by the following codes, Table 2.4.

Table 2.4

<table>
<thead>
<tr>
<th>Filler Coding</th>
<th>Filler Grade</th>
<th>Coating Level</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>no filler</td>
<td>-</td>
<td></td>
<td>N/F</td>
</tr>
<tr>
<td>Carbital 90</td>
<td>0%</td>
<td></td>
<td>C90</td>
</tr>
<tr>
<td>Polcarb</td>
<td>0%</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>Polcarb 60</td>
<td>0%</td>
<td></td>
<td>P60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>Queensfil 300</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Queensfil 20</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>no filler</td>
<td>-</td>
<td></td>
<td>N/F</td>
</tr>
<tr>
<td>Carbital 90</td>
<td>1%</td>
<td></td>
<td>1C90</td>
</tr>
<tr>
<td>Polcarb</td>
<td>1%</td>
<td></td>
<td>1P</td>
</tr>
<tr>
<td>Polcarb 60</td>
<td>1%</td>
<td></td>
<td>1P60</td>
</tr>
<tr>
<td>Queensfil 300</td>
<td>1%</td>
<td></td>
<td>1Q300</td>
</tr>
<tr>
<td>Queensfil 20</td>
<td>1%</td>
<td></td>
<td>1Q20</td>
</tr>
<tr>
<td>no filler</td>
<td>-</td>
<td></td>
<td>N/F</td>
</tr>
<tr>
<td>Carbital 90</td>
<td>1.90%</td>
<td></td>
<td>MC90</td>
</tr>
<tr>
<td>Polcarb</td>
<td>0.84%</td>
<td></td>
<td>MP</td>
</tr>
<tr>
<td>Polcarb 60</td>
<td>0.57%</td>
<td></td>
<td>MP60</td>
</tr>
<tr>
<td>Queensfil 300</td>
<td>0.43%</td>
<td></td>
<td>MQ300</td>
</tr>
<tr>
<td>Queensfil 20</td>
<td>0.38%</td>
<td></td>
<td>MQ20</td>
</tr>
<tr>
<td>Polcarb</td>
<td>0%</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>Polcarb</td>
<td>0.3%</td>
<td></td>
<td>0.3P</td>
</tr>
<tr>
<td>Polcarb</td>
<td>0.5%</td>
<td></td>
<td>0.5P</td>
</tr>
<tr>
<td>Polcarb</td>
<td>0.84%</td>
<td></td>
<td>0.84P</td>
</tr>
<tr>
<td>Polcarb</td>
<td>1%</td>
<td></td>
<td>1P</td>
</tr>
<tr>
<td>Polcarb</td>
<td>2%</td>
<td></td>
<td>2P</td>
</tr>
<tr>
<td>Polcarb</td>
<td>3%</td>
<td></td>
<td>3P</td>
</tr>
</tbody>
</table>
2.2.2 Dry Blending

Two high speed mixers were used during the course of this research; an 8 litre T.K. Fielder high speed mixer at IPTME, and a 40 litre Henschel high speed mixer at Cookson Central Research Laboratories. The general construction and principles of the two machines are the same, and have been discussed in Section 1.4.1, so only a schematic diagram of one, the Fielder, is shown in Figure 2.1.

Due to the dissimilar mixer sizes different charge weights were required for each machine, as shown in Table 2.5. These were thoroughly hand mixed and placed in the upper chamber of the mixer, which had already been preheated with a waste blend. Mixing took place at a predetermined set blade speed until the blend reached 120°C. The blend was then discharged through a pneumatic valve into a lower speed cooler mixer. From here the blend was discharged into a container; several hundred kilograms of dry blend were prepared in this way.

Blending conditions for each mixer are given in Table 2.6.
## Table 2.5

### 40 litre Henschel

<table>
<thead>
<tr>
<th></th>
<th>phr</th>
<th>charge weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corvic S68/173</td>
<td>100</td>
<td>10000</td>
</tr>
<tr>
<td>TBLS</td>
<td>2.0</td>
<td>200</td>
</tr>
<tr>
<td>NLS</td>
<td>1.2</td>
<td>120</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>0.4</td>
<td>40</td>
</tr>
<tr>
<td>Sasol HI</td>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>Filler</td>
<td>15.0</td>
<td>1500</td>
</tr>
</tbody>
</table>

Total charge weight = 11870g

### 8 litre Fielder

<table>
<thead>
<tr>
<th></th>
<th>phr</th>
<th>charge weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corvic S68/173</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>TBLS</td>
<td>2.0</td>
<td>20</td>
</tr>
<tr>
<td>NLS</td>
<td>1.2</td>
<td>12</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>0.4</td>
<td>4</td>
</tr>
<tr>
<td>Sasol HI</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Filler</td>
<td>15.0</td>
<td>150</td>
</tr>
</tbody>
</table>

Total charge weight = 1187g
### Table 2.6

**Blending conditions in Henschel**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Stage</th>
<th>Mixing</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jacket temp (°C)</td>
<td>50</td>
<td></td>
<td>ambient</td>
</tr>
<tr>
<td>Dwell time (min)</td>
<td>8 ± 3</td>
<td></td>
<td>5 ± 2</td>
</tr>
<tr>
<td>Rotor speed (rpm)</td>
<td>1500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge temp (°C)</td>
<td>120</td>
<td></td>
<td>30 ± 2</td>
</tr>
</tbody>
</table>

**Blending Conditions in Fielder**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Stage</th>
<th>Mixing</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jacket temp (°C)</td>
<td>50</td>
<td></td>
<td>ambient</td>
</tr>
<tr>
<td>Dwell time (min)</td>
<td>18 ± 3</td>
<td></td>
<td>5 ± 2</td>
</tr>
<tr>
<td>Rotor speed (rpm)</td>
<td>3000</td>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>Discharge temp (°C)</td>
<td>120</td>
<td></td>
<td>30 ± 2</td>
</tr>
</tbody>
</table>

The uncoated and 1% coated filler formulations were blended in the 40 litre Henschel, while the constant monolayer fraction coated fillers and the coated Polcarb series were blended in the 8 litre Fielder.

Five blends N/F, P, Q20, IP, IQ20 were run on both the Fielder and the Henschel so that a comparison could be made between mixers.
2.2.3 Milling

As recommended in BS 2782: Part 9 Method 901A: 1977, milled sheet was produced for the purpose of compression moulding (Section 2.2.4). The milling process proved necessary as compression mouldings of dryblended powders gave inadequate fusing of the PVC material. During milling minimum temperatures and times were chosen, through a series of trial and error experiments, such that a continuous sheet was formed with stabilisers absorbed into the PVC.

Milling conditions used are listed below:

- temperature: 166 °C
- time: 7 min
A two-roll mill was set at 166°C and fed with 300g of dry blend, producing a sheet approximately 1mm thick.

2.2.4 Compression Moulding

Flat sheets, 60mm x 70mm x 1mm, were compression moulded from the milled powder blends at temperatures ranging from 170 to 215°C. A 40 ton manually operated platen with electric heating and water cooling systems was used, to BS 2782: Part 9 Method 901A: 1977.

The processing conditions used are listed below:

- moulding temperature: 170 - 215°C
- preheating time: 15 min
- moulding time: 5 min
- moulding pressure: 2 ton
- cooling time: 5 min
- cooling pressure: 20 ton

Blends containing no filler and uncoated Carbital 90 filler were milled and compression moulded in this way.

2.2.5 Twin Screw Extrusion

The extrusion programme was carried out on two laboratory intermeshing counter-rotating twin screw extruders.

The Krauss-Maffei KMDL 25, at Cookson Central Research Laboratories, Perivale. This contained conical screws of diameter 50mm (at feed) and 25mm (at tip) and length 400mm.
Experimental 70

It was fitted with a pipe die producing pipe of external diameter 32mm and wall thickness 1mm.

The Göttfert, at Norsk Hydro Polymers, Newton Aycliffe fitted with screws of diameter 35mm and length 525mm, and with a pipe die producing pipe of external diameter 25.6mm and wall thickness 2mm.

Because of the small size of the laboratory extruders steady state operation was rapidly reached, and measurements could usually be taken after approximately 15 minutes. On either machine a single evaluation took only about 30 minutes and used about 7kg of blend. With each set of extrusions a control blend containing no filler was evaluated; this was considered necessary, not only because of the comparative nature of the study, but also to ensure that the instrumentation was functioning correctly.

In order to assess the processing characteristics of the dry blend being tested each extruder was equipped to measure melt pressure and temperature at several points along its barrel. The screw torque experienced during the processing operation was measured continuously, and the output once steady state had been achieved. Figures 2.2. and 2.3 depict the screw configurations, along with temperature/pressure zones and monitoring positions for the Krauss-Maffei and Göttfert respectively.

As can be seen from Figure 2.2, the Krauss-Maffei extruder was fed with a horizontal variable speed dosing screw which allowed the extruder to be flood fed at all
Experimental 71

times. In the case of the Göttfert the blend was loaded directly (by way of a stuff-feeder) on to the screws. Sizing in both cases was made in a water cooling/vacuum sizing bath (although a vacuum proved unnecessary in the case of the Göttfert).

The blends containing filler with no coating and a 1% coating level were run on the Krauss-Maffei, while the constant monolayer fraction covered filler blends and the coated Polcarb series were extruded on the Göttfert. The five blends (N/F, P, Q20, 1P and 1Q20) which were dry blended in both mixers were also processed on both extruders for comparison. Standard pipe extrusion conditions were chosen in each case, and these are given in Tables 2.7 and 2.8.

Table 2.7

Extrusion conditions on the Krauss-Maffei

<table>
<thead>
<tr>
<th>Location</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>rear barrel</td>
<td>180°C</td>
</tr>
<tr>
<td>front barrel</td>
<td>190°C</td>
</tr>
<tr>
<td>head</td>
<td>185°C</td>
</tr>
<tr>
<td>die</td>
<td>190°C</td>
</tr>
<tr>
<td>screw oil</td>
<td>120°C</td>
</tr>
<tr>
<td>main screw speed</td>
<td>15rpm</td>
</tr>
</tbody>
</table>
Table 2.8

Extrusion conditions on the Göttfert

set temperatures

<table>
<thead>
<tr>
<th>zone</th>
<th>temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>175</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
</tr>
<tr>
<td>4</td>
<td>185</td>
</tr>
<tr>
<td>5</td>
<td>185</td>
</tr>
<tr>
<td>6</td>
<td>190</td>
</tr>
</tbody>
</table>

screw speed 20rpm

Two complete processing temperature ranges, of blends containing uncoated Carbital 90 filler and 1% coated Carbital 90 filler, were also run on the Krauss-Maffei. The extrusion temperature ranges used are given in Table 2.9.

Table 2.9

Extrusion conditions for complete temperature range runs

<table>
<thead>
<tr>
<th>code</th>
<th>rear barrel (°C)</th>
<th>front barrel (°C)</th>
<th>head (°C)</th>
<th>die (°C)</th>
<th>screw oil (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>150</td>
</tr>
<tr>
<td>B</td>
<td>165</td>
<td>165</td>
<td>170</td>
<td>170</td>
<td>150</td>
</tr>
<tr>
<td>C</td>
<td>165</td>
<td>165</td>
<td>180</td>
<td>180</td>
<td>150</td>
</tr>
<tr>
<td>D</td>
<td>180</td>
<td>180</td>
<td>190</td>
<td>190</td>
<td>150</td>
</tr>
<tr>
<td>E</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>F</td>
<td>210</td>
<td>210</td>
<td>210</td>
<td>210</td>
<td>150</td>
</tr>
</tbody>
</table>

The screw speed was kept constant throughout at 15 rpm.
Figure 2.2 (a) Screw design Krauss-Maffei

Figure 2.2 (b) Instrumentation Krauss-Maffei

Figure 2.3 (a) Screw design Göttfert

Figure 2.3 (b) Instrumentation Göttfert
2.3 Characterisation of Dry Blend

2.3.1 Density Measurements

The bulk densities of PVC powder blends have been shown, by several workers, to be significantly affected by blending conditions and equipment. During twin screw extrusion, especially, density changes have a major effect on fusion and output rates, so to form a complete picture density measurements must be taken.

In this study bulk (tap) density measurements were made in accordance with BS 2782 :Part 6 :Method 6210 :1978 which involved weighing 100gm of powder into a measuring cylinder. This was then placed in a tap-pack volumeter and repeatedly tapped (at a rate of one drop per 2 seconds) until a constant volume was achieved. The tap density was obtained from the weight of powder per unit volume. Thus tap density depends on the closeness of the packing of the particles of which the powders are composed, and depends on the size and the shape of the particles.

2.3.2 Ash Analysis

Ash analysis was used to determine the final filler content of the blends following BS 2782 :Part 4 :Method 454A :1978 (which is the conventional way of determining the ash content of a PVC resin), but using a lower temperature to avoid the decomposition of calcium carbonate at 825°C. The following conditions were therefore chosen :-
Experimental 75

furnace temp. 600 ± 50°C
sample weight 5 ± 0.0005 gm

Powders were accurately weighed into crucibles, ashed, cooled in a desiccator, and reweighed until a constant mass was obtained. Two determinations were carried out on each sample and an average taken. This then gave a % ash content which was converted to a phr value.

2.3.3 Scanning Electron Microscopy

Powder blends were sputter coated with gold and mounted on aluminium stubs. Their examination was carried out under a SEM Cambridge Stereoscan 2A in conjunction with a calcium analyser. This gave a picture of the PVC grain surface topography, and the distribution of the filler particles over it.

2.3.4 Brabender Torque Rheometry

A Brabender torque rheometer was used to assess the fusion characteristics of the blends from the Henschel and Fielder laboratory mixers.

At the start of this work it was important to choose operating conditions of temperature, rotor speed and sample weight accurately so as to obtain a sufficiently broad spread of results. A constant sample weight rather than sample volume was chosen to allow for the variation in tap densities.
between the samples. A weight of 37g was deemed suitable after various trials.

The Brabender rheometer used consisted of an electrically heated mixing chamber with a capacity of approximately 55cc. The chamber enclosed two rotors with variable speeds from 0-250rpm. To ensure a constant feed-rate of test material to the mixer a feeding chute was attached to the top of the chamber and a ram forced material under a constant pressure into the mixing chamber, this also ensured reproducible filling. The operating conditions are given below:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jacket temperature</td>
<td>180°C</td>
</tr>
<tr>
<td>Rotor speed</td>
<td>80 rpm</td>
</tr>
<tr>
<td>Ram weight</td>
<td>1 kg</td>
</tr>
<tr>
<td>Sample weight</td>
<td>37 g</td>
</tr>
</tbody>
</table>

Traces with fixed temperatures and variable torques were obtained, a typical trace is shown in Figure 2.4. From these, fusion times and maximum and minimum torques were recorded.
2.4 Characterisation of Pipe

2.4.1 Solvent Testing

This test is one of the most widely used in the assessment of fusion levels of processed rigid PVC. Conditions stated in ASTM D 2152: (1986) were followed although this used acetone as a solvent instead of methylene chloride. The test procedure consisted of complete sections of pipe being immersed in methylene chloride. These were
allowed to stand for 20 minutes and then inspected for attack. Attack was taken as a lifting, raising, or removal, or both, of any material on the outside surface, inside surface, or mid-wall, of the specimen. Swelling or softening was not considered attack. As this test was purely visual, and thus based on operator judgement, it could not be used as the only test specification. However, it was useful for distinguishing between inadequately fused and adequately fused PVC.

2.4.2 Thermal Analysis

The heats of fusion of the processed pipe were determined using a Du Pont 990 Thermal Analyser fitted with a differential scanning calorimeter (DSC) cell. The calorimetry cell consists of a constantan disc enclosed within a silver heating block and lid. Sample and reference pans were positioned on two raised platforms within the cell which operated at a constant heating rate. The temperatures of the pans were monitored with chromel-constantan thermocouples formed by the junction of the constantan disc with a chromel wire at both platform locations. The signal difference between the two thermocouples was amplified and monitored on a recorder ($\Delta T$) against the sample temperature.

The temperature (X-axis) of the instrument was calibrated using pure samples of indium and tin metals having melting points 516.6°C and 231.9°C, and heats of fusion of 28.41 J/g and 59.16 J/g respectively.
During this work specimen sizes between 12-15 mg were scanned from room temperature to 240°C, at a heating rate of 20°C/min. under nitrogen, and with a Y-axis sensitivity of 1mV/cm. A minimum of three specimens were taken from each sample with no skin effects observed for these relatively thin pipe sections.

The areas of the endothermic curves (labelled 'A' in Figure 1.10) were measured with the aid of a planimeter and converted into heats of fusion from the following equation:

$$\Delta H_f = \frac{A}{m} \times (60 \times B \times E \times \Delta q_s)$$  \hspace{1cm} (2.1)

where
- $\Delta H_f$ - heat of fusion (J/g)
- $A$ - endothermic peak area (cm$^2$)
- $m$ - sample mass of PVC (mg)
- $B$ - time base setting (0.5 min/cm)
- $E$ - cell calibration coefficient characteristic of the calorimeter cell used, and evaluated from the areas of standard samples (value used 0.25 mW/mV)
- $\Delta q_s$ - y-axis sensitivity (mV/cm)

'B' onset temperatures were measured as shown in Figure 2.5, that is at the shoulder of the 'B' endotherm following the procedure of Gilbert and Vyvoda(102) and of Illers(97). It proves an accurate internal measure of the temperature experienced by the material.
Typical DSC trace

2.4.3 Optical Microscopy

Several optical methods were used to determine the location of the filler and the level of fusion in the pipes. For light microscopy a Zeiss universal transmission microscope fitted with a Zeiss M63 (35mm) camera was used throughout. Samples were microtomed in sections 3 microns thick direct from the pipe in a direction transverse to the direction of extrusion, shown in Figure 2.6. The microtome used was a Leitz 1400 fitted with a 'D' profile blade. These sections were then mounted between a glass slide and coverslip using cedarwood oil, a mountant of near matching refractive index to PVC.
To ascertain filler location common light microscopy was used; while acetone shearing, (using dark field illumination), was used to assess fusion.

Acetone shearing, as described in section 1.6.2, involved soaking approximately 2mm cube size specimens of PVC pipe in acetone for 5 hours. These were then sheared between microscopy slides (whilst still wet) and viewed via common light microscopy under dark field illumination. This method increases the sensitivity of the microscope system to refractive index fluctuations in the acetone-swollen PVC. From the photomicrographs fusion levels can be estimated by the amount of break-up of the samples; large chunks indicating high fusion levels while smaller chunks show up poorer fused areas.

2.4.4 Tensile Testing

Uniaxial tensile tests were carried out using a T5002 J.J Lloyd universal testing machine fitted with a 5kN load
cell and an X-Y chart recorder, according to ASTM D 638:(1972). The test specimens were, in all instances, cut from the pipe parallel to the extrusion direction. In the case of the thinner pipe, produced from the Krauss-Maffei (wall thickness 1mm), the tensile specimens could be stamped from the pipe using a single stroke of a press and knife-edged punch. However, pipe produced on the Göttfert (wall thickness 2mm) had first to be flattened, and then machined to shape by means of a high speed router-cutter guided by a shaped template. The test specimen profile is shown in Figure 2.7.

![Diagram of test specimen profile](image)

**Figure 2.7**

Test specimen dimensions

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Description</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>overall length</td>
<td>75mm</td>
</tr>
<tr>
<td>B</td>
<td>length of narrow parallel portion</td>
<td>30mm</td>
</tr>
<tr>
<td>C</td>
<td>width of narrow parallel portion</td>
<td>4mm</td>
</tr>
<tr>
<td>D</td>
<td>thickness</td>
<td>1mm</td>
</tr>
</tbody>
</table>

All marks as well as flaws, scratches or imperfections left from cutting the specimens were removed with abrasive
The final sanding strokes were in the direction parallel to the long axis of the specimens.

Ten specimens were tested of each sample at room temperature and at a crosshead speed of 5mm/min. From the force-crosshead displacement curves obtained values of tensile stress at yield and break were calculated from the following equation:

\[ \sigma = \frac{F}{A} \]  \hspace{1cm} (2.2)

where

- \( \sigma \) - tensile stress at yield or break (MPa)
- \( F \) - force at yield or break (N)
- \( A \) - initial mean cross-sectional area (mm\(^2\))

and the percentage elongation at break in relation to the initial gauge length from the following equation:

\[ E = \left[ \frac{(1-l_0)/l_0} \right] \times 100 \]  \hspace{1cm} (2.3)

where

- \( E \) - percentage elongation at break
- \( l_0 \) - initial gauge length (mm)
- \( l \) - displacement at break (mm)

Standard deviations of all the results were calculated from the following equation:

\[ s = \sqrt{\left( \sum x^2 - n \bar{x}^2 \right)/(n-1)} \]  \hspace{1cm} (2.4)
where

\[
\begin{align*}
    s & \quad \text{standard deviation} \\
    X & \quad \text{value of single observation} \\
    n & \quad \text{number of observations} \\
    \bar{X} & \quad \text{arithmetic mean of the set of observations.}
\end{align*}
\]

2.4.5 Impact Testing

A Rosand instrumented falling weight impact tester was used to assess the impact strength of complete sections of pipe. A schematic diagram of the Rosand is given in Figure 2.8. The impacting probe consists of a titanium shaft with a hardened and polished steel tip having a 10mm diameter hemispherical head. This is screwed into a force transducer/amplifier assembly, which is guarded with an aluminium alloy shield and measures the force as a function of time as the probe hits the sample. The very short duration of impact events necessitates accurate triggering of the data-capture system. This trigger is provided by a slotted opto-switch, through which a 'flag' attached to the weight passes. The assembly is equipped with a microprocessor system which controls the test cycle from the moment of initiation, from whence it measures; the initial impact velocity, measures and stores the force readings (transient recorder) and carries out calculations thereupon, drives a digital display of the calculated results, drives a monitor displaying force as a function of time or distance, and interfaces other controls within the system as a whole.
Thus values on force-time data and, through double integration, force-distance data are stored in the microprocessor, from which peak and failure energies, forces and deflections can be calculated.

