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IRRADIATION CROSSLINKING OF ORIENTED PLASTICISED PVC COMPOUNDS

by

ARUNEE TABTIANG

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

FEBRUARY 1995

Supervisor: M. Gilbert, Ph.D.

Institute of Polymer Technology
and Materials Engineering

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ACKNOWLEDGEMENTS

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Finally, I would like to thank my family and Rukchonlatee's family for all their support, and to Rich for the sacrifices he has made during the writing of this thesis.
SYNOPSIS

Plasticised polyvinyl chloride (PPVC) compounds were biaxially stretched, annealed in the drawn state and subsequently exposed to electron beam irradiation. During sample irradiation the crosslinking reaction was promoted by a radiation sensitising monomer, trimethylolpropanetriacrylate (TMPTMA), included in the PVC compound formulations. The influence of stabiliser type and level, TMPTMA level and irradiation dose on the network structure produced was investigated. A tin stabiliser, Stanclere TL, was selected for this study as it promoted the crosslinking reaction and it showed no interfering peaks in the wide angle x-ray diffraction (WAXD) traces which were used to follow the development of structural order. The appearance of gel, the material insoluble in THF, in irradiated oriented samples proved that a crosslinked structure was created. The gel formation increased with TMPTMA level and irradiation dose. The gel content was found to affect mechanical properties at elevated temperatures and produced an increase in the area shrinkage temperature. Sample thickness and the plasticiser content were found to have a major effect upon gel formation. The thicker the sample was, the smaller the quantity of gel that was formed. Samples containing 46.5phr plasticiser showed greater gel content than samples containing 25phr plasticiser as a result of the higher molecular mobility in the more plasticised samples. It was also found that the orientation of the film decreased the efficiency of network formation in PVC formulations with a 46.5phr plasticiser content but no significant change in gel content could be detected in those containing 25phr plasticiser.

Tensile properties and impact strength at room temperature were slightly improved in irradiated samples. The modified structure resulted in an improvement in tensile strength and penetration resistance at higher temperatures and an increased area shrinkage temperature. Crosslinking did not affect room temperature recovery or crystalline orientation; however irradiation crosslinking reduces crystalinity.
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1.1 GENERAL

The repeat unit of the PVC polymer chain is [-CH₂-CHCl-]. The polar groups in the molecule give rise to strong intermolecular bonds which join adjacent polymer chains rigidly together. Therefore, PVC is a stiff and inflexible material. The use of plasticiser converts the inherently hard PVC polymer into compositions with varying degrees of softness and flexibility, which are processable into a variety of products with diverse properties and uses. A plasticiser is a substance of low or negligible volatility, suitably compatible with the polymer into which it is incorporated. The significant consequences of plasticisation are the lowering of the glass transition temperature (Tg), softening temperature, reduction of strength and increased impact resistance.

PVC plasticisers are mainly organic esters with high boiling points. About two-thirds of the plasticisers in general use are diesters of phthalic anhydride with C₄-C₁₀ alcohols. Examples of plasticisers in this group are dioctyl phthalate (DOP), di-iso-octyl phthalate (DIOP), di-isodecyl phthalate (DIDP), etc. The other classes of more specialised plasticisers are triaryl phosphates, alkyl esters of dibasic alkyl acids, alkyl trimellitate esters, high-molecular-weight polyesters and epoxies. The important parameters for selecting the plasticiser for each system are:

1. compatibility and ease of mixing with the PVC polymer
2. effectiveness in producing the softness and flexibility of plasticised PVC
3. permanence
Dehydrochlorination is the initial step in the degradation of PVC when it is exposed to heat and mechanical shearing in the course of processing, or during service when the material experiences heat or ultraviolet light. The main products of this reaction are hydrogen chloride, as a toxic and corrosive gas, and polyene structures. The presence of degradation products in PVC components dramatically reduces their mechanical and electrical performance. The evolution of hydrogen chloride gas is obviously harmful to both machinery and those who operate it. The polyene structures produce colour in PVC materials containing degraded products, due to the absorption of light by the double bonds present within the polyenes. The decomposition process can be inhibited by the incorporation of stabilisers. Some reactions performed by stabilisers are summarised:\(^{(1-2)}:\)

- Reaction with hydrogen chloride. It is important to remove hydrogen chloride from the system as it further catalyses thermal degradation\(^{(3)}\).
- Reaction with allylic chlorides to stop further dehydrochlorination.
- Reaction with double bonds in polyene structures.
- Free radical absorption, since the degradation process proceeds by a radical path.

The stabiliser is thus, next to the polymer, the second most important constituent of every PVC composition. The compounds used as heat stabilisers for PVC may be divided (by chemical type) into the following general groups.

1. lead compounds
2. organotin compounds
3. compounds of other metals
4. organic stabilisers

The way of selecting a stabiliser or mixture of stabilisers depends on the application of
the final product and manufacturing costs.

Besides stabiliser and plasticiser, other components are often included in PVC formulation, mainly for easier processing and particular end-use properties. An external lubricant, e.g. stearic acid, counteracts sticking of the melt to hot equipment surfaces in processing. An internal lubricant, e.g. calcium stearate, reduces frictional effects between PVC grains. A processing aid is included to improve melt properties and fusion characteristics. An impact modifier is incorporated in the composition to impart toughness to the relatively brittle PVC polymer. Fillers are often incorporated as cheapening extenders, but in some cases the attendant effects on some properties may be useful, e.g. reduced shrinkage, increased hardness and stiffness.

PVC is well-known for its excellent properties such as good insulation, heat and fire resistance, high mechanical strength, toughness and formulation versatility and has been proved to be cost-effective for a wide variety of uses, for example cable insulation, sheathing and plastic pipe systems. However, this material presents some problems. The use of PVC may be limited, by its performance at higher pressures and temperatures. It has a tendency to flow and to have a reduced mechanical strength at elevated temperatures and it also lacks abrasion resistance. Ways to improve the properties of PVC have been extensively studied and crosslinking has been one of the methods used. Crosslinked PPVC shows an increased softening point, over PPVC, leading to a raising in its maximum service temperature.

When PVC is stretched and annealed, molecular orientation occurs and can strongly influence the properties of the system. The large change in properties on orientation is due to both crystalline and amorphous orientation. However, oriented PVC is not suitable for use at high temperature, due to its shrinkage.
1.2 MORPHOLOGY OF PVC

The morphology of PVC has been extensively studied. It was found that morphology is responsible for the physical property characteristics of the polymer. The morphology of a grain of PVC considerably affects the ability of the particulate polymer to absorb plasticiser. The morphology depends on many factors, including the ways of producing PVC resins. The four commercial processes are suspension, bulk, emulsion and solution polymerisation, but approximately 80% of PVC is produced by suspension polymerisation. PVC resins or grains prepared by this process are known to consist of irregularly shaped, porous granules of the order of 100 μm in diameter.

During suspension polymerisation, the first species formed are macro radical coils which aggregate rapidly to produce micro domains or basic particles. This species is unstable and aggregates to form domains. The domains also aggregate and form primary particles which continue to grow at the expense of the monomer to give grains of PVC approximately 150 μm in diameter. The simple representative of this mechanism was published by Allsopp as shown in Figure 1.1.

A number of investigators have tried to observe the micro domains by using a variety of techniques. Hattori et al. have studied the particle formation of suspension PVC by using electron microscopy. Approximately spherical 0.1 μm diameter particles were seen in the 10 μm diameter grains while the polymerisation reaction was in progress. They also observed that the 1 μm primary particles were broken down to form fibrils 10-30nm in thickness during powder extrusion. Their diagram of PVC powder morphology is shown in Figure 1.2. Neilson and Jabarin and Wenig revealed the existence of microdomains in unplasticised PVC (UPVC) using small-angle- x-ray scattering.
Chapter 1 Introduction

Coiled macro radicals

Micro domains

Domains

Primary particles

Primary particle aggregates

PVC grain

<table>
<thead>
<tr>
<th>SIZE</th>
<th>CONVERSION</th>
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<tbody>
<tr>
<td>&lt;1%</td>
<td></td>
</tr>
<tr>
<td>10-30 nm</td>
<td>1-2%</td>
</tr>
<tr>
<td>0.2-1.5 nm</td>
<td></td>
</tr>
<tr>
<td>1-2 um</td>
<td>4-10%</td>
</tr>
<tr>
<td>65-150 um</td>
<td>90%</td>
</tr>
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Figure 1.1 Scheme for polymer precipitation inside vinyl chloride droplets during polymerisation

Figure 1.2 PVC particle morphology
This composition of a PVC grain was also supported by determining the temperature torque profile of a PVC compound in a Brabender Plasticorder mixing chamber. Three characteristic peaks in the torque temperature trace were found and it is suggested that these peaks are associated with the breaking down of the PVC powder particles, microgranules, and primary particles.

1.3 Fusion of PVC

PVC products are produced by blending PVC powder with the necessary additives in a high speed mixer and followed by processing by an appropriate method e.g. compression moulding or extrusion. During processing, gelation or fusion, in which the powder grains are broken down to produce a continuous network, takes place. The fusion process is highly dependent on both shear and thermal history of the polymer. The fusion behaviour of grains is governed by the processing method, and also by the additives which are normally initially present at the grain surfaces. It has been suggested that the distribution of the additive on the powder influences grain fusion. Allsopp has suggested two routes for grain and primary particle fusion. The overall view of fusion, by Gilbert et al., postulating a melting and recrystallising process leading to network formation at the later stages of the process is shown in Figure 1.3.

The level of fusion is an important factor in determining the mechanical strength and fracture behaviour of processed products, therefore, various methods for assessment of fusion have been developed.
Tensile properties can be used to indicate fusion level, since the greater the fusion, the higher the tensile strength. In this test, a specified form of a large amount of sample is required, so it is not suitable for quality control process.

In solvent immersion tests for assessing fusion levels, processed PVC samples were immersed in a fairly compatible solvent, such as acetone or methylene chloride. This test is very convenient but it cannot be used to distinguish samples possessing a fusion level over about 70%\(^{(13)}\).

A rheological method for assessment of fusion was developed by Gonze\(^{(14)}\) and Lamberty\(^{(15)}\) and is used by a number of workers\(^{(11,16,17)}\). In this method, the capillary entrance pressure loss is measured while samples of varying states of fusion are extruded through a zero length die at a temperature below that of the processing.
temperature. By plotting capillary rheometry extrusion pressure against processing temperature, it is possible to produce a standard fusion curve.

Gilbert and Vyvoda\textsuperscript{(18)} used a thermal analysis technique for investigating gelation of rigid PVC components. They suggested that the area of the broad endotherm ranging from about 110°C to the maximum processing temperature in the thermogram appears to be related to the level of fusion since the energy of this endotherm arises from the breakdown of less ordered structures produced during cooling after processing. This suggestion was supported by Isles and Delatycki\textsuperscript{(19)} who used DSC to follow the changes within the microdomains due to processing.

1.4 CRYSTALLINITY

Crystallinity in PVC can be divided into two types: primary crystallinity and secondary crystallinity\textsuperscript{(20)}. Primary crystallinity is of relatively high order, occurring in virgin powder and single crystals prepared with special care. It is destroyed by heat during processing, while secondary crystallinity forms on subsequent cooling. This secondary crystallinity creates a network on fusion or gelation. Many workers\textsuperscript{(17,20,21)} have proved that recrystallisation or secondary crystallisation from a PVC melt produces a less ordered structure than the primary crystallinity. This results in a lower melting temperature, a lower heat of fusion and higher solvent sorption\textsuperscript{(21)}.

Natta and Corradini\textsuperscript{(22)} were the pioneers who investigated the structure of crystalline PVC by using wide angle x-ray diffraction (WAXD). Using oriented fibres of PVC, prepared with the aid of free radical catalysts, they found the crystal structure to be orthorhombic with unit cell dimensions $a = 10.4\AA$, $b = 5.3\AA$ and $c = 5.1\AA$. This structure has been supported by Wilkes et al.\textsuperscript{(23)} studying oriented mats of single
crystals with WAXD. Their results showed that the orthorhombic crystal unit cell is more compact than that of Natta and Corradini with the dimensions $a = 10.24\AA$, $b = 5.24\AA$ and $c = 5.08\AA$.

Mammi and Nardi\textsuperscript{(24,25)} studied the x-ray diffraction pattern of oriented and unoriented PVC samples. They have found that some reflections cannot be ascribed to the orthorhombic crystal form. They attributed these reflections to the so called mesomorphic or nematic structures which appear after annealing stretched fibres at 87-107$^\circ$C. These nematic structures consist of straight chains aligned in parallel with a distance between the axes of 5.4\AA. The reflection from nematic structures of PVC was also found by Lebedev et al.\textsuperscript{(26)} after annealing at a temperature above the glass transition temperature. Another work of Lebedev\textsuperscript{(27)} showed that samples annealed at 110$^\circ$C produced the reflections from orthorhombic and nematic structures at the same time, which means that the alignment of chains proceeds simultaneously with the formation of real orthorhombic crystallites.

In PVC, it is possible for the chloride atom to have two different arrangements about the polymer chain backbone. Consider the case where all the chlorine atom are found in the same relative position; the resulting structure is known as an isotactic chain.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {H};
\node at (0.5,0) {H};
\node at (1,0) {H};
\node at (0.25,0.5) {\text{-CH}_2\text{-}};
\node at (0.5,0.5) {C};
\node at (0.75,0.5) {\text{-CH}_2\text{-}};
\node at (1,0.5) {C};
\node at (1,1.25) {\text{-CH}_2\text{-}};
\node at (1,1.5) {C};
\node at (1,2.25) {\text{-CH}_2\text{-}};
\node at (1,2.5) {C};
\node at (0.5,1.75) {\text{-Cl}};
\node at (1,1.75) {\text{-Cl}};
\node at (1.25,1.75) {\text{-Cl}};
\node at (0.75,2.5) {\text{-Cl}};
\node at (0.25,2.5) {\text{-Cl}};
\end{tikzpicture}
\end{center}

\textit{isotactic}

If, on the other hand, the atoms are in alternating configuration, a syndiotactic chain is
A third possibility is where the chlorine atoms are positioned randomly, hence the structure is termed atactic.

It was found that PVC with a very high proportion of the syndiotactic structure was highly crystalline, and showed higher melting temperatures than those of atactic PVC grades\(^{(20)}\). This has led to the idea that only the syndiotactic parts in the PVC chains are able to form crystallites. However, commercial PVC have a tacticity of about 55% which means that the polymer is almost atactic but some crystallisation can occur.

Juijn et al.\(^{(28)}\) studied crystallinity in atactic PVC and said that the crystalline phenomenon in PVC cannot be explained by assuming that only the syndiotactic chain segments crystallise. Consequently, some isotactic chain segments must be able to crystallise. Another reason to support this idea is that the orthorhombic crystal form is independent of tacticity of the PVC: Natta and Corradini\(^{(22)}\), Smith and Wilkes\(^{(29)}\) and Nakajima and Hayashi\(^{(30)}\) studied atactic PVC, syndiotactic PVC and a combination of syndiotactic and atactic PVC, respectively, but they all found the orthorhombic lattice. However, the model of Juijn et al. is similar to that of Natta and Corradini except that the isotactic chain fits perfectly in the orthorhombic cell, surrounded by syndiotactic chains. (Figures 1.4-1.7)
Recently, Hobson and Windle\cite{31,32} have studied x-ray diffraction patterns of PVC with varying sample tacticity and identified a crystal structure in which both isotactic and syndiotactic sequences are incorporated within the same lattice. They presented a short summary of molecular and diffraction modelling results which show the effect of crystalline tacticity on the intensities of the 200 and 110 peaks.

The tacticity depends very strongly on polymerisation techniques. Highly syndiotactic PVC is obtained by polymerisation in the presence of butyraldehyde\cite{33} and irradiating the urea inclusion complex of vinyl chloride at -78°C\cite{34}. For the emulsion and suspension processes, the commercially important polymerisation techniques, the polymerisation temperature is the most important factor influencing the tacticity of the polymer. However, the crystallinity is not controlled only by the tacticity but also by the mechanical and thermal history of the PVC. For example, stretching increases the crystallinity of the material.

Commercial PVC is considered to contain about 55% of syndiotactic diads\cite{35}. X-ray diffraction has indicated that the level of crystallinity in UPVC is of the order of 10%\cite{9,36-40}. In 60 phr PPVC, the crystallinity was found to be reduced to about 4%\cite{39}. By DSC measurement, the PVC formulations containing 20-30% by weight of plasticiser was determined to have a crystallinity value of the order of 7-8%\cite{40}, therefore both UPVC and PPVC are known to be semicrystalline polymers. This semicrystallinity is accepted to be a three-dimension network structure in which the small crystallites act as crosslinks\cite{40-46} (Figure 1.8).
Figure 1.4 Model of the orthorhombic structure of polyvinylchloride

Figure 1.5 Comparison of the syndiotactic and isotactic straight chains.

Longitudinal section
Figure 1.6 Comparison of the syndiotactic and isotactic straight chains

Cross-section

Figure 1.7 Model of the structure of PVC. Combination of syndiotactic and isotactic chains segments in the orthorhombic lattice
Molecular orientation in a solid polymer may have a profound influence on the macroscopic physical properties of the polymer. Polymer fibres and films are the important commercial products, with their strength resulting from oriented crystal morphology, brought about by stretching and the subsequent crystallisation processes. Nowadays, this process is used not only in fibres and films but also in many application areas, for instance, pipe and stretch blow moulded bottles. However, orientation can be disadvantageous because it causes mechanical and optical properties to be anisotropic i.e. different properties in different directions. The biggest problem area is the undesirable orientation occurring during injection moulding and leading to anisotropy. As a result, the products have dimensional instability and poor mechanical properties.

Previous research on stress-induced crystallisation of polymer networks has been carried out by a number of workers. Katz, using x-ray diffraction, was among the first to investigate crystallite orientation and size in rubber-like synthetic substances which crystallise when stretched. Sometime later Flory evaluated the first
thermodynamic treatment of polymer crystallisation induced by stretching, which included two topics. Firstly, the strain over and above the isotropic equilibrium melting point causes melting point elevation. Secondly, he discussed the relationship between the increase in degree of crystallinity at constant elongation and temperature and the relative decrease in stress at crystallisation equilibrium with elongation and temperature. The latter relation was based on the assumption that crystallisation (nucleation and growth) at constant elongation occurred along the strain direction, suggesting the following: a) that the strain-induced nuclei had a fringed-micelle chain conformation, and b) that the resultant crystallites due to strain-induced crystallisation and/or additional thermally-induced crystallisation had dimensions comparatively greater in the strain than in the transverse directions. Such deduction about chain conformation and crystal dimensions from non-structural studies should be viewed with caution, especially since the deductions are based on an assumed crystal growth mechanism and direction that was shown to be wrong\(^\text{50}\). Nevertheless, these deductions seemed rather reasonable based on what was known at the time about polymer morphology, especially if it was assumed that the starting amorphous polymer had a random coil chain conformation. Stretching would be expected to extend and orient the randomly coiled macromolecules in the stretch direction. Upon phase transition, the aligned neighbouring segments would be expected to lead directly to crystallites with a fringed-micelle chain conformation that is not so different from the as-stretched chain conformation. Any crystal growth would also be expected to continue along the stretch direction rather than perpendicular to it.

Gent\(^\text{51}\) carried out a series of experiments including simultaneous volume and stress relaxation measurement from several polymers that were crystallised under strain at temperatures below their isotropic melting point. He concluded from the results that the crystal melting temperature which increased with the imposed extension, showed a
Jude and Stein\(^{(52)}\) studied axial length changes at constant load during crystallisation of crosslinked polyethylene from the melt. The results showed that the measured length always increased initially, but contracted later, especially at small loads, and eventually levelled off at long times. It was concluded that the increase in length is caused by a change in chain conformation to fringed micelles, followed by contraction due to chain folding during oriented crystallisation. This result was also supported by Keller and Machin\(^{(53)}\) who proposed a two step mechanism for formation of row-oriented lamellae, the first step resulting in an increase in the axial length began with strain-induced longitudinal nucleation of extended-chain crystals which they suggested occurred in the initial period and the second step followed with a thermally-induced lateral growth of chain-folded crystals, during which the length contractions took place. In addition, their study with wide angle x-ray scattering gave a good agreement with their proposal, consequently annealing at high temperature after stretching contributes to lateral alignment so that the original fibrillar morphology finally disappears and changes to an apparent lamellar type "row morphology", a nematic mesomorphic phase.

This two step mechanism was also supported by Yeh and Lambert\(^{(54)}\) and Yeh and Geil\(^{(55)}\) studying isotactic polystyrene and polyethylene-terephthalate, respectively. Furthermore, they have found that the transformation from a fibrillar morphology to a lamellar morphology can be either irreversible or reversible (leading to shrinkage), depending upon the temperature of the stretching and annealing processes. Another work of Yeh\(^{(56-57)}\) reported that the resulting morphology was very dependent upon the annealing conditions e.g. whether the specimens were free or restrained while annealing took place, and the magnitude of applied strain.
PVC is one of the polymers whose properties can be improved by orientation crystallisation. This polymer as produced contains 5-10% crystallinity but this value can be increased by many techniques\(^{(36,40,58-64)}\) e.g. drawing and annealing. The annealed highly syndiotactic sample made by the urea clathrate method gave the highest value of 76-78% crystallinity\(^{(61)}\).

Illers\(^{(65)}\) studied the influence of annealing on the physical state of technical PVC by calorimetric measurements, suggesting that heat treatment above \(T_g\) causes crystallisation and below \(T_g\) causes a decrease in free volume. Crystallinity changes were shown to have a greater effect on density, solvent sorption and shear modulus than free volume changes.

Molecular orientation behaviour of uniaxially stretched PVC was studied by several investigators\(^{(60-61,63,66-70)}\). For UPVC, tensile properties increased in the draw direction and decreased perpendicular to draw, resulting from the development of two-dimensional order. Annealing caused further changes in the structure, leading to the improvement of properties. Vyvoda et al.\(^{(60)}\) found that the maximum 2-dimensional order for UPVC occurs on annealing at 110°C. Plasticised polyvinylchloride (PPVC), having its \(T_g\) below room temperature, shrinks considerably after stretching. This shrinkage can be reduced by annealing in the stretched state because the ordered structures which hold the oriented chains in position behave as physical crosslinks in the system.

Improved tensile strength in both directions can be achieved by biaxial orientation. Brady\(^{(58)}\) assessed the influence of all the primary processing variables in the biaxial orientation process (temperature, rate and degree of extension) upon the tensile, dynamic mechanical and dielectric properties of non-impact modified PVC. In
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the same year, de Vries and Bonnebat\(^{(59)}\) studied uniaxial and biaxial stretching of PVC and chlorinated PVC sheet with a view to their behaviour in thermoforming process. Optimum forming condition were identified and the effect of biaxial orientation on various properties was also reported. Meijering \textit{et al.}\(^{(71)}\) have demonstrated the benefits of biaxial orientation particularly for properties relevant in gas pipe application.

Robinson \textit{et al.}\(^{(72)}\) compared the results from birefringence measurements of oriented plasticised PVC compounds with those of many workers\(^{(66,69,72-74)}\) and showed that an increase in plasticiser content or draw temperature produces a lowering of the birefringence for a given draw ratio.

Récemment, Gilbert and Liu\(^{(63-64)}\) studied the effect of uniaxial and biaxial orientation on UPVC and PPVC structure and properties. They found results similar to previous researchers. Furthermore, they found that in biaxial orientation the increase of two-dimensional order with draw ratio was much less than that observed after uniaxial orientation and that the amount of ordering is restricted by plasticiser molecules. They also proposed a model to describe the influence of uniaxial and biaxial orientation on the structure of UPVC and PPVC compounds. (Figure 1.9)

It can be concluded that in PVC, chain alignment induces crystallisation which further modifies properties and oriented PVC behaves like a much more crystalline polymer\(^{(64)}\).
1.6 Techniques to Investigate Orientation in PVC

The techniques used to evaluate molecular orientation give data for the orientation function in relation to the mathematical definition of orientation. Therefore, it is important to know how to explain these functions.

