The variation in physical and structural properties

with processing conditions of injection moulded rigid PVC.

By

Clive John Copsey MSc
Loughborough University of Technology

Submitted in partial fulfilment of the requirements for the award
of PhD of the Loughborough University of Technology.

1980

Director Professor A.W. Birley

Supervisors M. Gilbert PhD
D.E. Marshall PhD
Institute of Polymer Technology
© by C.J. Copsey 1980

I certify that this work has not been submitted to this or any other institution for consideration of a degree.

Acknowledgements

I would firstly like to thank B.P. for the supply of all the base polymer used in this work, and also the various members of the company for their most useful advice, especially in the interpretation of the ion etching results.

I would like to thank my two supervisors Dr. M. Gilbert and Dr. D. E. Marshall for their encouragement and guidance over the period of the work.

Also my thanks to the Science Research Council for the award of a grant to enable this work to be made possible.

Finally I would like to thank my typist who had to decipher my writing and to my wife for her patience when correcting this document.

SUMMARY

A blend of commercial PVC was injection moulded using two different
cavities: a small thin square plaque and a larger rectangular one of
a variety of thicknesses. The effects of changes in processing conditions
were related to the resulting properties and structure of these mouldings
and shown to vary with positioning in the plaque.

A virtually amorphous skin was discovered at the surface of the mouldings,
the thickness of which was shown to vary with processing conditions.
The thickness of skin was seen to be much greater with mouldings from
the square cavity than from the larger rectangular cavity for similar
processing conditions. It was shown to be greatest in the vicinity of
the gate decreasing towards the end of the plaque.

Physical properties such as the level of internal stress were shown to
be related to the amount of skin produced at a variety of processing
conditions. The greater the amount of skin the higher the internal
stress. Internal stress was greatest for the square plaque.

Density decreased as the thickness of skin increased and was shown to
increase as the amount of skin decreased. The density of the rectangular
plaques was greater therefore than that found for the square mouldings.

The amount of shrinkage released on heating (reversion) was seen to be
related both to the moulding conditions used and likewise to the thickness
of skin. The greatest shrinkage was reported in the vicinity of the gate
and was higher in the square plaque than the rectangular moulding.

An X-Ray diffraction technique was used to show that the structure of
injection moulded PVC was composed of very small imperfect crystallites

in a basically amorphous background. The size of these crystallite regions was seen to increase with increasingly higher temperature conditions used for moulding. The orientation of the crystallites was shown to vary with processing conditions.

Finally, differential thermal analysis showed that the glass transition temperature did not change significantly for either plaque. However, a broad endothermic melting peak was found and the peak area was related to enthalpy changes. The enthalpy change was shown to vary with processing conditions and position in the plaque and was seen to be greatest for the thicker rectangular moulding than for the thinner square plaque.

CONTENTS

CHAPTER 1 - INTRODUCTION

CHAPTER 2 - EXPERIMENTAL - MATERIALS AND PROCESSING

CHAPTER 3 - CHARACTERISTICS AND PROPERTIES OF MOULDINGS

CHAPTER 6   - CONCLUSIONS

CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

The aim of this research project was to study the effects of changes in the injection moulding process on the structure and properties of a commercial blend of PVC.

It is well known that temperature effects and also moulding effects produce differences in the resulting moulding. Although a lot of work has been conducted into these differences for a wide range of polymers very little work seems to have been conducted with PVC.

A range of processing conditions were to be used, and in particular the effects of changes to the melt and mould temperatures on the structure and properties of the mouldings estimated.

It was felt important that the results of this work could be related to what is likely to happen in practice to give a clearer understanding of the effects of the moulding process.

The changes in properties/structure with position in a moulding was also to be studied, so that perhaps the design of a moulding may be made with these positional changes in mind.

From this work it was hoped that it may be possible to predict the changes in structure and properties for the complete range of processing conditions possible. It was also hoped that these effects could be utilised when a moulding was being designed.

The techniques used to follow changes were such that they would be available to a major company or access to them would be possible.

1.2 LITERATURE SURVEY

1.2.1 Structural Properties In Mouldings

Because of the complex nature of the injection moulding process the resultant moulding is not homogeneous. In fact a number of workers have discovered distinct zones through the thickness of a moulding.

Many workers have attempted to relate the structure of a moulding and the moulding conditions under which it was produced.

Thermal history is shown by Waywell[1] to affect properties for high density polyethylene from polymerisation to moulded product, it was found that at each stage a change in structure occurred. Waywell has also shown that for polypropylene three seperate zones are found in a moulding namely a highly oriented non spherulitic skin, a shear nucleated intermediate layer and a spherulitic core. He shows that the amount of each of these layers varies with melt temperature and that the resulting composition influences the mechanical properties. Namely that tensile strength decreases with increasing melt temperature because of the reduction in the criented outer layers. He also says that any ordering present could be the result of growth centres formed at a stage prior to moulding. This is certainly the case for polyethylene and polypropylene where it has been shown that heat treatment at temperatures 40°c above the melting point for one hour does not destroy any memory of previous order.

For a different moulding material poly-4-pentene-1 (T.P.X.) Bevis and co workers[2] detected two zones in a moulded tensile bar;

Highly oriented
Structure

Equiaxed structure
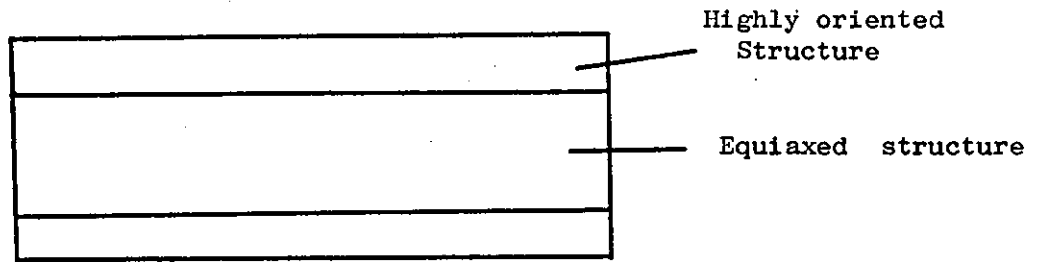
Fig. 1.1 Different zones in a tensile bar[2]

Band 1

Band 2

Band 3
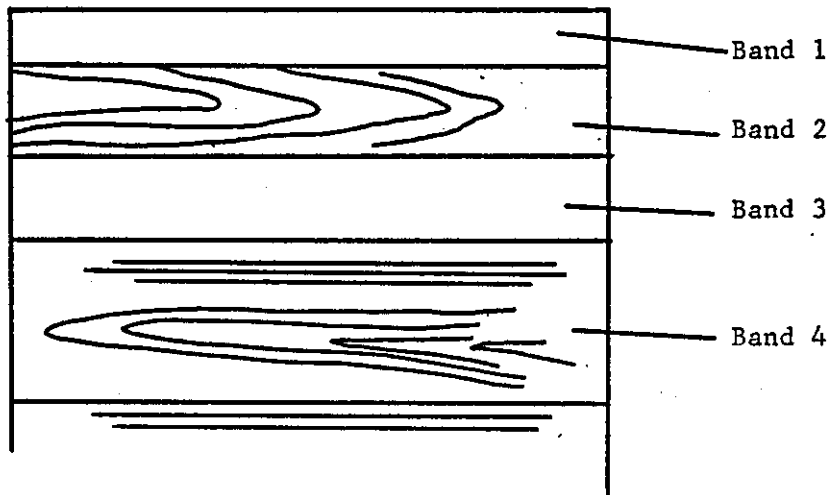
Band 4

Fig. 1.2 Optical micrograph[7] showing the band
structure and the opposing directions
of flow lines in Bands 2 and 4.

a highly oriented structure and a "crudely developed spherulitic".
These were in alternate bands (fig 1.1) with the centre having an
equiaxed structure.

The highly oriented skin is shown to decrease with increasing
barrel temperatures. The effect of mould temperature on the amount
of skin depends on the corresponding melt temperature. At the lower
barrel temperatures little change is seen in the thickness of the
oriented layers as a function of mould temperature. This is also
the case for the higher melt temperatures.

At an intermediate barrel temperature however, a rise in mould
temperature results in a greater amount of oriented material. These
results are in opposition to those determined by Henke et al[3] who
show that mould temperature has a significant effect on the
resulting structure when the material used was polypropylene.
They found that it was not the thickness of skin that changed with
moulding conditions but a region intermediate between the skin and
the core. The mechanical properties were also shown to be related
to the size of spherulites present, small spherulites which are
present in tensile bars moulded at high melt temperatures result in
higher impact strengths. The surface layer of the moulding was
shown to be amorphous and not to change very much with mould
temperature. Finally, it is interesting to note that the molecular
weight of the skin is higher than that of the centre regions.

Clarke[4] also shows the existence of three regions through the
thickness of an acetal moulding. He reports these regions (zones 1,
2 and 3) to be of different orientations. The orientation at the

surface is due to the combined effects of thermal gradients and surface nucleation, and the thickness of this layer is 0-0.2 mm. depending upon moulding conditions. It is also suggested that lamellae are present in the moulding perpendicular to both the surface and the injection direction in the 'skin'. The second layer is shown to consist of coarse and distorted spherulites this layer exists from 0.2 to 1.0 mm from the surface. In the centre layer of the moulding there is no preferred orientation direction and this core region is spherulitic. It is also confirmed that the thickness of zones 1 and 2 decrease when the mould temperature is increased.

Kantz[5] clearly states that the final properties of a moulding are dependent upon its morphology and the amount of orientation present. The levels of both for polypropylene may be controlled by the processing conditions used. He shows that injection pressure has little effect on tensile strength at constant melt temperature but that tensile strength does increase with increasing melt temperature. The existance of three distinct layers as found by previous workers are shown. Variations are much more significant in the case of impact strength which increases with increasing melt temperature.

He attributes the formation of a skin-core morphology not only to a temperature gradient between the inner and outer sections but also to higher shear stresses at the wall of the moulding, and a shear gradient. This is illustrated in a series of experiments with a viscometer in which extrudates below the critical shear stress for

flow instability exhibited no skin, whilst that above this critical

value showed a section typical of that found in injection mouldings.

The intermediate layer was found in both extrudates. This transitional

region is one in which the melt viscosity is low enough for relaxation

to occur, however unlike the core the crystallites appear to be

oriented along shear bands perpendicular to the flow direction. This

is due to high nucleation density along this shear band constraining

growth in one direction only.

In a similar study by Mencik[6] et al it was shown that the time to

fill which was proportional to shear rate, had a more significant

effect on the thickness of the transitional layer than variations

in melt temperature. The longer fill times produced corresponding

thicker surface layers presumably due to less severe shearing action.

Although these studies are with materials other than PVC some

of the results may be relevant to this work. Certainly Mencik[6] et al

when they describe an abrupt change in morphology at the boundary

of each layer suggest that this may also be so with other materials.

It is obviously much easier to detect a spherulitic structure in

polypropylene than it will be with a relatively low crystalline

material such as PVC.

Similar results were obtained by Callear[7] et al in which the

material used was polytetramethyleneterephthalate and four zones were

detected. They comment on this only to the extent to say that it was

due to a combination of barrel temperature and injection speed. The

various bands and flow lines of a section of a moulding (see fig1.2)

show that the flow lines in zone 2 are in an opposite direction to

those of the central zone 4. It is thought that this is a consequence
of moulding conditions used and that the central section was beginning
to solidify during filling of the mould. The increased viscosity
would create shear stresses and also cause changes in crystallinity.
The flow lines could then be said to represent changes in
crystallinity. This was also shown by Machin[8] who reported that
both pressure and shear stress altered the crystallisation process.
So it is assumed that the degree of crystallinity varies through the
thickness of an injection moulded bar.

In a paper by Kantz et al [9]. reference is made to a polypropylene
tensile bar in which the thickness of skin was shown to be independent of
injection pressure over a range of melt temperatures. The thickness
of the shear zone does however vary significantly with pressure as
well as melt temperature. If data for two different pressures is
recorded, the resulting extrapolation of the plot of thickness of
skin and shear zones versus melt temperature intersects at 165°c
the melting point of polypropylene. This means that a completely
oriented structure could be achieved (ie. all skin) if the material
could be moulded at this temperature. They conclude that one should
know the morphological state of the polymer, to be certain that
data from mechanical tests carried out subsequently are meaningful;
and also that a detailed knowledge of the structure may allow
fabrication of an injection moulded part having tailored mechanical
properties.

The surface 'skin' produced by the injection moulding process
has been studied in some detail by a number of workers in particular

Bowman et al [10] for T.P.X. have shown that a distinct surface layer
was easily distinguishable from the main central core of the moulding.
They show the 'skin' to be highly oriented and the thickness to vary
with barrel temperature. The extent of the surface layer in the
moulding is shown to decrease with increasing barrel temperature. An
increase in injection pressure is found to produce no significant
changes in the thickness of skin for the same temperature conditions.
On the other hand mould temperature has a considerable effect on the
amount of surface skin.

At low melt temperatures little variation in skin thickness with
mould temperature was observed, but as the temperature of the melt
was increased the effect of the quenching action at the mould walls
produced substantial changes in the amount of skin. As the
temperature of the mould was increased the amount of skin present
in the moulding was greater.

Further evidence of skin formation is shown [1] when the moulding
material is polypropylene. In this case however the amount of skin
decreases with increasing melt temperature and increasing injection
pressure. Relationships are found to exist between skin thickness
and tensile strength, where the strength of a tensile bar is
increased substantially with a greater amount of skin. Likewise
the shrinkage of the moulding is increased by larger amounts of skin.

A change in mould wall temperature in the production of acetal
tensile bars showed a definite increase of surface skin with
increasing mould temperature[4] The argument put forward to justify
the changes was that they were due to the effects of thermal

gradients produced by the differences in temperature between the melt and the mould walls.

In contrast to previous workers Henke et al[3] show that for injection moulded bars of a polypropylene-ethylene co-polymer no variation in skin thickness was found with a range of mould temperatures. They show that it is in fact an area just beneath the surface skin that changes with mould temperature. The molecular weight of the skin however was found to be substantially higher than in the rest of the bar. This they say is due to preferential crystallisation as a non spherulitic structure is formed compared with the spherulite growth away from the skin.

Physical properties of bars with differing thicknesses of the layer below the skin show no discernible trends for tensile strength, flexural modulus or elongation at yield for which they have no explanation except a suggestion that spherulite size and molecular orientation will have an effect on physical properties. They do show however that tensile impact does decrease with a reduction in the layer below the skin.

The tensile strength of the skin of high molecular weight, injection moulded polyethylene was shown to be much less than the central core due to the variation of crystallinity through the section; whilst D.S.C. thermograms taken at various positions through the moulding show a much smaller size of endotherm in the skin[11].

Kantz[5] shows the effects of melt processing variables on the skin-core relationship for polypropylene. He suggests that three

discrete phases exist, a non spherulitic skin with an essentially spherulitic core and an intermediate zone. The skin he shows to be highly oriented and to decrease with higher melt temperatures. The modulus and tensile yield strength of the oriented layers are shown to be greater than those of the core. Unlike others who relate the formation of a skin to only steep temperature gradients he says that a high shear stress at the wall and a shear gradient are sufficient. A change in shear stress alters the crystallisation process as predicted by Binsbergen[12].

A variation in the fill time of the mould has been shown[13], to produce the most noticeable differences in the thickness of the various layers for polypropylene. If the fill time (i.e. equivalent to a change in shear rate) is short the thickness of the surface layers is small whilst if increased ten fold it is ten times as thick. It must be made clear that it is the section of the moulding just below the skin that changes most with shear rate, whilst that of the skin remains virtually constant.

1.2.2 Structure In PVC

As with other polymers the stereoregularity of PVC may be of three types atactic, syndiotactic and isotactic. From the general formula for PVC viz $(CH_2 . CHCl)_n$ it is the chlorine atoms that can change their relative position on the PVC backbone. The isotactic position has the chlorine atoms on one side of the polymer chain whilst for the syndiotactic case it regularly alternates about the main backbone. Atactic polymers have no regular arrangement of the chlorine atoms. It is generally considered that it is a syndiotactic

formation that is produced as the polymerisation temperature is decreased, and it has been shown[14] that the syndiotacticity increases substantially as the polymerisation temperature is decreased. For instance Pezzin[15] showed that for polymer produced at 50°C a syndiotacticity of 55% was found whereas decreasing the polymerisation temperature to -60°C increases this value to 75%.

The amount of order possible in PVC has been shown to be dependent on the amount of branching . Baker et al[16] calculates that for a commercial PVC five to six branches per 1000 carbon atoms are found. Decreasing the polymerisation temperature leads to a decrease in branching and the possibility for an increase in crystallinity[17].

The macromolecular structure of suspension PVC has been studied[18] and found to be composed of globules $1-2\mu m$ in diameter formed from the polymerisation process. Mechanical action (rolling) and thermal treatment reduces the macroglobules to microglobules $0.1\mu m$ diameter. Specimen structure changes with an increase in temperature or time of 'rolling' to a fibrillar form. It is suggested that the structures observed during rolling will be formed to a certain extent during processing of PVC by extrusion, and injection moulding.

The morphology of injection moulded PVC using a variety of moulding conditions was studied by Knyazeva et al[19]. They showed that processing has a considerable effect on the structure of PVC. At low values of melt temperature and shear rate a predominantly globular structure is observed which they say indicates a retention of structure after processing as the unprocessed material exhibited a similar form. Increasing the melt temperature leads to the

formation of a 'wrinkled' globular structure up to $1 \mu m$ in length and 500 $\overset{\circ}{A}$ wide.

At high shear rates globules and bundles aggregate into large oriented systems giving a branch-like structure 5-10 μm long with a central stem and side branches that are 2000$\overset{\circ}{A}$ apart. A study of fragments of this regular structure reveals 'grape-shaped' associations of small globules 300-8000$\overset{\circ}{A}$ diameter that are joined to form the larger and more complex forms. Denser packing under these conditions that produced the fibrillar arrangement gave increases in tensile strength of up to 50% above that for the globular structures.

The extrusion of plasticised PVC shows that [20] any particle structure that was present prior to processing disappears at 200°C but reappears after cooling. Ultrathin sections showed the existance of particles about 0.03μm in diameter. Berens and Folt[21] are of the opinion that incomplete fusion of resin granules results in anomalous flow effects during the extrusion of suspension PVC. The relationship between these anomalies and the resin morphology is not well understood they conclude. Chartoff[22] however suggests that PVC granules are non homogeneous and vary in both particle shape and size. Electron micrographs of a granule show the existance of aggregates of particles of submicron size. Samples of suspension PVC particles with a tin stabiliser when heated to 190°C for four minutes retain the original particulate structure. He postulates that during processing at this temperature, which is within the normal processing range, fusion is complete. Even in samples heated to 220°C, which is above the usual processing temperature,

evidence of particle retention is found. Preliminary studies

suggests that a heterogeneous particulate morphology exists.

Bort et al[23] have shown by electron microscopy that during

polymerisation spherical particles 1μm are found. The number of

these particles does not change during polymerisation only the size

increases. Each particle consists of a number of microglobules.

The higher the temperature of reaction the smaller the number of

microglobules producing a more compact structure than polymerisation

at lower temperatures where a more open structure is obtained.

Shinai[24] however compares suspension PVC of different degrees of

polymerisation and shows that the particle diameter does not change

significantly.

1.2.3 Thermal Properties

There has been great debate on the true melting point of PVC

the value obtained varying with the method of determination.

Colbourne[25] used a variety of commercial polymers and found a range

of melting points from 174-232°C, using a Köfler bar, whilst Michel

and Guyot[26] found a much smaller range of 250-260°C by X-ray

diffraction.

By application of Flory's theory of melting Nakajima[27] et al and

Anagnostopoulous[28] arrive at melting points of 176°C and 233°C

respectively for commercial polymers under shear conditions.

For plasticised PVC over a range of temperatures using a

torsional pendulum and extrapolating to zero plasticiser content

Reding et al[29] show that the melting point of a number of PVC resins

varies with polymerisation temperatures. PVC that has been polymerised

at low temperatures (-80°C) had the highest melting point, in the region of 300°C, whilst those materials polymerised at 40°C had a melting point of 220°C.

The influence of thermal history on the properties of PVC has been shown by Illers[30] to be considerable. Using calorimetric measurements he investigated the effects of annealing above and below the glass transition temperature. As the quenching rate is increased the glass transition temperature is shifted to a lower temperature and a broad endothermal maximum occurs at approximately 175°C. Melting takes place over a wide temperature range due to the varying amount of crystalline material. Annealing below Tg produced maxima in D.T.A. traces close to the step change due to a superheating effect whilst annealing above Tg resulted in a shift to a higher temperature of these maxima. This latter effect is due to annealing producing more perfect crystallites. He goes on to say that the determination of the glass transition temperature of quenched polymers will always give incorrect results if the heating rates used in the calorimeter are not appreciably higher than the quenching rates.

Djumer et al[31] used thermal analysis to show that for injection moulded high molecular weight polyethylene different endotherms are found at varying distances from the surfaces of the moulding. Although they used very high injection pressures there is an underlying trend for the depth of the endotherms near the surface to be greater than those determined for samples taken at the centre of the moulding.

The effect of annealing on polymers in terms of the size of endotherm has been studied by McKinney and Foltz[32] who show that as the temperature and time of annealing are increased so the depth of the endotherm is increased. They attribute these findings to an increase in crystallinity, although this could not be corroborated by X-ray evidence as the increase was very small.

It has been suggested[33] that cold pressing and grinding of PVC reduces crystallinity to zero but that by subsequent heat treatment at temperatures greater than Tg the optimum degree of crystallinity is regained by the sample. A measure of crystallinity has been made by Yagfarov[34] based upon a comparison of two samples of differing amounts of crystallinity. There are two processes involved, he says, when partially crystalline samples are used in thermal measurements. Melting is associated with the crystalline phase whilst the transition from the glassy state(softening) is associated with the amorphous phase of the polymer. He shows that the level of crystallinity in polydimethylsiloxane is dependant upon previous heat treatment.

Dunn and Ennis[35] showed that where samples of PVC with additives of calcium stearate and dibutyltin dilaurate were examined by D.T.A. a synergistic relationship was observed i.e. the induction period to decomposition was longer than that predicted by simple addition of the increments due to each component. It is concluded that activation energies determined from a thermal analysis could be used to classify and evaluate stabiliser systems.

Evidence of structural changes occurring are shown by Ali and Sheldon[36] to take place in so called amorphous polymers such as

polystyrene, polymethylmethacrylate. and polyvinylacetate.when they are annealed at temperatures close to T_g or when they are cooled slowly through the glass transition temperatures. Such structural changes they say have an origin that is not clearly defined. They point out that contrary to previous descriptions of 'glassy' polymers as having a completely disorded arrangement of macromolecules there is growing opinion that such a description is an oversimplification. Furthermore they go on to say that it is not inconceivable that some order may exist at a low level and that the usual methods of determining crystallinity such as X-ray analysis cannot detect such order at this level.

The importance of taking great care in analysing the output from differential thermal analysis is stressed by Roberts and Sherliker[37]. Initially they found that with a sample of polyurethane not encapsulated in aluminium an exothermic step change occurs in the vicinity of T_g. Changes in the D.T.A. thermogram are reflections of changes in the thermal diffusivity of the sample. i.e. the value of ΔT on a thermogram is a function of the ease of conduction of heat through the sample. Polymers in a highly strained state show a bulk volume contraction at T_g and a difference in thermal conductivity producing an exothermic step change at T_g. If the sample were reheated no such contraction would occur and a 'normal' thermogram would be obtained. This shows the need to minimise the effects of sample thermal conductivity by encapsulating in aluminium foil they conclude.

Finally Gray[38] uses a wide variety of heat treatments to indicate that annealing below Tg causes changes in the structure of the amorphous phase in PVC. Whilst for heat treatment above the glass transition temperature crystallisation was shown to occur and therefore changes in the crystalline content may take place during processing.

1.2.4. Crystallinity And Its Measurement By X-Ray Diffraction

X-ray studies by a number of workers have been used to determine the crystal structure of PVC. The foundations were laid by Natta and co-workers[39] who looked at the dimensions of an orthorhombic cell but flat planar conformation.

This is not the only type of crystallinity possibility as May et al[40] explained. They looked at a calendered emulsion polymer and revealed as many as thirty additional peaks which had not previously been reported. These peaks were assumed to be a different crystal modification since they could not be attributed to additives and degradation as these were dismissed or identified. The size of the unit cell dimensions were estimated to be 9.3, 5.7 and 15Å(Natta's was 10.6, 5.4 and 5.1Å) this change they attributed to the formation of a new crystal lattice by deformation. This has proven to be the case for polypropylene and polyethylene[41,42].

Large deformations produced by the injection moulding process could lead to similar changes in structure being experienced. The work of May et al[40] for large crystallites and a high degree of order due to deformation and thermal treatment, may be present in part in injection mouldings.

Lebedev[43] showed that the degree of order of PVC can be changed by changing the conditions of polymerisation. He says that it is very difficult to produce a PVC 'melt' due to the fact that its degradation temperature is much lower than the melting point of its crystallites (which Reding[29] et al claim to be 220°C) Using Cu K_α radiation he detected two peaks in an amorphous trace at 24.0° and 40.4° 2θ and an extra broad peak at 17° for a quenched melt which he obtained by heating a sample for 1-2 min at 230°C in Wood's alloy and rapidly cooling in liquid nitrogen. He goes on to to confirm that PVC is a weakly crystalline polymer and that its crystallites are either very small or very defective. He shows that the sizes of crystallites in samples heated from room temperature to 175°C increase from 170 to 260Å respectively. Resulting changes in crystallinity diminished with temperature due he says to degradation. Other attempts at assessing crystallinity from infrared spectroscopy[17] have only ranked different types of PVC into ascending order of crystallinity e.g. for butyraldehyde polymerised PVC the ratio is D_{635}/D_{692}=4.7 and for commercial PVC 2-2.7.

Mammi and Nardi[44] confirm the two amorphous peaks from X-ray studies and the peaks present in a crystalline sample.

A number of authors[45-51] have investigated the degree of crystallinity in PVC by diffraction methods for a large number of polymerisation conditions and extents of crystalline order .

Nardi[52] and Lebedev[46] say that the position of the peaks of an unannealed oriented PVC sample at 24.5°(2θ) is independent of azimuthal angle whereas the 17.5°(2θ) halo is present in the

equatorial but absent in the fibre axis direction. They suggest
that this indicates a mesomorphous or nematic phase ordered in a
parallel arrangement of chains.They go on to say that this is
present in the unorientated sample.

Lebedev[53] considers the mesomorphous phase to be seperate
from an unordered amorphous region. Estimates of the percentage
crystallinity of mass PVC by the diffraction work of D'Amato[45] et al by
comparing so called amorphous samples with samples varying in order using
different polymerisation temperatures suggest a range of 5-10%
depending upon thermal treatment. This method, as with all other
methods where a comparison with an amorphous sample is used,
assumes that one can obtain a truly amorphous sample. It is thought
doubtful by many workers that order is totally destroyed upon
heating and quenching.

Work on small angle X-ray scattering[54] indicate the level of
order to be much lower than that obtained by other methods. Annealed
samples (6 days at 75°C) were found to have the same value within
experimental error of the original unannealed sample. This suggests
that the structure of PVC is not changed at this low annealing
temperature. Based on their results the crystalline content is
calculated to be a maximum of 0.5%. They say this result implies
that the concept of three dimensional order in PVC needs revision.

Rybnikar[55] working with both suspension and emulsion PVC
states that the crystallisation and recrystallisation process take
place similarly as in other partially crystalline polymers. The
crystallinity he says of PVC is low 10-20%.

Values of crystallinity vary from one review to another, a
range of 0 to 15% being the most common for commercial PVC depending
upon sample history.

Carrega[58] makes the point that only the uppermost thin layer
of sample exposed to radiation is analysed due to to the small
penetration of X-rays into PVC. For this reason moulded samples
must be relaxed to prevent orientation effects from marking the
true spectrum but he says this relaxation treatment might alter
the sample structure. So that in order to evaluate the true
crystallinty of a sample its exact thermal and mechanical history
must be known to draw any useful conclusions. Heating to 200 ^{o}C
 and quenching industrial PVC gives samples of minimum crystallinity
he continues, but is is not certain this minimum is nil.

Michel and Guyot[26] explain that changes in the X-ray patterns
of PVC samples heated from 80°C to 260°C do not show any marked
difference until 160°C. After this temperature, the width of the
peaks at 2θ values of 17.2^o and 19°, which Natta et al[39] attribute
to the orthorhombic cell, became narrower so the size of
crystallites up to 240°C increases from about 80Å to 150Å. The
crystallinity of these samples does not alter very much however.
They concluded by saying that crystallization occurs up to 240°C
as the size of the crystallites increases up to this temperature;
and that the crystallization involves better packing or ordering
of crystalline regions rather than a crystallization from amorphous
regions, as the crystallinity index does not change significantly.

Two types of crystallinity are shown by Juijn et al[59] to be of primary and secondary nature. The first formed by the polymerisation process and the second from annealing above the glass transition temperature. In contrast to Michel and Guyot[26] they show that the maximum crystallization effect is produced at 110°C for a commercial rigid PVC.

They confirm that it is only the syndiotactic parts in the PVC chain that crystallize and treat the material as a co-polymer with a crystallizable syndiotactic part and a non crystallizable isotactic part.

This general agreement that it is only the syndiotactic sequences that are crystallizable is supported by Pezzin,[60] and other workers have clearly shown [61-63] that the degree of syndiotacticity does correlate directly with the degree of crystallinity.

Several authors[64-66] give the maximum degree of crystallinity of commercial (nearly atactic) PVC to be less than 5 per cent (and others[45,46] not greater than 10 per cent) from X-ray studies, whilst the size of crystallites is put at 50-100Å.

1.2.5 <u>Structural Investigations By Electron Microscopy - Ion</u>

   <u>Etching.</u>

The erosion of a surface due to the ion bombardment of a cathode in a glass discharge was first observed in 1852 by Grove.[67] Since that time the possibility of utilising, the technique for the examination of microstructure has been attempted.[68-70] Initially with metals and later with polymers. The technique appears to have been used for materials where other forms of etching, such as chemical etching have proved difficult.

Although the basic principle of using the specimen as part of the cathode in a glass discharge has been used, design details of the apparatus have varied. This has resulted in the conditions required for etching to vary, with each type of equipment, giving little information for a standardised procedure.

Most employ an inert gas such as argon or krypton as the ionising atmosphere although some have used oxygen, neon and xenon, although oxygen has produced degradation problems in certain instances.

Etching times have varied from hours to minutes due to conditions of use.

The technique has been used to determine polymer morphology e.g. polystyrene, ABS and PVC in which structure of the order of 10-100nm have been observed. This order of magnitude has been predicted by Schoon[71] in a structural model resembling a string of pearls. He suggests that the molecular chain made up of monomer units forms a primary structure. These chains he says are more or less ordered and thus builds up a secondary structure which in turn order themselves to form 'pearls' as the tertiary structure which are finally linked to form a string of pearls, the quaternary structure. This latter structure is said to be in the range 10-100 nm. He was able to demonstrate by mechanical degradation that breakdown occurs only up to the tertiary unit, showing the exceptional stability above this unit.

Structures of this order of magnitude (as above) have been found in PVC.[72-74] These substructures build up to a longer globular structure of the order of $0.1 - 2 \mu m$.

In the case of PVC Hattori et al[75] have suggested the model below. According to this the raw material is composed of particles 1 μm in diameter when these globules are heated to 190°C they disappear and 'fibril' like structure with a diameter of 30nm are seen. It is suggested that these fibrils are virtually indestructable.

This type of structure has further been observed by Grosskurth[76] who showed that increasing deformation produces a distinct structural change in these fibrils. A line-like structure is shown consisting of parallel lines or 'lumps' of material the distance between which becomes smaller with increasing deformation. These parallel rows are oriented at right angles to the direction of stress; a most interesting result produced from ion etched polystyrene. It has been felt that specimens produced for microscopic work by ion etching could result in artefacts being produced at the surface. However Grosskurth is convinced that what he is seeing (ie. line-like structure) is unequivocally related to orientation.

Globules, of diameter 0.1-2 μm have been detected in PVC by Menges[77] and are said to be found in mass, suspension and emulsion polymerised material. The coarse particles are shown to remain present up to 160°C at which point they begin to fuse until they appear homogeneous above 200°C. It is however possible that the globules disappear only because additives diffuse from the particle core into the particle boundaries which have been etched away. This would be possible with lower melting point additives such as the waxes which are included as a processing aid he says.

The following is proposed to determine how the globules are held together and which material is etched away initially. It is

assumed that the globules are surrounded by:

Low molecular PVC molecules (from polymerisation)

emulsifiers where present (from polymerisation)

stabilisers and lubricants which are added during

compounding.

If this is the case then due to the lower molecular weight of
these additives for the processing conditions found in injection
moulding, the additives and the low molecular weight particles melt
and help to form a lubricant for the soft but unmelted PVC particles.
This 'coating' could then be preferentially etched away leaving
fragments of lubricant and other additives surrounding a PVC globule.
This has not been proven but for extruded pipes evidence of initial
particles produced by polymerisation is found. However the higher
temperatures and stresses produced by the injection moulding process
may show a different effect.

Grosskurth[76] did detect a coarse structure of non oriented
material at the centre of injection moulded test bars, whilst
towards the outer edges of the bar he found a highly stretched and
oriented material. This was shown by a line like structure similar
to that found by Menges.[77]

Although the usefulness of the structure revealed by ion
etching is open to debate it has been used successfully to give
information in other fields particularly for biological applications.
Spector[78] produced artefacts in red blood cells, but these became
less prominent as the accelerating voltage was increased revealing a
recognisable structure.

It is well known that the process can produce structural features which are not characteristic of the material but are artefacts. The presence of these may be confirmed as they produce random structures which are usually 'cone-like'. These were first observed by Guntherschulze and later by others (Thompson[79] and Wehner[81])[80].

Araldite has been used (Fitch[82]) to demonstrate that cones are produced in clusters which if subjected to further bombardment seem to disappear. A maximum height of 50nm was found before erosion of the cone took place. The surrounding material did give an indication of the true structure however. Artefacts were not produced if the specimen was rotated, but this resulted in a loss of structural features of the specimen.

It is suggested that the presence of a small number of cones may be beneficial as the beam direction may then be determined and structure perhaps formed by the action of the beam eliminated.

The effect of the process to increase the surface temperature of a polyethylene sample has been shown (Petrova[83]). In this case oxygen was used as the ionising gas, and temperatures could reach $130^{\circ}C$ under certain severe conditions but more usually only $50^{\circ}C$. This may or may not be signigicant certainly the higher temperatures would alter the surface morphology, but at temperatures less than T_g for PVC it is felt this may not occur.

Further evidence of surface cones is presented by Ducommun[84] who has written a computer program to predict the contour of these artefacts.

An interesting conlusion from ionic etching of aluminium was
that the cones were said to be formed by foreign matter (dust particles)
on the surface of the specimen. The material underneath the particles
was not subjected to etching so that an artefact was produced. A
similar effect was found with inclusions in the metal samples which
were not etched at the same rate as the surrounding matrix.

1.2.6. <u>Injection Moulding And Its Effects - Introduction</u>

Injection moulding is a method of converting a polymeric
material, usually granular or powdered, by the action of both
internal (shear) and external heating, with the application of
pressure, into a moulding which is a reproduction of the cavity of
the mould.

The very nature of the process suggests that changes in
processing conditions will result in corresponding changes in
compaction of the material i.e. density and the level of shrinkage
and orientation. Residual stresses set up during cooling will vary
with moulding temperatures and different flow patterns. Finally
the presence of a surface layer distinct from the main bulk of the
moulding will be found. All these effects will be illustrated
below by observations from previous workers.

1.2.7 <u>Flow In The Mould</u>

The injection moulding process has been studied by a large
number of people with different aims. Some [85-95] have concentrated
on analysing the flow in a mould by producing mathematical
expressions to explain mould filling.

It is not the purpose here to go into great detail regarding
the flow mathematically but rather as an empirical study.
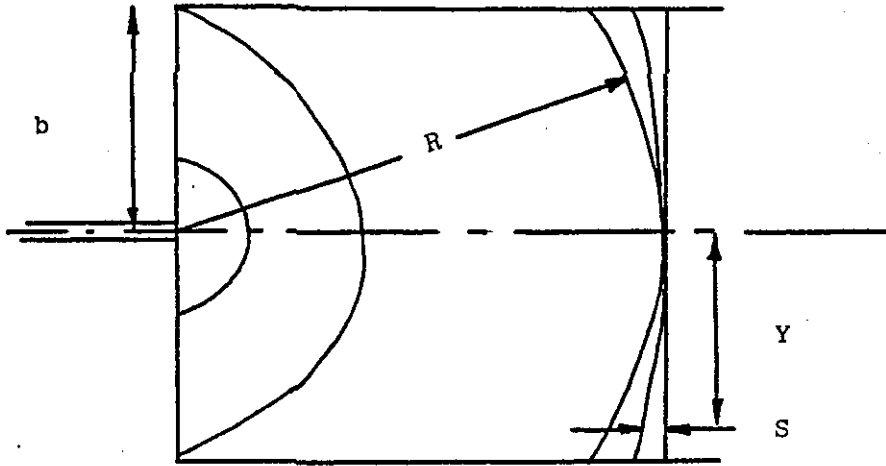
fig.1.3   Diagram for Kamals[96] flow studies with S(R,y)
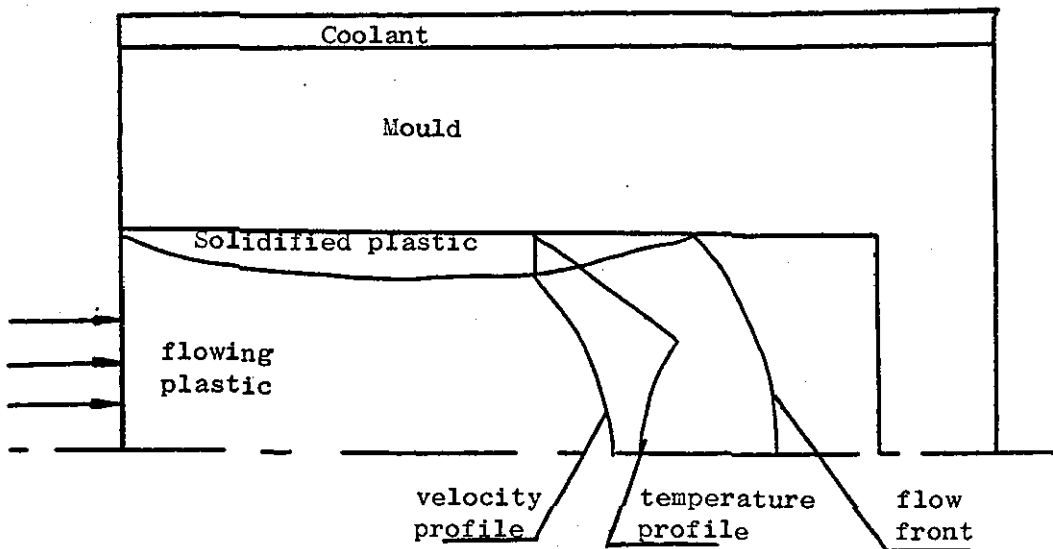
fig. 1.4   Polymer entering mould cavity in Lord and Williams [97] studies

Kamal[96] uses an extended version of a radial flow technique, previously used with a semi-circular cavity[85], to explain the flow in a rectangular cavity.

From high speed photography the shape of the melt front as it proceeds in the mould was determined. It can be seen (fig. 1.3) that the polymer spreads out radially from the gate until it reaches the side walls. Upon contact the melt front flattens out giving the appearance of plug flow.

Flow fronts for three commercial polymers polystyrene, high density polyethylene and low density polyethylene are shown to be very similar. A value 'S' which is "the axial distance between the actual front at a point located at a distance y from the axis and the straight line passing through the apex of the front at radial distance R from the gate" (Kamal[96] was measured and used to evaluate a constant K. The empirical factor K depends on resin properties and moulding conditions. It was found however that the dependance of K on moulding conditions was very weak. An average value of K was used for the three polymers above and good agreement between the predicted shape of the flow front and that measured was obtained.

Mould filling has similarly been studied by Lord and Williams[97] using production moulds in contrast to other workers[85-94] who analysed flow in simple circular or rectangular cavities.