Throughout this work it was observed that, during impact, the deflection of the top surface of the pipe was less than the internal diameter of the pipe. This meant that whole pipes could be tested on a 'VEE' block anvil (120°) with no fear of interference between pipe walls.

Each sample was tested ten times to give an average reading and standard deviation. The peak energy was found to be the most reproducible calculated result and was thus used to assess the different pipes.

A certain number of parameters were set before testing commenced and these values are given below :-

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>drop height</td>
<td>1000 mm</td>
</tr>
<tr>
<td>mass</td>
<td>25 kg</td>
</tr>
<tr>
<td>impact speed</td>
<td>4.5 m/s</td>
</tr>
<tr>
<td>temperature</td>
<td>19 ± 1 °C</td>
</tr>
<tr>
<td>sweep time</td>
<td>20 ms</td>
</tr>
<tr>
<td>range</td>
<td>2 kN</td>
</tr>
<tr>
<td>delay</td>
<td>10</td>
</tr>
<tr>
<td>filter</td>
<td>3 kHz</td>
</tr>
</tbody>
</table>
The sweep time sets the length of time that recordings will be taken after the data-capture system has been triggered. Delay values range from 0 to 10 and indicate the number of points recorded after the trigger, so that a delay of 0 means that all points recorded occurred before the trigger pulse was received, and a delay of 9 means that 90% are taken after the trigger signal.

The drop height was chosen on a trial and error basis such that it was a near minimum height to break all the pipes.
Figure 2.8

Schematic diagram of Rosand Instrumented Impact Tester
CHAPTER 3

CALCIUM CARBONATE FILLERS

3.1 Filler Selection

Five natural calcium carbonate fillers were selected for their wide range of particle sizes. They were all manufactured and supplied by ECC International Limited, St. Austell, and the technical references for the grades are as follows:

- Carbital 90 (C90)
- Polcarb (P)
- Polcarb 60 (P60)
- Queensfil 300 (Q300)
- Queensfil 20 (Q20)

The abbreviations used throughout this report are given in brackets, with typical properties of each filler listed in Appendix A.

3.2 Characterisation

The fillers were characterised according to their particle size distribution and specific surface area. These were measured by Andreasen, Sedigraph and Ladal techniques; and Flowsorb technique respectively.
3.2.1 Particle Size Analysis

The use of sedimentation techniques for particle size analysis is based on the fact that particles falling through a viscous medium quickly attain a terminal velocity, and settle at this constant velocity for the remainder of their descent. For spherical particles falling singly in an infinite sea of fluid the relationship between particle diameter and the properties of the system is given by Stokes' equation :-

\[ d = \frac{18 \eta V}{\left( \rho - \rho_0 \right) g} ^\frac{1}{2} \]  

(3.1)

where

- \( d \) - particle diameter (\( \mu \)m)
- \( \eta \) - fluid viscosity (poise)
- \( V \) - terminal velocity (cm/s)
- \( \rho \) - density of particle (g/cm\(^3\))
- \( \rho_0 \) - density of fluid (g/cm\(^3\))
- \( g \) - acceleration due to gravity (cm/s\(^2\))

If the fluid viscosity and density are kept constant the particle diameter is proportional to the square root of the terminal velocity for a given gravitational force.

\[ d = k \sqrt{V} \]  

(3.2)
Strictly speaking the equation only applies to spherical particles, though it has been found in practice that consistent results can be obtained with irregular particles where they are specified in terms of the diameter of a sphere of the same material that would have the same sedimentation velocity.

Many variations exist in the technique of using sedimentation velocity as a means of obtaining a particle size analysis, with a major division occurring between those using normal gravitational forces, and those using centrifugal forces to increase sedimentation rates.

The Andreasen technique uses gravitational sedimentation and Stokes' Law in its simplest form. Here the filler was dispersed in water and samples were taken from a predetermined depth and time, equivalent to a particular particle size, as determined by Stokes' Law. Samples were then evaporated to a constant weight and their particle size, as a % finer than, calculated. This technique was, however, very time consuming, and interference from such factors as convection, diffusion and Brownian motion meant that the smallest particles measurable were of the order 1-3μm.

The Sedigraph Particle Size Analyser also uses gravitational forces, but typically yields a particle diameter distribution over the range 50-0.18μm. Diameters outside these can be measured depending on particle density, liquid density and velocity. Analysis took place by means of a finely collimated beam of X-rays, which determined the
concentration of particles remaining in suspension at decreasing sedimentation depths as a function of time. The logarithm of the difference in transmitted X-ray intensity was electronically generated, scaled and presented linearly as 'Cumulative Mass Percent' on the Y-axis of an X-Y recorder. To minimise the time required for analysis the position of the sedimentation cell was continuously changed so that the effective sedimentation depth was inversely related to elapsed time. The cell movement was synchronised with the X-axis of the X-Y recorder to indicate the equivalent spherical diameter corresponding to the elapsed time and instantaneous sedimentation depth. The size information, 100-0.1μm, was presented logarithmically on a three cycle, semi-log graph.

A development of the sedimentation technique aimed at reducing the minimum measurable size is the application of centrifugal forces. By this method the settling rate is increased and interference from factors such as Brownian motion and/or convection reduced. The Ladal Pipette withdrawal centrifuge has been designed for particle size evaluation in the sub-micrometer range (approximately 2 to 0.01μm). The instrument consists of a horizontally rotating shallow disc-like bowl. In the centre of the disc is situated a sampling port which is connected to several sampling points set equal distances well out towards the circumference of the bowl. Figure 3.1.
A dilute dispersion of the sample to be examined was first prepared and a fixed volume sampled before charging the bowl of the centrifuge. The centrifuge disc was then set in motion at a constant speed, approximately 1500 rpm at constant temperature. At fixed time periods a set volume of dispersion was withdrawn from the centrifuge bowl via the sampling points. The concentration of the extracted sample was determined by drying and weighing.

Results from these tests are given in Table 3.1.
Table 3.1

<table>
<thead>
<tr>
<th></th>
<th>Andreasen</th>
<th>Sedigraph</th>
<th>Ladal</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;2μm</td>
<td>&lt;1μm</td>
<td>&lt;2μm</td>
<td>&lt;1μm</td>
</tr>
<tr>
<td>C90</td>
<td>90.4</td>
<td>75</td>
<td>46</td>
</tr>
<tr>
<td>P</td>
<td>85.5</td>
<td>87</td>
<td>51</td>
</tr>
<tr>
<td>P60</td>
<td>55.5</td>
<td>51</td>
<td>19</td>
</tr>
<tr>
<td>Q300</td>
<td>32.2</td>
<td>36</td>
<td>12</td>
</tr>
<tr>
<td>Q20</td>
<td>43.0</td>
<td>42</td>
<td>15</td>
</tr>
</tbody>
</table>

3.2.2 Specific Surface Area

The specific surface areas of the fillers were determined using a Flowsorb II 2300. This is designed to measure rapidly the surface area, on the molecular level, of stable, granulated or powdered materials (as well as pore volume). For powdered solids the surface area is measured by determining the quantity of gas that adsorbs as a single layer of molecules, a so called monomolecular layer, on a sample. This adsorption is done at, or near, the boiling point of the adsorbate gas. Under specific conditions the area covered by each gas molecule is known within relatively narrow limits. The area of the sample is thus directly calculable from the number of adsorbed molecules.

The gas used was a nitrogen/helium mixture 30/70%, and the conditions most favourable for the formation of a
monolayer of adsorbed gas were established at atmospheric pressure and the temperature of liquid nitrogen.

The sample to be analysed was placed in a clean dry test tube and, to remove all physically adsorbed material as rapidly as possible, treated to the highest temperature permissible (consistent with the thermal stability of the sample). Once degassed the sample tube was placed in liquid nitrogen and adsorption of the gas mixture took place. The value obtained gave the sample surface area in m$^2$, from which the specific surface area was determined in m$^2$/g from the weight of the sample.

The results are given in Table 3.2.

Table 3.2

<table>
<thead>
<tr>
<th>Filler</th>
<th>Flowsorb m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>C90</td>
<td>11.6</td>
</tr>
<tr>
<td>P</td>
<td>5.1</td>
</tr>
<tr>
<td>P60</td>
<td>3.5</td>
</tr>
<tr>
<td>Q300</td>
<td>2.6</td>
</tr>
<tr>
<td>Q20</td>
<td>2.3</td>
</tr>
</tbody>
</table>

3.3 Stearate Coating

To study the effects of different levels of stearate coating, which are often used in industry to facilitate handling and dispersion in the polymer matrix and prevent loss of mechanical performance, each filler was coated with
various levels of stearic acid. Coatings took place in a 101
Steele and Cowlishaw steam heated mixer under the following
conditions:-

<table>
<thead>
<tr>
<th>Temperature</th>
<th>120°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dwell Time</td>
<td>10 min</td>
</tr>
<tr>
<td>Rotor Speed</td>
<td>1000 rpm</td>
</tr>
<tr>
<td>Batch Size</td>
<td>2 kg</td>
</tr>
</tbody>
</table>

The fillers were prepared at three coating levels, see
Table 3.3 :-

1. Uncoated
2. Coated with 1% by weight stearic acid
3. Coated with approximately 75% of a
   predetermined monolayer coverage of stearic
   acid

One filler (Polcarb) was also chosen to be coated over
a complete range of stearic acid coating levels. This was
done to clarify the actual effects of the stearic acid. In
choosing the coating range the general recommendation was
followed that stearic acid should be added to formulations in
concentrations between 0.1 and 0.5 phr. At these levels they
do not delay the fusion process too strongly, whilst they
impart marginal improvements in the heat stability of the
compound. Polcarb was therefore coated over the following
range (by weight) :-
Table 3.3

Chosen coating levels

Stearic acid (% by weight)

<table>
<thead>
<tr>
<th></th>
<th>C90</th>
<th>P</th>
<th>P60</th>
<th>Q300</th>
<th>Q20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>monolayer</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1.90</td>
<td>0.84</td>
<td>0.56</td>
<td>0.43</td>
<td>0.38</td>
</tr>
</tbody>
</table>

3.3.1 Monolayer Coverage Calculations

The purpose of this series was to have no free stearic acid left in the blend, but rather to have it all bonded to the filler surface. To this end calculations were made as to the footprint area of stearic acid and how this compared to a value reported by Papirer et al. These two values were then used to estimate the weight of stearic acid required to coat the fillers with a monolayer coverage.
Footprint area of stearic acid

The footprint area calculations were based on the assumption that the stearic acid molecules would initially form a monolayered array of alkyl chains oriented so that their carboxylate groups were adjacent to the filler surface. Additional acid molecules would then be adsorbed in a second layer with their chains orientated tail-to-tail to the first molecular layer, as shown schematically below.

The double bond will divide equally between the two oxygens; the hydrogen atom is small enough in comparison to the carbon and two oxygens so that it can be ignored. To calculate the footprint area we need to find the base area of the cylinder.

It is known that in a carboxylate group

the $\text{O} \equiv \text{C} \equiv \text{O}$ bond angle $125^\circ$

and $\text{C} \equiv \text{O}$ bond length $1.27 \, \text{Å}$
Therefore the footprint distance between a carbon and oxygen atom

\[ = \sin 125 \times 1.27 = 1.13 \text{ Å} \]

It is also known that the

Van der Waals field surrounding carbon atom 1.8 Å
Van der Waals field surrounding oxygen atoms 1.4 Å

This gives us an area as shown below:

From this we can find the footprint area.

The Van der Waals field surrounding the carbon atom is calculated from

\[ \pi r^2 = 10.18 \text{ Å}^2 \]
The area each oxygen arc occupies can be calculated as shown below, considering one oxygen atom at a time.

Area of arc DEF = EBF + BAF - DAF

Find area EBF from angle EBF and cosine rule

\[ a^2 = b^2 + c^2 - 2bc \cos A \]

so,

\[ 1.8^2 = 1.4^2 + 1.13^2 - 2 \times 1.4 \times 1.13 \times \cos \hat{ABF} \]

\[ \hat{ABF} = 89.94° \]

and

\[ \hat{EBF} = 180 - 89.94 = 90.06° \]

therefore area EBF = 90.06/360 x \pi r^2 = 1.54 \text{ Å}^2
Similarly for area DAF

\[ 1.4^2 = 1.13^2 + 1.8^2 - 2 \times 1.13 \times 1.8 \cos \hat{DAF} \]

\[ \hat{DAF} = 51.06^\circ \]

therefore area DAF = \( \frac{51.06}{360} \times \pi r^2 = 1.44 \text{ } \mu^2 \)

For the area of BAF need to find perpendicular height CF

\[ CF = 1.4 \times \sin 89.94^\circ = 1.4 \text{ } \mu \]

area of triangle BAF = \( \frac{1}{2} \times \text{base} \times \text{height} \)

\[ = \frac{1}{2} \times 1.13 \times 1.4 = 0.79 \text{ } \mu^2 \]

Then area of arc DEF = \( 1.54 + 0.79 - 1.44 = 0.89 \text{ } \mu^2 \)

and footprint area = \( 10.18 + (4 \times 0.89) = 13.74 \text{ } \mu^2 \)

\[ = 0.1374 \text{ nm}^2 \]

**Experimental cross sectional value**

This is a much lower value than that reported by authors Papirer et al(135) who found, experimentally, stearic acid molecules to have a cross sectional area of \( 0.21 \text{ nm}^2 \).

In their work they examined the mechanism of reaction between calcium carbonate and stearic acid using a sensitive radiochemical method, and the change in surface properties in terms of surface energy variations using inverse gas chromatography.

They concluded that the stearic acid molecules are fixed perpendicularly to the filler surface and that their
long C\textsubscript{18} alkyl chains entirely shield this surface, decreasing dramatically its surface energy. This they claim both diminishes the particle-particle interactions and hence facilitates the dispersion of the filler in the PVC matrix, and enhances the compatibility between filler and matrix leading possibly to better mechanical performance of the material.

As there is no clear proof of how closely the stearic acid molecules pack together on the filler surface and as it was important in this series to have no free stearic acid in the blend the larger cross sectional area figure of 0.21\text{nm}^{2} was chosen. A monolayer coverage value based on this figure and presented as a percentage of weight for each filler specific surface area was calculated in the following manner:

Taking C\textsubscript{90} as an example:

Cross sectional area of stearic acid - 0.21 \text{nm}^{2}

C\textsubscript{90} filler specific surface area - 11.6 \times 10^{18} \text{nm}^{2}/\text{g}

Therefore to cover filler need

\[
\frac{11.6 \times 10^{18}}{0.21} = 5.52 \times 10^{19} \text{ molecules/gram}
\]

Molecular weight of stearic acid CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{16} COOH is 284

Thus from Avogadro's number

284g stearic acid contain 6.023 \times 10^{23} molecules

so 1 g contains 2.156 \times 10^{21} molecules
Need \(5.25 \times 10^{19}\) molecules/gram to cover filler therefore need \(0.0256\) g stearic acid for 1g of filler that is 2.56% by weight.

Using this method each filler’s monolayer coverage can be calculated to give the following values:

<table>
<thead>
<tr>
<th>Blend</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>C90</td>
<td>2.56</td>
</tr>
<tr>
<td>P</td>
<td>1.13</td>
</tr>
<tr>
<td>P60</td>
<td>0.77</td>
</tr>
<tr>
<td>Q300</td>
<td>0.57</td>
</tr>
<tr>
<td>Q20</td>
<td>0.51</td>
</tr>
</tbody>
</table>

**Chosen monolayer values**

These values are based on filler specific surface areas calculated by the adsorption of nitrogen onto the filler surface, using the Flowsorb technique described in section 3.2.2. There seems some doubt, however, as to whether the much bulkier stearic acid molecules would be exposed to, and could bond to, as large a surface area as the smaller nitrogen atoms. As it was important in this series to have no free stearic acid a slightly lower value, approximately 75% of that calculated, was chosen. The final values are given in Table. 3.4.
Table 3.4

<table>
<thead>
<tr>
<th>Blend</th>
<th>Stearic acid (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C90</td>
<td>1.90</td>
</tr>
<tr>
<td>P</td>
<td>0.84</td>
</tr>
<tr>
<td>P60</td>
<td>0.57</td>
</tr>
<tr>
<td>Q300</td>
<td>0.43</td>
</tr>
<tr>
<td>Q20</td>
<td>0.38</td>
</tr>
</tbody>
</table>

After every coating operation a small sample of the coated filler was tested to determine the exact level of stearic acid present. This was done by dissolving a known weight of sample in hydrochloric acid, washing out the stearic acid with chloroform and then evaporating this to leave the stearic acid from which a % weight could be calculated. From these tests stearic acid losses were shown to be consistently low (approximately 9%) and were thus ignored throughout this project.
CHAPTER 4

PROCESSING RESULTS

4.1 Dry Blending Studies

As previously mentioned two high speed mixers, a 40 litre Henschel and an 8 litre Fielder, were used in this work. The Henschel was used to prepare uncoated and 1% coated blends, whilst the Fielder blended the constant monolayer fraction and the Polcarb series. A control group comprising five samples (coded N/F, P, Q20, 1P, 1Q20) was prepared in both blenders so that a comparison could be made between the two mixers.

As the two blenders differed in both size and blade arrangement previous work by members of IPTME\(^{(89,130,131)}\) on the effects of different mixers on dry blend properties was studied carefully. The areas previously researched include observations on the effects of varying such parameters as jacket temperature, rotor speed and charge weight in different mixers on filler dispersion, particle size distribution, bulk density and blend fusion characteristics.

In this study the dry blending process was assessed by considering the blending time, the final filler content, the distribution of filler over the PVC grains and the final grain shape, the resultant powder density, and the fusion characteristics of the blend (this will be reported in Chapter 5).
4.1.1 Blending Characteristics

The blending time indicates the rate of heat build up in the mix and the total time required to reach the discharge temperature.

In either mixer the addition of 15phr of filler had little effect on the measured blending times, however, the Fielder mixer did show larger deviations between mixes than the Henschel. These findings support earlier work by Pepper(130) who considered the effect of mixer type, (using the same two dry blenders as used here) mixing conditions and filler loading on the dry blending process and subsequent properties of the dry blends. He found filler content at this comparatively low level to have generally little effect on blending times, although the Fielder mixer did show much larger variations in its time - temperature profiles than the Henschel.

As the results from series mixed on the same blender were similar an example of two typical series, one from each blender, is shown in Figure 4.1. These results clearly show the Fielder taking over twice as long as the Henschel to mix its blends. This large difference in mixing times between the two blenders can be attributed to the dissimilarities in blend size, and to the differences in the machines' blade arrangement. It is also expected that the larger filler loss in the Fielder (which will be discussed in section 4.1.2), which coated the inside of the chamber wall, not only reduced
the material available to generate frictional heat, but also reduced the heat input from the heated jacket.

The results do seem to show a general pattern of blending time with different filler type. This, however, was thought to be purely coincidental.

Figure 4.1

Comparison of Mixer Blending Times

4.1.2 Ash Analysis

The final filler content of the various blends was determined by ash analysis; obviously a low filler content apart from being unsatisfactory in terms of blend requirements, would suggest that the filler had been preferentially removed from the system. The results are given in full in Appendix B.
The blends from the Henschel mixer showed good agreement between the initial filler loading and the actual phr of filler left after ashing. On average less than 1phr of filler was lost during blending.

The Fielder blends, however, showed a wide discrepancy with only approximately half the filler remaining in the blend, that is between 7 and 8phr instead of 15phr. These results support those found from blending times, where a loss in filler content due to mixer fouling would reduce the effective mixing charge and therefore result in longer mixing times.

The results were again similar to those reported by Pepper(130) who found that the percentage of material lost varied greatly between the two mixers considered. He found the Henschel mixer to show correct proportions of filler up to a level of approximately 35phr, and that the blend produced was quite uniform and representative of the initial formulation. The Fielder mixer, however, lost a large proportion of the filler added to the formulation at all loading levels. He attributed this loss of filler in the Fielder to the formulation of a 'cake' around the metal surfaces which was most obviously seen on the heater mixer jacket wall. Various experiments including altering jacket temperature, rotor speed and discharge temperature did not prove successful in reducing this fouling.