The orientation of the chain in the uniaxially oriented polymer is specified by the angle $\theta$ between a particular direction in the polymer specimen, such as the direction of draw, and the molecular chain axis. The quantity, used as a measure of the distribution of the orientations, will be some function of this angle. For reasons of mathematical convenience it is sometimes preferable to express the results of studies of orientation in terms of the average values of the Lagendre polynomials $P_l(\cos \theta)$, where

- $P_0(\cos \theta) = 1$
- $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$
- $P_4(\cos \theta) = (3 - 30 \cos^2 \theta + 35 \cos^4 \theta)/8$
The biaxial orientation is defined in terms of angles $\phi_1$ and $\phi_2$ between the polymer chain axis and the machine 1 and transverse 2 direction. The orientation factors based on the $\phi_1$ and $\phi_2$ system are according to White and Spruiell\textsuperscript{(75)}:

\[
\begin{align*}
I_1 &= 2\cos^2\phi_1 + \cos^2\phi_2 - 1 \\
I_2 &= 2\cos^2\phi_2 + \cos^2\phi_1 - 1
\end{align*}
\]

For the case of isotropy, $I_1$ and $I_2$ are zero. For polymer chains perpendicular to the 12 plane, $I_1$ and $I_2$ are both -1. For equal biaxial orientation, $I_1$ and $I_2$ are equal.

It is possible to graphically present the state of biaxial orientation through a plot of $I_1$ and $I_2$. All possible states of orientation lie within an isosceles triangle with vertex at (-1,-1) and base stretching from (1,0) to (0,0) (Fig. 1.10).

Techniques used to study orientation are shown in Table 1.1\textsuperscript{(76)}. Each technique has its own limitations and different advantages. Therefore, different techniques are used to explain aspects of PVC orientation.
1.6.1 Birefringence

The measurement of birefringence is the most common method of characterising polymer orientation. In this technique, the difference between the refractive indices along two perpendicular directions is measured with polarised light along these directions. It results from anisotropic optical properties of an oriented molecule. This technique measures mean values over all the components and phases present, the details about distribution of orientation cannot be achieved by this technique. However, it has been used by a number of investigators\(^{63,70,72,77-79}\) to study orientation in PVC. It was found that the value of \((\Delta n)_{\text{in plane}}\) increases with draw ratio. By using this technique, Hibi et al.\(^{66}\) found that samples drawn above and below \(T_g\) have different molecular orientations for the same draw ratio because they gave different values of birefringence.

Kotnis and Spruiell\(^{80}\) used birefringence to study biaxially oriented films prepared from PVC/poly(methyl methacrylate co imide)(PI) blends. They chose a coordinate system for the film in which the \(Z\) axis was parallel to the first stretch direction and the \(Y\) axis was parallel to the second stretch direction, whilst the \(X\) axis was normal to the plane of the film. All of the biaxially oriented films had

\[
\Delta_{ZY} = 0
\]

indicating equal biaxial orientation with respect to the second stretch direction. They followed the level of orientation developed in the film by measuring the out-of-plane birefringence, \(\Delta_{ZX}\). The results showed increasing birefringence with draw ratio for each blend and with PI content in the blends. The rising of birefringence with draw ratio can be clearly ascribed to increasing molecular orientation.
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Table 1.1(76)

Methods for studying orientation in polymers

<table>
<thead>
<tr>
<th>METHOD</th>
<th>PART OF STRUCTURE BEING CHARACTERISED</th>
<th>ORIENTATION AVERAGES OBTAINED</th>
<th>EXPERIMENTAL LIMITATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birefringence</td>
<td>Crystalline + amorphous region; average over all chains in polymer</td>
<td>(&lt;P_7(\cos\theta)&gt;)</td>
<td>Transparent specimens required</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>Crystalline regions</td>
<td>Complete characterisation; any orientation average may be calculated</td>
<td>Difficult to quantify with low-crystallinity polymer</td>
</tr>
<tr>
<td>Infrared dichroism</td>
<td>Molecular bond or group, often in amorphous + crystalline regions but sometimes for specific region</td>
<td>(&lt;P_7(\cos\theta)&gt;) and (&lt;P_4(\cos\theta)&gt;)</td>
<td>Very thin specimens required; may set the limit in practice</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td>As infrared dichroism</td>
<td>(&lt;P_7(\cos\theta)&gt;) and (&lt;P_4(\cos\theta)&gt;)</td>
<td>Transparent optically homogeneous and non-fluorescent specimens required</td>
</tr>
<tr>
<td>Broad-line nuclear magnetic resonance</td>
<td>Usually amorphous + crystalline regions but sometimes for specific region</td>
<td>(&lt;P_7(\cos\theta)&gt;) and (&lt;P_4(\cos\theta)&gt;)</td>
<td>Magnetic anisotropy may not be large enough to be useful; detailed molecular structure must be known</td>
</tr>
<tr>
<td>Polarised fluorescence spectroscopy</td>
<td>Usually amorphous regions</td>
<td>(&lt;P_7(\cos\theta)&gt;) and (&lt;P_4(\cos\theta)&gt;)</td>
<td>If the polymer is non-fluorescent, a suitable marker molecule must be used</td>
</tr>
</tbody>
</table>
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This technique is very well known and results compare closely with other techniques such as NMR, fluorescence and Raman spectroscopy.

1.6.2 X-ray Diffraction (XRD)

XRD has been used by many workers to study the structure of PVC. Some examples of WAXD traces of non-crystalline PVC, consisting of a combination of the crystalline \( A_x \) and amorphous scattering \( A_\alpha \), are shown in Figure 1.11\(^{36}\). Order factors can be calculated as described by Rayner and Small\(^{85}\):

\[
\text{Order factor} = \frac{A_x}{A_x + A_\alpha} \times 100\%
\]

From this value, the crystallinity in the PVC sample can be measured. When PVC is oriented, the crystallinity is increased, therefore, a change in the WAXD pattern can be detected. Mammi and Nardi\(^{25}\) and Lebedev et al.\(^{27}\) reported that x-ray texture patterns of oriented PVC show the 24.5°2θ reflection to be independent of azimuthal angle whereas the 17.5°2θ halo is present in the equatorial but absent in the fibre axis direction. They attribute these results to a mesomorphic or nematic phase whose order consists in a parallel arrangements of chains. Brady and Jabarin\(^{68}\), Gilbert and Vyvoda\(^{62}\) and Vyvoda et al.\(^{60}\) have also observed an increase in the intensity of reflections showing a sharpening of 17°2θ peak in the WAXD pattern. Peaks in this angular region have been shown\(^{22}\) to be due to (010) (200) and (110) sets of the planes.
Figure 1.11 X-ray diffraction patterns for polymer annealed 5 hour:
(A) low temperature polymerised PVC ; (B) PVC2 at 100°C ; (C) PVC2 at 40°C

Vyvoda et al.\(^{(60)}\) have concluded that cold-drawing of compression-moulded material leads to a reduction in 3-dimensional order in the mouldings (a decrease in height of the 24°2θ peak) and an increase in 2-dimensional order (an increase in the 17°-19°2θ peak). As a result, after stretching the anisotropy of mechanical properties increases.

Liu and Gilbert\(^{(63-64)}\) noted that the order factor of uniaxially stretched PPVC increases with draw ratio, sharply at first, and then appears to reach a limiting value. Annealing temperatures are also shown the effect on order factor; the higher the annealing temperature, the greater the order factor. For the biaxially drawn samples, they reported that the value of the order factor is less than that observed in the uniaxially drawn samples.

More recently, Gilbert et al.\(^{(86)}\) used A-peak ratio to evaluate biaxial orientation of PVC. Figure 1.12 shows the change in the x-ray diffraction patterns of the UPVC samples at different draw ratios. The peak labelled A was ratioed to the equivalent
peak in an undrawn compression moulding. It was found that this ratio increases with draw ratio (Figure 1.13), and was highest for the UPVC.

![Graph](image)

**Figure 1.12 X-ray diffraction patterns for oriented samples**

1.6.3 IR Spectroscopy

The IR studies of PVC are focused on the influence of the configurational and conformational changes of the C-Cl groups stretching bands between 600-750 cm\(^{-1}\). It is a good tool for studying syndiotacticity and conformational fractions. Therefore, IR spectroscopy can provide qualitative information about orientation because the oriented PVC consists of a longer fraction of trans-trans or extent structure which can lead to the formation of crystalline areas during thermal treatment. The absorbance of two strong peaks at 602 and 640 cm\(^{-1}\) and a weak band at 690 cm\(^{-1}\) have been ratioed as follows: \(A_{602}/A_{690}\) and \(A_{640}/A_{690}\) are measures of the proportion of syndiotactic units in planar conformation and hence used as a measure of the crystallinity.\(^{(81)}\)
Infrared dichroism can also provide quantitative measurement of orientation by the use of dichroic ratios which relate to certain orientation functions characteristic of the average orientation of structural units within the polymer.

Theodorou and Jasse (67) studied orientation in pure and plasticised PVC by using FTIR. The results showed that orientation increases with draw ratio and that long all-trans syndiotactic sequences orient more readily than amorphous conformations. They also noted that a plasticiser does not affect the orientation of PVC at a given draw ratio. These results are in agreement with those of Shindo et al. (74) and Umemura (87), but in conflict with those of other workers (66, 69-70, 88), who suggested that orientation decreases with an increase in either temperature or plasticiser content.
1.6.4 Raman Spectroscopy

In this technique, the intensities of Raman scattering in C-Cl the stretching region of the infrared spectrum are measured and these data are analysed to give \( <P_2(\cos\theta)> \) and \( <P_4(\cos\theta)> \).

Amongst the pioneer workers, Robinson et al.\(^{(89)}\) and Maddams et al.\(^{(90)}\) studied the alteration of the stretching mode of C-Cl groups brought about by changes in tacticity, conformation and crystallinity of PVC. These properties were used to evaluate molecular orientation by Robinson et al.\(^{(72)}\) They reported that when PVC samples undergo cold drawing, the distribution of syndiotactic and atactic sequence orientations are identical, whereas hot drawing makes the syndiotactic fraction more oriented than the atactic fraction.

1.6.5 Fluorescence Spectroscopy

Since PVC is non fluorescent, it is necessary to add a suitable molecule to the PVC chain to create a fluorescing group in PVC molecule. Hibi et al.\(^{(91)}\) used the fluorescence of polyene and carbonyl groups produced by heat treatment to investigate the orientation behaviour of a non-crystalline chain and the molecular orientation behaviour in the uniaxially stretched film. This modified PVC is better than others created by the addition of fluorescent dyestuffs, because with the addition of dyes the distribution of orientation of the polymer chains must be related back to the orientation of the molecules of the additive. However, this method cannot be used directly to estimate the orientation distribution, because it is necessary to know the ratio of polyene to carbonyl-molecular distribution function to postulate the relationship. This is usually difficult, and is a significant disadvantage.
1.6.6 Nuclear Magnetic Resonance (NMR)

The broad line NMR measurements of the anisotropy of the proton magnetic resonance second moment at liquid nitrogen temperature for a series of drawn PVC samples have been studied by Kashiwaghi and Ward(69). The data were used to calculate orientation functions which characterise the molecular orientation. They found that the orientation functions for the drawn samples are shown to be consistent with those obtained from pseudo affine deformation of the aggregate units in the drawing process and there is a good correlation with birefringence data.

1.7 Effect of Irradiation on PVC

It is well known that crosslinking of PVC can be induced by irradiation with an electron beam or γ-rays, but the predominant reactions are dehydrochlorination and chain scission which lead to undesirable material properties. All reactions are largely dependent upon the radiation dose and radiation time. Crosslinking confers insolubility while the degradation becomes primarily evident by decolouration. Shapiro(92) and Alexander et al.(93) discovered these properties of PVC whilst they tried to crosslink PVC with high energy irradiation (>20 Mrad). Miller(94) found that the addition of radiation sensitisers, e.g. polyfunctional unsaturated monomers, lead to efficient crosslinking reactions with low dehydrochlorination at low irradiation doses, and therefore that specially formulated crosslinkable compounds containing a radiation sensitiser are required. Upon irradiation the sensitiser is polymerised and crosslinked into a three-dimensional network into which the PVC is incorporated via a grafting reaction(94-95). Polyfunctional monomers that have been shown to act as such crosslinking sensitisers for PVC include, allyl esters(96), dimethacrylates(94-95,97-98), trimethacrylate(95,97,99), triallyl isocyanurate(100), and triacrylates(95). The polyfunctional
methacrylates and acrylates were found to have the greatest sensitivity, especially trifunctional monomers such as trimethylol-propanetriacrylate (TMPTMA) and trimethylolpropanetriacrylate. Their use is highly advantageous because they are effective plasticisers for PVC, forming good contacts with the PVC chains and facilitating the grafting reaction. They also produce high yields of radicals during irradiation as a result of their high sensitivity to irradiation.

In addition, there are many variables affecting the occurrence of crosslinks such as irradiation dose, crosslinking monomer concentration, temperature of irradiation and the presence of plasticiser and stabiliser.

The mechanism of electron irradiation crosslinking of PVC using polyfunctional acrylic monomers was investigated by Salmon and Loan. During the first stage of the process, the radiation was found to produce free radicals on the PVC chains and monomers. In the second stage, the monomers were found to undergo rapid polymerisation. The final step involved grafting of the polymer chains formed by the polymerisation of the activated monomers onto PVC chains, to form a three-dimensional network. Polyfunctionality of the monomer was necessary for crosslinking to occur since butyl methacrylate containing only a single unsaturated bond did not crosslink readily. trimethylolpropane triacrylate, a triunsaturated compound, showed 40 times the radiation sensitivity of tetraethylene glycol, a diunsaturated compound. Based upon their mechanism, the radiation sensitisier TMPTMA would produce the irradiation crosslinking mechanism as displayed in Figure 1.
Figure 1.14 Irradiation crosslinking mechanism \(^{(87)}\)
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Hell et al. (103) examined the higher dose radiation crosslinking of PPVC in the presence of triallyl cyanurate as a sensitisier, DOP as a plasticiser and lead and tin stabilisers. Lead stabiliser gave very good crosslinking yields and the colour stability was good for radiation doses up to 150 kGy. Tribasic lead sulphate accepts HCl, formed in the dehydrochlorination reaction during thermal and irradiation processing, without inhibiting the crosslinking. Tin stabilisers conferred very good colour stability of samples even up to 300kGy doses, but they strongly inhibited the crosslinking process.

Kajima, Kumafuji and Ueno (104), in a study of discolouration of irradiated crosslinked PPVC found that the lower the irradiation dose, the less the discolouration of irradiated PVC. The optimum irradiation dose for PVC was under 12 Mrad. The irradiated PVC discoloured less when the amount of plasticiser was increased. It was caused not only by dilution of colour but also by the suppression of formation of the conjugated double bonds which are produced due to the interaction of the crosslinking agent with PVC molecules. PVC using tin or Ba-Zn stabilisers had less discoloration by irradiation in comparison with lead stabilisers, but after heat treatment, PVC using tin and Ba-Zn stabilisers discoloured remarkably. The Ba-Cd-Zn complex also was recognised to be a poor stabiliser against colour formation upon over-ageing (105).

de Hollain (106) found that different plasticisers bring about an altered network stability of the crosslink structure and changed crosslinking efficiency. He also found the effect of the increase in the free radicals, after storage for 3 weeks, brought about a reduction of tensile strength (which is then lower than that of unirradiated PVC). They suggested that the motion of these radicals can initiate a degradation process and even cause main-chain scission in PVC. This undesirable result was observed during earlier work carried out by Dobo (98), in an extensive study on radiation crosslinking of PVC.
with ethylene glycol dimethacrylate, which revealed an inexplicable increase in the concentration of free methacrylate radicals after storage of one week.

Bowmer et al.\(^{(107-109)}\) in a study on radiation crosslinking of PVC with TMPTMA, found that there was an initial preference for TMPTMA homopolymerisation using 30-40% of the available bonds after which the remainder of the double bonds grafted to PVC to form the network. Increasing the irradiation temperature up to 80°C increased all reaction rates but at temperatures greater than 80°C, the dehydrochlorination of the PVC began to compete with the grafting and crosslinking mechanisms. Furthermore, post-irradiation annealing may increase the crosslink density due to the reaction between the residual monomer molecules and the unreacted double bonds in the crosslinked network. The addition of phthalate plasticiser to the PVC composition considerably enhances the crosslinking reaction, and in its presence effective crosslinking may be achieved at room temperature\(^{(108)}\). As the phthalate plasticiser content increases the insoluble part also increases, due to a higher percent of the crosslinked material\(^{(110)}\). The added phthalate plasticiser acts as a lubricant between adjacent polymer chains and allows greater movement within the PVC molecules. The increased mobility of the chains leads to a higher rate of migration of the free and trapped radicals, which in turn increases the probability of radical collision\(^{(111)}\).

Nethsinghe and Gilbert\(^{(112)}\) investigated the structure and properties of irradiation crosslinked PPVC, using a PVC system containing DIOP as a plasticiser and TMPTMA as a crosslinking monomer. They found that increased irradiation doses at constant TMPTMA concentration markedly increased the crosslinking efficiency (gel yield). However, further increases in radiation intensity above 4 Mrad had less effect. From a crosslink density study, it was shown that crosslink density increased to
a maximum at an irradiation dose of 4 Mrad, then decreased as the irradiation dose is increased further. They explained that the initial network formed by the crosslinked TMPTMA broke down, at irradiation doses greater than 4Mrad, and the resulting radicals formed reacted with more PVC molecules to give a more open structure. In contrast, crosslinking density increased with TMPTMA concentration at constant irradiation dose, however the gel yield increased with TMPTMA loading. Part 2 of their paper documented work\(^\text{113}\) carried out on samples produced with varying concentrations of TMPTMA and with different radiation doses. Studies involved thermomechanical analysis and the determination of mechanical properties both at room temperature and 130°C. TMA traces showed the effect of the increased irradiation dose and the increased TMPTMA concentration. Crosslinking causes the development of a plateau in the TMA trace, which reflects the modulus of the sample, and an increase in the softening temperature of PVC. The crosslinking causes only minor changes in room temperature properties but a significant change in tensile properties at 130°C. The UTS increases with the irradiation dose and TMPTMA loading. Elongation at break increases with the irradiation dose, but rises to a maximum point and then falls away when plotted vs TMPTMA concentration. They explained that the difference in elongation behaviour as a function of the two variables must be attributed to the different types of network structure present. The difference in behaviour at the two temperatures is a consequence of chain mobility which is greater at high temperatures and hence the restriction in mobility caused by the crosslinks has a much more significant effect at higher temperatures. Flow in the unirradiated PVC is only prevented by the presence of small crystallites in the network, which act as physical crosslinks\(^\text{11}\). At 130°C crystallites partially melt, as can be seen from the endotherm starting around 100°C in the DSC thermogram\(^\text{18}\); in contrast chemical network structures still remain at higher temperatures.
1.8 Effect of Crosslinking on PVC

The mechanical performance of PPVC is very favourable, since the material’s usual operating temperature is well above $T_g$. The flow behaviour of PPVC is similar to that of a lightly cross-linked gel (i.e., a rubber type behaviour). This has been the subject of much debate, but the most reasonable explanation is the presence of a physical network consisting of a small crystallites\(^{(11)}\). An obvious way to increase the maximum useful operating temperature of PPVC products is to introduce a permanent chemical network (crosslinking structure) into the material.

Besides irradiation crosslinking (as mentioned in the previous section), chemical networks can be introduced by chemical crosslinking. Chemical methods involving reaction with organic peroxides are not satisfactory since degradation predominates over crosslinking and crosslinking would be introduced during processing\(^{(94)}\). Multifunctional organic mercapto compounds give very good results\(^{(114-119)}\) but practical applications are prevented especially by processing limitations and also by the decreased thermal stability of the products. Organosilanes are the alternative crosslinking agents that have been used by a number of investigators\(^{(120-125)}\). Chemical crosslinking is normally a two-step procedure. Firstly, compounding and forming must be performed under conditions which do not activate the crosslinking reactions, which are initiated in the second step, often by application of heat, usually by immersion in hot water. The process has its disadvantages, namely susceptibility to premature crosslinking and degradation of the PVC.

An early application area for irradiated PVC was general purpose wiring insulation for compact equipment such as radios, television sets, and computers since it gave good resistance to heat damage brought about by the use of soldering irons.
during assembly. Polytetrafluoroethylene (PTFE) shows the best properties for this purpose. Bennett(126) studied the hot soldering iron resistance and deformation resistance of PVC, crosslinked PVC and PTFE. He found that crosslinked PVC offered a practical degree of soldering iron resistance, but the irradiated crosslinked PVC additionally offered much improved mechanical deformation resistance in service. These advantages of crosslinked PVC in the field of wire insulation were also found by a number of researchers(105,127-132). The application of irradiated PPVC in pipes was studied by Hell et al.(101). They found that the resistance to internal pressure of crosslinked PPVC pipes at 80°C was higher than that of unirradiated PPVC pipes.

Hjertberg and Dahl(115) studied the co-operation between chemical and physical networks in crosslinked PPVC. DSC and penetration as a function of temperature were used to detect the change in melting behaviour and to follow the change in mechanical properties, respectively. Chemical crosslinking was performed by using a dithioltriazine. Figure 1.15 shows that even rather low degrees of crosslinking, hence low gel content, gave a substantial reduction in penetration over the temperature range 60-110°C, while a more complete crosslinking reaction prevented major penetration up to at least 200°C. The penetration curve of heavily crosslinked materials showed several plateaus and the transitions could be related to the melting of different crystallites formed by annealing at various temperatures. The physical network formed by the crystallites constitutes an important complement to the chemical network in PPVC crosslinked by dithioltriazine. Both the amount and the melting temperature of the crystallites increased after annealing. The introduction of the chemical network further improved the heat resistance of the crystallites. The presence of the two networks therefore shows a synergistic effect with respect to the mechanical properties at increased temperatures.
Some features of crosslinked PVC are summarised as follows$^{(133-134)}$:

1. Formulation flexibility - Crosslinked PVC can be compounded to meet varying property requirements.

2. Excellent abrasion resistance - Abrasion resistance is improved by a factor of 10 or better after irradiation.

3. Improved toughness - Resistance to cut through is upgraded markedly. This effect is enhanced at temperatures in excess of 100°C.
4. Resistance to high temperature deformation - Appropriately formulated crosslinked PVC will withstand application of a weighted solder iron at 350°C.

5. Reduced solubility in many solvents

6. Dimensional stability- Shrinkage effects at elevated temperatures are significantly reduced.

7. Opportunity to reduce thickness and weight - Due to excellent physical properties of crosslinked PVC.

8. Retention of the processing advantages of thermoplastic PVC - Because irradiation crosslinking is not carried out until forming operations have been completed.

In conclusion, the three dimensional polymeric network of crosslinked PVC gives rise to a superior range of properties and new application possibilities.

1.9 EFFECT OF ORIENTATION ON PVC

As stated in section 1.5, monoaxial orientation of UPVC resulted in increased tensile strength in the draw direction whilst reducing it in transverse direction. Similar effects can be induced in PPVC samples, providing that they are annealed in the stretched state prior to cooling. There is a keen interest in biaxial orientation (the planar orientation of molecules) since it produces good planar properties.
Work recently undertaken by Gilbert et al.\textsuperscript{(86,135)} has highlighted the relationship between biaxial conditions, properties and structure. They concluded that the draw ratio has the most significant influence on the mechanical properties of biaxially oriented samples of both UPVC and PPVC. It was shown that alteration of the draw and annealing temperatures delayed the onset of sample shrinkage upon heating. Tensile properties were measured in the biaxial stretch directions of the samples (0° and 90°) and also at 45° to these. The results were found that the tensile properties were the same over the whole of the plane of the film. It appears that molecular chains were uniformly aligned in the plane of the film by the stretching process. The presence of aligned polymer chains will increase strength, but restrict further chain extension so that elongation at break is reduced. Impact strength increased linearly with draw ratio as a result of alignment of PVC molecules in the plane of the film. In contrast, tear strength decreased with increased planar strain. They suggested that planar orientation will reduce the amount of chains and loops perpendicular to the sheet plane, thus tearing can occur more easily in the plane of the sheet. This effect was proved by scanning electron microscope (SEM) photographs of the tear surfaces. The undrawn sheet produced an irregular surface, whilst that for the biaxially drawn sheet shows regular parallel tears. It was apparent that biaxial orientation produced a laminar structure.