Lord and Williams,[97] see fig 1.4 , show that a layer of soldified polymer is formed and that the flow front is similar to that of Kamal[96]. The temperature of the flowing polymer is seen to be a maximum some distance between the wall and the centre of
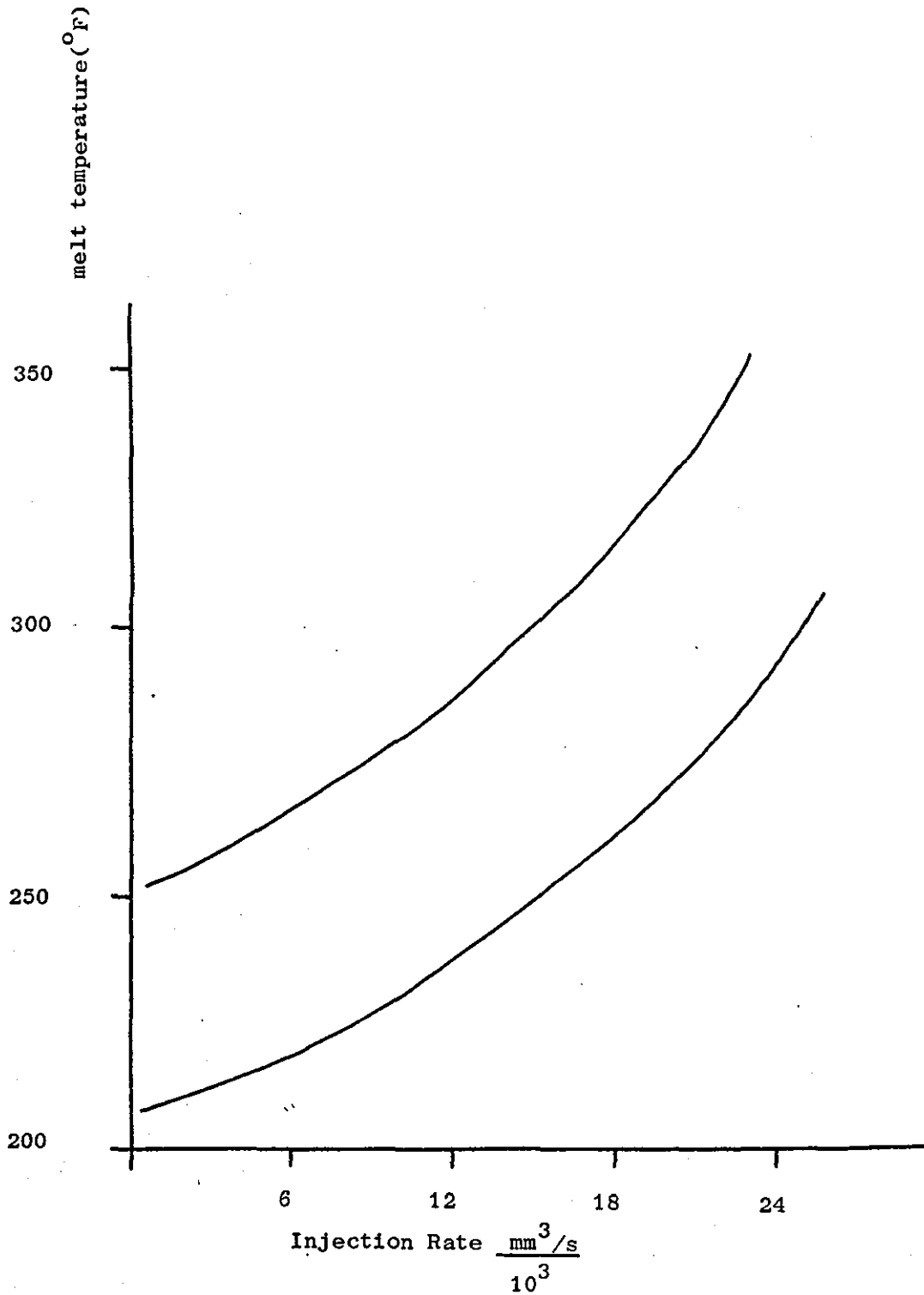
fig. 1.5[98] Variation in melt temperature with
injection rate.

the cavity. The thickness of the solidfied layer at the walls of the mould is shown to vary with distance from the gate decreasing as the flow front is approached. They also show that for a rectangular plaque of PVC the effect of cavity thickness on moulding conditions necessary to produce both a visually and mechanically satisfactory moulding is extremely important. Thinner sections require higher injection pressures in order to fill the cavity, together with an increase in the injection rate to maintain a minimum pressure drop across the cavity. For example a 1.5mm thick moulding requires an injection rate of approximately 16×10^3 mm /s at a pressure drop of $(10^4$ psi), whilst a 3mm moudling needs an injection rate of 4×10^3 mm /s at the same pressure. They continue that mould temperature has little effect on the pressure required to fill the cavity except at low injection rates $(4 \times 10^3$ mm /s) where a solidified layer of significant thickness forms and reduces the effective cavity thickness thus necessitating an increase in injection pressure.

The injection rate for a PVC telephone housing, was shown to[98] have a considerable effect on the temperature of the melt (fig. 1.5.) in the cavity. Modification to the length of the nozzle and the diameter of the sprue reduced the temperature of the melt in the cavity at constant injection rates, thus enabling faster filling and reduced cycle time. This makes the point that the conditions used for injection moulding in practice must result in an acceptable quality part for the shortest cycle time possible.

Deeley[99] has used a spiral mould in order to assess mouldability.

Another method[100] of describing the conditions necessary for production of a quality product was the control of melt viscosity in the range of 10^3 to 2×10^3 poise at a shear rate of 10^3 sec^{-1} at the moulding temperature used. This assumes that the polymer is thermally stable at this temperature which might not be the case for PVC.

Berger and Gogos[101] made one of the few studies of the flow of PVC in injection moulding. They developed a numerical solution to describe the cavity filling of a disc mould.

Variation in the thickness of the cavity shows that thinner discs have the largest radii at the flow front for similar flow rates. Even at relatively high flow rates sufficient material does not flow into the thicker discs to produce the same radii. It is further shown that mould temperature does not have as large an effect on the temperature of the polymer in the cavity as an increase in pressure does. So that if degradation was occurring in the PVC lowering the pressure and not the mould temperature would be more beneficial.

Gilmore and Spenser[102] studying the flow in a mould of polystyrene melts observed two types of flow one in which a uniformly expanding front emerges from the gate and another where jetting occurs.

Jetting has been observed by other workers[103,104] and is associated with small diameter gates and fast injection rates. Oda et al[105] describe experiments with polyethylene, polystyrene and polypropylene and extend their conclusions to other materials

Fig. 1.6   The effect of filling a cavity in a horizontal
or vertical mode[105].

(a)   (b)   (c)
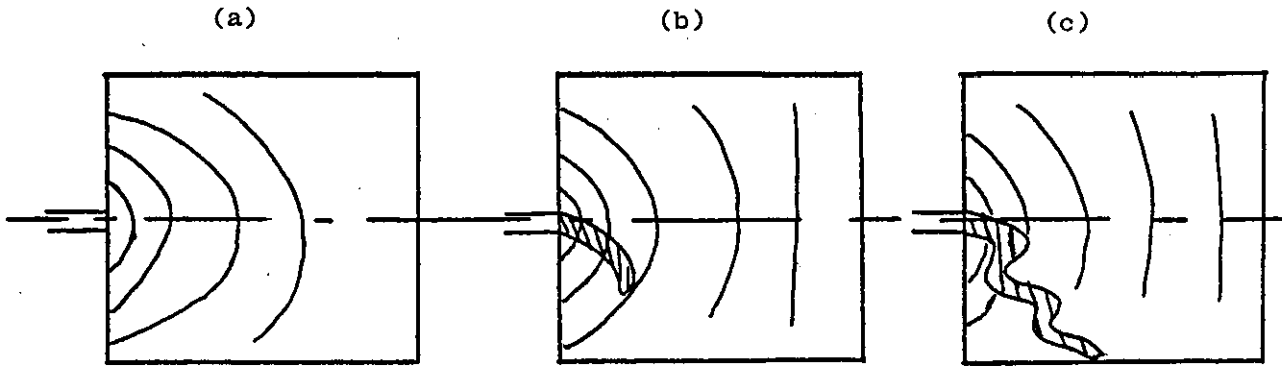
Filling horizontally of a rectangular cavity.

(a)   (b)   (c)
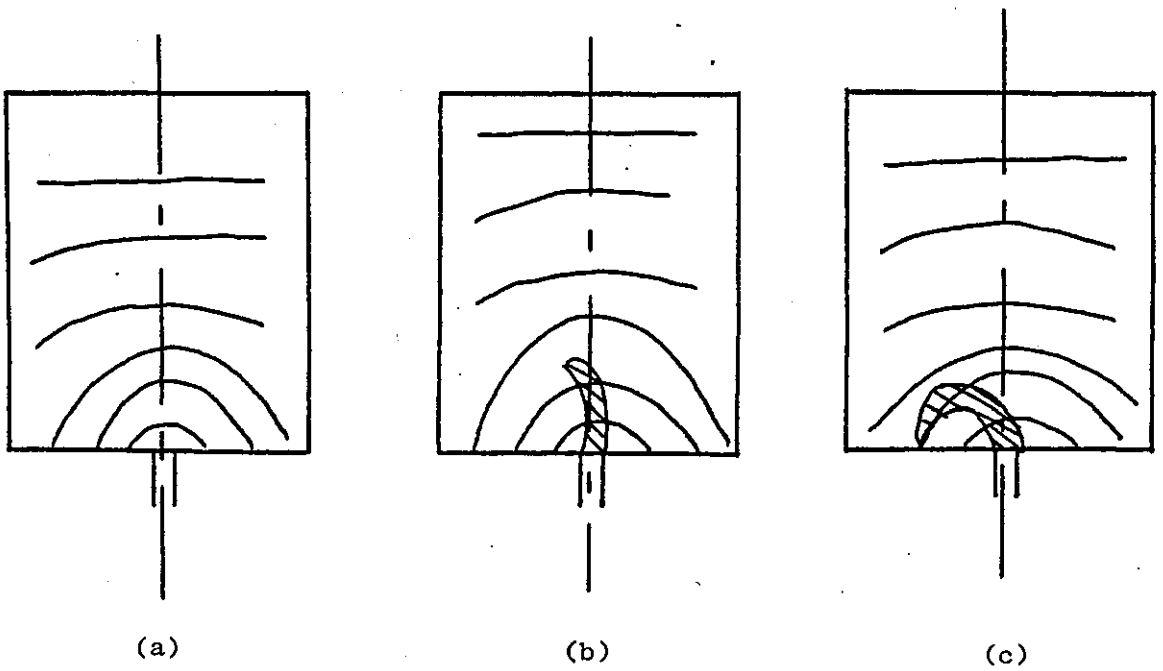
Filling vertically of a rectangular cavity

(a) Simple mould filling
(b) Mould filling at transition
(c) Jetting

in which they sought to decide whether a mould will fill uniformly or by jetting. The apparatus used was an Instron capillary rheometer to which was attached a mould with a range of cavities. In particular a simple rectangular cavity was used in which injection into the cavity could be vertically downwards, horizontal or vertically upwards.

Die swell ratio B, which is equal to d/D where d is the extrudate swell and D is the gate diameter, is shown to be related to d/h where h is the cavity thickness by the relationship

$$\frac{d}{h} = \frac{B}{h/D}$$

Jetting was seen to occur in moulds where large h/D ratios were found, and for smaller aspect ratios (h/D) only at low injection rates and high temperatures. It was found that situations in which the moulding thickness h, is greater than the extrudate swell d, results in jetting. If d ⇒ h a uniform material flow takes place which is obviously the more desirable. For all cases in which melts were injected horizontally into the cavity (and similarly for those cavities filled vertically at low filling rates jetting occurs and the jet is seen to fall to the bottom of the mould before it reaches the opposite wall. (fig. 1.6.)

Jetting may be avoided (fig. 1.7) by placing barriers near to the gates (a) or reservoirs of material prior to the gate (b), although this is somewhat a waste of material they conclude and suggest it is better where possible to change the moulding conditions.
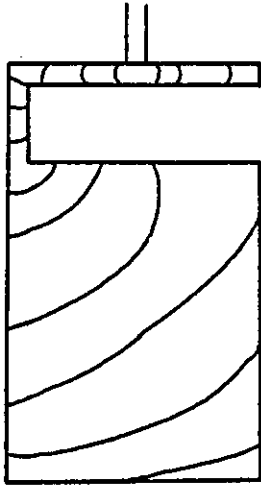
(a) Filling of a mould
    with a barrier near
    the gate to prevent
    jetting
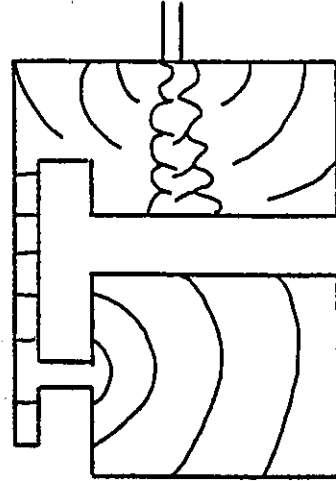
(b)　Filling of a mould with
    a reservoir to prevent
    jetting in cavity

Fig. 1.7.　Methods of preventing jetting [105]

Reports from other workers[106] suggest that jetting occurs

when the aspect ratio ($\frac{h}{D}$) is large, the temperatures of the

mould and melt are low, and the pressure is low which is in

agreement with the above.　However Sleeman[107] and White[108] mention

that jetting occurs when high injection pressure is used. Although

these views are inconsistent with each other Oda [105] et al show that

for polystyrene jetting can occur at both low and high injection

rates.　So that it is seen that jetting is a result of a number of

complex interacting conditions.

West[109] and Rose[110] describe a 'fountain effect' observed

near the fronts of Newtonian fluid slugs in a tube.　This phenomenon

has been used by White [111] to describe the flow in a rectangular

cavity, in which the melt, moving through the centre of the cavity,

seems to move out towards the cavity walls which then solidifies.

The velocity field is predicted to be in the shape of a semi-circle

near the gates whilst further into the cavity the melt separates

into two directions (fig. 1.8).
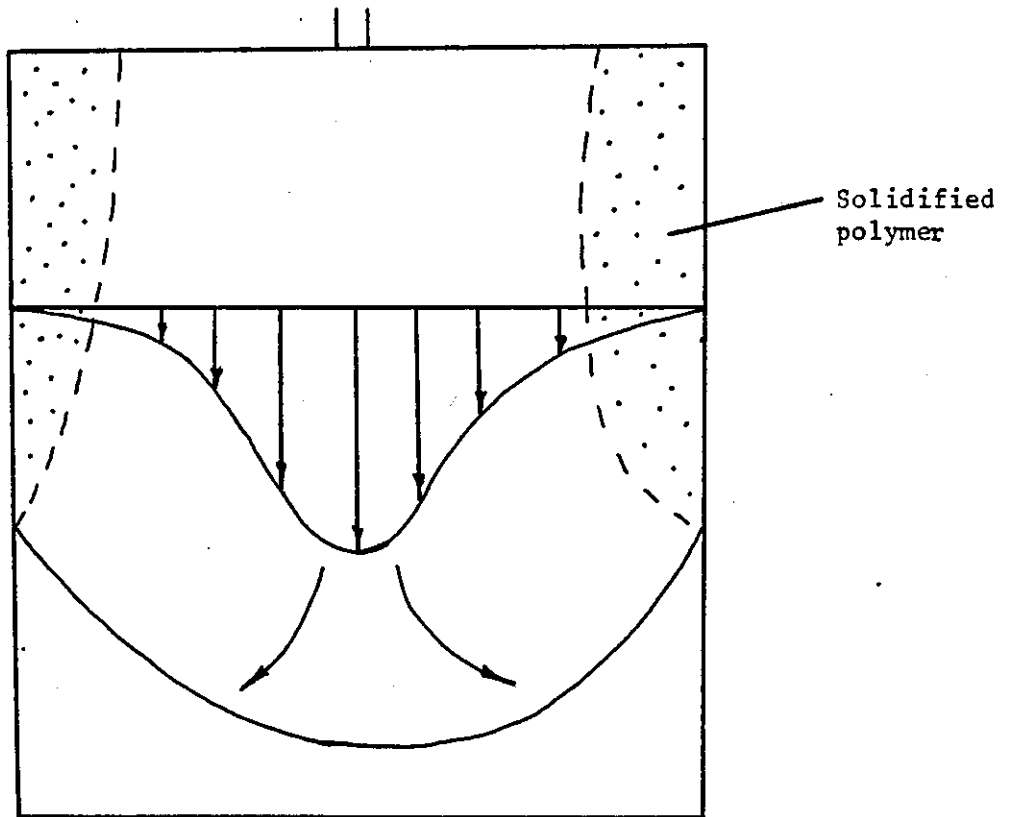
Fig. 1.8.   Fountain effect[111] showing melt

separation in a rectangular cavity

1.2.8. Factors Affecting Moulding

Bruce Rouzer[112] relates an amusing incident in explaining

some very practical problems facing a moulder when confronted with

PVC for the first time. The average moulder it is suggested enlarges

the diameter of the hole at the nozzle exit, sets the melt temperature

as low as possibe whilst still allowing the screw to turn and increase

the pressure to the maximum available. The first shot ejected looked

reasonable. On closer inspection a corner fell off, the part then

split and eventually crumbled. This combination of processing

conditions had resulted in a moulding which had been totally unfused

and it was held together only by the frozen skin. He cites the most

critical machine variables as melt temperature, screw speed, residence

time and mould temperature. Injection speed was not thought to be

a critical variable once problems with frictional burning that takes

place at high injection rates was avoided. The work does not take

into account variations in mechanical properties due to injection

speed. It is suggested that most of the problems arise from

incorrect temperature settings. Mould temperature control was found

to be essential for moulding stability and appearance.

Huber [113] details a number of machine settings necessary to

provide a good moulding together with a list of typical moulding

faults. Melt temperature he says should be achieved both by

correct barrel temperature and screw action. The temperature from

the feed end to the nozzle should be profiled from 150°C to 170°C.

The injection rate should be high enough to permit filling, which

is easier into a hot mould, but of a sufficient temperature that

will prevent any distortion during ejection.

This is confirmed by Bochm[114] when he says that the heat generated by injection varied with injection rate. He also makes the point that screw design is important. As the barrel heaters only contribute a small proportion of the heat necessary for melting of the material most of the thermal energy is generated by the action of the screw. So that the compression ratio of the screw should be between 1.6:1 and 2:1 with the pitch 0.8 to 1.00 depending on diameter.

In a practical situation Boehm[114] using a method previously suggested by Tulley and Harris[115] successfully moulded PVC without the use of external heat i.e. the shear heat generated by the screw was the only heat source after initial set up. A steep temperature profile was used to bring the material to the plasticising temperature. Once the material was soft enough to extrude from the barrel the cylinder heater bands were switched off and the melt temperature was maintained by judicious use of the back pressure and screw speed controls. It is claimed that the technique permits easy escape of volatiles through the rear of the cylinder and allows better control of temperatures, with minimum exposure to the temperatures which lead to decomposition This was achieved by "the self sustaining natural temperature gradient established by pellets being transformed into melt through shear rather than by some artificial profile provided by zoned heater bands".

Observations by Tulley and Harris[116] have shown that if the back pressure used is between $13.8 - 55 \times 10^6$ Pa, melt temperature will increase by $1^{\circ}C$ for every 3.4×10^6 Pa. A low compression ratio screw

permits a much wider range of back pressures and screw speeds to

be used providing greater control[116]. i.e. for screw 1.5:1 back

pressure range 0-6 x 10^6 Pa., screw speed 20 - 80 r.p.m. and for screw 2.5:1

back pressure range 0 - 3 x 10^6 Pa. with 20 - 40 r.p.m. The lower compression

ratio screw permitted the material to be worked much less severely than

the higher compression one. Besides producing a moulding of use

the process gave a 50% reduction in cycle time. These conditions

substantially increased the impact resistance of PVC.

1.2.9 Shrinkage And Orientation

Shrinkage of injection mouldings has been attributed to

molecular orientation produced by the moulding process[117-120] and expressed

as a percentage shrinkage of the dimensions of the moulding compared

to that of the cavity. It has been shown by Lebedev[121] for PVC also

to be highly dependent upon moulding conditions. He shows that

longitudinal shrinkage(ie measured in the injection direction)

is always less than transverse shrinkage for the conditions studied.

Increasing the melt temperature produces a more fluid material

whilst the orientation of the polymer chains decreases which results

in a reduction of both transverse and longitudinal shrinkage. An

increase in shrinkage is also found when hold on times are long.

As the temperature of the mould was raised a sharp increase

in the longitudinal shrinkage was observed at temperatures close

to the T_g of the material. This is attributed to greater relaxation

at these temperatures, whilst the transverse shrinkage is seen to

decrease with an increase in mould temperature due to better filling

of the cavity.

Orientation in injection moulding can be described in terms [122] of the changes in birefringence and specimens under polarised white light. An increase in birefringence is indicative of an increase in orientation and hence shrinkage. For polystyrene it is found that the birefringence decreases to zero towards the centre of a moulding predicting that there is little orientation and because of this there will be little shrinkage in this area. As cylinder temperature, mould temperature and cavity thickness are increased there is a corresponding decrease in orientation. In the case of mould temperature this is attributed to greater relaxation at higher mould temperatures. Whilst a thin cavity produces the greatest amount of orientation due to higher shear stresses as a result of a higher velocity than in a thicker cavity.

Variation in the shrinkage of polystyrene samples measured [123] after being placed in a hot oven to release internal stresses quickly show that the amount of shrinkage through the thickness of a rectangular moulding varied. It was greatest at the surface of the moulding with the lowest values found at the centre where the polymer chains have the greatest chance to relax. A local maximum however, was observed between the wall and the centre attributed to the balance of shear and thermal conditions in the region. This is at a position remote from the gate. Substantial increases in shrinkage as the gate is approached are seen as a result of increased orientation in this area. Tadmor [124] also predicted the development of orientation during filling of a cavity and is in agreement with the above.

Kantz et al [9] with tensile bars of polypropylene show that the amount of shrinkage is dependent upon the amount of surface 'skin' present. The surface layers of an injection moulding are highly oriented and as has been shown previously, shrinkage increases. with increasing molecular orientation. [125-127] A large amount of skin thus results in large amounts of shrinkage. This is confirmed by Waywell [1] working with polyethylene.

Changes in processing conditions produce corresponding changes in shrinkage of polyethylene. injection mouldings as observed by Tyiyama [147] who showed that whilst increases in melt temperature reduced shrinkage increases in injection pressure had little effect. He measured shrinkage in the 'as moulded' state and also after being subjected to various annealing temperatures. Changing injection speed appeared to have little effect on shrinkage whilst effects of mould temperature proved to be more complicated. For the 'as moulded' specimen shrinkage increased with mould temperature, whereas it was found to decrease for samples that had been annealed.

A linear relationship between the thickness of the skin layer and the amount of shrinkage was also found. X-ray diffraction patterns for injection moulded polyethylene however show that the skin is only slightly oriented whilst a transition layer and core show an appreciable degree of orientation.

Thickness variation of mouldings have been measured [10] and show that as the distance from the gate increases the thickness of T.P.X. tensile bars decreases. This is also true for higher melt temperatures i.e. as the melt temperature is increased the thicknesses

of the bars decrease. It is suggested that these changes are as
a result of a band close to the centre of the mouldings whose
molecular chain axis was perpendicular to the injection direction,
and that it is the relaxation of this band that is causing the
shrinkage. Mould temperature is shown to have little effect on
shrinkage.

Clark[4] for polyacetal mouldings shows that there was no
preferred orientation at the centre of tensile specimens; but
between an oriented skin, that consisted of lamellae that were
perpendicular to the moulded surface and the injection direction,
and the randomly oriented centre there existed a band whose lamellae
were oriented perpendicular to the surface only. The orientation
in the skin is caused by the combined effects of thermal gradients
and surface nucleation. However in the second layer some new
nucleation gives rise to spherulites but due to the strong thermal
differentials during crystallisation in this region, the spherulites
are greatly distorted. In the centre region of the bar crystallisation
occurs by spontaneous nucleation which, as there are no large
temperature differentials, results in the formation of spherulites
and no orientation of lamellae is seen.

1.2.10 Residual Stresses

1.2.10.1 Introduction

It is well known that internal stresses in metals may be
measured using stress relaxation data [128-133]. The methods used
are based on a power law relationship between stress and time
(see chapter 3) The approach is similar to the creep law which
relates stress and strain rate [134]. In fact for metals it has

been found that the relaxation method gives identical results to those determined by creep measurements.

Internal stresses have been shown to be related to structural defects such as dislocations and kinks[135] which are all associated with localised stress concentrations in a crystal[136]. Physical strengths in metals have been related to the presence of internal stress and it was thought by some that this philosophy may be extended to polymers[137].

1.2.10.2. Residual Stresses In Polymers

A difference of polymers is that flow can be interpreted as changes in free volume and relaxation times where internal stresses are not considered in the analysis.

In an early paper by Li[130] internal stresses were measured in cellulose and paper. Some of his assumptions were later applied to injection mouldings of a number of polymers[138]. Kubat et al[138] studied a number of moulded low density polyethylene samples which were subjected to various thermal treatments and then elongated or compressed a few per cent. This showed that a sample that had been compressed had a negative internal stress value whilst that of the elongated sample was positive in sign.

The Li[130] technique requires the data from a single stress relaxation experiment to be plotted as stress (σ) versus log t, (where t is time). The gradient of this is determined for a number of points along it and plotted versus the stress σ .(see figs 3.10, 3.11) If very short periods of time are neglected a straight line is obtained for $\frac{d\sigma}{d\log t}$ versus σ , the line is extrapolated until it intersects with the σ axis and the value at which the line intersects

is taken as the internal stress value σ_i . The analysis is based

upon a power low assumption to describe stress relaxation from a

theory of dislocation dynamics[130]. It is written as

$$\frac{\delta\sigma}{\delta t} = -B.E \; (\sigma - \sigma_i)^n$$

Where E is the modulus of elasticity and B and n are constants.

It is suggested that although the stress relaxation behaviour

in a polymer will rarely be a dislocation process the kinetics of

relaxation are similar.

Li[130] shows that for samples of high density polyethylene that were

annealed for 12 hrs at 90°c that there was no evidence of internal

stresses i.e. that the graph of $\frac{\delta\sigma}{\delta\log t}$ versus σ passes through

the origin. No explanation is offered for the difference in internal

stress detected in samples that had been elongated or compressed by

the same amount. However for samples that had been compressed a

negative stress was found whilst those that were elongated a

possitive value of σ_i was detected. Other materials were

injection moulded (polystyrene, acrylonitrile butadiene styrene

(ABS)) as well as polyethylene and negative internal stresses were

found suggesting that the moulding process produces compressively

stressed mouldings. All of these stresses can be made to virtually

disappear by annealing. It also seems likely from this work that

the amorphous polymers polystyrene and ABS have higher internal

stress levels than the crystalline polymers such as high and low

density polythylene.

Kubat et al[138] have shown with an adaptation of Li's

principle[130] (see experimental section later for method) that the

slope (m) from the plot of the maximum gradient of the σ versus

logt graphs against the original stress σ_o , varies significantly

with the material and processing conditions used. The values of

'm' range from 20 for the ethylene based polymers to about 100

for ABS.

Further work by Kubat[139] et al two methods of internal stress

determination are assessed showing a number of interesting findings.

Both high and low density polyethylene were used as the authors point

out that the structural properties are well known for these polymers.

Samples with different structures, produced by various heating

and cooling methods exhibited different relaxation curves and levels

of internal stress. The specimens for the cooler conditions that

had been cold stretched gave positive (tensile) internal stress

values which corresponded to about 10% of the maximum breaking

stress of the sample. For polyethylene it was suggested that tie

molecules are responsible for any internal stresses present. The

less oriented the tie molecules the lower the stress value. This

may not of course be so with PVC, but it does give an insight in

to the types of mechanism possible to explain residual stresses

in mouldings.

Work carried out[140] at the Illinois Institute of Technology

with polycarbonate and polymethyl-methacrylate (PMMA) determined

internal stresses for impact bars cut, annealed and quenched sheets.

Residual stresses were measured by a method developed by Treuting[141] et al

where the material stressed was a metal. It is based on measurements

of the curvature of a specimen after successive layers of material

have been removed. The resulting curvatures were plotted as a function of the depth of the material removed, and a formula developed which relates stress with these curvatures. In these tests the material was assumed to have similar stresses in the longitudinal and transverse directions. Although this is not the case for injection mouldings it was assumed in order to simplify the formula and gives an approximation of internal stress for mouldings which have a distinct skin-core morphology in which very different values for tensile modulus apply to these regions.

Results from these experiments show that residual stresses are present in the surface layers whilst tensile stresses were found in the interior of the specimen. The stress towards the centre of the sample was approximately half that in the outer layer. It is interesting to note that in the samples tested a zero stress level is produced at an identical distance from the surface for all heat treatments used although the levels of stress intensity varied with thermal treatment for the same thickness of sample. If the thickness were doubled the position of zero internal stress was likewise doubled. The distance from the surface at which this occurred was approximately 15% of the sample thickness. Stresses were obviously greater for the quenched samples than for those that were annealed.

1.2.11 Density

The determination of density of poly (vinylchloride) is complicated by the pores and cavities produced in the processed or unprocessed material according to Kostyuchenko[142].

Where the flotation method is used it is uncertain whether the pyknometric fluid penetrates these pores or cavaties. They show however that annealing specimens increased their density due to structural ordering.

Crystallinity determined from density results is complicated by the conflicting values of completely amorphous and crystalline samples. Values of the crystalline portion of PVC range from 1440 to 1530 kg/m^3 whilst those for the amorphous content vary between 1373 to 1412 kg/m^3. The values of density depend on the method of evaluation which is generally by a density gradient column or X-ray analysis [143,46,144,145].

The density of injection moulded polyethylene [146] is found to vary with the depth from the moulded surfaces i.e. the lowest density being at the surface where rapid cooling prevents the growth of large crystallites and reaching a maximum at the centre. It is also shown to vary with position from the gate. The densities at the gate are highest corresponding to the greater temperatures produced in the area of the gate. A gradual decline in density towards the mould wall across the moulding is shown. The variations in density are explained in terms of temperature differences. The distribution of density in the mouldings with position for the whole thickness of plaque is related to the composite structure of the moulding.

The variation in density with mould temperature for injection moulded propylene-ethylene copolymer shows no trend according to Henke et al[3]. Although they show that the density passes through

a maximum midway between their range of mould temperatures they are sceptical of their results and suggest' that their measurements may be imprecise.

Density measurements made on polyethylene injection mouldings show an increase from the outer skin to the centre of the moulding. The density also varies along the length of the moulding and through its thickness. Maximum values are shown to occur in the area of the gate at the centre of the moulding (centre here means centre of the thickness and width of the moulding). Density decreases in a complicated fashion towards the furthermost point from the gate. The changes in density induced by moulding effects due to the different rates of cooling injection moulded polyethylene samples.

Tyiyama[147] suggests that for mould temperature and injection pressure both are linearly related to density. Density is increased with increasing injection pressure and mould temperature. The effect of injection speed however is more complicated. He shows that there is a peak in density with a change in speed but is is suggested that as the changes in density are so small there may in fact be little effect. Cylinder temperature on the other hand substantially affects density. Increases in temperature lead to corresponding increases in density up to a maximum but further temperature rises have little effect. The reasons put forward for this are greater fluidity of the polymer at higher melt temperatures leading to greater packing in the mould and increases in crystallinity due to higher temperatures.

Density measurements made on polyethylene terephthalate by Ali and Sheldon[36] for samples annealed at temperatures below the glass transition temperature, show an increase in density up to T_g with a sudden decrease in density after this point.

An increase in the density of injection moulded PVC is found to be accompanied by a corresponding increase in tensile strength by some workers[19] whilst others[148] show that the strength does not change significantly.

CHAPTER 2

EXPERIMENTAL - MATERIALS AND PROCESSING

2.1 THE EFFECT OF ADDITIVES ON PROCESSING.

The additives present in a PVC compound may be numerous depending

upon both the processing technique and the end use.

The most important additive as far as PVC processing is concerned

is the stabilising system. Stabilisers fall into a few broad groups

namely the barium - cadmium systems, lead compounds and organo-tins.

The organo-tin system was used in the current work. The compounds

are derivatives of alkylated tin metal in which carbon tin bonds are

present. The alkyl groups in this case were octyl. The use of the

organo-tin systems give excellent high temperature colour stability.

They produce no plate out during processing which is an essential

property for any additive.

The organo-tin systems vary in their lubricating ability as a

function of their structure and are essentially classified as non-

lubricating. The compound therefore requires, a combination of

internal and external lubricants.

Studies have been made by Natov[149] et al: on the dispersion of stabiliser

in the polymer and resultant heat resistance by thermal analysis.

Experimentation showed that the Tg was altered (reduced) by an

amount depending on the particular stabiliser used.

Brecker[150] has shown that there is an interaction between the

stabiliser system used and the lubricant system which varies with

the type of stabiliser system.

Lubricants may be either internal or external and their effect

on processing is most dramatic. As well as preventing the material from sticking to the walls of the barrel (external) they also allow the material to flow more freely through the process (internal). Common lubricants are stearic acid, hydrocarbons including paraffin waxes, synthetic waxes of the ester and amide types and low molecular weight polyethylene.

Most lubricants have both an internal and external effect on processing. A combination of calcium stearate and paraffin wax is often used.

Calcium stearate has an effect on the fusion rate such that fusion rate is decreased at low levels but increased at high levels. (see fig. 2.1)[150]
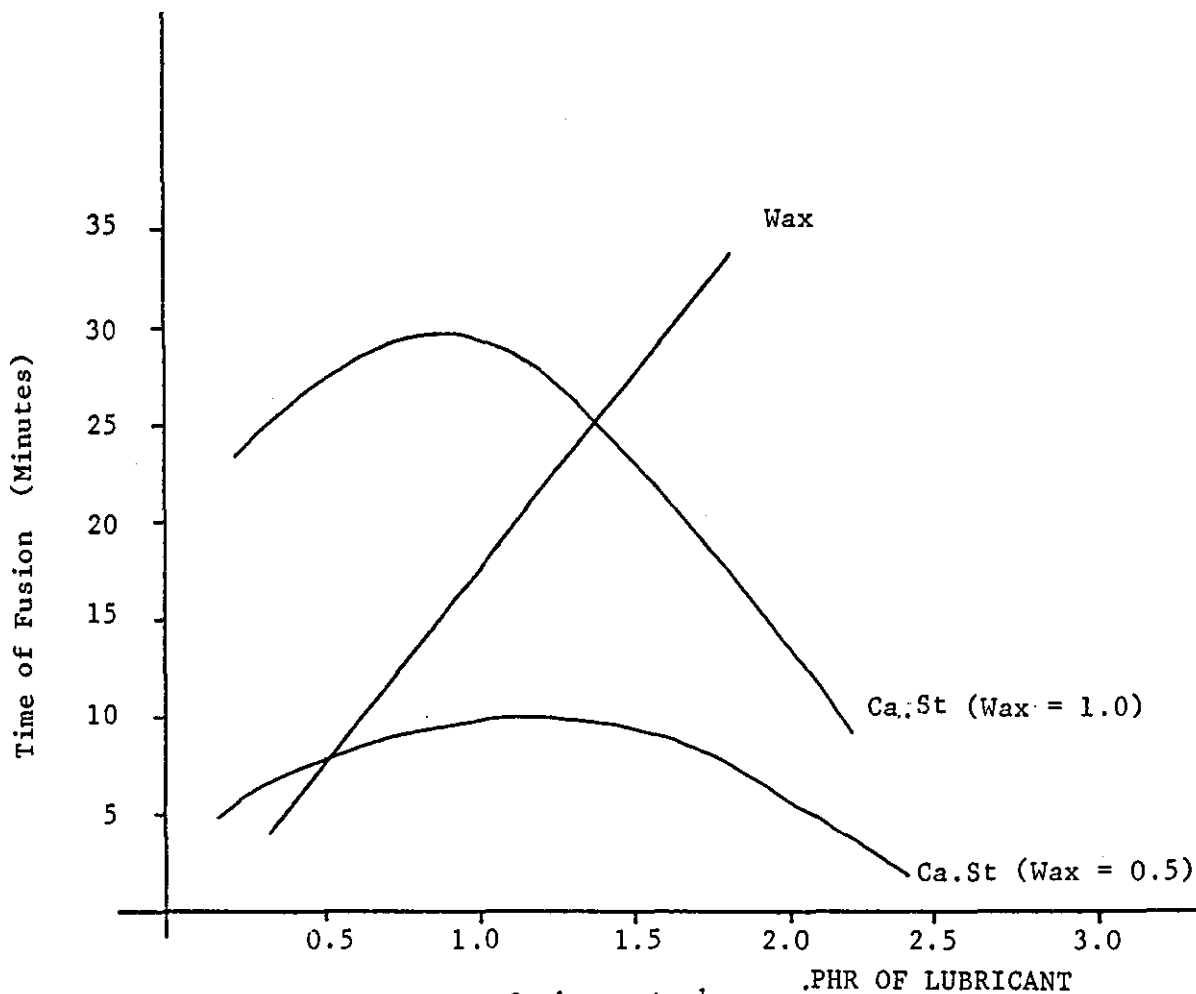
fig 2.1 Effect on fusion rate by addition of lubricants [150]

The combination of calcium stearate with wax shows that fusion may be delayed significantly by the addition of small amounts of wax as a lubricant. Wax does have the characteristic of imparting a yellow colour to the moulding which may be undesireable.

The right combination of lubricants is essential not only to control fusion but also for the development of physical properties such as impact and tensile strengths, and to reduce stock temperatures produced by the shear heating effect of moulding.

The impact strength of rigid PVC resin is low so that impact modifiers can be used to increase it. The commonly used ones are based upon graft polymers of styrene and acrylic monomers with a rubbery phase of butadiene or chlorinated polyethylene (up to 15phr). These additives are thought to deflect impact energy off the rubbery phase and back into the polymer matrix where it is eventually dissipated.

The MBS polymers (methacrylate-butadiene-styrene) are generally regarded as superior to the ABS polymers for colour and high temperature colour stability.

The impact strength not only varies with the type of additive but also of course by the processing conditions during moulding. Thus impact strength must be developed during processing and may be reduced substantially by over processing. (fig. 2.2)

	PHR
Breon M80/50	100.00
Stabiliser(Stanclere T126)	3.00
Wax O.P.	0.75
Processing Aid(Paraloid K120N)	4.00
Calcium Stearate	0.50

Table 2.1 Formulation of Material for Moulding

Processing Time (Arb. units)
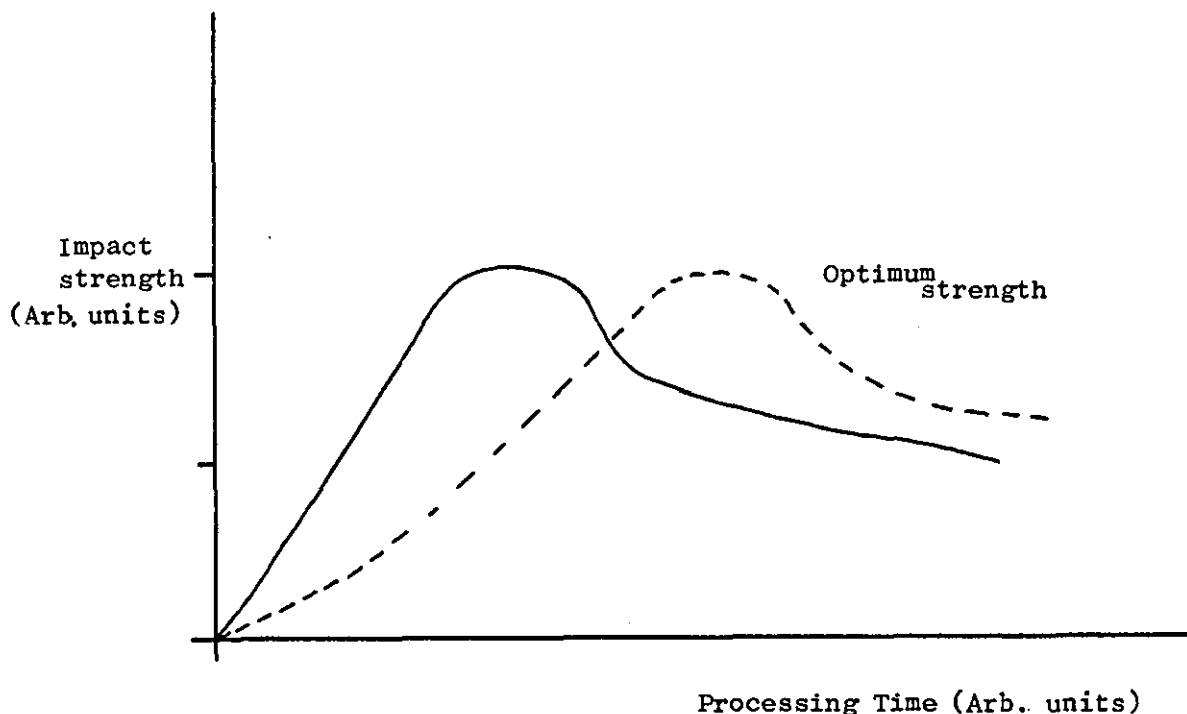
Fig 2.2   Reduction in impact strength with processing time. 150

2.2   INTRODUCTION TO BLENDING

The various PVC additives that go to make up a moulding

compound may be mixed in a variety of ways. Tumble blending

may be used but is not really very effective if the particle size is

small. High speed mixing is generally preferred as it gives a good

dispersion of additives and a better coating of the PVC particles

with stabiliser if in liquid form.

2.2.1   Conditions Of Blending.

The PVC base polymer in the form of a fine powder(table 2.1)was

weighed in 2 kg. batches. This, together with the dry powder additives

ie. wax, calcium stearate and Paraloid KI20N were placed in an 8 litre

Fielder Laboratory high speed intensive mixer. An initial mixing

time of ten minutes was used to disperse the additives at a mixing

speed of 2500 r.p.m. After this period of time with the blender

still operating the tin stabiliser was added and a further ten

minutes mixing allowed.

At the end of blending the material was immediately 'dumped'

into a container, the contents of which would be used for moulding

within forty-eight hours. During this period of time the material
was kept at room temperature ie. approximately 20°c.

A thermocouple in the wall of the blender recorded a final
temperature of approximately 60°c. An increase in temperature during
blending is thought to be beneficial in allowing the stabiliser to
coat the PVC granules more readily.

2.2.2 Processing Of PVC Compounds - Introduction

Due to its relative thermal instability PVC is very shear
sensitive. As the injection moulding process is basically one
involving significant amounts of shear heating, processing of PVC
has to be carried out in the knowledge that degradation of the
material may occur if excessive temperatures are produced. A guide
line for processing of PVC is to avoid significant amounts of
discolouration which occur very quickly at temperatures above 220°c.
The time to degradation increases as the temperature decreases.

Because of the chance of degradation there must be no point at
which stagnation of material can occur. Screw pre-plasticisation is
essential for production of a uniform melt to prevent local overheating
of the material which would happen with a plunger type machine. It is
also preferrable if the tip of the screw is tapered fitting closely
with the head of the barrel to prevent stagnation of material.

It is suggested [151] that the cylinder temperature profile should
be of the order:-

135, 150, 170, 180°c from feed end to nozzle.

A screw speed of between 30 and 45 rev./min. is usually satisfactory.
Excessive screw speeds produce large amounts of shear heating which
could lead to degradation whilst low speeds do not produce a

homogeneous melt and overload the screw motor.

To displace air that is introduced with the feed a back pressure
in the region of 0-6 x 10^6 Pa is necessary to ensure total loading
of the screw. The injection speed is one of the most critical
conditions that has to be selected when moulding PVC. Too high an
injection speed can cause decomposition by frictional heating. This
is usually shown as black streaks radiating from the gate which
usually remains hotter for longest. Too slow a speed will not
produce sufficient heat to ensure total filling of the cavity. It
must be borne in mind that heating of the material is from three
sources; barrel heaters, the screw action and shear heating produced
when the material is injected through the gate and runner system.
All three of these areas must be adjusted to produce a final melt
temperature in the cavity that is not excessive in order to avoid
degradation.

Mould temperatures in the region of 20-60°c should prove
adequate for most mouldings and yield sufficiently acceptable surface
finishes. Temperatures above 60°c could lead to distortion of the
moulding whilst too low a mould temperature may limit flow in thin
cavities and produce an unacceptable surface finish.

Cycle time ie. injection times and cooling times should be as
short as possible ie. injection time need be only of sufficient
duration to allow filling and solidification of the gate to occur.
Too long an injection time,that is the time the screw is in the
forward position,will produce mouldings that are internally stressed.
Likewise the cooling time should be set to allow the screw time to
retract and for the moulding to solidify so that distortion on
ejection does not happen.