Within this project the fouling problem was somewhat reduced in the following way. Initially twice the final
chosen charge weight was used, but large quantities of filler were found to be left on the barrel walls (especially in the heated chamber). This not only reduced filler levels but caused filler particles to agglomerate rather than disperse evenly throughout the blend. When these blends were then extruded filler separation was found to be at an unacceptable level. To try to remedy this situation a smaller charge weight was chosen along with a lower initial jacket temperature, thereby increasing the mixing time. This seemed to somewhat reduce the filler fouling and therefore alleviate the agglomeration and separation problems.

4.1.3 Scanning Electron Microscopy

Each powder blend was examined optically by scanning electron microscopy using X-ray analysis to produce a calcium element map capable of identifying the location of calcium carbonate filler on the surface of the PVC grains. Care must be taken in interpreting the results as calcium will only be detected on the side of the grain particles seen by the analyser.

This section will be divided into three parts covering: (i) the effects of various particle sized uncoated fillers on the PVC's grain structure during blending; (ii) what effect, if any, was seen when the filler was coated at first with a 1% stearate coverage and then a constant monolayer fraction coverage (the effect of coating level can
be looked at in more detail when examining the Polcarb series), (iii) the influence of the mixer and how this affected the powder blend.

**Effect of Uncoated Filler**

The blend containing no filler (sample code N/F) showed the distinctive rough surface of the PVC grains formed by the agglomeration of sub-grains, Figure 4.2. The addition of a fine filler (sample code C90) helped to smooth and reduce the size of the PVC grains both by its abrasive action in breaking off any irregularities on the surface of the grains, and by settling preferentially in the folds on the grain surface giving the grains a more even rounded shape, Figure 4.3(a,b). The distribution of filler in this way can be clearly seen from the calcium element maps which are the same field of view as their respective micrographs. As coarser fillers were added (sample code P to Q20) the filler particles themselves started to give the PVC grains a new slightly rougher surface, Figure 4.4(a,b).

**Effect of Coated Filler**

In general the introduction of a stearate coating seemed to have little effect on the shape of the PVC grains or on the distribution of the filler in the blend. In the 1% coated series irregularities were removed and folds between sub-grains filled in a similar manner to the uncoated series, Figures 4.5 to 4.7. In the Polcarb range a distinct covering
of filler could be seen (although it unfortunately had a much lower filler content than hoped), but there were no obvious differences between the various filler coating levels, Figure 4.8(a,b,c,d,e).

**Influence of Mixer**

The two mixers seemed to have profoundly different effects on the filler and PVC particles. Comparing the micrographs one can see that where there was no filler present both mixers produced a similar dry blend with agglomerated sub-grains clearly visible, Figure 4.9(a,b,c). However, once filler was added the mixers seemed to act in different ways, Figures 4.10 to 4.11.

In the Henschel, as mentioned earlier, the filler particles surrounded the PVC grains accumulating especially in the folds between the sub-grains. The fillers not only rounded the PVC grains in this way but also seemed to help break off any irregularities on the PVC particles' surface which would ultimately result in the particles packing more closely together.

In the Fielder the PVC grains were not coated as thickly with filler and individual sub-grains could still be clearly seen. Irregularities were still present in the PVC grain surface hindering the packing of grains which would give the resultant blends a low bulk density. This effect is clearly visible in the comparison blends, Figures 4.11(a,b) and 4.12(a,b).
These results support those found from ash analysis where the Fielder blends contained much lower quantities of filler. These huge differences in the resultant blends will affect their own blend characteristics as well as their processing characteristics both during extrusion and Brabender torque rheology.
Figure 4.2 N/F

Figure 4.3(a) C90

Figure 4.3(b) Ca Map

Figure 4.4(a) Q300

Figure 4.4(b) Ca Map

Micrographs of Powder Blends

150μm

Processing 112
Figure 4.5  N/F

Micrographs of Powder Blends

150µm

Figure 4.6(a) 1C90

Figure 4.6(b) Ca Map

Figure 4.7(a) 1Q300

Figure 4.7(b) Ca Map
Figure 4.8(a) P

Figure 4.8(b) 0.3P

Figure 4.8(c) 0.84P

Figure 4.8(d) 3P

Figure 4.8(e) Ca Map

Micrographs of Powder Blends

Processing 114

150μm
Micrographs of Powder Blends

Figure 4.9(a) N/F (uncoated)

Figure 4.9(b) N/F (1% coated)

Figure 4.9(c) N/F (monolayer)

Figure 4.10(a) P

Figure 4.10(b) MP
Figure 4.11(a) Q20

Figure 4.11(b) 1Q20

Figure 4.11(c) MQ20

Figure 4.12(a) Q20 (Fielder)

Figure 4.12(b) 1Q20 (Fielder)

Micrographs of Powder Blends
4.1.4 Powder Densities

A powder's tap density gives a measure of its ability to pack efficiently. This will be influenced by the particle's size distribution and shape. It can be seen from the results, Table 4.1, that it is the variation of the blenders that has the most profound effect on the densities of the blends rather than the presence of filler or coating.

Henschel

In the Henschel (uncoated and 1% coated series) the addition of all fillers markedly increased the tap density. With the uncoated series there seemed to be a slight increase in density as filler particle size was increased, this trend, however, is thought to be negligible in comparison to the overall filler effect, and once the filler was coated certainly disappeared. Tap densities in general varied very little between the uncoated and 1% coated series, Figure 4.13.

Fielder

In the Fielder mixer (constant monolayer fraction and Polcarb series) filler effects seemed to change, Figure 4.13. The addition of filler reduced the tap density in the constant monolayer fraction series with the coarser particles increasing this density slightly. Within the Polcarb series there were no clear trends, Figure 4.14. On the strength of previous results (ash analysis and SEM) these findings were
as expected, since they showed larger irregular grains remaining in the Fielder blends reducing the packing efficiency of the particles and therefore reducing the bulk density.

Not only were filled blend densities reduced, but even the unfilled blend had a lower density. This seems to suggest that the Fielder mixer, as well as losing a lot of filler through fouling and therefore losing part of the aggressive nature of the filler, is itself a much less effective mixer in terms of its ability to break down particles.

This effect can be clearly seen in the results from the comparison blends, where the bulk densities of Fielder blends are, in all cases, lower and less varied than those prepared in the Henschel mixer, Figure 4.15. These results support work by Higgs et al (131) who found a 10 litre Henschel mixer, as compared to an 8 litre Fielder, to give much larger variations in bulk (tap) and apparent densities when mixing parameters were varied.
Table 4.1

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Tap Density (g/cm^3)</th>
<th>Sample Code</th>
<th>Tap Density (g/cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henschel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/F</td>
<td>0.73</td>
<td>N/F</td>
<td>0.72</td>
</tr>
<tr>
<td>C90</td>
<td>0.76</td>
<td>1C90</td>
<td>0.78</td>
</tr>
<tr>
<td>P</td>
<td>0.77</td>
<td>1P</td>
<td>0.77</td>
</tr>
<tr>
<td>P60</td>
<td>0.79</td>
<td>1P60</td>
<td>0.78</td>
</tr>
<tr>
<td>Q300</td>
<td>0.79</td>
<td>1Q300</td>
<td>0.79</td>
</tr>
<tr>
<td>Q20</td>
<td>0.79</td>
<td>1Q20</td>
<td>0.78</td>
</tr>
<tr>
<td>Fielder</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/F</td>
<td>0.71</td>
<td>P</td>
<td>0.69</td>
</tr>
<tr>
<td>MC90</td>
<td>0.68</td>
<td>0.3P</td>
<td>0.71</td>
</tr>
<tr>
<td>MP</td>
<td>0.68</td>
<td>0.5P</td>
<td>0.70</td>
</tr>
<tr>
<td>MP60</td>
<td>0.70</td>
<td>0.84P</td>
<td>0.70</td>
</tr>
<tr>
<td>MQ300</td>
<td>0.70</td>
<td>1P</td>
<td>0.71</td>
</tr>
<tr>
<td>MQ20</td>
<td>0.70</td>
<td>2P</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3P</td>
<td>0.70</td>
</tr>
<tr>
<td>Comparison (Henschel/Fielder)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/F</td>
<td>0.73 / 0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.77 / 0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q20</td>
<td>0.79 / 0.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1P</td>
<td>0.77 / 0.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Q20</td>
<td>0.78 / 0.70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.13

Tap Density versus Filler Type

Legend
- uncoated
- IL treated
- metalized

Figure 4.14

Tap Density versus Polcarb Series
4.2 Extrusion Studies

4.2.1 Evaluation of Extrusion Characteristics

Both instrumented twin screw extruders allowed the processing characteristics of the blends to be evaluated from torque and pressure measurements as well as output rates. From this it was possible to monitor the influence of filler type and coating on the extrusion characteristics. These characteristics, due to equipment differences, could not, however, be compared directly from one extruder to another, even when extrusion conditions between the two machines were kept apparently constant. Unfortunately these extruder differences could not be investigated to any great extent, due to practical reasons related to the limited availability of both extruders. However, five blends coded N/F, P, Q20, 1P and 1Q20 were extruded on both machines in an attempt to clarify the results obtained from the two machines. Comparisons were further complicated by the use of two different dry blenders, as previously mentioned. Thus the results from the Krauss and Göttfert will be presented separately and only general trends, rather than actual figures, will be compared. All the results from the next four sections are tabulated in Appendix C.

4.2.1.1 Output Rate

It has been mentioned (section 1.4.2) that individual chambers are formed along the length of intermeshing counter rotating twin screw extruders creating a positive conveying
Figure 4.15

Tap Density versus Comparison Blends

![Graph showing tap density comparison]

Legend
- Filler
- Hematite

Figure 4.16

Extruder Output versus Filler Type

![Graph showing extruder output comparison]

Legend
- uncoated
- 1% coated
- 2% coated
- 3% coated
action with little material slip or leakage. Low pressures in the central region of the extruder also help to effectively separate the feed zone from the die and cause output rates to be dependent on the rate that material is introduced into the extruder and its screw speed, and not on the conditions at the die end. Increased output is obtained by increased screw speeds and bulk densities. It was therefore expected that in this study, where screws were flood fed at all times and screw speeds were kept constant within each extruder, output rates would follow bulk (tap) density trends.

Figures 4.16 and 4.17 present the results graphically and the curves obtained were as expected with output rates on both extruders generally tracing tap density trends.

The output from the Krauss increased with density, apart from sample P60 which, in both uncoated and 1% coated series was surprisingly low. The Göttfert, although giving a much higher output due to its higher screw speed, showed a similar increasing trend from fine to coarser filled blends. It is interesting to note that this trend is still very obvious even though these blends contained only approximately half the level of filler of those run in the Krauss extruder. It is also worth noting that the introduction of fine filler caused a fall in output as it had bulk density, and that it was only as coarser fillers were added to the blend that the output exceeded that of the unfilled blend. (The stuff
Figure 4.17
Extruder Output versus Polcarb Series

Figure 4.18
Extruder Output versus Comparison Blends
feeder used on the Göttfert is generally regarded as a means of increasing the output rate).

From the comparison blends it was observed, as expected, that in both the Krauss and Göttfert coarser fillers increased output. In the Göttfert the uncoated filler output was in both cases higher than the coated, whilst in the Krauss it was higher for sample Q20 but lower for sample P, Figure 4.18. Thus in general terms it could be concluded that the introduction of a coarser rather than finer filler increased the bulk density and thus the output, whilst coating the filler generally reduced the output. The Polcarb series, which showed a general reduction in output as the stearic coating level increased, was in agreement with this observation, Figure 4.17.

4.2.1.2 Torque

In general, torque readings do not provide a direct indication of the pattern of fusion of the material since contributions to the total torque arise from the material all along the barrel. However, in twin screw extruders the rear conveying part of the extruder is only partially full of material, thus reducing the torque in this region, and fusion is reported to take place in the metering zone, where the greatest torques will therefore be generated. The sensitivity of torque readings to varying formulation and processing conditions must therefore reflect variations in the viscosity and pattern of fusion of the material.
Torque values are of particular interest as a measure of the mechanical energy supplied to the material and can be defined as the specific energy consumption \( q \), that is the mechanical energy consumed per unit mass of material.

\[
q = \frac{2 \pi n (M - M_0)}{\dot{m}}
\]

where \( q \) - specific energy consumption
(rev.%/g or rev.Nm/g)

\( n \) - screw speed (15 or 21rpm)

\( M \) - screw torque (% or Nm)

\( M_0 \) - background torque (19.5% or 67.2Nm)

\( \dot{m} \) - mass output rate (g/min)

The background torque was estimated by running the two extruders empty at the same screw speed as used for extruding the dry blend, this was necessary to compensate for friction in the gear-box, for example.

From the results, Figure 4.19, it could be seen that in all cases the addition of filler increased the torque readings.

In the Krauss, taking the uncoated filled series first, it was found that the addition of any of the fillers increased the torque along with the mechanical energy requirement. Within the series a clear effect of filler particle size on torque was also seen with finer particles causing a greater increase in torque, this giving the pipe a
Figure 4.19
Extruder Torque versus Filler Type

Figure 4.20
Extruder Torque versus Comparison Blends
much glossier surface finish. In the 1% coated filler series again the addition of filler increased torque and the same relationship between filler particle size and torque was observed. However, in this case the spread of torques from fine to coarse fillers was much wider. Torques for the pipe samples P60 and 1P60 as in their output results were low.

The constant monolayer fraction series in the Götffert followed a near identical trend with the addition of filler increasing the torque, finer filler more so than coarser.

Results from the comparison blends show that in both extruders the presence of filler increased the torque, while coarser fillers tended to reduce this effect, Figure 4.20. In the Krauss, coating the finer filler slightly increased the torque while coating the coarser slightly reduced it. In the Götffert the opposite was true with coated fine filler having a reduced torque and coarser filler staying constant.

These results seemed to indicate that the presence of coating in the Götffert would reduce torque. Unfortunately, however, this effect was not seen in the Polcarb series where no clear effects of coating level were present, Figure 4.21.

4.2.1.3 Pressure

The Krauss-Maffei KMDL 25 twin screw extruder was fitted with four pressure transducers along its length. These were, in front of the compression zone of the screw
Figure 4.21

Extruder Torque versus Polcarb Series

(P1), in the metering zone of the screw (P2), in the adaptor piece (P3) and in the die (P4).

Pressure recorder (P1) detects bulk density differences in the formulation, and this can be clearly seen in the results (Appendix C.2) with the addition of filler increasing this pressure reading. The pressure recording (P2) was intentionally kept low to avoid the tendency for the material to be pushed out through the venting hole. The adaptor pressure (P3) measures the back pressure, indicating at the same time the highest pressure value. This, along with the die pressure (P4), has in previous work been found
to be dependent on the output rate\(^{(132)}\), the geometry of the flow channel in the head and die and the rheological properties of the material being extruded. Thus if the presence of fillers were to affect the materials' gelation behaviour it would be expected to be seen in these readings, and from the results there is a clear relationship between pressure readings and torque.

The Göttfert twin screw extruder was similar to the Krauss with four pressure transducers located at distances 9D, 14D and 20D along its barrel and one in the die itself. Referring back to Figure 2.3 it can be seen that these are in approximately the same position as the transducers on the Krauss, and it would thus be fair to assume that they would give us similar information about the state of the blend. However, as can be seen from the set of results in Appendix C.2 they do not give us the same relationships (pressure reading P4 at the die gives the highest reading), this may be due to differences in screw configuration and exact positioning of the transducers.

From the Göttfert results it can be seen that the values of P1 are practically irrelevant showing us no clear trends in the constant monolayer fraction series and being extremely low in the Polcarb series. They do, however, demonstrate that the feed zone can be regarded as a powder conveying section. In the metering zone (P2), which is full of material due to die resistance, pressures are transmitted backwards through leakage flows. These values therefore
become significant, and must depend on the length of fused material in the barrel. From here to the adaptor and die the pressure increases rapidly with expected relationships between the pressure and torque values. Thus pressure values can be readily used to characterise the formulation and processing characteristics of a blend.

(It must be noted that due to the practical impossibility of calibrating the pressure transducers the values here have only comparative significance).

The results from pressure readings thus support those already found from torque measurements with fine filler increasing pressures as compared to the unfilled blends. As coarser fillers are added pressures drop in both extruders, more so when the filler is coated in the Krauss, with coating having little effect in the Göttfert.

4.2.1.4 Temperature

Thermocouple/transducer probes were situated along the length of the barrel in both extruders monitoring the temperature of the extruder at specific points and therefore the operating conditions of the extruders. These readings, however, can not be used as an accurate measure of the material's melt temperature as this will be affected by several parameters independent of the temperature of the surrounding metal jacket. An internal measure of the highest temperature experienced by the pipe samples was therefore
calculated using thermal analysis to give the 'B' onset temperature. The technique used for this is described in section 2.4.2.

The uncoated filler series produced in the Krauss (Appendix C.3) gave an obvious trend from fine to coarse filler additions, (P60 gave perhaps a slightly higher than expected reading.) This trend was mimicked by the 1% coated series but at a temperature approximately 8°C higher than that experienced by the uncoated series, this could be explained by the long time gap between the two extrusion runs throughout which the extruder lay idle. Within this series 1P60 again gave an unexpectedly high reading which explains some of its behaviour during later fusion and mechanical tests.

The extrusion temperatures used in the Göttfert were set as closely as possible to those used in the Krauss. This produced pipe both in the constant monolayer fraction and Polcarb series with a 'B' onset temperature near to that experienced by the 1% coated Krauss series. The constant monolayer fraction series in the Göttfert again seemed less sensitive to changes in the filler particle size, with only MC90 standing out as experiencing a particularly high processing temperature. In the Polcarb series little variation in 'B' onset temperature was perceived.
CHAPTER 5

FUSION STUDIES AND RESULTS

5.1 Fusion Characteristics of Dry Blend

5.1.1 Brabender Torque Rheometry

The fusion characteristics of all the blends from both the Henschel and Fielder laboratory mixers were assessed using a Brabender torque rheometer, as described in section 2.3.4.

A constant sample weight rather than volume was used during these studies. This helped to reduce the effects that the large differences in bulk densities would otherwise have had on the results. It also meant that any variations observed between plastograms of different samples would be as a result of material property variations rather than bulk density variations.

The results from all four series along with the five comparison blends which had been mixed in both machines are given in Table 5.1. The torques are also shown in bar chart form, with fusion times plotted graphically.
### Table 5.1

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Minimum Torque (mg)</th>
<th>Maximum Torque (mg)</th>
<th>Fusion Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blended in Henschel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/F</td>
<td>920</td>
<td>1665</td>
<td>2.1</td>
</tr>
<tr>
<td>C90</td>
<td>1335</td>
<td>2235</td>
<td>0.9</td>
</tr>
<tr>
<td>P</td>
<td>865</td>
<td>1865</td>
<td>1.7</td>
</tr>
<tr>
<td>P60</td>
<td>800</td>
<td>1845</td>
<td>2.3</td>
</tr>
<tr>
<td>Q300</td>
<td>920</td>
<td>1925</td>
<td>2.3</td>
</tr>
<tr>
<td>Q20</td>
<td>935</td>
<td>1935</td>
<td>1.9</td>
</tr>
<tr>
<td>Blended in Fielder</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/F</td>
<td>1080</td>
<td>1800</td>
<td>2.5</td>
</tr>
<tr>
<td>1C90</td>
<td>1680</td>
<td>2210</td>
<td>1.1</td>
</tr>
<tr>
<td>1P</td>
<td>1165</td>
<td>1935</td>
<td>1.9</td>
</tr>
<tr>
<td>1P60</td>
<td>1040</td>
<td>1935</td>
<td>3.3</td>
</tr>
<tr>
<td>1Q300</td>
<td>985</td>
<td>1830</td>
<td>4.0</td>
</tr>
<tr>
<td>1Q20</td>
<td>920</td>
<td>1825</td>
<td>4.4</td>
</tr>
<tr>
<td>Comparison Blends (Henschel/Fielder)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/F</td>
<td>1665 / 1800</td>
<td>2.1 / 8.3</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>1865 / 2180</td>
<td>1.7 / 5.4</td>
<td></td>
</tr>
<tr>
<td>Q20</td>
<td>1935 / 1960</td>
<td>1.9 / 7.9</td>
<td></td>
</tr>
<tr>
<td>1P</td>
<td>1935 / 2055</td>
<td>1.9 / 6.4</td>
<td></td>
</tr>
<tr>
<td>1Q20</td>
<td>1825 / 1980</td>
<td>4.4 / 8.4</td>
<td></td>
</tr>
</tbody>
</table>
As mentioned earlier, using a constant charge sample weight removed the problem of comparing series with different bulk densities. The results thus gave a much clearer picture of the fusion characteristics of the different blends than those obtained from the two extruders, and depicted true coating level and filler effects. Brabender torques were not expected to follow the torques experienced during extrusion, particularly in the case of the Göttfert where blends were loosely packed and bulk densities extremely low.

Considering first the fusion time results for the three series uncoated, 1% coated and constant monolayer fraction, Figure 5.1, a family of curves was produced which clearly distinguished between different coating levels. "In general there was a reduction in fusion time when fine filler was introduced to the blend, with a subsequent increase as filler particle size was increased. "Any reduction in fusion time was at all times accompanied by an increase in the maximum torque experienced in the Brabender," Figure 5.3.