Gilbert and Hitt\textsuperscript{(86,136)} examined sample shrinkage caused by heating, using thermomechanical analysis (TMA). The effect of drawing and annealing temperatures upon the variation of area shrinkage with temperature is shown in Figure 1.16. An increase in annealing temperature modified the shrinkage behaviour, but the use of higher temperatures reduced the maximum possible draw ratio. The variation of elongation at break with temperature gave maximum values in the range 80-90°C for UPVC and PPVC compositions\textsuperscript{(137)}, therefore the decrease in maximum draw ratio at
temperatures greater than 90°C lead to sample failure. The samples were stretched at 90°C with the maximum draw ratio to achieve the highest tensile properties, followed by annealing at temperatures greater than 90°C. Consequently, tensile and shrinkage properties were controlled by selecting the most effective draw ratio and annealing temperature. They also investigated the room temperature recovery rate of biaxially oriented PVC\(^{138}\). The rate of recovery was found to increased with plasticiser concentration, while the sample areas decreased exponentially with time by two distinct steps; during the first day the samples recovered quickly followed by a slower recovery rate at later times. The area shrinkage observed in oriented PVC, both with temperature and time, is a disadvantage of the material.

![Figure 1.16 Effect of drawing and annealing conditions on area shrinkage](image)

1.10 AIMS OF THIS PROJECT

The experimental work outlined herein forms a part of a large programme being undertaken in the Institute of Polymer Technology and Material Engineering,
which is aimed at studying the relationships between biaxial stretching conditions, structure and physical properties of oriented PVC products. The overall programme is outlined in Table 1.2(139).

As mentioned in section 1.9 biaxial orientation can enhance the physical properties of PVC, however the shrinkage behaviour of oriented PVC limits the range of applications to which the material can be put, especially when high service temperatures are likely to be experienced, due to the loss of orientation which occurs under these conditions. Irradiation crosslinking modifies the properties of PPVC conferring improved physical performance at high temperatures and dimensional stability etc, therefore, it is of interest to combine these two methods to upgrade the polymer's properties.

To date investigations have been concerned with either oriented PVC or crosslinked PVC, and not with the effect of the combination of both techniques. This project was aimed at the enhancement of the properties of PPVC compounds by biaxial stretching followed by irradiation crosslinking. It was hoped that crosslinks introduced into the already oriented PPVC would prevent the loss of properties at high temperatures and reduce the room temperature recovery rate by holding molecules in the oriented state.

This work was divided into three stages: firstly, to confirm that a crosslinked structure can be introduced into the oriented samples; secondly, to study the effect of each component in the formulations and the effect of irradiation dose on physical properties of the material, and thirdly, to characterise the crosslinked oriented samples.
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Table 1.2

A. Construction of biaxial stretching stretching equipment

B. Measurement of optimum draw ratio Variables:
   Plasticizer content (0-70 phr)
   Temperature
   Stretching rate
   Molar mass of PVC

C. Preparation of selected biaxially stretched samples
   (a) Rigid, no annealing
   (b) Rigid, selected annealing conditions
   (c) Flexible, selected annealing conditions

D. Development of thermal analysis and x-ray techniques to detect structure

E. Measurement of:
   (a) sample shrinkage as a function of temperature
   (b) Tensile properties
   (c) Impact properties of rigid samples

Assessment of structure by:
   Thermal analysis
   X-ray analysis

G. Modifying drawing/annealing conditions to achieve optimum properties

H. Repeating steps E and F

I. Production of crosslinkable formulations:
   Drawing or drawing and annealing under optimum conditions
   Repeating steps E and F

Proposing relationships between formulation, drawing conditions, structure and properties, to enable:
   (i) Planning of new programmes related to specific applications;
   (ii) Identification of optimum processing conditions for oriented PVC products;
   (iii) Development of new products based on enhanced properties.
2.1 MATERIALS

2.1.1 Polyvinyl Chloride (PVC)

A commercial grade of suspension PVC homopolymer, supplied by European Vinyl Corporation (EVC plc), was used throughout the work carried out. This particular resin is specially designed for use in plasticised compositions. The polymer grains are irregular in shape and have a uniform and highly porous structure. The technical reference for the grade is CORVIC S71/102 (or SH7020) and its main characteristics are given in Table 2.1.

Table 2.1
Properties of Corvic S71/102

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>VALUE</th>
<th>TEST METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>K Value</td>
<td>71</td>
<td>a*</td>
</tr>
<tr>
<td>Molecular weight (Mw)</td>
<td>121000</td>
<td>b*</td>
</tr>
<tr>
<td>Molecular weight (Mn)</td>
<td>71000</td>
<td>b*</td>
</tr>
</tbody>
</table>

*Test methods:
a: Calculated from relative viscosity data obtained by method ISO-R174
b: Estimated by GPC
2.1.2 Trimethylol Propane Trimethacrylate (TMPTMA)

TMPTMA, a polyfunctional unsaturated monomer supplied by Ancomer UK, was used to promote irradiation crosslinking of PVC. The structure of the TMPTMA molecule is shown below. TMPTMA is a clear liquid at room temperature with a boiling point higher than 200°C @ 1mm Hg.

\[
\begin{align*}
 &\text{O} \\
 &\bigg\| \\
 &\text{CH}_3-\text{CH}_2-\text{C(}\text{CH}_2-\text{O-}\text{C-}\text{C=CH}_2)_3 \\
 &\quad \bigg\| \\
 &\text{CH}_3
\end{align*}
\]

\text{TMPTMA}

2.1.3 Stabilisers

Three commercial grade lead stabilisers and tin stabilisers were used. All stabilisers were supplied by Akzo Chemical, UK. The technical data on these additives are presented in Table 2.2.

2.1.4 Plasticiser and Lubricant

Di-isooctyl phthalate (DIOP), \(\text{C}_6\text{H}_4(\text{C}_8\text{H}_{17}\text{COO})_2\), a clear liquid with a density of 0.98 g/cm\(^3\), was used as a plasticiser and was supplied by Exxon. Stearic acid, supplied by Akzo Chemicals, was used as a lubricant.
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Table 2.2

Technical data on stabilisers

<table>
<thead>
<tr>
<th>STABILISER</th>
<th>FORM/COLOUR</th>
<th>SPECIFIC GRAVITY</th>
<th>MELTING POINT/°C</th>
<th>% LEAD CONTENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tribasic lead sulphate (TBLS) Pb\textsubscript{3}O\textsubscript{3}\textsubscript{2}\textsubscript{7}\textsubscript{2}O \textsubscript{5}</td>
<td>Powder/White</td>
<td>6.3</td>
<td>-</td>
<td>83.4</td>
</tr>
<tr>
<td>Lead stearate Pb\textsubscript{2}(O\textsubscript{2}C\textsubscript{17}H\textsubscript{15})\textsubscript{7}</td>
<td>Powder/White</td>
<td>1.8</td>
<td>104</td>
<td>28</td>
</tr>
<tr>
<td>Dibasic lead stearate (DBLS) 2Pb\textsubscript{2}O\textsubscript{3}\textsubscript{2}O\textsubscript{17}H\textsubscript{15}</td>
<td>Powder/White</td>
<td>2.0</td>
<td>-</td>
<td>51</td>
</tr>
<tr>
<td>Stanclere T186 (Dibutyltin mercaptophenyl) ((C\textsubscript{4}H\textsubscript{9})\textsubscript{2}Sn(\textsubscript{2}S\textsubscript{2}C\textsubscript{2}H\textsubscript{4}CO\textsubscript{2}))</td>
<td>Powder/White</td>
<td>-</td>
<td>110-130</td>
<td>-</td>
</tr>
<tr>
<td>Stanclere T184 (Dibutyltin substituted mercaptide) ((C\textsubscript{4}H\textsubscript{9})\textsubscript{2}Sn(\textsubscript{2}S\textsubscript{2}CH\textsubscript{2}CO\textsubscript{2}R))</td>
<td>Clear amber liquid</td>
<td>1.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Stanclere TL (Dibutyltindidecaneanoate or Dibutyltindilaurate) ((C\textsubscript{4}H\textsubscript{9})\textsubscript{2}Sn(O\textsubscript{2}C\textsubscript{11}H\textsubscript{17}))</td>
<td>Clear amber liquid</td>
<td>1.04</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2 Sample Preparation

2.2.1 Formulations

The formulations presented in Table 2.3 were used in this study. Formulations F1 and F2 were used in Chapter 3 for the purpose of studying the possibility of crosslinking oriented samples. Formulation F3-F13, which contained different types and concentrations of stabilisers, were used to evaluate the effect of stabiliser on crosslinked oriented samples. For the study into the effect of TMPTMA and stabiliser
Chapter 2 Experimental Procedures 45

Concentration upon the properties of PPVC products the formulation T2-T20 and S2-S6, were used, respectively. Formulation P25, which contained less plasticiser than the other formulations, was used to determine the influence of plasticiser on the properties of the final products.

2.2.2 Dry blending

An 8 litre T.K. Fielder laboratory high-speed mixer was used to prepare all formulations studied. The PVC resin and powder components were initially agitated in the mixer at 75°C, after a short time the plasticiser and crosslinking monomer were added. Mixing was continued, at a speed of 3,000 rev/min., until a temperature of 120°C was reached, after which the compound was discharged into the cooling chamber of the mixer where it was agitated and cooled to below 25°C.

2.2.3 Milling

According to the recommendations in BS 2782: Part 9 Method 901A: 1977, milled sheet was produced for the purpose of compression moulding (Section 2.2.4). The milling process is an essential step in sample preparation because fusion of the PVC takes place, whereas compression moulding of the dryblended powders directly resulted in inadequate fusing of the PVC material.

The powder blend was mixed on a two-roll mill for 5 min at 140°C to produce sheets of approximately 0.2 to 0.4 mm in thickness.
## Table 2.3

**Formulations (phr)**

<table>
<thead>
<tr>
<th>SAMPLE CODE</th>
<th>PVC</th>
<th>DIOP</th>
<th>STEARIC ACID</th>
<th>STABILISER</th>
<th>TMPTMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>TBLS</td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>TBLS</td>
<td>10</td>
</tr>
<tr>
<td>F3</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>Pb Stearate</td>
<td>DBLS</td>
</tr>
<tr>
<td>F4</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>F5</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>F6</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>F7</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>F8</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>F9</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>Stanclere T186</td>
<td>10</td>
</tr>
<tr>
<td>F10</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>F11</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>F12</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>P25</td>
<td>100</td>
<td>25</td>
<td>0.5</td>
<td>Stanclere T184</td>
<td>10</td>
</tr>
<tr>
<td>F13</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>T2</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>Stanclere TL</td>
<td>2</td>
</tr>
<tr>
<td>T5</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>T10</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>T20</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>S2</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>S3</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>S4</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>S6</td>
<td>100</td>
<td>46.5</td>
<td>0.5</td>
<td>6</td>
<td>10</td>
</tr>
</tbody>
</table>
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2.2.4 Compression moulding

The milled sheet was compression moulded to a thickness of approximately 0.25mm for samples to be used without stretching and approximately 0.5mm for samples to be subsequently stretched. Samples were moulded at 175°C for 5 min (after a five minute preheat period), at a pressure of 60MPa. The mould was then immediately transferred to a water-cooled press and cooling was effected under the same pressure. The mouldings used for the work outlined in chapter 3 had a thickened frame as shown in Figure 2.1 and those for the experiments described in chapters 4 and 5 flat sheets were used. Samples were marked with inked lines 10mm apart in both vertical and horizontal directions to form squares, and the sheet thickness at the centre of each square was recorded for the purpose of draw ratio calculation.

Figure 2.1 Compression moulding. (Dimension in mm)
2.2.5 Biaxial Stretching

The biaxial stretcher used in the preliminary investigation (chapter 3) is shown in its closed position in Figure 2.2(a) and in the extended position, with a sample present, in Figure 2.2(b). This attachment was designed to fit into the high temperature cabinet on an Instron tensile testing machine. The size of the unstretched sample required for this attachment is 55mm by 55mm.

For the rest of the study bigger samples, 116mm by 116mm, were used with the Biaxial Stretching Equipment (the BASE). The BASE was designed as an attachment for an Instron tensile testing machine (Figure 2.3). The full details of this equipment, including specifications, stretching mechanism and operating procedures, have been described by Hitt and Gilbert (140). The stretching head was located within the...
environmentally controlled cabinet, which can be operated at temperatures up to 200°C. The heating system works by circulating hot air through the cabinet. The stretching head has two draw rods which are perpendicular to each other (Figure 2.3). These two rods were moved simultaneously at the same rate to produce equally biaxially stretched samples. The stretching head of the BASE is shown in its zero position in Figure 2.4(a) and opened to a displacement of 160mm (both axes) in Figure 2.4(b). Samples were held by ten grips upon each edge, operated under nitrogen gas pressure, their function being to only apply a force in the direction in which the sample was being stretched. The grips were designed so as to allow the material held by them to draw down during stretching so that the elongation undergone by the material in the grips could equalise with that of the rest of the sample.

The samples were stretched at 80°C at a rate of 10 mm/min, followed by annealing whilst being held in the drawn state at the same temperature (unless stated) for 20min. Finally the samples were cooled down to room temperature in the stretching attachment. Figure 2.5 shows an undrawn sample, a sample after clamping and a stretched sample. The draw ratio(\(\lambda\)) of a stretched sample is defined by the equation given below:

\[
\lambda = \sqrt{\frac{t_b}{t_a}}
\] .... 2.1

where \(t_b\) = sheet thickness before stretching, at a given marked square
\(t_a\) = thickness at the same square after stretching
**Chapter 2 Experimental Procedures 50**

- Unstretched Sample
- Stretched Sample (maximum size)
  1. Crosshead of Instron
  2. Environmental Cabinet
  3. Draw Rod
  4. Hydraulic Cylinder
  5. Air Outlet Duct
  6. Air Inlet Duct
  7. Support Frame of BASE

---

**Figure 2.3 Schematic diagram of BASE**
Figure 2.4 The stretching head of the BASE (a) in zero position and (b) opened to 160 mm displacement

Figure 2.5 Samples before and after stretching. (a) an undrawn sample, (b) a sample after champing and (c) a stretched sample
2.2.6 Irradiation

Crosslinking was induced by exposing the samples to electron beam (EB) irradiation. The samples were irradiated on each side with a dose in the range of 2-8 MRad. All irradiation was performed under a nitrogen atmosphere.

2.3 CHARACTERISATION AND TESTING

2.3.1 Assessment of Crosslinked Structure

2.3.1.1 Percentage Gel Content

The gel content, the content of insoluble material in tetrahydrofuran (THF), is the most frequent method used to evaluate the degree of crosslinking. Gel content relates directly to network structures formed in the crosslinking process. The samples were examined for gel content by extracting the specimens with THF in a Soxhlet apparatus for 24 hours. Overnight extraction was used by many researchers\(^{(114,124,141)}\), to be certain that none of the dissolved material remained in the thimble. The extracted samples were vacuum dried at 60°C for at least 20 hours and the percentage gel content was determined from the remaining weight of all components which could be involved in gel formation, the plasticiser being excluded, as shown in equation 2.2.

\[
\% \text{ gel content} = \frac{W_g}{W_x - W_p} \times 100
\]  
\[\text{2.2}\]

where

- \(W_g\) = weight of gel
- \(W_x\) = weight of crosslinked specimen
Wp = weight of plasticiser in the specimen

2.3.1.2 Crosslink Density Measurements

The molar mass between crosslinks, $\overline{Mc}$, and the crosslink density in the gels, $1/(2\overline{Mc})$, were obtained from swelling measurements. Samples were allowed to swell in methyl ethyl ketone (MEK) for 4 days at 25°C. The weights of gel before swelling (deswollen weight, $W_d$) and after swelling (swollen weight, $W_s$) were recorded to calculate the volume fraction of PVC ($v_r$) in the network swollen to equilibrium. Crosslink density was calculated from the Flory-Rehner equation (145), shown below.

$$-[\ln(1-v_r) + v_r + \chi v_r^2] = \rho V_0 v_r^{\frac{1}{3}} \overline{Mc}^{-1}$$

where

- $\chi$ = the polymer - solvent interaction parameter
- $\rho$ = the density of PVC
- $V_0$ = the molar volume of solvent
- $v_r$ = the volume fraction of PVC in the swollen gel

2.3.2 Mechanical Properties

2.3.2.1 Tensile properties

Tensile tests were carried out both at room temperature and at elevated temperatures (70°C, 100°C or 130°C) using a Hounsfield tensile testing machine with a test speed of 50 mm/min. The tensile strength and elongation were determined at the fracture point of each specimen. Due to the limited sample area available and the requirement that specimens be of equal thickness for all crosslinked oriented materials,
a smaller tensile sample cutter than that specified in the British Standard (BS 903) was employed. A cutter with dimensions; 5mm width, 26.5mm in length and 10mm in gauge length was made specially for this purpose.

2.3.2.2 Impact Testing

A Rosand instrument falling weight impact tester was used to assess the effect of orientation and crosslinking on the samples' impact strengths. The tests were performed at room temperature, in accordance with BS 2782, Part 3, Method 352D. The impact velocity used was 3 m/s.

2.3.3 Thermal Analysis

2.3.3.1 Differential Thermal Analysis

The DSC traces were obtained using a Du Pont Instruments 2000 Thermal Analyser fitted with a 910 DSC cell. Specimens with sizes between 10-12 mg were scanned from -50°C to 150°C and from room temperature to 240°C, at a heating rate of 10°C/min, under a nitrogen atmosphere.

2.3.3.2 Thermomechanical Analysis (TMA)

2.3.3.2.1 Softening Temperature (Ts)

Softening temperatures were determined using a Du Pont 990 Thermal analyser fitted with a TMA attachment operating in the penetration mode. The temperature was
ramped from room temperature to 220°C at 10°C/min, with the probe loaded with a weight of 10g. The penetration of a probe into the sample was plotted against temperature. Ts was obtained from the experimental trace as shown in Figure 4.1.

2.3.3.2.2 Shrinkage Measurement

A Mettler TMA 40 Thermo Mechanical Analyser was used for shrinkage measurement, as shown in Figure 2.6 with its film & fibre attachment in position. The attachment is surrounded by a furnace, which was used to produce a heating rate of 10°C/min. The sample was held between two grips, the upper attached to the sample support and the measuring probe suspended from the lower. The probe was attached to the core of a differential transformer. The arrangement works by the fact that as the sample moves the core moves equally generating a signal proportional to the sample displacement. A micro processor converts the signal into a plot of displacement versus temperature. A calibration weight located within the TMA is used to apply a load to the measuring probe. The microprocessor controls the application of the load and for this study a load of 0.01N was used.

The dependence of displacement on temperature curve generated by the TMA is only a measure of linear shrinkage. The method used to calculated area shrinkage, which is more sensible measurement for a biaxially drawn material, was shown in Figure 2.7(136). Two strips are cut from a drawn sample (step A), one parallel to the vertical draw direction and one perpendicular to it. The linear shrinkage ($\Delta L$) is measured for each strip as a function of temperature (step B). The value of $\Delta L_1$ & $\Delta L_2$ can then be used along with the draw ratio of the sample to calculate the area shrinkage (AS) at any temperature (step C).
Figure 2.6 Mettler TMA40
A. Drawn sample

B. TMA curves

C. Area shrinkage (AS)

\[ DR = \text{Draw ratio} \]

\[ \text{AS maximum} = l_o^2 - (l_o/DR)^2 \]

\[ \text{AS at temperature } T = l_o^2 - (l_o - \Delta L_1)(l_o - \Delta L_2) \]

\[ \% \text{AS} = \frac{\text{AS at temperature } T}{\text{AS maximum}} \times 100 \]

\[ \% \text{AS} = \frac{l_o^2 - (l_o - \Delta L_1)(l_o - \Delta L_2)}{l_o^2 - (l_o^2 / DR^2)} \times 100 \]

\[ \% \text{AS} = \frac{(DR)^2}{(DR)^2 - 1} \left[ \frac{l_o \Delta L_1 + l_o \Delta L_2 - \Delta L_1 \Delta L_2}{l_o^3} \right] \times 100 \]

\[ \% \text{AS} = \frac{(DR)^2}{(DR)^2 - 1} \left[ \frac{\Delta L_1}{l_o} + \frac{\Delta L_2}{l_o} - \left( \frac{\Delta L_1}{l_o} \times \frac{\Delta L_2}{l_o} \right) \right] \times 100 \]

*Figure 2.7 Calculation of area shrinkage*
2.3.4 X-ray Diffraction Measurement

Wide angle x-ray diffraction (WAXD) traces were obtained using a JEOL DX-GE-25 generator, which was operated at 40 kV and 30 mA, and a DX-GO-S vertical goniometer. Ni-filtered Cu Kα was used under atmospheric conditions. Figure 2.8 shows a schematic diagram of reflection diffractometer geometry. Reflectance mode measurements at ambient temperature were made using flat rectangular samples (20mmx14mm) and the diffraction intensity in arbitrary units were obtained over the range 10°-50° 2θ with a 1° 2θ per minute scattering speed. No correction was made for air scattering; the variation of scattering intensity with 2θ was recorded.

Transmission X-ray measurements were made with samples of approximately 0.1-0.2 mm thickness and a sample to film distance of 5 cm. The exposure time was at least 24 hours. Scattered intensities were recorded photographically.

Figure 2.8 Diagrammatic arrangement of the x-ray diffraction
2.3.5 Birefringence

In this study, the optical anisotropy of the sample films was characterised in relation to three principal refractive indices, $\alpha$, $\beta$ and $\gamma$. It was found that the smallest index, $\alpha$, was perpendicular to the film plane, thus the birefringence measured in plane was $(\gamma-\beta)$ and those for out of plane were $(\gamma-\alpha)$ and $(\beta-\alpha)$. For equal biaxial orientation the average of these two values was used to represent out of plane birefringence; $[(\gamma-\alpha)+(\beta-\alpha)]/2$.

Measurements of birefringence were carried out using a microscopical method. Specimens were cut from a number of positions across the whole of the oriented sheet. In the determination of in plane birefringence $(\gamma-\beta)$, the specimens were mounted between a microscope slide and coverslip in glycerol (refractive index $n_D^0 = 1.54$) to reduce light scattering and depolarisation at the film surfaces. Three measurements were carried out on each specimen using a Zeiss Universal microscope equipped with crossed-polar:

1. The angle between the side of the specimen, which is parallel to the vertical direction of the sheet, and the nearest extinction position was measured.
2. The direction of $\gamma$ was determined using a one wavelength accessory plate.
3. The in plane birefringence was measured with a quartz Eringhaus compensator using light of wavelength 546.1 nm.

The OPD and $\Delta n$ can be calculated by the formulas\textsuperscript{146}:

\[
\text{OPD } \lambda = \frac{E}{\omega} \sqrt{(\alpha^2 - \sin^2 i) - (\varepsilon^2 - \sin^2 i)}
\]  \quad \text{..... 2.4}

\[
\Delta n = \frac{\text{OPD}}{t}
\]  \quad \text{..... 2.5}
where \( \text{OPD} \) = optical path difference in nm at wavelength \( \lambda \)
\( \lambda \) = wavelength in nm
\( \omega \) = refractive index of ordinary and
\( \varepsilon \) = refractive index of extraordinary wave in quartz for the wavelength \( \lambda \)
\( i \) = the angle of tilt of the plane relative to its zero position
\( t \) = the thickness of sample

According to Gifford values\(^{147}\) refractive index \( \omega \) is 1.661 and \( \varepsilon \) is 1.487 at the wavelength of 546.1 nm.

Conoscopy was used to measure out of plane birefringence. In this technique, the specimen on the stage of the microscope is illuminated with highly convergent light\(^{148,149}\). The light passing through the specimen is viewed at the back focus plane of the objective lens. The pattern of light seen in the back focal plane or detected by a camera is known as an interference figure. The interference figure consists of rings of polarisation colours in white light, or dark and bright 'fringes' in monochromatic light. These fringes correspond to the position in the back focal plane where the rays passing along an optic axis (OA) emerge (Figure 2.9). Superimposed upon this pattern are black 'brushes' or 'isogyres' marking where light passing through the specimen has encountered permitted vibration directions which are E-W and N-S.