2.2.3 Conditions Of Moulding

PVC is thermally unstable at elevated temperatures. (above $220^{\circ}c$); below $160^{\circ}c$. the material is not sufficiently fluid in its unplasticised form to flow. Therefore the processing range is fairly narrow.

PVC is also highly sensitive to injection speed, which leads to shear heating. This can be a problem but once its effects are recognised action can be taken to rectify it.

Cooling conditions have been shown [128] to influence the final properties of a moulding and the effect of mould temperature was also studied.

A Bipel (100g) injection moulding machine was used throughout the work with 31.8 mm diameter high pressure screw.

Melting of the PVC powder was controlled by electrical heater bands on the outside of the barrel the temperature of which were pre-set on the control panel of the machine. The barrel is divided into four zones (1-4) from the feed end (1)of the machine to the nozzle (4) (fig. 2.3). It is usual to have an increasing temperature gradient from the rear to the front of the barrel. The nozzle had its own heater band from which its temperature was controlled. The nozzle was a standard straight through design with a diameter at exit of 4.5mm.

A timing device was used to control the injection time which is in fact the injection time plus the hold on time to allow for solidification at the gate. A second timer then controls the screw back time plus cooling time.
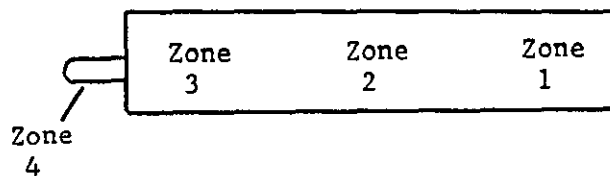
Fig 2.3   Temperature zones along the barrel
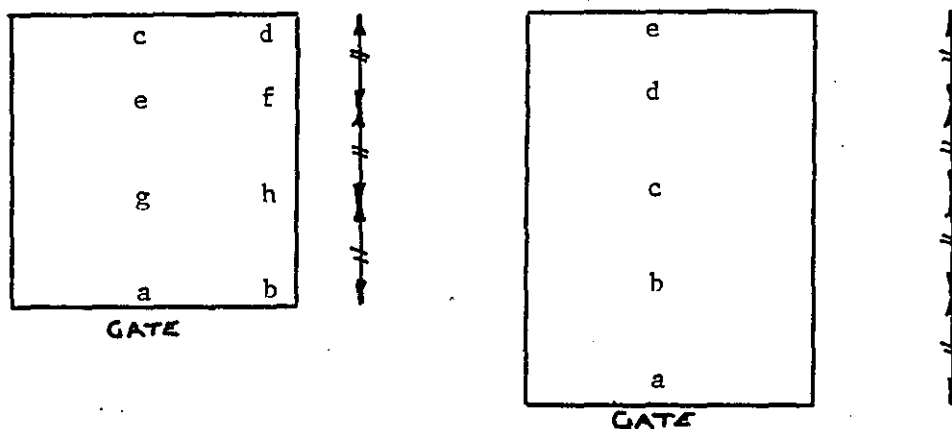
Fig 2.4   Positions in square and rectangular plaques for testing.

This time set on the machine was long enough to allow the screw to travel back to its pre-set position and for solidification to occur ready for ejection. For thin mouldings the mould could open immediately the screw stopped turning, as this would be a sufficiently long enough time for cooling. It can be seen from this that for thin mouldings it is the time for the screw to traverse that is controlling the point at which the mould will open; whilst for thicker mouldings it may be some time after the screw stops that the mould opens.

The temperature of the mould was controlled by passing water from a Churchill mould heater through the heating/cooling channels of the mould.

Initially processing conditions were chosen to produce what appeared to be a sound moulding at a number of different melt temperatures and injection speeds. In this project it was not

possible to measure the true temperature of the melt due to the lack
of instrumentation, so whenever a temperature is stated it is
assumed to be the value set on the control panel of the injection
moulding machine. Some measurements were taken of the temperature of
an air shot in order to assess any increase in temperature produced
by the shearing action of the screw and the passage of material
through the nozzle.

Initially square plaques were produced using an existing mould
which was part of a set of test mouldings as described in the mould
design section (2.3). Conditions of melt temperature, injection
rate and mould temperature were varied as shown in table 2.2.

Because of the large number of moulding conditions and moulding
shape the following was used to allow for easy identification : -

Thickness of the Plaque	1.6 mm	
Melt Temperature	175°c	Represented as
Time for Injection	0.6 sec	1.6, 175, 0.6, 40
Mould Temperature	40°c	

For the second stage of the work a new mould was used to produce
plaques of three thicknesses (see section 2.3) 3mm, 4mm and 6mm.
Moulding conditions were varied as previously to study the effect
of moulding thickness on properties/structure.

Some mouldings were made with the gate intended for the 6mm
thick moulding with the 3mm thick plaque. This was to enable the
effect of the dimensions of the gate to be studied. These mouldings

are differentiated from the usual conditions by the asterisk above

the thickness value in the code viz 3,155, 0.6, 40.

The final stage of the project was to show the effect of a

change in mould temperature on the mouldings. Four temperatures

were used 15, 30, 50 and 65°c. These were the steady temperatures

that the mould reached after a period of continual running (30 min.)

to stabilise the temperature conditions set on the machine. The

two lower mould temperatures were maintained by circulating a

methanol and dry ice mixture through the cooling channels of the

mould. The other mould temperatures were controlled as previously

by a Churchill mould heater.

Injection pressure was kept constant at 140 kN/m^{2} the maximum

for the machine. This is measured as the pressure on the rear of

the screw and not the pressure in the mould.

The speed at which material was injected into the mould could

be varied by a flow valve at the rear of the screw. This was

controlled by the number of turns closed from the fully open

(maximum speed) position.

Screw speed was kept constant at 60 r.p.m. as suggested in the

literature [151].

Finally, after moulding the samples were wrapped in polyethylene

and kept at -20°c to minimise any storage effects which are known

to occur at room temperature.

The positions at which tests were made are shown in fig. 2.4.

MOULDING CONDITIONS TABLE 2.2

Series 1

Moulding Thickness (mm)	Set Melt Temperature (°c)	Actual Melt Temperature (°c)	Injection Time (sec) (Measured)	Mould Temperature (°c)	Injection Time (sec) + Hold On Time	Cooling Time (sec)
1.6	120,130,140,155	175	0.6	40	6	30
1.6	120,130,140,155	175	1.0	40	6	30
1.6	135,140,155,165	183	0.6	40	6	30
1.6	135,145,155,165	183	1.0	40	6	30
1.6	180,130,140,155	175	0.6	60	6	30
1.6	180,130,140,155	175	1.0	60	6	30
1.6	135,145,155,165	183	0.6	60	6	30
1.6	135,145,155,165	183	1.0	60	6	30

Series 1 continued

Moulding Thickness (mm)	Set Melt Temperature (^{o}c)	Actual Melt Temperature (^{o}c)	Injection Time (sec) (Measured)	Mould Temperature (^{o}c)	Injection Time (sec) + Hold On Time	Cooling Time (sec)
1.6	150,160,170,185	210	0.6	40	6	30
1.6	150,160,170,185	210	1.0	40	6	30
1.6	150,160,170,185	210	0.6	60	6	30
1.6	150,160,170,185	210	0.8	60	6	30
1.6	150,160,170,185	210	1.0	60	6	30
1.6	145,155,165,175	195	0.6	40	6	30
1.6	145,155,165,175	195	1.0	40	6	30
1.6	145,155,165,175	195	0.6	60	6	30
1.6	145,155,165,175	195	1.0	60	6	30

	Moulding Thickness (mm)	Set Melt Temperature (^{o}c)	Actual Melt Temperature (^{o}c)	Injection Time (sec) (Measured)	Mould Temperature (^{o}c)	Injection Time (sec) +Hold On Time	Cooling Time (sec)
Series 2	3	120,130,140,155	175	0.6	40	6	20
	3	120,130,140,155	175	0.8	40	6	20
	3*	120,130,140,155	175	0.6	40	6	20
	3*	120,130,140,155	175	0.8	40	6	20
	3	150,160,170,185	205	0.8	40	6	20
	3*	150,160,170,185	205	0.8	40	6	20
	4	120,130,140,155	175	0.6	40	6	25
	4	120,130,140,155	175	0.8	40	6	25
	4	150,160,170,185	205	0.8	40	6	25
	6	120,130,140,155	175	0.6	40	6	25
	6	120,130,140,155	175	0.8	40	6	25
	6	150,160,170,185	205	0.8	40	6	25
Series 3	3	120,130,140,155	175	0.8	15	5	20
	3	120,130,140,155	175	0.8	30,	5	20
	3	120,130,140,155	175	0.8	55	5	20
	3	120,130,140,155	175	0.8	65	5	35

2.3 MOULD DESIGN

2.3.1 Introduction

The selection of a suitable moulding to be used in the work
was based upon a number of criteria:-

1. The shape of the moulding must be simple to prevent any
    material flow problems that would hinder analysis after
    testing.

2. The size and form of the cavity must be such that all the
    test procedures envisaged may be performed on the resulting
    moulding.

3. The shot weight in PVC could not exceed approximately
    120 gm. which is the maximum output of the injection
    moulding machine available.

4. The mould must allow for inter changeable cavities to be
    used.

It was decided that the shape of the moulding should be a thin
square plaque initially. This would be large enough to allow all
the necessary tests to be performed at various positions in the
moulding and would also simplify any flow (orientation) problems
that might result from a circular moulding. It was fortuitous
that a mould with such a cavity was immediately available within
the department (see fig. 2.4). The intention was then to use
this existing mould and from the observations and subsequent testing
of the mouldings a further mould and cavity could be designed.

From this initial work the following points were seen to
influence the choice of design of a new mould:-

1. The flow in the cavity was fairly simple.

2. The length of the moulding should be increased whilst
   maintaining the same width to show this effect on flow
   and properties.

3. The thickness of the moulding should be increased to show
   the effect of moulding thickness on properties and structure.

4. Different gates should be used to show their influence on
   the filling of the cavity.

5. The cooling of the cavity should allow the preset mould
   temperature to be maintained.

2.3.2 Design Of The Cavity

As previously stated the maximum shot weight of the machine
with the existing screw and barrel is approximately 120g this limits
the volume of the moulding to about $60 \times 10^3 mm^3$ for PVC . The width
of the moulding is to be maintained at 75 mm. so that a comparison with
the previous square plaque may be made. This means therefore that the
product of the length and the thickness of the cavity must not
exceed $800mm^2$. It is known that very rarely in practice does a
moulding exceed 6mm, due to problems of distortion and mould cooling
times being excessively long. This was chosen as the maximum
thickness of moulding to be produced which means the lengths cannot
be greater than 130mm. In fact 125mm was fixed as the length of the
cavity which would allow the same distance between positions at which
tests would be made as with the square plaque.

With the overall size of the cavity now fixed two other thicknesses
of moulding could be selected which would show the variation of
properties and structure with moulding thickness at the various
processing conditions. Three millimetres and four millimetres were
chosen to complete the range.

2.3.3 The Feed System

The flow path from the nozzle to the cavity is known as the feed system. This comprises a sprue, a runner and the gate to the moulding. It is a requirement that the length that the material has to travel be a minimum to prevent heat and pressure losses.

2.3.3.1 The Runner

The cross sectional shape of the runner is usually one of three forms circular, square or a modification of the trapezoidal form. The criteria of efficient runner design as suggested by Pye[152] is that the runner should provide a maximum cross sectional area from the pressure transfer standpoint and a minimum contact at its periphery to prevent heat loss. The ratio of the cross sectional area to the periphery will give a measure of the efficiency of the runner design. The circular runner has the highest 'efficiency' unfortunately it is difficult to match the two halves of the mould. A square runner has the same efficiency but is difficult to eject, so a modified form of this i.e. a trapezoidal shape is recognised to allow good flow whilst minimising heat and pressure losses and is also able to be ejected easily.

The size of the runner is determined by the general relationship

$$D = \frac{\sqrt{W} \cdot \sqrt[4]{L}}{8}$$

> Where D = the runner diameter
>
> W = the weight of the moulding
>
> L = the length of the runner.

For PVC it is suggested the diameter is increased by 25% of the calculated value above.

In practise the calculated diameter of the runner is rounded to the nearest standard cutter diameter.

The formula shows that as the distance from the sprue to the impression increases so the melt has further to flow giving a greater resistance, making it necessary to use a larger runner diameter. Too large a diameter could increase the cooling time and hence . , the cycle time to an unacceptable level.

For the size. of cavities used in this work the corresponding runner diameters are shown in table 2.3. and 2.4.

2.3.3.2 Gate Design

The choice of gate, which is the section connecting the runner with the impression, depends upon the shape of the component and the moulding material used. For solid block type mouldings a tab gate or film gate is often used (fig 2.5.). The gate has a number of functions to fulfil :-

(1) It should leave a small witness mark after degating for most production mouldings.

(2) The small cross sectional area of the gate allows the melt to freeze quickly so the screw of the machine may be retracted whilst still maintaining pressure in the cavity, thus increasing the speed of the moulding operation.

(3) It gives better dispersion of additives than just mixing.

(4) The gate constriction increases the melt temperature through shear heating.

The tab gate (fig. 2.5) is particularly useful for feeding solid block mouldings. One of the problems with moulding large flat areas is that if fed from the end of the moulding 'jetting' may occur. It is not usually practicable to feed into the flat surface of the moulding as an unsightly witness mark would be left, and certainly for this work the orientation produced would not be desireable. A restriction in the path the material has to take minimises any jetting that might occur. In the tab gate the melt is turned through 90° and material flows uniformly into the cavity.

The gate is divided into two regions, the tab and the rectangular section (see fig. 2.5). The size of the tab is determined from the empirical relationship[152].

   10. Y (tab width mm) = D (where D is the diameter of the runner)

   10. X (tab depth mm) = 0.9 t (where t is the thickness of the
                                                   moulding)

   10. Z (tab length mm) = 1.5 D minimum.

The size of the rectangular section is determined by the values of the gate width (w) depth (h) and its land length (L). (see fig.2.5)

The land length L should be as small as possible to prevent pressure losses, it is recommended[152] that land lengths of 0.5 mm - 0.75 mm. are used and a value of 0.75mm was chosen here.

Again, there is very little published work on the size of gates, with most designers basing the dimension on past experience. However empirical relationships do exist for the depth of the gate (h) in terms of the thickness of moulded section and a constant for the material (n)

viz. $h = n.t$ (cm) the value of n for PVC is 0.9.

The width of the gate (W) is likewise given by the empirical relationship

$$W = \frac{n.\sqrt{A}}{30}$$

Where A is the surface area of the moulding.

The other form of gate used in the work for the square plaque was a film gate. This is really a long rectangular gate extending almost across the whole width of the moulding (fig 2.6). Gates of this type are commonly used where a large flow area gives a quick fill time, although at high injection rates jetting may occur.

The size of the gate is found by

$h = 0.7$ nt where n and t are defined as previously.

It is conventional to extend the runner slightly beyond the width of the moulding and the width of the gate can be anything up to the width of the moulding. Obviously the greater the width the easier the flow of material into the cavity will be. Because of the length of the runner and gate a thin wall of steel exists between the cavity and the runner, this land length (fig 2.6) must be 1.25 mm or more to prevent it from collapsing.

The diameter of the runner was determined as before and allows an even flow of material to the gate. The sizes for the gate and runner are shown in table 2.4.

Moulding Thickness		3	4	6
Runner diameter	D	5.6	6.5	7.8
Gate width	W	3.4	3.4	3.4
Land length	L	0.75	0.75	0.75
Gate depth	h	2.7	3.6	5.4
Tab depth	X	2.7	3.6	5.4
Tab length	Z	11.5	11.5	11.5

Table 2.3   Runner and gate dimensions (mm) for the rectangular plaque

Moulding Thickness		1.6
Runner diameter	D	6.0
Gate width	W	65.0
Land length	L	1.5
Gate depth	h	1.0

Table 2.4 Runner and gate dimensions (mm) for the square plaque
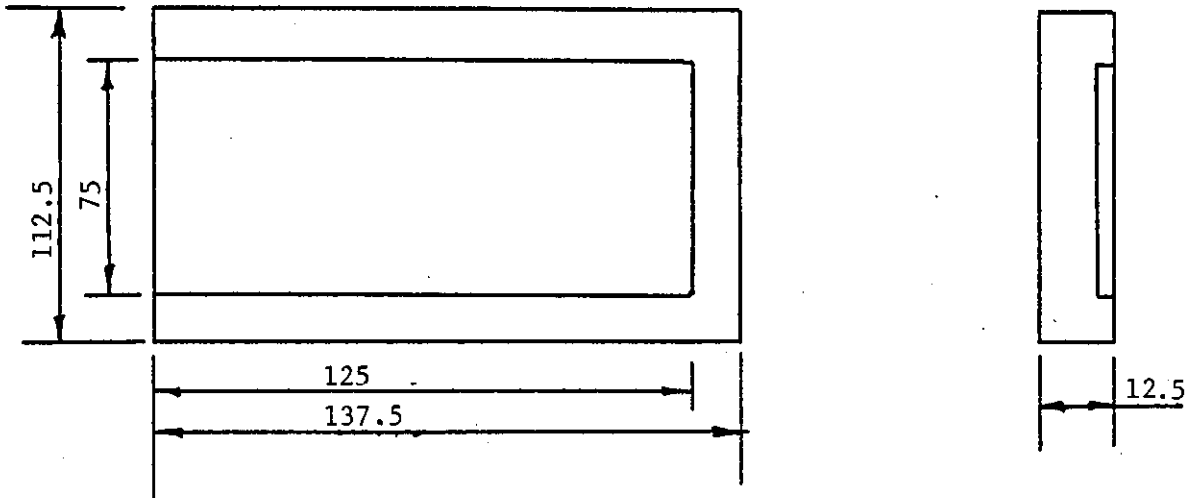
Cavity Insert
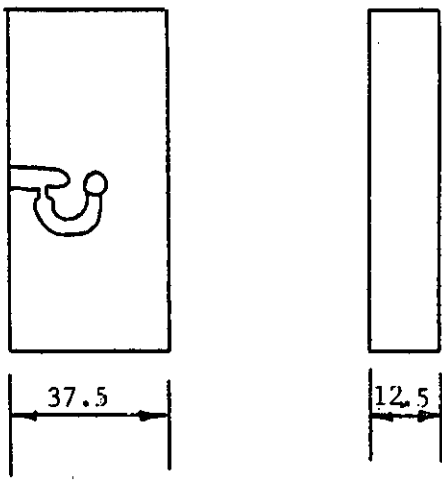
Gate Insert

Fig 2.5   Diagram of the
cavity and gate blocks
with their respective
dimensions for the
rectangular plaque

(Dimensions are in mm)

Tab Gate
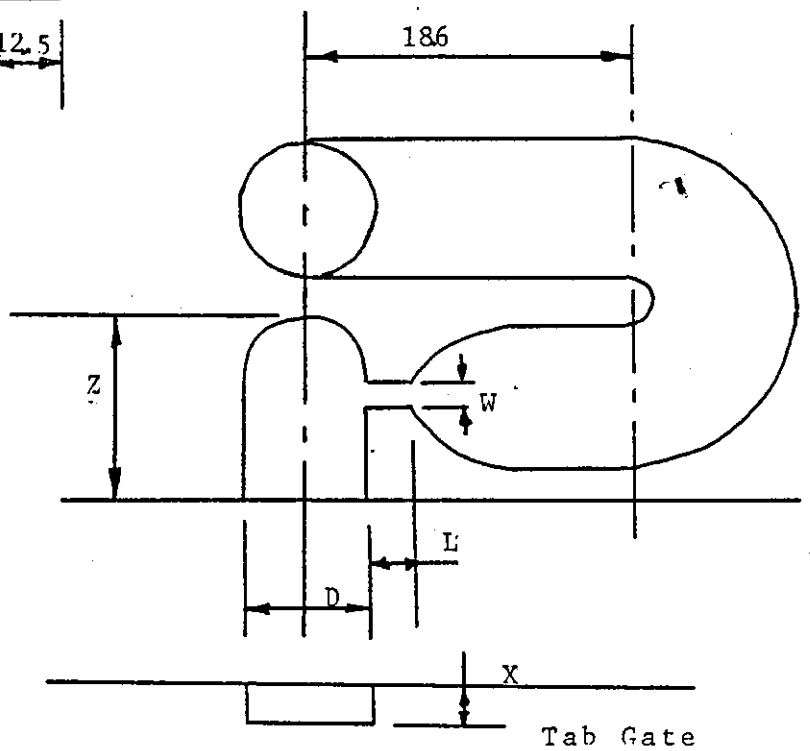
2.3.4 Cavity, Runner & Gate Plates.

The provision for interchangeable cavity sizes was made by
having three inserts one for each depth of moulding. These are
shown in fig 2.5. They were secured in place by four cap head
screws. As it was also necessary to change the gate and runner
configuration to study their effect on moulding a seperate insert
was used. This meant that for the three depths of cavities and
the two different forms for each thickness of gate eighteen possible
arrangements could be used to show the effect of type and size of
gate on mould filling. It was thus a simple matter of removing
four screws for the runner system to be changed without dismantling
the whole mould. If the cavity needed to be changed however, the
rear half of the mould had to be removed from the moulding machine
and the back plate taken off to reveal the ejector plate. Different
lengths of ejector pins were necessary to produce the three
thicknesses of moulding and although the cavity insert could be
removed without taking the complete mould down this had to be done
to remove the ejector pins. It was useful however to be able to
change the cavity size without stripping down the mould to show
the effect of moulding conditions or gate size with cavity thickness.

2.3.5 Mould Cooling

It is necessary to control the temperature of the cavity to
assist mould filling, to keep the cycle time within acceptable limits
for the production moulding shop and to produce the required
properties of the moulding and level of surface finish.

Mould cooling may be achieved by a flow of liquid usually
water or oil circulating in close proximity in channels around the

cavity/core. The channels may be machined in the cavity and core directly in which case seals are necessary to prevent coolant leakage, or copper pipe may be placed in the channels and liquid passed through the pipe. The second method was used in this work and copper tube approximately 9mm in diameter was formed into the circuit shown in fig 2.7. This allows the temperature of the mould plates (and therefore the cavity) to be controlled within $\pm 1^{\circ}c$.
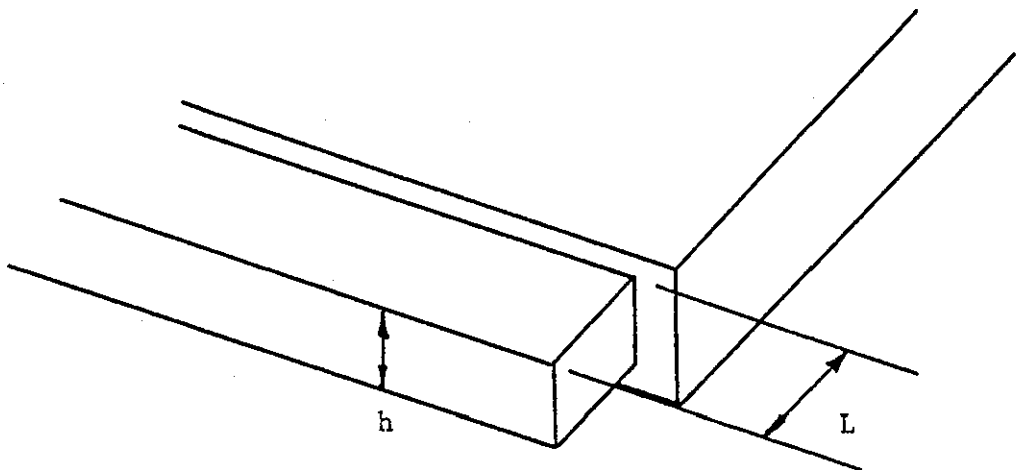
Fig 2.6 Film gate used to produce the square plaque
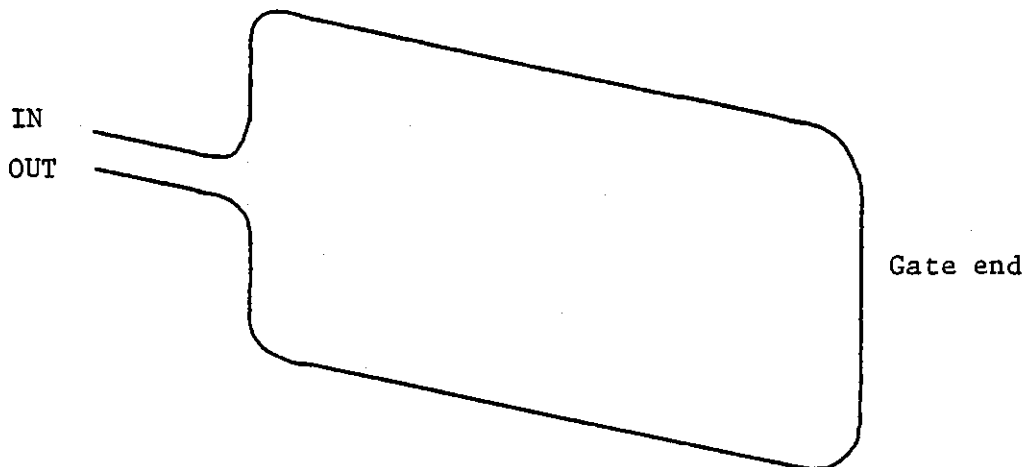
Fig 2.7 Cooling water circuit

CHAPTER 3

CHARACTERISTICS AND PROPERTIES OF MOULDINGS

3.1.1 X-Ray Diffraction - Introduction

X-ray diffraction is a useful technique for the determination
of crystallinity, crystallite size and orientation. If a beam of
electrons impinges upon a solid (or a liquid) the beam is diffracted.
If the material were completely without order a photographic plate
placed behind it would be evenly blackened. However it is said[153]
that solids are hardly ever totally without order and that at least
short range order exists. Areas of order in supposedly amorphous
polymers have been detected; this order being attributed to
aggregation[153].

If a beam of X-rays is incident on a crystal in which the atoms
are arranged in a three dimensional lattice the X-rays are diffracted
from different sets of planes in the crystal. If an analogy with
light is made and the beam of X-rays is considered as a beam of
light, the rays can be taken to be "reflected" from atomic planes.
As shown in fig. 3.1.
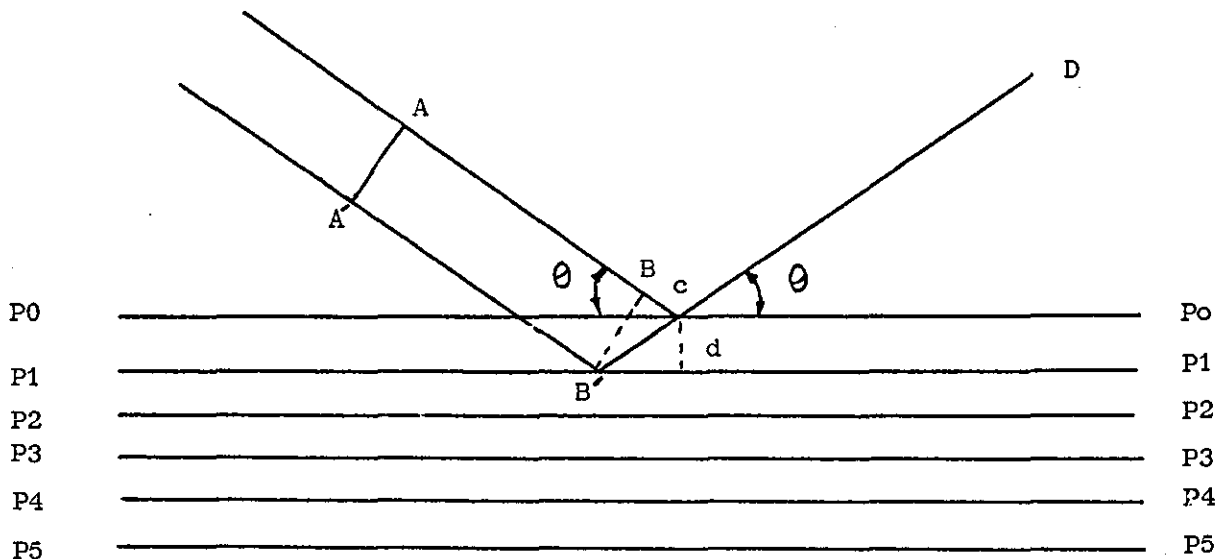
Fig. 3.1 Geometry of Bragg reflection analogy

The parallel lines P0 P0,P1 P1etc.represent a set of atomic planes with a constant interplanar spacing 'd' parallel to a crystal face. AB, A'B' are X-rays of wavelength λ striking the plane and being 'reflected' in the direction CD. For reinforcement of waves from B' and C to occur, the wave from B' must arrive at C in phase with the wave ABC. This is the case if the path difference is a whole number of wavelengths(n) ie:-

$$B'C - BC = n\lambda \quad \ldots \quad (1)$$

but
$$B'C = \frac{d}{\sin\theta} \quad \ldots\ldots \quad (2)$$

and
$$BC = B'C \cos 2\theta = \frac{d(\cos 2\theta)}{\sin\theta} \quad \ldots\ldots\ldots \quad (3)$$

which if substituted in (1) gives

$$\frac{d}{\sin\theta}(1 - \cos 2\theta) = \frac{d}{\sin\theta}(2\sin^2\theta) = n\lambda \ldots\ldots (4)$$

which gives $n\lambda = 2d\sin\theta \quad \ldots\ldots\ldots \quad (5)$

This is the Bragg equation where in a crystal of a given d spacing at a particular wavelength λ the various orders of "reflection" occur only at the angle θ which satisfies equation (5). At other angles there is no observed beam as a result of interference. The "reflection" of X-rays is not the same as that of light which is only reflected at the surface. The X-rays penetrate several million atomic layers into the material before being absorbed and at each layer a portion of the X-ray beam may be thought to be 'reflected'. If these reflected beams are to emerge as a single beam, the small individual beams must not be absorbed by any of the layers to the surface and as mentioned above the beams must not interfere with each other.

With a knowledge of the d spacing, information about the
unit cell dimensions can be obtained.

The X-ray pattern displayed by PVC is not distinct for a
number of reasons. Crystallinity in PVC is generally attributed
to the syndiotactic parts of the polymer chain and as such the
intensity of diffraction is limited. Consequently the isotactic
portions of the chain will contribute to the overwhelming amorphous
background. Ordering is similarly restricted in the 'a' and 'b'
axes leading to an increase in the amorphous background. Any
crystallites that are present in PVC due to processing are likely
to be small and will thus increase the line broading effect.

3.1.2 Experimental Procedure

The X-ray equipment used was a Jeol Dx/gE/2S 3 kw generator,
fitted with a D x/G0/S vertical goniometer. The apparatus was
operated in the usual symmetrical reflection condition for specimens
with a flat surface as shown in figure 3.2.
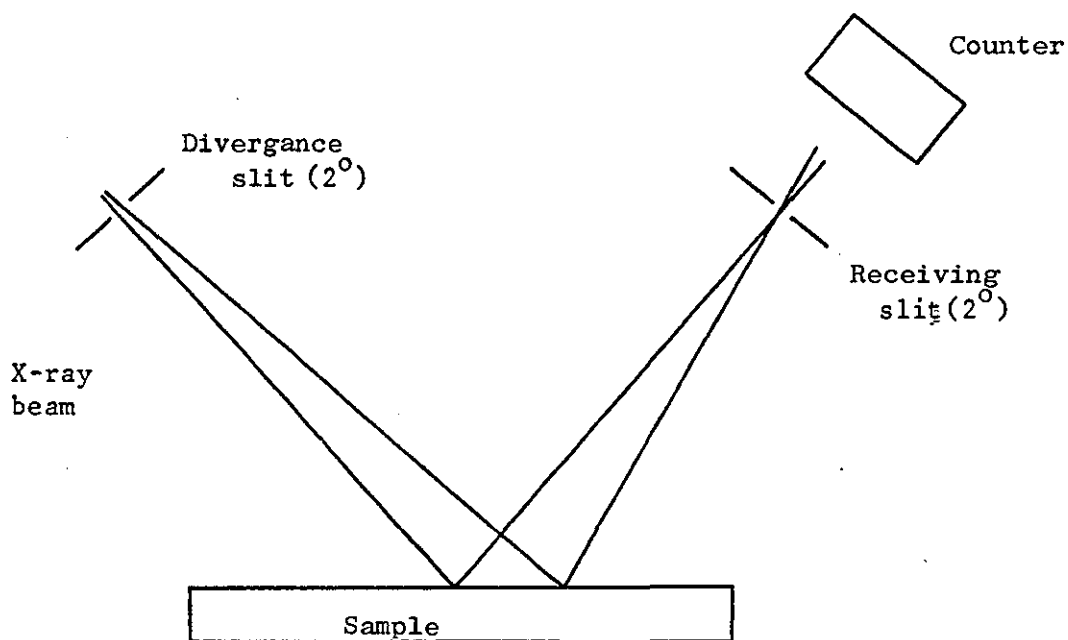
fig. 3.2 Symmetrical reflection arrangement

The diffracted beam is registered by the counter and passed through an electronic system which amplifies and scales the intensity of the beam located by the counter. The intensity of the diffracted beam measured over an angular range of $12^{\circ}(2\theta)$ to $36^{\circ}(2\theta)$ was recorded on a strip chart recorder. This angular range was considered to be sufficient to show the characteristics of PVC. A typical trace is shown in fig. 3.3. The actual operating conditions of the equipment were 40 kV and 30 mA with a $1^{\circ}/min.$scan.

Nickel filtered copper $K\alpha$, X-rays were used with a wavelength of 0.1542nm generated from a copper anode. The angles in fig 3.2 were maintained by a gear drive system which kept the angular relationship between the specimen and the counter constant so the beam always converged at the receiving slit.

It can be seen from above that due to the poor diffraction pattern from PVC high current and voltages were necessary to produce an acceptable trace. These values of current and voltage were the maximum that could safely be used with the equipment. It was also necessary to operate the equipment with a number of divergent and receiving slits to determine the most satisfactory arrangement. It had to be borne in mind that too large a divergent slit could produce spurious diffraction from the equipment whilst too small a slit would substantially reduce the intensity of the trace. Likewise similar problems are associated with the receiving slit. The arrangement of slits eventually used was arrived at after some experimentation with different combinations of slits.

Sample specimens were taken from positions along the centre line of the rectangular mouldings as in fig. 3.4. and with the
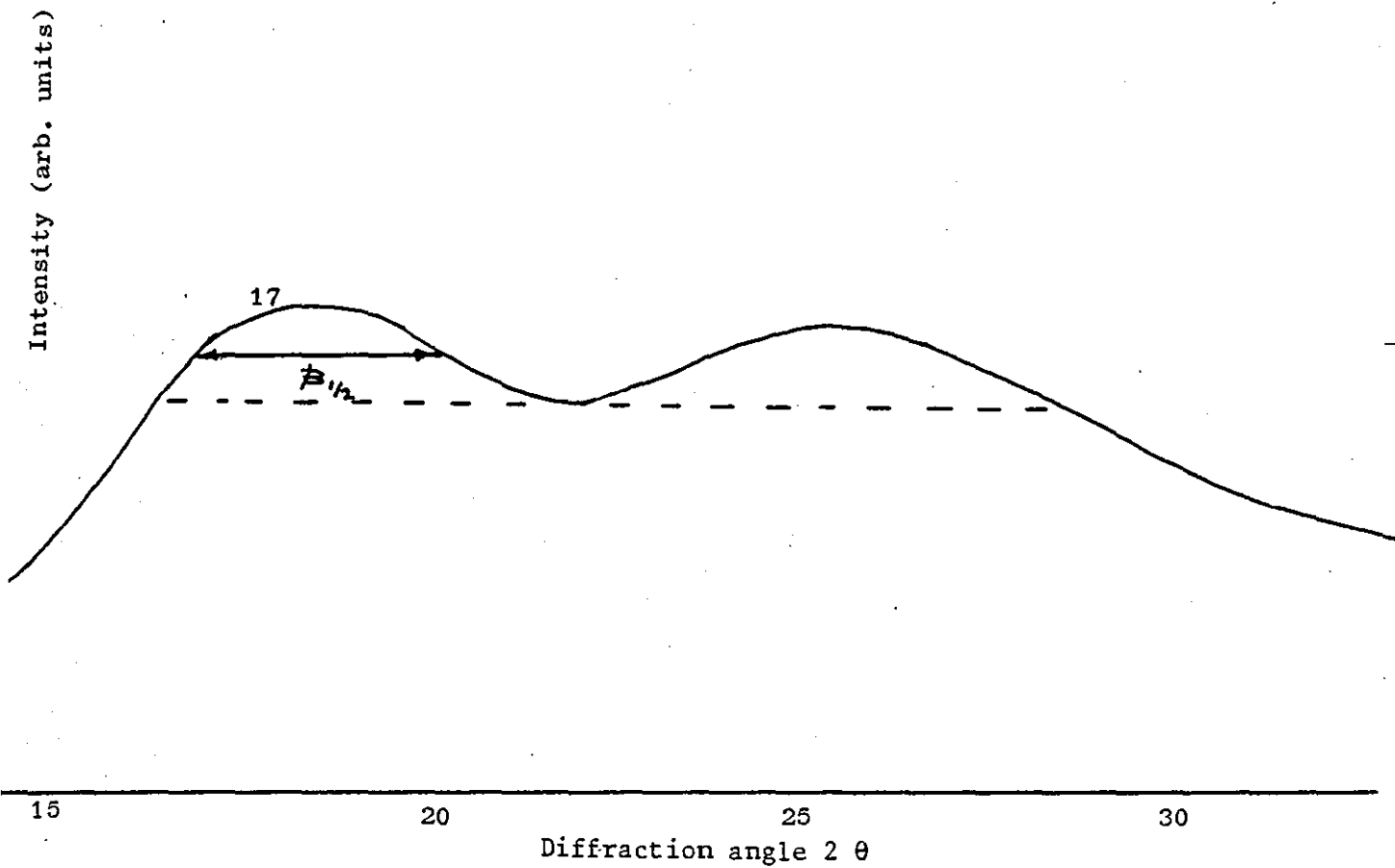
fig.3.3 Typical X-ray diffraction trace
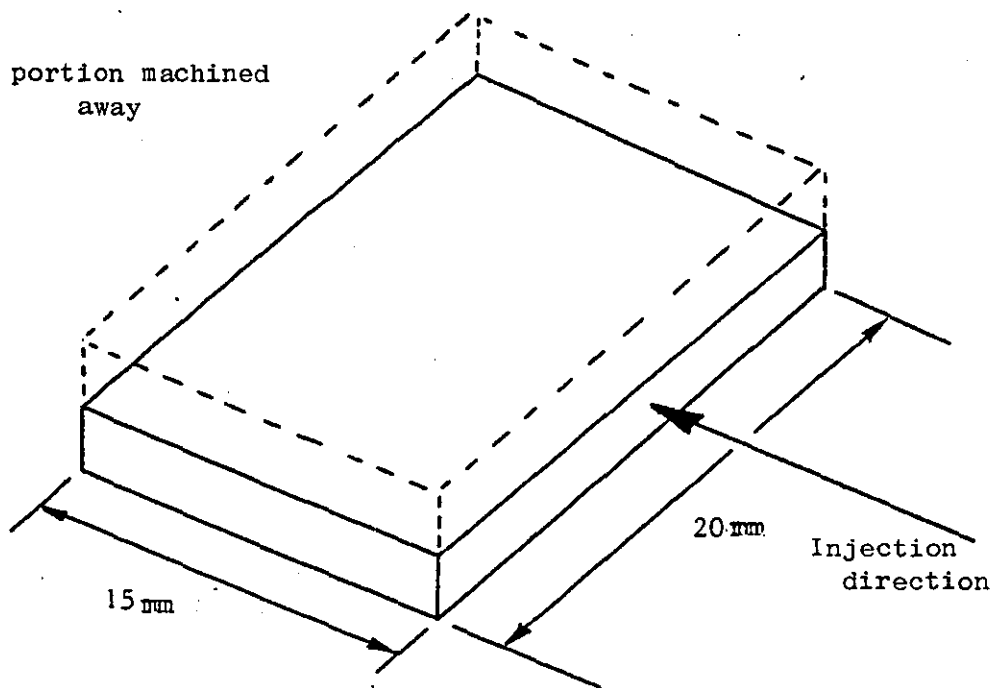
fig. 3.4 Diagram showing the surface presented
to the X-ray beam

plane of the X-ray beam perpendicular to the injection direction.

The surface of the specimens examined was at the centre of the

moulding (see fig.3.4), this was to eliminate orientation effects.

The upper layer of the plaque was machined away carefully to

prevent any temperature rise which could alter the structure of the

surface. The surface finish produced by milling was not as good as

the moulded one but was thought to be adequate for X-ray purposes,

and was similar for all samples.

A measure of crystallite size was made from the two predominant

peaks of the traces using the Scherrer equation:-

$$L_{(h,k,l)} = \frac{K \lambda}{\beta_{\frac{1}{2}} \cos \theta}$$

where $L_{(h,k,l)}$ is the mean dimension of the crystallites perpendicular to the planes (h,k,l) (nm).

$\beta_{\frac{1}{2}}$ Is the breadth at half maximum intensity in radians (fig 3.3).

λ Is the wavelength of the X-ray beam (nm).

K Is a constant taken to be unity for this work.

The above expression does not take account of effects due to

lattice distortions which contribute to broadening of the reflections.

The results do however give an indication of crystallite size.

Measurement of crystallinity in polymers is not always easy due

to both the polymer concerned and the difficulties associated with the

X-ray technique. Crystallinity in PVC has been shown in the literature

survey to be low and there are difficulties in obtaining wholly.

amorphous samples of PVC. Previous methods based on an χ-ray

diffraction pattern from a so-called amorphous sample are thought

too unreliable, it is not certain whether all traces of order can

or has been destroyed. A better term would be crystallinity index

which is based upon the maximum and minimum intensity patterns from

samples of the same polymer species. This obviates the need to

consider corrections for air scattering since all the samples have

similar air scatter components, more importantly however it is not

necessary to compensate for incoherent scattering since it is the

same for both crystalline and amorphous regions.

3.2 DIFFERENTIAL THERMAL ANALYSIS

3.2.1 Introduction

Differential thermal analysis (D.T.A.) was originated in 1887

by H. Le Chatelier when it was used in the analysis of clays.

The process was further instrumented by Roberts - Austen twelve

years later and his apparatus forms the basis of the present day

instruments.

The technique involves the heating (or cooling) of a test

sample and an inert reference sample and the measurement of the

temperature difference between them. This temperature (ΔT), is

then plotted against the sample temperature.

An exothermic peak is found if heat is evolved from the sample

or endothermic if heat is absorbed by the sample.

