Surface properties of poly(bisphenol-A-carbonate)

Thesis

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SURFACE PROPERTIES OF
POLY(BISPHENOL-A CARBONATE)

by

D.G. Kamal E. WEERAPPERUMA, MSc

A thesis presented to the Open University in partial fulfilment
of the degree of DOCTOR OF PHILOSOPHY

March 1980
None of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institution of learning.
Education, a fundamental step towards egalitarianism is the urgent requirement of the peoples of today.

This thesis is dedicated to the tea estate workers of Sri Lanka.
ABSTRACT

The work presented in this thesis consisted of several strands of research. A technique to measure surface energy was developed, and this change was observed by ellipsometry. Stringent temperature control was achieved using this technique. A surface free energy of approximately 0.121 J m\(^{-2}\) (14 J cm\(^{-2}\)) at 174°C was measured for polycarbonate using this method.

An increase in the polishing rate was found to increase the thinning rate but not the extent of polishing or etching. The condition of the sample during polishing was found to affect the growth of the etching and etching phases. A degree of molecular orientation and residual stress was primarily responsible for fracture and mechanical failure. The high birefringence of the moulding was predominantly attributed to molecular orientation and residual stress.
The work presented in this thesis consists of several strands:

(a) the development of a technique to measure surface free energies of amorphous polymers
(b) an investigation of chemical polishing and
(c) the problems of injection moulded polycarbonate.

Grooves inscribed in an amorphous polymer surface change in dimensions on thermal annealing, and this change observed by interferometry forms the basis of the surface free energy measurement technique. Stringent temperature control and accurate temperature monitoring during thermal annealing is an essential feature of this technique. A surface free energy of approximately 0.121 J m$^{-2}$ (121 ergs cm$^{-2}$) at 174°C was measured for polycarbonate using this method.

An increase in the polishing temperature was found to increase the thinning rate but not the extent of polishing or etching. The position of the sample during polishing was found to affect the growth rate of the viscous layer and hence polishing and etching phases. An activation energy of 26.0 kJ (mol)$^{-1}$ was measured for the thinning process.

A high degree of molecular orientation and residual stress (a major reason for premature mechanical failure) was primarily attributed to cold moulding and poor mould design coupled with inadequate testing of the finished product. The high birefringence observed in the moulding was predominantly attributed to molecular orientation and residual stress.
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March, 1980
PREAMBLE

The work presented in this thesis is primarily aimed at improving the understanding of the surface properties of poly(bispheno1-A carbonate) and three broad areas of research were conducted to fulfil this aim.

The initial part of the research program was devoted to the development of an independent method of estimating surface free energies (by monitoring the extent of thermal decay of a single scratch groove) of PC. In this technique, surface grooving was done by mechanical rulling followed by a process of chemical thinning which removed stresses induced by the rulling process.

The second part of this thesis described an investigation of the said phenomena of chemical polishing (etching, thinning) with particular reference to changes in surface topography, the effects of change in temperature and finally the mechanisms governing the chemical polishing.

In the final part of the work, chemical polishing was developed to obtain a situation of uniform thinning, the basis of the layer removal technique used in the observation of molecular orientation and residual stresses through various layers of injection moulded PC samples.

The surface properties of PC researched into in this thesis, in particular the use of chemical polishing, connects the three areas of research conducted in this thesis.
CHAPTER I

INTRODUCTION

1.1 AN INTRODUCTION TO POLYCARBONATES

1.1.1 Development of Polycarbonates

Polycarbonates are basically linear thermoplastic polyesters of carbonic acid with aliphatic or aromatic dihydroxy compounds, and may be represented by the general structure in Figure (1.1). Polyesters were first prepared in 1863 by Lourenço (1) from succinic acid and ethylene glycol while linear polyesters of carbonic acid were first prepared by Einhorn (2) in 1898 by reaction of phosgene with resorcinol, and hydroquinone in pyridine. The first successful systematic investigation and the preparation of relatively high molecular weight polycarbonates were done by Carothers and co-workers (3) in 1929. Subsequently Peterson improved this method to obtain high molecular weight polycarbonates that could be made into fibres and films with useful technological properties. (4) The preparation of aromatic polycarbonates from bisphenol-A with potential technological utility was carried out by Schnell and co-workers of Farbenfabriken Bayer AG. (5) Technical procedures were rapidly developed in 1958, and Farbenfabriken Bayer AG began commercial production followed by Mobay Chemical Company and General Electric Company in the USA.

1.1.2 Properties of Poly(bisphenol-A carbonate)

Relatively little is known about the properties of aliphatic and aliphatic-aromatic polycarbonates. However, a significant amount
of work has been done on Poly(bisphenol-A carbonate) due to its commercial importance; and its chemical structure is as in Figure (1.2). Poly(bisphenol-A carbonate) is a tough and stiff plastic and maintains its properties over a wide temperature range of -100°C to +120°C. Ballistic experiments conducted on the material showed extraordinary high-impact behaviour (6) and this may be associated with its low ductile-brittle transition of -100°C (29) and the aspect of cold drawing (see Figure 1.3).

Mechanical properties of injection-moulded Poly(bisphenol-A carbonate) having a weight average molecular weight (\( \bar{M}_w \)) between 32,000 and 35,000 (\( \bar{M}_w/\bar{M}_n = 3 \)) is given in Table (1.1), showing its combination of unique and desirable properties. However, it should be mentioned that the properties of this material are very strongly dependent on its molecular weight and if \( \bar{M}_w \) is below 10,000 (corresponding to the entanglement molecular weight; see Section 3.4.5) the material is brittle, and between 10,000 and 25,000 (\( \bar{M}_w/\bar{M}_n = 3 \)) low strengths are observed (7).

Crazing, the development of microscopic planar defects (generally a narrow zone of highly deformed and voided polymer) within the material, under stress or under the action of a solvent (usually a combination of both) is common in Poly(bisphenol-A carbonate) as in other polymers; and hence, it is of importance with respect to its mechanical properties. (18,19,20) Embrittlement, the change in mechanical properties on annealing is also evident in this material. (8,9)

At first sight, it is apparent that low cold flow, good electrical properties, high transparency, biological inertness and resistance to acids, oils, fats and oxidising agents make it a desirable polymeric material. However, crazing and fatigue failure under a continuous dynamic load are the disadvantages of this material.
<table>
<thead>
<tr>
<th>Property</th>
<th>Method DIN No.</th>
<th>Value</th>
<th>Property</th>
<th>Method ASTM No.</th>
<th>Value</th>
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<tr>
<td>Density [g/ml]</td>
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<td>1.20</td>
<td>Impact strength (izod) notched [ft.lb/in]</td>
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<td>11c 10-6</td>
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<td>2.8-3.2x10⁵</td>
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<td>Elongation at yield [%]</td>
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<td>5-7</td>
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<tr>
<td>Elongation ultimate [%]</td>
<td>53 455</td>
<td>&gt;60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus of elasticity [kg/cm²]</td>
<td>53 455</td>
<td>22-25,000</td>
<td></td>
<td></td>
<td></td>
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</table>
1.1.3 Processing of Poly(Bisphenol-A carbonate)

Injection moulding, extrusion, blow moulding and solvent casting are the major processing techniques available for polycarbonate. It is important to understand the nature of this material, particularly the high, Newtonian melt viscosity\(^{(30)}\) and hence, its processing conditions: an aspect often overlooked by the manufacturers, usually reflected by the poor quality of the finished product.\(^{(21,22)}\)