A typical interference figure for a biaxial specimen in the 45° position is shown in Figure 2.10. Upon rotation of the specimen to the 0° position the pattern changes to that shown in Figure 2.11. The maximum distance \( (d) \) between these two isogyres (in the 45° position) was used to calculate out of plane birefringence. The optical axial angle \( (2V) \) is the angle between the optical axes which is a characteristic feature for biaxial specimen as the differences in \( d \) are caused by the differences in \( 2V \). In practice
the angle between the emerging rays (2E) was calculated from via d by equation 2.6, because the light refracts at the surface of the specimen (Figure 2.12).

\[ d = k \sin E \] ..... 2.6

The constant k can be calculated from the measurement of d of mica, which was used as a known crystal, under the same conditions experienced by the samples. For mica, 2V is 45° and n_2 is 1.582. By using equation 2.6 and 2.7, the constant k was achieved.

\[ \sin E = n_2 \sin V \] ..... 2.7

2E of specimen can be converted to give 2V using equation 2.7 (where n_2 is the intermediate refractive index). Out of plane birefringence of specimen (β-α) was calculated by using Malliad's rule (149) (equation 2.8), where (γ-β), in plane birefringence, was measured by a quartz Eringhaus compensator.

\[ \tan 2V = \frac{\beta - \alpha}{\gamma - \beta} \] ..... 2.8

Figure 2.9 Surfaces of equal retardation around the optic axes of a biaxial crystal
Figure 2.10 Interference figure at 45° position

Figure 2.11 Interference figure at extinction position (0°)

Figure 2.12 Real and apparent optic axial angles
2.3.6 Density Measurement

The densities of samples were measured using a Davenport density gradient column at 23.0±0.1°C. The column was filled with aqueous calcium nitrate and calibrated with glass floats with accurately known densities. The height at which each specimen floated in the column was recorded and converted to density by the standard calibration curve plotted between heights and densities of the glass floats. The average of three measurements was used for each sample.

2.3.6 Ageing Study

The effect of stabiliser upon heat stability of materials used was assessed using ASTM: D 2115-67. Samples were exposed in an oven at a temperature of 177±0.5°C for one hour, and the change in colour of samples was noted.
CHAPTER 3

RESULTS AND DISCUSSION

I. PRELIMINARY INVESTIGATION

3.1 INTRODUCTION

The aims of this part of the project were firstly to find the most effective stretching temperature, secondly to investigate whether crosslinks could be introduced into oriented PPVC and thirdly to see how properties were modified in the samples produced. The formulations F1 and F2 were used in this study. Formulation F2 was shown to be an effective composition for irradiation crosslinking by Nethsinghe and Gilbert\(^{112-113}\) (as discussed in section 1.7). The crosslinked products were found to have high percentage gel contents and improved tensile properties, especially at higher temperatures. Formulation F1 was used as a comparative material because the crosslinking monomer (TMPTMA) was excluded in this composition. A radiation dose of 4 Mrad was used to irradiate each side of the undrawn samples, as this dose gave the best properties for this formulation according to Nethsinghe and Gilbert\(^{112}\). The drawn samples were irradiated with a dose of 2 Mrad on each side. The reason for using a smaller radiation dose for the drawn samples than for the undrawn samples was to make sure that the materials in all samples were exposed to the same total energy because the drawn samples were thinner. However, the doses 2 and 4 Mrad were approximate values. A more detailed study of the effect of sample thickness on properties is considered in Chapter 5. The results obtained from the experiments carried out will be discussed under the following heading: stretching temperature,
Chapter 3 Preliminary Investigation 65

percentage gel content, softening temperature, shrinkage, tensile properties and WAXD study.

3.2 EFFECT OF TEMPERATURE ON PERCENTAGE ELONGATION AT BREAK

The purpose of this section was to find the optimum orientation temperature for PPVC F2. Samples were tensile tested at a range of temperatures. The plot of elongation at break as function of temperature for PPVC F2 before crosslinking is shown in Figure 3.1. It can be observed that elongation at break rises to the maximum at the temperature of 80°C and then decreases. This shape of this curve has been seen before by Hitt and Gilbert(137). They found that all of the curves for 0, 30, 50, 70 and 100 phr plasticised PVC have a peak elongation in the temperature range 80°C-90°C. Hence, throughout this study, a stretching temperature of 80°C was selected to give the maximum draw ratio of the drawn samples.

3.3 PERCENTAGE GEL CONTENT

Gel content is used as a measure of the amount of insoluble, i.e. crosslinked PVC in a sample. Table 3.1 shows that the gel content of both drawn and undrawn samples increases after irradiation. This suggests that crosslinked structures were formed during exposure to an electron beam. The unoriented sample gave the highest percentage gel content, because it was irradiated with a higher dose of radiation than the stretched samples. The thickness of specimens was also considered, as the difference in sample thickness led to the variations in the total irradiation intensity experienced by each test specimen. The effect of sample thickness upon percentage gel content will be discussed in detail in Chapter 5.
Figure 3.1 Elongation at break as a function of temperature for PPVC F2
Table 3.1

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>SOFTENING TEMPERATURE/°C</th>
<th>%GEL CONTENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>F2 (unirradiated)</td>
<td>93.5</td>
<td>0</td>
</tr>
<tr>
<td>F2 (irradiated)</td>
<td>103.0</td>
<td>51.7</td>
</tr>
<tr>
<td>SF2 (irradiated) (λ=1.3)</td>
<td>-</td>
<td>35.5</td>
</tr>
<tr>
<td>SF2 (irradiated) (λ=1.6)</td>
<td>-</td>
<td>36.3</td>
</tr>
</tbody>
</table>

SF2=stretched F2, λ=draw ratio

3.4 THERMOMECHANICAL ANALYSIS

3.4.1 Softening Temperature

Figure 3.2 shows TMA traces of unirradiated and irradiated PPVC F2. It can be noted that the irradiated sample gave the longer temperature range for penetration resistance than the unirradiated sample. This was further evidence for a modified structure in the irradiated specimens. However the softening temperature of irradiated PPVC given in Table 3.1 was not improved as much as was expected. For the oriented samples measurements were unsuccessful due to the rapid shrinkage of samples at higher temperatures.
Figure 3.2 Penetration resistance for irradiated and unirradiated samples
3.4.2 Shrinkage

The area shrinkages of the drawn samples before and after irradiation are shown in Figure 3.3. It can be seen that crosslinking PVC affected the area shrinkage of the irradiated samples. The unirradiated specimens showed shrinkage at temperatures as low as 40°C, whereas the irradiated compounds did not shrink until temperatures around 50°C were reached. This result indicates that crosslinking induced in the molecular structure held the molecules in the drawn position. Changing the draw ratio had minor effect upon percentage area shrinkage.

3.5 TENSILE PROPERTIES

The effects of draw ratio and irradiation on tensile strength at room temperature and at 70°C are shown in Table 3.2. These properties had been previously tested at 130°C, which was selected for higher temperature tensile testing of PVC by many researchers (113,122,125), but this temperature resulted in shrinkage of the drawn samples. The testing was carried out at 70°C to reduce this problem, since it was known that shrinkage was less at this temperature. The results showed that, for the samples with the same formulation, tensile strength increased with draw ratio, as reported before in several papers (58-60,63-64). The tensile strengths of F1 samples were higher than those of F2 both in undrawn and drawn specimens due to the addition of TMPTMA, which acts as a plasticiser. It was observed that the irradiated samples gave higher tensile strengths when compared with the unirradiated samples at the same draw ratio. This effect was brought about by the crosslinked structure in PPVC. This effect will be discussed in detail in Chapter 5.
Figure 3.3 Percentage area shrinkage as a function of temperature for F2
Table 3.2

Tensile Strength at Room Temperature and at 70°C

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TENSILE STRENGTH/MPa</th>
<th>BEFORE IRRADIATION</th>
<th>AFTER IRRADIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ROOM TEMPERATURE</td>
<td>70°C</td>
</tr>
<tr>
<td>F1</td>
<td>26.5</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>SF1 (λ=1.3)</td>
<td>34.0</td>
<td>10.3</td>
<td>-</td>
</tr>
<tr>
<td>SF1 (λ=1.6)</td>
<td>39.6</td>
<td>10.8</td>
<td>-</td>
</tr>
<tr>
<td>F2</td>
<td>23.7</td>
<td>7.9</td>
<td>25.2</td>
</tr>
<tr>
<td>SF2 (λ=1.3)</td>
<td>31.0</td>
<td>11.7</td>
<td>33.3</td>
</tr>
<tr>
<td>SF2 (λ=1.6)</td>
<td>35.1</td>
<td>13.4</td>
<td>38.4</td>
</tr>
</tbody>
</table>

3.6 WIDE ANGLE X-RAY DIFFRACTION (WAXD)

The WAXD pattern of drawn specimen F2 at the draw ratio of 1.3 is illustrated in Figure 3.4. It can be observed that there are a number of distinctive peaks which do not belong to PVC (WAXD trace of PVC was already shown in Figure 1.10). These peaks were from the TBLS stabiliser. Hence, the x-ray diffraction technique cannot be used to confirm the crystallisation occurring in these PVC compounds.

3.7 CONCLUSION

Crosslinking in stretched and unstretched PPVC can be induced by irradiating samples with electron beam radiation. This is shown by the appearance of crosslinked structures or gel content in irradiated samples. Crosslinked stretched samples gave higher tensile strengths and lower percentage area shrinkage values than the stretched
Figure 3.4 X-ray diffraction pattern for stretched PPVC sample F2 at the draw ratio of 1.3
samples without irradiation of the same formulation. Therefore, by introducing crosslinking to drawn PPVC the properties of this material can be improved. Having established the feasibility of this approach more detailed studies were carried out. These are reported in Chapters 4-6.
CHAPTER 4

RESULTS AND DISCUSSION

II SELECTION OF A SUITABLE FORMULATION AND CROSSLINKING CONDITIONS

4.1 INTRODUCTION

Crosslinking of the oriented PVC compound (F2) containing TMPTMA as the crosslinking agent and TBLS as the stabiliser was discussed in Chapter 3. It was found that electron beam radiation promoted crosslinking in stretched PVC samples. The formulation of the PVC compound studied in chapter 3 was not suitable for studying the effect of orientation by using WAXD because some of the peaks arising from TBLS coincide with several of those from the PVC itself. No attempt has been made to optimise formulation F2 for use with electron beam radiation.

Stabilisation of the irradiated formulation is very important, since it affects the colouration, crosslinking efficiency and physical properties of the samples. Several publications\(^{(103-104)}\) have documented the effects of stabilisers upon radiation crosslinking of PVC compounds. The stabilisers investigated were of the tin group, the barium-zinc group and the lead group. The lead group, e.g. TBLS and DBLS, was found to be the most effective in the formation of crosslinked structures, but the tin and barium-zinc groups gave better colour stability.

The aim of this part of the programme was to find a suitable formulation to study the crosslinking of oriented PVC compounds. The lead stabilisers, namely normal lead stearate and DBLS, and tin stabilisers, namely Stanclere T186, Stanclere
Chapter 4 A Suitable Formulation and Crosslinking Conditions

T184 and Stanclere TL, were used in the formulations prepared for irradiation crosslinking. The effects of the amounts of each additive, i.e. TMPTMA and stabiliser, and irradiation doses were studied to find out suitable conditions for the next experiment.

The study was divided into two parts. In the first part, sections 4.2 to 4.5, formulations F3 to F13, S2, S4, S6, and T2 to T10, shown in Table 2.3, were used in sheet form (undrawn samples) with thicknesses in the range 0.2mm to 0.3mm. The effects of the stabiliser type, TMPTMA level and irradiation dose upon the percentage gel content, crosslink density and softening temperature were investigated. Specimens with different stabilisers were examined using WAXD to ensure that the stabiliser would not mask the x-ray diffraction pattern from the PVC. The heat stability of each formulation was also determined. The stabiliser found to be most suitable was then employed in the second part of the study, outlined in section 4.6, in which the effects of stabiliser concentration and radiation dose upon the properties of drawn samples were determined. Drawn samples of formulations S2, S3, and S4 were used at draw ratios in the range 1.5 to 1.6; the thicknesses of these ranged from 0.15mm to 0.20 mm.

4.2 Effect of Stabiliser

Initially three powder stabilisers, normal lead stearate, DBLS and Stanclere T186 were used in this investigation. Two liquid stabilisers, Stanclere T184 and Stanclere TL were introduced the later stages of the work specifically to study WAXD as explained in section 4.2.5. The formulations employing these stabilisers are shown in Table 2.1. Normal lead stearate was used in F3-F4; a mixture of normal lead stearate and DBLS was used in F5; samples F6-F8 contained DBLS stabiliser at various levels;
Stanclere T186 was used in F9-F11; Stanclere TL and Stanclere T184 were used in F12 and F13, respectively. All the stabilisers described in this paragraph were effective, since the irradiated samples showed no signs of discolouration. The experimental data showed the effect of stabiliser upon the following factors: percentage gel content; oven heat stability; softening temperature and WAXD.

### 4.2.1 Percentage Gel Content

The relationships between stabiliser type and percentage gel content, for the formulations studied, are presented in Table 4.1. In the unirradiated state, all the formulations were completely soluble in THF. After irradiation, F3 and F4 gave lower percentage gel contents in comparison with the other formulations. The mixture of normal lead stearate and DBLS used in F5 produced better results than normal lead stearate alone. The highest percentage gel content was found in F8, which was stabilised by DBLS, and hence DBLS was the best additive in the group of stabilisers given in Table 4.1. Formulations F6, F7 and F8, using DBLS at levels of 4, 6 and 8phr respectively, showed increased gel contents with DBLS concentration. It can be concluded that at higher DBLS levels, i.e. in the more stable system, the crosslinking efficiency was optimised. In formulations using Stanclere T186 it was observed that the higher the stabiliser content, the lower the percentage gel content in irradiated specimens. F12 stabilised with Stanclere TL showed a reasonable gel content; the gel content of F12 was found to be 43.6%. The formation of crosslinked structures in F12 was found to be less extensive than in the formulations stabilised with Stanclere T186 and DBLS.
Table 4.1
Percentage Gel Content and Softening Temperature
for Unirradiated and Irradiated PPVC Formulations F3-F12

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>%GEL CONTENT</th>
<th>SOFTENING TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unirr.</td>
<td>irr.</td>
</tr>
<tr>
<td>F3 (4phr normal Pb stearate)</td>
<td>0</td>
<td>21.0</td>
</tr>
<tr>
<td>F4 (6phr normal Pb stearate)</td>
<td>0</td>
<td>23.7</td>
</tr>
<tr>
<td>F5 (3phr normal Pb stearate + 3phr DBLS)</td>
<td>0</td>
<td>46.9</td>
</tr>
<tr>
<td>F6 (4phr DBLS)</td>
<td>0</td>
<td>52.3</td>
</tr>
<tr>
<td>F7 (6phr DBLS)</td>
<td>0</td>
<td>54.4</td>
</tr>
<tr>
<td>F8 (8phr DBLS)</td>
<td>0</td>
<td>67.5</td>
</tr>
<tr>
<td>F9 (4phr Stanclere T186)</td>
<td>0</td>
<td>59.3</td>
</tr>
<tr>
<td>F10 (6phr Stanclere T186)</td>
<td>0</td>
<td>51.7</td>
</tr>
<tr>
<td>F11 (8phr Stanclere T186)</td>
<td>0</td>
<td>47.4</td>
</tr>
<tr>
<td>F12 (4phr Stanclere TL)</td>
<td>0</td>
<td>43.6</td>
</tr>
</tbody>
</table>

These results show good agreement with Hell et al.\textsuperscript{103} who found that the use of basic lead stabiliser permitted the formation of high levels of crosslinking, but tin stabiliser strongly inhibits the irradiation crosslinking process.

Rodriguez\textsuperscript{125} in a study of aminosilane crosslinking of PPVC also found that organotin stabiliser containing PPVC samples gave lower gel contents than a formulation stabilised by basic lead, barium, cadmium or zinc stabilisers. The
formulations containing tin had good resistances to premature crosslinking, i.e. crosslinking was kept to a minimum until the crosslinking activation process was carried out. The author explained that the reactivity of PVC with the stabiliser is higher than that with the aminosilane, and therefore the grafting reaction of the aminosilane is less extensive.

In systems containing lead stabilisers, the main stabilisation mechanism is thought to be by the neutralisation of hydrogen chloride. This is supported by the fact that lead chloride is formed in lead stabilised PVC materials during their heat treatment and service. The effectiveness of the stabilising action of the lead compounds depends upon the amount of lead in the stabiliser. DBLS is a mild external lubricant as well as a stabiliser; normal lead stearate is similar to DBLS but provides greater lubricity and a lower stabilising strength, which can be explained: DBLS [2PbO.Pb(O₂CC₁₇H₃₅)₂] contains a considerably higher percentage lead content than normal lead stearate, as shown in Table 2.2; this implies that DBLS gives better stabilising performance through hydrogen chloride scavenging. Normal lead stearate also has limited compatibility with PVC.

In conclusion, for the lead stabilisers the greatest gel contents were found in formulations F9, F10 and F11, containing DBLS; the formulation with the highest stabiliser concentration (F11), and hence the most stable compound, also gave greatest gel content, as seen in Table 4.1. Apparently the degradation reactions taking place in the formulations with lower stabiliser concentrations limit the effectiveness of the crosslinking process. For the same reason, F5 that was stabilised by a mixture of normal lead stearate and DBLS gave a higher gel content than F3 and F4, but the gel content of F5 was found to be lower in comparison to F9, F10 and F11.
Chapter 4 A Suitable Formulation and Crosslinking Conditions

R$_n$SnX(4-n) is the general chemical formula of organotin compounds, where R is an alkyl group (normally butyl or octyl) and X is a saturated or unsaturated carboxylate, mercaptide or mercaptide ester such as a mercapto-acetate or a mercapto-propionate. It was first noticed by Frye et al.$^{(154)}$ that the X component of an organotin stabiliser became chemically bound to the polymer during the thermal ageing of stabilised PVC. Klemchuk$^{(155)}$ studied the reactions of organotin compounds using models compounds in place of PVC. The author used 4-chloropent-2-ene and 2-chloro-2-metyl butane as the allylic and tertiary chloride models. The results showed that organotin stabilisers reacted instantly with the allylic chlorine atom. This indicated that the stabilisers functioned not only as an acceptor of hydrogen chloride but also replaced the allylic chloride formed by dehydrochlorination. This reaction eliminated further hydrogen chloride formation.

$$2-\text{CH} = \text{CH} - \text{CH} - + R_2\text{SnX}_2 \rightarrow 2-\text{CH} = \text{CH} - \text{CH} - + R_2\text{SnCl}_2 \cdots$$

The high effectiveness of the stabilising action of organotin compounds can be explained by their ability to suppress free radical chain processes. Dibutyltin stabilisers were shown to lower the degree of radiation-induced grafting of styrene and acrylonitrile onto PVC and it was concluded from ESR studies that they inhibited the free radical reaction$^{(156)}$. Mori et al.$^{(157)}$ also found that organotin stabilisers were effective in the deactivation of radicals. It was mentioned in section 1.7 the irradiation crosslinking reaction starts with radical formation, and hence this stage can be interrupted by the action of the tin stabiliser. It can be concluded that this results in the low level of gel formed in formulations in which they were used, compared with samples employing DBLS. The formulations with organotin stabilisers (Stanclere T186 in F9 F10 and F11; Stanclere TL in F12), however, gave higher gel contents than F3.
and F4 that were stabilised by normal lead stearate. This result shows that the formulation stability conferred by the organotin compounds limits the negative effects that the degradation reactions have upon the crosslinking mechanism; the benefit of the extra stability gained outweighs the hindering effect that organotin stabilisers have directly upon the crosslinking reaction.

The irradiated sample containing 4phr Stanclere T186 (formulation F9) had a greater gel content than the formulation employing 4phr Stanclere TL (F12), as a result of the greater stability conferred to the system by the action of T186(158-159).

4.2.2 Softening Temperature

A TMA 'softening temperature' was obtained to assess the increased resistance to flow caused by irradiation. These temperatures were obtained from the experimental traces as shown in Figure 4.1 for F12 and irradiated F12(IF12). The curves have been offset to make them clearer. The softening temperatures of unirradiated and irradiated F3 to F12 are listed in Table 4.1. As expected in all samples the softening temperatures of the irradiated samples were higher than those of unirradiated samples. It is interesting that all the irradiated samples had softening temperatures in the narrow range of between 172°C and 180°C, but the spread of their gel contents was considerable (in the range of 21.0 to 67.5%). It can be seen that the compounds stabilised with the same stabiliser at different levels show very similar softening temperatures. Slight differences in softening temperatures are detected in formulations containing different stabilisers. Compounds containing DBLS, F6 to F8, soften at higher temperatures than compounds stabilised by tin stabiliser, F9-F12. It is suggested that different types of network structure are formed under the varying stabilising conditions. It is possible that F6 to F8 have network structure with higher numbers of
Figure 4.1 Penetration resistance for irradiated F12 and unirradiated F12
linkages between PVC chains. The gel contents played a significant role in shaping the TMA traces in the temperature range 80°C to the softening temperature. The effect of crosslinking on the TMA trace will be discussed later.

4.2.3 Ageing properties

The ageing properties of F6 to F13 were assessed by placing specimens of each of the formulations in an oven set at 177±0.5°C for one hour; any colour changes were noted. F3 to F5 were not studied further since they showed low crosslinking efficiency. The colours of samples before and after the tests are listed in Table 4.2. The distinct change in colour for F6 to F8 indicated that DBLS provided poor resistance to colour formation upon oven ageing. Stanclere T186 in F9 to F11 and Stanclere TL in F12 gave good performances since these samples only discoloured slightly. These results are consistent with the results of Hell et al.(103), who found that tin stabilisers gave better colour stability than lead stabilisers. F13 stabilised by Stanclere T184 became yellow during the test. Stanclere T184 thus had inferior stabilisation properties compared with the other two tin stabilisers, and hence was not used in any further tests.

Colour formation in PVC is directly affected by the extended polyene sequences formed as a result of dehydrochlorination reactions. One of the most important stabilising reactions of organotin stabilisers is the elimination of labile chlorine atoms, as already shown in reaction 4.1. This elimination reaction can stop further dehydrochlorination that increases the amount of polyene sequences. This results in greatly improved thermal stability. In addition, organotin stabilisers can react with double bonds in polyene sequences. An example of this was shown in reaction 4.2. The mercapto compounds that are released during the reaction between organotin
mercaptides and hydrogen chloride are able to add to double bonds\(^\text{160-162}\); hence the stabilising performance of organotin stabilisers is higher than that of DBLS.

\[
\text{C}_8\text{H}_{17}\text{O}\text{CO}+\text{CH}≡\text{CH}≡\text{CH}≡\text{CH}≡\text{CH}→\text{C}_8\text{H}_{17}\text{O}\text{CO}+\text{CH}≡\text{CH}≡\text{CH}≡\text{CH}≡\text{CH} S
\]

Table 4.2

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>ORIGINAL COLOUR</th>
<th>COLOUR AFTER HEATING</th>
</tr>
</thead>
<tbody>
<tr>
<td>F6 (4phr DBLS)</td>
<td>white translucent</td>
<td>tan</td>
</tr>
<tr>
<td>F7 (6phr DBLS)</td>
<td>white translucent</td>
<td>dark tan</td>
</tr>
<tr>
<td>F8 (8phr DBLS)</td>
<td>white translucent</td>
<td>copper</td>
</tr>
<tr>
<td>F9 (4phr Stanclere T186)</td>
<td>colourless transparent</td>
<td>pale yellow</td>
</tr>
<tr>
<td>F10(6phr Stanclere T186)</td>
<td>colourless transparent</td>
<td>pale yellow</td>
</tr>
<tr>
<td>F11(8phr Stanclere T186)</td>
<td>colourless transparent</td>
<td>pale yellow</td>
</tr>
<tr>
<td>F12(4phr Stanclere TL)</td>
<td>colourless transparent</td>
<td>pale yellow</td>
</tr>
<tr>
<td>F13(4phr Stanclere T184)</td>
<td>colourless transparent</td>
<td>yellow</td>
</tr>
</tbody>
</table>

As mentioned in section 4.2.1, Stanclere T186 is the best thermal stabiliser among stabilisers employed in this part of the programme. In this test the performances of Stanclere T186 and Stanclere TL appeared very similar. It would be expected that a greater level of differentiation may be obtained if the heating time was longer. The stabilising action of dibutyltin dilaurate (Stanclere TL) and dibutyltin
bis(dodecylmercaptide), which has a similar structure to Stanclere T184, (C₄H₉)₂Sn(SCH₂CO₂R), were found to be similar. The oven heat stability of the formulation containing Stanclere T184 was slightly poorer than the formulation employing Stanclere TL. The reason for this is not clear, as the stabilising action of the organotin stabilisers is complex and many factors are involved in the system. A thorough search of available literature has not elucidated the reason for the action of the Stanclere TL stabiliser; published findings are conflicting.