In the uncoated series the addition of any of the fillers generally reduced the Brabender fusion time and increased the maximum torque. Within this general reduction there was a clear trend from fine to coarse filler particles. The pattern seen in the maximum torques was very similar to that observed in the extruder. The finest filler (sample code C90) greatly increased the torque experienced in the Brabender, with a corresponding decrease in fusion time, as compared to the unfilled blend. As coarser fillers were
added to the formulation the torque readings fell and fusion times increased.

When the filler was coated with 1% by weight stearic acid this filler trend was exaggerated. Again, compared to the unfilled control blend fine fillers increased torque and reduced fusion time, but to a slightly lesser degree; as coarser coated fillers were added the torque again decreased and the fusion time rose, however, this effect compared to the uncoated fillers was greatly enhanced, such that fusion times were greater than those experienced with the unfilled blend.

With the constant monolayer fraction series a similar trend to the uncoated series was seen; the addition of filler in all cases increased torque and reduced fusion time. The results also followed the uncoated blends in that the fusion times for the filled blends never rose above that of the unfilled blend, as it had done in the 1% coated formulations. It is interesting to note that although the torques experienced by the constant monolayer fraction series are very similar to those of the uncoated and 1% coated series, fusion times were greatly increased. This may be caused by the low tap density of the constant monolayer fraction blends which therefore took longer to be compacted within the Brabender mixing chamber. This effect can be seen if one examines the traces obtained from the different series. Two such traces are shown in Figure 5.5.
Figure 5.1

Brabender Fusion Time versus Filler Type

Legend
- uncoated
- PE coated
- PE coated

Figure 5.2

Brabender Fusion Time versus Polycarb Series
Figure 5.3

Brabender Torque versus Filler Type

![Brabender Torque versus Filler Type graph]

Legend:
- Open bars: uncoated
- Closed bars: coated
- Horizontal lines: monolayer

Figure 5.4

Brabender Torque versus Polcarb Series

![Brabender Torque versus Polcarb Series graph]
Figure 5.5

Typical traces from Henschel and Fielder blends

A typical trace from a blend mixed in the Henschel shows a constantly increasing torque from its minimum to maximum value. A Fielder blend, however, starts to fuse and then appears to go through a period of further compaction before the final phase of fusion can commence, and maximum torque result. This gives a trace with similar torque values to those of the Henschel blends, but greatly different fusion times. This effect can be seen in the results from the comparison blends, Figure 5.6 and 5.7 where much larger discrepancies are seen between fusion times than torque levels.
Figure 5.6

Brabender Fusion Time versus Comparison Blends

Figure 5.7

Brabender Torque versus Comparison Blends
In the coated Polcarb series a low level of coating reduced fusion times while a high level increased these times (Figure 5.2). The uncoated filled blend (sample code P) lay between the 0.84% and 1% coating level. This trend can be picked out in the other results, if for example the fusion times of the blends MP and the two comparison blends P and IP are compared; the uncoated filler again lies in the middle (fusion times corresponding to MP, P and IP are 3.4, 5.4 and 6.4 respectively).

It is also interesting to note that when uncoated filler or constant monolayer fraction covered filler was added to the blend the resulting fusion time was less than that of the unfilled blend. However, once an excess of lubricant was added to the blend the fusion time increased rapidly so that it became greater than that of the unfilled blend.

5.2 Fusion Studies of Extrudate

5.2.1 Solvent Testing

All the extrudated pipe samples were subjected to a methylene chloride immersion test, described in section 2.4.1, used as a simple method of assessing fusion levels during processing. The only failures came from the two complete processing temperature range series in which processing profiles A and B failed. Profile C showed signs of severe swelling, which in itself does not constitute a
failure, but also slight lifting and splitting of the pipe wall.

5.2.2 Acetone Shearing Test

This technique was applied to pipe samples from all four series in an attempt to detect variation in fusion levels caused by changes in filler particle size or coating level. From the resultant micrographs it proved difficult to distinguish differences between the various extrudates, as seen in Figures 5.8 to 5.10. This suggested that each sample was well fused although the technique is purely qualitative and exact fusion levels could not be determined. It therefore proved necessary to use a much more sensitive quantitative technique to distinguish between the various extrudates; thermal analysis was chosen.

5.2.3 Thermal Analysis

The technique of thermal analysis, as described in section 2.4.2, was used to evaluate the heat of fusion ($\Delta H_f$) of all the processed samples. This was done by measuring, by means of a planimeter, the areas of the endothermic peaks 'A' and using equation 2.1 to calculate from this the heat of fusion. To convert this heat of fusion (J/g) value into a comparable percentage fusion figure complete heat of fusion curves covering a broad span of processing temperatures were constructed. This was done either by milling and compression
Acetone Shearing Test: Dark Field Illumination

Figure 5.8
Sample N/F

Figure 5.9
Sample C90

Figure 5.10
Sample 1Q20
moulding over a 170 to 215°C temperature range, or by extruding over a similar temperature range.

In an ideal world a standard curve would be produced for all the compounds on both twin screw extruders since complete fusion curves depend on both shear and heat history. However, as mentioned before, access to the two extruders was limited and in the first instance it was only possible to construct complete curves through milling and compression moulding. Subsequently time permitted only two complete runs to be carried out on the Krauss-Maffei extruder. Results from both methods are included here for completeness.

A maximum heat of fusion value was taken from these curves and using the following equation the values for $\Delta H_f$ could then be related to a percentage fusion level:

\[
\% \text{ fusion} = \frac{\Delta H_f}{\Delta H_{\text{max}}} \times 100
\]

(5.1)

where $\Delta H_f$ - experimental value for heat of fusion (J/g)

$\Delta H_{\text{max}}$ - maximum heat of fusion (J/g)

The heat of fusion values were calculated as an energy value per gram of PVC. Therefore the values obtained from the filled compositions were corrected on a weight basis from ashing results, thus providing a comparable energy value.
5.2.3.1 Compression Moulded Samples

The technique used for the production of compression moulded plaques is described in sections 2.2.3 and 2.2.4. This produced samples which had been exposed to a range of temperatures from 170 to 215°C. From these, small specimens were taken and assessed for their heat of fusion ($\Delta H_f$) and their 'B' onset temperature. Two blend formulations were assessed in this way, samples N/F and C90, both of which had been blended in the Henschel mixer. The results are listed in Table 5.2 and plotted in Figure 5.11.

Table 5.2

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>'B' Onset Temp. (°C)</th>
<th>$\Delta H_f$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/F</td>
<td>169</td>
<td>1.6</td>
</tr>
<tr>
<td>N/F</td>
<td>172</td>
<td>2.0</td>
</tr>
<tr>
<td>N/F</td>
<td>181</td>
<td>4.1</td>
</tr>
<tr>
<td>N/F</td>
<td>188</td>
<td>5.4</td>
</tr>
<tr>
<td>N/F</td>
<td>205</td>
<td>8.6</td>
</tr>
<tr>
<td>N/F</td>
<td>213</td>
<td>9.3</td>
</tr>
<tr>
<td>N/F</td>
<td>218</td>
<td>10.1</td>
</tr>
<tr>
<td>C90</td>
<td>167</td>
<td>1.2</td>
</tr>
<tr>
<td>C90</td>
<td>182</td>
<td>3.4</td>
</tr>
<tr>
<td>C90</td>
<td>193</td>
<td>4.9</td>
</tr>
<tr>
<td>C90</td>
<td>194</td>
<td>5.3</td>
</tr>
<tr>
<td>C90</td>
<td>197</td>
<td>6.6</td>
</tr>
<tr>
<td>C90</td>
<td>210</td>
<td>9.3</td>
</tr>
<tr>
<td>C90</td>
<td>217</td>
<td>10.2</td>
</tr>
</tbody>
</table>
5.2.3.2 Complete Extrudate Range

Two blends, sample code C90 and 1C90, were extruded in the Krauss-Maffei extruder over a complete processing temperature range, as given in Table 2.9. The resultant pipes were similarly assessed for their heat of fusion ($\Delta H_f$) and 'B' onset temperature. It unfortunately proved impossible to form a pipe from temperature profile A. However, as it was the high end of the temperature scale (profiles E and F) which was important in finding a maximum heat of fusion value, profile A was ignored. The results from each temperature range are listed in Table 5.3 and plotted in Figure 5.12.

Table 5.3

<table>
<thead>
<tr>
<th>Thermal Analysis of Complete Extruded Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipe Code</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>C90B</td>
</tr>
<tr>
<td>C90C</td>
</tr>
<tr>
<td>C90D</td>
</tr>
<tr>
<td>C90E</td>
</tr>
<tr>
<td>C90F</td>
</tr>
<tr>
<td>1C90B</td>
</tr>
<tr>
<td>1C90C</td>
</tr>
<tr>
<td>1C90D</td>
</tr>
<tr>
<td>1C90E</td>
</tr>
<tr>
<td>1C90F</td>
</tr>
</tbody>
</table>
Figure 5.11

Thermal Analysis of Compression Moulded Samples

Figure 5.12

Thermal Analysis of Complete Extrudate Range
As expected in all four fusion curves the degree of fusion increased with increasing processing temperature, with a distinct transition taking place around 200°C. It can be seen that between 185 and 200°C small changes in the melt temperature produced substantial increases in the degree of fusion, while beyond 200°C relatively large changes in the melt temperature produced little change in the degree of fusion. Similar findings have been reported by several authors\(^1,74,76\) who have shown that the transition is due to changes in flow units in the melt. At low melt temperatures (180°C) primary particles are the main flow units present in the melt, allowing few sites for cross-linking. As the melt temperature increases many of these primary particles are destroyed and secondary crystallites form upon cooling. It is at this stage that a small increase in temperature produces a large increase in the degree of fusion. Above 200-205°C no primary particles remain, therefore little further change can take place and curves tend to level off.

It is interesting to note that blends exposed to comparable temperatures in the two processing routes had much higher fusion levels when extruded. This is as expected as both temperature and shear affect fusion level.

5.2.3.3 Heats of Fusion

From the complete fusion curves the maximum heat of fusion was taken as 9.9 J/g. That is, the maximum value from the complete extrusion runs; as this had obviously followed
the same fusion mechanism as that of the series pipe samples. Percentage fusion levels for the pipe samples were calculated according to equation 5.1. The results are given in Table 5.4.

A family of curves was produced from the three series uncoated, 1% coated and constant monolayer fraction, Figure 5.13. In all cases the addition of fine filler greatly increased the fusion level in the pipe. This effect decreased as coarser fillers were added to the blend. When fusion percentage is plotted against filler specific surface area this effect becomes even more obvious, Figure 5.14.

Considering first then the uncoated series, fine filler dramatically increased fusion levels, such that at quite normal processing temperatures (as used in this project) the pipe was almost 100% fused. As filler particle size was increased fusion levels dropped rapidly, to almost plateau out at slightly under unfilled levels as the coarsest fillers were added.

The coating of the filler with 1% stearic acid seemed to generally reduce the fusion level. This seems particularly true if one considers that the 1% coated series saw, on average, an 8°C higher processing temperature than the uncoated series. It is also a clear effect if one considers the results from the Göttfert comparison blends, Figure 5.15. (Sample 1P60 gave a particularly high reading due to the high processing temperature it was exposed
to, Appendix C.3.). The fusion level reduction was also similar to that achieved through Brabender work.

Within the constant monolayer fraction series fusion level variations were not as great as might be expected. This could possibly be due to the loss of filler during blending, with only 8phr remaining in the blend, and the low bulk density of the powder blends. A similar effect of particle size on fusion level was however present, and can be demonstrated if one plots percentage fusion against filler specific surface area (Figure 5.14).

From this figure it is clear that the presence of 14phr of filler in the blend produces a broad range of fusion levels whether the filler is coated or not. In the constant monolayer fraction series, containing only 8phr filler, the spread of fusion levels is much smaller, although each filler does have an obvious effect on fusion. It is interesting to note that the finest particle sized filled blend (sample code MC90) raises the fusion level to as high a value as sample code 1C90 (containing 14phr of filler).

It is when one looks at the Polcarb coated series that one sees an obvious effect of coating level, Figure 5.16. Here fusion levels were only increased from the uncoated sample when very small levels of stearic acid were introduced into the blend (sample code 0.3P). As more stearic acid was added fusion levels fell in a very constant manner. This effect was similar to that experienced in the Brabender, where the more highly coated fillers caused fusion times to
### Table 5.4

**Heat of Fusion of Pipe Samples**

<table>
<thead>
<tr>
<th>Pipe Code</th>
<th>°C Onset Temp.</th>
<th>$H_f$ (J/g)</th>
<th>% Fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/F</td>
<td>185</td>
<td>5.8</td>
<td>58.6</td>
</tr>
<tr>
<td>C90</td>
<td>187</td>
<td>9.6</td>
<td>97.0</td>
</tr>
<tr>
<td>P</td>
<td>186</td>
<td>7.4</td>
<td>74.7</td>
</tr>
<tr>
<td>P60</td>
<td>186</td>
<td>5.9</td>
<td>59.6</td>
</tr>
<tr>
<td>Q300</td>
<td>185</td>
<td>5.7</td>
<td>57.6</td>
</tr>
<tr>
<td>Q20</td>
<td>183</td>
<td>5.6</td>
<td>56.6</td>
</tr>
<tr>
<td>N/F</td>
<td>192</td>
<td>5.9</td>
<td>59.6</td>
</tr>
<tr>
<td>1C90</td>
<td>194</td>
<td>8.9</td>
<td>89.9</td>
</tr>
<tr>
<td>1P</td>
<td>194</td>
<td>7.3</td>
<td>73.7</td>
</tr>
<tr>
<td>1P60</td>
<td>199</td>
<td>8.0</td>
<td>80.8</td>
</tr>
<tr>
<td>1Q300</td>
<td>192</td>
<td>5.7</td>
<td>57.6</td>
</tr>
<tr>
<td>1Q20</td>
<td>191</td>
<td>5.2</td>
<td>52.5</td>
</tr>
<tr>
<td>N/F</td>
<td>190</td>
<td>5.4</td>
<td>54.5</td>
</tr>
<tr>
<td>MC90</td>
<td>200</td>
<td>8.9</td>
<td>89.9</td>
</tr>
<tr>
<td>MP</td>
<td>193</td>
<td>6.9</td>
<td>69.7</td>
</tr>
<tr>
<td>MP60</td>
<td>194</td>
<td>7.4</td>
<td>74.7</td>
</tr>
<tr>
<td>MQ300</td>
<td>193</td>
<td>6.8</td>
<td>68.7</td>
</tr>
<tr>
<td>MQ20</td>
<td>193</td>
<td>7.0</td>
<td>70.7</td>
</tr>
<tr>
<td>P</td>
<td>195</td>
<td>7.6</td>
<td>76.8</td>
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<tr>
<td>0.3P</td>
<td>194</td>
<td>7.7</td>
<td>77.8</td>
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<tr>
<td>0.5P</td>
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<tr>
<td>0.84P</td>
<td>194</td>
<td>7.1</td>
<td>71.7</td>
</tr>
<tr>
<td>1P</td>
<td>193</td>
<td>6.9</td>
<td>69.7</td>
</tr>
<tr>
<td>2P</td>
<td>193</td>
<td>6.8</td>
<td>68.7</td>
</tr>
<tr>
<td>3P</td>
<td>193</td>
<td>6.4</td>
<td>64.6</td>
</tr>
</tbody>
</table>

**Comparison Blends (Krauss/Gottfert)**

<table>
<thead>
<tr>
<th>Pipe Code</th>
<th>°C Onset Temp.</th>
<th>$H_f$ (J/g)</th>
<th>% Fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/F</td>
<td>185 / 190</td>
<td>5.8 / 5.4</td>
<td>58.6 / 54.5</td>
</tr>
<tr>
<td>P</td>
<td>186 / 197</td>
<td>7.4 / 7.6</td>
<td>74.7 / 76.8</td>
</tr>
<tr>
<td>Q20</td>
<td>183 / 195</td>
<td>5.6 / 7.2</td>
<td>56.5 / 72.7</td>
</tr>
<tr>
<td>1P</td>
<td>194 / 196</td>
<td>7.3 / 6.8</td>
<td>73.7 / 68.9</td>
</tr>
<tr>
<td>1Q20</td>
<td>191 / 196</td>
<td>5.2 / 5.7</td>
<td>52.5 / 57.6</td>
</tr>
</tbody>
</table>
Figure 5.13
Heat of Fusion versus Filler Type

Figure 5.14
Heat of Fusion versus Filler Surface Area
Figure 5.15

Heat of Fusion versus Comparison Blends

Figure 5.16

Heat of Fusion versus Polcarb Series
increase, and the uncoated blend (sample code P) lay between the 0.84% and 1% coated samples.

From these results it would seem that at high filler levels, in the Krauss extruder, filler particle size has a much greater effect than coating level on fusion, whilst at lower filler levels in the Göttfert the reverse is true.
CHAPTER 6

MECHANICAL PROPERTY RESULTS

Extrudates were tested for uniaxial tensile strength using a J.J Lloyd universal testing machine and for impact strength using an instrumented tester, the Rosand instrumented falling weight impact tester (type 5A), as described in sections 2.4.4 and 2.4.5 respectively.

6.1 Tensile Testing

Although several authors (77,79,103,105,124) have previously investigated tensile properties of rigid PVC, and how these are affected by changes in fusion levels, it is evident from literature (section 1.8.1) that there are still many conflicting opinions.

Yield parameters have generally been reported to be independent of fusion levels (79,103,104,124), although some authors (77,105) have found other relationships. Post-yield parameters have, in general, shown a different trend, either by increasing with increasing fusion (75,79,105), or by exhibiting an optimum value (77,111). Throughout the literature however, little work has been carried out on either the effect of filler particle size or filler coating level on the final tensile properties of the extrudate.

Thus with the aim of establishing a relationship between fillers, fusion and tensile properties all extrudates
were tensile tested. The specimens were cut in a direction parallel to the direction of extrusion and tested at room temperature at a rate of 5mm/min. The details of the experimental procedure along with methods of obtaining the tensile parameters are presented in section 2.4.4.

A series of the typical force-extension curves obtained is shown in Figure 6.1. As can be seen, an extension produced an instantaneous elastic response which became increasingly non-linear as plastic deformation was introduced and increased in magnitude. All the samples showed a well defined yield point, from which yield stress could be determined very precisely. At this yield point a neck was formed, and the formation of bands of sheared material and voids through crazing caused stress whitening to occur. The specimens did not elongate uniformly, but a constriction formed at the yield in the specimen where very large molecular orientation was developed. The restricted area 'grew' in both directions towards the specimen clamps. The cross sectional area of the drawn portion remaining constant during the stretching until eventually local stresses caused failure of the specimen.\(145\)

The results of yield stress, stress at break and elongation at break measurements from all four filled series are given in Table 6.1. From standard deviation measurements (equation 2.4) it was clear that experimental scatter was quite high. This was particularly true for those measurements made at break, where the effect of flaws in the
pipe would be much greater. It should be noted here that the elongation at break measurements were not made using an extensometer, but simply by measuring the specimen's extension from the force-distance graphs.

When considering the results from the comparison blends it should be remembered that the two coated blends extruded in the Krauss experienced a higher 'B' onset temperature (approximately 8°C higher). Although this did not seem to affect dramatically their fusion levels, Figure 5.15, it obviously had some effect on their tensile properties. This effect can be clearly seen if one compares the results from the two unfilled control blends (N/F) in the uncoated and the 1% coated series.

As an additional study the series of blends extruded over a complete processing temperature range (used to construct complete fusion curves) were also tensile tested under identical conditions. This gave an indication of the effect of processing temperature on the tensile strength of filled pipe with the same formulation as used in this project, the results are presented in Table 6.2.

6.1.1 Yield Stress

The results indicate that variations in the filler particles' specific surface area had little effect on the pipes' yield properties, Figure 6.2. However, it is clear that the addition of 14phr of filler does, in all cases, reduce the pipes' strength at yield. The introduction of
Figure 6.1

Figure 6.2

Yield Stress versus Filler Type

Legend
- uncoated
- 1% coated
- monolayer
filler to the constant monolayer fraction series (extruded in
the Göttfert) seemed to have no obvious damaging effect on
the yield stress ($\sigma_y$). This was probably due to the much
lower levels of filler present (approximately 7 to 8 phr),
Figure 6.2.

A significant difference in $\sigma_y$ was observed between the
uncoated and 1% coated series. This increase observed on
coating was supported by the results from the comparison
blends, where the $\sigma_y$ of both filled samples extruded in
either extruder was increased by coating the filler with
stearic acid, Figure 6.3. This effect was much larger than
that obtained by a change in filler particle size. However,
it must be noted that the unfilled pipe sample (N/F in the 1%
coated series) also had an increased $\sigma_y$. These differences
are therefore thought to be partially due to the time lapse
between testings, and the different processing temperatures
experienced by the two series (Appendix C.3).