Differential scanning calorimetry (D.S.C.) differs from D.T.A.

in that individual heat sources and temperature sensors are present

at both the sample and reference positions and the energy to

maintain a zero temperature difference between them is plotted.

The ordinate of a D.S.C. curve thus represents the rate of energy absorption by the sample relative to the reference material.

D.T.A. and D.S.C. are said to be equally useful in the testing of materials. D.T.A. equipment generally covers a wider temperature range than D.S.C. instruments whilst differential scanning calorimeters produce better results at very low heating rates.

The apparatus used in this work consists basically of a heating chamber into which are mounted two thermocouples, one to monitor the sample temperature, whilst the other is so arranged as to record the temperature difference between the sample and the reference.

A temperature programmer is used to heat the furnace at a constant rate and a recording system to display the temperature differences between sample and reference materials. This is shown in block form in figure 3.5.

It is generally considered that lowering the heating rate produces the same effects as lowering the sample weight ie. sharper peaks are produced and the resolution is increased A heating rate of 10° c/min is usually sufficient for most purposes, although some workers[38] have used much higher heating rates and claim greater sensitivity.

3.2.2. Experimental

The operating conditions of the instrument which was a Du Pont 900 Thermal Analyser used in conjunction with a D.S.C. cell were as shown in the table below.
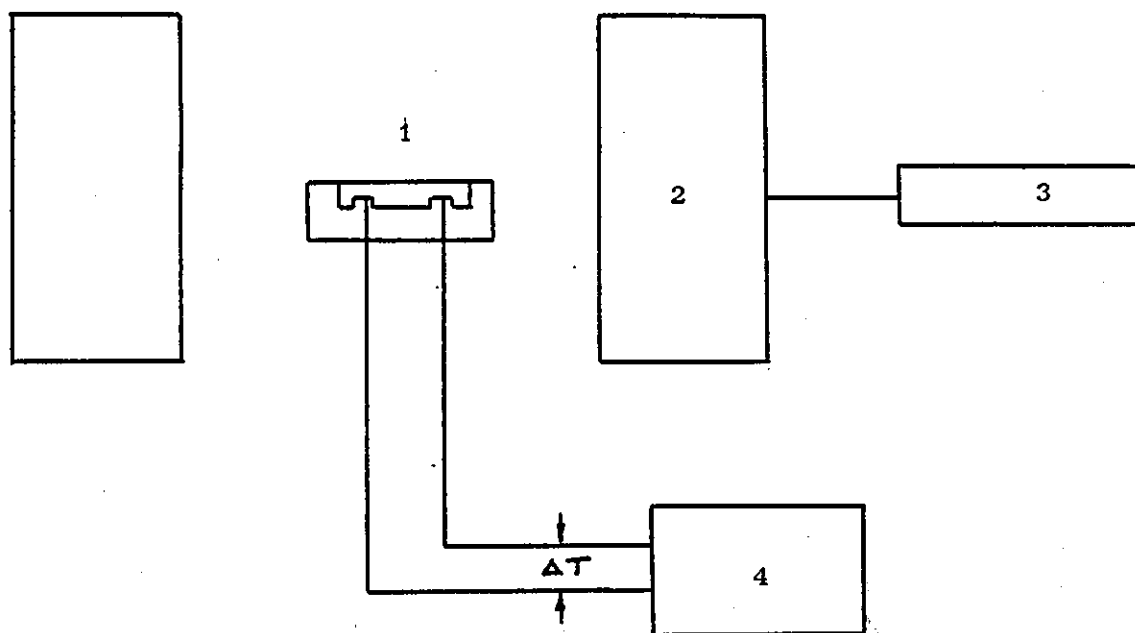
1   Sample holder

2   Furnace

3   Temperature programmer

4   Recorder

fig. 3.5 Block diagram of D.T.A. apparatus

Sample Weight (mg)	Start Temperature (^{o}c)	Final Temperature (^{o}c)	Heating Rate (^{o}c/min)	Atmosphere
15 $\pm$ 1 mg	-40	200	30	air

Table 3.1   Operating conditions for differential thermal analysis.

A number of experimental points of interest arise from this study. Firstly aluminium pans were used to hold the sample and an empty pan was used as the inert reference material. It was necessary to crimp the edges of the sample pan to prevent movement of the sample on heating. It was noticed that if this occurs, which it did for the samples initially tested, due to relaxation, totally false traces are produced. This is because the area in contact with the pan is greatly reduced and localised melting of this small portion of the sample occurs. This is prevented if the sample is in a crimped pan and lid.

Furthermore the start temperature (-40°C) had to be sufficiently far removed from the temperature range to be studied to allow the temperature differences between the cell and sample to equilibrate. The cooling was achieved with liquid nitrogen.

The heating rate was chosen based upon the previous work of Gray[38] where it was felt that a high heating rate with a small sample weight would prevent any changes occuring in the structure during testing.

Finally after a test run when the cell was cooled, the next sample was placed into the instrument at approximately 20°c to minimise any annealing effects that might take place.
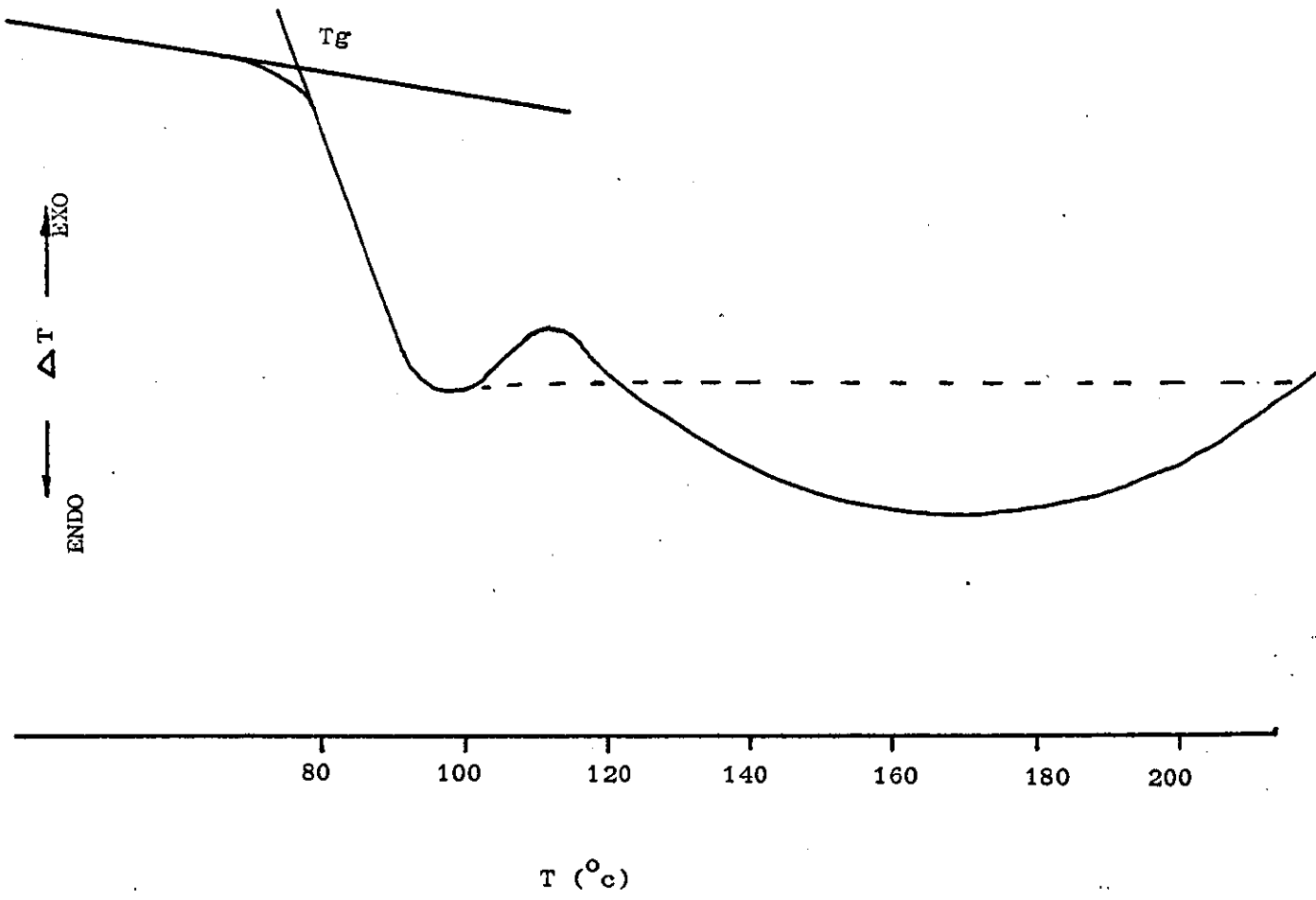
fig. 3.6 Typical D.T.A. trace

The information obtained from the D.T.A. traces is shown in tables (26-30). Here the glass transition temperature, Tg, is taken as the intersection of the line of maximum slope of the peak with the extrapolated baseline.

Information about the morphology of a sample can be obtained from the D.T.A. trace by relating the area of certain peaks present to crystallinity. If one follows the specimen trace in fig. 3.6 it is seen that a shift in baseline occurs at approximately $80^{\circ}C$ which is taken as the Tg after which an exothermic peak may or may not be present at approximately $95^{\circ}C$ depending on the position in the plaque from which the sample was taken. After this the broad endothermic melting peak is found. The area of any peaks present may be related to enthalpy change and in some cases crystallinity. In order to achieve this a sample of known heat of fusion must be used for calibrating purposes. In this instance indium was used, as its melting temperature lies within the range studied. As the enthalpy of fusion of indium is known ($28.5 \: Jg^{-1}$) it may be used to calibrate the instrument to find the constant (c).

ie. for a sample of indium:-

$$\frac{\text{Peak area of indium trace}}{\text{Weight of indium}} = \text{known enthalpy change of indium x constant(c)}$$

so that for a sample of PVC:-

$$\frac{\text{Peak area of PVC trace}}{\text{Calibration constant (c) x weight}} = \text{enthalpy change for PVC sample (J)}$$

These enthalpy changes are shown in tables (26-30). The positions in the plaque at which tests were made are as shown in fig 2.4.

0 - 5000V

Coolant (CO$_2$)

Ion
Beam

Argon
Supply

Sample

Vacuum
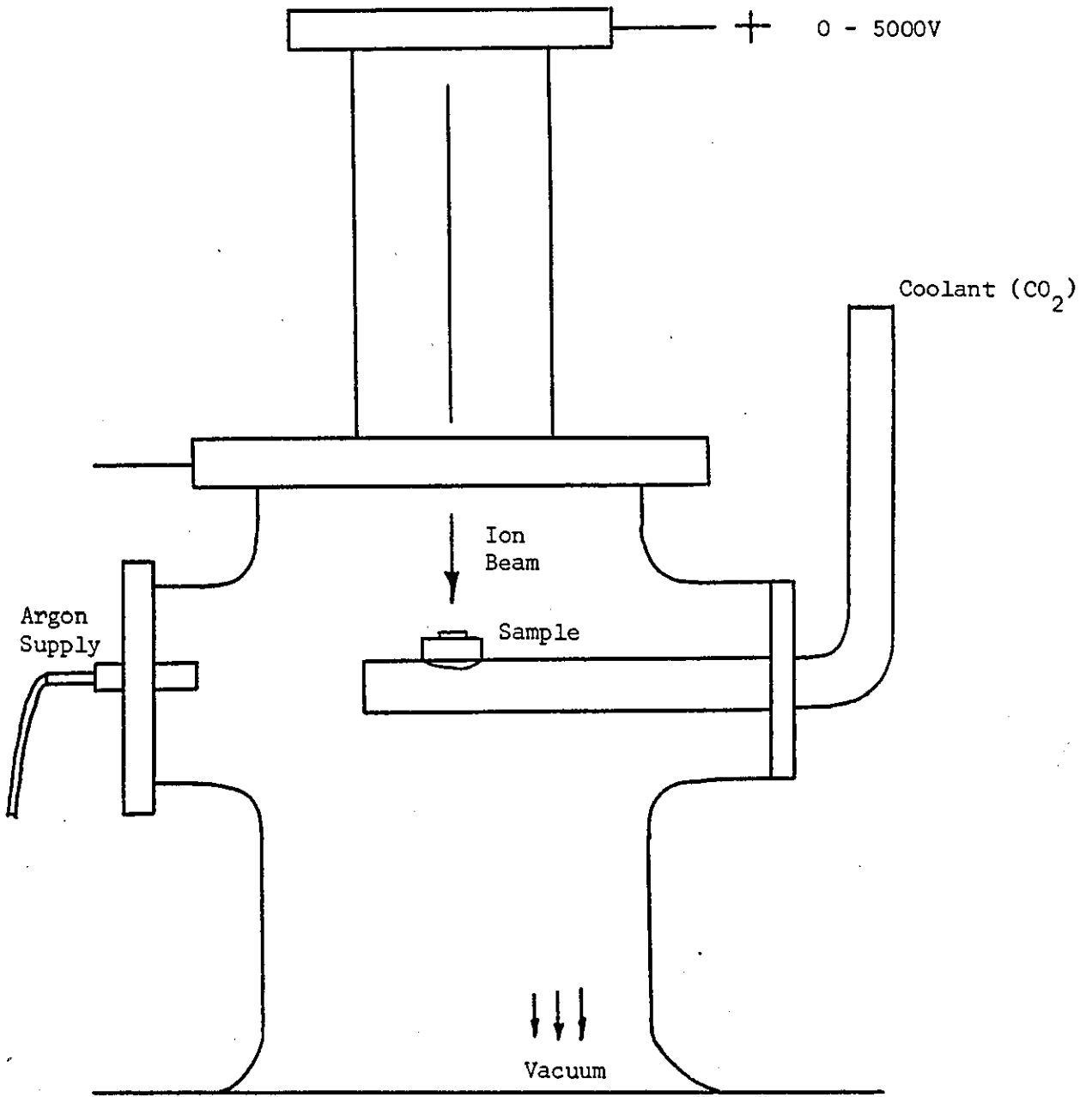
fig 3.7. Ion Etching Apparatus

3.3 ION ETCHING

3.3.1 Introduction

It has long been known that if a surface is bombarded with ions
material is removed from it. This process is known as sputtering.
In ionic etching a pure gas (usually argon) is passed into an evacuated
vessel which is at a low pressure (- 2.6 N/m^2) and a high frequency
field is produced which activates the gas molecules. These are
then accelarated through a voltage field and erode away the specimen
surface. The rate at which erosion takes place depends upon a
number of things:-

1. The specimen material - especially if this is non
    metallic, since beam heating may damage the exposed
    surface.

2. The power of the beam - this must not be too great as
    it may destroy any structure present.

3. Etching time - this must be selected with reference to
    the other conditions of etching to give satisfactory
    results.

4. Pressure - the pressure in the vessel must not be too
    high or ionisation will not occur, nor too low or there
    will not be sufficient molecules to ionise.

5. Ionising gas - an inert gas is used to avoid chemical
    degradation.

So it is seen that to achieve successful etching the correct
combination of the above parameters must be maintained.

The actual process of erosion is thought to occur when the
energy of the accelarated ions is greater than the chemical

bonding of the atoms of the material.. Thus this level of energy

varies between solids and is said to be in the range 5 - 40 eV

and is related also to crystallographic orientation of the samples

and the mass of the incident ion[67].

In order for an atom to be ejected from the specimen surface

the energy given to it by the accelarated ion must be sufficient

to remove it from that surface. The efficiency of this process is

known as the sputter yield ie. the number of atoms ejected per

incident ion. Increasing the beam energy increases the efficiency

of the process up to a value at which further increases in intensity

will result in beam damage of the specimen. Typical values of

<10kV are quoted as satisfactory for efficient etching[68].

3.3.2 Experimental Procedure

The equipment used for the examination of structure by the

method of ion beam etching is illustrated in fig. 3.7. It is seen

that it consists basically of a glass vessel with two electrodes

attatched to a d.c. supply capable of being operated up to 5kV . A

vacuum pump capable of operating at pressures below-1.33 N/m^2 was

attached to one opening of the glass flask.

The specimen was attached to a copper tube through which a

mixture of dry ice and methanol could be passed to act as a cooling

medium.

Argon was used as the ionising gas and was leaked into the

discharge tube by a needle valve at a controlled rate, this was

found by necessity to be quite low, due to extraneous arcing

at high flow rates.

A high voltage was applied to the electrodes and a discharge occurred depending upon the flow of gas and the pressure in the chambers. After some initial trials the operating conditions in table 3.2 were established to give a stable and reproducible glow discharge. Etching was found to affect the surface of the specimen when a drop in discharge current with a corresponding increase in voltage occurred. It was from this point that the time of etching was recorded.

All specimens were etched on the same surface of the moulding ie. the side in contact with the moving half of the mould. The plaques used for investigation were the final set of mouldings in which the effect of mould temperature was studied. Positions tested in the plaque correspond to those in fig. 2.4.

After etching the chamber was brought to atmospheric pressure again and the sample removed. It was then transferred almost immediately to a mounting stud for examination in the scanning electron microscope. The etched surface was coated with a gold-paladium conducting surface layer to be viewed by the scanning electron microscope (S.E.M.) The magnifications necessary to show detail of any structure present were found to be 2500X. Some typical etched surfaces are shown in fig 4.1.

Voltage	Current	Beam current	Vacuum
0.56kV	6.5mA	0.25mA	~1.3 N/m^2

Table 3.2   Operating conditions for ion etching

3.4 DENSITY MEASUREMENTS

Changes in the density of injection moulded samples have been reported (see section 1.2.11).to be related to their thermal history. These changes may be of use in assessing the effect of the moulding operation on the final properties of a moulding.

Samples of mouldings for density measurement were taken from the areas shown in fig. (2.4). The size of these samples was approximately 6mm x 6mm.

The flotation method of determining density was used utilising a Davenport density gradient column filled with a solution of calcium nitrate in water. The column was calibrated with glass beads whose density was known to $0.1kg/m^3$, the maximum length of column being used to cover the expected range of densities to increase the accuracy of measurement.

Samples were cut from the plaque with a small hacksaw and all rough edges cleaned with a scalpel. It is very important that the edges of samples are smooth to prevent air bubbles attaching themselves and creating a false reading. Ethanol was used to clean the samples which were then dried in tissue and placed in a solution of calcium nitrate to thoroughly wet the surfaces further to prevent air bubbles adhering to them.

Three plaques at each moulding condition were used and the densities at identical positions were averaged. Identification was made easier by cutting different shapes for each area of the plaque. Readings were taken after three hours when an equilibrium condition was reached.

Due to the necessity of having various additives to assist processing, the measured densities were not the density of PVC alone. A correction factor could be applied but the project was intended as a practical study of the effect of processing on a commercial blend of PVC and not its effects on PVC alone. It was thus felt that the measured values of density would be of sufficient use to record any changes due to processing.

A further complication was that the moulding was not of uniform structure but a composite with different densities in each layer (see chapter 5) . Any measurement would thus be an average of the sum of the densities in each layer. However this'layered' effect is a result of the processing conditions used, so that it is possible to follow the changes in overall density due to the variation in moulding conditions.

Although only the positions in fig. 2.4 were used for examination, one plaque was subjected to an intensive study (measurements were taken at 81 different positions) to try to map the variation in density across the complete moulding, this is illustrated in fig 4.7   Tables 1 -9 and figs 4.2 - 4.6 show the dependance of density on melt temperature, mould temperature and plaque thickness.

3.5   SHRINKAGE MEASUREMENTS

Shrinkage was determined both for the complete moulding and also at particular positions within the plaque.

3.5.1   Moulding Shrinkage Due To Cooling

The dimensions of the cavity for the square plaque were .75 mm by 75. mm , whilst for the rectangular cavity they were 75 mm wide by 125mm long. .

Measurements were taken of the moulded plaques and the difference between moulded dimensions and actual cavity size was converted to a percentage shrinkage.   The effects of a change in processing conditions on the dimensions of the moulding can clearly be seen in fig 4.8   and fig 4.9.

3.5.2   Reversion

Samples approximately 25mm x 125mm were cut from mouldings at positions shown in fig. 2.4, the dimensions of which were measured to .01 mm with a micrometer.   These were placed in a reversion jig, which had reached a constant temperature of 130°c, for 3 hrs.   The reversion was the percentage change in the dimensions of the sample as measured in the injection direction.   The contraction in this case was caused by extensional flow in the mould.   The elongated molecular chains relax a certain amount whilst in the mould (mould shrinkage) until the material is cooled by the surfaces of the mould to prevent this from happening.   The resultant frozen in stresses are relieved when the polymer is subjected to a temperature sufficiently great to release them.   The rate at which relaxation occurs is a function of the temperature to which the sample is subjected, this must be above its Tg but below its melting point

if the sample shape is to be maintained. It was found that at a

temperature of 130$^{\mathrm{o}}$c relaxation occurred fully within 3 hrs.

Three samples were used at each moulding condition and the

mean shrinkage value is recorded in tables 17 - 25 and figs 4.10 - 4.13.

3.6. MICROSCOPIC EXAMINATION OF THE SKIN

It has been shown by previous workers that a skin is formed at

the surfaces of an injection moulded sample in contact with the walls

of the mould.

Samples were cut from a moulding at the positions shown in fig 2.4

Microtomed sections 15μm thick by approximately 6mm long in the

injection direction were placed in cedarwood oil between two glass

slides. The section was then viewed between crossed polars using

a Reichart polarising microscope with a magnification of 10 x . A

clearer image of the skin is seen if a quartz analyser is placed between the

sample and the light source, a typical section is shown in fig 3.8.

Each sample was photographed and the thickness of the surface

layer was measured directly from the photograph.

Although the thickness of the 'skin' was similar on both sides

of the moulding values were always recorded from the surface in

contact with the moving half of the mould. This prevents any

temperature differences between the fixed and moving halves of the

mould influencing the measured skin thickness.

It is possible to view sections of the moulding in either the

injection direction or transverse to it, however as the skin is more

birefringent parallel to the injection direction it is easier to

see when viewed in this mode. Variations in skin thickness are shown

in tables 10 - 16, and figs 4.14 - 4.16.
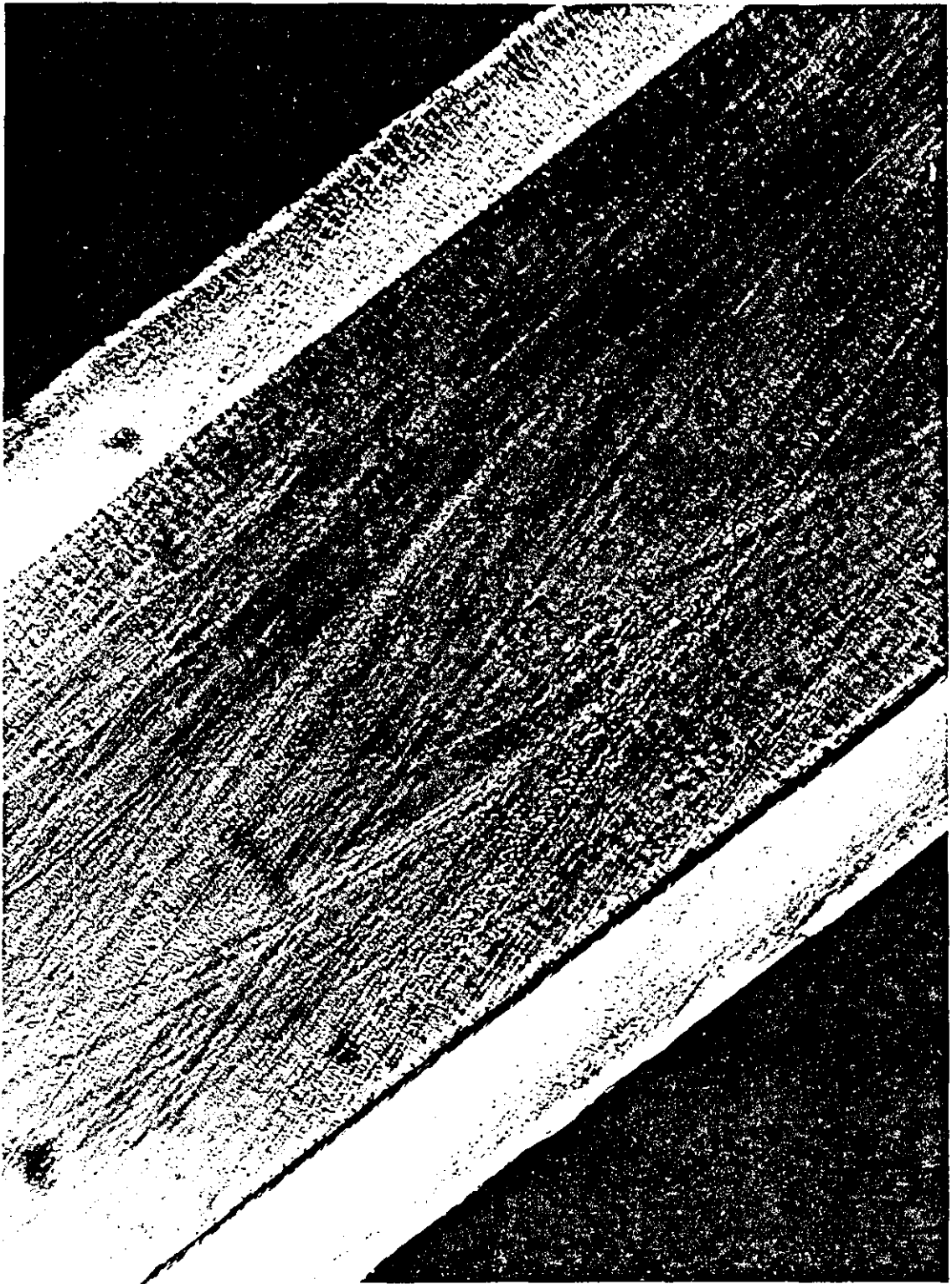
Fig 3.8 Micrograph of a microtomed section showing skin and flow lines

Other interesting features can also be seen from the sections, showing the existance of a number of different shear zones through the thickness of the moulding, these are indicated in fig 3.8.

It was not practicable nor very informative to take measurements at any more positions than those shown for each moulding condition but one plaque was tested in 81 places to show the complexity of the overall pattern see fig. 4.17.

3.7 FLOW IN THE MOULD

Many studies have been made with a view to examining what is happening inside the mould during filling. Some of these involve the use of high speed photography through glass windows let into the mould. Other less sophisticated means involve the dispersion of coloured particles in the blended material to follow flow. Mathematical theories of flow are expounded, most of which are based on unreal conditions to be of little practical use.

In the present work no means of following flow in the mould as it was happening was available nor was this considered to be a major part of the project. However it was considered useful, in order to explain some of the physical properties, to make some attempt of following the changes in flow patterns with changes in moulding conditions.

The means by which flow was studied was simply from short shots and visual inspection of the surfaces of the moulding. A short shot is one in which only part of the cavity has been filled with polymer. This is achieved by altering the amount the screw of the machine is allowed to move back to pick up fresh material.

The short shot shows the flow front and how it changes with position in the mould.

Some information about flow can also be found from observations of the surface of the moulding; this was more as a consequence of material freezing on the mould walls however.

Some typical flow patterns are illustrated in figs 4.18 - 4.19.

3.8. INTERNAL STRESS MEASUREMENT

3.8.1 Introduction

For metals there appear to be well defined relationships between flow rate and effective stress, which is the difference between the applied and the internal stresses present in a material. The relationship for metals is usually of the exponential or power law type[133].

Flow for polymers however is analysed in terms of free volume changes and relaxation time spectra where internal stresses are not taken directly into account[30].

Non uniform cooling in the mould of the injection moulding process leads to a difference in orientation stresses. Different rates of relaxation therefore set up compressive or tensile stresses in the moulding, these may be determined by a number of means including optical methods[15,4]. The method used in this work however is that based upon the work of Li[130] and extended to polymers by Kubat and Rigdahl[138,139].

The method uses a number of stress relaxation curves with different initial stresses(fig. 3.10.). If the maximum slope of these curves of stress versus log. time is plotted against the
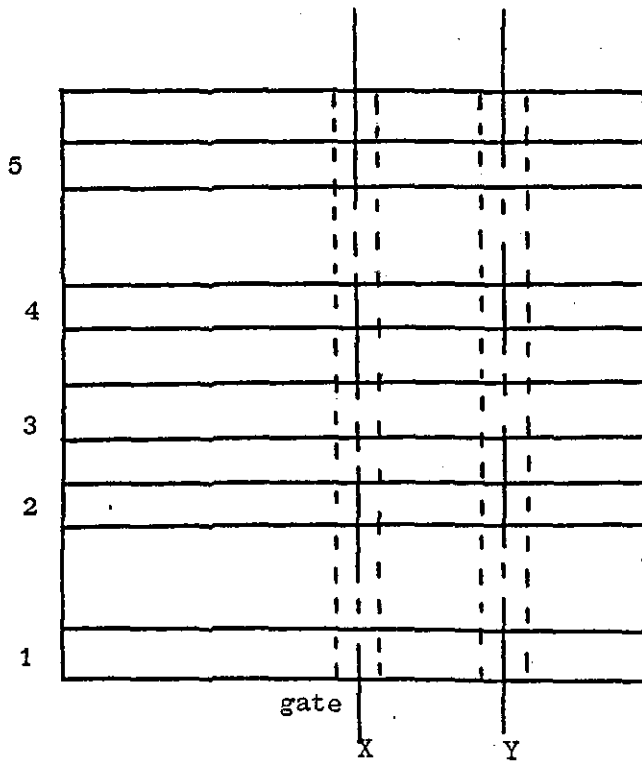
fig. 3.9   Position of test specimens for internal stress.
measurements.
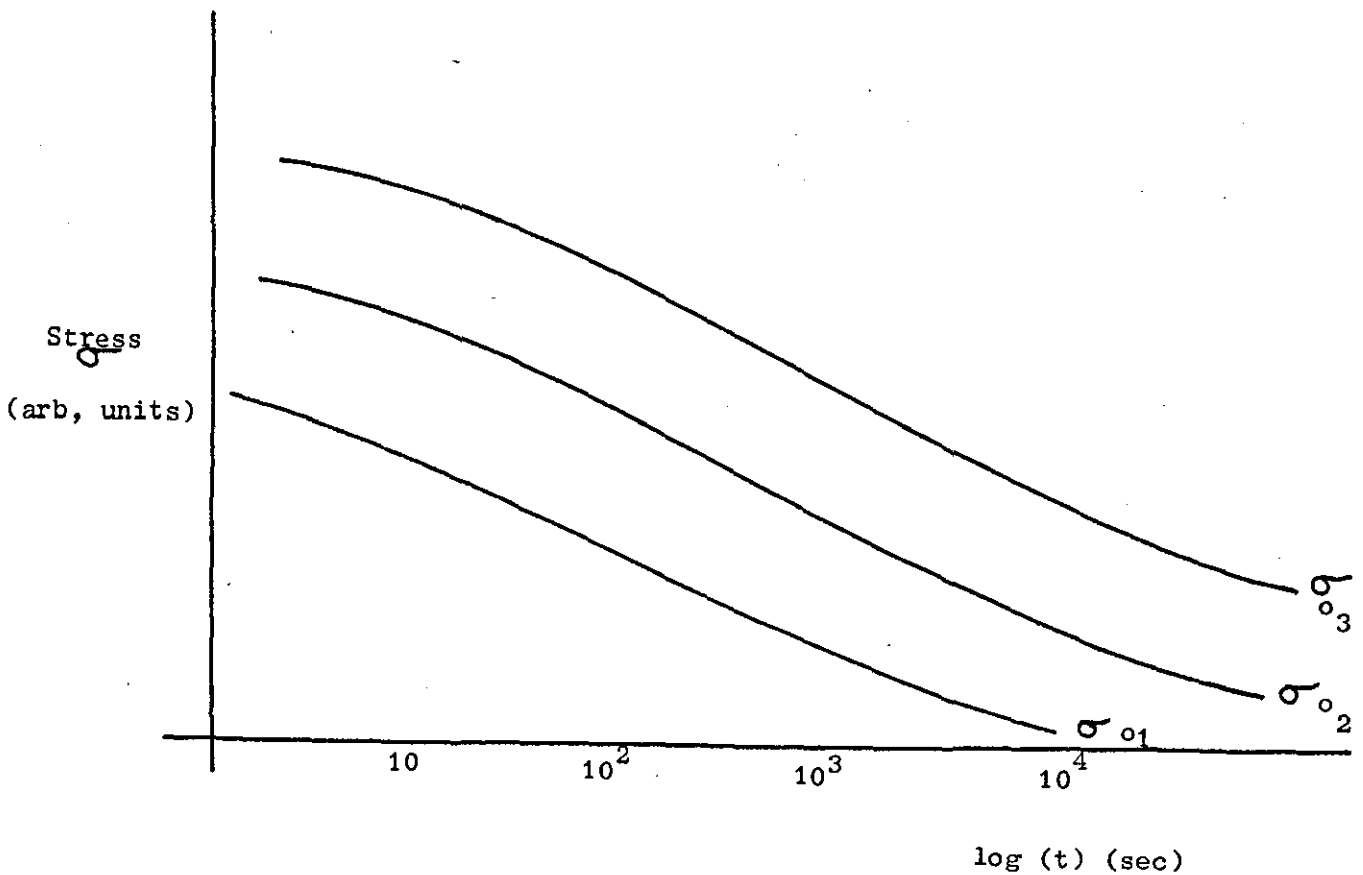
fig. 3.1C Stress relaxation curves (schematic)

initially applied stress a linear relationship is found whose
intercept with the 'x' axis is taken as a measure of the internal
stress of the sample.

The formula for uniaxial extension relating stress and strain
is

$$\frac{\dot{\sigma}}{E} + B\sigma^n = \dot{e} \qquad \ldots \ldots (1)$$

Where σ is stress in uniaxial extension

E is Young's modulus

$\dot{e}$ is strain rate

$\dot{\sigma}$ is rate of stressing

B and n are constants and $\dot{e} = 0$ for stress relaxation

$$\dot{\sigma} = -E.B.\sigma^n \qquad \ldots \ldots (2)$$

For internal stresses σ is replaced by $(\sigma - \sigma_i)$ as the
effective stress σ_{eff}. When $\dot{\sigma_i} = 0$, the internal stress
level is assumed to be unaffected by flow, equation (2) becomes

$$\dot{\sigma} = -E.B(\sigma - \sigma_i)^n \qquad \ldots \ldots (3)$$

The solution of which is

$$\sigma = (\sigma_o - \sigma_i)(1 + mkt)^{-\frac{1}{m}} + \sigma_i$$

Where k is E. B. $(\sigma_o - \sigma_i)^m$ and m = n-1

also σ_o is the initial stress.

The slope of the relaxation curves $d\sigma/d\log t$

is $\qquad S = -K(\sigma_o - \sigma_i) t (1 + mkt)^{-\frac{(m+1)}{m}} \qquad \ldots \ldots (5)$

eliminating t gives

$$-S = \frac{\sigma - \sigma_i}{m}\left[1 + \left((\sigma - \sigma_i)\big/(\sigma_o - \sigma_i)\right)^m\right] \ldots$$
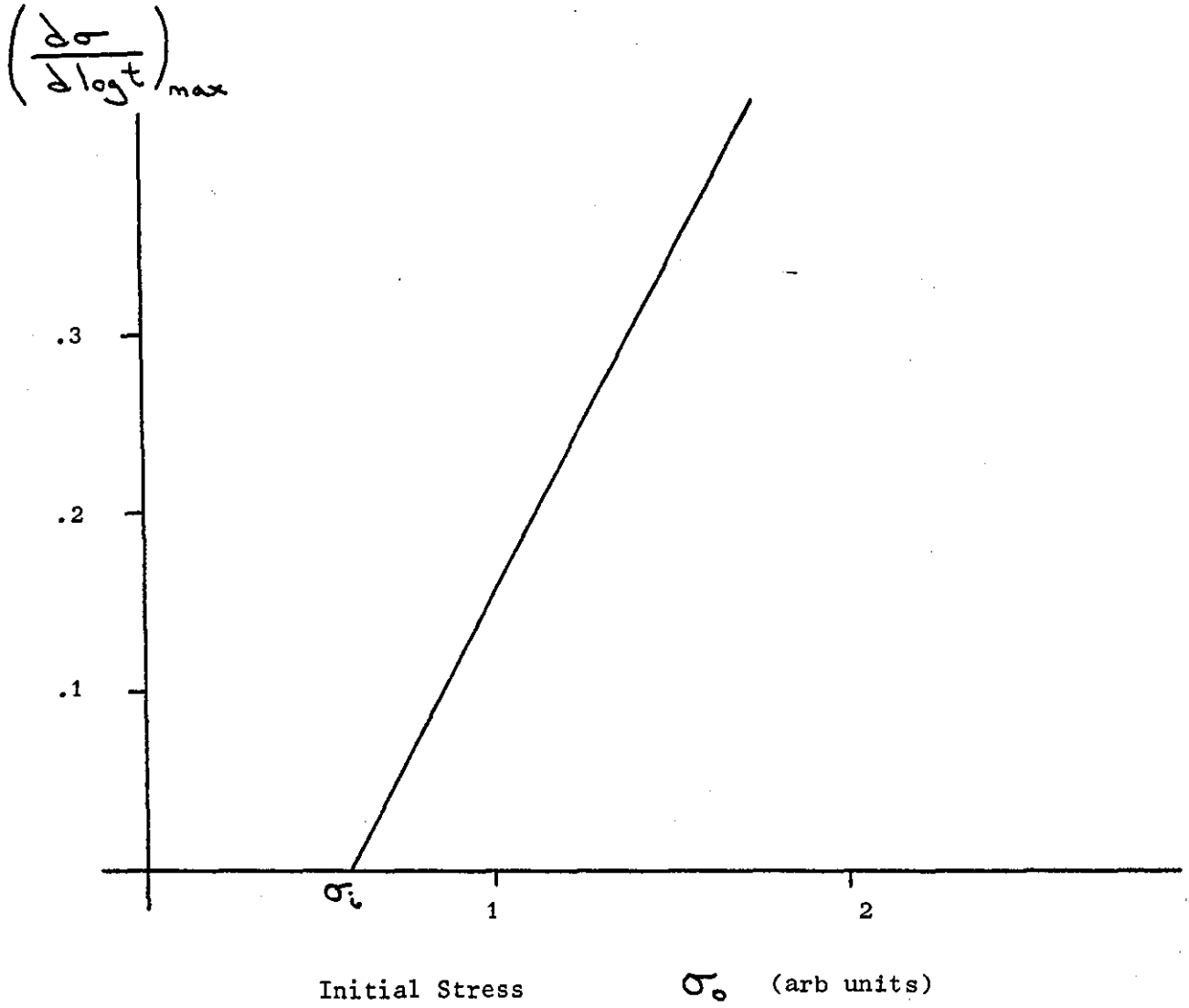
fig. 3.11 Determination of internal stress from
maximum slope of the relaxation curves.

This is the method according to Li[130] where the slope of the graph σ versus log t is used to determine σ_i the internal stress. 'S' values from a single relaxation curve are plotted versus σ to produce an intercept which is the internal stress value. This is sufficiently meaningful if the curvature of the σ versus log (t) graph is great enough. When the slope of the relaxation curve of σ versus log (t) is plotted against the stress at the same point on the curve, the slope is plotted numerically as $\dfrac{\delta\sigma}{\delta\log t}$ versus σ

In the present case however the plot of σ versus log (t) is virtually linear so that Li's method is used in a slightly modified form. The method involves the use of a number of relaxation curves with different initial stresses (σ_0) instead of just one for Li's method. The maximum slope of each is plotted versus σ_0 , the intercept is then a measure of the internal stress of the sample (fig. 3.11).

Denoting the maximum slope by F, from equation (6)

$$F = n^{-n/n-1} \; (\sigma_0 - \sigma_i) \qquad \ldots\ldots (7)$$

The slope of the graph of F versus σ_0 is $n^{-n/n-1}$, so that for a sample without any internal stress

$$\frac{F}{\sigma_0} = n^{-n/n-1} \qquad \ldots\ldots (8)$$

Furthermore if the value log ($\sigma - \sigma_i$) is plotted versus log (t) then the reciprocal, of the slope m, denoted by $\dfrac{1}{m}$ has often been used for metals to give information about the mechanism of flow, it is also found of interest in the present context.

Values of both internal stress and the 'm' values associated with them are given in tables 31 - 34.

3.8.2. Experimental Procedure

Samples were cut from the mouldings transverse to the injection direction and routed to produce dumbell specimens. Five specimens per moulding were taken at positions corresponding to positions 1 - 5 in fig 3..9 and three samples tested for each moulding condition.

The theoretical basis for the relaxation method assumes that small extensions are used, corresponding to the initial linear portion of the stress strain curve. For the PVC mouldings the maximum percentage extension before necking or fracture was approximately 7%. In all four different values of extension were used with a maximum of 4.6%, at each position along the plaque.

The tensile testing equipment used was an Instron with an environmental chamber for heating the specimen. The tests were performed at an elevated temperature in order to accelarate the relaxation rate. A temperature of 60°c was used this being high enough to speed up the testing but not too close to the glass transition temperature at which any frozen in stresses would be relaxed almost instantaneously. A temperature of this order over the relatively short timescale of the test does not affect the level of stress significantly.

The specimens were allowed a warming up period of ten minutes in the chamber prior to testing. A cross head speed of 25mm/min as suggested by ASTM was used for initially extending the sample by the pre-set amount, and the decay in the level of the load was plotted versus time.

From the relaxation plot a graph of stress (σ) versus
log time was plotted, and the maximum slope (F) used to give the
graph of F versus σ_o the initial stress. The intercept of the
line of best fit, obtained by linear regression, with the axis
is taken to be the internal stress of the sample.

It is seen in tables 31 - 34 that the levels of stress present
are low, and either negative or positive indicating a tensile or
compressive stress depending upon the moulding conditions used.
Values of the corresponding slope 'm' are also given.

CHAPTER 4

RESULTS

4.1 Introduction

The results that follow are an attempt to assess the changes
brought about by the moulding process. In this chapter tables of
results that are referred to may be found in the appendix 1. Some
of the results in this chapter are presented in graphical form
in order that trends may be followed more easily. As mentioned
earlier (Chapter 2) the work falls broadly into three moulding
series :

- i) initial moulding using an existing mould with a
square cavity;

ii) a subsequent design of a rectangular cavity using
similar moulding conditions as for the square moulding;

iii) and finally the effect of mould temperature on properties
for the rectangular plaque.

The results are therefore described in this manner.

It may be useful to refer to Chapter 2 for details of the
positions in the plaques that were tested.

4.2 X-ray Results

The results from X-ray examination of specimens fall into
two groups as described in the experimental section, namely the
determination of crystallite size and the height of the two main
peaks.