4.2.4 Wide Angle X-ray Diffraction

The WAXD traces of PPVC samples with the three stabilisers, lead stearate, DBLS and Stanclere T186 are illustrated in Figures 4.2 to 4.4, respectively. It can be seen that all the traces contain distinct peaks that suggest that crystals of the stabilisers or their reaction products are responsible. The positions of the peaks were found to match with the x-ray diffraction patterns of the stabilisers alone. Some overlapping peaks occurred in the regions 16° to 18° 2θ and 24° to 25° 2θ that were used to study the change in the crystalline structures in PVC due to orientation. Thus these three stabilisers are not suitable for the purposes of this project.

To avoid crystal stabiliser interference liquid stabilisers were used. Two types of liquid tin stabilisers, Stanclere TL and Stanclere T184 were selected to prepare PVC samples according to formulation F12 and F13 in Table 2.1. As a result of the discolouration of F13 in the oven heat stability test, this sample was no longer used. The WAXD pattern of F12 in Figure 4.5 shows a very satisfactory trace without interfering peaks. Consequently, Stanclere TL was the most promising stabiliser used in formulation for the WAXD study.
Figure 4.2 X-ray diffraction pattern for PPVC sample with lead stearate
Figure 4.3 X-ray diffraction pattern for PPVC sample with DBLS
Figure 4.4 X-ray diffraction pattern for PPVC sample with stanclere T186
Figure 4.5 X-ray diffraction pattern for PPVC sample with Stanclere TL
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4.2.5 The Preferred Stabiliser for this Study

From the results of the WAXD study it was found that Stanclere TL was the only stabiliser that did not hinder the assessment of orientation by x-ray diffraction. This measurement was very important for the drawn samples in the subsequent experiments. The non-discolouration of F12 in the ageing tests demonstrated that Stanclere TL also provided effective stabilisation. The results of gel content analyses and softening temperature measurements confirmed that a crosslinked structure was created in this formulation. The tin stabiliser was found to inhibit the crosslinking reaction, but this effect was kept under control by the lowest level of stabiliser possible to maintain adequate stabilisation. In addition, gel formation was improved by other factors such as increasing the irradiation dose and TMPTMA level. Hence, Stanclere TL was selected as the stabiliser for the formulation used in the study of irradiation crosslinking of oriented PPVC compounds.

4.3 Effect of Stabiliser Content

The effect of stabiliser level on the irradiated samples was examined using Stanclere TL at concentrations of 2, 4 and 6 phr in formulations S2, S4 (F12) and S6, respectively. The level of TMPTMA was kept constant at 10 phr in all formulations. The samples were used in the undrawn form. Before irradiation S4 and S6 were colourless and transparent but S2 was slightly yellow. When exposed to an irradiation dose of 4 Mrad S4 and S6 were not discoloured, but S2 became dark yellow.
New photocopying cards

The Library has implemented a re-usable photocopying card system over the summer.

These are for use on all the Library's copiers and can be purchased from dispensers on Level Three of the Pilkington Library for £3.00. This includes £1.00 for the cost of the card, £1.00 of photocopying credits and a £1.00 refundable deposit.

This card should be retained throughout your course and can be "topped up" by using either the note or coin revaluers next to the card dispensers. Users wishing to buy or revalue their cards using switch, should ask at the Information and Enquiries Desk or Issue Desk on Level Three. Please note that the minimum switch card transaction is £5.00.

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- A4 colour: 70p
- A3 black and white: 10p
- A3 colour: £1.40
- Acetates: 40p

Acetates for black and white copying are now available by selecting tray 2 on designated machines. Colour acetates should be purchased from Information and Enquiries Desk.

Please note that some copiers on each level will still have an old card reader attached to allow users to use up any outstanding units on their old cards.
Chapter 4 A Suitable Formulation and Crosslinking Conditions

4.3.1 Percentage Gel Content and Crosslink Density

Gel contents and crosslink densities of S2, S4 and S6 are exhibited in Table 4.3 and Figure 4.6. No gel content was found in any of the unirradiated samples. It can be seen that gel content decreased with the increase in Stanclere TL level. This indicated that the higher the Stanclere TL concentration, the lower the amount of crosslinked structures that can be produced. It was reported that good high temperature tensile strength can be achieved from crosslinked PVC with a gel content of 40% or over. Hjertberg and Dahl found that a relatively small amount of gel can be enough to give rather large improvements in penetration resistance at temperatures in the interval 60 to 110°C, which perhaps is the most important for practical applications. The gel content produced in these formulations would be expected to give rise to good high temperature mechanical properties.

Table 4.3

Percentage Gel Content, Mγ, Crosslink Densities and Softening Temperature

for Unirradiated and Irradiated PPVC S2, S4 and S6

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>%GEL CONTENT</th>
<th>Mγ (g/mol)</th>
<th>CROSSLINK DENSITIES (mol/g)</th>
<th>SOFTENING TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unir</td>
<td>irr</td>
<td>unir</td>
<td>irr</td>
</tr>
<tr>
<td>S2</td>
<td>0</td>
<td>47.4</td>
<td>1.159x10⁴</td>
<td>4.3x10⁻⁵</td>
</tr>
<tr>
<td>S4</td>
<td>0</td>
<td>43.6</td>
<td>1.283x10⁴</td>
<td>3.9x10⁻⁵</td>
</tr>
<tr>
<td>(=F12)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>0</td>
<td>33.2</td>
<td>1.34x10⁴</td>
<td>3.7x10⁻⁵</td>
</tr>
</tbody>
</table>
The results from swelling measurements showed good agreement with gel content results. A decrease in molecular weight between crosslinks or an increase in crosslink density was observed when the stabiliser loading was decreased.

The gel content can be improved by reducing the amount of this stabiliser. S2 gave the highest gel content, but discoloured after irradiation indicating that it was not stabilising the system to a great enough extent. Stanclere TL in PVC at 4phr showed good stabilisation properties. Considering all of the results together, a formulation containing 3phr Stanclere TL was introduced into the study of the irradiation of drawn samples (section 4.6). It was expected to allow higher gel contents than S4, whilst still maintaining stabilisation properties.
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4.3.2 Thermomechanical Analysis

The softening temperatures of S2, S4 and S6 are presented in Table 4.3. Figure 4.7 illustrates the TMA traces of irradiated S3, S4 and S6, along with unirradiated F12 (S4) as a comparison. The softening temperature increased in irradiated samples as a result of the presence of crosslinked structures. The softening temperatures of these three formulations were similar although a difference between the gel contents was observed. The presence of gel affected the penetration resistance in the TMA traces. The TMA traces in Figure 4.7 show that S2 had the highest resistance until the softening temperature was reached. S4 had a lower penetration resistance than S2 and S6 had the poorest performance. It can be concluded that the higher the gel content, the greater the penetration resistance.

4.3.3 Tensile Properties

The tensile properties of S2, S4 and S6 at room temperature and at 130°C are given in Table 4.4 and 4.5 respectively. The room temperature tensile strength was slightly increased in irradiated samples: e.g. the UTS of S4 was increased by 5.5%. The increase of UTS at 130°C was considerable. The increase in the UTS of S2 was 80% and for S6 it was 40%. Elongations at break at room temperature for the irradiated samples were lower than those for the unirradiated samples of the same formulation. This means that the ductility of the material decreased after crosslinking. At 130°C the increase in elongation at break after irradiation was caused by the increased strength of crosslinked material. The linkages between polymer chains allow the neighbouring polymer chains to slip over one another; consequently the tensile specimens are more able to extend.
Figure 4.7 Penetration resistance for irradiated IS2, IS2 and IS6
Figure 4.8 illustrates the influence of stabiliser level on UTS of the irradiated samples both at room temperature and at 130°C. It was noted that UTS fell at higher stabiliser concentrations. This result can be attributed to the effect of the crosslinked network in the samples. The influence of the crosslinked network relates directly to the UTS: the higher the gel content, the greater the strength of the material. Figure 4.9 presents the elongations at break of irradiated S2, S4 and S6 at room temperature and at 130°C. At room temperature the effect of stabiliser level was not very clear, as all of the tensile test results gave similar values. Elongation at break at 130°C increased to a maximum and then decreased with increasing stabiliser level. Corresponding with the low gel content in the crosslinked sample, S6 was the weakest material. The extent of the network structures in S4 was higher than that in S6, so that S4 was stronger than S6. The elongation at break of S4 was increased. The highest gel content in S2 restricted in chain mobility which resulted in a decrease of elongation at break.

Table 4.4

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>UTS AT ROOM TEMPERATURE (MPa)</th>
<th>%ELONGATION AT BREAK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unirr.</td>
<td>irr.</td>
</tr>
<tr>
<td>S2</td>
<td>25.1</td>
<td>26.5</td>
</tr>
<tr>
<td>S4</td>
<td>25.6</td>
<td>27.0</td>
</tr>
<tr>
<td>(=F12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>24.2</td>
<td>25.3</td>
</tr>
</tbody>
</table>
Table 4.5

Tensile Strength and elongation at break at 130°C for Unirradiated and Irradiated PVC S2, S4 and S6

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>UTS (MPa)</th>
<th>%ELONGATION AT BREAK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unirr.</td>
<td>irr.</td>
</tr>
<tr>
<td>S2</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>S4</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>(=F12)</td>
<td>0.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Figure 4.8 Tensile strength at room temperature and at 130°C as a function of stabiliser level
4.4 EFFECT OF TMPTMA LEVEL

In order to study the effect of level TMPTMA, specimens of samples T2 to T20 were prepared. Before being irradiated T2, T5 and T10(F12) were colourless and transparent but sample T20 was slightly yellow. Under an irradiation dose of 4 M.rad, none of the specimens which were initially colourless were discoloured but the yellow specimens became dark yellow.

4.4.1 Percentage Gel Content and Crosslink Density

Variations in percentage gel contents and crosslink densities with TMPTMA concentration are shown in Table 4.6. Samples containing 2phr TMPTMA did not
yield sufficient gel for analysis. The gel content of unirradiated T20 is rather high when compared with the other unirradiated samples. The reasons for this are that this sample contains a very high concentration of TMPTMA and it was prepared and kept at room temperature for long a time before the tests were carried out. As a result crosslinking occurred prematurely.

Table 4.6

Percentage Gel Content, $\bar{M}_c$, Crosslink Densities and Softening Temperatures for Unirradiated and Irradiated PPVC T2-T20

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>%GEL CONTENT</th>
<th>$\bar{M}_c$ (g/mol)</th>
<th>CROSSLINK DENSITIES (mol/g)</th>
<th>SOFTENING TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unirr</td>
<td>irr</td>
<td></td>
<td>unirr</td>
</tr>
<tr>
<td>T2</td>
<td>0</td>
<td>13.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T5</td>
<td>0</td>
<td>26.5</td>
<td>1.858 x 10^4</td>
<td>2.7 x 10^-5</td>
</tr>
<tr>
<td>T10</td>
<td>0</td>
<td>43.6</td>
<td>1.282 x 10^4</td>
<td>3.9 x 10^-5</td>
</tr>
<tr>
<td>(=F12)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T20</td>
<td>26.8</td>
<td>55.6</td>
<td>0.605 x 10^4</td>
<td>8.3 x 10^-5</td>
</tr>
</tbody>
</table>

From Figure 4.10 it can be seen that the higher the TMPTMA content, the higher the gel content and crosslink density. This implies that increased TMPTMA concentration increases the efficiency of crosslinking. This effect was observed previously by Nethsinghe and Gilbert(112).
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Figure 4.10 Gel content and crosslink density as a function of TMPTMA level.

TMPTMA homopolymerisation took place in the initial stage followed by grafting to PVC to form the crosslinked structure.\(^{107-109}\). The increase in TMPTMA level caused a greater amount of polyTMPTMA which in turn increased the number of linkages between PVC chains; consequently a more effective crosslinking system was achieved.

4.4.2 Thermomechanical Analysis

The softening temperatures of T2, T5, T10 and T20 before and after irradiation are listed in Table 4.6; none of the softening temperatures were significantly affected by TMPTMA content except for T20. In the latter case an increase was caused by premature crosslinking in the unirradiated specimen. The higher gel content in irradiated T20 caused the higher softening temperature.
TMA traces showing the effect of increased TMPTMA concentration are shown in Figure 4.11. The effect of network structures can be seen in the traces between about 80°C and the softening temperature. The penetration decreases with increasing degree of crosslinking or TMPTMA level. The trace of irradiated sample T20 shows a very small penetration until the softening temperature is reached, also inferring that the amount of crosslinked structure in this sample is very high.

It can be seen that the traces for irradiated T2(IT2) and irradiated T5(IT5) show an increase in the gradient towards the end of plateau region over the temperature range 110°C-140°C in comparison to the trace of unirradiated F12. The penetration resistance in this range is controlled by the physical network. The increase in penetration resistance of IT2 and IT5 is possibly attributable to the lowering of crystallinity, which may be partially destroyed by the electron beam radiation. This decrease in crystallinity in the irradiated materials was discovered by using DSC as discussed in section 6.2.1. This effect, however, cannot be detected in the TMA traces of the irradiated samples with higher gel contents e.g. IT10, IT20, IS2, IS4, IS6, I4, I6 and I8; neither is the effect seen in the TMA trace for the sample I2 (Figure 4.15) with a lower gel content. It is suggested that in the samples with higher gel contents the chemical networks can compensate for the reduction in crystallinity, therefore the penetration resistance is maintained. The result for sample I2 depends on two factors. Firstly, a lower irradiation dose was employed for I2. This might have caused less damage in the physical network. Secondly, although its gel content is rather low, it appears that the crosslinked network produced is quite dense, as shown by crosslink density values 5.7x10^{-5} (Table 4.6) and 2.7x10^{-5} (Table 4.9) for I2 and IT5, respectively. These structures are responsible for the plateau region in TMA trace.
Figure 4.11 Penetration resistance for F12, IT2, IT5, IT10 and IT20
4.4.3 Tensile Properties

Tables 4.7 and 4.8 present the tensile properties at room temperature and at 130°C for T2, T5, T10 and T20 before and after irradiation. As expected, the increase in tensile strength by the effect of irradiation was slight at room temperature but considerable at 130°C. The percentage elongation at break of the irradiated samples was found to rise at room temperature; conversely a decrease in the percentage elongation at break was noted when the test was performed at 130°C. The effect of premature crosslinking in T20 can be seen clearly by the fact that the percentage elongation at break was remarkably low. Figure 4.12 shows that the tensile strength of the irradiated samples rose with increased TMPTMA level; this effect was much clearer when the test was carried out at 130°C. At elevated temperatures the physical network formed by the crystallites is partially destroyed, so that the strength of the materials must depend upon the chemical network. The study of crystallinity by DSC will be discussed in section 6.2.1.

Table 4.7

Tensile Strength and Elongation at Break at room temperature for unirradiated and irradiated PPVC T2-T20

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>UTS AT ROOM TEMPERATURE (MPa)</th>
<th>%ELONGATION AT BREAK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unirr.</td>
<td>irr.</td>
</tr>
<tr>
<td>T2</td>
<td>25.7</td>
<td>26.0</td>
</tr>
<tr>
<td>T5</td>
<td>25.3</td>
<td>26.5</td>
</tr>
<tr>
<td>T10</td>
<td>25.6</td>
<td>27.0</td>
</tr>
<tr>
<td>(=F12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T20</td>
<td>26.5</td>
<td>27.5</td>
</tr>
</tbody>
</table>
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Table 4.8

Tensile Strength and Elongation at break at 130°C for unirradiated and irradiated PPVC T2-T20

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>UTS (MPa)</th>
<th>%ELONGATION AT BREAK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unirr.</td>
<td>irr.</td>
</tr>
<tr>
<td>T2</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>T5</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>T10</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>(=F12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T20</td>
<td>0.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The plots of elongation at break of irradiated samples as a function of TMPTMA level are shown in Figure 4.13. The difference between the two test temperatures can be clearly seen. At room temperature the greater the TMPTMA level, the lower the elongation at break. The decrease of room temperature elongation at break with increased TMPTMA level implied that the irradiated PVC sample became stronger and harder. The plot of elongation at 130°C against TMPTMA concentration passed through a maximum, which corresponded to the sample with 10 phr TMPTMA. These results are similar to the results of Nethsinghe and Gilbert(112), who explained that chain mobility is greater at higher temperatures. Elongation at break increased in parallel to the increase in strength, but above 10 phr TMPTMA the elongation at break decreased due to the reduction of chain mobility when the crosslink density increases further.
Chapter 4 A Suitable Formulation and Crosslinking Conditions

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**Figure 4.12** Tensile strength at room temperature and at 130°C for crosslinked PPVC compounds as a function of TMPTMA level

---

**Figure 4.13** Elongation at break at room temperature and at 130°C for crosslinked PPVC compounds as a function of TMPTMA level
4.4.4 The selection of TMPTMA Level

In this study the gel content was improved by increasing the level of TMPTMA in the PVC formulations. The formulation with 20 phr TMPTMA was found to produce some gel before the irradiation process took place. This occurrence may lead to difficulties in further processing steps introduced into the procedure. The residual unsaturation in irradiated PPVC samples which included TMPTMA in their formulations was measured by Infrared Spectroscopy\textsuperscript{(112)}. The results showed that this unsaturation could be attributed to the presence of unreacted double bonds of TMPTMA. The percentage of remaining unsaturation in samples containing increasing TMPTMA concentrations was found to be similar until the TMPTMA loading reached 10 phr. Between 10 phr and 20 phr TMPTMA the remaining unsaturation increased proportionally with the radiation sensitiser level. The presence of unsaturation was undesirable since it is known to promote oxidative degradation in the polymer which reduces the service life of the crosslinked product, particularly when exposed to ultraviolet light or elevated temperatures. 10 phr was therefore selected as the optimum concentration of TMPTMA.

4.5 Effect of Irradiation Dose

In order to study the effect of irradiation dose, thin sheet specimens of sample F12 were prepared. Irradiation was performed at doses of 2, 4, 6 and 8 Mrad. None of the irradiated specimens were discoloured.
4.5.1 Percentage Gel Content and Crosslink Density

The influence of irradiation dose upon gel content and crosslink density is illustrated in Table 4.9 and Figure 4.14. It can be seen that an increased irradiation dose at constant TMPTMA level produced an increased gel content, but crosslink density was correspondingly decreased. Crosslink density was considerably reduced in specimens 12 to 14, but fell only slightly between specimens 14 to 18. It has been suggested\(^{112}\) that at an irradiation dose which is higher than the optimum dose, the initial network formed by the crosslinked TMPTMA breaks down and the resulting radicals formed react with more PVC molecules to give a more open structure. It is not possible to conclude that the irradiation dose at 2 Mrad is the optimum dose for this study, since the gel content in 12 was not high enough to modify the mechanical properties at elevated temperatures. Therefore the effect of irradiation dose on the properties of the stretched samples with different levels of stabiliser was investigated and will be discussed in section 4.6.

**Table 4.9**

*Percentage Gel Content, M<sub>c</sub>, Crosslink Densities and Softening Temperature for 12-18*

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>%GEL CONTENT</th>
<th>M&lt;sub&gt;c&lt;/sub&gt; (g/mol)</th>
<th>CROSSLINK DENSITIES (mol/g)</th>
<th>SOFTENING TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unirr</td>
<td>irr</td>
<td>unirr</td>
<td>irr</td>
</tr>
<tr>
<td>I2</td>
<td>-</td>
<td>22.1</td>
<td>0.871x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>5.7x10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
<tr>
<td>I4</td>
<td>-</td>
<td>43.6</td>
<td>1.283x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>3.9x10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
<tr>
<td>(=F12)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I6</td>
<td>-</td>
<td>57.0</td>
<td>1.416x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>3.5x10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
<tr>
<td>I8</td>
<td>-</td>
<td>71.2</td>
<td>1.504x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>3.3x10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
4.5.2 Thermomechanical Analysis

TMA traces showing the effect of increased irradiation dose are shown in Figure 4.15. As expected the penetration resistance increased with the gel content and irradiation dose. The trace of I8 showed the best performance as its gel content was the highest. Although the crosslink density was found to decrease at irradiation doses higher than two Mrad, it was found not to have much effect on the development of a plateau in the TMA trace, however the softening temperature of I2 was higher than those of I4, I6 and I8, as shown in Table 4.9. The small amount of network structures with high crosslink density in I2 caused the raising of its softening temperature.
Figure 4.15 Penetration resistance for I2, I4, I6, I8 and F12
4.5.3 Tensile properties

Table 4.10 and Figures 4.16 to 4.17 show the influence of irradiation dose upon tensile strength and elongation at break both at room temperature and at 130°C. As expected the effect is more significant at higher test temperatures. The tensile strength also increased with longer irradiation doses. This implied that the effect of the gel content on this property had a greater influence than that of crosslink density. The gel content increased with irradiation dose but crosslink density fell at larger irradiation doses.

The elongation at break of I2 at 130°C was slightly greater than that of the same formulation in the unirradiated form due to the small amount of gel present in this sample. Elongation at break markedly increased from I2 to I4 and then levelled off over the range I4 to I8, even though the gel contents of each were much different (they were 43.6, 57.0 and 71.2, respectively). This observation showed the combination of the effects of gel content and crosslink density. If the effect of gel content alone was considered, the plot would be expected to pass through a maximum in a similar manner to the plot between percentage elongation at break at 130°C and TMPTMA content. The decrease in crosslink density in samples exposed at higher radiation doses permitted greater mobility in network structures which allowed the greater percentage elongation at break.
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Table 4.10
Tensile Strength and Elongation at Break at room temperature and at 130 °C for I2-I8

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PROPERTIES AT ROOM TEMPERATURE</th>
<th></th>
<th>PROPERTIES AT 130°C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UTS/MPa</td>
<td>%EB</td>
<td>UTS/MPa</td>
<td>%EB</td>
</tr>
<tr>
<td>I2</td>
<td>26.5</td>
<td>237</td>
<td>0.6</td>
<td>115</td>
</tr>
<tr>
<td>I4</td>
<td>27.0</td>
<td>251</td>
<td>0.8</td>
<td>196</td>
</tr>
<tr>
<td>(=F12)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I6</td>
<td>28.0</td>
<td>245</td>
<td>1.0</td>
<td>178</td>
</tr>
<tr>
<td>I8</td>
<td>27.0</td>
<td>226</td>
<td>1.4</td>
<td>176</td>
</tr>
</tbody>
</table>

Figure 4.16 Tensile strength at room temperature and at 130 °C for crosslinked PPVC compound as a function of irradiation dose
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Figure 4.17 Elongation at break at room temperature and at 130°C for crosslinked PPVC compound as a function of irradiation dose

4.6 STUDY OF ORIENTED SAMPLES

In this section the work was focused upon the combined effect of stabiliser level together with irradiation dose on the properties of crosslinked oriented samples with draw ratio in the range of 1.5 to 1.6. As stated in section 4.3.1 the gel content can be improved by keeping the stabiliser level as low as possible. From section 4.5.1 it was found that the higher the irradiation dose used, the greater the gel content that was formed. A compromise between these two variables was sought, as both affect the stability of the system. TMPTMA at a concentration of 10 phr was used in this experiment. Levels of stabiliser at 2, 3 and 4 phr (samples S2, S3 and S4 in Table 2.1) and irradiation doses of 3, 4 and 6 Mrad were chosen. Percentage gel contents were measured together with tensile properties at 100°C. The temperature of 100°C was selected instead of 130°C in order to reduce the amount of shrinkage of the drawn
samples and reserve some part of the crystallites which melt at temperatures higher than 100°C. These crystallites retard the plastic flow behaviour, leading to more precise results in tensile tests. The tensile strength data in Tables 4.5, 4.8 and 4.10 are very low because at 130°C the majority of the crystallites melt and the samples become soft.

Table 4.11

Percentage gel content and tensile strength at 100°C for irradiated drawn S2, S3 and S4 at the dose of 3, 4, and 6Mrad.

<table>
<thead>
<tr>
<th>SAMPLE (λ=1.5-1.6)</th>
<th>%GEL CONTENT</th>
<th>UTS AT 100°C (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3Mrad</td>
<td>4Mrad</td>
</tr>
<tr>
<td>S2</td>
<td>30.1</td>
<td>37.0</td>
</tr>
<tr>
<td>S3</td>
<td>28.1</td>
<td>34.9</td>
</tr>
<tr>
<td>S4</td>
<td>27.0</td>
<td>32.6</td>
</tr>
</tbody>
</table>

The results of these tests are displayed in Table 4.11 and Figures 4.18-4.19. The irradiation dose at 6 Mrad showed the greatest effect both in gel formation and in improvement of tensile strength at 100°C. The gel content decreased with an increase in stabiliser content at all irradiation doses. Tensile strength also decreased with increased stabiliser concentration at the irradiation doses of 3 and 4 Mrad. After the specimens were exposed at 6 Mrad, the lowest tensile strength was found in S2 and the highest one was found in S3. This can be attributed to the stabilisation effect. It is possible that the molecules in S2 broke down at this irradiation dose, due to the inadequate concentration of stabiliser. From these experimental observations the stabiliser level at a concentration of 3phr was selected in order to maintain the desired
Figure 4.18 Gel content as a function of stabiliser level

Figure 4.19 Tensile strength as a function of stabiliser level
stabilisation, whilst still enabling crosslinking to occur using an irradiation dose of 6Mrad.