In injection moulding a viscosity average molecular weight \((\bar{M}_v)\) between 32,000 and 35,000\(^{(7)}\) and processing temperatures between 260°C and 310°C\(^{(21)}\) are preferred. The pellets of the moulding compound should be dry as excessive water content produces poor surface appearance on mouldings and also causes degradation and hence a decrease in molecular weight.\(^{(10,21)}\) The high Newtonian melt viscosity of polycarbonate makes it important to provide short sprues of ample cross-sectional area, making runners short as possible, and keeping wall thickness above 0.7 mm.\(^{(11,12)}\) High mould temperatures up to 120°C are required to minimize molecular orientation (see Section 1.4) and residual stresses\(^{(13)}\) of the finished product. Finally the resident time of the polymer melt, temperature control at all stages, excessive shear and pressure are some of the other important processing aspects which undoubtedly would influence the quality of the final product.\(^{(14)}\)

Aromatic polycarbonates may be extruded to form films, sheets, pipes, rods and various other tubular products by the usual techniques.\(^{(12,15,16)}\) The high melt viscosity of poly(bisphenol-A carbonate) is advantageous in extrusion and molecular weights \((\bar{M}_n)\) up to about 50,000 may be used \((\bar{M}_w/\bar{M}_n = 2.5)\). In order to minimize internal stress, in film making it is important not to chill the material as it leaves the die but to adjust the temperature of the take-up rolls or the
environment as appropriate.

Blow moulding, blowing up a short piece of extruded tube inside a mould before the material leaves the plastic state\(^{17}\) is a good method of manufacturing hollow shaped objects. Cold forming and compression moulding are some other processing methods available for poly(bisphenol-A carbonate). Processing from solution is also possible due to its solubility, especially in chlorinated hydrocarbons, thus giving the advantage of processing high molecular weight polycarbonate.\(^*\)\(^\text{(7)}\)

1.1.4 The Uses of Polycarbonate

The most important polycarbonate from a commercial point of view is that derived from bisphenol-A, due to its wide range of desirable properties mentioned in Section 1.1.2.

Polycarbonate films formed by casting or extrusion are used in radios, television sets, coils, wires, capacitors\(^\text{(23)}\) etc., in the form of insulators. Injection moulded enclosures and safety shields are used for television sets, plugs, telephone housing, battery cases\(^\text{(24)}\) etc.; while camping utensils, dishes, refrigerator parts have entered the domestic market. As an engineering thermoplastic its applications include (a) various metering and regulating 'apparatus covers' where transparency is of importance (e.g. filter vessels\(^\text{(25)}\)), (b) as a shatterproof glazing\(^\text{(26)}\), (c) as wall panelling and various electrical apparatus in marine applications. Covers for street and industrial lamps have been produced by thermoforming, blow moulding or injection moulding.\(^\text{(27)}\) In the medical field the material has been used as syringes etc.\(^\text{(27)}\) (due to its resistance to sterilization) and finally for the manufacture of dental prostheses.\(^\text{(28)}\)

\(^*\) Poly(bisphenol-A carbonate) will be referred to as 'polycarbonate' or 'PC' in the rest of this work.
1.2 SURFACE ENERGETICS

1.2.1 The Definition of Surface Free Energy

Molecules at the surface of a solid or a liquid are subject to unbalanced molecular forces and hence possess additional energy, in contrast to those inside a solid or a liquid. In liquids the surface energy manifests itself as an internal force which tends to minimise the surface area. A solid surface, as that of a liquid, possesses additional free energy, but due to the lack of molecular mobility this free energy is not directly observed and must be measured indirectly. This additional free energy at the interface between two condensed phases may be considered as the interfacial energy. The importance of surface and interfacial energy is seen by its controlling influence in many practical applications such as polymer adhesion, spinning, stability of dispersions and wetting of solids by liquids (e.g. in printing).

The specific free surface energy of a material is the excess energy per unit area due to the existence of the free surface; it is also the thermodynamic work per unit area of surface extension.

Gibbs free energy, \( G \), is defined by the equation

\[
G = U + PV - TS \tag{1.1}
\]

where

- \( U \) is the internal energy
- \( P \) is the pressure
- \( V \) the volume
- \( T \) the temperature and
- \( S \) entropy of the system.

Following the method of Defay and Prigogine\(^{75}\) the energetic properties of a surface may be defined as follows:

\[
G^s = U^s + PV^s - TS^s \tag{1.2}
\]
The superscript 's' refers to surface with reference to the bulk material.

From the above equation it can be shown (1,2) that for a multicomponent system

\[ dG^S = - S^S dT + V^S dp + \gamma dA + \Sigma \mu_i^S \, dn_i^S \]  \hspace{1cm} (1.3)

where

\[ \mu_i^S = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_i} \]  \hspace{1cm} (1.4)

\( n_i^S \) is the number of moles of the component 'i' in the surface layer and \( \gamma \) the surface tension.

At constant temperature and pressure, the above equation may be reduced to

\[ dG^S = \gamma dA + \Sigma \mu_i \, dn_i^S \]  \hspace{1cm} (1.5)

and it can be shown that

\[ \frac{G^s}{A} = \gamma + \Sigma \mu_i \Gamma_i \]  \hspace{1cm} (1.6)

where

\[ \Gamma_i = \frac{n_i^S}{A} \]  \hspace{1cm} (1.7)

A being total area of free surface. It can also be shown that at constant composition

\[ \left( \frac{\partial G^S}{\partial A} \right)_{T,P} = \gamma \]  \hspace{1cm} (1.8)

The above equation shows that surface tension is, in general, not equal to the surface free energy. They are identical in the case of a single component system, as shown by Dupre (75,83), when dividing is chosen such that \( \Gamma = 0 \). It was noted by Defay and Prigogine (75) that surface
free energy can be made equal to surface tension if Gibbs diving surface is chosen such that $\Sigma (\Gamma_1 \nu_1^5)$ is identically zero.

1.2.2 Parameters affecting surface free energy

The most important factor that affects surface free energy is due to the imbalance of intermolecular forces and its contribution is denoted by the term $U^S$ in equation (1.2). The other important parameters affecting surface free energy are temperature, orientation and adsorption.

The dependence of surface tension on temperature may be given by the following equation:

$$\frac{dY}{dT} = -S_s$$  \hspace{1cm} (1.9)

However, if adsorption occurs the situation changes as shown by Shewman and Robertson (32) in equation (1.10):

$$\frac{dY}{dT} = \Delta S_m + \frac{\theta \Delta H_a}{T}$$  \hspace{1cm} (1.10)

where $\theta$ is the quantity of impurity absorbed per unit area of surface, $\Delta H_a$ the heat of adsorption and $\Delta S_m$ the entropy of melting.*

Jones and Leak (35) considered a more general case of this equation:

$$\frac{dY}{dT} = -S = (S_s - S_a)$$  \hspace{1cm} (1.11)

* The surface entropy is approximately equal to the entropy of melting. (33)
where $S_s$ is the entropy of a clear surface and $S_a$ accounts for this adsorption. Positive values of $\left( \frac{dS}{dT} \right)$ have been thus explained, in terms of strong adsorption on the basis of equations (1.10) and (1.11). A review by Jones and Leak(36) on zero-creep data on metals has shown surface entropy values could be high as 3 mJ m$^{-2}$ (deg.C)$^{-1}$ in contrast to the generally expected value of 0.5 x mJ m$^{-2}$ (deg.C)$^{-1}$ and have accounted for this increase in terms of surface impurities.