4.2.1. Crystallite Size and Peak Heights

The size of any crystallites present was found to vary
with both processing conditions and position in the moulding. It
is seen in table 35 that the greatest crystallite size is at

position 'b', some distance from the gate, with a gradual decrease

in size towards the end of the plaque. This is the case for most

melt temperatures and injection speeds used at this mould temperature

of 40°c.

The largest crystallites were found in the plaque moulded

at the highest melt temperature. Whilst injection rate appeared

to have a small effect on size of the crystalline content, slight

decrease in dimensions was noted for the slower injection rate.

A more dramatic effect was found for plaques moulded using

a variety of mould temperatures. The lowest mould temperature

(15°c) produced the smallest crystallites of all the moulding

tested, these were in fact almost half the size of the crystallites

found in mouldings made at a mould temperature of 65°c.

A similar variation with position emerges in the crystallite

size for the plaques produced at different mould temperatures as

exists for those mentioned above (at 40°c); namely that there is

a maximum at position 'b'. The smallest crystallites were

found in the remotest regions from the gate.

At the highest mould temperature used (65°c) not only were

the largest crystallites produced but the plaque appears to be

composed of more uniform structure as the variation in crystallite

dimensions is minimal.

It is interesting to note that the results for the plaques

with a mould temperature of 40°c lie between those samples whose

mould temperatures were 30° and 50°c. This shows the moulding

process and X-ray procedure is reproducible, as the sets of mouldings

were made at different times during the course of the work.

Changes in the peak height on the X-ray trace at 17° (2θ) are shown in table 36. The height is seen to vary with both position in the plaque and the moulding conditions used. The peak height for the plaque moulded with the highest injection rate shows a change in height at positions 'd' and 'e' only. A decrease in injection rate for the same melt temperature increases the height of the peak.

For samples made at different mould temperatures the pattern of results is slightly different from above. At the coldest mould temperature the peak height is seen to be a maximum for the set of moulding conditions used. Increasing the mould temperature to 30°c produces a uniform size of peak height over the length of the moulding, but lower than for the samples produced at 15°c. Further increases in the temperature of the mould produce a decrease in the numerical value of the peak height to a minimum at position 'a' for the mould at 65°c.

An increase in melt temperature has the effect of reducing the peak heights to the minimum values found for any condition of moulding in this work. The height of peak is very similar for all the positions tested at the high melt temperature.

4.3 Differential Thermal Analysis

Values of the glass transition temperature remained constant (80°c) within experimental error for all the moulding conditions and positions of testing examined.

Differences were observed however for the traces; from the D.T.A. equipment in the depth of the endothermal peak. It can be seen from the specimen trace (fig. 3.6) that after the glass transition temperature (Tg) there is generally a broad endothermic peak extending between approximately 120°c and 200°c. It is the area of this peak that has been converted into an enthalpy change, the results of which are shown in table 30 for the 3mm plaque and tables 26 to 29 for the 1.6mm plaque.

The enthalpy change varies very systematically over the processing range used and the positions in the moulding that were tested. The greatest change is found at the gate and diminishes steadily as the end of the plaque is approached for the 3mm thick plaque.

The enthalpy change also increases as the temperature of the mould is raised. The increase from a mould temperature of 15°c to one of 60°c produces a corresponding increase in the enthalpy change of approximately 33% for all positions tested.

A higher injection rate produces a small increase in enthalpy change. Whilst for plaques moulded at the higher melt temperature little variation is seen when compared with the results for the plaques produced at the lower melt temperature.

Although numerically the difference in the values of enthalpy

change is low the effect on the physical properties of even small

differences is thought to be significant.

For the thinner plaque the variation in enthalpy change is

much less straightforward than for the 3mm thick plaque. As a set

of results all the values of enthalpy change for the thinner plaque

are less than those for the 3mm thick plaque.

Although the results (table 26) show a steady increase from

the end of the plaque to the gate there are a number of anomalous

situations in the results presented in tables 26 to 29.

There is generally an increase in the value of the enthalpy

change with an increase in melt temperature certainly for the

positions tested along the centre of the plaque. The situation

for the samples tested along the edge of the plaque 'b', 'd', 'f'

and 'h' is not quite so clear . Samples from position 'b' in

the moulding are particularly irregular in their predictable

enthalpy change.

An increase in injection rate produces a greater enthalpy

change in the main, although numerically the size of the increase

varies with position in the mould. Some enthalpy changes remain

very similar with position in the mould whilst others may change

by as much as 100%.

Changing the mould temperature from 40°c to 60°c produces a

slight increase in the depth of the endotherm and hence a slight

increase in enthalpy change. Although this is more noticeable at

the higher melt temperatures.

The greatest enthalpy change is frequently at a position some

distance from the gate ie. at 'g' with the smallest change at 'c'

for the central positions. The samples examined at the edge of the
moulding do not show the same pattern of results as those in the
central region. Often the corner of the moulding ('b') has the
largest enthalpy change along the edge of the moulding.

4.4 Ion Etching Results

Ion etching has the effect of removing a small amount of
material from the surface that has been bombarded. It is suggested
that material is removed preferentially depending upon structure
and material composition at the surface.

The results from a small number of tests are not fully
reproducible and are subject to too much interpretation. It is
evident however that the effect of ion bombardment is to produce
a surface with characteristic 'spikes'. These thermal spikes
although artefact do show a linear pattern along the length of the
moulding. Between the rows of spikes are 'craters' which vary in
size depending upon the length of time of etching and the moulding
condition.

Specimens from some of the moulding conditions are discussed
in Chapter 5, and shown in fig 4.1.

4.5 Density Measurements

Density results for the square plaque are shown in tables 1 - 5
and in graphs in figures 4.2 - 4.6. Density does not change
significantly for moulding temperatures up to approximately 195°c
above this temperature there is a sudden dramatic increase, this is
true for all positions in the plaque for the faster injection speed.

Injection
direction

Sketch of sea shore structure exposed by
ion etching.
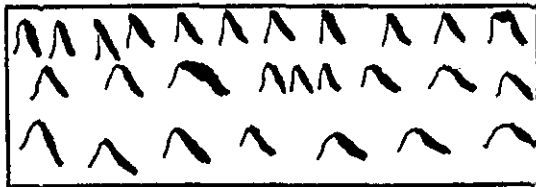
injection
direction

Spiked   artefacts caused by over etching
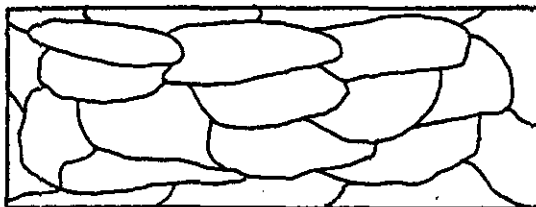
injection
direction

Plate like structure

Fig. 4.1 Examples from etching

fig. 4.2 Density Vs Mould Temperature 1.6mm x 75mm Plaque

185,0.6
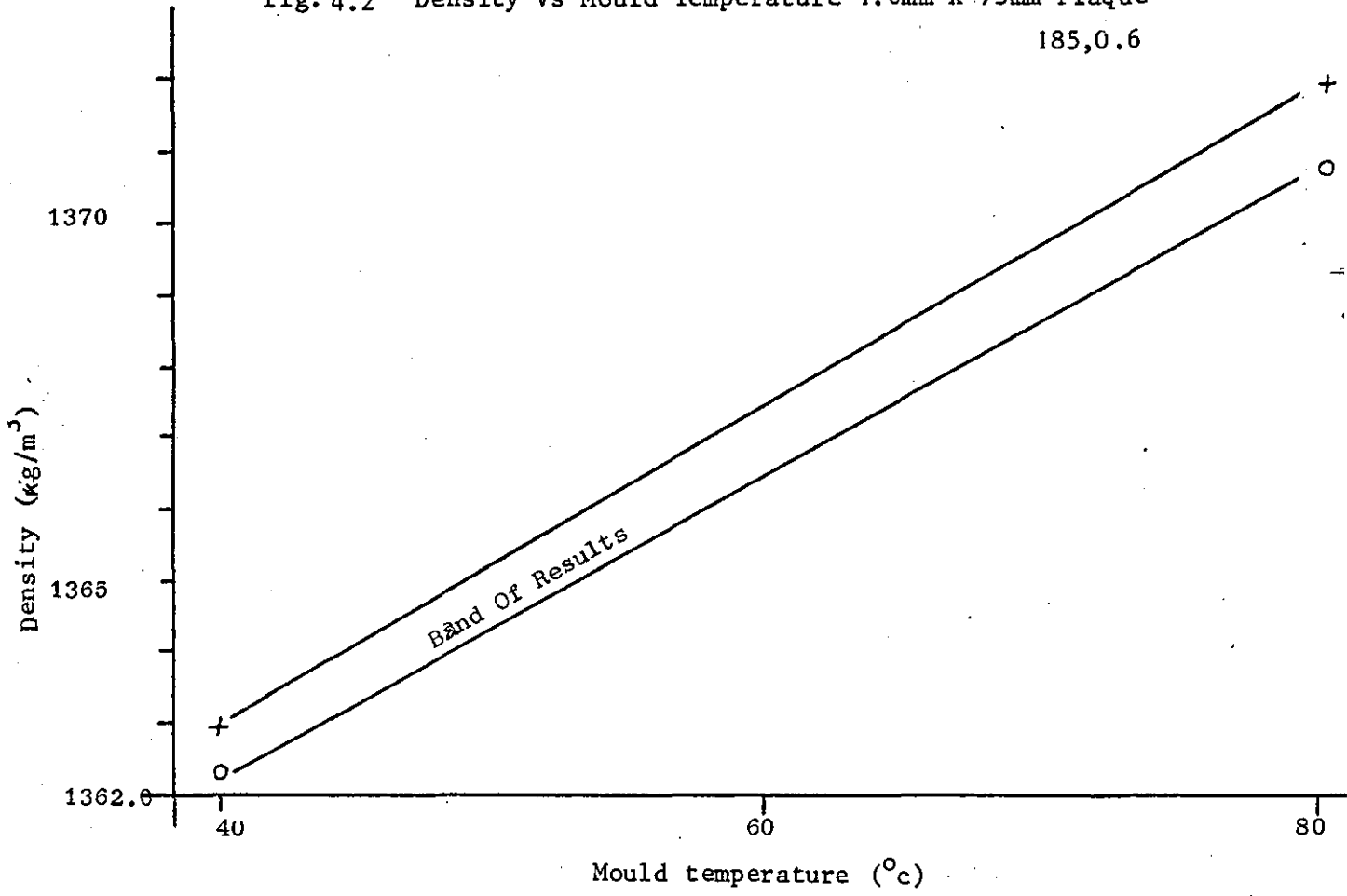
fig 4.3 Density Vs Mould Temperature 3mm x 125 mm Plaque

155,0.8
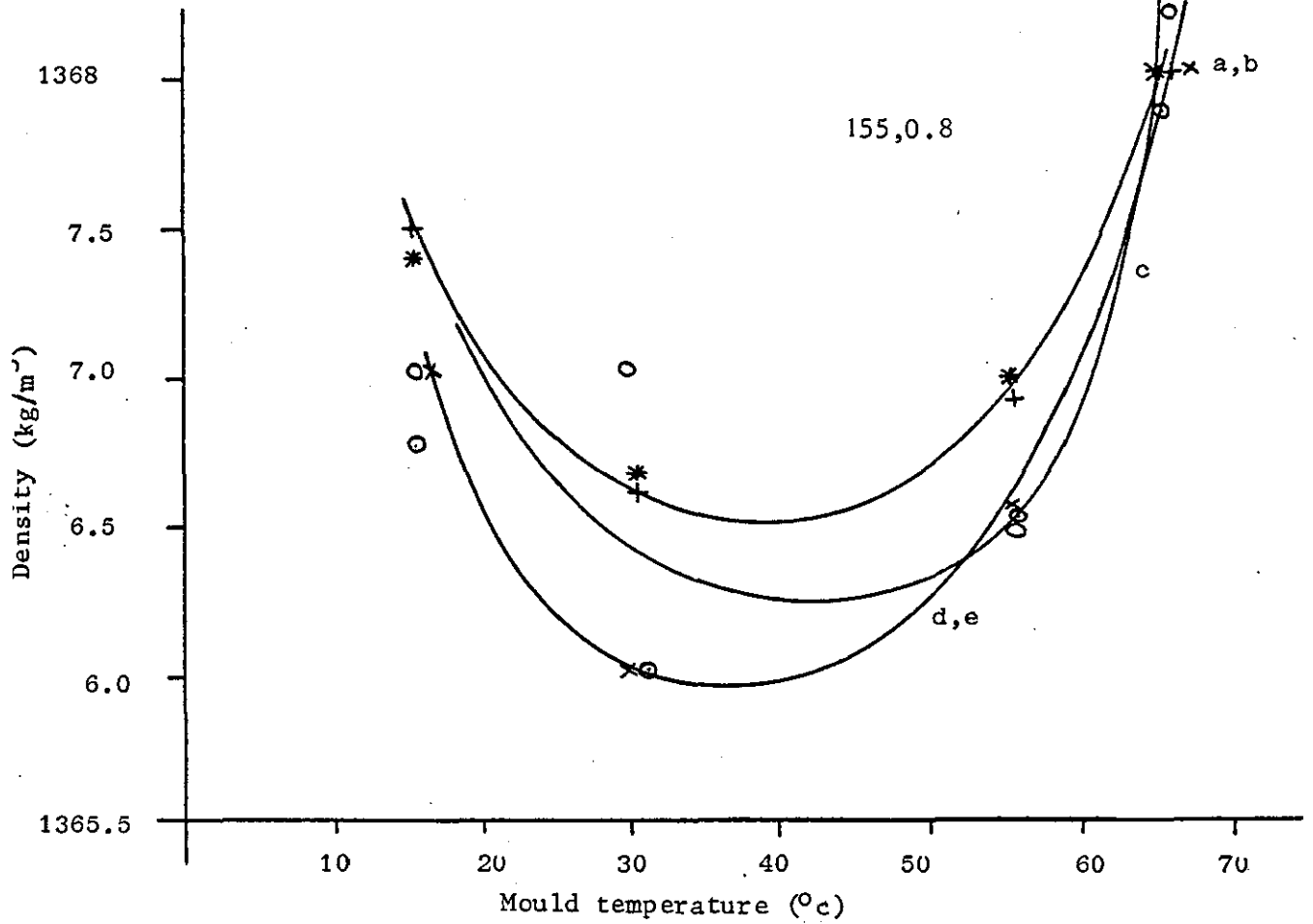
fig 4.4   Density Vs Plaque Thickness

155, 0.6, 40
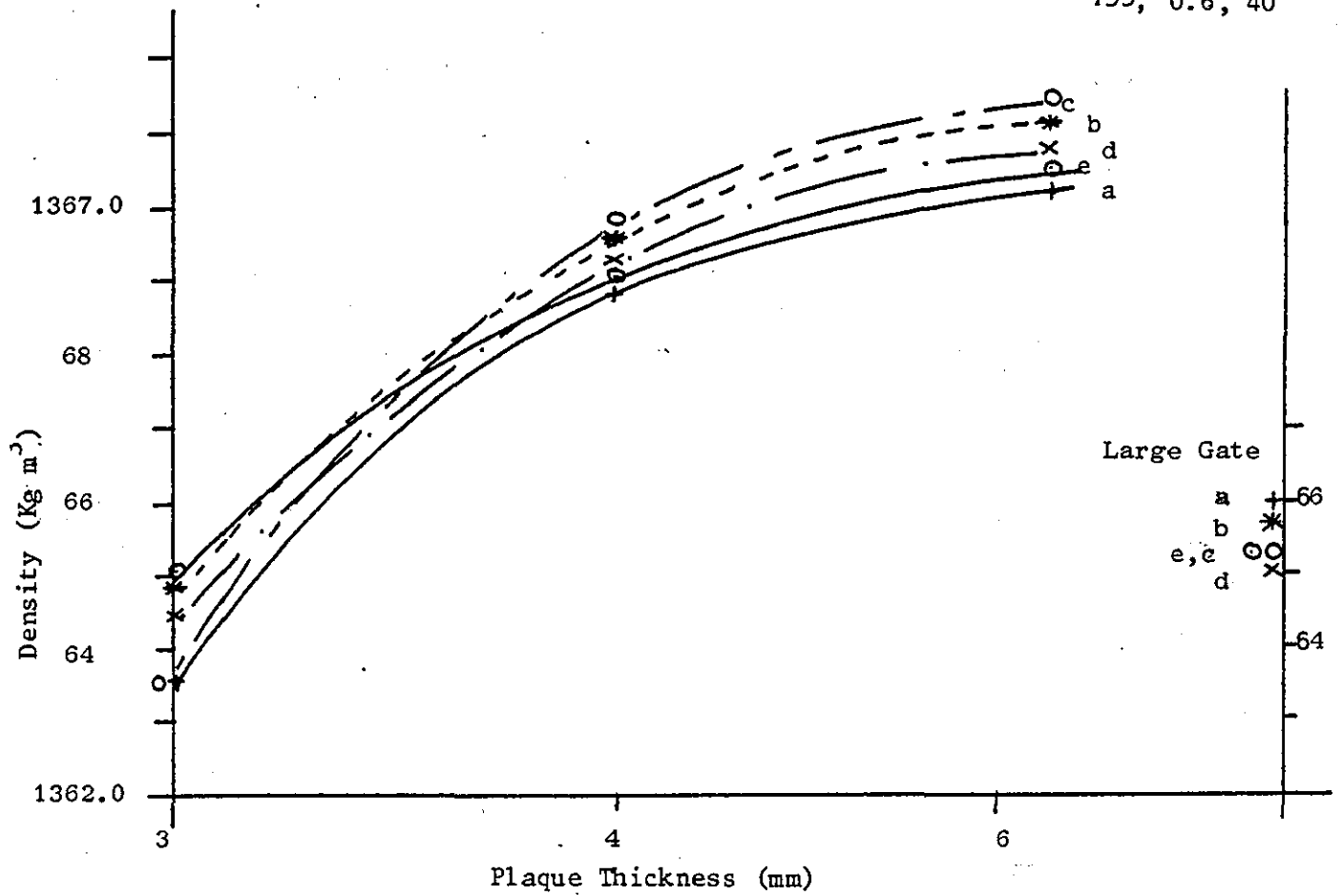
fig 4.5 Density Vs Plaque Thickness

155, 1.0, 40
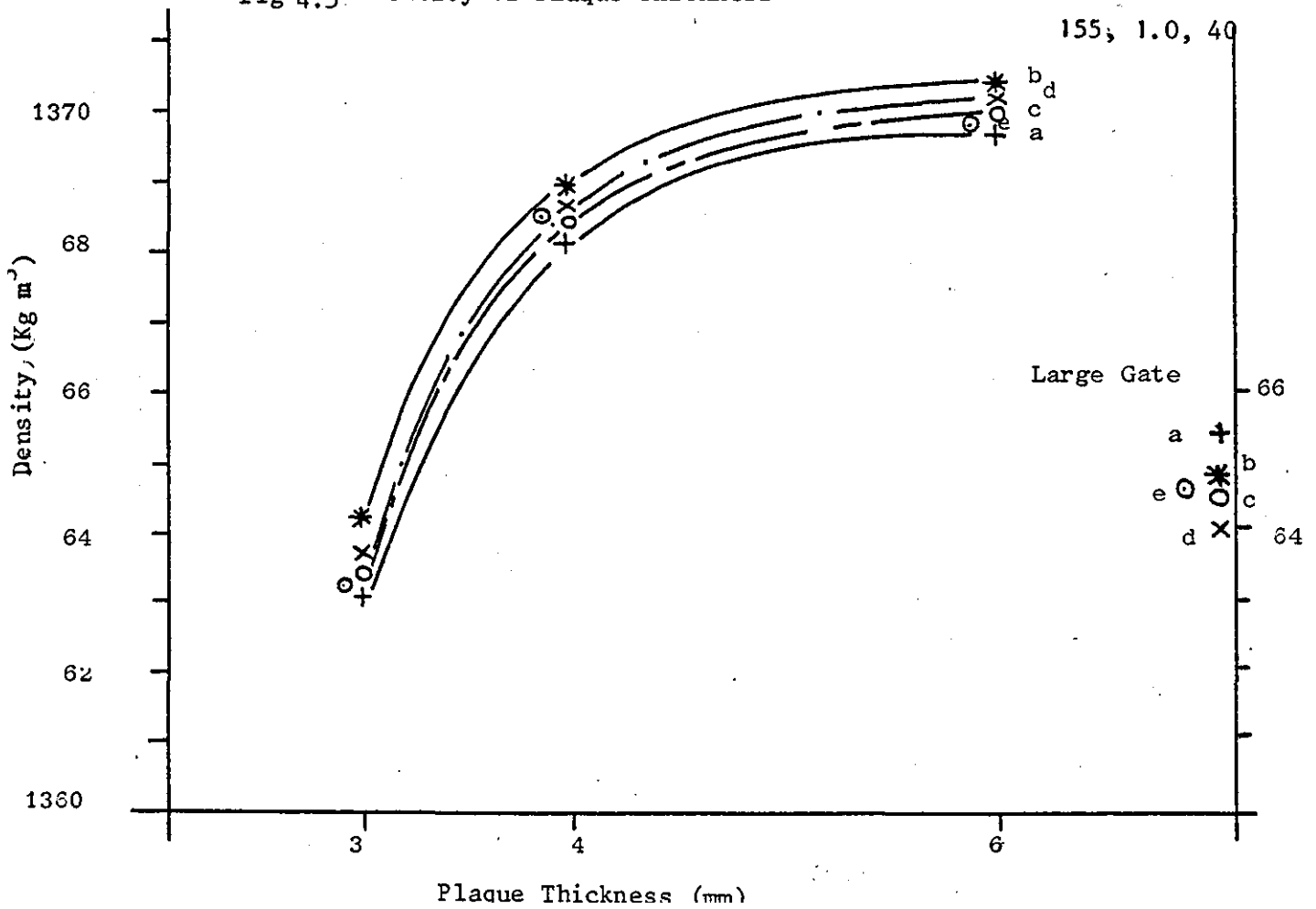
Fig 4.6 Density Vs Plaque Thickness
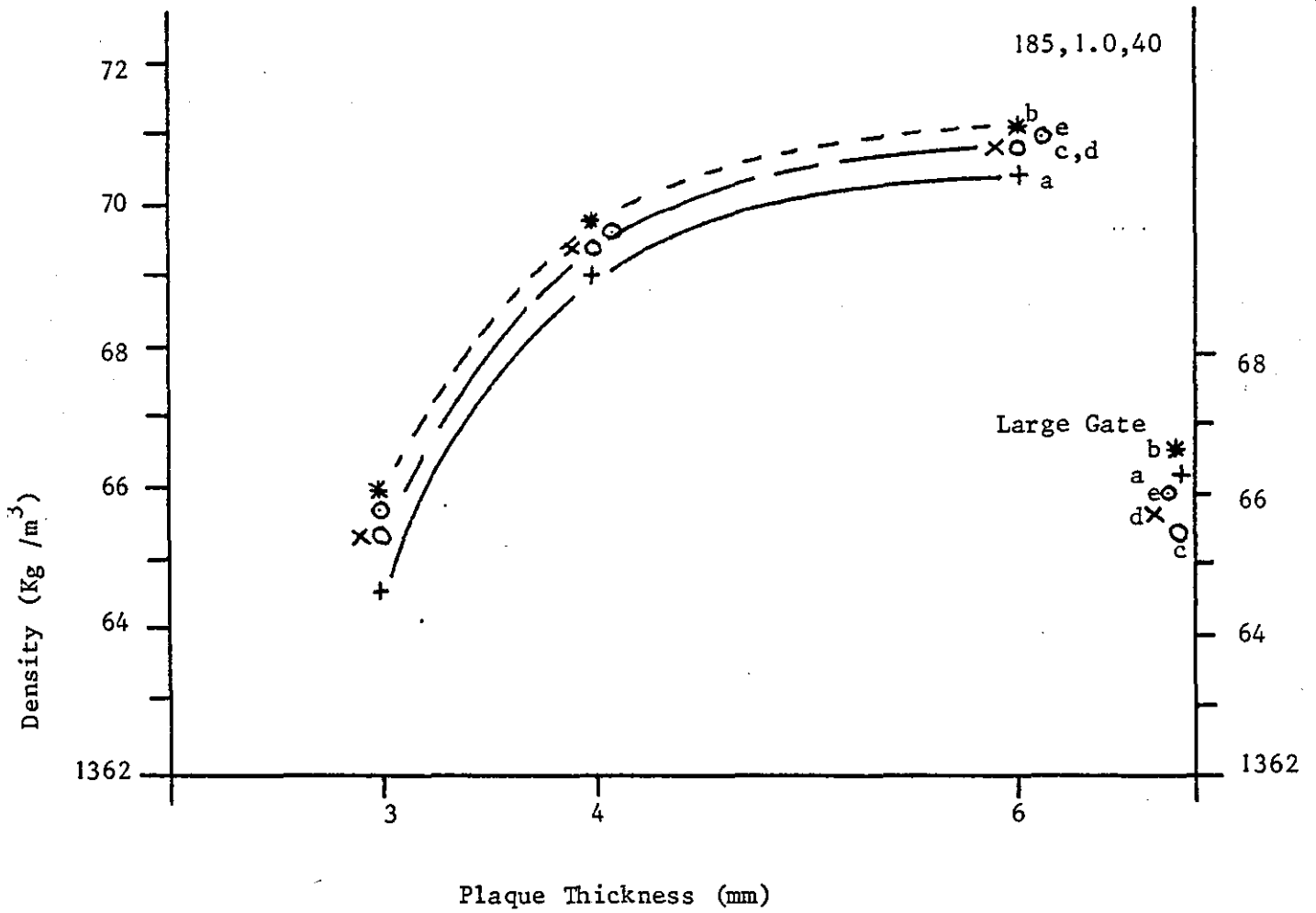
1.36905	1.36890	1.36845	1.36875	1.3684	1.3686	1.3701
1.36940	1.3693	1.3695	1.3697	1.36925	1.3692	1.3681
1.36980	1.36957	1.3696	1.3694	1.3691	1.3692	1.3697
1.37005	1.3687	1.3703	1.36925	1.36958	1.3704	1.3704
1.37035	1.3694	1.3698	1.36863	1.3704	1.3697	1.3704
1.3704	1.3705	1.3704	1.3689	1.3704	1.3699	1.3701

GATE END

Fig 4.7 Density Measurements for Square Plaque (165,0.8,40)

If the injection rate is decreased a much narrower range of density changes is found for all positions except 'a' however, where there appears to be a minimum for the intermediate melt temperature.

As well as injection speed mould temperature has an effect on density (table 9) for the rectangular plaque. Densities at low melt temperatures again appear to be fairly constant although there is an increase for the mouldings at 195°c at the slower injection speed. The most striking points to note are the increase in density for high temperature condition and the much reduced spread of density with the plaque at this temperature. This is the type of moulding which would be considered an optimum.

The spread of densities at a particular melt temperature appears to be similar for all the moulding conditions used, with generally the lowest densities in the area surrounding the gate.

It seems that comparison is easier if the density at a particular melt temperature is considered. At 195°c positions 'a' and 'b' have the lowest densities, 'e','f' and 'g' a slightly higher value whilst for the other positions comparison is not possible.

It is probably better therefore to look at density changes for the overall plaque rather than too closely at individual positions at this stage (fig 4.7).

Density changes with injection speed for the square plaque with a minimum density at 0.8 sec. At this value positions 'a', 'b' and 'c' have the lowest densities whilst at the other positions the

density increases to approximately the same value of 1366.0 kg/m^3.

The temperature of the mould seems to be a significant factor in determining moulding density . With reference to the graph in fig 4.2, it can be seen that a surprisingly linear relationship exists density increasing with increasing mould temperature. This is only for one particular set of moulding conditions and must not be thought of as being true for all melt temperatures and injection rates. The moulding conditions chosen for these results were selected to give the smallest spread of density within the plaque.

For the rectangular moulding the effect of a change in the size and thickness of moulding produces changes in the density of the plaque at similar moulding conditions. It is seen that density increases with increasing plaque thickness, this is true for all moulding conditions subsequently used.

The spread of density within a plaque is less than with the much thinner mouldings.

The lowest values of density occur in the gate area as with the thinner mouldings.

An increase in the cross sectional area of the gate produces a corresponding increase in density for all positions within the plaque and at all processing conditions used. It also has the effect of changing the position of maximum density in the plaque generally to the vicinity of the gate.

Increases in melt temperature for the same injection rate, produce a denser moulding for the 3 and 4mm thick plaques but

appears to have little effect on the 6mm thick moulding. This is

also the case with a change in injection rate.

In contrast to the original moulding (1.6 mm thick) where there

was a linear relationship between density and mould temperature for

the thicker (3mm) plaque the situation is more complex. It is true to

say that at the highest mould temperature studied 65°c, that the

densest mouldings are produced. However there is a minima   at

a mould temperature of 30-40°c. This is in conflict with initial

thoughts that a colder mould would produce a thicker skin and thus

a lower density.(see chapter 5.) Positions further most from the

gate seem particularly sensitive to a change in mould temperature.

4.6 Shrinkage measurements

The effect of the moulding process on shrinkage, both the

mould shrinkage measured as the difference between mould and

moulding dimensions, and the relaxation of 'frozen in' orientation

stresses are shown in tables 17 - 25 and figs 4.8 - 4.13.

For the thinnest plaque (1.6mm) shrinkage, as measured in the

injection direction, is greatest at low moulding temperature. This

is regardless of injection rate and mould temperature, although these

are clearly closely linked with melt temperature. It is seen that

the percentage shrinkage is greatest in the vicinity of the gate

at the highest melt temperatures. For the lower melt temperatures

however there is a shift away from the gate to positions 'c' and

'd' where the maximum occurs. For the other positions values lie

within the extremes.

It is noticeable that at positions 'b' an anomalous situation

fig 4.8   MOULD DIMENSIONAL SHRINKAGE 3mm x 125mm PLAQUE
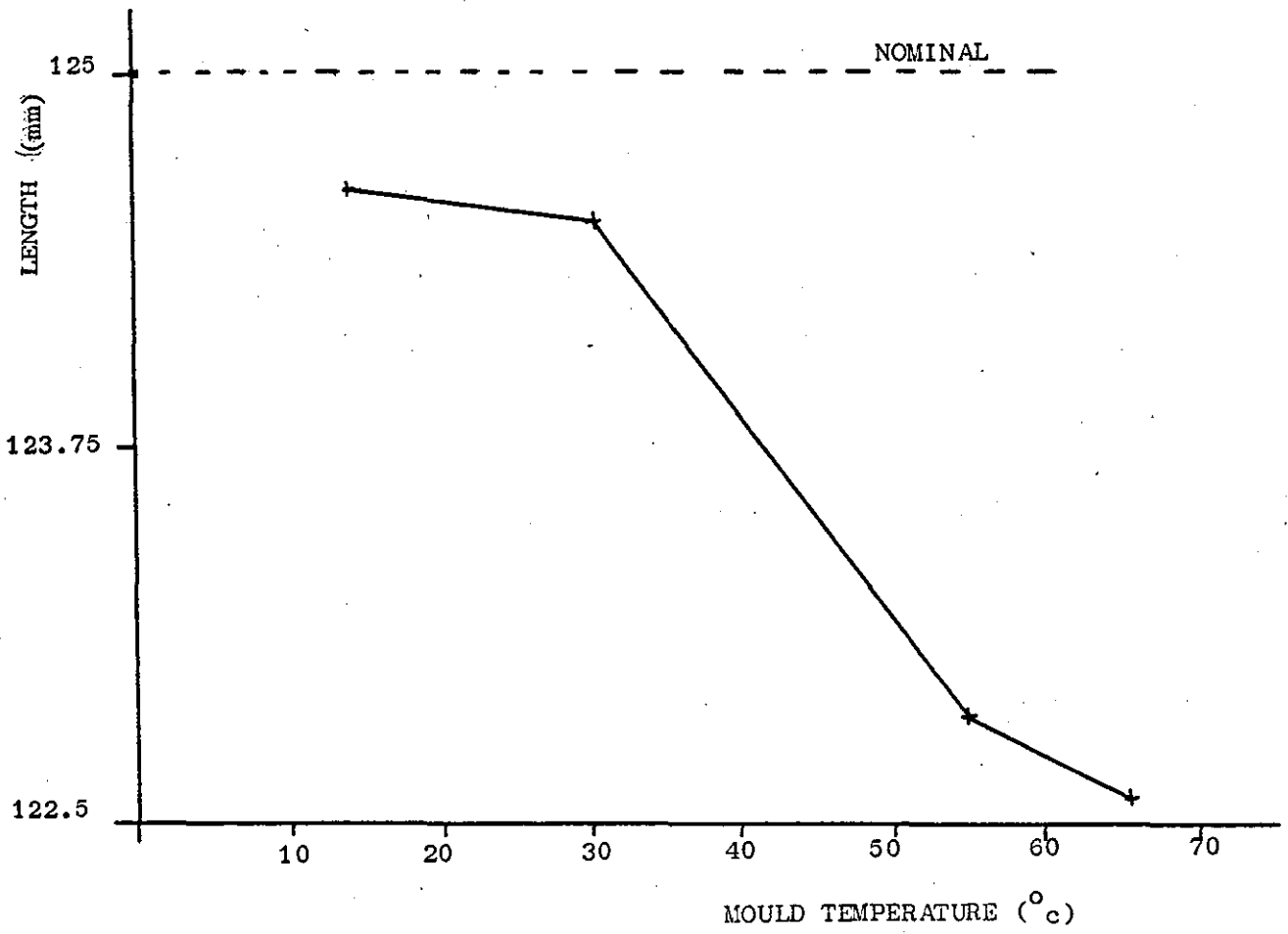
fig 4.9   MOULD DIMENSIONAL SHRINKAGE 1.6mm x 75mm PLAQUE
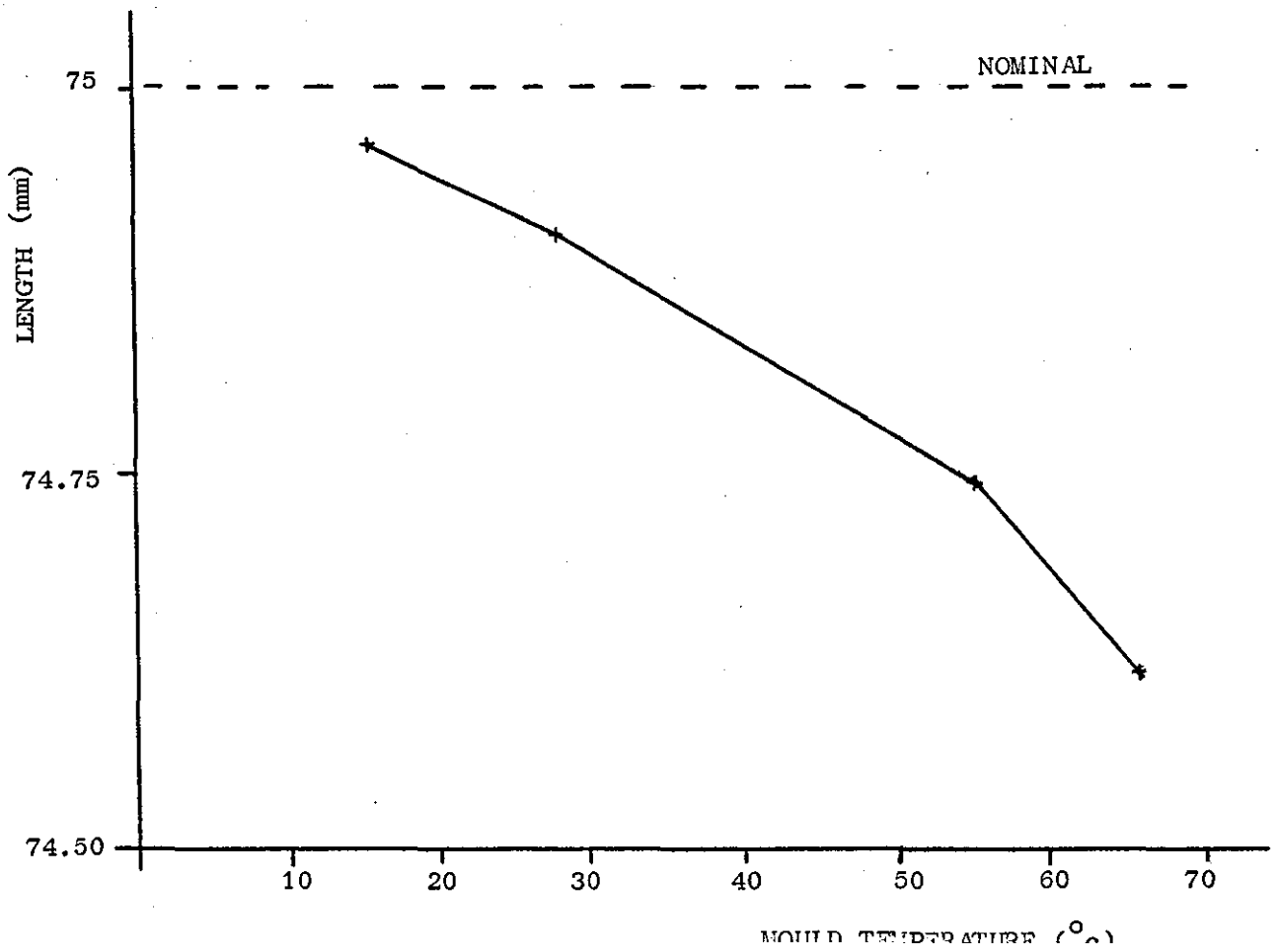
Fig 4.10 Shrinkage Vs Plaque Thickness

155,0.6,40

% Shrinkage

Plaque Thickness (mm)
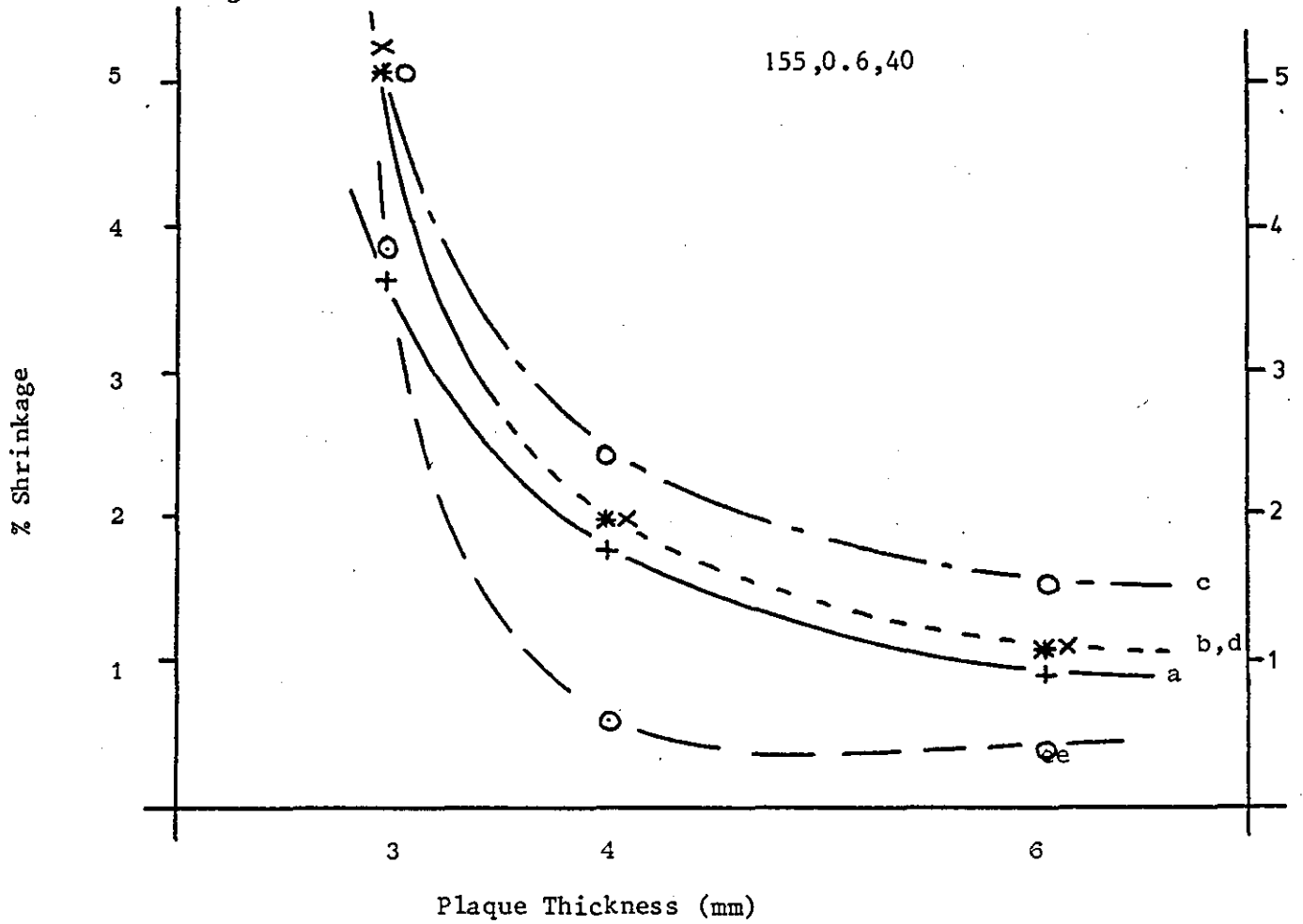
Fig 4.11 Shrinkage Vs Plaque Thickness