4.7 CONCLUSION

The liquid tin stabiliser Stanclere TL was found to be the most suitable stabiliser for PVC in the study of crosslinking of oriented PPVC compounds. The optimum concentrations of TMPTMA and stabiliser were 10 phr and 3 phr respectively. An irradiation dose of 6 Mrad was found to provide satisfactory crosslinking conditions.
5.1 INTRODUCTION

The experimental work outlined in chapter 4 showed that formulation S3 and an irradiation dose of 6 Mrad provided the optimum formulation and post processing conditions respectively; this system was employed as the basis for the work in this section. To study the effect of plasticiser content on the properties of irradiated samples, formulation P25 (which contained a low plasticiser concentration) was also used in this section. The glass transition temperature (Tg) of sample S3 and P25 were -21°C and -5°C, respectively. The values of Tg were obtained by thermomechanical analysis (TMA) using a DuPont 990 thermal analyser, at heating rate of 10°C.

The aim of this part of the research programme was to examine the influence of crosslinked structures and/or oriented structures upon tensile and impact properties. Additionally the effect of sample thickness upon gel formation was investigated, because the drawing process reduces sample thickness, which in turn may affect the result of the irradiation process.

5.2 EFFECT OF SAMPLE THICKNESS

When a film sample is irradiated it has been shown that the maximum dose occurs within the body of the material and not at the incident surface. This is due to
the elastic collisions with atomic nuclei which tend to scatter the incident electrons in all directions. Wide-angle elastic scattering causes the build-up in the dose in the body of the material close to the sample surface (the distance from the surface is controlled by the sample density) and a gradual reduction in the dose beyond the maximum point. Figure 5.1(a) shows the variation in electron beam radiation dose with product thickness. The dose distribution through the product can be improved by irradiating the sample from two directions, as shown in Figure 5.1(b).

![Diagram of dose distribution](image)

**Figure 5.1 (a) The dose distribution from a mono-directional irradiation(I) of product with mono-energetic electrons (b) The effect of a two-sided(I+II) irradiation of a thicker product**

The applicability of the established theory described above to the system under investigation in this work was examined. The effects of specimen thickness of moulded sheets and undrawn samples of formulations S3 and P25 were studied. The results were related to gel formation and tensile properties.
5.2.1. Percentage gel content

The relationships between specimen thickness of undrawn samples S3 and P25 and gel content is shown in Figure 5.2 and Table I.1 in Appendix I. It was found in both formulations that gel content decreased with increasing sample thickness. The dose of electron beam radiation in the middle of sample decreases with increasing sample thickness, as shown in Figure 5.1(b); it was found in section 4.5.1 that the formation of gel was enhanced at higher radiation doses, and hence in the thicker samples the formation of crosslinked structures is reduced.

Gel formation in S3 was found to be more sensitive to sample thickness than that of P25. The differences in behaviour between these two samples are related to the different plasticiser contents in each formulation. This result shows good agreement with Kojima et al.\textsuperscript{(104)} who found that the gel content ratios in irradiated PVC were
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- Nottingham Trent University
- University of Leicester
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larger when the plasticiser level was increased. This effect was also found by Bowmer et al.\cite{109} in the study on the effect of diundecylphthalate (DUP) on the radiation crosslinking of PVC with TMPTMA. Their results showed that the introduction of DUP, as a plasticiser, into the mixtures enhanced TMPTMA polymerisation, TMPTMA grafting and the rate of the PVC crosslinking reaction. It is also possible that the dissimilar performances of S3 and P25 are related to the formation of unlike types of crosslinked networks in each material, due to the changed crosslinking reaction environment in each formulation.

5.2.2. Tensile properties

The shapes of the tensile stress-strain curves were similar to those found in section 4.3.3 and 4.4.3; this behaviour is directly related to the material gel content. Figure 5.3 and Table 1.2 present the variations in tensile properties at 100°C with specimen thickness. The results show that tensile strength rises with an increase in gel content in the sample. The plot of elongation at break against sample thickness, shown in Figure 5.3, contains a maximum corresponding to a sample thickness of about 0.3mm. The portion of the curve up to a sample thickness of 0.3mm may be explained by the following argument: in the thinnest specimen, the most extensive crosslinked network is formed and as a consequence the movement of polymer chains is highly restricted. This results in a low tensile elongation at break. As sample thicknesses increase, the extent of crosslink formation in the materials decreases, which is detected by the lowering of the measured gel contents; since there are fewer tie points between adjacent molecules, neighbouring polymer chains are freer to slip over one another and hence the tensile specimens are more able to extend. As sample thicknesses increase over the range 0.3mm to 0.5mm the proportion of crosslinking sites, which is directly related to gel content, in the test specimen becomes so low that there are insufficient
forces holding the PVC chains together and the polymer molecules rapidly slip over one another; this leads reduced elongations. Similar results were also found in the sample containing 25phr DIOP, as shown in Figure 5.4

5.2.3. Selection of Sample Thickness

It can be seen clearly that the sample thickness has a large influence upon crosslink formation; the thicker the sample, the lower the gel content and hence tensile strength. To eliminate this effect, drawn and undrawn samples were produced at the same thickness. A very small sample thickness was employed to enhance gel content formation. Practically it is only possible to produce even specimen thicknesses with good precision up to the nearest tenth of a millimetre in PVC moulded sheets. It is more difficult to control sample thickness for drawn samples, as the stretching step in the sample preparation reduces thickness further. To tackle this problem a number of samples were prepared from which were cut mechanical test specimens; specimens of very similar thicknesses were employed for comparative work. The thicknesses of test specimens were in the range of 0.21mm to 0.22mm.

5.3 Effect of Draw Ratio

As stated in section 1.9, draw ratio is the most significant variable affecting the mechanical properties of the oriented PVC samples. In this section, the investigation was concentrated on the effect of draw ratio upon gel formation and the changes of tensile and impact properties of samples after irradiation. Sample S3 and P25 were prepared and stretched to different draw ratios, followed by electron beam irradiation at a dose of 6 Mrad. To limit the influence of thickness variations upon the mechanical
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Figure 5.3 Effect of sample thickness on tensile properties at 100°C for S3.

Figure 5.4 Effect of sample thickness on tensile properties at 100°C for P25.
properties, all test specimens were cut from drawn and undrawn samples with thicknesses in the range 0.21mm to 0.22mm

5.3.1. Percentage gel content

Table 5.1 displays the effect of draw ratio on the gel contents of irradiated samples of formulations containing 46.5 phr DIOP (S3) and 25phr DIOP (P25). It can be seen that the highest gel content was found in undrawn sample S3, whilst similar gel contents were measured in samples with draw ratios in the range 1.3 to 1.7. This implies that the efficiency of the crosslinking reaction taking place in the undrawn samples is higher than in the drawn samples. After sample drawing and annealing in the stretched state, the formation of small crystallites locks the oriented polymer chains into position, which leads to reduced chain mobility; the crosslinking reaction was less extensive in the drawn sample, resulting in reduced gel formation. This result shows good agreement with Nikolova and Mateev(170) in the study into irradiation of oriented LDPE films. They found that the orientation of polyethylene films decreased the formation of networks induced by irradiation. The gel content of drawn samples was found to be independent of draw ratio in the range studied, although the mobility of chains related directly to draw ratio. It is possible that the draw ratios employed in this work are not high enough to play a significant role in the reduction of chain mobility.

It can be seen that for samples with lower plasticiser contents, the effect of orientation is insignificant; the gel contents in the drawn and undrawn samples with the lower plasticiser contents over the draw ratio range 1.4 to 1.9 were similar. Although the mobility of chains in the oriented samples was expected to be lower than before stretching, the difference in gel formation was not distinctive. Over the range of draw
ratios studied, it is suggested that the reduction of the mobility of polymer chains by orientation had a very small effect upon the crosslinking reaction.

Table 5.1
Effect of draw ratio on % gel content

<table>
<thead>
<tr>
<th>FORMULATION</th>
<th>DRAW RATIO</th>
<th>% GEL CONTENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3</td>
<td>1.0</td>
<td>44.01</td>
</tr>
<tr>
<td>(46.5 phr DIOP)</td>
<td>1.26-1.28</td>
<td>37.19</td>
</tr>
<tr>
<td></td>
<td>1.39-1.41</td>
<td>36.93</td>
</tr>
<tr>
<td></td>
<td>1.52-1.54</td>
<td>37.32</td>
</tr>
<tr>
<td></td>
<td>1.66-1.70</td>
<td>38.39</td>
</tr>
<tr>
<td>P25</td>
<td>1.0</td>
<td>29.94</td>
</tr>
<tr>
<td>(25 phr DIOP)</td>
<td>1.34-1.40</td>
<td>30.84</td>
</tr>
<tr>
<td></td>
<td>1.62-1.64</td>
<td>30.86</td>
</tr>
<tr>
<td></td>
<td>1.82-1.86</td>
<td>32.97</td>
</tr>
</tbody>
</table>

5.3.2 Tensile Properties

Figure 5.5 and 5.6 show typical stress-strain curves obtained in tensile tests of specimens of S3 and P25 respectively. The ultimate tensile strength of both formulations at both temperatures falls in the sequence:

UTS unirr. undrawn < UTS irr. undrawn < UTS unirr. drawn < UTS irr. drawn
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The plasticisers used in both formulations examined in this work resulted in rubber like physical performances of the materials under tensile test conditions. As expected, the UTS of unirradiated undrawn P25 was found to be higher than that of S3. Tensile strength is generally reduced by the addition of plasticiser since the stress developed is reduced because of the lower molecular cohesion(143). None of the curves for S3 displayed in Figure 5.5A and B show clearly defined yield points. The results show that orientation results in an increase in modulus at 100% strain (which is referred to as 100% modulus). The crosslinked structures also improve the 100% modulus in both drawn and undrawn samples. Similar performances were observed in the tensile properties of P25 at room temperature (see Figure 5.6A). The yield points observed in the tensile tests performed on P25 at room temperature are more pronounced than those in all the other plots. When the tensile tests were performed at 100°C, the 100% modulus of irradiated drawn P25 was found to be lower than that of the corresponding unirradiated drawn sample. The reasons for this are as yet unclear.

The results of tensile strength and elongation at break measurements at room temperature and at 100°C of S3 and P25 are given in Tables I3 and I4 and Figures 5.7 to 5.10. Tensile strength was found to be enhanced at increased draw ratios. The explanation was that biaxial stretching raises the number of crystallites lying in the plane of the film; x-ray diffraction studies reported in section 6.3 support this argument. The number of crystallites was found to increase with increasing sample draw ratio. These crystallites contribute to the mechanical property modification in the plane of the film which is higher in the more highly oriented sample, that is at larger draw ratios. The increase in room temperature tensile strength produced by the effect of irradiation for both formulations was small. A significantly improved tensile strength of the irradiated materials over the unirradiated samples can be seen when tensile tests were performed at 100°C. It is concluded that the strength at room temperature is
Figure 5.5 Stress-strain curves of S3 (A) at room temperature and (B) at 100°C.
Figure 5.6 Stress-strain curves of P25 (A) at room temperature and (B) at 100°C.
Figure 5.7 Effect of draw ratio on tensile properties at room temperature of S3
Figure 5.8 Effect of draw ratio on tensile properties at room temperature of P25
Figure 5.9 Effect of draw ratio on tensile properties at 100°C of S3
(The explanation of draw ratio(*) will appear in Appendix III.)
Figure 5.10 Effect of draw ratio on tensile properties at 100°C of P25

(The explanation of draw ratio(*) is given in Appendix III.)
largely controlled by physical networks, as the gel content of the samples was not high enough to influence this property. At elevated temperatures the chemical networks significantly affect the ultimate tensile strengths of the materials since some parts of the physical network melts, and thus leaves the resistance to the applied tensile load to the chemical network, which still remains at higher temperatures. The melting of these crystallites will be discussed in section 6.2.1.

The effect of crosslinked structures on tensile strength is more pronounced in the formulation containing 46.5 phr DIOP (S3) in comparison with material containing less plasticiser (P25). This result is associated with the gel content that is higher in S3.

Elongations at break of the biaxially drawn samples were found to fall with increasing draw ratio. As mentioned in section 1.9, the presence of aligned polymer chains in the plane of the film not only increases strength but also restricts further chain extension, so that elongation at break is reduced. At room temperature the effect of irradiation upon elongation at break was insignificant for all samples except undrawn S3 (Figure 5.7B and 5.8B) for which the elongation at break was greatly decreased upon irradiation. This reduction is caused by the restriction of molecular chains due to the presence of the crosslinked network. It seems that the higher mobility system is more sensitive to changes in the internal structure, since the irradiation crosslinked structures shows no effect on the elongation at break of undrawn P25.

The significantly increased elongations at break at 100°C for irradiated samples of both compounds are highlighted in Figures 5.9B and 5.10B. At this temperature the physical network formed by the crystallites is partially destroyed (see section 6.2.1); consequently the polymer molecules in unirradiated specimens slip past one another,
leading to failure at lower strains. The crosslinks in the irradiated samples prevent PVC chains from completely slipping away from one another as a result in the higher strength and elongation at break in crosslinked samples.

5.3.3. Impact Properties

The formulation containing 46.5phr DIOP was employed in the study of the dependence of impact properties on draw ratio and crosslinked structures. An undrawn sample and a series of drawn samples were prepared and exposed to electron beam radiation at the dose of 6 Mrad. Impact testing was performed using a Rosand instrumented falling weight impact tester; the experimental details are given in section 2.3.2.2.

The mode of fracture of all samples appears to follow the same ductile fracture mechanism. Typical force-extension plots are displayed in Figure 5.11; (A) for unirradiated undrawn S3; (B) for irradiated undrawn S3; (C) for unirradiated drawn S3 (D.R.=1.3) and (D) for irradiated drawn S3 (D.R.=1.3). The summary of the impact study is shown in Table 1.5 and Figures 5.12-5.13. Considering first the unirradiated series it can be seen that both maximum force and energy to peak force rise with the increasing draw ratio. The alignment of PVC molecules in the plane of the film results in an increased resistance to impact under falling weight impact test conditions.(85)

The maximum impact forces measured for the irradiated series were higher than those for the unirradiated series; as crosslinking takes place in the compound, the chemical bonds in the network formed link adjacent PVC molecules, which results in a greater resistance to specimen deformation under the applied impact load. The plot of energy to peak force versus draw ratio also shows the improvement in impact
Figure 5.11 (A) A typical force-extension plot for unirradiated undrawn S3

Figure 5.11 (B) A typical force-extension plot for irradiated undrawn S3
Figure 5.11 (C) A typical force-extension plot for unirradiated drawn S3

Figure 5.11 (D) A typical force-extension plot for irradiated drawn S3
Figure 5.12 Effect of draw ratio on maximum force for S3

Figure 5.13 Effect of draw ratio on energy at maximum force for S3
performance that is promoted by the presence of the crosslinked structures. The trend is not as pronounced as the plot of maximum force versus draw ratio. This is the consequence of the presence of plateau at the top of the force-extension plot (see Figure 5.11), and hence the measurement of peak force is more precise than that of energies to peak force.

5.4 EFFECT OF ANNEALING TEMPERATURE

Specimens of sample formulation S3 were biaxially drawn at 80°C at draw ratios in the range 1.5 to 1.6 and then were annealed under strain at 80°C, 90°C and 100°C for 20 minutes. The results obtained from percentage gel content and tensile property measurements are discussed in the following sections.

5.4.1 Percentage Gel Content

The variation of percentage gel content with annealing temperature is illustrated in Figure 5.15 and Table 5.6. The results show that the gel contents of samples annealed at 90°C and 100°C were slightly lower than the sample which was annealed at 80°C. It is known from studies into irradiation crosslinking of polyethylene by many investigators\(^{(171-173)}\) that the irradiation process preferentially induces the formation of crosslinks in the amorphous phase. The degree of crystallinity of PVC increases with increasing annealing temperature from above T\(_g\) up to 130°C\(^{(62)}\). These observations lead to the possible explanation that at annealing temperatures higher than 80°C the increase in crystallinity or the reduction of mobility of molecular chains is responsible for the fall in the level of gel formation. The values obtained for gel contents in samples annealed at 90°C and 100°C are very similar; it is suggested that this is related to the near identical crystallinities determined in these two samples.
5.4.2. Tensile Properties

The plots of tensile strength and elongation at break versus annealing temperature are displayed in Figures 5.15 to 5.16 and Table I.7. The tensile properties measured at room temperature are consistent with those reported by Gilbert et al.\(^{(86)}\), that is the annealing temperature appears to have little effect upon tensile performance. Tensile properties at elevated temperatures, are however, increased by the presence of crosslinking structures. The elongation at break at 100°C of the sample annealed at 80°C shows the greatest increase over the corresponding unirradiated sample under the same test conditions. This is related to the fact that the highest gel content was found in this sample, which leads to the greatest resistance to polymer flow at elevated temperatures.

![Figure 5.14 Effect of annealing temperature on % gel content for oriented S3 at draw ratio range of 1.5-1.6](image-url)
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Figure 5.15 Effect of annealing temperature on tensile strength for S3

Figure 5.15 Effect of annealing temperature on elongation at break for S3
5.5 CONCLUSIONS

Sample thickness was found to influence gel formation. The thinner the specimen, the higher the gel content that can be produced; this results in the attainment of the most desirable tensile properties. The macromolecular chain mobility in each compound was found to affect gel formation; compound S3, containing 46.5 phr DIOP, contained a greater gel content than formulation P25, with 25 phr DIOP.

Tensile and impact properties were observed to improve with the increasing draw ratio. The crosslinked structures formed within the PVC compounds, which were induced by electron beam irradiation, result in the improvement in mechanical properties of the drawn samples. A significant improvement was found in tensile properties when tensile tests were carried out at elevated temperatures.

The annealing temperature appeared to have only a small effect upon gel formation and tensile properties of the formulation containing 46.5 phr DIOP. The annealing temperature at 80°C was selected for this programme as at this temperature the highest gel content and draw ratio, as shown by the maximum elongation at break in Figure 3.1, were achieved in this compound.
6.1 INTRODUCTION

The aim of this part of the programme was to investigate the changes in structures after PPVC has been modified by stretching and/or irradiation crosslinking. DSC and density measurements were carried out to ascertain crystallinity changes; XRD was employed to examine crystallite orientation. Molecular orientation was followed by birefringence determinations. Thermal shrinkage and room temperature recovery rate were also studied to investigate the stability of modified structures. Structure-property correlations were drawn from the experimental data.

6.2 CRYSTALLINITY MEASUREMENTS

6.2.1 Differential Thermal Analysis

DSC traces of specimens cut from moulded sheets of two of the formulations used in this study are shown in Figure 6.1. The traces are very similar in appearance and show three characteristic peaks. According to Juijn et al.\(^{28}\) endotherm B corresponds to the melting of relatively well developed crystalline structures known as 'primary crystallinity'. Gilbert and co-workers\(^{11,18}\) have shown that endotherm A arises because of the melting of secondary crystallites in PVC; 'secondary crystallinity' is produced as a PVC network develops. It was also noted that the onset temperature
Figure 6.1 DSC thermograms for compounds S3 and P25
of endotherm B coincides with the actual processing temperature employed during sample preparation; in this work the moulding temperature of 175°C for S3 and P25 was used. Endotherm C relates to the melting of secondary crystallinity produced during room temperature storage; as described by Juijn et al.\(^{28}\). The DSC study in this programme was primarily concerned with these three endotherms.

**Endotherm C**

The effect of oriented structures on secondary crystallinity was investigated by measuring the change in the enthalpy of endotherm C with sample age; samples of formulation S3 in undrawn and drawn states, with draw ratios of 1.3 and 1.6, were used for this purpose. The results given in Figure 6.2 show that the enthalpy of endotherm C of both undrawn and drawn samples fall on the same line. It may therefore be concluded that orientation has no effect upon endotherm C. All of measured enthalpies increase with time; at a high rate over the first three weeks, followed by a slower rate of increase thereafter.

The effects of orientation and the formation of crosslinked structures upon the enthalpy of endotherm C, for formulations S3 and P25 at the same age, were studied; the findings are presented in Table 6.1. For a given formulation it can be seen that the enthalpy of endotherm C is neither affected by sample drawing nor by electron beam radiation treatment, and hence it may be concluded that neither orientation nor irradiation has any effect upon secondary crystallinity. This observation was surprising because it was expected that orientation and crosslinking would hinder molecular chain movement, leading to a reduction in crystallinity formed during room temperature annealing. It is possible that the draw ratios employed in the oriented samples are not high enough to affect the formation of these crystallites. A similar argument can be
Figure 6.2 The variation of the change in enthalpy of endotherm C with time for undrawn and drawn samples S3

made for the crosslinked samples: the gel content may not be great enough to prevent
the movement of molecular chains.

-Endotherms A and B

The effect of orientation and crosslinking upon endotherms A and B of sample
formulations S3 and P25 are presented in Table 6.2 and Figures 6.3-6.4. Considering
firstly the effect of orientation, it is noteworthy that the drawn samples shrink upon
heating; this movement of molecular chains might affect the measurement of the
melting endotherms, which are very broad due to the existence of a wide range of
Table 6.1

The effect of orientation and crosslinking upon enthalpy of endotherm C

<table>
<thead>
<tr>
<th>SAMPLE/D.R.</th>
<th>ENTHALPY OF ENDO THERM C (J/g)</th>
<th>UNIRR. SAMPLE</th>
<th>IRR. SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3 / 1.0</td>
<td>1.675</td>
<td>1.656</td>
<td></td>
</tr>
<tr>
<td>S3 / 1.25</td>
<td>1.893</td>
<td>1.653</td>
<td></td>
</tr>
<tr>
<td>S3 / 1.4</td>
<td>1.688</td>
<td>1.882</td>
<td></td>
</tr>
<tr>
<td>S3 / 1.6</td>
<td>1.877</td>
<td>1.730</td>
<td></td>
</tr>
<tr>
<td>P25 / 1.0</td>
<td>2.298</td>
<td>2.464</td>
<td></td>
</tr>
<tr>
<td>P25 / 1.35</td>
<td>2.456</td>
<td>2.251</td>
<td></td>
</tr>
<tr>
<td>P25 / 1.6</td>
<td>2.287</td>
<td>2.267</td>
<td></td>
</tr>
<tr>
<td>P25 / 1.8</td>
<td>2.402</td>
<td>2.264</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.2

The effect of orientation and crosslinking upon enthalpy of endotherm A and B

<table>
<thead>
<tr>
<th>SAMPLE / D.R.</th>
<th>ΔH OF UNIRR. SAMPLE (J/g)</th>
<th>ΔH OF IRR. SAMPLE (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ENDOTHERM A</td>
<td>ENDOTHERM A</td>
</tr>
<tr>
<td>S3 / 1.0</td>
<td>10.104</td>
<td>4.224</td>
</tr>
<tr>
<td>S3 / 1.25</td>
<td>9.907</td>
<td>4.282</td>
</tr>
<tr>
<td>S3 / 1.6</td>
<td>10.014</td>
<td>4.051</td>
</tr>
<tr>
<td>P25 / 1.0</td>
<td>8.500</td>
<td>5.083</td>
</tr>
<tr>
<td>P25 / 1.35</td>
<td>8.687</td>
<td>4.676</td>
</tr>
<tr>
<td>P25 / 1.8</td>
<td>8.548</td>
<td>4.800</td>
</tr>
</tbody>
</table>
crystallite sizes and/or levels of perfection. As a result the accuracy of measurement of the enthalpy is limited. The results in Table 6.2 show that the differences in endotherms A and B between the undrawn and drawn sample for both formulations are not significant. As mentioned in the beginning of this section, the B endotherm is related to primary crystallinity and the A endotherm corresponds to secondary crystallinity that is produced as a PVC network develops. The crystallinities of the oriented samples were expected to be higher than those of the undrawn samples, according to the findings about polymer crystallisation induced by stretching\(^{47-57}\). At this stage, further interpretation of the effect of PPVC orientation on crystallinity is probably not justified due to uncertainties in the measured enthalpy of the stretched samples.