The dependence on orientation of a surface may be represented by a polar plot of surface free energy as a function of the direction normal to the corresponding surface and is known as a 'γ-plot'.(31) All surfaces of a liquid or amorphous material would be equivalent, and the corresponding 'γ-plot' would be a sphere. However, the presence of a crystalline structure will alter the surface free energy and the 'γ-plot' will not be spherical.(31,34) Shewmon and Robertson(32) have reviewed the main experimental techniques(37,38,39) for measuring the anisotropy of γ in metals.

1.2.3 Techniques of Determining Surface Free Energies

Several experimental techniques are available for the measurement of surface free energy for metals and these have been reviewed by Mills(40). Of particular interest to polymers are the following methods:

(a) Estimation of the surface tension of a solid by measuring the contact angle between different liquids and the solid.(41)
(b) By determination of the critical surface tension of wetting ($\gamma_{cr}$) and assuming that $\gamma_{cr}$ is approximately equal to the surface tension of the solid.\(^{(42)}\)

(c) Extrapolation of surface tension data of polymer melts to room temperature; the pendant drop method.\(^{(43)}\)

(d) Estimation of surface tension of a solid polymer from an additive function; introduced by Sugden\(^{(44)}\) termed 'Parachor'.\(^{(45)}\)

(e) Estimation of surface free energy by the controlled cleavage process.\(^{(46)}\)

(f) The measurement of surface free energy using a single or multiple groove decay technique has been of considerable success for metals.\(^{(40,47,48,49,50)}\) This technique has now been modified and extended to polymers, which forms the basis of Chapter 2 of this thesis.

(g) Evaluation of surface free energy by measurement of crystal growth rates of polymers.\(^{(84)}\)

Finally, it must be mentioned that all methods of surface free energy measurements have limitations and each method must be judged by its own merits. In certain instances the measurement of surface tension and surface free energy of solids have been widely criticised\(^{(45,50)}\) due to the nature of this formidable task. However, no attempts have been made by these authors to suggest alternatives. One of the major criticisms (quite justifiably) of the decay technique is that of the relaxation of residual stresses* (introduced during sample preparation) on annealing.\(^{(50)}\) In the work presented in Chapter 2 this aspect of

* Molecular orientation may also be present.
the problem has been solved by a novel technique of chemical polishing (see Section 1.3 and Chapter 3).

1.3 POLISHING AND ETCHING OF POLYMERS

1.3.1 Introduction

The progressive smoothening of surface irregularities (polishing) is a basic requirement in the examination of structural details of a material in the bulk state. The development of electropolishing and chemical polishing\(^{(51,52)}\) of metals led to the production of surfaces free of scratches and structural disturbances, in contrast to mechanical polishing which caused surface damage. This undoubtedly was a great asset for metallurgical research.\(^{(53,54)}\) Etching, polishing and thinning of polymers have a similar importance to that of metals, but the subject is still at its infancy.

Etching of polymers in morphological studies have been known for some time. Hot nitric acid has been used as an etchant for polyethylene\(^{(55,56,57)}\) while hot chromic acid has been used for polypropylene\(^{(58,59,60)}\). However, it should be noted that the etching times for the above methods are relatively long, ranging from 4 to 100 hours. Etching of poly(ethylene terephthalate) (PET) by ethylamine\(^{(61)}\), methylamine\(^{(62)}\) and n-propylamine\(^{(63)}\) and also polyamide using hydrazine hydrate\(^{(64)}\) have been carried out by aminolysis. The thinning of polycarbonate has also been observed by aminolysis\(^{(65)}\) and the rates of thinning of various etchants are shown in Table (1.2).

As a condensation polymer, polycarbonate is sensitive to hydrolytic degradation by alkalis; this effect has been used by geologists in the study of fission tracks of mineral samples. The technique is to coat the relevant material with a polycarbonate film; charged particles
## THINNING OF POLYCARBONATE

<table>
<thead>
<tr>
<th>Cyclics</th>
<th>Thinning Rate $\mu$m min$^{-1}$</th>
<th>Condition of Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrroloidine</td>
<td>23.1</td>
<td>thinning/etching</td>
</tr>
<tr>
<td>piperdine</td>
<td>5.9</td>
<td>good polish</td>
</tr>
<tr>
<td>morpholine</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td><strong>linear aliphatic amines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>methyamine solution (33% ethanol)</td>
<td>5.1</td>
<td>surface film and etching</td>
</tr>
<tr>
<td>ethylamine (33% ethanol)</td>
<td>7.7</td>
<td>surface film and etching</td>
</tr>
<tr>
<td>n-propylamine</td>
<td>23.5</td>
<td>polish</td>
</tr>
<tr>
<td>isopropylamine</td>
<td>2.8</td>
<td>surface film</td>
</tr>
<tr>
<td>n-butylamine</td>
<td>9.0</td>
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</tr>
<tr>
<td>isobutylamine</td>
<td>4.3</td>
<td>surface film and etching</td>
</tr>
<tr>
<td>sec. butylamine</td>
<td>2.1</td>
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</tr>
<tr>
<td>tert. butylamine</td>
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<td></td>
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<tr>
<td>n-amylamine</td>
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<td></td>
</tr>
<tr>
<td>ethylamine (33% ethanol)</td>
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<td>surface film and etching</td>
</tr>
<tr>
<td>diethylamine</td>
<td>1.5</td>
<td>crystalline, brittle</td>
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<td>triethylamine</td>
<td>0</td>
<td>surface opaque</td>
</tr>
<tr>
<td>hydrazine hydrate</td>
<td>5.7</td>
<td>quite good polish</td>
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<tr>
<td>1,2-diaminoethane</td>
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</tr>
<tr>
<td>approx. 6.5N methanolic caustic potash</td>
<td>1.2</td>
<td>excellent polish</td>
</tr>
</tbody>
</table>

**TABLE (1.2)**

After Anderton (65)
leave traces in the film which are etched out using 6N aqueous NaOH at 70°C for 10 minutes (72). Paretzke et al (67) have also reported the etching of polycarbonate by aqueous sodium hydroxide (6.25N, 40°C), due to hydrolytic degradation (see Figure 1.4a). These investigations undoubtedly prompted further studies of alkaline reagents to be used as etchants and possibly polishers (66, 70, 71).

1.3.2 Thinning, Etching and Polishing of Polycarbonate

Preliminary work on chemical thinning of polycarbonate (68) (shown in Figure (1.4b)) indicated a methanolic solution of KOH as a good thinning agent.

The action of alkaline hydrolysis of polycarbonate by interfacial chain degradation is thought to provide a viscous boundary layer (provided the chain fragments are soluble) at the solid interface so that the surface projections are attacked preferentially (66). An analogous situation is observed in metal polishing, where the diffusion barrier may either be a viscous boundary layer or a thin solid layer or a combination of both on the surface (69). A scratch decay technique combined with interferometry (described in detail in Chapter 3) had been used to evaluate the polishing and etching action of methanolic KOH on polycarbonate. It was found that etching always preceded polishing and that a balance, (strongly dependent on crack size and KOH concentration) between etching and polishing was evident (66).

The change from an initial etching phase to a polishing phase is thought to be due to the formation of the viscous boundary layer; etching occurring before a stable viscous layer has built up. The formation of the viscous boundary layer is thought to be much slower than the initial scission reaction. Hence, shorter reaction times favour etching and longer times, (i.e. after a stable viscous boundary layer has formed), favour polishing.
The expected sequence of events of the polishing process of polycarbonate is shown in Figure (1.6) and has been described\(^\text{(66)}\) as follows:

\(\text{(a)}\) Equilibration of KOH and methanol forming methoxy ions
\[
\text{KOH} + \text{MeOH} \xrightarrow{\text{K}^+ \text{MeO}^- + \text{H}_2\text{O}}
\]

\(\text{(b)}\) These ions initiate random chain scission at the polymer surface, the chain fragments passing into solution from a viscous boundary layer.