The higher $\sigma_y$ of the constant monolayer fraction series
was thought to be mainly due to the variation in filler level
actually present in the pipe. Pepper (136) recently found
increasing filler levels in the 0 to 20phr range dramatically
reduced $\sigma_y$. Higher $\sigma_y$ could also be as a result of the
different method of sample preparation, or the increased
thickness of the samples, which although corrected for in the
calculations would reduce the influence of flaws or scratches
in the specimen.
Figure 6.3

Yield Stress versus Comparison Blends

Figure 6.4

Yield Stress versus Polcarb Series
For the pipe extruded in the Krauss where high levels of filler were present the coating of the filler obviously improved the yield properties. One would expect this effect to be clearly seen in the fourth series where one filler was coated over a range of levels. However, the loss of filler during dry blending reduced the filler effect on yield so coating had virtually no effect on the $\sigma_y$. This can be seen from the coated Polcarb series Figure 6.4.

Thus the level of addition of filler obviously has a marked effect on yield properties. The difference between Krauss-Maffei extruded pipe (containing approximately 14phr of filler) and Göttfert pipe (containing approximately 8phr of filler) is clearly evident, the higher filler levels dramatically reducing the strength of the pipe. This effect seemed to be somewhat alleviated when the filler was coated.

### 6.1.2 Post Yield Parameters

#### 6.1.2.1 Stress at Break

The pipe samples' stress at break ($\sigma_B$) and percentage elongation at break ($\varepsilon_B$) were analysed and the results given in Table 6.1.

Considering first the five comparison blends one can see very similar trends present to those obtained from yield stress results, Figure 6.5. Once again the difference in filler level between the Göttfert and Krauss blends has a marked influence on the effect the filler has on tensile properties. As with yield, when 14phr of uncoated filler was
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<tr>
<th>Pipe code</th>
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<th>Stress at break (MN/m²)</th>
<th>Elongation at break (%)</th>
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<td>41.7 3.0</td>
<td>161 4.5</td>
</tr>
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<td>176 3.6</td>
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<td>160 6.1</td>
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<td>159</td>
<td>3.8</td>
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<td>7.8</td>
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<tr>
<td>0.84P</td>
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<td>4.8</td>
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</tbody>
</table>

Comparison Blends (Krauss/Göttfert)

<p>| | | | | |</p>
<table>
<thead>
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<th></th>
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<tbody>
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<td>N/F</td>
<td>41.3</td>
<td>50.7</td>
<td>186</td>
<td>175</td>
</tr>
<tr>
<td>P</td>
<td>37.0</td>
<td>49.5</td>
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<td>171</td>
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<td>42.9</td>
<td>51.5</td>
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<td>172</td>
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<tr>
<td>1Q20</td>
<td>43.2</td>
<td>51.8</td>
<td>156</td>
<td>175</td>
</tr>
</tbody>
</table>

added the pipes' $\sigma_B$ property was greatly reduced. As the filler particle size was increased this deterioration was somewhat improved. Coating the filler produced a vast improvement in $\sigma_B$ and seemed to even-out filler particle size effects. In the less highly filled Gottfert blends these effects could still be seen, but to a much lesser extent.

When one looks at the uncoated series, Figure 6.6, one can see the effect of increasing filler particle size gradually increasing the ultimate strength of the pipe; after
Figure 6.5

Break Stress versus Comparison Blends

Figure 6.6

Break Stress versus Filler Type
the initial decrease through the introduction of the filler. The increase in $\sigma_B$ seemed to reach a plateau, with pipe sample Q20 (containing the largest filler particles) actually showing a slight decrease in $\sigma_B$. This effect is by no means certain, however, due to the relatively large recorded experimental scatter.

Once the fillers were coated with stearic acid the pipes' ultimate strength properties in general improved; Figure 6.6, although these results may again be somewhat affected by the increased processing temperature experienced in the pipe. This effect, however, was not true of sample 1C90 which contained the smallest particle sized filler. Here $\sigma_B$ remained low in comparison to the other coated blends.

In the constant monolayer fraction series, Figure 6.6, where a lower level of filler was present, ultimate strength properties did not obviously drop with the presence of filler, and only a slight increase in $\sigma_B$ was seen with increasing filler particle size. At this low filler addition level variation of stearate coating level also seemed to have very little effect on the pipes' ultimate strength; as seen from the coated Polcarb series, Figure 6.7. Variations within this series were inside the band of experimental scatter, apart from the highest coated sample, 3P, which had a slightly lower ultimate strength.

Previous workers have in general found post yield parameters (both $\sigma_B$ and $\varepsilon_B$) to be sensitive to variations
in fusion level. Covas (124) found that for test temperatures below \( T_g \) both \( \sigma_B \) and \( \epsilon_B \) reached a maximum for fusion levels between 65 and 85% corresponding to a processing temperature in the range 193-203°C.

If one studies the results from thermal analysis work (section 5.2.3) one can see that in each series the sample containing the smallest particle sized filler (samples C90, 1C90, and MC90) lies above the 85% fusion level; while five coarser samples (Q20, 1Q20, Q300, 1Q300 and P60) lie below 65% fusion. From the results presented here it would seem that the ultimate strength of the pipe is very sensitive to highly fused pipe, which greatly reduces this parameter, but not so sensitive to less well fused pipe, Figure 6.8. In particular, once coated, particle size and thus fusion level seems to have less effect, although the highly fused 1C90 blend still has a very poor \( \sigma_B \) value. Once the filler level in the pipe drops to 8phr these effects become a lot less obvious although similar trends are still present.

As far as the coated Polcarb series is concerned only sample code 3P has a particularly low fusion level, explaining its lower tensile strength.

6.1.2.2 Elongation at Break

In general elongation at break results closely resembled those of stress at break. Experimental scatter was, in all cases, high and results should not be taken as an
Figure 6.7

Break Stress versus Polcarb Series

Figure 6.8

Break Stress versus Fusion Level

Legend:
- uncoated
- 1% coated
- monolayer
accurate measure as an extensometer was not used. They are, however, included here for completeness.

6.1.3 Processing Range Samples

An attempt was made to clarify the effect of fusion level on the tensile properties of the pipe produced in this project. To do this the two pipe samples which had been extruded over a wide processing temperature range (and which had been used to construct complete fusion curves, section 5.2.3.2) were tensile tested. The results are given in Table 6.2, with elongation at break plotted graphically in Figure 6.9.

From the results obtained it can be seen that yield parameters are insensitive to variations in the degree of fusion. This insensitivity agrees well with results reported by other authors\(^{(79,103,124)}\), and helps confirm the theory that yield is independent of the relative coherence of the entanglement network or the number of crystalline junctions, and that it must be related to a molecular relaxation processes.

Post yield parameters, however, are clearly more dependent on fusion levels, with an optimum fusion level for \(\sigma_B\) existing between, very approximately, a 75 and 95% fusion level. This corresponds to a processing temperature of between 185 to 199°C. The highest \(\sigma_B\) values seemed to lie at a higher fusion level when the filler was coated.
Elongation to break results, Figure 6.9, tend to show a general increasing effect with fusion level reaching a maximum at a processing temperature of approximately 205°C. The very low figure for $\varepsilon_B$ calculated for sample 1C90 F is though to be a dubious result due to its large standard deviation figure.

Table 6.2

<table>
<thead>
<tr>
<th>Pipe code</th>
<th>(% fusion)</th>
<th>Yield stress ($\sigma_y$)</th>
<th>Stress at break ($\sigma_B$)</th>
<th>Elongation at break ($\varepsilon_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C90 B</td>
<td>(43)</td>
<td>42.8 1.9</td>
<td>43.5 3.7</td>
<td>103 8.8</td>
</tr>
<tr>
<td>C</td>
<td>(78)</td>
<td>40.5 0.9</td>
<td>44.0 3.4</td>
<td>135 7.7</td>
</tr>
<tr>
<td>D</td>
<td>(84)</td>
<td>38.6 2.3</td>
<td>43.8 2.9</td>
<td>163 6.7</td>
</tr>
<tr>
<td>E</td>
<td>(99)</td>
<td>38.1 1.5</td>
<td>40.8 2.5</td>
<td>167 8.5</td>
</tr>
<tr>
<td>F</td>
<td>(100)</td>
<td>40.0 3.0</td>
<td>40.2 3.7</td>
<td>168 7.1</td>
</tr>
<tr>
<td>1C90 B</td>
<td>(17)</td>
<td>42.1 2.3</td>
<td>40.2 1.2</td>
<td>87 6.8</td>
</tr>
<tr>
<td>C</td>
<td>(67)</td>
<td>40.2 2.0</td>
<td>39.8 2.7</td>
<td>113 6.8</td>
</tr>
<tr>
<td>D</td>
<td>(83)</td>
<td>40.7 0.5</td>
<td>41.1 2.7</td>
<td>139 6.6</td>
</tr>
<tr>
<td>E</td>
<td>(93)</td>
<td>43.1 2.0</td>
<td>44.0 1.4</td>
<td>140 5.9</td>
</tr>
<tr>
<td>F</td>
<td>(97)</td>
<td>42.8 1.0</td>
<td>40.5 2.0</td>
<td>120 13.0</td>
</tr>
</tbody>
</table>
6.2 Impact Testing

Numerous reports can be found in literature as to the behaviour of the impact strength of rigid PVC with varying fusion level. Most agree that an increase in impact strength is observed with increased fusion level, although the presence of a maximum is as yet unclear. Comparisons between authors are complicated by the existence of various impact test types and procedures.

Few reports exist, however, on the effect of filler particle size and coating level on impact strength. Recently Pepper (136) studied the effect of varying filler levels on the impact strength of rigid PVC pipe. He used a similar procedure to that used here and found the presence of filler
greatly affected the impact strength of the pipe, such that an increase in filler addition from 10 to 20phr reduced the pipes' failure energy from 10 to 2 J/mm.

In this study complete sections of pipe from each sample were tested on a Rosand instrumented drop weight impact tester; the experimental details are given in section 2.4.5. The results from all four series are tabulated in Table 6.3, with the results from the processing range extrudates given in Table 6.5.

The Rosand impact tester measured both peak and failure values, however, only the results from the peak values will be presented here as interference between the two pipe walls often produced unrealistic failure readings. As can be seen from the tabulated results trends in the series were demonstrated by all three parameters: peak force, deflection and energy. However, when comparing the pipe samples impact strength peak energy values will be used as these gave the most reproducible results. (The peak force results frequently had a standard deviation of between 80 to 100.)

As pipes of different thickness were being tested (wall thickness 1mm and 2mm from the Krauss and Göttfert respectively) pipe sections were measured and peak values were standardised. Although this then produced similar results from the two extruders the effects on impact strength of such large differences in wall thickness is not thought to be normalised that easily, and direct comparison of results from the different extrusion series should not be made.
6.2.1 Filled Series

Considering first the uncoated series, it is initially interesting to note the mode of failure of the pipe. From the tests it was clear that the unfilled pipe failed in a ductile/brittle manner, with the introduction of filler at 14phr producing a more brittle pipe. As coarser fillers were added to the blend this brittleness increased, independent of the fusion level of the pipe. This effect can be clearly seen from the shape of the force-distance graphs. A typical force-extension plot of each sample is shown in Figures 6.10 to 6.15.

From this argument it seems reasonable that as the brittleness of the pipe increased so the peak energy should decrease. This, however, was clearly not the case, with the peak energy going through a maximum value as coarser fillers were added to the blend, Figure 6.16. This optimum value corresponded to a fusion level in the pipe of between approximately 60 to 70% which agrees well with the findings of other authors.

![Figure 6.10 N/F](Image)

![Figure 6.11 C90](Image)
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Figure 6.12 P

Figure 6.13 P60

Figure 6.14 Q300

Figure 6.15 Q20

Figure 6.17 N/F

Figure 6.18 1C90

Figure 6.19 1P

Figure 6.20 1P60
Once the filler was coated with 1% stearic acid the pipe generally seemed to become more brittle, this can be seen from the force-distance graphs, Figures 6.17 to 6.22. The embrittlement reduced the peak impact energy of the pipe but left it still with a well defined maximum value at the same 60 to 70% fusion level, Figure 6.23.

The monolayer covered series which contained only 7phr of filler did not show increasing embrittlement as coarser fillers were added. Instead peak energy values remained quite constant fluctuating only slightly with the fusion level in the pipe, Figure 6.23. It is evident from this, and from the two series previously discussed, that the presence
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of filler in a pipe can improve its impact performance. It is also clear that the level of filler, its particle size and coating, and the fusion level in the pipe can have a dramatic effect on impact properties.

When considering the coated Polcarb series one must remember again that only 7phr of filler were present. Fluctuations in fusion and thus impact energy were slight in comparison to the higher filled blends. However, a trend corresponding to changes in fusion level was again evident, with peak impact energies lying between 60 to 73% fusion.

Coating the filler at a low level initially increased the fusion level above 77% fusion, as more stearic acid coating was added the fusion level dropped to 71.7% (sample code 0.84P) where impact strength was at its greatest. Increased coating dropped the fusion level further until at sample code 3P it was as low as 65%, with a corresponding slight fall in impact strength, Table 6.3, Figure 6.24.

Figure 6.21 1Q300  Figure 6.22 1Q20
Figure 6.23

Impact Strength versus Fusion Level

Figure 6.24

Impact Strength versus Polcarb Series
<table>
<thead>
<tr>
<th>Pipe code</th>
<th>Peak force (N/mm)</th>
<th>Peak defl. (mm)</th>
<th>Peak energy (J/mm)</th>
<th>Mode of failure</th>
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<td>1444</td>
<td>21.15</td>
<td>18.78</td>
<td>2.91</td>
</tr>
</tbody>
</table>

Mode of failure
- **D** ductile
- **DB** ductile / brittle, failure takes place after peak force has been reached
- **BD** brittle / ductile, failure takes place before peak force has been reached
- B brittle, failure takes place after elastic deformation only
6.2.2 Comparison Blends

From the comparison blend results, Table 6.4 and Figure 6.25, one can see that the addition of filler slightly embrittles the pipe. This is particularly noticeable when filler is added at the higher level of 14phr. At this higher level coarser fillers have a much more damaging effect upon impact energies than finer ones. The addition of filler at 14phr or 7phr can have a beneficial effect upon impact energy, however, to achieve this fusion in the pipe must remain at the 60 to 70% level.

Table 6.4

<table>
<thead>
<tr>
<th>Pipe code</th>
<th>Peak force (N/mm)</th>
<th>Peak defl. (mm)</th>
<th>Peak energy (J/mm)</th>
<th>Mode of failure</th>
</tr>
</thead>
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<td>17.81 / 19.89</td>
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<td>1421 / 1459</td>
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</tr>
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<td>1244 / 1531</td>
<td>28.25 / 20.87</td>
<td>14.31 / 19.95</td>
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</tr>
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</tr>
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<td>1266 / 1483</td>
<td>28.85 / 20.73</td>
<td>14.61 / 18.90</td>
<td>BD/B / DB</td>
</tr>
</tbody>
</table>

6.2.3 Processing Range Samples

Results from the complete extrusion processing temperature range are presented in Table 6.5 and Figure 6.26, and are included here for completeness. They indicate that impact strengths can remain high for fusion levels of up to 85% and also seem to indicate that the addition of a 1%
stearic acid coating although only slightly reducing fusion levels greatly reduces impact strength.

Table 6.5

<table>
<thead>
<tr>
<th>Pipe code</th>
<th>(% fusion)</th>
<th>Peak force (N/mm)</th>
<th>Peak defl. (mm)</th>
<th>Peak energy (J/mm)</th>
<th>Mode of failure</th>
<th>s.d</th>
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<td>C90 B</td>
<td>(43)</td>
<td>804</td>
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<td>7.98</td>
<td>1.46</td>
<td>B</td>
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<td>C</td>
<td>(78)</td>
<td>888</td>
<td>24.63</td>
<td>10.54</td>
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<td>D</td>
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<td>1387</td>
<td>30.41</td>
<td>17.51</td>
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<td>1214</td>
<td>29.90</td>
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<td>27.31</td>
<td>11.67</td>
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Figure 6.25
Impact Strength versus Comparison Blends

Impact Strength versus Processing Samples

Legend
- Kraus
- Gutflecht

Legend
- C20
- C30
CHAPTER 7

DISCUSSION OF RESULTS

7.1 Introduction

Although several authors (20, 23, 27, 28, 31, 33) have previously studied the effect of fillers in rigid PVC, the most recent being Pepper (136) who examined the effect of filler level on fusion and properties, there are still no clear explanations as to many of their characteristics. This is particularly true in relation to their particle size where reports are varied and often conflicting.

The objectives of this project were thus to understand more fully the effects that different particle sized calcium carbonate fillers, and different filler coating levels, have on the fusion and properties of rigid PVC. To this aim the discussion will be based on the results presented in Chapters 4 to 6, and will include hypotheses from previous workers, where these are relevant.

The chapter will be divided into several sections considering firstly the effect of the two different processing routes used in this project. The remaining discussion will be split into two sections covering:
- the effects of various particle sized uncoated fillers and the consequences of coating these fillers with 1% by weight stearic acid
the effects of the same fillers coated by a constant monolayer fraction coverage and the results of coating one chosen filler over a range of levels.

Throughout the course of these discussions one must be aware of the influence that the various processing routes had on the fusion and final properties on the pipe. To clarify these effects a control consisting of five blends was prepared by both processing routes, that is; the Henschel mixer and Krauss-Maffei extruder, and the Fielder mixer and Göttfert extruder. The findings from this control will be presented here as comparisons between series cannot be made without a basic understanding of these influences. (The five blends used in the control were coded N/F, P, Q20, 1P, 1Q20).

7.1.1 Analysis of Dry Blenders

During the course of this project two dry blenders were used, a 40 litre Henschel and an 8 litre T.K. Fielder. The Henschel was used to prepare two series, the uncoated and the 1% coated, while the Fielder blended the constant monolayer fraction series and the coated Polcarb series. The blend properties were compared by use of ash analysis, scanning electron microscopy and bulk density, with the results presented in section 4.1.

It was clear from these studies that the two mixers produced widely different blends, with two dissimilarities being particularly apparent.
One became clear from ash analysis results, which gave an indication of the level of filler remaining in the mix after blending. These results showed that those mixes blended in the Henschel gave an average final filler level of 14.3phr, whether coated or uncoated, as compared to the 15phr initially hand mixed into the blends, while the mixes blended in the Fielder gave a much lower final filler level of 7.6phr. The loss of filler in the Fielder was clearly seen in the form of a 'cake' coating the walls of the heated mixing chamber. Attempts were made to reduce this 'cake' by both increasing the mixing time (by reducing the initial mixing chamber jacket temperature), and by reducing the charge weight of blend; these proved slightly effective. The formation of the 'cake' seemed to be unaffected by the presence of a stearic acid filler coating.

The formation of a 'cake' on the chamber wall surface also had the effect of reducing the heat transfer rate from the heated jacket to the blend, and reducing the number of particles present to create frictional heat. The blends in the Fielder thus took over twice as long to reach their discharge temperature as those in the Henschel.

The other marked difference between the blends was their bulk (tap) densities. From the tap density results of the comparison blends mixed in the Henschel it was clear that filler increased the final blend's bulk density, with coarser fillers having the greatest positive effect. Filler did not so obviously increase the bulk densities of the comparison
blends mixed in the Fielder, although increases were again seen from fine to coarse fillers, Figure 7.1.

To understand this behaviour the dry blends were examined using a scanning electron microscope fitted with X-ray analysis facilities; this produced micrographs of the blends accompanied by calcium element maps. From these both the PVC's final grain shape, and the location of filler over the grain's surface, could be investigated.

From these micrographs it became clear that the mixing process in the two blenders was quite different. In the Henschel mixer the presence of the filler had a beneficial effect, both breaking down and rounding off the PVC grains. The final blend thus contained much smaller PVC particles with the filler located between the folds of the sub-grains. With the addition of coarser fillers the filler particles themselves gave the PVC grains a slightly rougher surface, although this did not seem to affect the particles packing ability. (The presence of a stearate coating on the filler did not seem to affect their abrasive role). Through this process the blends greatly increased their tap densities, an obvious advantage for a blend to be later processed through extrusion.

In the Fielder the filler presence was much less obvious, with the final PVC grain shape being very similar to that of the virgin polymer irrespective of the presence of filler in the blend. The filler again packed in the folds of the sub-grains although less was present, a lot being lost in
the 'cake' formation, but the packing ability of the grains was not enhanced and low tap densities resulted. Within the filled blends a slight increase in tap density was seen with the addition of coarser fillers, with the filler coating again having little effect.

When the two unfilled comparison blends were compared it became clear that even without the presence of filler the Henschel produced a much more compact blend, and as such seemed a more suitable mixer for the production of extrusion dry blends.

7.1.2 Analysis of Twin Screw Extruders

The differing properties of the blends produced by the two mixers obviously affected their extrusion characteristics. These differences were further complicated by the use of two different twin screw extruders (a Krauss-Maffei and a Göttfert). An attempt will be made to explain their effects.

The extrusion characteristics of the blends were evaluated in several ways including studying, output rate, extrusion torque and pressure and melt temperature.