The effect of crosslinked structures on the thermogram is clearly seen in Figures 6.3 and 6.4 for formulation S3 and P25, respectively; the full set of data is presented in Table 6.2. It is can be seen that irradiation produces a lowering of the enthalpy of endotherm A. This implies that the introduction of chemical networks by irradiation partially destroys crystallinity although the crosslinking reaction mechanism is not at present understood. The decrease of crystallinity was also found to reduce the penetration resistance of the crosslinked samples with low gel contents, as discussed in section 4.4.2.

The baseline in the thermogram is not distinct, and due to the close proximity of peak A and B changes in the size of either one of these peaks will affect the measurement of the other; it is thought that this is the reason for the reduction in the enthalpy of peak B. In actuality the primary crystallinity is not changed by irradiation, as shown later in the WAXD results.
Figure 6.3 Effect of irradiation and orientation upon endotherm A and B for compound S3
Figure 6.4 Effect of irradiation and orientation upon endotherm A and B for compound P25
6.2.2 Density Measurement

The densities of samples of formulation S3 were measured using a Davenport density gradient column operated at 23.0±0.1°C, as described in detail in section 2.3.6. The results are displayed in Figure 6.5 and Table II.1 (in Appendix II). The density of a sample that was unirradiated, drawn and annealed at 100°C is also included in the graph to investigate the effect of annealing temperature upon density. Considering first the unirradiated series, it is seen that density slightly increases with draw ratio. The density of the sample annealed at 100°C was considerably higher than that of the undrawn sample and the sample drawn and annealed at 80°C. The increase in density was attributed to the rise in crystallinity in the sample annealed at the greater temperature(18). It can be seen that orientation has a very small effect upon density in comparison to the effect of the change in crystallinity by annealing, and hence it may be concluded that biaxial orientation does not have a major influence upon the change in crystallinity of PPVC. This deduction is consistent with the results from the study of uniaxially oriented PVC(63,79). It was suggested(79) that the change in density with draw ratio is most likely related to conformation changes and ordering rather than true crystallisation, since these changes are extremely small.

The effect of irradiation on density is much more pronounced than the effect of orientation on density; this is highlighted in Figure 6.5. Apparently the densities of the crosslinked samples are considerably higher than those of the uncrosslinked. The observed increase was attributed to the fact that crosslinking causes additional restrictions to the flexibility of the molecules, with a corresponding reduction in free volume. This effect is widely known in vulcanised rubber systems. In the series of crosslinked samples, the density was found to be independent of draw ratio. This
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shows that the influence of crosslinking on molecular arrangement is greater than that of orientation.

![Figure 6.5 Effect of irradiation and crosslinking upon density for compound S3](image)

6.2 MEASUREMENT OF BIREFRINGENCE

The birefringence of the undrawn and drawn samples of formulation S3 were carried out using optical microscopy. A quartz Ehringhaus compensator was used for in-plane birefringence determinations of all materials and the out of plane birefringence measurements on the undrawn samples. To determine out of plane birefringence, sections of different thicknesses were cut from the sample plaque; the birefringence of each was recorded. The slope of a plot of birefringence against sample thickness yielded the value for out of plane birefringence. The out of plane birefringence of drawn samples was measured by conoscopy. This technique cannot be used for the undrawn samples because the distance (d) between two isogyres (see section 2.3.5) is
out of the measurable range. The positions of drawn samples used for determination of
birefringence are shown in Figure 6.6.

![Figure 6.6 Schematic representation of the positions from which samples were cut for birefringence determinations](image)

Figure 6.7 shows the changes of plane orientation (the average value of the
two out of plane birefringence values) with draw ratio. It can be seen that all the plane
orientation values are extremely small (in the range $0.4 \times 10^{-4}$ to $3.2 \times 10^{-4}$) in comparison to the values in the range $1 \times 10^{-3}$ to $5 \times 10^{-3}$ for uniaxially and biaxially oriented UPVC\cite{72,78,79,88}; variations in plane orientation with draw ratio for the samples used in this study do not show any clearly defined trends. Figure 6.8 compares the birefringence values obtained herein with some published data\cite{174} for oriented UPVC materials.

Equation 6.1\cite{79} shows that the total birefringence is a combination of the
birefringence arising from both crystalline and amorphous regions.
Figure 6.7 Effect of draw ratio upon plane orientation for compound S3

Figure 6.8 Comparisons of the measured birefringence of biaxially oriented PPVC and UPVC
\[ \Delta n_T = X_{C,V} \Delta n_C^+ (1 - X_{C,V}) \Delta n_a + \Delta n_f \] .... 6.1

where \( \Delta n_T \), \( \Delta n_C \), \( \Delta n_a \) and \( \Delta n_f \) are the total, crystalline, amorphous and form birefringence, respectively; and \( X_{C,V} \) is the volume degree of crystallinity.

The crystalline orientation, measured by WAXD, was found to increase with draw ratio (see section 6.4.1). Due to the very low crystallinity in PVC, birefringence arises primarily from amorphous regions. The relaxation of the chains seems to be extensive in the PPVC formulation containing 46.5 phr; the total size of the specimen shrinks from 289 cm\(^2\) to 242 cm\(^2\) immediately after release from the BASE (see Figure 6.22). This probably is the reason for the very low birefringence. Residual stresses remaining in the specimen from the compression moulding process may well affect the final stress state after biaxial stretching. It can be concluded that molecular orientation cannot be detected by this method.

6.4 Crystalline Orientation

Crystalline orientation was examined by using two x-ray diffraction techniques: firstly in the reflectance mode, to produce WAXD patterns and secondly in the transmission mode to produce x-ray diffraction patterns on photographic plates. The results are presented in the following sections.

6.4.1 Wide Angle X-ray Diffraction (WAXD)

Figure 6.9 and 6.10 illustrate WAXD traces of undrawn and drawn samples of formulations S3 and P25, respectively. It can be clearly seen that every pattern contains a peak at \(-17^\circ\theta\), with a second peak on its shoulder at \(-18.5^\circ\theta\), and a
broad peak centred at \(-24.5^\circ\). It is suggested that the peak at \(-28.7^\circ\) belongs to a component in the plasticiser, since this peak is smaller in the formulation with a lower plasticiser content. The peak at \(17^\circ\), arising from x-ray reflections by the (200) plane in the PVC crystallites, was used to follow crystalline orientation. Figure 6.11 shows the orthorhombic unit cell of PVC, with the (200) plane highlighted; the polymer chains lie parallel to the c-axis (known as the chain direction). This peak is referred to as the A-peak, following the system used in the work of Gilbert et al.\(^{86}\). The ratios of the A-peak in the diffractograms of the drawn samples to the equivalent peak for undrawn samples were calculated; the results are plotted against draw ratio in Figure 6.12. Considering firstly the oriented sample series, it can be seen that the A-peak ratio increases with draw ratio. These findings show that biaxial stretching increases the number of crystallites lying in the plane of the film. This results in a significant increase in mechanical properties in the plane of the film.

![Figure 6.9 WAXD traces of undrawn and drawn samples for compound S3](image-url)
Figure 6.10 WAXD traces of undrawn and drawn samples for compound P25

Figure 6.11 Orthorhombic unit cell of PVC showing the (200) plane
The A-peak ratio values are higher for the sample containing less plasticiser (P25); this is attributed to the higher stability of crystalline orientation. It appears that crosslinking does not significantly affect crystalline orientation, since the A-peak ratio of the irradiated samples followed the same trend as that of the unirradiated. S3 annealed at 100°C was found to give a slightly lower A-peak ratio compared with S3 annealed at 80°C at the same draw ratio. The observed decrease was caused by the greater degree of relaxation of orientation that occurred in the sample that was annealed at the higher temperature.

It is noteworthy that the increase in the A-peak ratio is probably not due to the increase in crystallinity of the material. It was stated in the DSC study (in section 6.2.1) that biaxial orientation of PPVC has no effect upon either the enthalpy of endotherm A or B. The increase in density because of orientation is very small, as
discussed in section 6.2.2. In the study of biaxially drawn rigid PVC\textsuperscript{(174)}, the increase in density with draw ratio was also found to very small. Hence it seems reasonable to suggest that biaxial stretching does not affect crystallinity.

6.4.2 X-Ray Diffraction Photograph

The directions through which x-ray transmission analyses were taken are illustrated in Figure 6.13; the normal direction is defined when the x-ray beam is perpendicular to the plane of the film.

*Figure 6.13 'Normal direction' and 'through thickness direction' employed for transmission x-ray studies*

The x-ray diffraction patterns of the PPVC films are displayed in the photographic plates in Figures 6.14 and 6.15 for S3 and P25, respectively. The pattern of the unstretched specimen S3 obtained in the normal direction, Figure 6.14(a), shows two circular halos corresponding to the lattice spacings d = 5.2\textdegree and d = 4.6\textdegree and a
broader circular halo corresponding with \( d = 3.58\text{Å} \). The first two halos correspond to the peaks at positions \( 17°\theta \) and \( 18.5°\theta \) in the reflectance mode diffractograms (figure 6.9); \( d = 3.58\text{Å} \) appears as a broad peak centred at \( 24.5°\theta \). The presence of these rings shows that PVC is semicrystalline material. This is explained in the following paragraph.

Crystalline materials contain a multitude of tiny crystallites with faces oriented at all angles to the incident x-ray beam. Some of these crystallites are positioned such that one set of parallel planes is at the correct angle (\( \theta \)) to reflect the incident x-rays. There are many crystallites with this orientation and because the crystallites are small, the spots on a photographic plate coalesce and appear as a ring to the naked eye. Since crystallites have several sets of planes that are capable of reflecting, several diffraction rings are produced \(^{173}\). Crystalline polymers, when analysed in powder or unoriented film forms, produce x-ray diffraction patterns characterised by sharp rings. In the case of PVC the rings are blurred and broad as a result of the low level of crystallinity present; the presence of imperfect crystallites also adds to this effect.

Figure 6.14(b) presents the diffraction photograph in the normal direction of the biaxially drawn sample S3. It can be seen that all the rings are sharper in comparison to the undrawn sample (Figure 6.14(a)). The reason for this is that the crystallites become oriented in certain directions by the effect of biaxial stretching. In these alignments, the number of sets of parallel planes that can produce reflections is higher than in unoriented specimens, and hence sharper rings appear in the photograph.

It was mentioned in the WAXD discussions presented in section 6.3.1, that the c-axis of the unit cell (see Figure 6.11) in biaxially drawn samples is aligned parallel to the plane of the film; the a-axis and b-axis have mixed orientations. If the orientation of
the c-axis is observed through the sample thickness (see Figure 6.13), uniaxial orientation has occurred; x-ray transmission studies were carried out in this direction, parallel to the plane of the film of biaxially stretched specimens, to see if uniaxial orientation had occurred preferentially ahead of biaxial orientation. The photographs displayed in Figure 6.14(c) show the presence of rings instead of arcs in the diffraction patterns. It was expected that arcs or spots would be seen in, especially in the two inner rings, since these rings correspond to the (200) and (110) planes that lie parallel to the c-axis. This axis was found to be oriented as a result of biaxial stretching. Since (200) and (110) are oriented, they should produce reflections showing spots or arcs on the photograph. This observation leads to the deduction that only a small quantity of the crystallites are oriented; the draw ratio is not high enough to produce more oriented structures and the high relaxation takes place after sample preparation. As the photograph is not clear, it is difficult to detect any differences in intensities within the ring. It is suggested that if an azimuthal scan was possible, the change in intensity may be detected.

Similar results were found for samples P25 as shown in Figure 6.15(a),(b) and (c). The diffraction photograph for the through sample thickness direction in Figure 6.15(c) seems to show an arc, although the picture is not very clear. As expected, crystalline orientation in the less plasticised formulation is more pronounced; this was also found in the reflection mode work, where the A-peak ratio of P25 was more sensitive to changes in draw ratio than S3 (see Figure 6.12).

6.5 SHRINKAGE MEASUREMENTS

The stability of macromolecular structures depends on the strength of inter-molecular interactions and on the polymer chain conformations. Oriented polymers
(a) undrawn sample  \hspace{1cm} (b) drawn sample (D.R.=1.6), normal direction  \hspace{1cm} (c) sample (b), through thickness direction

*Figure 6.14 X-ray photograph for S3*
(a) undrawn sample  
(b) drawn sample (D.R. = 1.8), normal direction  
(c) sample (b), through thickness direction

*Figure 6.15 X-ray photograph for P25*
may lead to a thermodynamically less stable arrangement. Extended chain elements tend to decrease their end-to-end distances in such situations and to assume more coiled conformations. The stability of orientation therefore depends on the changes in internal energy that are determined by interactions between neighbouring elements of the polymer chains. If the closer packing of oriented segments results in an energy decrease that compensates for the drop in entropy, the molecular orientation will be stable. Such a situation takes place if cohesive forces between polymer chains are sufficiently strong; for example, in the regions of high crystallinity in semicrystalline polymers. In amorphous regions the state of molecular orientation is not stable and may be maintained only after cooling the system below Tg where molecular motion is short-range and so slow that the orientation is practically "frozen-in". In conclusion the chain-extended conformations are stabilised by the lowering of the energy of the macromolecular system; if this energy is then somehow increased, extended macromolecules tend to relax or shrink, reaching more stable coil formations\(^{(144)}\).

The glass transition temperatures of PPVC compounds S3 and P25 are lower than room temperature, and hence the stability of oriented structures is expected to be very low. It was found that the samples shrunk after drawing, cooling and removal from the grips; the compound containing 46.5 phr DIOP (S3) reverted almost to its original size. Subsequent annealing in the stretched state reduced this shrinkage, due to the formation of ordered structures that held the oriented chains in position. It was found that the sample with 25 phr DIOP (P25) did not shrink after annealing; sample S3, however, still showed some shrinkage. The higher Tg of P25 in comparison with S3 implies that the molecular cohesion of P25 is greater than that of S3. This leads to the more stable oriented structures produced in P25.
It was mentioned previously the physically crosslinked structures created during the annealing period were not strong enough to halt the shrinkage process. The introduction of chemically crosslinked networks was expected to modify the shrinkage behaviour of the oriented samples. The aim of this experiment, therefore, was to investigate the effect of crosslinked structures on shrinkage properties.

6.5.1 Thermal Shrinkage

Thermal shrinkage measurements were determined using a Mettler Thermo-mechanical Analyser as described in section 2.3.3.2.2. The study was focused on the effect of draw ratio, %gel content and annealing temperature.

6.5.1.1 Effect of Draw Ratio

Compound formulations S3 and P25 were investigated in this experiment. The percentage area shrinkage (%AS) was calculated and plotted against temperature as shown in Figure 6.16 and 6.17 for S3 and P25, respectively. To compare the behaviour of different samples, temperatures corresponding to 5% AS and 50% AS, as displayed in Figure 6.18 were read off the resulting trace; the data are displayed in Figures 6.19 and 6.20.

It can be seen that in both compounds %AS increases with temperature until a maximum %AS was reached. This relaxation of orientation was attributed to the fact that the motion of molecules in amorphous regions increases upon heating and that the system tends to resume more highly coiled conformations, as mentioned earlier. The draw ratio was found to have a very small effect on both the maximum %AS and %AS temperature at 5% and 50%. In the irradiated series of S3, it can be seen clearly that
Figure 6.16 Percentage area shrinkage as a function of temperature for S3
Figure 6.17 Percentage area shrinkage as a function of temperature for P25
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Figure 6.18 Temperature at 5% AS ($T_{5\%}$) and at 50% AS ($T_{50\%}$)

Figure 6.19 Effect of draw ratio upon temperature at 5 and 50% AS for S3
crosslinked structures have the effect of reducing %AS, when compared with the unirradiated (see Figure 6.16), most significantly at higher temperatures, resulting in a decrease in the slope of the curve between 45°C to 100°C. No difference can be detected in the temperature range 30 to 45°C. The maximum %AS was reduced from 100% to 80% by the irradiation effect. %AS temperatures at 5% and 50% were found to be increased in the irradiated series; the improvement of the temperature at 50% AS was shown to be more pronounced. These results confirmed that irradiated crosslinked structures can modify shrinkage properties distinctly at elevated temperatures.

Similar results were discovered in the study of P25; the effect of irradiation, however, was less noticeable as shown in Figure 6.17. The maximum %AS was reduced from 100% to somewhere in the range 90 to 95%. The different behaviours of S3 and P25 can be seen in Figure 6.19 and 6.20; irradiated P25 shrunk to 50% at a lower temperature than crosslinked S3. No effect on the temperature at 5% AS was
detected. These phenomena are related to the lower gel content in P2s (see Table 5.1) and the lower shrinkage.

6.5.1.2 Effect of Gel Content

The effect of gel content on %AS was examined using oriented samples S3 with a draw ratio of 1.5. These samples were treated by electron beam radiation at varying doses to produce different gel contents in the products. The plots of %AS versus temperature of three samples with %gel contents of 26.2, 34.2 and 42.4 are shown in Figure 6.21. As expected, the maximum %AS decreases with increasing gel content. This shows that at higher temperatures the cohesive forces between adjacent PVC chains are controlled by chemical networks; the greater the gel content, the more stable are the oriented structures at elevated temperatures. The shrinkage behaviour at low temperatures, from 25°C up to 50°C, was found to be independent of gel content. This is consistent with the conclusion that at low temperatures the physical crosslinked structures play an important role. Upon heating these physical networks start to melt and the properties of the material will be controlled by the chemically crosslinked network.

6.5.1.3 Annealing Temperature

The effect of annealing temperature on %AS of unirradiated and irradiated S3 at draw ratio 1.5 is displayed in Figure 6.22. Apparently the shrinkage curve is shifted significantly to the right when the annealing temperature is increased from 80°C to 100°C. Similar results were found previously by Gilbert and co-workers(86). Two distinct slopes of the plot can be seen between the onset shrinkage temperature and the temperature at which the maximum %AS takes place. The gradient of the first part of
Figure 6.21 Percentage area shrinkage as a function of temperature for irradiated S3
Figure 6.22 Percentage area shrinkage as a function of temperature for S3
the curve is smaller than that of the second; the second part starts approximately at the annealing temperature. The smaller gradient arises as a result of improvements in the structural order that serve to fix the oriented structure in position. The increased slope in the second part is caused by the melting of the physically crosslinked structures formed during the annealing period. Chemically crosslinked structures also shift the shrinkage curve to the right and reduce the maximum %AS. The annealing temperature is very effective in modifying shrinkage behaviour. It can be concluded that the physical network is an important complement to the irradiation crosslinked network in PPVC. This effect is similar to that reported by Hjertberg and Dahl[6] who used penetration to follow the effect of crosslinking on mechanical properties. They found that the enlarged physical network created by annealing alone can improve penetration resistance in the interval 60°C to 110°C and major penetration can be avoided by the reinforcement conferred by the chemical network.

Annealing temperature shows no effect upon tensile properties, as discussed in section 5.4.2. The increasing annealing temperature introduces one problem though; the natural draw ratio of the sample is lower at temperatures above 80°C. If samples are drawn to their maximum draw ratio at 80°C and then are annealed at a higher temperature, failure will occur; the conditions for preparing samples need to be optimised to maximise mechanical properties and minimise shrinkage.

6.5.2 Room Temperature Recovery Rate

Two sets of three samples of formulation S3 were drawn to the total area of 289cm² in the stretcher head and were subsequently annealed at 80°C, 90°C and 100°C; their sizes were recorded with time. The plots of sample size against time are displayed in Figures 6.23 and 6.24. Clearly the samples show a rapid initial recovery
Figure 6.23 Total area of compound S3 vs time (in the first 2 days)

Figure 6.24 Total area of compound S3 vs time
The rate of recovery is fast in the first 110 days and then becomes very slow thereafter. The shrinkage was found to be reduced by increasing the annealing temperature, as shown by the increase in gradient of the plot in Figure 6.24 with decreasing annealing temperature. Structures produced with greater order at higher annealing temperatures will be more highly stable, as discussed in the previous section. It seems that irradiation shows has no effect on the recovery rate. This result confirms that crosslinked structures only affect the modification of physical properties at elevated temperatures.

6.6 SUMMARY OF THE RELATIONSHIP BETWEEN STRUCTURE AND PROPERTIES

The modified properties of PPVC after irradiation and orientation can be explained by the influence of oriented and crosslinked structures.

6.6.1 Effect of Orientation

Orientation has a significant influence upon tensile and impact properties; both of these were found to increase with draw ratio. This result is supported by the evidence collected in the WAXD study: the rise in the A-peak ratio with draw ratio indicates that the number of crystallites parallel to the plane of the film increases with draw ratio. These structures lead to the improvement of the properties in the plane of the biaxially stretched film.

It seems that the molecular orientation cannot be detected from the findings of birefringence studies, since the measured values are extremely small and clear relationships between birefringence and draw ratio are not discernible. This implies
that amorphous orientation cannot be maintained in biaxially stretched PPVC due to the extensive relaxation in the amorphous regions.

Orientation was found to have no significant effect upon endotherm C, measured by DSC, corresponding to the structural order produced during room temperature storage. Biaxial orientation has no detectable effect on either endotherm A or B. It is suggested that biaxial orientation in the range of draw ratios studied does not affect the crystallinity of PPVC. This is supported by the density measurements, in which the change of density with draw ratio was found to be extremely small.

It was shown that ultimate tensile strength and x-ray A-peak ratio increase with draw ratio. The x-ray A-peak ratio is plotted against the UTS of undrawn and drawn samples in Figure 6.25; there is a linear relationship between UTS and A-peak ratio in both cases. It can be concluded that the crystallite orientation present in biaxially drawn PPVC has a strong influence upon its mechanical properties. Even though the crystallinity of commercially produced PVC is very low (~10%), it has been found to significantly affect its processing, properties and applications as reviewed in reference 150.

Oriented PPVC suffers from shrinkage at higher temperatures and during storage under ambient conditions, leading to the reduction of its mechanical properties; this can be improved by annealing stretched PPVC at higher temperatures. The physical crosslinks, however, are destroyed upon heating, and hence the introduction of chemical crosslinks into the oriented structures to hold the chains in the oriented positions was investigated.
6.6.2 Effect of Irradiation Crosslinking

The development of crosslinked structures, signified by gel formation, was found to increase tensile strength slightly and to reduce elongation significantly at break at room temperature. A dramatic improvement in the tensile properties was observed at elevated temperatures, when the physical network melts; linkages formed in the crosslinking reaction holding the polymer chains together. The tensile properties are controlled by the gel content in the compound, as shown in the plot between the ultimate tensile strength and gel content for 46.5phr PPVC, irrespective of the formulation, in Figure 6.26. Ultimate tensile strength rises slightly with gel contents in the range 0% to 40%, after which point there is a sharp increase. This observation is consistent with some results reported by Rodriguez (125) in a study of chemical crosslinking of PPVC with aminosilane.
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It appears that the crosslinked network produced is very loose since the average molecular weights between crosslinks, shown in Tables 4.3, 4.6 and 4.9, are high in relation to Mn.

![Graph showing the dependent of UTS on %gel content for S3.](image)

*Figure 6.26 Dependent of UTS on %gel content for S3.*

The softening temperatures of the crosslinked compounds were found to be higher than those of the uncrosslinked materials. The gel content has very little effect upon the softening point, but the sample with the higher gel content gives the greatest penetration resistance. In chemically crosslinked PPVC, the penetration resistance is not only controlled by gel content but also by the physical crosslinks. The study of the physical network complementing the chemical one is shown in reference(115).

The differences in the tensile properties between irradiated and unirradiated oriented PPVC at the same draw ratio are more distinct at 100°C than at room temperature. Crosslinking was found to have no effect on crystalline orientation, since
the variation of x-ray A-peak ratio with draw ratio was the same for both irradiated and unirradiated samples. Irradiated stretched PPVC therefore maintains the property improvements gained from the effect of molecular orientation at increasing draw ratios.

Secondary crystallinity, measured by DSC, was found to be partially destroyed by irradiation. The chemical bonds created during irradiation link polymer chains together; mechanical properties are maintained at room temperature, whilst at elevated temperatures they are improved. These covalent bonds cause additional restriction to the flexibility of the molecules, with a responding reduction in free volume. This explains the increase in density of irradiated samples in comparison to unirradiated compound.