\(\text{(c)}\) As the thickness of the diffusion layer increases the concentration of the methoxy ions at the polymer surface decreases, due to the reaction of the methoxy ions with the low molecular weight polymer fragments present in the viscous layer, and also, due to the greater distance for diffusion. Hence, as the thickness of the viscous layer increases the polishing rate increases and the overall thinning rate decreases (see Figure 1.6).

\(\text{(d)}\) The ultimate product of degradation by this reaction is an equimolar mixture of esters and phenols which is comparable to products found by Parentzke et al\(^\text{(67)}\) for the degradation of polycarbonate using hot, aqueous NaOH.

### 1.3.3 Parameters Affecting Polishing, Etching and Thinning of Polycarbonate using a KOH/MeOH Solution

The thinning, polishing and etching rates of polycarbonate are strongly dependent on the KOH concentration. A maximum rate of thinning at a KOH concentration of 4.8\text{N} was observed by Anderton\(^\text{(70)}\) as shown in Figure (1.7).
The logarithmic crack depth ratio \( \log_e(b_0/b) \) against the amount of material removed from the surface \( u \), was plotted for various KOH concentrations, and crack width (see Figures (1.5) and (1.8)) by Lewis and Ward.\(^{(66)}\) These results clearly show etching and polishing phases, etching always preceding polishing. The depth of etching seems to be inversely proportional to the KOH concentration and inversely related to the crack width. When the gradient of the graphs becomes positive polishing occurs, and the smaller cracks are polished more rapidly than the larger ones. The best polishing solution for all cracks is that of maximum KOH concentration. Crack widening at lower KOH concentration was also observed by Lewis and Ward\(^{(66)}\) and this result has been successfully used in the study of craze morphologies by Ward\(^{(71)}\) and Hawkins.\(^{(9)}\)

When samples were rotated in the polishing solution, the rate of polishing was found to be inversely proportional to the rate of rotation for all KOH concentrations and crack width\(^{(70)}\) as shown in Figures (1.9) and (1.10). This is probably due to the reduction in height of the viscous layer and is additional evidence of its existence.

From the work discussed so far it is clear that (a) the thickness of the viscous layer, (b) the rate of build up of the viscous layer, (c) the analysis of the chain fragments in the viscous layer and finally (d) the effect of temperature on process of chemical polishing, etching or thinning needs to be investigated for a comprehensive understanding of the subject; which forms the basis of Chapter 3.
1.4 MOLECULAR ORIENTATION AND RESIDUAL STRESS IN INJECTION MOULDINGS

1.4.1 Introduction

A polymer is said to contain molecular orientation when the polymer molecules are elongated and aligned in a specific direction in contrast to its usual randomly coiled configuration. Residual stress could be considered as the local, elastic (energy) stresses that exist in a solid body in the absence of all external forces. However, it must be mentioned that the terms 'frozen-in', 'locked-in', 'built-in', 'internal' stresses and strains, which relate to the non-equilibrium configurations of molecular orientation and residual stress are often used in literature.

In injection mouldings, the molecules align in the direction of the melt flow and if the cooling of the mould is sufficiently rapid the molecules freeze in their orientated state and relaxation to an equilibrium state is not possible. Molecular orientation does not exhibit any local mechanical stress, below the glass transition temperature ($T_g$) of the moulding, in contrast to residual stresses. This fact is revealed if a moulding was to be sectioned; the change in shape being observed as mechanical equilibrium is restored in a residual stress situation, and no change in shape observed in a moulding with only molecular orientation. However, when a moulding with molecular orientation is heated above the $T_g$, relaxation of the polymer chains to its randomly coiled position can cause mechanical strain. The relatively low temperature of the mould results in an inhomogeneous temperature distribution of the polymer melt which results in contraction of one part of the moulding with respect to the other. Hence, for the body to be in equilibrium the residual stresses must be set up in such a manner so as to introduce tension in the parts of the body undergoing relative volume contraction, and compression in
the case of relative volume expansion.

In a typical injection moulding, both residual stresses and molecular orientation exists. The problem that is often encountered is the difficulty of assessing the contribution of each factor, and moulding an object minimising (or maximising) these effects for the advantage of the finished product in its applications.

1.4.2 Experimental Methods Used in Assessing Residual Stress and Molecular Orientation

The through-thickness birefringence (interference due to the difference in refractive indices in the two orthogonal directions $x$ and $y$; the sample being in the $xy$ plane) measurements of plastics as a function of thickness is commonly used in estimating molecular orientation and residual stress.\(^{(9,73,74)}\) The basic limitation in this type of measurement is the necessity for a second method to separate residual stress from molecular orientation.

The successive removal of layers from a surface may result in disturbing the force and the bending moment equilibrium of the specimen, and hence, may cause to alter its length and curvature in order to re-establish equilibrium. The residual stress of the removed layer, may be considered as a function of the magnitude of change in length and curvature of the specimen,\(^{(73,76)}\) and hence, the residual stress may be calculated. The above mentioned method is used in conjunction with the through-thickness birefringent measurement technique for assessing molecular orientation and residual stress in plastics. However, these methods have the following shortcomings:

(a) The observation of curvature or the change in length of a specimen is practicable, only above a particular threshold of residual stress. This restricts the detection of relatively low residual
The layer removal technique generally employed is that of mechanical cutting and may result in damaging the specimen. Polishing the surface may also be necessary (after cutting) for birefringence measurements. A novel chemical layer removal technique for poly(bisphenol-A carbonate) is described in Chapter 3.

Ennos and Thomas have used a holographic interferometric technique\(^{(77)}\) in measuring the distortion of injection moulded glass fibre filled polypropylene specimens, due to the relaxation of internal stresses. White, Coxon and Sandilands\(^{(78)}\) have calculated internal stress parameters for injection moulded high density polyethylene and polystyrene from stress-relaxation data using the analysis of Li\(^{(79)}\) and Kubat and Rigdahl.\(^{(82)}\)

The measurement of residual stresses has been done in alloys and metals by using a blind hole drilling technique.\(^{(80,81)}\) The use of a similar method for plastics is discussed in Chapter 4.
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Figure 1.1 The general chemical structure of polycarbonates

Figure 1.2 The chemical structure of poly(bisphenol-A carbonate)

Figure 1.3 A typical polycarbonate tensile stress-strain curve
Figure 1.4(a) Alkaline hydrolysis of PC using 6.25N aqueous NaOH at 40°C, after Paretzke et al.

Chemical thinning of polycarbonate (static conditions, 25°C)

Weight loss (%) vs. time (hrs.)

KOH(s)/H₂O
KOH/H₂O/MeOH
KOH+MeOH ⇌ KOMe + H₂O
KOH/MeOH (5N)

Figure 1.4(b) Thinning rates of PC in various KOH solutions, after Ward (68)
Figure 1.5b (After Lewis and Ward) Thinning curves for a 45-µm wide crack on a polycarbonate surface. The etching region is largest at about 4.24 N solution concentration, the crack becoming deeper more rapidly at lower normalities. The polishing rate is a very sensitive function of concentration, the most rapid polishing occurring at highest normalities.

Figure 1.5a (After Lewis and Ward) Thinning curves for a 120-µm crack ruled on a polycarbonate surface as a function of solution normality (KOH-MeOH). The etching phase becomes progressively larger as normality is decreased. The rate of polishing increases as a function of normality.