**Output Rate**

The output rate from a twin screw extruder is generally regarded to be dependent on screw speed and blend bulk density. As the screw speeds in the two machines were kept constant (although not equal) throughout this work output
rates were expected to follow bulk density trends. This indeed happened; in the Krauss output clearly increased as filler was added to the blend, while in the Göttfert the output did not rise so rapidly, although larger variations were experienced between filled blends. Again an increase in filler particle size generally increased output in both extruders, as it had increased density (this effect was particularly obvious in the Göttfert's output where huge increases in output were experienced). Once the filler was coated output rates generally fell in both extruders the Krauss losing the filler's particle size effect while the Göttfert amplified it, Figure 7.2.

Output rates from the Göttfert were much higher than those from the Krauss-Maffei although blend densities were lower. This was thought to be due to the different screw speeds in the two machines (15rpm in the Krauss, 20rpm in the Göttfert) although the different forms of hopper feeder could also have had a small effect. (The Krauss-Maffei was fed with a horizontal variable speed dosing screw which allowed the extruder to be flood fed at all times. While the Göttfert was fitted with a vertical stuff-feeder which fed the powder blend directly onto the extruder screws; this therefore introduced the powder at the highest possible rate and could subsequently have produced a higher output rate).
Figure 7.1
Tap Density versus Comparison Blends

Figure 7.2
Extruder Output versus Comparison Blends
Extrusion Torque and Pressure

Torque readings could not be compared directly as the two extruders measured them in different units, however, the same general trends were observed in both machines. These were that the introduction of fine filler dramatically increased torque, with coating slightly reducing the effect seen in the Göttfert. This observation supports findings from previous authors who have speculated that fillers increase the melt viscosity of the polymer(141). In the presence of coarser fillers torques fell, in the Göttfert to the same level as the unfilled blend. It seems from these results that the Göttfert is a more sensitive extruder showing large differences in both torques and outputs in the presence of much smaller quantities of filler, Figure 7.3.

Pressure readings in the adaptor and die closely followed those of torque indicating that the introduction of finer fillers produced an increase in melt viscosity in both the Krauss and Göttfert.

Melt Temperature

Although extrusion temperatures on both machines were set as near to one another as possible broad variations were seen in the actual melt temperatures measured by thermal analysis. The uncoated series saw the lowest extrusion temperature at approximately 185°C with the other three series experiencing temperatures in the range 190 to 200°C. These were obviously due to equipment variations and not
to changes in formulation as the comparison blends exhibited the same deviations.

7.2 Uncoated and 1% Coated Series

This section of the discussion centres on the two series processed by way of the Henschel blender and the Krauss-Maffei extruder. That is the uncoated and 1% by weight stearic acid coated series. In both series six pipe extrudate compositions were studied - comprising five containing natural calcium carbonate fillers with varying specific surface areas (either uncoated or 1% coated), and one unfilled control composition. Each filler was incorporated into an identical base formulation.

7.2.1 Dry Blending Studies

Filler loss during blending in the Henschel was for both series consistently low with an average final filler level of approximately 14.3phr. This value supported work by Pepper(136) who, using the same blender, only experienced serious loss when filler was present in concentrations of 40 to 50 phr. Because filler loss was consistently low blending time variations between mixes were also kept to a minimum, with the only trend being a slight reduction in blending time in the presence of filler. This would have been caused by the additional frictional heat created by the presence of the filler.
Apart from characterisation through ash analysis, bulk densities of the dry blends were also measured, giving an indication of the packing ability of the particles. Here the presence of filler had a dramatic effect on results greatly increasing the bulk density of the blends. This effect was investigated further by use of SEM micrographs which showed filled blends to contain rounded smoother PVC particles. The abrasive nature of fillers has been noted by other authors\(^{(136,140)}\) and indeed the fillers do obviously wear away irregularities on the polymer grains. This produces smaller\(^{(140)}\) and more regular particles with the fillers finally preferentially filling the folds on the grain's surface. It is interesting to note that the filler's particle size did not greatly affect the final bulk density of the blend. The reason for this lies with the preferential filling of the grain folds, where even the coarsest fillers were not obtrusive enough to restrict the packing of the PVC grains.

The presence of filler coating had little effect on this process, and it therefore seemed that a high quality dry blend could be produced (on this blender) irrespective of the filler's particle size or coating.

7.2.2 Processing and Fusion Characteristics

Twin screw extrusion and Brabender torque rheometry were used to assess the influence of the various fillers, both uncoated and coated, on processing and thus fusion.
7.2.2.1 Twin Screw Extrusion

Pipe extrusions of all the samples were carried out on a laboratory sized twin screw extruder, the Krauss-Maffei KMDL 25. Four parameters were measured to assess extrusion characteristics and these were output, torque, pressure and melt temperature.

Mass output has been shown to be independent of the conditions at the die end of twin screw extruders and to depend instead on the screw speed and material bulk density. As screws were flood fed at all times and speeds kept constant output followed bulk density trends. Thus output increased as bulk density increased, and also slightly as filler specific surface area decreased, with little variation between uncoated and coated samples.

In all twin screw extruders, torque levels are designed to be kept low, and it is now widely accepted that in these conditions a fusion mechanism exists which involves the compaction, densification, fusion and elongation of the grains (CDFE mechanism)\(^{(66,85)}\). In this mechanism grains are not initially broken down, rather they are compacted together eliminating any free space between them. This process continues as primary particle agglomerates and finally primary particles themselves are compacted. As the temperature increases interparticle fusion starts to take place; but grain boundaries remain in the melt until they pass through the high shear adaptor and head regions of the extruder. Here grain elongation takes place, finally
Figure 7.3
Extruder Torque versus Comparison Blends

Figure 7.4
Extruder Torque versus Filler Type
creating a network of molecules linked by small or imperfect crystallites formed during cooling.

From the torque results, which are reprinted here for ease of reference Figure 7.4, it can be seen that the presence of filler dramatically increased the torque in the extruder, which in turn reflected variations in the viscosity and fusion pattern of the melt. The filler must therefore be having some effect on the fusion and elongation stages of the melt. These stages take place once the resin has been fully compacted, and here the abrasive nature of the filler may help to break down the final grain and primary particle boundaries to form a fully fused homogeneous pipe. If this were the case then it would be expected that the finer fillers with their larger specific surface areas would be more effective in breaking down the boundaries and increasing the fusion rate. This would be especially true of the finest filler Carbital 90 which is derived from marble deposits, the other fillers all being based on softer chalk deposits.

Whatever the explanation fine fillers produced much higher torques during extrusion. This trend was exaggerated in the presence of filler coating with fine fillers producing higher torques and coarse fillers lower. The coating had a similar effect on Brabender torques and an explanation of this will be given in the following section.

One unexplained result from the processing studies was the large increase in processing temperature experienced by the 1% coated blends and determined through thermal analysis.
This result was thought to be independent of the formulation changes, and caused instead by equipment variation due to the time gap between the two series' extrusion runs, during which the Krauss-Maffei was left idle.

7.2.2.2 Brabender Torque Rheometry

The Brabender torque rheometer is commonly used in industry as a quick and simple method of collecting data (such as fusion times and torque levels) on a material in an environment similar to that which it would experience in an extruder. In this study it was hoped that the Brabender fed with a constant charge weight would not be as greatly affected by bulk density variations as the extrusion characteristics, the results would therefore give a clearer indication of the effects of the filler's particle size and coating level on fusion and torque. Recent research has shown that the PVC resin in a Brabender undergoes a different fusion mechanism to that which occurs in a twin screw extruder (66), so direct comparisons should not be made.

It is now widely accepted that in high torque machines, of which the Brabender is one, the PVC grains are broken down into primary particles. These particles are then compacted and sintered with interdiffusion taking place between them and their microdomains. The boundaries between the primary particles thus disappear, and an entangled three dimensional network is finally formed. (This fusion mechanism can be
related more directly to a single screw rather than a twin screw extruder, where much lower torques were experienced).

Thus, from the findings of previous authors(62,77), it is clear that the PVC resin follows different mechanisms of fusion in the two processes. It is therefore quite probable that the filler itself plays a different role, though as can be seen from the results, Figure 7.5, their final effects are similar.

In the high shear Brabender torque rheometer where resin grains are first comminuted it is reasonable to imagine that the abrasive filler particles, which were so effective in smoothing down the PVC grains during dry blending, would aid this process. Following this argument it could be assumed that finer filler particles, which present a larger specific surface area, would be more effective in assisting comminution than coarser filler particles, especially the harder marble based filler Carbital 90. This in turn would lead to a reduction in fusion times, more so for the finer than the coarser filled blends. This explanation fits neatly with the results, where the presence of fine filler dramatically reduced the fusion time. With the introduction of coarser filler this effect was reduced.

As with extruder torques, Brabender torques were also affected by filler coating. Here coating the fine fillers produced a slight reduction in torque, with torques falling faster as coarser coated fillers were introduced.
The presence of coating therefore had a profound effect on the processing torque, particularly at the coarser end of the filler range. Part of the effect can be simply explained if one considers that the stearic acid coating was acting in the same manner as extra external lubricant. However, if this was purely the case torque would have been reduced by the same extent in each sample. This was clearly not the case and if one examines the Brabender fusion time results which are plotted in Figure 5.1 and reproduced here, Figure 7.6, one can see that the delayed fusion effect increased as coarser fillers were introduced. The three coarsest filled blends, where a 1% coating level would have exceeded a monolayer covering of the filler surface, actually had fusion times which were longer than that for the unfilled blend. The explanation to this must lie with the filler's specific surface area, and one idea based on the interaction of stearic acid with the calcium carbonate filler is given below.

Considering for a moment the coating process, it is known that at the coating temperature of 120°C the layer of stearic acid in contact with the calcium carbonate particle reacted and converted to calcium stearate, which was then bound to the filler surface. This reaction converted the nature of the bonded coating from that of an external lubricant (stearic acid) to an internal lubricant (calcium stearate).
Figure 7.5

Brabender Torque versus Filler Type

![Bar graph showing Brabender Torque versus Filler Type with sample codes N/F, C90, P, P60, Q360, and Q20.]

Legend:
- Uncoated
- 1% coated

Figure 7.6

Brabender Fusion Time versus Filler Type

![Line graph showing Brabender Fusion Time versus Filler Type with sample codes N/F, C90, P, P60, Q360, and Q20.]

Legend:
- Uncoated
- 1% coated
Discussion

\[ \text{CaCO}_3 + 2\text{CH}_2(\text{CH})_16\text{COOH} \rightarrow (\text{CH}_2(\text{CH})_16\text{COO}^-)_2\text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \] (7.1)

From this it follows that the larger the surface area of the filler the more internal lubricant would be present, and the less unbonded free stearic acid would be left in the blend. During processing external lubricants are known to reduce torque and fusion rates while internal lubricants have less of a deleterious effect, indeed they may even be beneficial. Thus as all the fillers were coated at the same level the coarser filled blends contained more stearic acid and thus fused more slowly.

7.2.3 Assessment of Extrudate Fusion Level

Three tests were used to evaluate the level of fusion in the pipe samples.

**Solvent Testing**

Solvent testing, due to its simplicity, has become a common internal quality control test used by many extruders of PVC pipe. In this project specimens of PVC pipe were immersed in methylene chloride for a given length of time after which they were examined for surface attack. (Experimental detail is given in section 2.4.1). Although this method readily distinguished poorly processed pipe, its
interpretation was subjective and difficult to quantify. This can be explained by the fact that in a sample where a fusion network existed swelling had little effect on the cohesion of the particles because of the restraining effect of the network. Sufficient swelling would, however, dislodge particles in low fused areas where particles were held together at best by sintering. Thus swelling in itself was not deemed to constitute failure although delamination or disintegration was.

All the pipe sample from both the uncoated and 1% coated series passed this test, with no visible differences between samples being detected. This therefore indicated that all the pipe samples had achieved a reasonable level of fusion.

Acetone Shearing Test

A slightly more sensitive test based on solvent immersion, developed by Summers and Rabinovitch(92) and improved by the use of transmitted light dark field microscopy(84) was used to produce micrographs in which primary particle fusion was clearly visible. In this method high temperature well fused PVC swelled and sheared to show fibrils and an absence of primary particles, while PVC processed at lower temperatures showed primary particles with only a few interconnecting fibrils. However, differences between well fused pipe still proved difficult to distinguish (a selection of micrographs is given in Figures 5.8 to 5.10).
thus tests only really supported results gained earlier from solvent testing.

Both the aforementioned tests gave a qualitative measure of fusion, and depended on the measurement or otherwise of the molecular entanglement in the sample. To give a quantitative measure of the level of fusion in the pipe a further technique using thermal analysis was used.

Thermal Analysis

The level of fusion obtained by twin screw extrusion was determined by using a Du Pont 990 thermal analyser fitted with a Du Pont DSC cell, previously described in section 2.4.2. This measured the heat necessary to raise a specimen of the test material through a selected range of temperatures and displayed the endothermic and exothermic effects encountered. The degree of fusion was then calculated from the area of endotherm 'A' (Figure 1.10, equation 2.1) which gave a measure of the extent of imperfect ordered regions in the sample which melted on reheating.

The degree of fusion was then converted to a percentage value, as is common(77), by way of equation 5.1. This conversion required standard fusion curves to be produced by extruding a blend of identical formulation over a complete processing temperature range. From the complete fusion curves a maximum heat of fusion value was taken as 9.9 J/g; this value agreed well with a maximum range of 10-12 J/g suggested by Gilbert et al(84).
Discussion

Plotting percentage fusion for the uncoated series against their 'B' onset temperature showed that the level of fusion was related to the processing temperature that the pipe saw. However, when percentage fusion was plotted against filler specific surface area, Figure 5.14, a much more direct relationship was formed, indicating that fusion level was very closely related to the filler's particle size. Thus the addition of fine filler particles greatly enhanced the fusion level in the pipe, while coarser grains had less of an effect. This was true to the extent that the very coarsest grains actually had a retarding effect upon fusion producing a pipe with a level lower than that in the unfilled pipe.

These results support the previous hypothesis which suggested that finer fillers would prove more beneficial in breaking down the PVC particles, thus aiding fusion. The filler particle size effect on fusion was also seen in the Brabender fusion time results, further supporting this hypothesis.

As expected from previously discussed results the degree of fusion in the 1% coated pipe samples was lower than that in their respective uncoated counterparts. (This was not true for sample code 1P60 which saw an unexpectedly high processing temperature). The differences between the fusion levels in the 1% coated and uncoated blends become even
greater when one considers that the coated blends experienced a much higher (approximately 8°C) processing temperature, which is usually accompanied by a rise in fusion level.

All these results seem to indicate that the stearate coating acts in the same manner as an extra lubricant, reducing both the internal friction and the friction between the polymer and the metal surfaces to a greater or lesser degree, depending on the amount of free and bonded stearic acid present.

7.2.4 Mechanical Properties of Extrudate

Tensile and impact tests were carried out to determine the mechanical properties of the extrudates. The tensile tests gave an important indication of the strength of the material, giving both a measure of the force necessary to pull the specimen apart and the amount of stretching that occurred before break. From the resultant force-extension plots three parameters were calculated. These were: (1) the yield strength - the stress at which nonelastic deformation began; (2) the ultimate strength - the maximum stress the specimen withstood at point of rupture; (3) ultimate elongation - the total amount of extension the specimen underwent.

The impact strength of each sample was measured from the work done in breaking the specimen, thus giving an indication of its toughness. This could have been
approximated from the area under the tensile stress-strain curve. However, in the impact tests the rate of applied load was significantly faster than that used in the tensile tests, and as complete pipes were tested an idea of the performance of the pipe as a whole was gained.

Several previous authors\(^{(137,138)}\) have shown that the behaviour of rigid PVC in mechanical property tests, from linear deformation up to break, is controlled by its molecular structure and by the density and shape of the defects induced during processing. The structural heterogeneities induced by the processing of PVC or by the presence of the filler dispersed in the matrix changes the local stress distribution in the material. Depending upon their constitution, shape, dimensions and compatibility these heterogeneities can be:

- either zones or concentrations of stresses which will locally initiate fractures and decrease the impact resistance of the product,
- or zones of energy dispersion which will increase the minimum energy needed for the propagation of the fracture and improve the impact resistance of the PVC.

Several studies have shown that coating fillers improves the pipe's mechanical properties\(^{(21,22)}\). One explanation for this improvement is that the calcium stearate on the filler's surface may promote the adhesion and degree of fusion to and around the filler particle\(^{(33)}\). The PVC
around the particle is thus tougher and more resistant to crack initiation and propagation.

7.2.4.1 Tensile Properties

Tensile tests were carried out as specified in section 2.4.4 with results presented in section 6.1. From these it was clear that the addition of 14.3phr of uncoated filler, irrespective of particle size, reduced the pipe's yield stress ($\sigma_y$). This influence has been seen by other authors including Chauffoureaux (32) who studied the effect of two grades of calcium carbonate filler (0.07μm and 2.4μm) at two different concentrations (10 and 20%) on the mechanical properties of PVC. He found that the inclusion of filler in all cases reduced $\sigma_y$, while at the high 20% concentration level the fine filler depressed $\sigma_y$ more than the coarser filler. He related this adverse effect to the agglomeration of the filler particles, which is a common occurrence when using fine fillers (35), and gives a result which is similar to using a grade of filler with a coarser top cut. Within the results presented here a small drop in $\sigma_y$ was apparent with the finer filler grades. This slight deterioration in $\sigma_y$ was similar to that experienced by Pepper (136) who found $\sigma_y$ to fall when substantial quantities of filler were added and poorly dispersed in rigid PVC.

To establish if filler agglomeration was the problem a method previously used by Gotham and Hitch (139) and Pepper (136) to identify regions of poorly fused pipe was
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used. The technique used dark field optical microscopy to examine thin sections cut from the pipe. Under these conditions PVC showed as dark areas while the additives appeared bright. A well processed powder containing evenly distributed filler particles was readily identifiable, whereas a poorer processed material contained clearly defined dark areas, which were polymer grains, and bright agglomerations of filler particles. Micrographs taken in such a way of the uncoated series are shown in Figures 7.7 to 7.12. These do indicate that slight agglomeration of the filler particles took place in the finest filled blend coded C90. It is interesting to note that once the fillers were coated $\sigma_y$ properties were both improved (although this could have been caused by the higher processing temperature they experienced) and the filler particle size effect was lost, the coating perhaps removing the agglomeration problem.

The $\sigma_y$ parameter appeared relatively insensitive to changes in fusion level, in agreement with previous authors (79,103,104), thus reinforcing the idea that yield properties were independent of the number of crystalline junctions or the relative coherence of the entanglement network. (This insensitivity could be seen from the results of the processing range series in Table 6.2).

Post yield parameters of rigid PVC have for a long time been thought to be dependent on the fusion level, which affects the ability of the test specimen to neck and then cold draw. For both stress at break ($\sigma_B$) and elongation at
Micrographs of Pipe Specimens: Dark Field Illumination

Figure 7.7
Sample N/F

400μm

Figure 7.8
Sample C90

Figure 7.9
Sample P
Micrographs of Pipe Specimens: Dark Field Illumination

Figure 7.10
Sample P60

Figure 7.11
Sample Q300

Figure 7.12
Sample Q20
many authors have presented evidence for either an increase with increasing fusion level \((75,79,103,104)\) or an optimum fusion level in the range 45 to 85% fusion \((77,78,111,124)\). From the results presented here it was therefore difficult to decipher whether trends were due to fusion or filler particle size effects. Chaffoureaux\(^{32}\) who found filler particle size to affect \(\sigma_Y\), also found it to affect \(\sigma_B\) in a similar manner with 20% of fine filler having the greatest adverse affect on \(\sigma_B\). Sample C90 which contained the finest filler particles and had the highest fusion level (97%) gave the lowest \(\sigma_B\) value, while the two coarsest filled blends with fusion levels within the optimum fusion range mentioned before produce the highest \(\sigma_B\) values.

It therefore seems that post yield tensile properties are very dependent on fusion levels, more so than they are on filler particle size. The effect of fusion level on tensile properties can be seen from the processing range series (the results are given in Table 6.2), from these one can see that optimum tensile properties lie approximately in the fusion range of 70 to 90% fusion.

As discussed in section 6.1 the tensile strength of the pipe samples at both yield and break were improved by coating the filler, while elongation at break values were reduced. This effect was seen both in the two series discussed here and the processing range series. However, in the Göttfert control blends, which admittedly only contained 7.6phr of filler, all three properties were seen to increase with a 1%
coating on the fillers, Table 6.1. It seems therefore that it can be concluded that both $\sigma_Y$ and $\sigma_B$ improve with coating in a manner independent of the filler's specific surface area (perhaps relying on the improved bonding between polymer and filler produced by coating) whereas $\varepsilon_B$ results are less definite and should be confirmed with an extensometer. The reduction in $\varepsilon_B$ in the 1% coated series, may have been due to the increased embrittlement in the pipe resulting from its higher processing temperature. This increased embrittlement is discussed in the impact results.

7.2.4.2 Impact Properties

The results from the uncoated series, reprinted here with the 1% coated series in Figure 7.13, indicate that the presence of filler can greatly improve the impact performance of PVC pipe. However, selection of filler particle size and processing temperature must be made with care.