155,1.0,40

% Shrinkage

Plaque Thickness (mm)
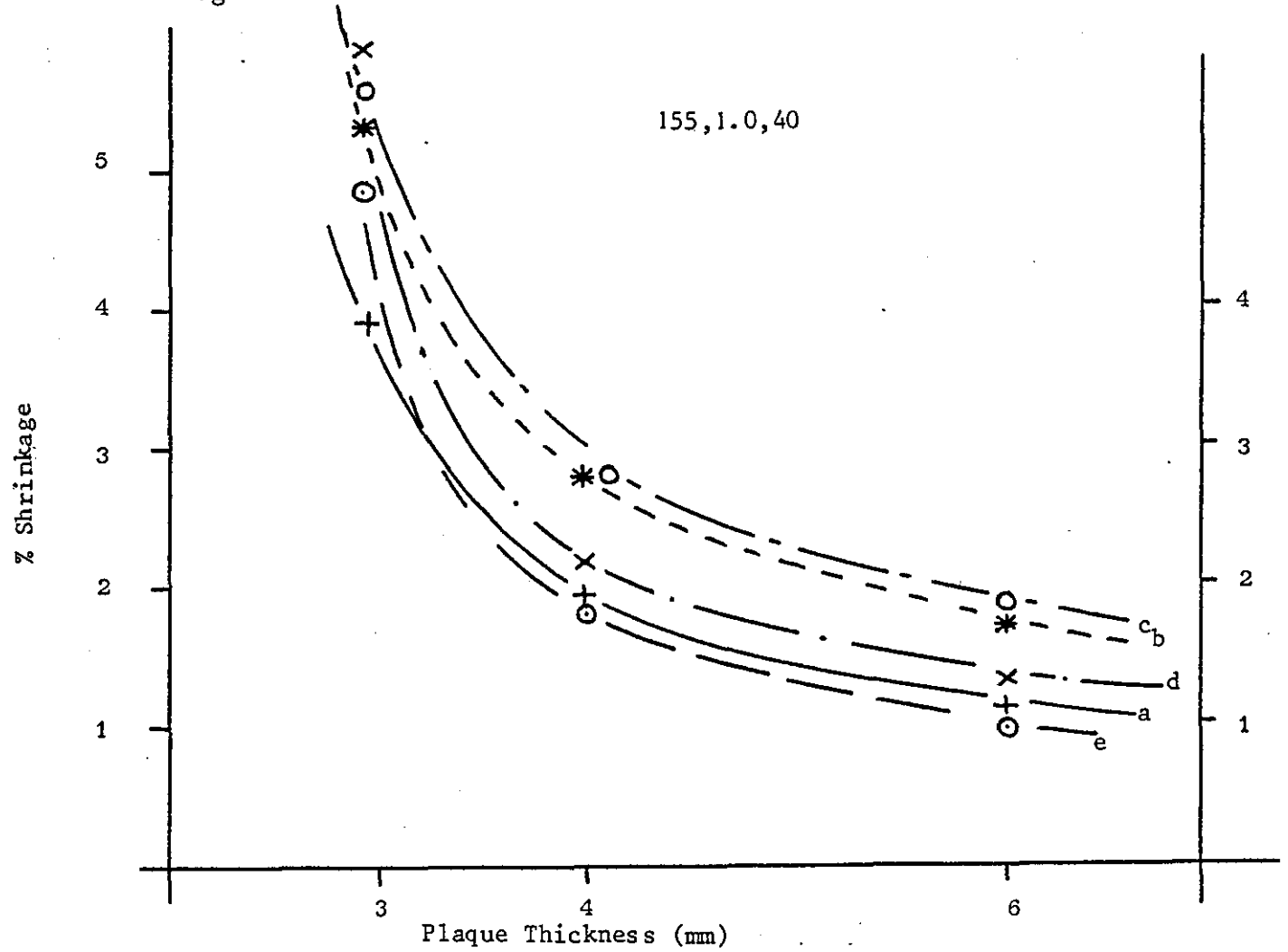
Fig 4.12   Shrinkage Vs Plaque Thickness   125 mm long Plaque

185, 1.0,40
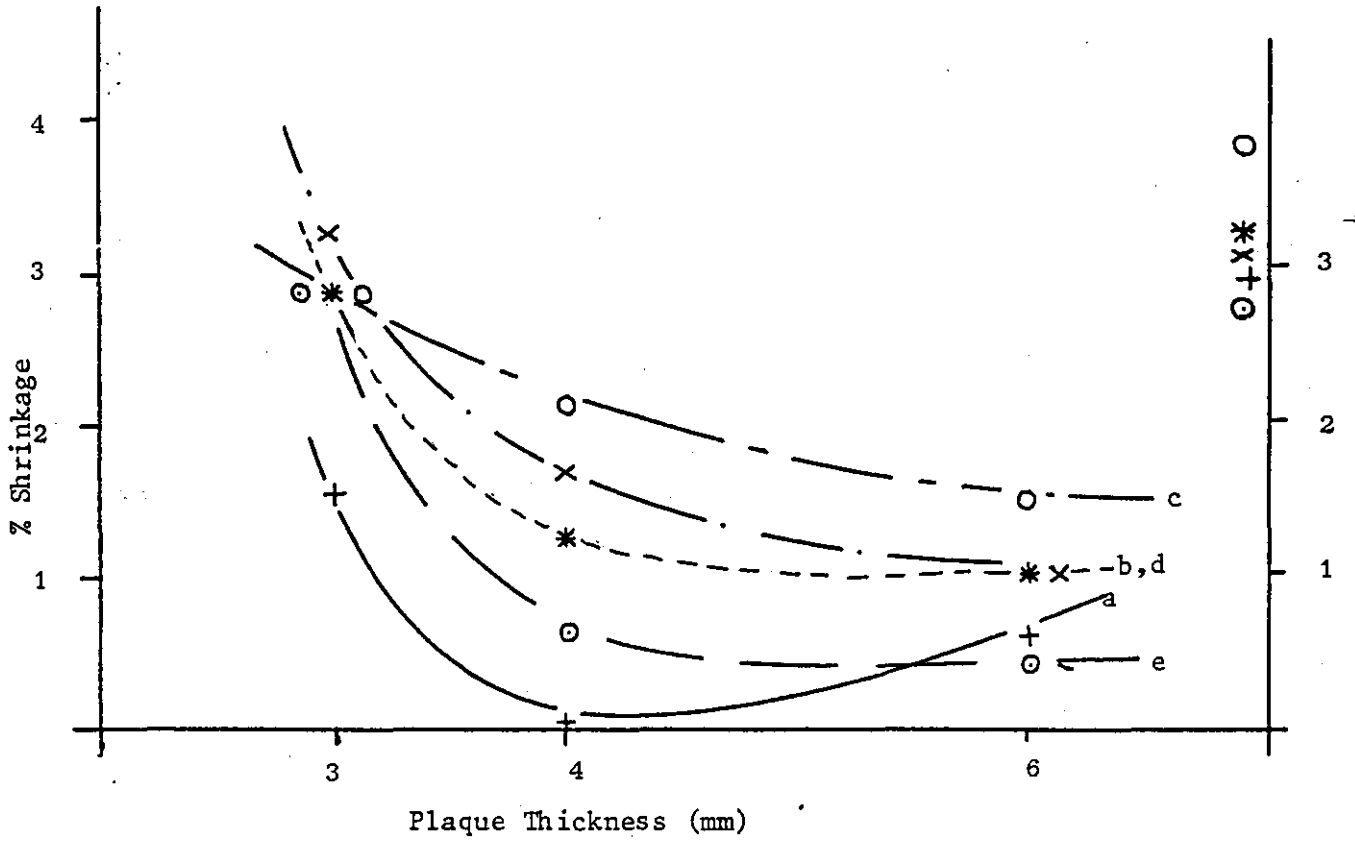
Fig 4.13   Shrinkage Vs Mould Temperature   3mm x 125mm Plaque
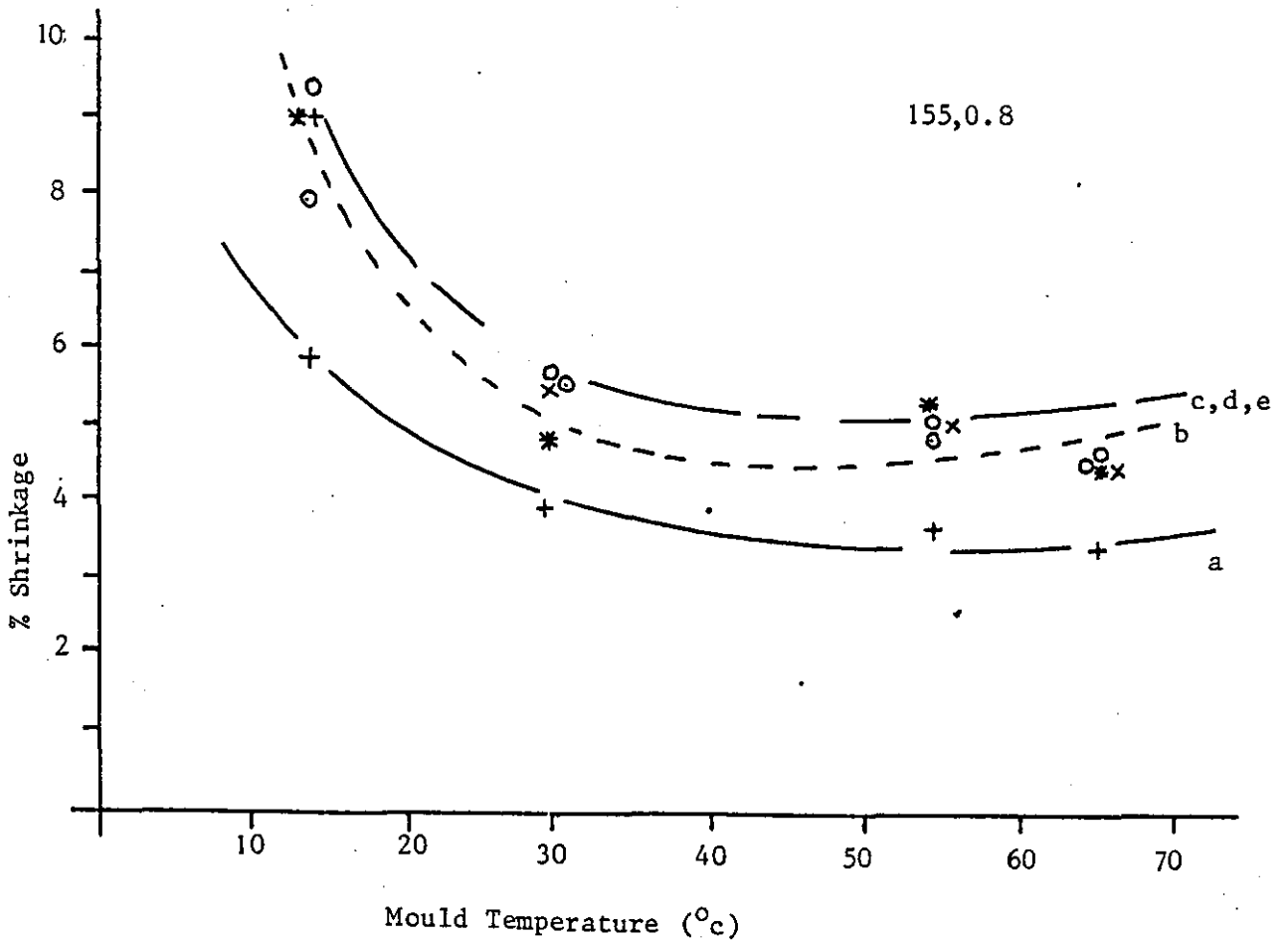
arises where the percentage shrinkage decreases as the melt
temperature is decreased,the reasons for this will be discussed
in chapter 5.

A change in the mould temperature from 40 to 60°c does not
seem to have a great effect on shrinkage although slight increases
are seen for the cooler mould at lower melt temperatures.

If percentage shrinkage is compared with injection speed, in
tables 17 and 18, a slight increase in shrinkage is apparent for the
slower injection times, probably due to less shear heating and
corresponding mould filling problems. Again anomalies are seen
this time at positions 'a' and 'c' ie. at the nearest and farthest
from the injection point.

A change in plaque thickness and its effect on shrinkage is
shown in tables 22 - 24. Shrinkage is very much reduced with an increase
in moulding thickness. All of these thicker mouldings (3, 4 and
6mm) have been produced at the lower melt temperature of 155°c
and give values of shrinkage approximately one third or less than
those observed for the thinner plaque at the same temperature.

The greatest shrinkage in this case is at position 'c'
(previously it was at position 'a') with the least amount again
furthermost from the gate.

Injection rate does not seem to have very much effect on this
property, although an increase does result in less shrinkage
especially in the thicker mouldings (4 and 6 mm) and particularly
at position 'c' where values less than 1% are found.

An increase in melt temperature significantly reduces
shrinkage (to zero in one case). There is still a fall in

shrinkage with increasing plaque thickness. As the percentage

values are low any change in the dimensions of a moulding especially

at room temperature would be small.

It is interesting to note that more or less the same

positional order is found (ie ·'e','a';'b','d';'c') · for all the

processing conditions used for the rectangular plaque. This might

lead one to believe that the relationship between moulding

history and properties might be more easily understood than is

the case for the thinner (1.6mm) plaques.

A larger gate produces a greater amount of shrinkage for all

conditions of moulding used in producing the rectangular plaques

for this second series of moulding.

Finally the effect of mould temperature on shrinkage is

seen (table 25) to be more significant at the lower temperatures

which produce a substantial increase in shrinkage. The spread of

results within the plaque is reduced, even for the coldest mould,

although samples in the gate area (exhibiting the least shrinkage)

are significantly different from the other positions.

4.7   Skin Thickness Measurements

The thickness of a skin, produced by the injection moulding

process when the molten plastic comes into contact with the

relatively cold mould surface can also be related to moulding

conditions (Tables 10 - 16 and figs. 4.14 - 4.17).

It is apparant that there is generally a gradual linear ·

decrease to zero in the thickness of skin produced along the centre

of the square moulding from the gate to the opposite end of the

moulding.

Fig 4.14 Skin Thickness Vs Plaque Thickness

155,0.6

Large gate

Plaque Thickness (mm)

Fig 4.15 Skin Thickness Vs Plaque Thickness

185, 1.0

Large gate

Plaque Thickness (mm)
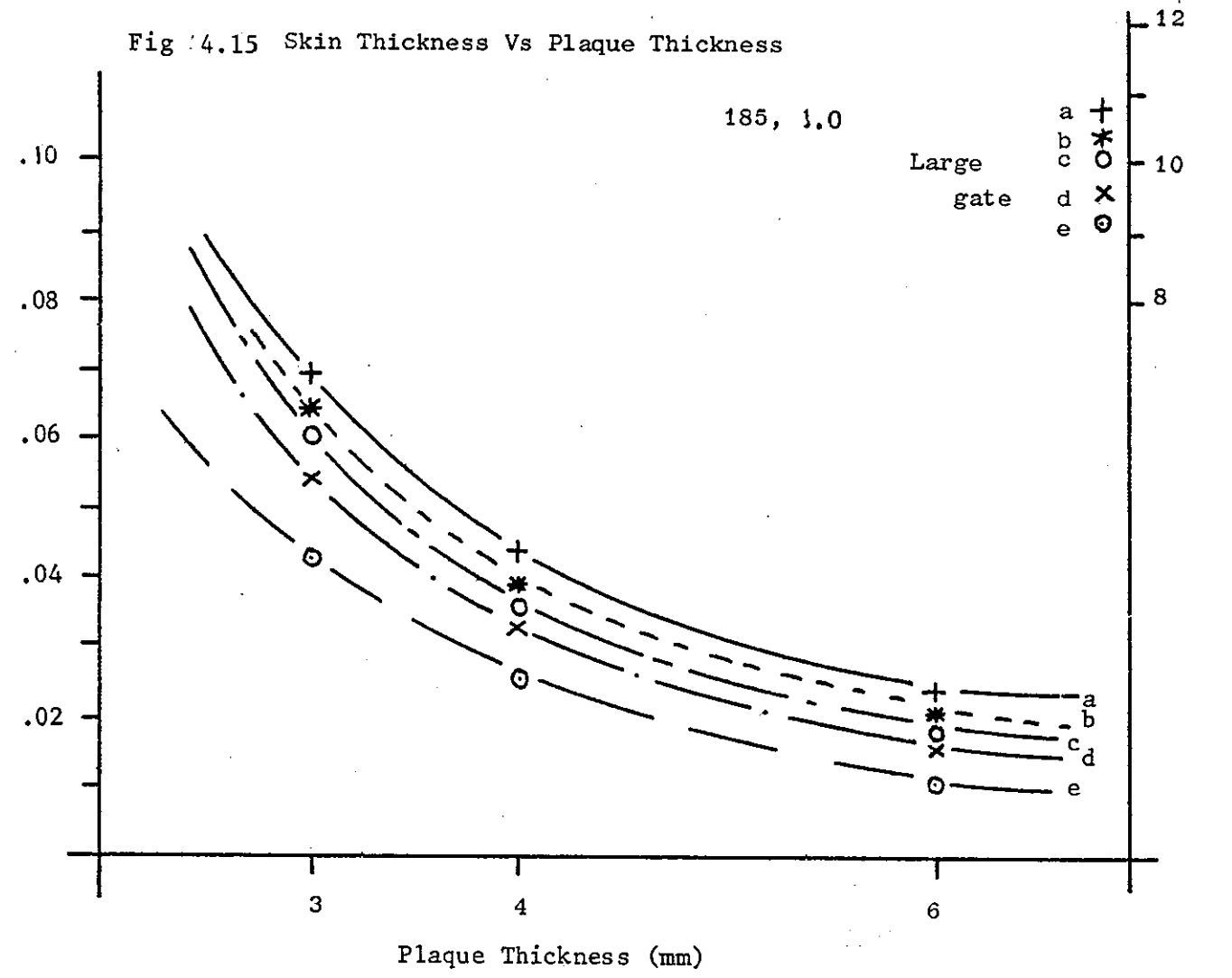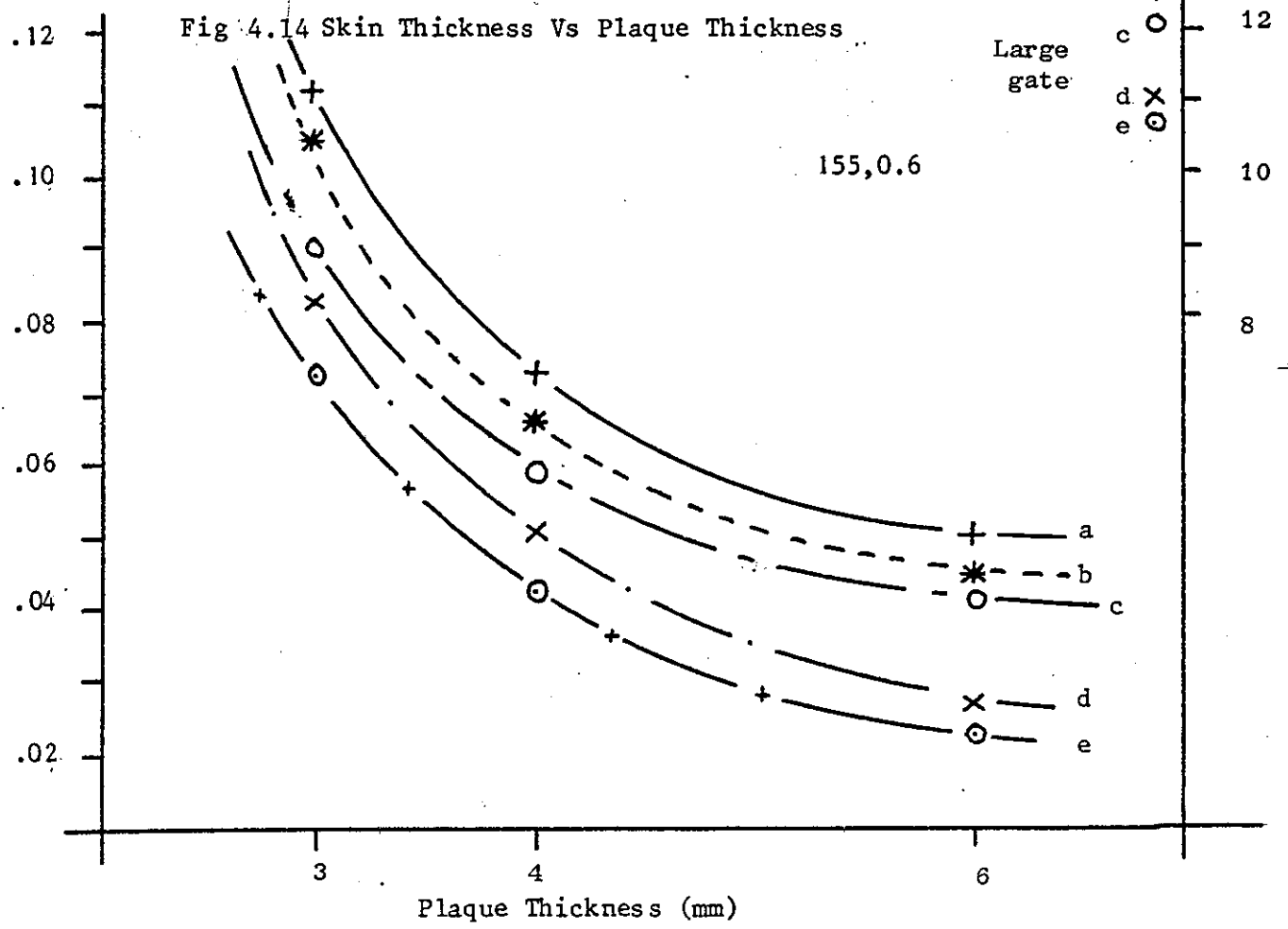
Fig 4.16   Skin Thickness Vs Mould Temperature 3mm x 125mm Plaque

Mould Temperature (^{o}c)
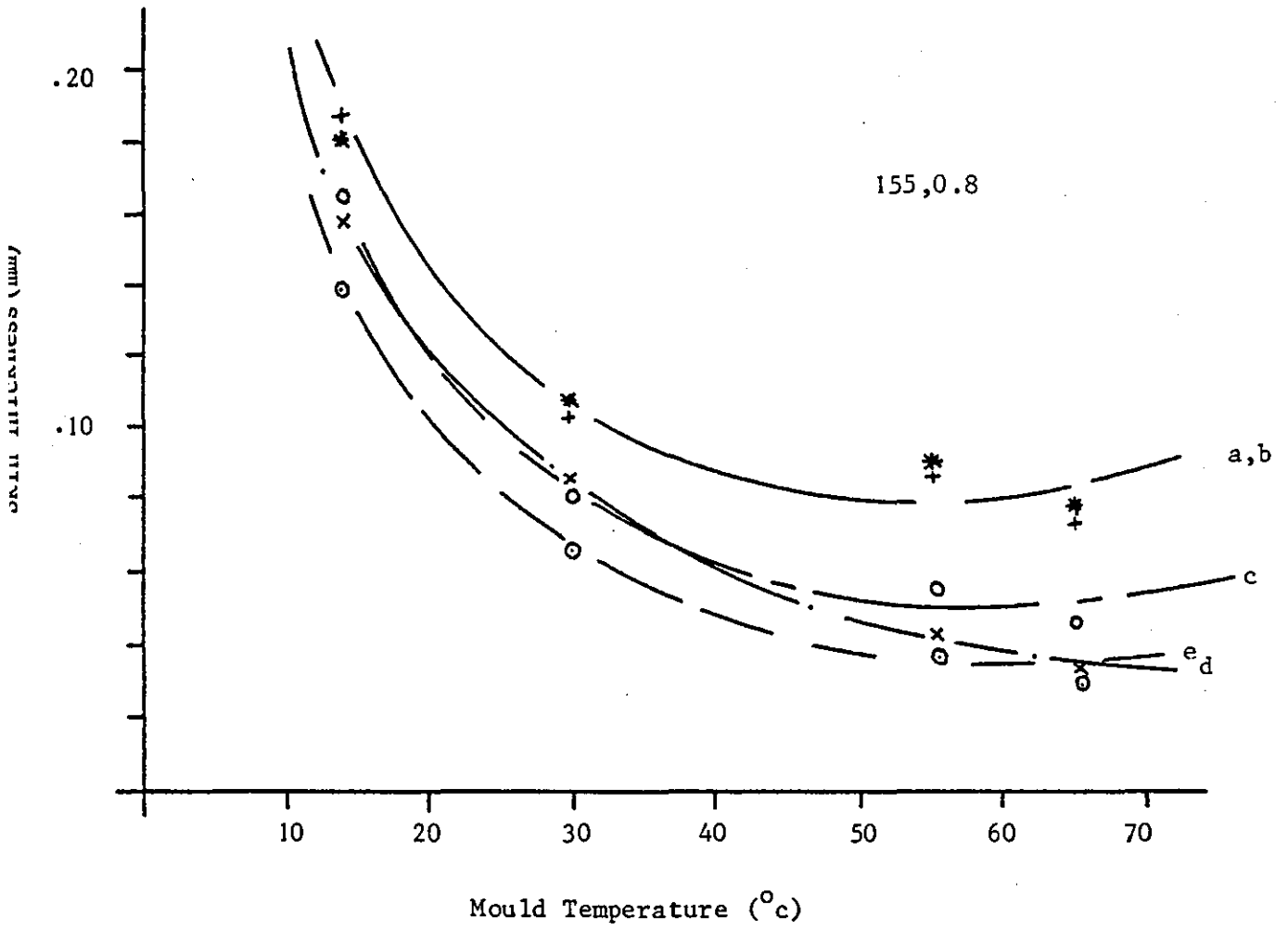
5	0	0	0	.5	1	1	1	1	1	1	0	0	.5
1	3	2	3	2	2	3	4	3	4	4	4	3	3
1	5	3	2	4	5	3	5	5	6	6	5	5	4
7	7	5	6	6	6	4	6	6	6	6	6	5	3
9	9	5	5	7	5	4	6	6	8	8	8	8	5
10	10	9	5	8	5	4	4	6	6	6	7	7	10
12	11	8	5	8	9	5	5	8	8	8	8	11	10

GATE

$\times 10^{-4}$ m

fig 4.17 Skin Thickness profile for square plaque (165, 0.8, 40)

The thickness of skin also diminishes with an increase in melt temperature for the positions examined. The skin may account for as much as one third of the total thickness of the moulding at the lower melt temperatures.

There is some confusion for the position 'b' (bottom corner) of the moulding, although positions 'd','f' and 'g' show a similar profile as the central region.

Injection rate does not seem to have a very significant effect on skin thickness at lower melt temperatures, but there is a much reduced thickness of skin at the higher melt temperatures for a higher injection speed.

An increase in mould temperature from 40°c to 60°c for the square plaque does reduce the thickness of the surface layer, especially at low melt temperatures where the temperature differential between the mould and the melt is less.

Positions 'a','f' and 'h' appear to have a similar thermal history as the thickness of skin is similar for the mould temperatures used.

A change to the rectangular plaque does not produce a linear relationship between skin thickness and plaque thickness but the amount of skin does diminish with increasing moulding thickness. The thickness of the surface layer is very much reduced compared to the thinner square plaque. An increase in melt temperature, as with the 1.6mm thick plaque leads to a reduction in skin thickness.

The injection rate seems to have a greater significance for

the thickest plaque (6mm) where the amount of skin prevailing is less and more constant over the length of the plaque than for the 3 and 4 mm thick plaques.

An enlargement of the gate, permitting easier flow, gives an increasing thickness of skin for all processing conditions used. This is especially so with plaques moulded at the highest melt temperature.

Mould temperature is one of the controlling factors in the formation of a skin. It is seen (table 16) that as the temperature difference between the melt and the mould is diminished the amount of skin formed is reduced. The skin, certainly in the case of the colder mould does not appear as distinctive as at other moulding conditions but is seen more as a layer of material whose boundary is indistinct. It therefore seems to be less of a chilling effect which forms a skin, but more of a restriction to flow. This is illustrated furthermore by the presence of flow lines on the surface of the moulding. (see mould flow diagram fig 4.18).

The thickness of skin at positions 'a' and 'b' is almost identical for all the mould temperatures used.

4.8 Mould Filling Profiles

The flow within any mould is dependant upon a number of factors, not least of which is the geometry of the gate and the cavity shape. For simple square or rectangular cavities the flow front, that is the leading edge of the melt as it proceeds through the mould, is both well documented [109,110] and of a simple shape. It was felt however that some knowledge of the flow of PVC material under the various moulding conditions used in the work might be of value to explain some of the physical test data.

The flow front was examined by arranging for the cavity to be incompletely filled ie. a short shot (at a distance of approximately 2.5 and 5.0 cm from the gate) was produced. This was achieved by decreasing the feed on the moulding machine. A typical flow front is shown in fig. 4.18, for a position 5cm from the gate. It is regarded as of the "double bow" type and is well known for these type of cavities using other moulding materials. The shape of this front does vary with moulding conditions as shown in figs 4.18, 4.19 the double bow effect is seen to be more pronounced for the square cavity than for the rectangular one.

4.8.1. Square cavity

The amount by which the front is "bowed" seems to vary with moulding conditions. Low mould temperatures produce a more pronounced bow whilst at the increased mould temperature of 60°c the flow front is more parabolic in shape.

Increasing the melt temperature has an effect on the flow front that now resembles a parabola.

Low melt temperature 40°c
    melt temperature 185°c
    injection speed (0.6)

Higher mould temperature 60°c
melt temperature 185°c
injection speed (0.6)
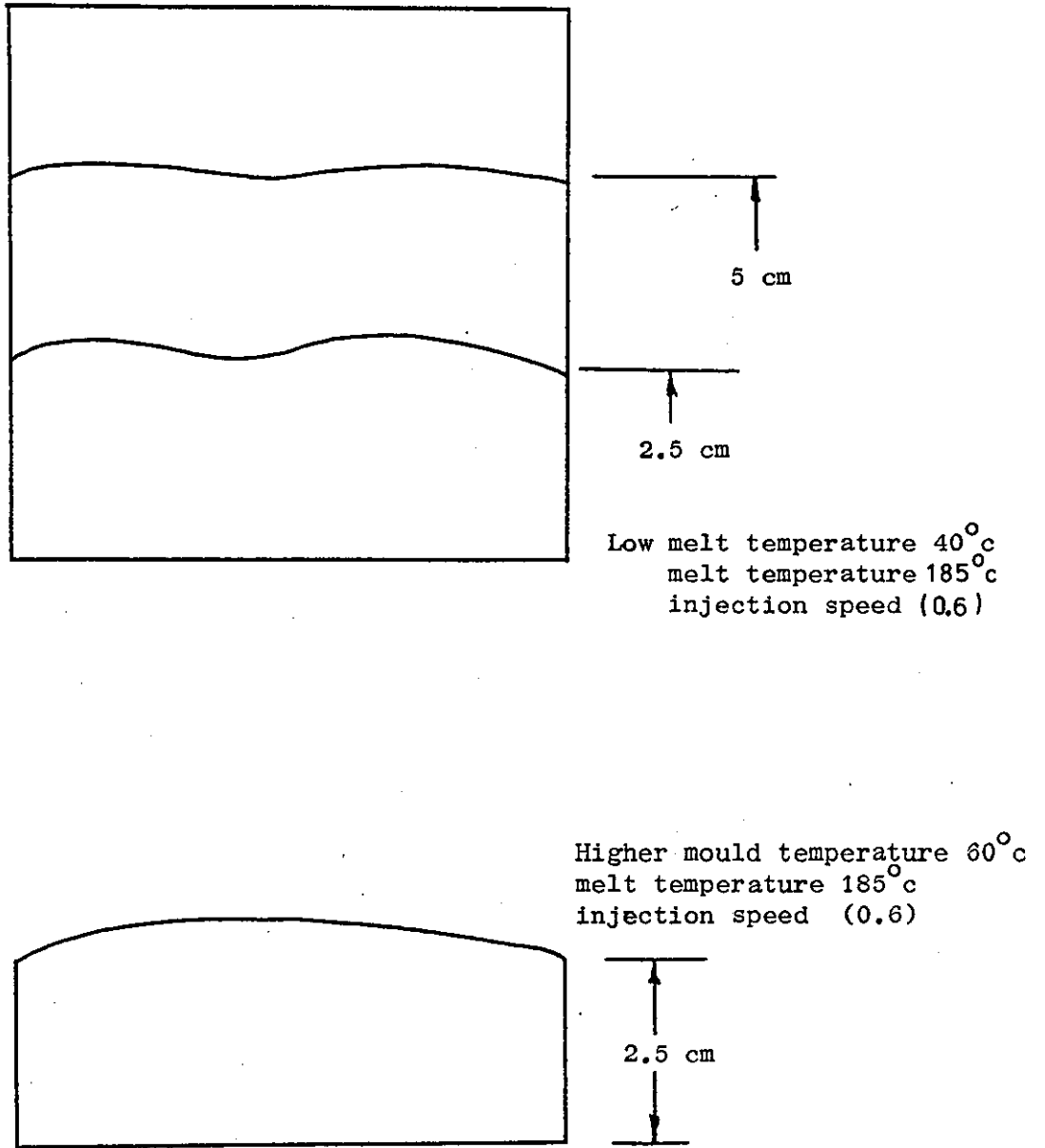
Fig. 4.18 Flow fronts for square plaque
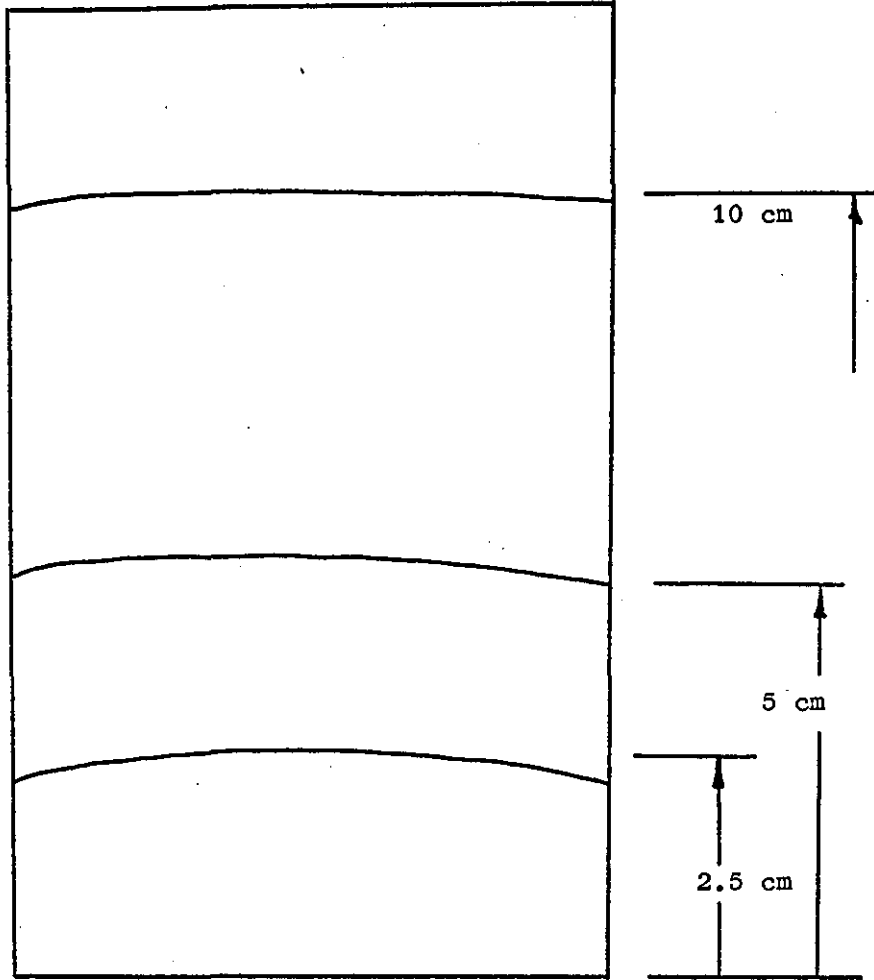
Fig.4.19 Flow fronts at various positions along plaque 3mm thick for most moulding conditions used.

Changes in injection speed produce flow fronts very similar to those for changes in melt temperature viz. higher injection speeds result in a more parabolic profile.

4.8.2. Rectangular cavity

The profiles of the flowfront in the rectangular cavities do not seem to be quite so non-linear as the square cavity ie. they appear more parabolic in shape.

The depth of the parabola 'd' ie. the distance from the extremity of the front to where it touches the mould walls, varies with processing conditions.

The colder mould temperatures give greater values of depth for the same melt temperature.

A hotter melt results in a shallower profile other conditions remaining constant.

Some observations were made for a position approximately 10cm from the gate, the profile appeared to be virtually constant for all the processing conditions used. As is seen in fig.4.19 the front is almost perpendicular to the injection direction with a curved form at the walls of the mould.

4.9   Stress Relaxation

The results from this series of tests are shown in tables 31-34 and are produced from graphs similar to fig.3.11 which are prepared from the original load - time plot as described in chapter 3.

4.9.1. Square Plaque

The internal stress of samples for all moulding conditions used is seen to vary significantly tables 31-32. What is also of

interest however is the gradient 'm' of the graphs of F versus the initial stress σ_o .

For low melt temperatures the values of m is high, whilst as melt temperature is increased the magnitude of m diminishes. This is the case whether the sample is taken from the centre of the moulding position 'x' or from position Y some distance away from the centre of the moulding.

The magnitude of internal stress diminishes to almost zero at a melt temperature of 210°c which is of the order of a 90% decrease in the level of stress at 175°c.

The speed of injection has a significant effect on internal stress. Higher stresses are found for the slower injection speed (1.0 sec) and greater values of the slope 'm'. A wider variation in stress is seen for the slower speed over the same range of melt temperatures, with a gradual decrease in stress as the melt temperature is increased.

Mould temperature is seen to have a fairly marked influence upon the level of stress produced. For the same conditions of melt temperature and injection speed the stress at a mould temperature of 40°c is approximately 25% greater than at 60°c.

The gradient 'm' is higher with the colder mould for the range of melt temperatures and injection speeds used.

4.9.2. Rectangular Plaque

Stress measurements made on the 3mm thick rectangular plaque show that when tested in the injection direction the internal stress is always negative.

A gain, the stress increases as the melt temperature is reduced and increases as the injection speed is reduced. This is the case for those samples taken centrally from the plaque and for those taken some distance from the centre.

The slope 'm' does not seem to change significantly for this set of moulding conditions of series 2.

When the temperature of the mould is altered the internal stress changes. As mould temperature is increased so the level of stress reduces substantially e.g. at (155, 0.8, 15) the stress is 50×10^3 Pa. whilst at (155, 0.8, 60) the stress has dropped to almost zero. The gradient also reduces as mould temperature is increased.

For samples tested in the transverse direction to injection table 34 there are a number of positive internal stresses at some positions in the moulding. The stress changes both with conditions of moulding and position in the plaque. The same overall effects are found as for the previous measurements viz. a decrease in stress with increasing mould and melt temperatures and an increase in injection speed; however there are substantial changes in stress with position in the plaque. There is a point some distance from the gate that has a maximum value of internal stress, this is at position 'b' for most moulding conditions.

The minimum stress is usually at the extreme point from the gate, although at the highest melt temperature and the hottest (60°c) mould temperature the minimum occurs at the gate. The highest mould temperature also creates positive internal stresses for all positions tested in the plaque.

At certain moulding conditions there appears to be no internal stress present at all for positions 'a' and 'e'. Where there is a lack of detected internal stress it is usually accompanied by positive stresses at the other positions in the moulding.

CHAPTER 5

DISCUSSION

5.1 DISCUSSION OF RESULTS

The results from this work will be discussed under two broad

headings of the effect of processing on properties and the effects

of processing on structure. An attempt will then be made to relate

both properties and structure directly to the moulding process.

5.2. The Effect Of Processing Upon Properties

The physical properties of injection mouldings are dependant

both upon the process variables produced by the machine and those

produced by the mould. The relationship between these processing

variables and the physical properties of injection mouldings has

been investigated by Machin[11] who tries to catalogue the work of

others and comes to the conclusion that because of the unsteady

state of the process and the complex interactions of the variables

contradictions occur between these published works. This shows that

these relationships have not been clearly explained even though in

some cases complex instrumentation has been used to measure melt

temperatures and pressures at various stages in the moulding process.

In this work a practical solution was sought which could be

directly applied in an industrial setting. Unlike previous workers

in this field where tensile specimens or the like are used this

work takes square and rectangular plaques and investigates the

effect of moulding for various positions within these plaques, at

edges and corners for instance. This may enable a comparison to

be made in the case of actual mouldings in a production environment.

5.2.1. Density and Skin Effects

Focusing on table 1 with results for the square plaque which shows density changes for a number of different melt temperatures one can begin to see not only the differences in density due to a change in melt temperature but also the change with position within a moulding. It might be expected that as the hottest place is assumed to be at the gate for an injection moulding a greater density would be achieved in this area. Certainly this is not the case for these set of results where the greatest density is seen to be some distance away from the gate.

Density changes occur because of differences in flow rates and cooling rates in moulding produced both by a variation in processing variables and also when passing through the mould.

When a hot melt is injected into a relatively cold mould, material is almost instantly frozen at the walls of the mould, the structure of which will be discussed later. (This has the effect of insulating the material passing over it.) The shear rate and hence the melt temperature will thus vary depending upon the thickness of this frozen layer. The thickness of the surface layer will depend upon the temperature of the melt and mould and will vary, as heat is extracted from the melt when passing through the mould.

As density is dependant upon both compaction and reorganisation of structure varying with temperature, density will vary throughout a moulding. The moulders aim is to produce a moulding whose density is constant which suggests constant temperature and pressure histories at all points in the moulding.

Referring again to table 1 the lowest melt temperature produces a plaque that is overall less dense than one at the highest melt temperature.

The reasons for this as just explained are due to thermal differences produced by the process; this has the effect of producing a multilayered structure. This is a condition which has previously been reported for other materials[1-12] but never before for PVC as far as can be determined. The density, it is suggested varies throughout the thickness because of a changing temperature and shear profile. This being the case any density that is measured is really an average of the sum of the individual densities through the thickness of the moulding.

It might be pertinent at this stage to introduce the concept of a distinct surface layer which can be measured directly. Results of the measurement of this layer are found in tables 10-16. The surface layer (skin) is formed, as suggested earlier, by the contact of the melt against the relatively cold mould wall. The relationship between processing conditions and the thickness of skin for the various positions tested in the plaques are shown in tables 10-16.

If reference is made to table 10 it can be seen that with melt temperature as the variable, the thickness of skin varies with position in the plaque. Positions at or near the gate tend to have a thicker surface skin tapering to a much thinner skin at the remote regions from the gate. It is postulated that when the hot melt enters the cavity there is an instant freeze situation so that at the gate area heat is extracted by the mould and a skin is formed. The melt can then be seen to be passing thorugh an insulated layer which is reducing the thickness of the channel

through which the melt can pass. There are two interacting
features here, one which is preventing any further heat loss from
the melt and the other which is allowing an increase in shear heat-
ing due to the decreased cross section. So that based solely on
the fact that there is initial insulation and then an increase in
shear heating causing a rise in melt temperature, one might expect
a surface skin to be thickest at the feed point and progressively
decreasing with increasing distance from it. . This is the case
for the square plaque in table 11 and for all the rectangular
plaques tested, however tables 10 and 12 show a slight deviation
from the norm. Certainly in all cases the thickest skin is found
close to the gate but not always at the point of injection. At
the slower injection speed table 11 there does appear to be a
pattern along the central region of the plaque with the greatest
amount of skin at the gate and the least at the far end. For
the faster injection speed however(tables 10 & 12) the greatest
amount of skin is found 25mm from the gate for the lower melt
temperatures. This suggests not suprisingly that the amount of
skin formed is shear sensitive. The results from both tables 10
and 12 were for a fast injection speed. It is possible that a
surface layer is formed in the same way as for the slower speed
but that as the shear rate is greater part of the skin is remelted
for some distance along the moulding.