FIGURE (1.5)
The growth of the viscous boundary layer and the explanation for polishing

FIGURE (1.6)
Rate of Thinning as a Function of Normality for Static Conditions

FIGURE 1.7 (After Anderton)
Figure 1.8a (After Lewis and Ward) Thinning results for polycarbonate immersed in 2.60 N methanolic KOH at 15°C. The logarithmic crack depth ratio is plotted against the amount of material removed from the surface. Etching occurs during removal of the first 60 µm of surface, and is then followed by a slow polishing mode. The narrowest cracks are polished and etched most rapidly.

Figure 1.8b (After Lewis and Ward) Polishing and etching of four cracks in 6.92 N methanolic KOH at 15°C. The cracks deepen during removal of the first 20 µm of surface but are then rapidly polished. All cracks have returned to their original depth after 40-60 µm, and the 18 µm wide crack has been completely removed after 80 µm of surface depletion.

FIGURE 1.8
FIGURE (1.9) Plots of the rate of polishing versus the velocity of rotation. (After Anderton)
FIGURE (1.10) Plots of the rate of polishing versus the velocity of rotation. (After Anderton)
CHAPTER II

THE DEVELOPMENT OF A SCRATCH DECAY TECHNIQUE
FOR THE EVALUATION OF SURFACE FREE ENERGY

2.1 SINUSOIDAL PROFILE DECAY

2.1.1 Introduction

It is known that an irregular surface relaxes in order to minimise its overall free energy. The driving force for this relaxation is the result of the chemical potential of the atoms in a surface; and this is a function of the surface curvature as shown by Gibbs-Thomson equation.

\[ \mu_1 - \mu_2 = \bar{v} 2 \gamma k \] 

(2.1)

where \( \mu_1 \) and \( \mu_2 \) are the chemical potentials on the concave and the convex sides respectively, \( \bar{v} \) the specific volume, \( \gamma \) the surface free energy and \( k \) the curvature of the surface. Herring\(^{(1)}\) proposed that mass transport on a surface could occur by four distinct mechanisms (surface diffusion, volume diffusion, evaporation-condensation and viscous flow), while Mullins\(^{(2)}\) extended Herring's theory to the case of flattening of nearly plane surfaces. Mullins' special case development of the thermal decay of sinusoidal grooves (using simplifying assumptions) is of particular interest to the work presented in this chapter. However, it must be mentioned that a single scratch model has also been developed for evaporation-condensation, surface diffusion and volume diffusion.\(^{(47,48,49,50)}\)
2.1.2 The Transport Phenomenon of Sinusoidal Profile Decay

The work presented in this section is a direct adoption of Mullins' work.

Consider an initial surface parallel to the y axis with a trace on the xy plane (see Figure 2.11) given by $z = w(x, o)$. Now

$$w(x, o) = a \sin \left( \frac{2\pi}{\lambda} x \right) \quad (2.2)$$

where $\lambda = \text{the wavelength of the groove}$

$a = \text{the amplitude of the groove}$

and $\omega = \frac{2\pi}{\lambda}$

hence equation (2.2) may be written as

$$w(x, o) = a \sin \omega x \quad (2.2)$$

The simultaneous action of all four processes of transport, namely, viscous flow, evaporation-condensation, volume diffusion and surface diffusion would result in a total change of the surface contour and may be given by:

$$\frac{\partial w}{\partial t} = \left( \frac{\partial w}{\partial t} \right)_{\text{vis}} + \left( \frac{\partial w}{\partial t} \right)_{E_1} + \left( \frac{\partial w}{\partial t} \right)_{E_2} + \left( \frac{\partial w}{\partial t} \right)_s \quad (2.3)$$

where $\left( \frac{\partial w}{\partial t} \right)_{\text{vis}} = \text{the change in the surface contour due to the viscous flow}$

$\left( \frac{\partial w}{\partial t} \right)_{E_1} = \text{the change due to evaporation-condensation}$

$\left( \frac{\partial w}{\partial t} \right)_{E_2} = \text{the contribution due to volume diffusion; evaporation-condensation}$

and $\left( \frac{\partial w}{\partial t} \right)_s = \text{the contribution due to surface diffusion}$.

Now

$$\left( \frac{\partial w}{\partial t} \right)_{\text{vis}} = -F \omega w \quad (2.4)$$

and

$$\left( \frac{\partial w}{\partial t} \right)_{E_1} = -A \omega^2 w \quad (2.5)$$
Hence from equation (2.3) to (2.8) we have

$$\left(\frac{\partial W}{\partial t}\right)_s = -B\omega^4 W$$

(2.8)

where

$$\left(\frac{\partial W}{\partial t}\right)_F = -\left[ F\omega + A\omega^2 + (A' + C)\omega^3 + B\omega^4 \right] W$$

(2.9)

where

$$F = \frac{\gamma}{2\mu}$$

(2.10)

$$A = \frac{P_o \gamma \Omega}{(2\pi M)^{1/2}(kT)^{3/2}}$$

(2.11)

$$A' = \rho_o D_G \gamma \Omega^2 /kT$$

(2.12)

$$C = D_V \gamma \Omega /kT$$

(2.13)

$$B = D_S \gamma \Omega^2 N/kT$$

(2.14)

where

- $P_o$ is the equilibrium vapour pressure over the flat surface
- $\Omega$ is the atomic volume
- $\gamma$ is the surface free energy per unit area
- $M$ is the mass of a molecule of the solid
- $N$ is the atomic surface density
- $D_S$ is the surface self diffusion coefficient
- $D_V$ is the volume diffusion coefficient
- $\rho_o$ is the equilibrium vapour density over a flat surface
- $D_G$ is the diffusion coefficient of vapour molecules in the inert atmosphere
- $k$ is the Boltzmann constant
- $T$ is the absolute temperature
- $\mu$ is the coefficient of viscosity.
The movement of a surface due to viscous flow is associated with a change in pressure, normal to the surface, and just beneath it. Such a change (in pressure) is associated with the surface free energy, \( \gamma \), by the Gibbs Thompson relation. This forms the basis of the physical process behind the derivation of equation (2.4) and hence equation (2.20) (see page 26).

From equation (2.9) we have

\[
\frac{dw}{w} = -(F \omega + A \omega^2 + D \omega^3 + B \omega^4) \, dt
\]  

(2.9a)

Integrating between the limits of \( t \) and \( t = 0 \) we have

\[
\frac{w(x,t)}{w(x,0)} \ln w = -(F \omega + A \omega^2 + D \omega^3 + B \omega^4) t
\]  

(2.9b)
Hence the solution of equation (2.9) for the time dependent contour under the simultaneous action of all processes is

\[ w(x, t) = - \exp \left[ F_0 \omega + A_0 \omega^2 + D_0 \omega^3 + B_0 \omega^4 \right] t \]  

(2.15)

where \( D = (A' + c) \)

\[ w(x, 0) = a \sin \omega x \]  

(2.2)

Hence from equations (2.2) and (2.15) we have

\[ \frac{w(x, t)}{w(x, 0)} = - \exp \left[ F_0 \omega + A_0 \omega^2 + D_0 \omega^3 + B_0 \omega^4 \right] t \]  

(2.16)

The equation can be more generally written as

\[ \frac{w(x, t)}{w(x, 0)} = - \exp \left[ \sum_{i=1}^{4} k_i \omega^i \right] t \]  

(2.17)

or

\[ \ln \left( \frac{w(x, 0)}{w(x, t)} \right) = \sum_{i=1}^{4} k_i \omega^i t \]  

(2.18)

However, in practice all four transport mechanisms may not be active; for example, if it were to be assumed that the viscous flow is the dominant mechanism equation (2.18) may be reduced to

\[ \ln \left( \frac{w(x, 0)}{w(x, t)} \right) = k_1 \omega t \]  

(2.19)

where \( k_2 = k_3 = k_4 = 0 \),

\[ k_1 = F = \frac{\gamma}{2\mu} \]  

(2.10)

and \( \omega = \frac{2\pi}{\lambda} \)

Hence equation (2.19) becomes

\[ \ln \left( \frac{w(x, 0)}{w(x, t)} \right) = \frac{\gamma \pi t}{\mu \lambda} \]  

(2.20)
2.1.3 The WLF Model

If the dominant mechanism of thermal decay of surface profiles is assumed to be viscous flow, the relevant decay equation is 2.20 (see section 2.1.2). From equation 2.20 it is clear that the decay is very much viscosity dependent and hence, it is vital to estimate accurately the viscosity of the polymer at the corresponding decay temperature.