From either series it is clear that the addition of filler at this level (14.3phr) reduced the ductility of the pipe, and that this reduction was dependent on the filler's particle size, coarser fillers having a more detrimental effect. However, the final impact strength was not wholly dependent on the ductility, or otherwise, of the pipe and was clearly affected by the pipe's fusion level.

Thus in the uncoated series finer fillers, although having less of a detrimental effect on ductility, increased the extrusion torque causing very high fusion levels in the
pipe and poor impact properties. Pipe containing a slightly coarser filler resulting in a lower fusion level gave much better impact properties, indicating that fusion level played an important role. Once the coarsest fillers were added to the blend, producing an almost brittle pipe, impact strengths fell significantly.

Figure 7.13

Impact Strength versus Filler Type

It seems reasonable to assume that a finer filler particle size has a more beneficial effect on impact strengths. This could be due to a number of reasons: the smallest particle size fillers could be equated to perfect spheres which quickly debond from the polymer matrix and spin
to absorb and deflect the energy; the larger size fillers cause larger discontinuities in the PVC matrix allowing easier crack initiation and propagation. However, in a process with insufficient shearing forces a too large filler surface area can lead to dispersion problems or uncontrollable viscosities. The non-divided filler agglomerates then act as a coarser top cut. This may be happening in the low shear twin screw extruders.

Previous authors\(^{77,78,106,143,143}\) have also found impact strengths to go through an optimum value with fusion level, and it is thought that it is these two influences together which produce the results presented here.

In the 1\% coated series the impact strength again showed a maximum as Polcarb was added to the blend, corresponding to a 74\% fusion level. In general, the impact strength of the series was however much lower than that experienced previously, with the filled samples never exceeding the impact strength of the unfilled pipe. The pipe became very brittle as the coarsest fillers were introduced into the blend giving extremely poor properties.

7.3 Constant Monolayer Fraction and Coated Polcarb Series

To simplify the problems raised from the 1\% coated series, where both free stearic acid and bonded calcium stearate were present in varying degrees in each formulation, the constant monolayer fraction series was examined. This was based on a calculation of the footprint area of stearic acid
and the specific surface area of each filler grade (section 3.3.1), and gave a value for the weight of stearic acid required to cover each filler with a monolayer stearate covering. In practice a value slightly less than the calculated monolayer value was used in order to ensure that no free stearic acid was left after coating the fillers, and thus this series was termed the constant monolayer fraction series.

The final series was chosen to examine in more depth the true effect of coating level on processing, fusion and end product properties. To this end one filler (Polcarb) was chosen and coated using a range of coating levels.

The processing equipment used in both these series was different to that used in the aforementioned ones, and consisted of an 8 litre T.K. Fielder dry blender and a Göttfert twin screw extruder.

7.3.1 Dry Blending Studies

As previously mentioned the Fielder blender produced a dry blend with entirely different properties to that obtained from the Henschel blender. These dissimilarities have already been discussed in section 7.1.1. Suffice to say that the resulting dry blends had a filler content of approximately 7.6phr (as compared to 14.3phr from the Henschel), and a bulk density of approximately 0.69 g/cm³ as compared to 0.78 g/cm³ from the Henschel). These differences
stem from the fact that the Fielder was a much less effective mixer depositing vast quantities of filler on the wall of the heated mixing chamber. This loss of filler reduced the effectiveness of the filler's abrasive action in partially breaking down and rounding off the PVC grains, which would eventually have produced a more tightly packed and thus higher density dry blend. These dissimilarities in both filler content and bulk density could be clearly seen from the SEM micrographs of the dry blends, Figures 4.2 to 4.12, and will obviously affect the results.

The loss of filler during blending meant that in the constant monolayer fraction blends bulk densities did not dramatically rise in the presence of the filler, in fact they fell slightly indicating perhaps that the filler particles were not situated so neatly in the folds between the sub grains, but in fact lay exposed on the PVC's grain surface separating the grains even further. The presence of coarser fillers in this series did increase the density slightly, as with the Henschel mixed blends. In the coated Polcarb series bulk densities were again low with no obvious differences being seen between different coating level samples, although the presence of coating did in all cases seem to improve the blend's density. The coating level on the surface of the filler perhaps helping initially to adhere it to the polymer.
7.3.2 Processing and Fusion Characteristics

As before twin screw extrusion and Brabender torque rheometry were used to assess the effect of fillers and stearate coating on processing and thus fusion.

7.3.2.1 Twin Screw Extrusion

For these two series a Göttfert twin screw extruder was used. The complexity of twin screw extruders presents many problems when attempting to relate results from one machine to another, so although the important extrusion characteristics, ie. output, torque, extrusion pressures and melt temperatures could be monitored in both machines comparisons between these and previous results must be made with care. From the comparison blends it had previously been noted that output rates were higher from the Göttfert, due to increased screw speeds, although blend bulk densities were lower. The two machines recorded torques in different units and pressures at different position along the barrel so direct comparisons of these parameters could not be made. However, the same trends were followed in the two extruders, although differences between torque readings corresponding to variations in filler particle size and the presence of coating were more exaggerated in the Göttfert. Actual melt temperatures fluctuated somewhat, although set temperatures were kept as constant as possible, the result being that the constant monolayer fraction series and the coated Polcarb series saw a temperature approximately the same as the 1%
coated series, while the uncoated series experienced one 8°C lower.

Consider first the extrusion characteristics measured for the constant monolayer fraction series. Here results followed very closely those experience by the two previous series, reinforcing the suggestions made earlier on the effects of fillers on extrusion. These were that:

(1) output rate increased as filler and progressively more so as coarser filler was added to the blend. (In the series considered here output rate initially fell from the unfilled to the finest filled blend corresponding to the measured drop in bulk density).

(2) extrusion torques and pressures also rose as filler was introduced to the blend. In this case torque and pressures were highest for the finest filled blends indicating that the fillers (especially fine ones) increased the melt viscosity of the polymer. Because output rates varied less than torques specific energy consumption results closely followed torque readings, see Appendix C.1.

The effects of the constant monolayer fraction coating were hard to decipher from these results as comparisons could only be made with an uncoated and 1% coated series extruded on a different machine; however, comparisons could be made between these results and the comparison blends. From these one could compare two filled blends which had both been extruded uncoated, and coated over two levels ie.
constant monolayer fraction and 1% coated (taken from Appendix C.1).

<table>
<thead>
<tr>
<th>Coating level</th>
<th>Output (g/min)</th>
<th>Torque (Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N/F  P  Q20</td>
<td>N/F  P  Q20</td>
</tr>
<tr>
<td>0</td>
<td>166.7 170.0 183.3</td>
<td>160 205 160</td>
</tr>
<tr>
<td>monolayer</td>
<td>166.7 176.7 183.3</td>
<td>160 225 200</td>
</tr>
<tr>
<td>1</td>
<td>166.7 153.3 175.0</td>
<td>160 185 160</td>
</tr>
</tbody>
</table>

Comparisons could also be made from the Polcarb coated series which within its series had the same filler coated at the same three levels - results are given below.

<table>
<thead>
<tr>
<th>Coating level</th>
<th>Output (g/min)</th>
<th>Torque (Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>0</td>
<td>163.3</td>
<td>210</td>
</tr>
<tr>
<td>monolayer</td>
<td>166.7</td>
<td>210</td>
</tr>
<tr>
<td>1</td>
<td>156.7</td>
<td>192</td>
</tr>
</tbody>
</table>

The results seem to indicate that both output and torque readings go through a maximum as fillers are first uncoated, then coated with a monolayer coverage such that no free stearic acid remains in the blend, and then coated with an excess of stearic acid. It therefore seems that there is a critical coating level at which all stearic acid is
converted to calcium stearate producing optimum torque and output results. These results were partially confirmed by those found in the coated Polcarb series where output rates were found to be high for blends containing less than a monolayer coverage of stearate coating, once this level was exceeded outputs fell. Unfortunately, however, neither torque nor pressure readings gave any clear trends.

7.3.2.2 Brabender Torque Rheometry

The same Brabender torque rheometer, using a constant sample weight, was employed for all four series so in principle direct comparisons between blends should be possible.

From the fusion time results one can see a very similar trend present in the constant monolayer fraction as in the 1% coated series although fusion times for the constant monolayer fraction series were considerably longer. The one striking difference was that in the constant monolayer fraction series the fusion time of the filled samples was always less than the fusion time of the unfilled blend, Figure 7.14. In this respect the results were more similar to those obtained from the uncoated series. The torques experienced in the Brabender again followed more closely those of the uncoated series although sample's coded MC90 and MP were particularly high.

The large differences experienced in the times to fusion between these and the two previous series can be
explained by the differences in bulk densities. In the constant monolayer fraction series where particles were loosely packed and bulk densities low the compaction stage in the Brabender took a lot longer to be reached, and fusion took longer to commence. Once fusion had started the rate at which it proceeded was very similar to that in the aforementioned uncoated and 1% coated series.

Brabender torques and fusion times responded clearly to the presence of varying quantities of filler coating. When low levels of coating were added to the blend the torques rose and fusion times decreased. As coating levels increased the torques systematically fell and fusion times rose beyond that of the uncoated filler. It seems likely from this that when coating was added to produce a monolayer covering, or less, on the filler surface calcium stearate was created slightly improving the fusion behaviour of the pipe. As more stearic acid coating was added it became free and acted in the same manner as that of extra external lubricant.

This effect can be seen if one considers the results from the constant monolayer fraction series, the comparison blends and the coated Polcarb series, as shown below (taken from Table 5.1).
If one looks solely at the coated Polcarb series it becomes evident that the presence of a stearate coating initially reduced the fusion time, up to the point where the monolayer coverage was exceeded and free stearic acid was left in the blend. The fusion time then increased dramatically to a value greater than that of the uncoated blend, although additional increases in coating level did not seem to delay fusion further, Figure 7.15.

7.3.3 Assessment of Extrudate Fusion Level

As with the previous series no differences could be detected between the various blends using solvent and acetone shearing tests. These methods thus proved again to be worthwhile only as quick and simple quality control tests, confirming that all the pipe samples had reached a relatively high degree of fusion.
Figure 7.14
Brabender Fusion Time versus Filler Type

![Chart showing Brabender Fusion Time versus Filler Type](image)

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Figure 7.15
Brabender Fusion Time versus Polcarb Series

![Chart showing Brabender Fusion Time versus Polcarb Series](image)
Thermal Analysis

Considering first the constant monolayer fraction series similar trends to the 1% coated series and perhaps more closely the uncoated series were seen. These two series behaved with great similarity in that the addition of filler to the blend, irrespective of particle size, always increased the fusion level in the pipe. In the 1% coated series the coarsest filled blends exhibited a fusion level below that of the unfilled blend. This phenomenon supports the theory of the effect of free and bonded stearic acid.

It is interesting to note the effect of filler level on fusion from these results. The fall in filler level seemed to be accompanied by a drop in the fusion level, in the same way as it had increased the fusion time in the Brabender torque rheometer. These results do not agree with those presented recently by Pepper(136) who found that the addition of substantial quantities of filler did not appear to influence the level of fusion in the pipe.

Again it is interesting to look at the three series constant monolayer fraction, comparison blends and coated Polcarb series to understand more fully the effect of coating level on fusion (taken from Table 5.4).
From the results it seems that the coating does not have the same effect that it does in the Brabender. Here the addition of coating decreased the fusion level. It is only when one looks at the coated Polcarb series and the very lowest coated level that one sees an increase in the fusion level as compared to the uncoated blend.

### 7.3.4 Mechanical Properties of Extrudate

Pipe produced from the Göttfert had a wall thickness approximately twice that of the Krauss pipe, thus to partially eliminate the effect of this on results all samples were normalised by dividing the individual results by the thickness of the specimens. Further problems arose from the sample preparation of tensile specimens as the thicker Göttfert pipe could not be physically punched and samples had to be routed out. Due to these differences results from these and previous series should not be compared too closely.
7.3.4.1 Tensile Properties

The tensile strength of the constant monolayer fraction samples at both yield and break showed a substantial improvement on the previous two series. This result is thought to reflect the large variation in filler levels between the uncoated and 1% coated series and those series discussed here.

At this point it is interesting to note some of the results from Pepper's work on the study of the effect of filler level on tensile properties. At yield he found stress to be dependent upon filler level such that an increase in filler level caused a decrease in stress - this he attributed to a dilution effect of the inert filler. He also found yield parameters to be insensitive to variations in fusion level. Post-yield parameters were not so dramatically effected by filler level and it was only the very highly filled samples (30-40phr of filler) which showed a dramatic reduction in ultimate stress due to the poor filler dispersion affecting neck stability.

Agreement was seen with Pepper's results in that a change in filler level from 7.6 to 14.3 phr produced a vast reduction in $\sigma_Y$ but only a small reduction in $\sigma_B$. However, at the filler addition level used here, a level lower than any used by Pepper, the yield stress was increased in the presence of filler while both stress and elongation at break were reduced. From the constant monolayer fraction series $\sigma_Y$ seemed insensitive to both the filler's specific surface
area and the fusion level in the pipe. The post yield properties, however, were very dependent on fusion level the finest filled blend, with the highest fusion level of 90%, giving the worst properties. This was not thought to be due to filler agglomeration as no effects had been seen in the $\sigma_y$ parameter.

To look more closely at the effect of coating level one can again examine the comparison blends and the monolayer series. From these results it seems that tensile properties of the finer filled blend (sample code P) increased as more coating was added to the filler. Tensile strength properties from the coarser filled blend (sample code Q20) seemed to go through a maximum. This could be feasible as here a great deal more free stearic acid would be left in the blend at the 1% coating level (the filler having a smaller surface area to absorb the stearic acid) thus reducing the fusion level further in the pipe (results taken from Table 6.1).

<table>
<thead>
<tr>
<th>Coating level</th>
<th>Yield strength (MPa)</th>
<th>Ultimate strength (MPa)</th>
<th>Ultimate elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N/F P Q20</td>
<td>N/F P Q20</td>
<td>N/F P Q20</td>
</tr>
<tr>
<td>0</td>
<td>50.7 49.5 50.5 54.3 52.8 54.4 175 171 173</td>
<td></td>
<td></td>
</tr>
<tr>
<td>monolayer</td>
<td>50.7 50.0 52.3 54.3 53.3 55.8 175 171 172</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>50.7 51.5 51.8 54.3 54.6 55.4 175 172 175</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Discussion 225

If the stearic acid was having an effect on tensile properties it should become clear in the coated Polcarb series. However, trends in the series were more obscure with three points becoming clear:

(1) the presence of coating at this relatively low filler addition level had little effect on the tensile properties of the pipe,
(2) the highest coated filled blend, coated at 3% by weight stearic acid, exhibited the worst post yield properties due to its low fusion level,
(3) the blend containing filler coated at near monolayer coverage level showed the best post yield properties of the coated blends.

7.3.4.2 Impact Properties

Impact strength values, as mentioned previously, were normalised to allow for thickness variations, but again differences in thickness can produce disproportionate results.

Within the constant monolayer fraction and coated Polcarb series impact strength results were considerably higher than those measured for the previous series. This was clearly the effect of filler level and has been noted by previous authors principally Pepper(136) who found impact strengths to be greatly reduced as filler content was raised from 8 to 14phr. Changes within the mode of failure were also less dramatic in this series, due again to the lower
filler levels. In the highly filled pipes failure changed from that of an almost ductile break to a virtually brittle break. However, in the constant monolayer fraction and coated Polcarb series little variation was seen in the mode of failure as filler was added to the blend.

Considering first the constant monolayer fraction series impact strengths rose from an initial fall with the introduction of the finest fillers to a value greater than that of the unfilled blend. It seems from this work therefore that both the fusion level and the filler particle size play a role in determining the final impact strength. In this series, as before, the optimum impact strength is obtained at a fusion level in the range 60 to 75%. The addition of finer fillers often increasing the fusion level in the pipe above this value causing a reduction in mechanical properties. However, if fusion levels are kept within this range fillers can improve the pipe's impact strength, perhaps by creating areas of stress concentration which then transmit the impact energy to the PVC matrix by way of microcracks.

Considering now the coated Polcarb series and the general effect of coating level let us again consider the monolayer series with two comparison blends, (taken from Table 6.3).
<table>
<thead>
<tr>
<th>Coating level</th>
<th>Peak energy (J/mm)</th>
<th>Polcarb series (% fusion)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N/F</td>
<td>P</td>
</tr>
<tr>
<td>0</td>
<td>19.89</td>
<td>19.88</td>
</tr>
<tr>
<td>monolayer</td>
<td>19.89</td>
<td>18.77</td>
</tr>
<tr>
<td>1</td>
<td>19.89</td>
<td>19.96</td>
</tr>
</tbody>
</table>

It was hard to distinguish between the effect the coating had directly upon impact strength and the effect it had by way of altering the fusion level in the pipe. It would seem, however, from these results that it was the effect upon fusion which was most important (as long as no filler agglomeration occurred). From the comparison and constant monolayer fraction blends the peak energy results do not follow any clear trends, other than that of following the fusion level in the pipe. Within the coated Polcarb series the maximum too follows fusion levels and lies in the range 65 to 70% fusion.
CONCLUSIONS

Dry Blending Studies

From Henschel blender results the following was concluded:

- The addition of filler increased the dry blend's bulk density. This was achieved by the fillers abrasively removing irregularities from the PVC grain surface. The fillers themselves finally accumulated in the folds between sub-grains producing rounder, smoother PVC grains. Both these processes aided bulk density by improving the packing ability of the particles.

- Neither the filler's particle size nor the presence or otherwise of stearic acid coating greatly affected the blending process, although the coarser filled blends exhibited slightly higher bulk densities.

- Filler loss in the Henschel was consistently low, and the high bulk density blends produced were particularly suited to the twin screw extrusion process.

From Fielder blender results the following was concluded:

- The Fielder mixer proved much less effective in producing high bulk density filled dry blends suited for twin screw extrusion.

- In the Fielder almost half the added filler was lost in the blending process. The lost filler formed a 'cake' around the inside of the heated chamber mixer.
Conclusions

- The loss of filler reduced the number of particles producing frictional heat and abrasively wearing down the PVC grains. The 'cake' also reduced the heat flow from the heated jacket to the mix. Thus blends took over twice as long to reach their discharge temperature as those mixed in the Henschel, resultant blends having very low bulk densities.

- Both coarser filler and the presence of coating slightly improved the blend's bulk density.

- From these discoveries it must be concluded that care should be taken in the choice of dry blender as different machines with dissimilar blade arrangements and chamber sizes produced vastly different dry blends.

Twin Screw Extrusion Studies

- Under extrusion conditions of constant screw speed and flood feeding the output rate followed, and generally enhanced, the bulk density trends.

- Thus output was generally improved by the presence of fillers, coarser fillers having the most beneficial effect although their improvement on bulk density had been slight.

- As the level of coating on the fillers was increased so output rate went through a clear maximum. This maximum corresponded to an approximate monolayer coating on the filler surface. No such optimum had been seen from bulk density results and this was therefore purely due to the effect coating had on the extrusion process.
Conclusions

- Extrusion torques increased in the presence of filler, finer filler having the greatest effect. The finest filler, which was the only grade based on marble rather than softer chalk deposits, gave a particularly high extrusion torque reading. It therefore seemed that fillers aided the extrusion process by breaking down the PVC grains.

- In the Krauss the presence of a 1% coating level slightly increased the torque experienced by the fine fillers (where all the stearic acid had been converted to calcium stearate), and greatly reduced the torques of the coarser fillers (where free stearic acid remained in the blend).

- In the Gottfert, with only 7.6phr of filler in the blend, coating each filler with an approximate monolayer coverage produced torque results which exhibited similar trends to those experienced by the uncoated fillers. Varying the coating level, at this low filler addition level, produced no obvious trends.

- Melt temperatures were consistent within series but did not closely follow set temperatures. Thermal analysis, giving 'B' onset temperatures, proved a successful method of determining the actual temperature seen by the melt.

- Pressure readings in both extruders were low at the feed end of the barrel. Pressures at the adaptor and die followed similar trends to torque reading.

- It proved difficult to decipher the effect of filler level variations on extrusion characteristics as two
extruders had been used. However, it seemed that the presence of filler at the low level of 7.6phr had an equally dramatic effect on output (probably because of the higher screw speed), torque and pressure although coating effects were not as dramatic as hoped.

**Brabender Torque Rheometry**

- Using a constant charge weight during Brabender experiments reduced the effects of bulk density on fusion and torque, and gave a clearer picture of filler particle size and coating level effects.
- The very low bulk densities of the Fielder blends caused long Brabender fusion times by increasing the time it took for powders to compact.
- Fusion times were also influenced by the average size of particles in the blend. The Fielder mixed blends (due to filler loss) had a larger average particle size in comparison to the Henschel blends. This resulted in them creating less frictional heat, due to their smaller surface area, and therefore taking longer to fuse.
- As in the extruders the presence of fillers, particularly fine fillers, helped to break up the PVC grains thereby increasing the torque and reducing the fusion time.
- A distinct optimum was experienced for both Brabender torque and fusion time as filler coating levels were increased. During the coating process the stearic acid in contact with the calcium carbonate filler reacted and
converted to calcium stearate (an internal lubricant), which was then bound to the filler's surface. Once a monolayer coverage of calcium stearate was formed around the filler particle additional stearic acid (an external lubricant) remained unreacted and free in the blend. Maximum torques and minimum fusion times were experienced when the maximum amount of calcium stearate, ie. a monolayer coverage, was present. As more stearic acid was added to the blend the torques fell and fusion times increased, finally exceeding those of the unfilled blends.