The changes along the edges of the square plaque in skin
thickness are predictable i.e. least skin at the farthest point
from the gate, however the bottom corner fluctuates from 0.5mm to
zero. There does not appear to be any logical reason why this

should be so but it is probably concerned with the geometry and
filling pattern in the corner.

Other relationships are as might be expected i.e. the amount
of skin decreases for higher mould temperatures and higher melt
temperatures.

Skin thickness is very much reduced for the rectangular
plaques (table 13-15) due to the much larger volume of melt being
sheared creating higher melt temperatures and is only about 10% of
that of the square plaque.

A larger gate creates less shearing of the melt leading to
lower temperatures and consequently more skin.

One of the most important processing variables appears to be
mould temperature. Table 16 shows the results for mould temperatures
from 15-65°c for the 3mm thick plaque. A very cold mould produces
a substantial skin even under the much higher shear conditions of
the rectangular plaque. The same overall pattern is shown with
position as for previous results and likewise with melt temperature.

It is comforting to note that the results from this part of
the work agree with what had been previously determined at a much
earlier date by the author for the square plaque.

Previous workers have shown that a surface skin is visible for
polypropylene, and polyethylene. the presence of a skin, and that it
varies inversely with melt temperature.[5-10]

Callear and Shortall[7] confirm that the thickness of skin
decreases from the point of entry to a cavity for polytetramethylene
terephthalate.

Kantz[5] found for polypropylene that the skin thickness varied
linearly but inversely with melt temperature.

Tyiyama [147] working with polypropylene shows a decreasing
amount of skin with increasing cylinder temperature and injection
speed but shows mould temperature as having little effect.

This latter point is in contradiction in the present work, but
he interestingly shows that for an impact bar which was gated closer
to one surface than the other very similar skin thicknesses were
found. The suggestion that this should be so leads one to think
that for thin sections i.e. less than say 2.5mm. similar skin
formations would be found. However for larger moulding thicknesses
a thicker skin would be found at the surface farthest from the
gate.

In this work skin thickness determination was made from one
side only of the plaques as the rate of heat extraction from the
fixed and moving halves may have been different. There was how-
ever no noticeable difference in the thickness of skin for either
surface. For larger mouldings this difference would have to be
considered and cooling circuits adjusted to cater for the
differences in heat extraction in each half of the mould.

It can be seen therefore from the above discussion that when
considering changes in density with processing conditions that the
amount of skin needs to be taken into account.

The density of skin was found to be less than that of the bulk
of the moulding for the square plaque. This is because the
structure of the surface is less ordered than that of the central
core as it is almost instantaneously frozen and can be considered
almost amorphous.

Ty.iyama [147] showed that density increases linearly with mould

temperature, increases to a maximum and then slightly decreases,

with cylinder temperature for polypropylene.

The square plaque which consisted for some moulding conditions

of almost all skin close to the gate requires a knowledge of the

amount of skin and the thermal history at any particular point to

be established before any statement of density may be made.

Where there is a greater amount of skin it is expected that

the overall density of the section tested would be less than a

section with less skin. This argument is sound if taken in

isolation but the effect of pressure and changes in structure need

to be considered and will be later in this chapter. It has been

shown [147] that density increases linearly with increasing injection

pressure for polypropylene. Although injection pressure was not

altered in this work the pressure effects must change with melt

conditions and the distance from the gate. There is a pressure

drop along the cavity and assuming the gate remains open for long

enough packing will occur in the vicinity of the gate leading to

higher densities in this region. It was certainly found in this

work that density in the main decreased with remoteness from the

gate.

Other workers [155] have shown for different types of mouldings

that density varies not only with the distance from the gate but

with the type of moulding. Figure 5.1 shows density variations

for an acetal copolymer. Although the density is shown to vary

along the length of a moulding it does not vary significantly for

the first 150mm in the case of the tub and is obviously different
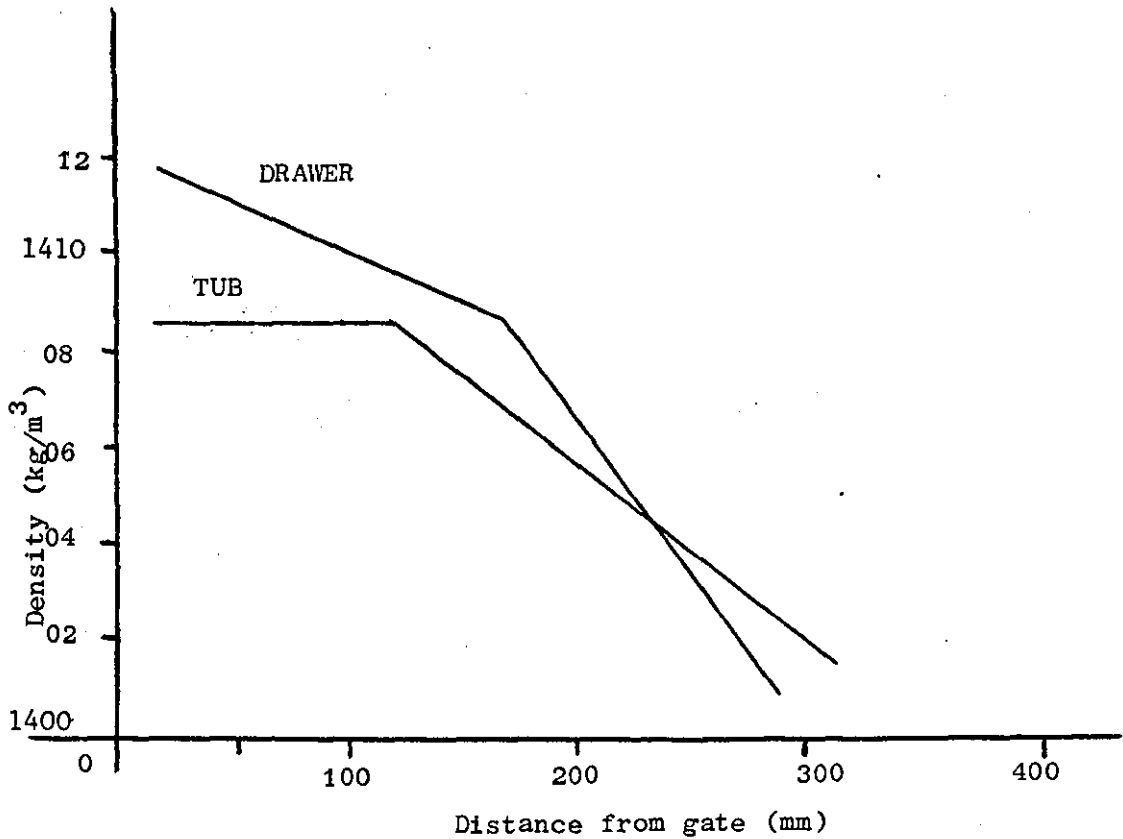
Fig. 5.1. Density variation as a function of distance from the gate (Serle and Lantos[155])

for the drawer moulding. This shows that it is not possible to categorically state that density varies with distance from the gate for all mould configurations and processing conditions. In the present work where simple mould shapes were used it should be easier to detect trends than for the more complex mouldings found in practise. If this is the case then the density pattern for non basic mouldings must be extremely complex.

One moulding was tested at a large number of positions to detect density changes and the overall pattern is complex as shown in fig. 4.7 .. In particular the area of the plaque around the corners closest to the gate are highest in density. There does not appear to be very much order in the changes in density with position in the moulding. This fact is strange in that one might

expect some symmetry within the moulding so that the density at the top left in the plaque would be the same as that at the top right, this is not the case.

The reasons for this complicated pattern of density is I think, a combination of factors. Firstly as already seen, the variation in skin thickness where the density of skin has been found to be significantly lower than that of the core. For this particular plaque the density of the skin at the gate is shown to be 13667 kg/m^3 which is substantially less than the density of the total thickness of sample at the gate of 1368·9kg/m^3. Thus the greater the amount of skin the lower the density of a sample.

Secondly, density increases with increasing pressure for injection moulding due to increases in shear heating resulting in a lower viscosity melt and greater compaction. It might be reasonable to assume that compaction into the bottom corners would be greater than that at the upper corners due to temperature variations i.e. material would be much hotter at the gate. This appears to be so with this plaque.

Returning to the square plaques tested to produce tables 1-4, density tends to be more uniform for the positions tested at the higher melt temperatures presumably because a more uniform heating pattern exists.

An increase in shear rate increases density due to an increase in melt temperature, greater compaction and a longer time for structural reordering .

There is some confusion however for a direct comparison between mould temperatures i.e. tables 1 and 2, and tables 3 and 4

where for the lower melt temperature of 175°c there is very little difference in density (tables 3&4) For the slightly higher temperature of 195°c the density is higher for the 40°c mould temperature and at 210°c the highest densities are found in the hotter mould. There is no clear reason for this anomaly at the middle melt temperature tested, but Henke[3] et al showed this to be the case for polyethylene over a range of mould temperature and suggested that this trend was due to imprecise measurements. Although, as will be shown later the enthalpy changes were different in the present case.

If the density variations presented in table 1, are carefully studied there is only an overall trend for these processing conditions (i.e. an increase in density with increasing melt temperature) as the individual positional changes are not very clear. This result appears to be freak for this set of processing conditions only.

Changes in density with injection rate (time) were found by some workers[147] to be unclear. It is possible that rather than the minimum condition shown in table 5, that the results for the injection times of 0.6 and 0.8 are the same within experimental error. This would suggest an increase in density with a greater amount of shear heating which is understandable.

The rectangular plaques show much greater predictability in that the thicker the plaque the greater the density for all moulding conditions. This is because of a slower overall cooling rate and an increase in shear heating as a result of greater volumes of material being injected. It has been confirmed by Steinbuch[156]

working with nylon-6.He showed that density increased from 1094 kg/m^3 at 20°c to 1122 kg/m^3 at 100°c.

A larger gate which reduces the amount of shear heating giving a cooler melt and should therefore lead to lower densities. However a larger gate will remain open for longer than a smaller one and will thus allow more material to be fed in and compacted before the gate seals. This is apparantly what is happening in tables 6-8 where the density of the 3mm thick plaques with the larger gate are higher than with a smaller gate.

As cavity thickness is increased the amount of shear heating is reduced for the velocity of the melt is reduced. Consequently the shear rates of corresponding radial positions are lower for a considerable part of the time whilst the cavity is filling than in the thinner cavities. This argument however assumes that the gate size is the same. Consider the case, where for the same gate size the cavity thickness is doubled. In this instance the amount of shear heating will be greatest for the thinner cavity giving a hotter melt and greater compaction. The material entering the thicker cavity will not receive as much shear heat but will retain its heat for longer as it is a larger mass of material and will allow greater relaxation, and therefore lead to higher densities. Although the skin thickness will be greater for the thinner mould-ing this is offset by the greater amount of time for re-ordering for the thicker moulding. It is possible, therefore that the overall density of these two plaques are very similar.

If, not only the cavity thickness is changed but the gate size (depth) is altered the problem is doubly complex. From studies of

flow length versus thickness of gate Backofen [157] showed that for
polycarbonate flow length increased proportionately as the thick-
ness of gate increased. This is because the resistance to flow
has been altered and the pressure drop at the gate is now less.
In the present work the larger the gate size the greater the time
that pressure is maintained on the cavity before the gate freezes.
As the gate depth is given as 0.9 x thickness of moulding there
exists a linear relationship between the pressure exerted in the
cavity the gate depth and therefore the thickness of moulding.
This is really saying that the shear condition for each thickness
is linearly related. There does appear to be almost a linear
relationship of density difference and cavity thickness.

There is a corresponding increase in density with increasing
melt temperature which would be expected as with the thinner
plaques.

The density gradient along the length of the moulding for the
rectangular plaques show a slight increase   25mm from the gate
and then a progressive decrease to the remotest point from the
gate. This is indeed similar to Bakerdjian[146] who found a maximum to
exist some distance along from the gate tailing off to a minimum
at the farthest point from the gate for polyethylene. It is
thought to be because of temperature variations as measured along
the length of the moulding.

Mould temperature affects density in different ways depending
upon the material and the workers involved. Tyiyama[147] suggests
that density increases linearly as mould temperature increases

for polypropylene. Henke[3] et al obtains a peaking effect at about

55°c for polypropylene. In this work a trough is found (fig 4.3)

at about 40°c-50°c depending upon the position in the plaque. Higher

values of density for the coldest mould used,than for other temperatures

up to 50°c seem to contradict all that has been said previously. There

is a substantial increase in skin thickness for the coldest mould

temperature used (15°c). It is possible that this layer was much

thicker and acted as an insulating layer. However, with the reduced

channel thickness, increases in temperature occurred due to shearing

of material. With the increase in temperature, some of the frozen

skin re-melted thus reducing the insulating effect and the eventual

equilibrium condition achieved.

5.2.2. Shrinkage Effects Produced by Changes in Processing Conditions

The physical properties of injection moulded items are affected

both by temperature and velocity domains during the moulding cycle

and vary within the item. Whilst filling, layers of the polymer

which are flowing at different velocities through the thickness of

the moulding, generate both shear and elongational stresses and

cause the polymer chains to be oriented in the same direction as

this stress. Orientation is changing through the thickness due to

thermal gradients and leads to anisotropic properties.

Several studies[102,117-120] of the effect of orientation on the

properties of injection mouldings have been made. Birefringence

measurement is a good method of determining the degree of orientation.

That is, when examined under plane polarised white light an

injection moulded item shows a repeating series of coloured fringes,

each colour of which indicates a fixed amount of molecular

orientation. The birefringence can be calculated[122] and gives a

measure of orientation. This procedure was attempted for this work but was abandoned due to the very low and very similar levels of birefringence measured. Reversion was used to give an indication of frozen in stresses as a result of differing amounts of orientation.

Orientation is usually thought to decrease as melt temperature, mould temperature and cavity thickness increases. It increases as gate size increases[122]. Tables 17-20 show that for the square plaque orientation (% shrinkage) decreases with increasing melt and mould temperature.

Shrinkage decreases with an increase in plaque thickness (tables 22-24) and increases with a large gate size.

The amount of shrinkage is also reduced as the mould temperature is increased.

Taking each of these observations in turn, Ballman and Toor[122] have shown that orientation of a rectangular bar decreases with cylinder temperature for polystyrene and this is confirmed for PVC by Lebedev[121]. Orientation has been shown to be synonomous with shrinkage[115-124]. Orientation has been shown by these workers to vary through the thickness of a moulding with little or no orientation at the surface, increasing to a maximum just below the surface and decreasing to a minimum as the centre of the moulding is approached. Figure 5.2. shows this variation, the dotted line shows the effect of orientation and the solid line the combined effect of orientation and relaxation. The difference between the two is the loss of orientation due to relaxation.
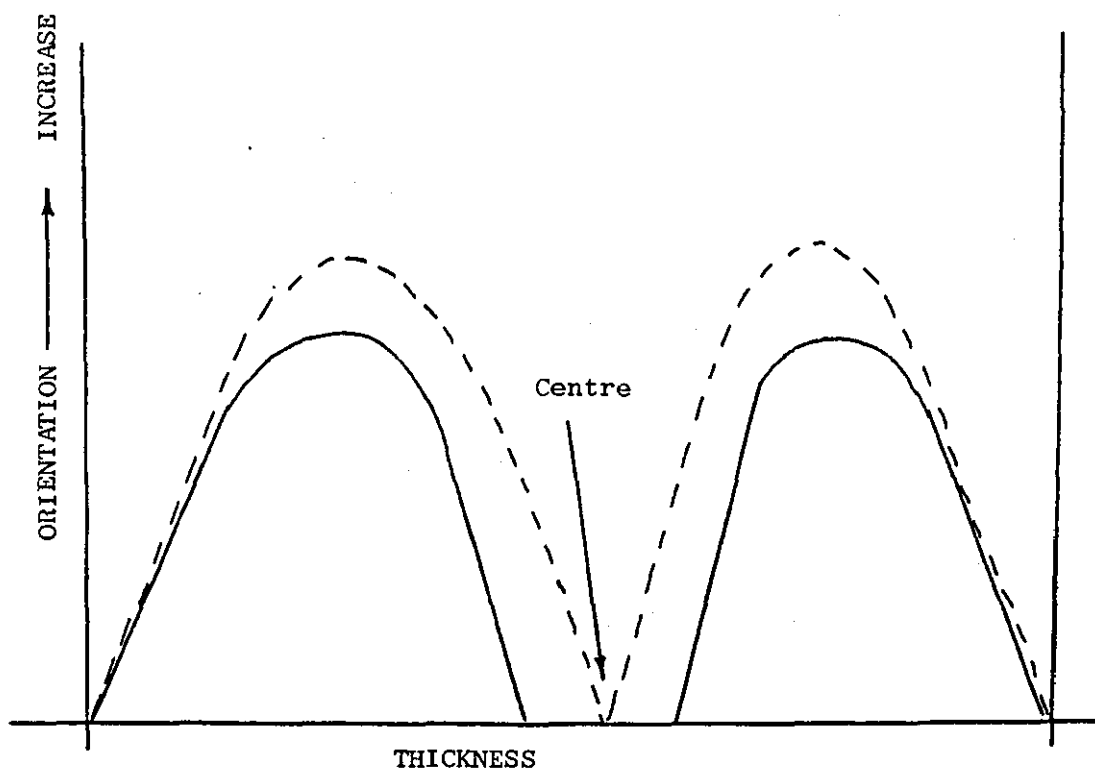
Orientation profile across the thickness of a
polystyrene moulding [122].

FIG. 5.2

Ballman and Toor[122] suggest that the orientation profile is

similar to the temperature profile exhibited in the moulding. So

that the hotter material along the centreline of the channel will

relax most and completely erase all orientation.

Certainly in the present work X-ray evidence will be shown

later that suggests there is little   orientation at the centre

of the moulding. There was not quite the same effect in the

present work of an absence of orientation in the skin. Microtomed

sections of skin were heated and shrinkage seen purely as an

observational exercise to determine whether there was   indeed

orientation present. This was confirmed subsequently by X-ray analysis where a difference in traces was shown for samples taken parallel to and at right angles to the polymer flow direction.

If one considers polymer melt flowing in a flat plaque mould the cavity walls are at a temperature less than the melting point of the polymer and as previously observed the material in contact with the walls freezes. The pressure at the cavity entrance is highest and decreases to zero at the flow front. As the shear stress causing orientation is related to the pressure gradient it is suggested that the orientation is a maximum at the cavity entrance and decreases to a minimum at the flow front. The velocity at the wall is obviously zero so that there must be flow away from the centre of flow to fill the cavity. This material is unoriented and freezes almost immediately leaving a layer of virtually unoriented material at the surface. Further into the cavity thickness other material cools less quickly and is able to be sheared before it freezes giving rise to orientation. As the shear stress is a minimum at the centre, orientation decreases to a minimum. This is in combination with the thermal effects of the process whereby material remains hottest for longer at the centre and allows greater relaxation.

As has already been seen skin thickness is greatest some distance from the cavity entrance and likewise shrinkage is found to be greatest at an identical position. This suggests that there is orientation in the skin even though at the very outer edge of the moulding for a minute thickness there is indeed no orientation.

It is not certain what is happening to the shear stress across the section. In an isothermal case there would be a maximum shear

stress at the walls of the cavity. As the moulding process is non-isothermal shear stress will vary from the inner surface of the skin to the centre of the moulding in the normal way. Butwhat is happening across the skin is unclear. There is obviously some shear stress in this region but it is likely to have a different gradient than in the rest of the thickness.

So the effect of an increase in melt temperature on orientation and hence shrinkage is to reduce viscosity and therefore shear stress and orientation. There is also a greater amount of relaxation possible at higher melt temperatures. However there is also the point to consider that there is a greater pressure transmission with a reduced viscosity during filling which will increase shear rate and hence orientation. It is felt that the relaxation caused by hotter material will make the last comment void.

The effect of an increase in shear rate giving less shrinkage can be explained as above because of greater relaxation in the mould at the higher generated temperatures.

There is an anomaly for the square plaque at the corner position nearest the gate where there is zero shrinkage at low melt temperatures and a greater amount as melt temperature is increased. This is the case for all processing conditions used for the square plaque and suggests this is because of the flow in this area and possibly greater packing, as the density is quite often higher in this area than those adjacent to it (tables 1-4).

Much less shrinkage is found for the thicker rectangular plaques due to the possibly higher temperatures prevailing for longer in a larger mass of material.

The shrinkage at different positions along the rectangular plaques suggests that material is hottest at the gate position giving less shrinkage than at positions further along, until the end of the plaque is reached where shrinkage decreases markedly due to much colder material. This is confirmed by density and skin thickness measurements where there is little skin and a lower density at the remotest point from the gate.

A larger gate allows a greater amount of time for pressure to be applied to the cavity before the gate seals. Thus less relaxation could occur for the same cycle times and a greater density will prevail (tables 6-8).

The above arguments show I think, that shrinkage can be explained by two effects firstly the molecular orientation due to shear forces during injection. Secondly relaxation in the mould after filling has ceased.

It is further suggested that although growth of the surface skin will be greatest at the gate the amount of skin will be least due to new hot material being fed to the cavity. Therefore there should exist a skin profile with a maximum some distance from the cavity entrance decreasing to a minimum towards the end of the cavity. This did in fact appear to be the case for the square plaque where skin thicknesses were found to be greatest some distance (2.5mm) from the gate. This was not the case for rectangular plaques probably due to the larger mass of material being sheared.

Finally fig 5.3 shows a definite relationship between skin thickness and percentage shrinkage ie. as the amount of skin increases so the percentage shrinkage increases.
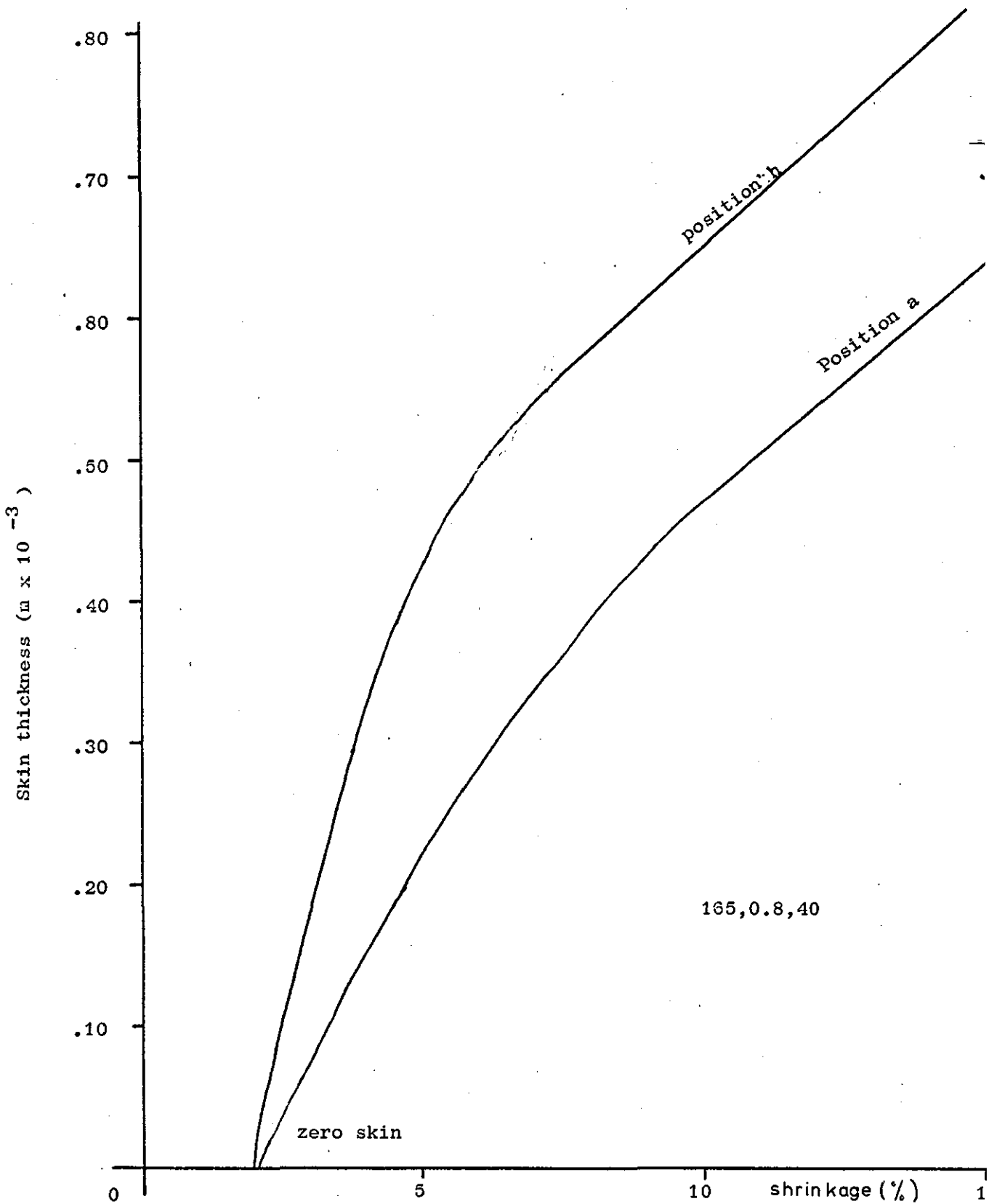
Fig 5.3 Skin thickness Vs % shrinkage square plaque.

5.3 The Effect of Processing upon Structure

5.3.1. Structural Changes Detected by Differential Thermal Analysis

As with the other tests in this work thermal measurements were made at eight positions from each plaque to determine changes in structure.

A typical thermogram is shown in fig 3.6 it is seen that there is a baseline shift at approximately 80°c followed by an exothermic peak and then finally a broad endothermic peak after which degradation occurs. The baseline shift has been widely attributed to the glass transition temperature, for the present work there was no noticeable difference in Tg for any of the moulding conditions used. It is thought that differences in Tg do occur but these are too small to be recorded by the instrument with any great accuracy.

The small exothermic peak is thought to be as a consequence of crystallisation and is confirmed by a number of workers including Illers[30] and Gray[38]. The size of this peak varied with moulding conditions and the relative position in the plaque. Its peak temperature however remained fairly constant at approximately 115°c. The hotter conditions of moulding ie. greatest shear and thermal conditions gave the smallest peaks, whilst those conditions that resulted in the material being cooled much more rapidly gave substantially larger peaks. This is due to the time the material is kept above room temperature as well as the thermal conditions used. This agrees broadly with Gray[38] who showed that for longer annealing times the exothermic peak disappeared altogether. The form of the trace of this work was similar to Gray's shortest annealing times.

The final broad peak is attributed to the melting of crystallites formed during moulding.

One of the major difficulties between the current work and that of most previous workers is that the specimens used are taken from injection mouldings and not compression moulded items. This has the effect of not only introducing a different temperature profile through the thickness of the moulding but also of creating a stressed moulding. It is therefore not so easy to relate the thermal history of the specimen with what is being detected by the thermal analysis equipment. The specimen as has been shown is composed of a number of distinct layers produced by the moulding process and any results from D.T.A. show an average for the complete thickness of moulding. This means therefore that where enthalpy changes are determined and found to be identical for two different moulding conditions it does not mean that the structure through the thickness of the moulding is the same only that the average is the same.

Tables 26-29 show the enthalpy change for the square plaque and broadly indicate an increase for all moulding conditions of the change in enthalpy with melt temperature.

An increase in the enthalpy change for mouldings at a higher mould temperature is also shown.

Samples were kept for a short time (approximately 30 minutes) at room temperature before being placed into a freezing cabinet.

It has been shown [30] that structural changes can occur very rapidly particulary above Tg, but also below. This obviously produces a change in the crystalline portion of the structure for a change in the amorphous content at temperatures below Tg. However these changes are thought to be minimal at this temperature (20°c).

So that the changes in enthalpy for the different moulding conditions of the tables 26-29 are in the main changes exhibited in the crystalline content of the structure of the material. All of the results for this part of the work can be explained by changes in shear heating, moulding temperature and particularly mould temperature. It is suggested that the changes in the crystalline content remain approximately the same for all changes in the melt temperature and injection rate but the amount observed is influenced most strongly by mould temperature. Obviously the hottest part of the moulding will be at the centre, and this central zone varies considerably with mould temperature viz. changes in skin thickness shown previously. Therefore as the thickness of the central zone is changing so will the endothermic peak size and consequently the enthalpy value.

The results in table 30 confirm this hypothesis and show that the enthalpy change is significantly greater for higher mould temperatures. The achievement of a more equilibrium structure by raising the mould temperature is confirmed by a rise in density of specimens. This result is confirmed by amongst others Savelev et al [158].

Differences with position in the plaques of enthalpy change must be considered from both a temperature point of view ie. specimens taken at or near the gate are hottest for longer as well as the amount

of skin present. It has previously been suggested (5.2.1) that some
remelting of the skin initially formed, may occur, this causes
further complications when analysing the structure. The final
condition of the moulding is being considered however and as such
deeper explanations are thought to be too speculative.

5.3.2. Internal Stresses in Mouldings

The amount of internal stress present in a moulding determines
a number of crucial properties including heat distortion, stress
cracking, impact strength etc.[134-140]. It is suggested that the
largest stress present in injection moulding is formed by orientation
of polymer chains during processing. As the molten polymer flows
through the mould a velocity front occurs (fig1.4). The inner core
is flowing at a greater velocity as it is hotter than the colder
outer layers. The polymer chains are stretched because of the shearing
action occurring between the different layers of the polymer. The
greater the differences in the velocity between layers the greater
is the shear rate and consequently the higher the orientation. The
degree of orientation will obviously be influenced greatly by melt
temperature as this changes the melt viscosity and hence the velocity
profile. The lower the melt temperature the greater the viscosity
and the corresponding stressing.

The amount of orientation varies through the thickness as
will be shown later by X-ray analysis. Thus there is a velocity
gradient formed by the changing temperature and velocity of the melt
through the thickness of a moulding. As the material enters the cavity
the hot central core moves out to the relatively cold walls of the
mould and freezes. The very outer edge of the material is orientation free

as it freezes almost instantaneously and is not subjected to

shearing forces. The rate of cooling slows as the centre is

approached. As the viscosity of the melt increases whilst flow

is still continuing and material is hottest at the centre of the

moulding greater relaxation can occur as the centre is reached.

This relaxation ceases when injection is completed and the material

cools.

So it would be expected that the internal stresses detected

in this work would vary with processing conditions this is shown

to be the case in tables 31-34. where stress is measured both in

the injection direction and perpendicular to it. A stress gradient

is formed along the length of a moulding as well as through its

thickness. The greatest stress will be encountered at or near

the gate especially if packing is excessive. The change in stress

with melt temperature is fairly self explanatory. As the melt

temperature increases, greater relaxation can occur both along the

moulding and through its thickness. So and Broutman[140] have shown

that the stress varies through the thickness of a moulding by

removing successive layers, a technique which may be suspect if not

performed correctly. They also show that the stress is compressive

in the outer layers and tensile at the centre. This finding was

confirmed in the shrinkage measurements of this work. Kubat and

Rigdahl[139] show that for the total thickness of moulding internal

stress as measured in the injection direction could be positive or

negative depending upon both moulding conditions and material.

Furthermore the level of stress could be reduced to zero by

annealing.

In this work negative stresses were encountered for almost

all the results except for those at the higher mould temperatures.

This is because for the lower mould temperature conditions there is

produced a greater amount of stressed layers.

It has been suggested by others[1-11], and confirmed in this work

that the moulding thickness is made up of a number of layers of

differing structure. This is particularly noticeable for polypropylene

and other crystalline materials.
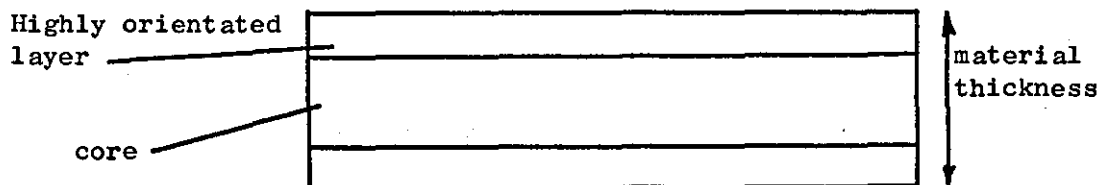
fig. 5.4 Layer model

Figure 5.4 shows the two regions that are suggested by this

work. An outer highly oriented skin and a second zone that is

unoriented. As mentioned earlier in this chapter the skin was

shown to be highly oriented by shrinkage measurements. The internal

stress as determined will therefore vary with the amounts of skin

and this appears to be the case. The greatest stresses are formed

at the lowest melt temperatures which have the greatest amounts of

skin.

Injection rate, as it changes the shear and consequently the

temperature of the melt also alters the internal stress level. The

higher shear condition reflecting the lower values of stress

because of the argument in the preceding paragraph.

The variation in internal stress of samples along the centre

line of the plaque and those tested of samples taken some distance

away show that those along the centre line have a greater stress

value. This is because of the pressure distribution and thermal

differences. Internal stress has been shown to be greater along

the centre line[138] than away from centre. This was so in this

work where the stress value to the side of centre was on average

12% lower than that measured along the centre line.

In the experimental section the analysis used was based upon

a power law relationship for the final part of the stress relaxation

curve as it is linear over the time interval chosen. This approach

does not of course take into account the initial portion of the

curve that would appear to obey an exponential relationship. A more

correct approach may be a combination of the two laws, however for

this work a good understanding of the way internal stress varies

with processing conditions has been achieved even though the values

may not be absolute.

Internal stress as measured in the transverse to injection

direction was very low this has been experienced by other workers[138]

too. Values approximately 10% of those experienced in the injection

direction. There was a variation with processing conditions, where

the lower mould and melt temperatures gave the greatest values.

A gradual increase in mould temperature altered the stress value

from negative to positive ie. from compressive to tensile. This is

thought to be because of the almost negligible amount of stressed skin and the greater amount of relaxation possible.

There has been some speculation using stretched polyethylene fibres,[160] that tie molecules relax and lose their orientation when annealed and also their internal stress. It is possible therefore that as the bulk of oriented chains lie in the injection direction, that what is being experienced in this work is a relaxation of the polymer chains. It has been said however that in order for this relaxation to occur temperatures in excess of 60°c must be experienced. For the present work relaxation of tie molecules would only be expected of the inner core and as most stress is found in the skin even in the transverse direction it is more likely to be because of a reduction in the amount of skin than any molecular activity.

The exponent 'm' values that were taken are intended to reflect the changing structural condition of the sample of a plaque. A high 'm' value indicates a high stress level whilst a decrease in 'm' suggests a more annealed type structure. Certainly the exponent varied in this way , with the corresponding level of internal stress detected. Values of 'm' were found to be similar to those for low density polyethylene[138]. Whilst this exponent did follow a trend it is not thought to be of too much use as its actual value besides being dimensionless only indicates a very broad assessment of structure. It has not been established qualitively the difference between say m=10 and m=12.

5.3.3. Flow in the Mould

The flow of material into the cavity was influenced by temperature and speed of injection. Figures 4.18 and 4.19 show the flow fronts produced in both the square and rectangular plaques. It can be seen that for the square plaque the flow front shape is of the double bow type for low temperature conditions of melt and mould. It is created by material freezing at the walls of the mould and consequently is related to the velocity profile. The slow moving material being towards the edges of the mould. The effect has been shown by numerous workers[98-110].

For the square plaque material entering the cavity through the edge gate initially in an almost radial fashion is hindered both on the faces of the mould and at the edges by the freezing action as mentioned above. The shape of the front can be explained in terms of the amount of material that is allowed to freeze on the mould walls. For low shear conditions the temperature of the melt is low,thus the growth of the stationary layer is allowed to progress. The temperature reduces along the cavity of the bulk material and the time for the outside layer to form is longer than at higher shear rates. The velocity profiles are not very flat and shearing occurs mainly in the region where temperature is low and viscosity consequently high. The required pressure to fill is high because of the restricting channel through which the molten polymer may flow due to the large amount of skin. It is only in the region close to the flow front where the temperature is hottest and skin formation has not had time to develop that the pressure gradient is lower for low injection rates.

At a high shear rate the maximum temperature of the melt is closer to the wall. The high temperature prevents skin formation and gives an increase in bulk temperature along the mould. This then leads to a decrease in viscosity reducing the pressure profile and thus the flat velocity profile is obtained.

This section of the work was purely observational but it was hoped that some useful conclusions were drawn based upon what is thought to be happening in the cavity during filling.

5.3.4. Structural Changes Detected from Ion Etching

Despite its importance as a commercial material little work with PVC has been conducted into the relationship of morphology to processing conditions. Several means are possible for evaluating structure in polymers including X-ray techniques, freeze fracture and ion etching. This last technique was attempted for this study, and used equipment which hitherto had been used for work with thermo-set materials. The results produced were by no means conclusive and it is believed that further work with this technique is needed before any meaningful conclusions may be drawn as to the relationship of processing conditions to morphology.

However, some of the photographs from the electron microscope do show interesting features. It is well known that over etching results in the characteristic 'spike' array (fig 4.1). This was experienced especially at high power and long times of exposure to the beam (greater than 5 minutes) and is caused by melting of the surface being bombarded. What was interesting to note however was that the spiking effect was different for different conditions of moulding. This indicated that there are differences in the surface

structure produced by the moulding process. It has been suggested[144]

that the surface artefacts produced by etching are not caused by

the 'etching' process but by a restructuring of partially etched

material. Restructuring should be prevented by the presence of tie

molecules which are present in the amorphous phase. However etching

should preferentially etch the amorphous phase thus fracturing

these tie molecules and relaxation of the surface will occur. This

it is believed is what happened in some of the samples tested.

Figure 4.1 shows what could be described as a wavelike appearance.

It is postulated that is is formed by the relaxation of oriented

material and the 'rows' are shown to be at right angles to the

injection direction which supports this theory.

The spiky artefacts also appear to be directional and arranged

in rows and where the beam has eroded the rows into 'spikes'.

The most interesting photographs taken, showed what appeared

to be platelike entities. Bonart[70] shows these lamellae for ion

etched PVC also. There are a number of possibilities that may

exist for the morphology of low crystalline polymers; there may be

very small perfect crystallites in an amorphous matrix, a larger

number of imperfect crystallites or an irregular defective lamella

structure. If the ion etching technique follows the theory behind

it, that amorphous regions should be etched preferentially to any

crystalline portion then what we should see is small clumps of

material representing something of the order of 7% of the surface

in view. This was not the case as is seen in the sketches and it

is suspected that the etching conditions were not satisfactory to

produce the desired result.

Returning briefly to the lamellar structure exposed by etching it is possible that this is not really a structural arrangement, but more of a flow phenomena as the size of the lamellae is much larger than would be expected ie. in the 100Å range and were approximately 1μ in diameter.

The results therefore were disappointing but.it is still felt that the technique has some potential and might subsequently be of use in the future.

5.3.5. X-Ray Analysis

Structure was also examined by X-ray analysis and the crystallite size measurements derived from the diffraction traces are shown in table 35. It can be seen that the size of the crystallites was very small 2.4 - 5.2nm. depending upon moulding conditions and the position in the plaque. Results are only shown for the rectangular plaque as the diffraction traces were identical for the square plaque at all processing conditions. This it may be assumed means that the size difference of any crystalline regions is so small as to be undetected by X-ray diffraction.

The size of crystallite is seen to increase markedly with mould temperatures from 2.4nm at 15°c to 4.4nm at 65°c for the same melt conditions. This is significant because the measurements were made from reflections of the centre of the moulding where mould temperature as such does not seem to play a very important role in structure formation. It is presumably associated with the greater amount of heat extraction at the colder mould temperatures.

Traces were taken from the centre of the moulding because of orientation effects at the surface. It was shown that the traces were substantially different for samples taken in the direction of flow of material in the mould to those taken perpendicular to the flow. It was not the case at the centre of the moulding where orientation effects were found to be negligible.

The mean size was, on the whole smaller than that reported by other workers [38,43], who show crystallite sizes in the 5.0-6.0nm range. Most of these results have been for compression moulded samples of PVC where the shearing forces and the temperatures reached would not give complete breakdown of the PVC particles nor give so refined a structure.

It would seem therefore that the structure at the centre of the moulding is composed of very small crystallites in the overall amorphous matrix. The central portion for the rectangular plaque was, as was shown earlier almost the whole thickness of the plaque. This was one reason why the density of this plaque was greater than that of the square plaque of a lower thickness. The other major reason was of course the increased thickness of skin for the square plaque which was shown to be of a much lower density than the central core.

The X-ray determined method for evaluating crystallite size gives only a mean value. The D.T.A. evidence reported earlier showed that there was a very considerable range of crystallite size by the broad melting endotherm.

The size of crystallites has been shown[46] to vary with heat treatment eg. the mean size was increased from 17nm for an

original sample of commercial PVC to 20 and 26nm after heating

at 145°and 175°c respectively. Gray[38] showed that the sizes of

crystallites remained fairly constant over the range of heat

treatments used 40°c to 160°c. He did show however that the

crystallinity developed during heat treatment increased at

annealing temperatures in excess of 100°c. Illers[30]confirms

this finding for samples annealed at temperatures above Tg.

For the present work no differences in crystallinity could be

determined for any of the traces using the method of separating

the amorphous and crystalline portion of the curve, so results

are not reported.

It is suspected that the method is not accurate enough to

cope with the very small changes in order for the weakly crystalline

polymer. There may also have been small differences in the

surface finish presented to the X-ray beam as a consequence of the

machining operation. The diffraction beam would be scattered at

angles that might not be detected and would reduce the size of

the signal producing the trace.

Density measurements did not yield any useful information

concerning crystallinity for two reasons. Firstly that the

samples were composed of two distinct regions ie.a skin and a core

of suspected quite different crystallinity values. To be of any

real use measurements would have to be made on both the skin and

the core separately for the same sample to give an average for

the sample. It was not considered useful, nor very pratical for

this approach to be taken as an average value of crystallinity
in this case would not produce any meaningful conclusions. This
was more relevant of course for the square plaque where the skin
content was greater than for the rectangular plaque. Secondly,
and this is true also for the X-ray technique, a truly amorphous
sample is thought impossible to produce. Illers[30] says that the
recrystallisation process may occur so rapidly that quenching would
not produce a truly amorphous sample. Amorphous density for PVC
has been shown to be 1410 kg/m^3 for instance which is greater than
some of the measurements of samples from the present work.