In viscoelastic materials time and temperature are equivalent to the extent that data at one temperature can be superimposed upon data taken at different temperatures merely by shifting curves along the time axis. The distance shifted represents the logarithm of the shift factor $a(T)$. An empirical equation for the shift factor was proposed by Williams, Landel and Ferry (51,52) (WLF equation).

$$
\log_{10} a(T) = \log_{10} \left( \frac{\eta(T_s)}{\eta(T)} \right) = \frac{c_1 (T - T_s)}{c_2 + T - T_s}
$$

(2.21)

where $c_1$ and $c_2$ are the WLF constants, $T_s$ the reference temperature and $\eta(T)$, $\eta(T_s)$ the viscosity at temperature $T$ and $T_g$ respectively. The average values of $c_1$ and $c_2$ had been first obtained by fitting on a large number of polymers, and estimated to be 17.44 and 51.6 respectively; the reference temperature $T_s$ is taken as the glass transition temperature, $T_g$, of the polymer (52). However, for accurate estimations it is necessary to use the appropriate WLF constants and the reference temperatures to suit the polymer in question. Mercier et al (54) used the values of 16.14 and 56 for $c_1$ and $c_2$ respectively, and a reference temperature of $T_1$ ($T_1 = T_g + 5^\circ C$) and found very good agreement between the calculated and the experimental curves (except at $T - T_1 = -20^\circ C$ where the time temperature superposition principle becomes less certain and the WLF equation is probably not applicable) for poly(bisphernol-A carbonate).
2.2 EXPERIMENTAL TECHNIQUES

2.2.1 Introduction

The measurement of surface free energy by thermal decay of a polymer surface profile requires several demanding experimental techniques including precise temperature control and measurement.

A scratched sample was heated under controlled conditions with continuous monitoring of its temperature, the profile being recorded before and after each experiment using Interferometry. Measurement of bulk viscosity, the glass transition temperature and an assessment of the extent of thermal degradation during the heating process were supporting experiments in the evaluation of surface free energy.

2.2.2 Specimen Preparation and Surface Measurements

The specimens used, and the initial preparation was the same as that described in Section 3.2.1. However, after scratching the specimens (as in 3.2.1) they were chemically thinned by approximately 3 μm using a 5.8N KOH solution in methanol (see Chapter 3) so that the surface layer (which would probably contain residual stress due to the scratching process) would be eliminated. The surface profile of the chemically thinned specimen was recorded using interferometry as described in Section 3.2.3 before and after the thermal annealing. Figure (2.1) shows a typical set of interferograms before and after annealing.

2.2.3 The Development of the Annealing Technique

2.2.3.1 The Initial Attempt of Annealing

The first attempt of annealing PC was done by placing the sample on a metal slide, which was heated using a Reichert micro hot-

* molecular orientation may also be present.
stage in conjunction with a Reichert 'TC 400' control unit. The
temperature of the hot-stage was recorded by using a built-in
platinum resistance thermometer (PRT), while the temperature of
the surface of the sample was monitored using a Nickel/Chromium-
Nickel/Aluminium thermocouple in conjunction with a cold cell and a
chart recorder.

The results obtained by this method were not reproducible and
an extra thermocouple attached to the sample indicated the presence
of thermal gradients as high as 20°C per mm of thickness. Furthermore,
the disturbance of the ambient conditions of the room (e.g. temperature
variations due to convection currents etc.) clearly had an effect on
the surface temperature of the sample. Finally, the temperature
control also proved to be very difficult. A temperature overshoot of
about 15°C and final fluctuations of about ± 4°C were not uncommon.

Although this attempt of the experiment was not successful it
indicated the necessary requirements for a successful experiment i.e. :

(i) * A better system of temperature control

(ii) The heating of the specimen has to be done on all sides
    (e.g. by the use of a furnace) to minimise the temperature
    gradient in the sample

(iii) * Improvement of temperature measurement

(iv) To observe the effect of adsorption on the polymer
    surface (e.g. by conducting the experiment in a
    vacuum or under a particular gaseous environment)

(v) An assessment of the degree of thermal degradation, if
    any.

* The aspects of instrumentation, especially temperature control and
  measurement are treated separately in Section 2.2.4.
2.2.3.2 Annealing Using the Second Rig

A second experimental rig based on the first four of the above modifications was set up. Firstly temperature control was improved by using an AEI temperature controller with proportional, differential and integral controls (the latter being fixed at a particular setting) in conjunction with a phase angle firing thyristor unit (see Section 2.2.4.2). Two sets of heating chambers as shown in Figures (2.2) and (2.3) were designed in such a manner that only the edges of the sample came into contact with the heating chamber, and primarily, the sample was heated by (a) radiation from top and bottom of the sample chamber and (b) by conduction and convection due to the gas in the sample chamber. This ensured uniform heating of the sample (the thickness kept to a minimum of 1 mm) thus, reducing thermal gradients through its thickness.

The hot-stage used in the previous experiment was employed to heat the 'heating chamber', which in turn contained the sample. The hot-stage was controlled by the 'temperature controller' mentioned previously, with the aid of a feedback thermocouple placed just below the sample (see Figure 2.4) The temperature gradient within the inner surfaces of the sample chamber was minimal due to high thermal conductivity of the heating chamber (made of copper).

The temperature measurements of the surface profile was done by using a BICC KSK2B10* thermocouple while the temperature on the other side of the sample was monitored by using a KSK4B20* thermocouple. The second thermocouple in KSK4B20 was used as a control thermocouple. The thermocouples used were calibrated against a National Physical Laboratories calibrated platinum resistance thermometer (PRT) and the EMF generated was converted to temperature using a British Standards Conversion Table(4). The EMF generated by the thermocouples were

* See Appendix 2.2
measured using a Solartron Digital voltmeter with a resolution of 10 μV or an Oxford 3000 series potentiometric chart recorder (see Appendix 2.2).

Finally the hot-stage and a heating chamber with the thermocouples were placed in a vacuum furnace (see Figure 2.4) enabling either to create a vacuum of $10^{-6}$ mm of mercury or alternatively using an atmosphere of a desired gas.

Annealing was done using (a) vacuum of $10^{-6}$ mm of mercury, (b) an atmosphere of Nitrogen; (c) an atmosphere of Helium and (d) in air.

The annealing process was not reproducible as expected and an error margin of 100 to 200% was observed in all four cases (of the annealing process described above). Temperature overshoot of approximately 3°C and the limited accuracy of temperature measurement (± 0.5°C) were inadequate. The problem was two-fold. Firstly, incorporating the temperature fluctuations in the decay equation (2.20) and secondly the measurement of these variations accurately.