**Fusion Studies**
- Both solvent testing and acetone shearing proved useful as quality control tests to determine the approximate fusion level in the pipe. However, neither of these methods could detect variations between well fused pipe.
- The thermal analysis technique proved a very useful method of assessing fusion level in the pipe once a standard curve had been constructed.
- The presence of filler, irrespective of particle size, generally increased the fusion level in the pipe. The exception to this came when the filler was heavily coated with stearic acid.
- The level of fusion in the pipe was directly related to the filler's specific surface area, such that fine fillers improved fusion more so than coarse grained ones.
Conclusions

At the two levels of filler addition studied it seemed that as the filler level was increased its effect became more pronounced, i.e. increasing fusion in the case of the finer filled blends, and either not affecting it or retarding it with the coarser coated grains.

At the lower filler level of 7.6phr, where the effects of coating were studied, coating the filler initially increased fusion, and then reduced it as more stearic acid became free in the blend.

Coating the filler at a 1% coating level reduced fusion in both extruders at both filler levels. Fusion levels in the Krauss may have been affected by the variations in processing temperature.

Tensile Properties

From the Krauss extruded pipe containing 14.3phr of filler the following could be concluded:

- The yield stress was reduced by the addition of filler, fine fillers having a greater detrimental effect due to the formation of filler agglomerates.
- Coating the filler somewhat improved the pipe's yield stress, perhaps by improving the bond between the filler and polymer matrix.
- Once the fillers were coated their particle size had no effect on yield stress. Coating may have removed the agglomeration problem.
- Yield stress proved insensitive to fusion level,
confirming previous reports that yield must be related to a molecular relaxation process.

- Post yield parameters were always reduced by the addition of 14.3phr of filler.
- The stress at break of the uncoated filled series proved sensitive to both filler specific surface area and fusion level, properties falling as either finer filled highly fused or coarser filled poorly fused pipe was tested.
- Coating the finest filler, although improving the filler agglomeration problem, did not greatly improve the post yield properties of the pipe, which still suffered from a high fusion level.

From the Gottfert extruded pipe containing 7.6phr of filler the following could be concluded:
- The addition of filler at this lower level enhanced the yield stress of the pipe, fine fillers by the same degree as coarser ones, indicating that there were no agglomeration problems with the coated fillers.
- With no agglomeration problems there were no effects of filler particle size nor were there any of coating level or fusion level.
- Post yield properties were reduced as filler was added to the blend and were sensitive to the fusion level in the pipe; the worst properties seen in the highest fused pipe containing the finest particled fillers.
- Variation in filler coating level had little effect on post yield properties; only when fusion was greatly
Conclusions

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diminished in the highest coated blend did these properties fall.

Thus the general conclusions from the tensile tests were:

- The yield stress of the pipe seemed extremely sensitive to the filler level in the pipe, the addition of low levels of filler actually increasing this property.
- Where the addition of fine filler caused agglomeration problems the pipe's yield stress was greatly reduced. Coating the fine filler removed this problem.
- Yield stress proved insensitive to both the fusion level in the pipe and the coating level on the filler.
- Post yield properties were generally reduced by the presence of filler, irrespective of the filler level.
- Post yield properties were a lot less sensitive than yield to filler level; and a lot more sensitive to the effect that filler particle size had on fusion level.
- A high fusion level in the pipe caused the most detrimental effect on post yield parameters, a condition brought about by the addition of fine fillers to the pipe.
- Filler coating level had little effect on post yield properties; only when the coating level significantly affected the fusion level was stress at break reduced.
Impact Properties

Conclusions from the Krauss extruded pipe:
- The presence of 14.3phr of filler altered the mode of failure of the pipe from one breaking in a ductile/brittle manner to, in the presence of the coarsest fillers, an almost brittle one.
- The processing temperature experienced by the 1% coated series was approximately 8°C higher than the uncoated series. Although this did not greatly alter the fusion level in the pipe it did embrittle it, thereby reducing impact strength.
- Impact strength was dependent upon fusion level with a maximum seen between 60% and 80% fusion.
- Pipes filled with this level of filler did in some instances have improved impact strengths. The fine fillers proved most beneficial in that they had less effect on the ductility of the pipe. However, care is needed in blending to prevent filler agglomeration, and in extrusion so that their fusion levels do not exceed approximately 80%.

Conclusions from Gottfert extruded pipe:
- At this lower filler addition level of 7.6phr the fillers did not have such a detrimental effect on pipe ductility, and no differences in mode of failure were detected between finer and coarser filled pipe.
- Maximum impact strength again lay between 60% and 80%; the coarsest filled pipe, having a fusion level of 70%, exhibited the best impact properties.
Coating the pipe affected its impact strength through fusion, such that the pipes with fusion levels in the range 60 to 70% exhibited the best properties. This occurred when the filler was coated with an approximate monolayer coverage.

**General Conclusions**

- The addition of fillers, particularly those with large specific surface areas, increase the fusion level in PVC pipe. This in turn affects the mechanical properties of the pipe, though not always in a beneficial manner.

  Fine filler while having a small effect on pipe ductility may cause excessively high fusion levels damaging impact and post yield tensile properties. Fine fillers also have an increased tendency to agglomerate, a problem that can usually be cured by coating although the presence of coating and its effect on fusion must then also be taken into consideration. Coarser fillers, on the other hand, substantially reduce pipe ductility, again reducing impact and elongation properties. Thus from the results of this project it would seem that a fine grained filler (say Polcarb) coated with a monolayer coverage of stearic acid and processed to give a final fusion level of approximately 70% would produce a pipe with optimum mechanical properties.
SUGGESTIONS FOR FURTHER STUDY

1. Throughout this work the variations in dry blend properties caused by using different dry blenders has been very apparent, yet few references can be found in literature as to the effects of different blender's blade arrangements and chamber sizes. This could therefore be an interesting area for further research, especially as blend properties effect many of the extrusion characteristics.

2. One could not only examine different blenders but also look more closely at the mixing process itself and the effects of additives on this process. Suggestions have been made that advantages could be gained from initially mixing the filler and polymer together, thus reaping the full benefits of the abrasive nature of the filler before adding the rest of the ingredients. This idea could be further investigated.

3. In this study filled pipes were only compared with unfilled pipe which had been processed at the same temperature. This resulted in the unfilled pipe having a much lower level of fusion, than that of the filled pipe, in which some grain memory may still have been present. This grain memory may act in a similar manner to filler particles when mechanically tested, and thus to see the full effect of
filler particles it would be interesting to compare a filled pipe with an unfilled pipe of an identical high fusion level.

4. From the results gathered here it seemed that filler particle size, irrespective of coating level, had a clear effect on extruder output with coarser fillers increasing output although they had had little effect on bulk density. It might be interesting to study this observation further.

5. Initial studies of the reaction of stearic acid coating to calcium stearate on the surface of the filler particles was carried out using infrared fourier transformation spectrometry. However, although results did show a conversion taking place they were inconclusive, and it would be interesting to not only study this in more depth but also the idea of free and bonded coating. Free stearic acid could perhaps be removed after mixing (possibly by using a soxhlet extraction with chloroform) to estimate how much is bonded to the filler.
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## APPENDIX A

### TECHNICAL DATA FOR FILLERS

Table A.1

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Carbital 90</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃%</td>
<td>96.5</td>
</tr>
<tr>
<td>pH</td>
<td>9.0 - 0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 53 micron (% max)</td>
<td>0.01</td>
</tr>
<tr>
<td>+ 10 micron (% max)</td>
<td>1.5</td>
</tr>
<tr>
<td>- 2 micron (%)</td>
<td>90 ± 3</td>
</tr>
<tr>
<td>specific gravity (solid)</td>
<td>2.7</td>
</tr>
<tr>
<td>specific surface area m²/g</td>
<td>11.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Optical properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>brightness % (ISO)</td>
<td>93.0 ± 1.0</td>
</tr>
<tr>
<td>yellowness %</td>
<td>1.5 ± 0.5</td>
</tr>
<tr>
<td>mean refractive index</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Carbital 90 is an ultra-fine natural calcite with extremely high brightness, derived from the Italian Carrara marble deposits.

Table A.2

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Polcarb</th>
<th>Polcarb 60</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃%</td>
<td>98.5</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>9.5 ± 0.5</td>
<td>9.0 ± 0.5</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 53 micron (% max)</td>
<td>0.02</td>
</tr>
<tr>
<td>+ 10 micron (% max)</td>
<td>0.5</td>
</tr>
<tr>
<td>- 2 micron (%)</td>
<td>86 ± 3</td>
</tr>
<tr>
<td>specific gravity (solid)</td>
<td>2.7</td>
</tr>
<tr>
<td>specific surface area m²/g</td>
<td>6.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Optical properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>brightness % (ISO)</td>
<td>85.0 ± 1</td>
</tr>
<tr>
<td>yellowness %</td>
<td>3.5 ± 0.5</td>
</tr>
<tr>
<td>mean refractive index</td>
<td>1.56</td>
</tr>
</tbody>
</table>
Polcarb is a very fine particle size calcium carbonate based on chalk from Salisbury and characterised by a minimum of coarse particles and a narrow particle size distribution. Polcarb 60 is also based on chalk but originates from Beverley, Hull. It is a medium particle sized filler with minimal coarse particles.

Table A.3

Queensfil 300    Queensfil 20

Chemical properties

<table>
<thead>
<tr>
<th></th>
<th>Queensfil 300</th>
<th>Queensfil 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃%</td>
<td>96.15 ± 0.5</td>
<td>8.5 ± 0.5</td>
</tr>
<tr>
<td>pH</td>
<td>9.0 ± 0.5</td>
<td>8.5 ± 0.5</td>
</tr>
</tbody>
</table>

Physical properties

<table>
<thead>
<tr>
<th></th>
<th>Queensfil 300</th>
<th>Queensfil 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 53 micron (%) max</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>+ 10 micron (%) max</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>- 2 micron (%)</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>specific gravity (solid)</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>specific surface area m²/g</td>
<td>2.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Optical properties

<table>
<thead>
<tr>
<th></th>
<th>Queensfil 300</th>
<th>Queensfil 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>brightness % (ISO)</td>
<td>82.0 ± 1.0</td>
<td>83.5 ± 1.0</td>
</tr>
<tr>
<td>yellowness %</td>
<td>5.9 ± 0.5</td>
<td>5.0 ± 0.5</td>
</tr>
<tr>
<td>mean refractive index</td>
<td>1.56</td>
<td>1.56</td>
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</tbody>
</table>

Queensfil 300 and 20 are coarser grade fillers derived from the Beverley chalk deposits.
## APPENDIX B

**ASH ANALYSIS**

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<tr>
<th>Blend Code</th>
<th>Actual Filler Level (phr)</th>
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<tbody>
<tr>
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</tr>
<tr>
<td>C90</td>
<td>14.1</td>
</tr>
<tr>
<td>P</td>
<td>14.8</td>
</tr>
<tr>
<td>P60</td>
<td>14.0</td>
</tr>
<tr>
<td>Q300</td>
<td>14.5</td>
</tr>
<tr>
<td>Q20</td>
<td>14.0</td>
</tr>
<tr>
<td>N/F</td>
<td>0.0</td>
</tr>
<tr>
<td>1C90</td>
<td>13.9</td>
</tr>
<tr>
<td>1P</td>
<td>14.0</td>
</tr>
<tr>
<td>1P60</td>
<td>14.0</td>
</tr>
<tr>
<td>1Q300</td>
<td>14.9</td>
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<tr>
<td>1Q20</td>
<td>14.3</td>
</tr>
<tr>
<td>N/F</td>
<td>0.0</td>
</tr>
<tr>
<td>MC90</td>
<td>7.9</td>
</tr>
<tr>
<td>MP</td>
<td>7.2</td>
</tr>
<tr>
<td>MP60</td>
<td>7.3</td>
</tr>
<tr>
<td>MQ300</td>
<td>8.0</td>
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<tr>
<td>MQ20</td>
<td></td>
</tr>
</tbody>
</table>
### APPENDIX C

**EXTRUSION CHARACTERISTICS**

#### Table C.1

<table>
<thead>
<tr>
<th>Pipe Code</th>
<th>Output (g/min)</th>
<th>Torque (%)</th>
<th>q (rev. %/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/F</td>
<td>88.3</td>
<td>49</td>
<td>31.5</td>
</tr>
<tr>
<td>C90</td>
<td>106.7</td>
<td>83</td>
<td>56.1</td>
</tr>
<tr>
<td>P</td>
<td>111.7</td>
<td>76</td>
<td>47.6</td>
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<tr>
<td>P60</td>
<td>100.0</td>
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<tr>
<td>Q300</td>
<td>116.7</td>
<td>70</td>
<td>40.8</td>
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<td>Q20</td>
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<td>71</td>
<td>41.0</td>
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<td>39</td>
<td>20.8</td>
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<td>116.7</td>
<td>79</td>
<td>48.0</td>
</tr>
<tr>
<td>1P60</td>
<td>105.0</td>
<td>52</td>
<td>29.2</td>
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<tr>
<td>1Q300</td>
<td>113.3</td>
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<td>38.7</td>
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<td>1Q20</td>
<td>113.3</td>
<td>66</td>
<td>38.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pipe Code</th>
<th>Output (g/min)</th>
<th>Torque (Nm)</th>
<th>q (rev. Nm/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/F</td>
<td>166.7</td>
<td>160</td>
<td>73.4</td>
</tr>
<tr>
<td>MC90</td>
<td>150.0</td>
<td>270</td>
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<tr>
<td>MP</td>
<td>176.7</td>
<td>225</td>
<td>117.8</td>
</tr>
<tr>
<td>MP60</td>
<td>180.0</td>
<td>205</td>
<td>101.0</td>
</tr>
<tr>
<td>MQ300</td>
<td>173.3</td>
<td>205</td>
<td>104.9</td>
</tr>
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<td>MQ20</td>
<td>183.3</td>
<td>200</td>
<td>95.6</td>
</tr>
<tr>
<td>P</td>
<td>163.3</td>
<td>210</td>
<td>155.4</td>
</tr>
<tr>
<td>0.3P</td>
<td>163.3</td>
<td>210</td>
<td>115.4</td>
</tr>
<tr>
<td>0.5P</td>
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<td>105.4</td>
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<td>0.84P</td>
<td>166.7</td>
<td>210</td>
<td>113.0</td>
</tr>
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<td>156.7</td>
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<td>105.1</td>
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<td>205</td>
<td>116.0</td>
</tr>
</tbody>
</table>

**Comparison Blends (Krauss/Gottfert)**

<table>
<thead>
<tr>
<th>Pipe Code</th>
<th>Output (g/min)</th>
<th>Torque (Nm)</th>
<th>q (rev. %/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/F</td>
<td>88.3 / 166.7</td>
<td>49 / 160</td>
<td>31.5 / 73.4</td>
</tr>
<tr>
<td>P</td>
<td>111.7 / 170.0</td>
<td>76 / 205</td>
<td>47.6 / 106.9</td>
</tr>
<tr>
<td>Q20</td>
<td>118.3 / 183.3</td>
<td>71 / 185</td>
<td>48.0 / 101.4</td>
</tr>
<tr>
<td>1P</td>
<td>116.7 / 153.3</td>
<td>79 / 185</td>
<td>48.0 / 101.4</td>
</tr>
<tr>
<td>1Q20</td>
<td>113.3 / 175.0</td>
<td>66 / 160</td>
<td>38.7 / 70.0</td>
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### Table C.2

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<thead>
<tr>
<th>Pipe Code</th>
<th>P1 (Bar)</th>
<th>P2 (Bar)</th>
<th>P3 (Bar)</th>
<th>P4 (Bar)</th>
<th>Die (Bar)</th>
</tr>
</thead>
<tbody>
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<td>161</td>
<td>102</td>
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<td>C90</td>
<td>14</td>
<td>130</td>
<td>261</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>11</td>
<td>115</td>
<td>226</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>P60</td>
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<td>47</td>
<td>171</td>
<td>105</td>
<td></td>
</tr>
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<td>86</td>
<td>175</td>
<td>110</td>
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<td>Q20</td>
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<td>88</td>
<td>174</td>
<td>110</td>
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<tr>
<td>N/F</td>
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<td>27</td>
<td>165</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>1C90</td>
<td>10</td>
<td>140</td>
<td>274</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>1P</td>
<td>7</td>
<td>116</td>
<td>228</td>
<td>132</td>
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<tr>
<td>1P60</td>
<td>0</td>
<td>34</td>
<td>149</td>
<td>80</td>
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<td>1Q300</td>
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<td>95</td>
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<table>
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<th>(9D)</th>
<th>(14D)</th>
<th>(20D)</th>
<th>Die</th>
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</thead>
<tbody>
<tr>
<td>N/F</td>
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<td>10</td>
<td>155</td>
</tr>
<tr>
<td>MC90</td>
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<td>10</td>
<td>265</td>
</tr>
<tr>
<td>MP</td>
<td>20</td>
<td>20</td>
<td>210</td>
</tr>
<tr>
<td>MP60</td>
<td>20</td>
<td>40</td>
<td>205</td>
</tr>
<tr>
<td>MQ300</td>
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<td>30</td>
<td>205</td>
</tr>
<tr>
<td>MQ20</td>
<td>0</td>
<td>25</td>
<td>200</td>
</tr>
</tbody>
</table>

| P    | 0     | 5     | 207  | 270 |
| 0.3P | 0     | 5     | 205  | 265 |
| 0.5P | 0     | 5     | 187  | 245 |
| 0.84P| 0     | 5     | 205  | 265 |
| 1P   | 0     | 5     | 182  | 250 |
| 2P   | 0     | 5     | 202  | 257 |
| 3P   | 0     | 5     | 187  | 245 |

**Comparison Blends (Krauss/Gottfert)**

<table>
<thead>
<tr>
<th>Pipe Code</th>
<th>P1 / P2</th>
<th>P3 / P4</th>
<th>Die / Die</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/F</td>
<td>1 / 10</td>
<td>25 / 10</td>
<td>161 / 155</td>
</tr>
<tr>
<td>P</td>
<td>11 / 10</td>
<td>115 / 10</td>
<td>226 / 200</td>
</tr>
<tr>
<td>Q20</td>
<td>12 / 15</td>
<td>88 / 15</td>
<td>174 / 174</td>
</tr>
<tr>
<td>1P</td>
<td>7 / 10</td>
<td>116 / 10</td>
<td>228 / 175</td>
</tr>
<tr>
<td>1Q20</td>
<td>7 / 0</td>
<td>62 / 10</td>
<td>135 / 165</td>
</tr>
</tbody>
</table>
Table C.3

'B' Onset Temperature

<table>
<thead>
<tr>
<th>Pipe Code</th>
<th>'B' Onset Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/F</td>
<td>185</td>
</tr>
<tr>
<td>C90</td>
<td>187</td>
</tr>
<tr>
<td>P</td>
<td>186</td>
</tr>
<tr>
<td>P60</td>
<td>186</td>
</tr>
<tr>
<td>Q300</td>
<td>185</td>
</tr>
<tr>
<td>Q20</td>
<td>183</td>
</tr>
<tr>
<td>N/F</td>
<td>192</td>
</tr>
<tr>
<td>1C90</td>
<td>194</td>
</tr>
<tr>
<td>1P</td>
<td>194</td>
</tr>
<tr>
<td>1P60</td>
<td>199</td>
</tr>
<tr>
<td>1Q300</td>
<td>192</td>
</tr>
<tr>
<td>1Q20</td>
<td>191</td>
</tr>
<tr>
<td>N/F</td>
<td>190</td>
</tr>
<tr>
<td>MC90</td>
<td>200</td>
</tr>
<tr>
<td>MP</td>
<td>193</td>
</tr>
<tr>
<td>MP60</td>
<td>194</td>
</tr>
<tr>
<td>MQ300</td>
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<td>MQ20</td>
<td>193</td>
</tr>
<tr>
<td>P</td>
<td>196</td>
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<tr>
<td>0.5P</td>
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<td>0.84P</td>
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<tr>
<td>1P</td>
<td>195</td>
</tr>
<tr>
<td>2P</td>
<td>195</td>
</tr>
<tr>
<td>3P</td>
<td>195</td>
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</tbody>
</table>

Comparison Blends (Krauss/Gottfert)

<table>
<thead>
<tr>
<th>Pipe Code</th>
<th>'B' Onset Temp. (°C)</th>
</tr>
</thead>
<tbody>
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<td>185 / 190</td>
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<tr>
<td>P</td>
<td>186 / 197</td>
</tr>
<tr>
<td>Q20</td>
<td>183 / 195</td>
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<tr>
<td>1P</td>
<td>194 / 196</td>
</tr>
<tr>
<td>1Q20</td>
<td>191 / 196</td>
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</tbody>
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