At present therefore in injection moulded samples the order
is simply assumed to be low and no quantitative value is considered
meaningful.

Finally, one noticable difference between X-ray traces produced
by samples at different moulding conditions was the variation in peak
height at 17° (2 θ). A change in peak height has been shown [162] to
be as a consequence of a change in orientation of crystallites. As
the amount of orientation increases so the X-ray peak height increases.
A change in the peak height at 24.5° (2 θ) has been assigned to
variations in the level of crystallinity. No difference in the
height of this peak was found in this work, suggesting, it is thought,
that the changes in crystallinity are so small as to be undetected
by X-ray analysis.

The variations in peak height are shown in table 36. At
the lowest mould temperature the peak height was found to be greatest
probably due to the increase in orientation brought about by moulding

at this low temperature. Increasing the mould temperature and thus
reducing any orientation effects reduces the height of the X-ray
peak.

An increase in melt temperature should have the effect of
reducing orientation due to relaxation; this is shown in table 36
by a reduction in peak height.

Changes in peak height with position in the plaque are small
at any one set of moulding conditions.

The peak heights for positions close to the gate are very
similar ie. 'a', 'b', 'c', but at positions 'd' and 'e' there is
an increase in height of peak corresponding to an increase in orientation.
This is probably due to a chilling effect on the material as it passes
through the relatively cold mould, giving rise to an increase in
orientation.

CHAPTER 6

CONCLUSIONS

6.1 Conclusions

Processing conditions have been shown to influence both structural and physical properties in injection moulding. The most striking discovery was the presence of a surface skin. This was something that hitherto had not been detected in any published work for injection moulded PVC.

The skin thickness was found to be very much greater for the square plaque than for the rectangular one because of the greater amount of shear and larger mass of hot material in the latter moulding. The plaques were shown to consist of a highly oriented amorphous skin surrounding a central core region.

The thickness of skin was found to vary both with processing conditions and position in the plaque. At the higher temperature conditions less skin was found.

It was shown that an increase in surface skin gave mouldings of a lower density because the density of the skin was less than that of the central core. This shows therefore that in injection mouldings any properties/structure measurements are an average for the thickness of sample because at each point through the thickness there exists a different heat history. The rectangular plaques exhibited the greatest density due to the least amounts of skin. It was also found that as the thickness of plaque increased,.

so too did its density, due to the greater amount of shear
heating and the ability of the larger mass of material to
stay hotter for longer.

The amount of shrinkage found which was due to orientation
was also shown to be dependant upon the thickness of skin. The
greatest shrinkage was shown therefore to occur in samples
taken from the square plaque. Shrinkage in the rectangular
plaque was found to be very much less - usually less than
half depending upon the position in the plaque.

The greatest shrinkage and skin thickness were found
to be in the vicinity of the gate with a gradual decline towards
the ends of both the square and rectangular plaques. This would
mean that any mouldings produced in practise would exhibit
different physical properties at different points in the
moulding, and these conditions of service would need to be
known to determine whether this would be of importance.

The correlation of skin thickness and shrinkage was
shown to be very high, thus suggesting that it would usually
be desirable to produce mouldings with the least amount of
skin possible. The ultimate condition of moulding would be
one whose thermal history was the same throughout. This is
not thought to be possible but may be approached by moulding
at the highest mould and melt temperatures practical and
economically feasible.

It is usually thought detrimental to produce mouldings
that are highly stressed due to the reduction in such properties

as impact strength and tensile strength. Whilst the level
of internal stress was not thought to be high for the mouldings
in this work it is probably more desireable to minimise the
level of stress. Internal stress was shown to vary with the
amount of skin thickness present and therefore with moulding
conditions. The highest level of stress was shown to be
for the square plaques with the greatest amounts of surface
skin. The rectangular plaques, because of the smaller amounts
of skin, exhibited very much lower values of stress compared
with the square plaque produced at the same processing
conditions.

The results from the ion etching work that were supposed
to give an indication of structure in the plaques proved to
be disappointing. The technique needs further refinement
as the conditions used were shown to be too severe for use
with PVC.

Differential thermal analysis showed that enthalpy
changes could be related to changes in processing conditions.
Greater enthalpy changes occurred at higher melt and mould
temperatures. The enthalpy changes were 100% greater for
the rectangular plaque than for the square plaque,due to the
higher temperatures achieved in the thicker rectangular plaque.

The determination of crystallite size from X-ray
diffraction traces for samples from the rectangular plaque
showed that any crystallites present were very small. The
samples were taken from the centre of the moulding thickness

to minimise any orientation effects present near the surface. Because the samples from mouldings were not homogeneous the crystallite sizes determined were only true for the centre of the plaque. The peak height variation at $17^{o}(2\theta)$ showed some interesting trends for the rectangular plaque at various moulding conditions used. Peak height was shown to vary with processing conditions and to be indicative of a change in crystallite orientation.

In conclusion, therefore, it has been shown using a variety of test procedures that it is possible to follow trends of structural and physical changes produced by the variations in conditions of moulding. The mouldings were seen to be composed of layers of polymer with different heat histories and therefore when analysing a moulding this point must be borne in mind.

6.2 Recommendations For Further Study

Whilst the presence of a layered structure was found, a greater amount of work could be done in determining the properties and structure for each individual layer and how they contribute to the overall moulding.

A greater amount of instrumentation to determine actual temperature and pressure conditions in the mould during moulding could be investigated. This would enable a more detailed study to be made using actual moulding conditions existing in the mould. In the present work the moulding conditions were measured at a point before the mould entrance.

Ion etching did not reveal the structural information that it was intended to. Further investigation using a modified version of this technique would yield very valuable information to the structural formation in PVC during moulding. This would then enable a better assessment to be made of the contribution changing structure has on physical properties.

Flow in the mould was not evaluated in detail for this work and a great deal of useful information could be given to moulders. This would then enable the design of injection moulded components to be undertaken with more certainty and the effect of the design upon resulting properties. This type of work could be extended using a range of mould cavities of differing forms.

Although some measurements were taken regarding the effect of changes in gate dimensions of the mould on properties, a wider range of gate types would produce mouldings whose shear history was different. This effect could be evaluated in terms of the structure and properties produced and the optimum design of gate determined for a particular type of moulding.

The current work used only one formulation of stabiliser, processing aid etc. and although the mouldings produced were considered satisfactory, different formulations with varying amounts of each additive could be used with a view to determining the most economic and optimum property producing formulation.

APPENDIX 1

DENSITY (Kg/m^3) CHANGE FOR SQUARE

PLAQUE

TABLE 1

MOULDING CONDITIONS		175,1.0,40	195,1.0,40	210,1.0,40
POSITION IN PLAQUE	a	1366.8	1366.0	1366.5
	b	1367.5	1367.0	1367.8
	c	1365.8	1367.5	1367.1
	d	1366.3	1366.9	1366.6
	e	1366.9	1366.9	1366.3
	f	1366.6	1367.4	1367.8
	g	1366.3	1366.9	1366.3
	h	1367.2	1367.3	1367.7

DENSITY (Kg/m^3) CHANGE FOR SQUARE

PLAQUE

TABLE 2

MOULDING CONDITIONS		175,1.0,60	195,1.0,60	210,1.0,60
POSITION IN PLAQUE	a	1362.0	1362.2	1366.8
	b	1362.2	1362.4	1366.8
	c	1362.2	1362.6	1366.4
	d	1362.4	1363.2	1366.8
	e	1362.6	1362.6	1366.8
	f	1362.8	1362.8	1366.6
	g	1362.9	1362.3	1366.8
	h	1361.9	1363.0	1366.8

TABLE 3

DENSITY (Kg/m³) CHANGE FOR SQUARE

PLAQUE

MOULDING CONDITIONS		175,0.6,60	195,0.6,60	210,0.6,60
POSITION IN PLAQUE	a	1362.2	1363.5	1368.0
	b	1362.4	1363.1	1368.3
	c	1362.5	1363.9	1367.1
	d	1362.7	1363.7	1367.3
	e	1362.8	1364.0	1367.8
	f	1362.8	1363.8	1367.3
	g	1362.9	1364.4	1367.8
	h	1362.1	1363.8	1368.1

<u>DENSITY (Kg/m^3) CHANGE FOR SQUARE</u>

<u>PLAQUE</u>

<u>TABLE 4</u>

MOULDING CONDITIONS		175,0.6,40	195,0.6,40	210,0.6,40
POSITION IN PLAQUE	a	1362.4	1367.2	1366.9
	b	1362.8	1367.3	1367.3
	c	1362.6	1365.7	1367.8
	d	1362.7	1366.2	1366.5
	e	1362.8	1365.9	1367.0
	f	1362.5	1366.6	1366.9
	g	1363.0	1365.9	1367.8
	h	1363.0	1365.6	1367.5

CHANGES IN DENSITY (Kg/m³) FOR SQUARE PLAQUE WITH VARIATION IN INJECTION TIME

TABLE 5

INJECTION TIME (SEC)		1.0	0.8	0.6
POSITION IN PLAQUE	a	1366.6	1365.2	1368.0
	b	1366.6	1365.3	1368.3
	c	1366.3	1365.3	1367.1
	d	1366.6	1365.9	1367.2
	e	1366.6	1366.0	1367.7
	f	1366.5	1365.8	1367.2
	g	1366.6	1366.0	1367.7
	h	1366.6	1366.5	1368.1

MOULDING CONDITIONS :-
MOULD TEMP 60°C
MELT TEMP 210°C

DENSITY (Kg/m^3) VARIATION WITH PLAQUE THICKNESS FOR

RECTANGULAR MOULDING

TABLE 6

PLAQUE THICKNESS (mm)		3	4	6	3*
POSITION IN PLAQUE	a	1363.7	1368.7	1370.1	1366.0
	b	1364.7	1369.2	1370.9	1365.8
	c	1363.7	1369.5	1371.1	1365.3
	d	1364.3	1369.0	1370.4	1365.0
	e	1365.0	1368.8	1370.2	1365.0

Moulding Conditions

155, 0.6, 40

* with large gate

DENSITY (Kg/m^3) VARIATION WITH PLAQUE THICKNESS FOR

RECTANGULAR MOULDING

TABLE 7

PLAQUE THICKNESS (mm)		3	4	6	3 *
POSITION IN PLAQUE	a	1363.0	1368.0	1370.1	1365.5
	b	1364.1	1369.0	1370.7	1364.7
	c	1363.1	1368.2	1370.4	1364.5
	d	1363.5	1368.6	1370.3	1364.0
	e	1363.3	1368.3	1370.1	1364.0

MouldingConditions:-
155, 1.0, 40

* With large gate.

DENSITY (Kg/m^3) VARIATION WITH PLAQUE THICKNESS FOR

RECTANGULAR MOULDING.

TABLE 8

PLAGUE THICKNESS (mm)		3	4	6	3 *
POSITION IN PLAQUE	a	1364.5	1369.0	1370.3	1366.2
	b	1365.8	1369.7	1370.7	1366.5
	c	1365.2	1369.2	1370.5	1365.6
	d	1365.0	1369.2	1370.5	1365.7
	e	1365.0	1369.0	1370.6	1366.1

MOULDING CONDITIONS
185, 1.0, 40

* With large gate.

DENSITY (Kg/m³) VARIATION WITH MOULD TEMPERATURE FOR

3mm RECTANGULAR PLAQUE

TABLE 9

MOULD TEMPERATURE (°C)		15	30	55	65
POSITION IN PLAQUE	a	1367.5	1366.7	1366.8	1368.0
	b	1367.3	1366.7	1366.4	1368.0
	c	1367.0	1367.0	1366.5	1368.2
	d	1367.0	1366.0	1366.5	1368.0
	e	1366.8	1366.0	1366.5	1367.8

MOULDING CONDITIONS:-
155 0.8,

SKIN THICKNESS VARIATION (mm) FOR SQUARE PLAQUE WITH

MELT TEMPERATURE

TABLE 10

MELT TEMP (^{o}C)		175	185	195	210
POSITION IN PLAQUE	a	0.55	0.56	0.50	0.43
	b	0	0	0.53	0.40
	c	0.22	0.10	0.0	0.0
	d	0.30	0.31	0.30	0.20
	e	0.48	0.48	0.40	0.30
	f	0.44	0.44	0.42	0.40
	g	0.73	0.74	0.52	0.40
	h	0.62	0.63	0.53	0.36

MOULDING CONDITIONS:-

MOULD TEMP. 60°C

INJECTION TIME 0.6 sec.

SKIN THICKNESS VARIATION (mm) FOR SQUARE PLAQUE WITH

MELT TEMPERATURE

TABLE 11

MELT TEMP. (^{o}c)	175	185	195	210
POSITION IN PLAQUE a	0.74	0.71	0.70	0.60
b	0.23	0.0	0.0	0.40
c	0.20	0.16	0.0	0.0
d	0.21	0.22	0.17	0.16
e	0.60	0.58	0.50	0.40
f	0.52	0.53	0.45	0.43
g	0.73	0.71	0.62	0.55
h	0.74	0.67	0.66	0.54

MOULDING CONDITIONS:-
MOULD TEMP   60°c.
INJECTION TIME 1.0 sec.

SKIN THICKNESS VARIATION (mm) FOR SQUARE PLAQUE WITH

MELT TEMPERATURE

TABLE 12

MELT TEMP (^{o}c)		175	185	195	210
POSITION IN PLAQUE	a	0.60	0.6	0.50	0.45
	b	0.32	0.0	0.55	0.50
	c	0.36	0.0	0.22	0.0
	d	0.30	0.35	0.26	0.25
	e	0.60	0.60	0.40	0.35
	f	0.50	0.54	0.44	0.36
	g	0.80	0.80	0.55	0.42
	h	0.47	0.70	0.53	0.43

MOULDING CONDITIONS

MOULD TEMP 40°c
INJECTION TIME 0.6 sec.

SKIN THICKNESS VARIATION (mm) WITH PLAQUE THICKNESS FOR

RECTANGULAR MOULDING

TABLE 13

PLAQUE THICKNESS (mm)		3	4	6	3*
POSITION IN PLAQUE	a	0.099	0.060	0.031	0.105
	b	0.092	0.055	0.027	0.103
	c	0.086	0.049	0.022	0.098
	d	0.076	0.042	0.017	0.090
	e	0.074	0.041	0.016	0.082

MOULDING CONDITIONS :-

MELT TEMP 155°c

INJECTION TIME 0.6 sec.

* with larger gate

SKIN THICKNESS VARIATION (mm) WITH PLAQUE THICKNESS FOR

RECTANGULAR MOULDING

TABLE 14

PLAQUE THICKNESS (mm)	3	4	6	3 *
POSITION IN PLAQUE a	0.115	0.070	0.049	0.130
b	0.105	0.067	0.048	0.124
c	0.090	0.060	0.044	0.120
d	0.082	0.048	0.026	0.110
e	0.072	0.043	0.022	0.108

* with larger gate

MOULDING CONDITIONS:-

MELT TEMP 155°c

INJECTION TIME 1.0 sec

SKIN THICKNESS VARIATION (mm) WITH PLAQUE THICKNESS FOR

RECTANGULAR MOULDING

TABLE 15

PLAQUE THICKNESS (mm)		3	4	6	3*
POSITION IN PLAQUE	a	0.070	0.046	0.025	0.108
	b	0.064	0.041	0.023	0.104
	c	0.059	0.038	0.021	0.102
	d	0.055	0.035	0.020	0.097
	e	0.043	0.028	0.016	0,093

MOULDING CONDITIONS :-

MELT TEMPERATURE 185°c
INJECTION TIME 1.0 sec

* with larger gate

<u>SKIN THICKNESS VARIATION (mm) WITH MOULD TEMPERATURE FOR</u>

<u>RECTANGULAR (3mm) PLAQUE</u>

<u>TABLE 16</u>

MOULDING CONDITIONS:-

MELT TEMPERATURE 155°c
INJECTION TIME 0.8 sec

MOULD TEMPERATURE (^{o}C)	15	30	50	65
TEMPERATURE DIFFERENCE BETWEEN MELT & MOULD ^{o}C	140	125	105	95
POSITION IN PLAQUE a	0.185	0.107	0.095	0.080
b	0.190	0.110	0.092	0.078
c	0.167	0.085	0.062	0.056
d	0.160	0.088	0.056	0.043
e	0.140	0.070	0.047	0.040

REVERSION (% SHRINKAGE) FOR SQUARE PLAQUE AT VARYING

MELT TEMPERATURES

TABLE 17

MELT TEMPERATURE (°c)		175,1.0,40	185,1.0,40	195,1.0,40	210,1.0,40
POSITION IN PLAQUE	a	14.0	11.4	9.0	6.8
	b	Q	Q	5.5	6.8
	c	6.6	5.6	5.7	2.7
	d	7.3	5.8	4.2	3.7
	e	14.0	10.0	6.9	4.7
	f	14.0	10.3	7.8	5.7
	g	17.0	12.8	9.7	7.2
	h	16.1	12.2	8.7	6.3

REVERSION (% SHRINKAGE) FOR SQUARE PLAQUE WITH VARYING

MELT TEMPERATURES

TABLE 18

MELT TEMPERATURE (^{o}c)		175,0.6,40	185,0.6,40	195,0.6,40	210,0.6,40
POSITION IN PLAQUE	a	14.2	10.5	7.0	6.4
	b	0	0	4.7	6.3
	c	6.5	5.4	3.3	2.3
	d	7.4	5.4	3.7	3.3
	e	16.3	11.5	5.3	3.8
	f	14.0	10.8	6.0	5.3
	g	17.9	13.2	7.0	5.5
	h	18.6	14.4	7.8	5.5

REVERSION (% SHRINKAGE) FOR SQUARE PLAQUE WITH

VARYING MELT TEMPERATURES

TABLE 19

MELT TEMPERATURE (^{o}c)	175,1.0,60	185,1.0,60	195,1.0,60	210,1.0,60
POSITION IN PLAQUE a	13.5	11.0	9.5	7.6
b	0	0	6.4	4.8
c	4.7	3.7	2.2	2.0
d	5.3	4.5	3.0	2.9
e	13.5	9.1	5.0	5.0
f	13.0	9.8	6.9	5.8
g	15.3	10.3	6.7	6.5
h	15.0	12.8	8.7	6.5

REVERSION (% SHRINKAGE) FOR SQUARE PLAQUE WITH VARYING

MELT TEMPERATURES

TABLE 20

MELT TEMPERATURE (^{o}c)	175,0.6,60	185,0.6,60	195,0.6,60	210,0.6,60
POSITION IN PLAQUE a	14.4	11.2	8.9	9.0
b	1.2	2.0	5.0	3.5
c	6.3	5.4	3.0	3.3
d	4.7	5.2	4.0	3.6
e	14.2	13.3	5.5	4.3
f	13.5	10.4	6.7	5.5
g	17.4	15.2	7.5	5.9
h	15.7	13.7	8.8	6.5

CHANGES IN REVERSION (SHRINKAGE %) FOR SQUARE PLAQUE

WITH INJECTION TIME

TABLE 21

INJECTION TIME (SEC)		0.6	0.8	1.0
POSITION IN PLAQUE	a	6.5	8.2	6.8
	b	4.7	5.3	6.8
	c	2.2	0.7	2.7
	d	3.3	3.4	3.6
	e	3.9	4.3	4.7
	f	5.3	4.7	5.7
	g	5.5	5.6	7.1
	g	5.4	5.0	6.3

MOULDING CONDITIONS :-
MOULD TEMP 40°c
MELT TEMP 210°c

REVERSION (% SHRINKAGE) FOR RECTANGULAR PLAQUE OF

DIFFERENT THICKNESSES

TABLE 22

PLAQUE THICKNESS (mm)	3	4	6	3 *
POSITION IN PLAQUE a	3.40	1.70	1.00	4.00
b	5.10	1.90	1.25	5.30
c	5.00	2.40	1.60	5.25
d	5.20	0.60	0.50	4.40
e	3.80	0.60	0.50	4.40

* WITH LARGE GATE

MOULDING CONDITIONS :-

155, 0.6, 40

REVERSION (% SHRINKAGE) FOR RECTANGULAR PLAQUE OF

DIFFERENT THICKNESSES

TABLE 23

PLAQUE THICKNESS (mm)		3	4	6	3*
POSITION IN PLAQUE	a	3.85	1.90	1.25	4.60
	b	5.10	2.80	1.75	5.60
	c	5.40	2.80	1.85	5.50
	d	5.70	2.10	1.30	6.00
	e	4.70	1.80	1.15	5.10

* WITH LARGE GATE

MOULDING CONDITION:-

155, 1.0, 40

REVERSION (% SHRINKAGE) FOR RECTANGULAR PLAQUE OF

DIFFERENT THICKNESSES

TABLE 24

PLAQUE THICKNESS (mm)	3	4	6	3*
POSITION IN PLAQUE a	1.50	0.0	0.60	2.75
b	2.80	1.30	1.00	3.25
c	2.80	2.30	1.45	3.70
d	3.20	1.60	1.10	3.00
e	2.70	0.50	0.40	2.60

MOULDING CONDITIONS :-
185, 1.0, 40

* WITH LARGE GATE

REVERSION (% SHRINKAGE) OF 3mm THICK PLAQUE WITH VARYING

MOULD TEMPERATURE

TABLE 25

MOULD TEMPERATURE (^{o}c)		15	30	55	65
POSITION IN PLAQUE	a	6.0	3.9	4.0	3.8
	b	9.2	5.0	5.7	4.7
	c	9.5	5.8	5.5	4.9
	d	9.2	5.6	5.3	4.7
	e	8.1	5.8	5.1	4.9

MOULDING CONDITION:-

155, 0.8

ENTHALPY CHANGE (KJ/kg) FOR

SQUARE PLAQUE

TABLE 26

MOULDING CONDITIONS	175, 0.6, 40	185, 0.6, 40	195, 0.6, 40	210, 0.6, 40
POSITION IN PLAQUE a	1.4	1.4	1.8	2.1
b	1.0	3.0	1.8	1.9
c	1.2	2.0	1.6	1.9
d	1.4	1.4	1.5	1.7
e	1.3	1.4	1.6	2.0
f	1.3	1.4	1.9	2.0
g	1.4	1.4	1.8	2.2
h	1.6	1.4	1.8	2.2

ENTHALPY CHANGE (KJ/Kg) FOR SQUARE PLAQUE

TABLE 27

MOULDING CONDITIONS		175,1.0,40	185 ,1.0,40	195,1.0,40	210,1.0,40
POSITION IN PLAQUE	a	1.2	1.4	1.5	1.8
	b	0.6	1.0	2.3	1.0
	c	0.7	1.0	1.1	1.5
	d	1.0	1.0	1.2	1.3
	e	1.0	1.2	1.2	1.6
	f	0.8	0.9	1.0	1.3
	g	1.0	1.4	1.5	1.8
	h	1.4	1.3	1.6	1.8

ENTHALPY CHANGE (KJ/Kg) FOR SQUARE

PLAQUE

TABLE 28

MOULDING CONDITIONS		175,0.6,60	185,0.6,60	195,0.6,60	210,0.6,60
POSITION IN PLAQUE	a	1.4	1.4	2.0	2.4
	b	2.0	2.3	1.5	2.6
	c	1.3	2.0	1.6	2.2
	d	1.4	1.6	1.5	2.0
	e	1.8	1.8	1.9	2.2
	f	1.6	1.6	1.5	1.7
	g	1.8	1.8	2.2	2.8
	h	1.8	1.8	2.0	2.4

ENTHALPY CHANGE (KJ/kg) FOR SQUARE

PLAQUE

TABLE 29

MOULDING CONDITIONS	175,1.0,60	185,1.0,60	195,1.0,60	210,1.0,60
POSITION IN PLAQUE a	1.4	1.5	1.7	2.0
b	1.8	2.8	2.4	2.2
c	1.0	1.0	1.4	1.8
d	1.0	1.3	1.4	1.5
e	1.5	1.6	1.8	2.0
f	1.6	1.4	1.5	1.5
g	1.5	1.6	2.0	2.4
h	1.6	1.5	1.8	2.0

ENTHALPY CHANGE (KJ/kg) FOR 3mm THICK PLAQUE

TABLE 30

Processing Conditions	a	b	c	d	e
155, 0.8, 15	3.3	3.1	3.2	3.2	2.9
155, 0.8, 30	3.9	3.8	3.5	3.6	3.5
155, 0.8, 50	4.3	4.0	3.8	3.7	3.6
155, 0.8, 60	4.5	4.2	3.9	3.8	3.8
155, 0.6, 40	4.3	4.3	4.0	3.9	3.7
155, 0.8, 40	4.1	4.0	3.8	3.7	3.6
185, 0.8, 40	4.1	4.1	3.9	3.8	3.5

INTERNAL STRESS MEASUREMENTS TESTED IN INJECTION DIRECTION -

SQUARE PLAQUE

TABLE 31

MELT TEMPERATURE °c		175 STRESS m		185 STRESS m		195 STRESS m		210 STRESS m	
POSITION IN PLAQUE	x	−35	20	−38	18	−19	16	−4	13
	y	−30	20	−28	19	−11	15	−2	12

MOULDING CONDITIONS :- MOULD TEMPERATURE 40°c
INJECTION TIME 0.6 sec.

MELT TEMPERATURE °c		175 STRESS m		185 STRESS m		195 STRESS m		210 STRESS m	
POSITION IN PLAQUE	x	−50	24	−50	25	−30	20	−12	17
	y	−43	23	−40	24	−28	19	−8	16

MOULDING CONDITIONS :- MOULD TEMPERATURE 40°c
INJECTION TIME 1.0 sec.

STRESS − Pa x 10^3

INTERNAL STRESS MEASUREMENTS TESTED IN INJECTION DIRECTION –

SQUARE PLAQUE

TABLE 32

MELT TEMPERATURE °c	175 STRESS 'm'		185 STRESS 'm'		195 STRESS 'm'		210 STRESS 'm'	
POSITION IN PLAQUE x	-48	25	-50	25	-27	20	-10	16
y	-40	22	-28	23	-19	19	-6	15

MOULDING CONDITIONS:- MOULD TEMP 40 °c

INJECTION TIME 0.6 sec.

MELT TEMPERATURE °c	175 STRESS 'm'		185 STRESS 'm'		195 STRESS 'm'		210 STRESS 'm'	
POSITION IN PLAQUE x	-63	31	-59	29	-39	20	-20	12
y	-55	28	-45	26	-26	18	-12	10

MOULDING CONDITIONS :- MOULD TEMP. 40°

INJECTION TIME 1.0 sec.

STRESS – Pa x 10^3

INTERNAL STRESS MEASUREMENTS - TESTED IN INJECTION DIRECTION

FOR 3mm RECTANGULAR PLAQUE

TABLE 33

POSITION IN PLAQUE	x STRESS*	'm'	y STRESS	'm'
155, 0.8, 15	-50	18	-35	16
155, 0.8, 30	-30	12	-20	11
155, 0.8, 50	-10	8	-3	6
155, 0.8, 60	-2	8	0	6
155, 0.6, 40	-18	8	-16	8
155, 0.8, 40	-26	11	-20	10
185, 0.8, 40	-15	7	-10	7

* STRESS - Pa x 10^3

INTERNAL STRESS MEASUREMENTS TESTED PERPENDICULAR TO
INJECTION DIRECTION FOR 3mm THICK PLAQUE

TABLE 34

POSITION IN PLAQUE	STRESS*a	STRESS b	STRESS c	STRESS c	STRESS e
155, 0.8, 15	-30	-40	-36	-30	-26
155, 0.8, 30	-18	-25	-28	-20	-8
155, 0.8, 50	+1	-12	-8	-3	0
155, 0.8, 60	+4	+20	+16	+8	+2
155, 0.6, 40	0	+20	+16	+6	+2
155, 0.8, 40	-16	-23	-23	-18	-6
185, 0.8, 40	0	+18	+8	+6	0

* STRESS - Pa x 10^3

MEAN CRYSTALLITE SIZE (nm.) FOR '210' REFLECTION PLANE

FOR 3mm THICK PLAQUE

TABLE 35

Processing Conditions	POSITION IN PLAQUE				
	a	b	c	d	e
155, 0.6, 40	4.08	4.32	3.82	3.82	3.60
155, 0.8, 40	3.10	3.60	3.60	3.80	3.40
185, 0.8, 40	4.80	5.2	4.60	4.68	4.30
155, 0.8, 15	2.4	2.8	2.6	2.5	2.2
155, 0.8, 30	2.9	3.3	3.4	3.2	3.0
155, 0.8, 50	3.40	4.2	3.80	3.80	3.20
155, 0.8, 65	4.4	4.0	4.2	4.0	4.0

TABLE 36

Processing Conditions	POSITION IN PLAQUE				
	a	b	c	d	e
155, 0.6, 40	3.1	3.1	3.0	3.4	3.4
155, 0.8, 40	3.2	3.2	3.3	3.6	3.6
185, 0.8, 40	2.0	2.0	2.0	2.2	2.2
155, 0.8, 15	4.8	4.8	5.1	5.2	5.4
155, 0.8, 30	3.6	3.6	3.8	4.1	4.1
155, 0.8, 50	2.7	3.3	2.9	3.0	3.0
155, 0.8, 65	2.2	2.2	2.3	2.3	2.3

APPENDIX 2

REFERENCES

1. D. Waywell - P.P.G. Symp. May 1976.

2. M. Bevis , J. Bowman, N. Harris - Plastics and Polymers 19,42,1974.

3. S. Henke, C. Smith and R. Abbott - Polym. Eng. Scie.
   15, 79, 1975.

4. E. Clarke - S.P.E.J. 23, 46, 1967.

5. M. Kantz - International J. Polymeric Mater, 3, 245, 1974.

6. I. Mencik and D. Fitchmun - J. Polym. Scie, Polymer Physics.
   Edition 11, 1973, 1973.

7. J. Callear and J. Shortall - J. Mat. Scie 12, 141, 1977.

8. H. Machin -J. App. Polym Scie. 13,1767. 1969

9. M. Kantz, H. Newman and F. Stigate - J. App. Polym. Scie.
   16, 1249, 1972.

10. J. Bowman, N. Harris, M. Bevis - J. Mat. Scie. 10, 63, 1975.

11. K. Djurner and J. Kubat - Kunstoffe 66, 511, 1976.

12. F. Binsbergen - Nature 211, 516, 1966.

13. D. Fitchman - J. Polym. Scie. 11, 951, 1973

14. J. Fordham - ibid 39, 321, 1959.

15. E. Pezzin - Plastics and Polym. 37, 295, 1965

16. C. Baker, W. Maddans, G. Park, B. Robertson - Makromol.
    Chem. 165, 321, 1973.

17. T. Stafford - Rapra Technical Review 66 Part 2.

18. L. Vidyaikina, N. Oklandov and B. Shtarkman - Vysokomol soyed
    8, 390, 1966.

19. V. Knyazeva, V. Knyazev, G. Lukyanova and V. Berezkin-
    Plasticheskie Massey 2, 44, 1974.

20. H. Munstedt - Angew. Makromol. Chem. 47, 229, 1975.

21. A. Berens and V. Folt - Trans. Soc. Rheol. 11, 96, 1967.

22. R. Chartoff - Polymer 16, 470, 1975.

23. D. Bort, V. Zegel'man and V. Kargin   Polym. Scie USSR 10, 1498, 1968.

24. Y. Shinai - Plastics Industry News May, 65, 1973

25. R. Colbourne - J. Appl. Polym. Scie. 14, 127, 1970.

26. A. Michel and A. Guyot - J. Polym. Scie. C33, 75, 1971.

27. N. Nakajima, H. Hamada and S. Hayashi- Makromol. Chem. 60, 103, 1973.

28. C. Anagnostopoulous, A. Coran and H. Gamrath - J. Appl. Polym. Scie. 4, 181, 1960.

29. F. Reding, E. Walter and F. Welch - J. Polym. Scie. 56, 225, 1962.

30. K. Illers - Makromol. Chem. 127, 1, 1969.

31. K. Djurner, J. Kubat, M. Rigdahl - Polymer 18, 1068, 1977.

32. P. Mckinney and C. Foltz - J. Appl. Polym. Scie. 11,1189,1967.

33. E. Passaglia - S.P.E. Trans. 4, 169, 1964.

34. M. Yagfarov - Vysokomol. soyed A10, 1267, 1968.

35. P. Dunn and B. Ennis - J. Appl. Polym. Scie. 14, 355, 1970.

36. M. Ali and R. Sheldon - ibid 14, 2619, 1970.

37. R. Roberts and F. Sherliker ibid 13, 2069, 1969.

38. A. Gray - Ph. D. Thesis Loughborough 1975.

39. G. Natta and P. Corradini - J. Polym. Scie. 20,251, 1956.

40. M. May and C. Walther - Plast. u. Kautschuk 19, 485, 1972.

41. H. Sobue and J. Tabula - J. Polym. Scie. 39, 427, 1957.

42. R. Pierce and J. Tordella - J. Amer. Chem. Soc. 74, 282, 1952.

43. V. Lebedev - Polymer Scie. USSR. 9, 553, 1967.

44. M. Mammi and V. Nardi - Nature 247, 1963.

45. R. D'Amato and S.Strella - Appl. Polym, Symp. 8, 275, 1969

46. V. Lebedev, N. Okladnov, K. Minsker and B. Shtarkman - Poly. Scie. USSR 7, 724, 1965.

47. V. Lebedev, V. Zegelman and D. Yan. Tsvankin ibid 14, 2119, 1972.

48. V. Zegelman, M. Shlykova and S. Svetozarskii ibid 10, 133, 1968.

49. G. Rehage and H. Halborth - Makromol. Chem. 119, 235, 1968.

50. J. Manson, S. Iobst and R. Acosta - J. Polym. Scie. 10, 179, 1972.

51. A. Brunner - Polym. Letters 10, 379, 1972.

52. V. Nardi - Nature 563, 1961.

53. V. Lebedev, D. Tsvankin and Y. Glazkovskii - Poly. Scie. USSR 14, 1123, 1972.

54. R. Straff and D. Uhlmann - J. Polym. Scie. 14, 353, 1976.

55. F. Rybnikar - Makromol. Chem. 140, 91, 1970.

56. E. Gouinlock - J. Polym. Scie. 13, 961, 1975.

57. V. Lebedev - Vysokomol. Soedin. Ser. A14, 1010, 1972.

58. M. Carrega - Lecture Polymer Symp. 1976. France.

59. J. Juijn, J. Gisolf and W. De. Jong - Koll. Zeit. Zeit. Polym. 251, 456, 1973.

60. G. Pezzin - Plastics and Polym. 194, 5, 1964.

61. K. Hellwege - Koll. Zeit. Zeit. Polym. 194, 5, 1964.

62. G. Garbuglio, A. Rodella, G. Borsini and E. Gallinella- Chim. Ind. (Milan) 46, 166, 1964.

63. G. Talamini and G. Vidotto - Makromol. Chem. 100, 48, 1967.

64. H. Halborth- Ph. D. Thesis Rheimisch - Westfaelischen Technischen Hochschule, Auchen 1965.

65. H. Wilski - Koll. Zeit. Zeit Polym. 198, 17, 1964

66. A. Prietzschk - ibid 156, 8, 1958.

67. G. Grove - Plastics Progress 132, 1959

68. D. Coleman - Private communication

69. R. Colbourne - J App. Polym Scie 14, 127, 1970

70. G. Bonart - J. Mater, Scie 10, 833, 1973

71. E. Schoon - Kunstoffe 25, 487, 1972.

72. H. Behrens - Plast. u. Kautschuk 22, 2, 1975.

73. R. Tregan - Plastiques Modernes et. Elastomers 23, 220, 1971.

74. C. Singleton - Polym. Eng. Scie. 14, 371, 1974.

75. T. Hattori, K. Tanaka and M. Matsuo - ibid 12, 199, 1972.

76. E. Grosskurth - Polym Eng. Scie 12, 265, 1973

77. G. Menges - Kunstoffe 11, 735, 1976

78. M. Spector - I.I.T.R.I. Chicago 3, 665, 1974.

79. B. Guntherschulze - Physics 119, 685, 1942

80. M. Thompson - J. Mater. Scie. 4, 56, 1969.

81. G. Wehner - J. App. Phys. 42, 1145, 1971.

82. R. Fitch - J. Mater. Scie. 12, 1225, 1977.

83. I. Petrova - Vysokomol. soyed A15, 1421, 1973.

84. J. Ducommun - J. Mater. Scie. 9, 725, 1974.

85. M. Kamal - Polym. Eng. Scie. 12, 294, 1972.

86. M. Kamal - ibid 12, 302, 1972.

87. S. Kenig - Ph.D. Thesis, Megill University, 1972.

88. J. Berger - Polym. Eng. Scie. 13, 102, 1973.

89. Z. Tadmor - S.P.E. Tech. Conf. 19, 122, 1973.

90. W. Bauer - Kunstoffe 53, 210, 1963.

91. I. Barrie - Plast. Polym. 37, 463, 1969

92. I. Barrie - ibid 3, 47, 1970.

93. D. Harry - S.P.E.Tech. Papers 15, 448, 1970.

94. D. Harry - Polym. Eng. Scie. 10, 209, 1970.

95. W. Gloor - S.P.E.Trans. 3, 270, 1963.

96. M. Kamal - Polym. Eng. Scie. 15, 863, 1975.

97. H. Lord and E. Williams - ibid 15, 569, 1975.

98. V. Koita - ibid 14, 840, 1974.

99. C. Deeley - Mod. Plast. 42, 111, 1965.

100. F. Karas - ibid 41, 140, 1963.

101. J. Berger and C. Gogos - Polym. Eng. Scie. 13, 102, 1973.

102. E. Gilmore and R. Spenser - Mod. Plast. 28, 117, 1951.

103. M. Sleeman and G. West - Brit. Polym. J. 6, 109, 1974.

104. J. White and H. Dee - Polym. Eng. Scie. 14, 212, 1974.

105. K. Oda, J. White and E. Clarke - ibid 16, 585, 1976.

106. S. Yamaguchi - Res. Rpts. Kogalevin University 24, 71, 1968

107. M. Sleeman - Brit. Polym. J. 6, 109, 1974

108. J. White - Polym. Eng. Scie. 14, 212, 1974.

109. G. West - Proc. Royal. Soc. 86A, 20, 1911.

110. W. Rose - Nature 191, 242, 1961.

111. J. White - Polym. Eng. Scie. 15, 44, 1975.

112. B. Rouzer - S.P.E.Tech. Conf. Chicago Section 1, 1975.

113. M. Huber - P.R.W. Feb. 18, 1977.

114. R. Boehm - S.P.E.Tech. Conf. Chicago Section 10, 1975.

115. F. Tulley and B. Harris - S.P.E.Encyclopaedia of PVC vol III
     chapter 24 Marcel Dekkers Inc. 1976.

116. F. Tulley and B. Harris - Ethyl Corp. Tech. Bulletin Ethyl
     7042 compound Ethyl Corp. , Baton Rouge, Louisiana.

117. H. Hogberg - Swedish Plast. Fed. Oct. 1956.

118. R. Horsley and D. Lee - Brit. Plast. 29, 152, 1956.

119. D. Lee - Symp. Plast. Polym. Group Soc. Chem. Ind. 1958.

120. R. Spenser and D. Gilmore - Mod. Plast. 28, 97, 1950.

121. V. Lebedev. - Poly Scie USSR 7,366, 1965

122. R. Ballman and H. Toor - Mod. Plast. 8, 113, 1960.

123. Z. Bakerdjian and M. Kamal - Polym. Eng. Scie. 17, 76, 1977.

124. Z. Tadmor - J. App. Polym. Scie. 18, 1753, 1974.

125. H. Keskkula and J. Schmidt - ibid 9, 2681, 1965.

126. H. Wiegand and H. Vetter - Kunstoffe 56, 761, 1966.

127. H. Vego and S. Hushino - J. App. Polym. Scie. 14, 317, 1970.

128. M. Tyiyama - Kobunshi Ronbun. 32, 581, 1975.

129. K. Djurner and M. Rigdahl - Polymer 18, 1068, 1977.

130. J. Li - Canadian J. Phys. 45, 463, 1967.

131. R. Rohde - Mat. Scie. Eng. 12, 179, 1973.

132. M. Simha - Phil. Mag. 28, 591, 1973.

133. R. De Batist - Phys. Status Solidi 21, 591, 1974.

134. A. Jenkins - Polym. Scie. North Holland Pub. Co. London 768, 1972.

135. J. Peterman - Phil. Mag. 25, 813, 1972.

136. W. Pechold - Koll. Zeit. Zeit. Polym. 228, 1, 1968.

137. B. Thakker - Ph.D. Thesis Illinois Inst. 1976.

138. J. Kubat and M. Rigdahl - Int. J. Polym. Mat. 3, 287, 1975.

139. J. Kubat, J. Petermann and M. Rigdahl - Mat. Scie. Eng. 19, 185, 1975.

140. P. So and L. Broutman - Polym. Eng. Scie. 16, 785, 1976.

141. R. Treuting and W. Read - J. App. Phys. 22, 130, 1951.

142. A. Kostyuchenko - Vysokomol. soyed A10, 2604, 1968.

143. N. Nakajima - Makromol. Chem. 95, 40, 1966.

144. C. Wilkes, V. Folt and S. Krimm - Macromol. 6, 235, 1973.

145. P. Burleigh - J. Amer. Chem. Soc. 82, 749, 1960.

146. Z. Bakerdjian - Polym. Eng. Scie. 17, 98, 1977.

147. M. Tyiyama - Kobunshi Ronbun. 33, 182, 1976. Rapra Abst. 42071

148. A. Savelev, V. Braginskii, N. Zubarera and E. Sereda - Soviet Plast. No. 6 1971.

149. M. Natov and T. Gancheva - Vysokomol. soyed 14, 2354, 1972

150. L. Brecker - SPE Conference Chicago October 1975

151. I.C.I. Tech. Service Note W114

152. R. Pye - Injection Mould Design

153. H. Klug and P. Alexander - X-Ray Diffraction Procedures
J. Wiley and Son 1962

154. E. White and B. Murphey - Polym. Lett. 7, 157, 1969

155. A. Serle and P. Lantos - S.P.E. Antec. tech. Pap.12
Session xi, Paper 1, 6 (1966)

156. R. Steinbuch - Br. Plast. 37, 12, 678, 1964

157. W. Backofen - Plastics 26, 50, 1961

158. A. Savelev, V. Kotenkor and V. Braginskii - Plast. Massy,6, 32, 1974

159. V. Tan and M. Kamal - J. App. Polym. Scie. 22, 2341, 1978

160. O. Borkman - J. Polym. Scie 3, 3399, 1965

161. G. Gleng - J. Polym. Scie. 9, 1191, 1971

162. J. Vyvoda, M. Gilbert and D. Hemsley - Polymer 21, 109, 1980