Armed with these results it was decided to build a third annealing rig (see Section 2.2.4) with the following improvements:

(i) Improve the accuracy of the temperature measurements coupled with a digital logging system enabling the data to be directly processed in a computer (see Section 2.2.4.2).

(ii) The use of the above-mentioned data in the decay equation (2.20) via a numerical integration so that the temperature fluctuations are accounted for in the process of decay.

(iii) Calibration of the thermocouples (using a PRT) for each experiment and finally, observing a relative temperature measurement rather than an absolute one, thus increasing the reliability of the measurement.
(iv) To improve further temperature control.

(v) The effect of the type of environment on the annealing process was assumed to be a second order problem (judging from the feedback of the previous annealing experiment) compared with the limitations of the temperature measurement technique, and hence it was decided to anneal in air rather than in a controlled environment. However, should this assumption prove to be false (depending on the feedback of annealing experiments to be conducted from improvements (i), (ii), (iii) and (iv)) provisions for further modifications (in order to anneal in a specific environment) were made.

(vi) Design of a new furnace so that the temperature gradient through the thickness of the sample would be further reduced.

2.2.4 The Annealing Technique

2.2.4.1 Introduction

The technique described in this section is a direct development from the feedback of the annealing attempt described in Section 2.2.3.2. The improvements (i), (ii), (iii), (iv) and (vi) suggested (in Section 2.2.3.2) were implemented. Figure (2.5) shows a flow diagram of the procedure of temperature control and measurement, calibration of the thermocouples, data capture and analysis, while Figure (2.6) shows a photograph of the experimental rig.

The furnace used for annealing was redesigned so that its own heaters were incorporated on both sides of the sample (see Figures 2.7 and 2.8) thus, further reducing the temperature gradient in the
sample. Secondly, the design was such that the furnace with the thermocouples and the sample could be sealed so that it may be immersed in an oil bath for thermocouple calibrations.

Initially the sample was heated using the temperature controller* attached to a control (feedback) thermocouple* placed on one side of the sample. The temperature on either side of the sample was monitored by thermocouples* at regular intervals (approximately 11 seconds) in addition to the electrical interference level (see Section 4.2.4.2(b)) using the data logging system developed.* The data was initially stored in the buffer of the computer* and was transferred on to floppy disk as and when the available buffer space was used up. After annealing for approximately 30 mins, the furnace was allowed to cool in air to approximately 140°C and then immersed in an oil bath* (see Figure 2.9), very accurately thermostated at 135°C. When the temperature of the oil bath was stabilized at 135°C (usually about 30 mins after immersing the furnace) the thermocouples* in the furnace were calibrated against the PRT* which was initially placed in the oil bath. These measurements were then recorded on floppy disk. Finally using the computer program 'SENERGY' (see Section 2.3 and Appendix 2.1) the data was analysed and surface energy calculated.

2.2.4.2 Instrumentation

(a) Temperature control

A crude form of manual control may be automated using a thermostat to provide a feedback signal. When the temperature is below a set level the power is switched on and when the temperature

* The equipment used for temperature control, measurement and recording are listed in Appendix (2.2).
is above this level the power is switched off. The result is a temperature variation as in Figure (2.10(a)). The response of the detecting transducer to the changes in the heating power is affected by (a) the distance between the heater and the detecting element (known as the transport or distance lag), (b) the thermal process where heat is transferred through 'thermal resistance' (transfer or exponential lag).

This system may be improved by replacing the on-off system by a proportional control system where the correction signal is proportional to the error between the set value and the measured value (set in the correct sense to reduce the error to zero). Such a system enables the controller to regulate the power supply proportional to the deviation. However, such control is restricted over a very limited range of load changes; and hence, it is necessary to introduce some amplification of the control signal. The relationship between the deviation and the controller output is called the proportional band. As the system requires a deviation to operate, there is always a sustained deviation (offset) present, dependent on the proportional band-width. As the proportional band is decreased, deviation is reduced, but reaches a point where the system is unstable and the temperature oscillates. A compromise proportional band-width which maintains a stable system must be used, but this gives a slow response, a considerable degree of overshoot, and a steady-state deviation (see Figure 2.10(b)).

The steady-state deviation may be reduced by an alternative signal of sufficient magnitude to provide an output, if a steady-state deviation exists. Such a signal may be provided by an integrator giving a constantly increasing output for a steady-state value input. The use of a proportional and integral control would result in reducing the steady-state deviation. However, it must be
mentioned that too much integral term control causes the system to be unstable and oscillations are observed. In general an increase in the integral term reduces the steady-state deviation but increases the time the system takes to settle after a disturbance (i.e. the overall response time).

If the controller' output is boosted by a signal proportional to the rate of change of deviation, which is added to both integral and the proportional control outputs, then the system would pre-act to sudden changes and prevent large deviations. The derivative term does not have any effect upon any steady-state deviations but reduces the settling time by reducing the number of oscillations.

In this control system the correction applied is proportional to the magnitude of error (proportional), the time of error during which it exists (integral) and the rate of change (derivative) of such error. Such an arrangement is known as a proportional + integral + derivative (P + I + D) or three term control (see Figure 10c).

A Eurotherm three term controller (type 090-002-97-151-02-04-61-00)\(^{(5)}\) was used in conjunction with a Eurotherm thyristor (type 031-080-06-42-00)\(^{(6)}\) for the temperature control of the furnace. The setting of the proportional, derivative and integral controls was done as follows:

(i) The proportional band and the power limit were set to a maximum with the derivative and integral controls switched off.

(ii) The proportional band was progressively reduced until oscillations (say period T) were observed (at a band setting A say).

(iii) The proportional control was set to 1.7A and integral
and derivative controls to T/2 and T/8 respectively.

(b) Temperature Measurement and Recording

Accurate temperature measurement, especially when rapid temperature changes occur is a formidable task. Figure (2.5) shows a flow diagram of the temperature measurement and recording technique used, while Appendix (2.2) lists the details of the equipment used.

Firstly, the measuring transducer must have a very fast 'response time' to any change in temperature and secondly, it should have a low thermal capacity so that transducer does not alter the temperature of measuring region to an appreciable extent. A fast 'response time' and low thermal capacity is characteristic of thermocouples but they inherit other problems such as hysteresis effects and low resolution. Also, the EMF generated by the thermocouples are rather low (approximately 40μV per degree C, for Chromel-Alumel thermocouples) which immediately presents the problem of microvolt measurement. However, if a PRT were to be used it would be a sacrifice of fast response time and low thermal capacity for a higher degree of accuracy. It was decided to overcome this dilemma by using thermocouples and calibrating them against an NPL calibrated PRT, at a temperature of approximately 30°C below that of annealing. This calibration was done immediately after each experiment (see Section 2.2.4.1) thus, minimising the hysteresis effect: as only relative (to the calibration temperature) temperature measurements were conducted (rather than absolute ones*).

A major problem in microvolt measurement is that of 'electrical

* If the annealing temperature is 170°C and the thermocouple has a 1% error, then true error of

(i) a relative temperature measurement of 30°C (with respect to the calibration temperature approximately at 140°C) would be 0.3°C
(ii) an absolute measurement of 170°C would be 1.7°C

This illustrates the importance of relative temperature measurements.
interference' which is due to a) thermo-electric or electro-chemical effects (steady interference), b) inductive coupling from alternating current power supplies (alternating interference), c) intermittent operation of inductive loads (random interference). These three forms of interference may appear at the input terminals of an equipment in one of two modes, a) an interference voltage, usually at mains frequency, common to all terminals of a signal circuit with respect to a reference point, usually the earth (common or parallel mode interference); b) an interference voltage that appears across the terminals of a signal circuit (series or differential mode).