Crosslinking was found to reduce the shrinkage of oriented samples especially at elevated temperatures; no effect was apparent on the onset of shrinkage temperature (the chemical networks were expected to increase the onset temperature that would have lead to an increase in the service temperature of the PPVC products); upon heating above this temperature, crosslinked samples shrunk to a lesser extent than the uncrosslinked ones. The crosslinked structures reduce the maximum %AS; this effect becomes more pronounced with increasing gel content. No significant effect of irradiation crosslinking can be seen upon room temperature recovery rate. It is possible that the amount of chemical crosslinks is not high enough to prevent the relaxation of polymer chains that occurs at increased temperatures and during storage at room temperature (the gel contents of irradiated stretched samples are in the range of 30% to 38%). Another possible reason is that the crosslinked structure produced is loose, and hence the number of linkages is not high enough to hold the molecular chains in the oriented state. It may be possible to avoid shrinkage by choosing a system with a
very high gel content. This value should be higher than 50%, as can be seen from Figure 6.26, where a gel content greater than 50% produces dramatically modified properties. The annealing temperature is more effective in modifying shrinkage behaviour: an increase in this value can significantly delay the maximum and onset of shrinkage.

6.6.3 Conclusions

The properties of crosslinked oriented PPVC are modified by the effect of molecular orientation and by chemical linkages between polymer chains. The improvement of tensile properties and shrinkage are more significant at elevated temperatures. The dimensional stability of drawn PPVC can be modified by an increase in annealing temperature.

Finally, a schematic diagram summarising the effect of stretching and irradiation crosslinking upon PPVC is presented in Figure 6.27.
Figure 6.27 Schematic representation of irradiation crosslinked, biaxially stretched, plasticised PVC
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CHAPTER 7

GENERAL CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

7.1 GENERAL CONCLUSIONS

Stretched and unstretched PPVC formulations containing TMPTMA as a radiation sensitiser, are readily crosslinked upon exposure to electron beam radiation; this is shown by the appearance of gel in the irradiated samples.

The liquid tin stabiliser Stanclere TL was found to be the most suitable stabiliser for PVC in the study of crosslinking of oriented PPVC compounds. The amount of gel formed was found to increase with irradiation dose and TMPTMA level, but was found to decrease with increasing concentration of organotin stabiliser. The optimum concentrations of TMPTMA and stabiliser were ten and three parts per hundred, respectively. An irradiation dose of six Mrad was found to provide satisfactory crosslinking conditions.

The irradiation process gives rise to significant changes in the physical properties of PPVC compounds. Improvements in tensile properties are more pronounced at elevated temperatures than at room temperature. These are controlled by the gel content in the compound. The crosslinked structures also improve the penetration resistance at higher temperatures.

Sample thickness influences the extent of gel formation: the thinner the specimen, the higher the gel content that is produced upon irradiation. This results in the attainment of the most desirable tensile properties. The macromolecular chain
mobility in each compound was found to affect gel formation; compound S3, with a DIOP content of 46.5 phr, contained a greater percentage gel than formulation P25, with 25 phr DIOP.

Tensile and impact properties were found to improve with increasing draw ratio. The crosslinked structures formed within the PVC compounds, which were created by electron beam irradiation, result in the improvement of the mechanical properties of the drawn samples. A significant improvement was found in tensile properties when testing was carried out at elevated temperatures.

The annealing temperature seems to have only a small effect upon gel formation and tensile properties of the formulation containing 46.5 phr DIOP.

From the DSC study, both orientation and crosslinking were found to have no significant effects upon endotherm C, corresponding to the structure order produced during room temperature storage. Biaxial orientation shows no detectable effect on either endotherm A or B. In contrast, a reduction of crystallinity was discovered in irradiated samples, which is signified by the lowering of the enthalpy of endotherms A and B.

The effect of orientation upon density seems to be very small, whilst crosslinking significantly increases the density.

It seems the molecular orientation can not be detected by the measurement of birefringence, since the measured values are extremely small and clear relationships between birefringence and draw ratio are not discernible.
Chapter 7 Conclusions

The results from WAXD studies produce strong evidence that the properties of the PVC films are improved by crystallite orientation. This is attributed to the fact that the number of crystallites parallel to the plane of the film increases with draw ratio, as shown by the rise in the A-peak ratio with draw ratio. Crosslinking was found to have no effect on the alignment of crystallites.

Finally, crosslinking reduced the shrinkage of oriented samples, especially at elevated temperatures; no effect was apparent on the onset of shrinkage temperature. Upon heating above the onset temperature, the shrinkage of crosslinked samples was reduced compared to the uncrosslinked ones. The crosslinked structures reduce the maximum %AS; this effect becomes more pronounced with increasing gel content. No significant effect of irradiation crosslinking can be seen upon room temperature recovery rate. Annealing temperature was discovered to strongly influence shrinkage both at higher temperatures and at room temperature.

7.2 Suggestions for Further Study

Residual unreacted double bonds from TMPTMA were found in the crosslinked product; these are known to promote oxidative degradation in polymer, which can lead to undesirable properties. The degradation reactions and their effects upon the properties of irradiated samples after ageing at room temperature should be studied. Functional groups produced by the degradation reactions, e.g. carbonyl groups may be detected by infra-red spectroscopy. The study of the change in tensile properties over time would reveal the effect of unsaturation upon the long term properties of the irradiated products.
It was found that the increase of A-peak ratio with draw ratio in the WAXD study can be clearly ascribed to crystallite orientation. Additional x-ray work would complete this study; the use of pole figure analysis is suggested. With this technique, it would be possible to depict the distribution of the c-axes.

The gel content, and hence the mechanical properties, can be improved by increasing the irradiation dose, however the level of degradation also increases. Crosslinking via a chemical reaction route may be an alternative approach, as it would be possible to produce very high gel contents in the crosslinked product by varying the concentration of the components and the conditions.
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References

**Appendix I**

**Table I.1**

*Effect of sample thickness upon percentage gel content for S3 and P25.*

<table>
<thead>
<tr>
<th>SAMPLE THICKNESS/mm</th>
<th>%GEL CONTENT*</th>
<th>SAMPLE THICKNESS/mm</th>
<th>%GEL CONTENT*</th>
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<tr>
<td>0.14</td>
<td>50.9</td>
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<td>30.1</td>
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<td>44.1</td>
<td>0.35</td>
<td>24.9</td>
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<td>0.24</td>
<td>39.7</td>
<td>0.49</td>
<td>18.1</td>
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<td>0.28</td>
<td>36.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.31</td>
<td>29.9</td>
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<td></td>
</tr>
<tr>
<td>0.35</td>
<td>26.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Percentage gel content values presented in this programme are the average of at least two measurements;*

Arithmetic means ($\bar{x}$) were calculated:  

$$\bar{x} = \frac{\sum n_i x_i}{N}$$

Sample standard deviations (σ) were calculated:  

$$\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N - 1}}$$

where $n_i$ is the number of results of magnitude $x_i$ and $N$ is the total number of results.

e.g. for formulation S3:

<table>
<thead>
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<th>D.R.</th>
<th>%gel content (3 measurements)</th>
<th>Average</th>
<th>σ</th>
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<td>1.40-1.44</td>
<td>36.12 / 37.56 / 37.11</td>
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Table I.2

Effect of sample thickness upon tensile properties at 100°C for S3 and P25

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<th>SAMPLE THICKNESS/mm</th>
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<th>P25</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UTS/MPa</td>
<td>%EB</td>
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<tr>
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<td>6.07(02)</td>
<td>354(8)</td>
</tr>
<tr>
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<td>571(8)</td>
</tr>
<tr>
<td>0.35</td>
<td>4.23(07)</td>
<td>425(8)</td>
</tr>
</tbody>
</table>

*UTS and %EB values presented in this programme are the average value of at least three measurements. The standard deviation (σ) is shown for each sample in the parenthesis.*

Table I.3

Effect of draw ratio upon tensile properties at room temperature for unirradiated and irradiated S3 and P25

<table>
<thead>
<tr>
<th>UNIRRADIATED SAMPLE</th>
<th>S3</th>
<th>IRRADIATED SAMPLE</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE /DRAW RATIO</td>
<td>UTS/MPa</td>
<td>%EB</td>
<td>UTS/MPa</td>
</tr>
<tr>
<td>S3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>24.1(5)</td>
<td>304(29)</td>
<td>1</td>
</tr>
<tr>
<td>1.23</td>
<td>31.5(1)</td>
<td>215(4)</td>
<td>1.32</td>
</tr>
<tr>
<td>1.37</td>
<td>33.3(1.2)</td>
<td>193(5.5)</td>
<td>1.44</td>
</tr>
<tr>
<td>1.51</td>
<td>36.3(1.1)</td>
<td>174(14)</td>
<td>1.56</td>
</tr>
<tr>
<td>1.63</td>
<td>38.0(5)</td>
<td>172(8)</td>
<td>1.67</td>
</tr>
<tr>
<td>P25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>38.8(2.9)</td>
<td>226(19)</td>
<td>1</td>
</tr>
<tr>
<td>1.35</td>
<td>53.1(2.1)</td>
<td>173(68)</td>
<td>1.35</td>
</tr>
<tr>
<td>1.63</td>
<td>54.1(1.8)</td>
<td>138(1.4)</td>
<td>1.65</td>
</tr>
<tr>
<td>1.9</td>
<td>59.0(1.2)</td>
<td>131(26)</td>
<td>1.93</td>
</tr>
</tbody>
</table>
Table I.4

*Effect of draw ratio upon tensile properties at room temperature for unirradiated and irradiated S3 and P25.*

<table>
<thead>
<tr>
<th>UNIRRADIATED SAMPLE</th>
<th>IRRADIATED SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE /DRAW RATIO</td>
<td>UTILITY</td>
</tr>
<tr>
<td>S3</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.16(.01)</td>
</tr>
<tr>
<td>1.22</td>
<td>3.27(1)</td>
</tr>
<tr>
<td>1.36</td>
<td>3.54(04)</td>
</tr>
<tr>
<td>1.52</td>
<td>4.22(01)</td>
</tr>
<tr>
<td>1.63</td>
<td>4.29(1)</td>
</tr>
<tr>
<td>P25</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.12(.09)</td>
</tr>
<tr>
<td>1.37</td>
<td>6.08(.13)</td>
</tr>
<tr>
<td>1.64</td>
<td>6.38(.2)</td>
</tr>
<tr>
<td>1.9</td>
<td>7.19(.27)</td>
</tr>
</tbody>
</table>

| SAMPLE /DRAW RATIO  | %EB               |
| S3                  | 399(9)            |
| 1                   | 1                 |
| 1.22                | 234(3)            |
| 1.36                | 210(13)           |
| 1.52                | 203(.7)           |
| 1.63                | 189(19)           |
| P25                 | 265(23)           |
| 1                   | 1                 |
| 1.35                | 177(5)            |
| 1.65                | 137(17)           |
| 1.9                 | 124(7)            |

| SAMPLE /DRAW RATIO  | %EB               |
| S3                  | 1                 |
| 1                   | 1.33              |
| 1.22                | 3.27(1)           |
| 1.36                | 3.54(04)          |
| 1.52                | 4.22(01)          |
| 1.63                | 4.29(1)           |

| P25                 | 1                 |
| 1                   | 1.35              |
| 1.37                | 1.65              |
| 1.64                | 1.93              |
| 1.9                 | 1                 |

|          | S3           |                  |
| SAMPLE  | UTILITY     | %EB              |
| S3      | 4.81(.19)   | 462(22)          |
| 1       | 6.24(.2)    | 348(28)          |
| 1.22    | 6.67(.09)   | 316(26)          |
| 1.33    | 7.08(.16)   | 286(18)          |
| 1.45    | 7.3(,24)    | 199(20)          |
| 1.52    | 7.42(.12)   | 190(12)          |

Table I.5

*Effect of draw ratio upon impact properties for unirradiated and irradiated S3.*

<table>
<thead>
<tr>
<th>UNIRRADIATED SAMPLE</th>
<th>IRRADIATED SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRAW RATIO</td>
<td>PEAK FORCE</td>
</tr>
<tr>
<td>SAMPLE</td>
<td>PEAK ENERGY</td>
</tr>
<tr>
<td>N/mm</td>
<td>J/mm</td>
</tr>
<tr>
<td></td>
<td>N/mm</td>
</tr>
<tr>
<td></td>
<td>J/mm</td>
</tr>
<tr>
<td>1</td>
<td>702(22)</td>
</tr>
<tr>
<td>1.19</td>
<td>848(38)</td>
</tr>
<tr>
<td>1.30</td>
<td>922(11)</td>
</tr>
<tr>
<td>1.44</td>
<td>1033(28)</td>
</tr>
<tr>
<td>1.63</td>
<td>1149(46)</td>
</tr>
</tbody>
</table>

| SAMPLE              | PEAK ENERGY       |
| S3                  | 5.7(32)           |
| 1                   | 715(25)           |
| 1.22                | 861(20)           |
| 1.36                | 965(28)           |
| 1.52                | 1069(12)          |
| 1.63                | 1178(34)          |

| P25                 | 7.3(.24)          |
| 1.37                | 8.2(.43)          |
| 1.65                | 9.3(.83)          |
| 1.9                 | 9.9(.87)          |
**Table I.6**

Effect of sample annealing temperature upon percentage gel content for S3

<table>
<thead>
<tr>
<th>Tanneal</th>
<th>%GEL CONTENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>37.7</td>
</tr>
<tr>
<td>90</td>
<td>34.4</td>
</tr>
<tr>
<td>100</td>
<td>34.7</td>
</tr>
</tbody>
</table>

**Table I.7**

Effect of sample annealing temperature upon tensile properties at room temperature for unirradiated and irradiated S3

<table>
<thead>
<tr>
<th>UNIRRADIATED SAMPLE</th>
<th>IRRADIATED SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tanneal.  °C</td>
<td>UTS/MPa</td>
</tr>
<tr>
<td>80</td>
<td>36.3(1.1)</td>
</tr>
<tr>
<td>90</td>
<td>33.4(8)</td>
</tr>
<tr>
<td>100</td>
<td>34.7(.1)</td>
</tr>
</tbody>
</table>

**Table I.8**

Effect of sample annealing temperature upon tensile properties at 100°C for irradiated and irradiated S3

<table>
<thead>
<tr>
<th>UNIRRADIATED SAMPLE</th>
<th>IRRADIATED SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tanneal.  °C</td>
<td>UTS/MPa</td>
</tr>
<tr>
<td>80</td>
<td>4.22(.1)</td>
</tr>
<tr>
<td>90</td>
<td>3.9(.4)</td>
</tr>
<tr>
<td>100</td>
<td>3.68(.2)</td>
</tr>
</tbody>
</table>
### Appendix II

**Table II.1**

*Effect of draw ratio upon density for unirradiated and irradiated S3*

<table>
<thead>
<tr>
<th>UNIRRADIATED SAMPLE</th>
<th>IRRADIATED SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRAW RATIO</td>
<td>DENSITY/g/cm²</td>
</tr>
<tr>
<td>1.0</td>
<td>1.2372</td>
</tr>
<tr>
<td>1.27</td>
<td>1.2380</td>
</tr>
<tr>
<td>1.40</td>
<td>1.2388</td>
</tr>
<tr>
<td>1.64</td>
<td>1.2359</td>
</tr>
<tr>
<td>Ta=100°C/1.5</td>
<td>1.2407</td>
</tr>
</tbody>
</table>

---

**Table II.2**

*Effect of draw ratio upon x-ray A-peak ratio for unirradiated and irradiated S3 and P25.*

<table>
<thead>
<tr>
<th></th>
<th>S3</th>
<th>P25</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNIRRADIATED</td>
<td>IRRADIATED</td>
<td>UNIRRADIATED</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1.23</td>
<td>1.16</td>
<td>1.23</td>
</tr>
<tr>
<td>1.36</td>
<td>1.26</td>
<td>1.43</td>
</tr>
<tr>
<td>1.7</td>
<td>1.44</td>
<td>1.7</td>
</tr>
<tr>
<td>Ta=100</td>
<td></td>
<td>Ta=100</td>
</tr>
<tr>
<td>1.43</td>
<td>1.28</td>
<td>1.43</td>
</tr>
</tbody>
</table>
A simple experiment was devised to measure the force exerted due to the relaxation of orientation during the heating period when oriented specimens were tensile tested at 100°C; it is possible that this force may contribute to the overall measured tensile load. A drawn sample with known thickness and width was placed between the grips in the tensile testing machine. After a ten minute heating period, the shrinkage force, specimen thickness and width were measured.

The results for S3 in Table III.1 show that the load exerted is very low. This may be caused by the reordering of the oriented structure that takes place in the sample upon heating; orientation is retained in the longitudinal (tensile) direction because the sample is restrained in this direction, but is lost in the transverse direction; the data in table III.2 show that the specimen widths reduce when heated. Therefore equal biaxial orientation is converted to unequal biaxial or uniaxial orientation after heating. The plot of intended planar strain, \((D.R.)^2\), against actual planar strain is displayed in Figure III.

Similar results were obtained for P25, as shown in Tables III.3-4 and Figure III.2.

\(D.R.(*)\) in Figures 5.9-5.10 is related to intended planar strain as \(D.R.(*)\) is the draw ratio of sample before heating. Hence, \(\left[D.R.(*)\right]^2 = \) intended planar strain.
### Table III.1

**UTS and shrinkage stress of unirradiated and irradiated S3**

<table>
<thead>
<tr>
<th>UNIRRADIATED S3</th>
<th></th>
<th></th>
<th>IRRADIATED S3</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DRAW RATIO</strong></td>
<td><strong>UTS at 100°C /MPa</strong></td>
<td><strong>SHRINKAGE STRESS /MPa</strong></td>
<td><strong>DRAW RATIO</strong></td>
<td><strong>UTS at 100°C /MPa</strong></td>
<td><strong>SHRINKAGE STRESS /MPa</strong></td>
</tr>
<tr>
<td>1.3</td>
<td>3.27</td>
<td>0.01</td>
<td>1.3</td>
<td>6.24</td>
<td>0</td>
</tr>
<tr>
<td>1.5</td>
<td>4.22</td>
<td>0.20</td>
<td>1.5</td>
<td>6.67</td>
<td>0.19</td>
</tr>
<tr>
<td>1.8</td>
<td>4.52</td>
<td>0.46</td>
<td>1.8</td>
<td>7.20</td>
<td>0.39</td>
</tr>
<tr>
<td>1.5/Ta=90°C</td>
<td>3.90</td>
<td>0.27</td>
<td>1.5/Ta=90°C</td>
<td>5.80</td>
<td>0.23</td>
</tr>
<tr>
<td>1.5/Ta=100°C</td>
<td>3.68</td>
<td>0.04</td>
<td>1.5/Ta=100°C</td>
<td>5.60</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table III.2

**Planar strain before and after heating of unirradiated and irradiated S3.**

<table>
<thead>
<tr>
<th>D.R.</th>
<th>PLANAR STRAIN\textsuperscript{a}</th>
<th>THICKNESS /mm</th>
<th>WIDTH /mm(A)</th>
<th>THICKNESS /mm</th>
<th>WIDTH /mm(B)</th>
<th>D.R.\textsuperscript{*}</th>
<th>PLANAR STRAIN\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>1.3x1.3</td>
<td>0.284</td>
<td>2.40</td>
<td>0.368</td>
<td>1.89</td>
<td>1.0</td>
<td>1.3x1.0</td>
</tr>
<tr>
<td>1.5</td>
<td>1.5x1.5</td>
<td>0.169</td>
<td>2.40</td>
<td>0.264</td>
<td>1.51</td>
<td>1.0</td>
<td>1.5x1.0</td>
</tr>
<tr>
<td>1.8</td>
<td>1.8x1.8</td>
<td>0.227</td>
<td>2.40</td>
<td>0.399</td>
<td>1.33</td>
<td>1.0</td>
<td>1.8x1.0</td>
</tr>
<tr>
<td>1.5*</td>
<td>1.5x1.5</td>
<td>0.186</td>
<td>2.40</td>
<td>0.268</td>
<td>1.62</td>
<td>1.0</td>
<td>1.5x1.0</td>
</tr>
<tr>
<td>1.5**</td>
<td>1.5x1.5</td>
<td>0.219</td>
<td>2.40</td>
<td>0.283</td>
<td>1.89</td>
<td>1.2</td>
<td>1.5x1.2</td>
</tr>
<tr>
<td>Irr.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>1.3x1.3</td>
<td>0.234</td>
<td>2.40</td>
<td>0.289</td>
<td>1.91</td>
<td>1.0</td>
<td>1.3x1.0</td>
</tr>
<tr>
<td>1.5</td>
<td>1.5x1.5</td>
<td>0.219</td>
<td>2.40</td>
<td>0.319</td>
<td>1.65</td>
<td>1.0</td>
<td>1.5x1.0</td>
</tr>
<tr>
<td>1.8</td>
<td>1.8x1.8</td>
<td>0.197</td>
<td>2.40</td>
<td>0.294</td>
<td>1.53</td>
<td>1.15</td>
<td>1.8x1.15</td>
</tr>
<tr>
<td>1.5*</td>
<td>1.5x1.5</td>
<td>0.213</td>
<td>2.40</td>
<td>0.270</td>
<td>1.95</td>
<td>1.2</td>
<td>1.5x1.2</td>
</tr>
<tr>
<td>1.5**</td>
<td>1.5x1.5</td>
<td>0.211</td>
<td>2.40</td>
<td>0.253</td>
<td>2.08</td>
<td>1.3</td>
<td>1.5x1.3</td>
</tr>
</tbody>
</table>

1.5* = Draw ratio for sample annealed at 90°C.
1.5**= Draw ratio for sample annealed at 100°C.

D.R.* = Draw ratio in perpendicular direction in tensile bar.[D.R.*=Bx(D.R./A)]

Planar strain\(^i\) = Intended planar strain.

Planar strain\(^a\) = Actual planar strain.

### Table III.3

**UTS and shrinkage stress of unirradiated and irradiated P25.**

<table>
<thead>
<tr>
<th>UNIRRADIATED P25</th>
<th>IRRADIATED P25</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRAW RATIO</td>
<td></td>
</tr>
<tr>
<td>D. R.</td>
<td></td>
</tr>
<tr>
<td><strong>UTS at 100°C</strong></td>
<td><strong>UTS at 100°C</strong></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>6.08</td>
</tr>
<tr>
<td>1.6</td>
<td>6.38</td>
</tr>
<tr>
<td>1.9</td>
<td>7.19</td>
</tr>
</tbody>
</table>

### Table III.4

**Planar strain before and after heating of unirradiated and irradiated P25.**

<table>
<thead>
<tr>
<th>D.R.</th>
<th>PLANAR STRAIN(^i)</th>
<th>THICKNESS /mm</th>
<th>WIDTH /mm</th>
<th>THICKNESS /mm</th>
<th>WIDTH /mm</th>
<th>D.R.*</th>
<th>PLANAR STRAIN(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>unirr.</td>
<td>1.4x1.4</td>
<td>0.229</td>
<td>2.40</td>
<td>0.349</td>
<td>1.64</td>
<td>1.0</td>
<td>1.4x1.0</td>
</tr>
<tr>
<td></td>
<td>1.6x1.6</td>
<td>0.224</td>
<td>2.40</td>
<td>0.376</td>
<td>1.50</td>
<td>1.0</td>
<td>1.6x1.0</td>
</tr>
<tr>
<td></td>
<td>1.9x1.9</td>
<td>0.306</td>
<td>2.40</td>
<td>0.517</td>
<td>1.37</td>
<td>1.1</td>
<td>1.9x1.1</td>
</tr>
<tr>
<td>Irr.</td>
<td>1.4x1.4</td>
<td>0.224</td>
<td>2.40</td>
<td>0.294</td>
<td>1.83</td>
<td>1.1</td>
<td>1.4x1.1</td>
</tr>
<tr>
<td></td>
<td>1.6x1.6</td>
<td>0.216</td>
<td>2.40</td>
<td>0.329</td>
<td>1.57</td>
<td>1.05</td>
<td>1.6x1.05</td>
</tr>
<tr>
<td></td>
<td>1.9x1.9</td>
<td>0.214</td>
<td>2.40</td>
<td>0.329</td>
<td>1.47</td>
<td>1.15</td>
<td>1.9x1.15</td>
</tr>
</tbody>
</table>
Figure III.1 Intended planar strain against actual planar strain for S3.

Figure III.2 Intended planar strain against actual planar strain for P25.