The 7065 series solartron voltmeter (see Appendix 2.2) used was engineered to overcome these problems by

a) the use of the ±15µv offset control to back-off any spurious voltages at the start of the experiment.

b) rejection of A.C. signals by averaging the input voltage over the integration time (1.28 seconds set for this experiment); the integration time being an exact multiple of the mains period (20 ms at 50 Hz). This reduced 'series mode interference' to a very great extent. It should be mentioned that a phase angle firing thyristor (see Appendix 2.2) was used (in conjunction with the temperature controller) which generated alternating interference and hence, 'series mode rejection' was an essential feature of the measurement technique.

c) and finally the rejection of 'common mode interference' by the use of 'Guard Techniques'.

In addition to the above mentioned methods, interference was minimised by using closely twisted pairs of thermocouple wire (to eliminate inductive coupling effects) wrapped in aluminium foil (in
order to provide an electrical screening effect). Finally a dummy channel was used to monitor the extent of electrical interference not suppressed.

The calibration of the thermocouples was done by taking measurements from the thermocouples and the PRT, once the temperature in the oil bath stabilised (see Section 2.2.4.1). This measurement was done by changing the mode of measurement from volts (for the thermocouple) to ohms (for the PRT) in the digital multimeter. This change in mode was accomplished by a modification of command system in the data logger. Thirty such readings were the basis of the thermocouple calibrations.

2.2.5 Supplementary Experiments

Three sets of additional experiments were conducted to provide additional information necessary for the evaluation of surface free energy:

(a) The assessment of the extent of thermal degradation in the annealing process.
(b) The measurement of viscosity of polycarbonate.
(c) The measurement of the glass transition temperature.

The details of these experiments are as in Appendix (2.3).

2.3 DEVELOPMENT OF COMPUTER PROGRAMS FOR THE EVALUATION OF SURFACE FREE ENERGY

2.3.1 Introduction

All computer programs were written in 'BASIC' for a 'Horizon North Star*' computer and five programs named (a) 'SENERGY', (b) 'DATLPT', (c) 'DATVDU', (d) 'DATRST' and (e) 'DATCAP' were used for the surface energy evaluation. (All programs are listed in Appendix 2.1.)

* See Appendix (2.2)
DATCAP was used initially to capture the incoming data from the data logger, and then to write it on to floppy disk. DATVDU transferred the data from floppy disk to a visual display unit (VDU)* for examination. Data was printed using DATLPT and a printer*. The calculation of surface free energy and recording the results on floppy disk was done by SENERGY. Finally, DATRST was used to obtain a hard copy of the results from the floppy disk using a printer*.

2.3.2 The Surface Free Energy Program (SENERGY)

SENERGY is the most important program and is responsible for analysing the data and the final evaluation of surface free energy. The following operations are done by this program:

(a) Firstly, it opens and labels a file in the second floppy disk corresponding to the data to be analysed (already in the first disk). This has to be requested by the operator through the keyboard of the VDU.

(b) Then the computer responds by requesting the reference temperature, the temperature from which effective annealing occurs and the WLF constants.

(c) It then calibrates the thermocouple constants against the PRT using its NPL calibration\(^8\). (The NPL calibration has been written into the program.)

(d) Having obtained the appropriate thermocouple constants it converts the thermocouple output voltage to temperature using a British Standards conversion chart\(^4\), which was incorporated into the program.

(e) The next step would be the calculation of the viscosity of the sample at the annealing temperature. This is

* See Appendix (2.2)
done by using the well known WLF equation (see Section 2.13) and a viscosity measurement made at an elevated temperature (see Appendix 2.3a).

(f) The program then executes the numerical integration; from equation (2.20) we have

$$\ln \left( \frac{A_1}{A_2} \right) = \frac{\tau}{\mu} \frac{Y}{\lambda} t$$

(2.21)

where $A_2 (= w(x,t))$ is the final depth of groove

$A_1 (= w(x,0))$ is the initial depth of groove

$\gamma$ is the surface free energy

$\mu$ the viscosity

$\lambda$ the width of the groove*

$t$ the time of annealing.

Hence

$$\frac{\lambda}{\tau} \frac{\ln A_1}{\ln A_2} = \frac{t}{\mu(t)}$$

(2.22)

The right hand side of equation (2.22) was subjected to a numerical integration using Simpson's Rule(11) over the effective time and temperature range of annealing.

$$\frac{\lambda}{\tau} \left[ \ln \left( \frac{A_1}{A_2} \right) \right] = \sum_{i=1}^{n} \left[ \left( \frac{t_{i+1} - t_i}{3} \right) \left( \frac{1}{\mu_{i-1}} + \frac{4}{\mu_i} + \frac{1}{\mu_{i+1}} \right) \right]$$

(2.23)

$$\frac{\lambda}{\tau} \left[ \ln \left( \frac{A_1}{A_2} \right) \right] = k$$

(2.24)

where $k = \sum_{i=1}^{n} \left[ \left( \frac{t_{i+1} - t_i}{3} \right) \left( \frac{1}{\mu_{i-1}} + \frac{4}{\mu_i} + \frac{1}{\mu_{i+1}} \right) \right]$

where $\mu_i$ and $t_i$ are the $i$th interval of viscosity and time respectively. Hence the right hand side of equation (2.23) was thus calculated.

(g) The computer then responds by requesting the operator

* Identification of $\lambda$ with the width of a single scratch is discussed on page 45.
for A₁, A₂ and λ values and then evaluates surface free energy (γ) using equation (2.23) for each particular set of A₁, A₂ and λ values.

2.4 RESULTS

In the surface free energy calculations for polycarbonate, a glass transition temperature (Tₙ) of 140.5°C and a viscosity value of 1.42 x 10⁵ poise (at 223°C) was used. The measurement of these two values is detailed in Appendix (2.3) Sections (b) and (a) respectively. An assessment of the extent of degradation, if any, during the annealing process was done and is as in Appendix (2.3) Section (c).

Three sets of experiments H₁, H₂, H₃ were conducted.

The annealing curves for the three experiments are shown in Figure (2.12) while Table (2.1) summarises the surface free energy values evaluated.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Appropriate annealing Temperature (°C)</th>
<th>SUREFACE FREE ENERGY (mJm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(see Fig. 2.12)</td>
<td>Groove width 25μm WLF cond.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A*</td>
</tr>
<tr>
<td>H₁</td>
<td>168</td>
<td>184</td>
</tr>
<tr>
<td>H₂</td>
<td>174</td>
<td>94</td>
</tr>
<tr>
<td>H₃</td>
<td>see Fig. 2.12</td>
<td>75</td>
</tr>
</tbody>
</table>

**TABLE (2.1)**

* The WLF constant C₁ and C₂ and the reference temperature Tₛ, (see section 2.1.3) for conditions 'A' and 'B' are as follows:

<table>
<thead>
<tr>
<th></th>
<th>C₁</th>
<th>C₂</th>
<th>Tₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>condition 'A'</td>
<td>17.44</td>
<td>51.6</td>
<td>140.5</td>
</tr>
<tr>
<td>condition 'B'</td>
<td>16.14</td>
<td>56.8</td>
<td>145.5</td>
</tr>
</tbody>
</table>

** The accuracy of the surface free energy values are not indicated in Table 1.2 but are discussed separately in sections 2.5 and 2.6.
TABLE 2.2

Experimental values of surface tension ($\gamma$)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Surface tension (mJ m$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>140°C</td>
</tr>
<tr>
<td>Linear polyethylene</td>
<td>35.7</td>
<td>28.8</td>
</tr>
<tr>
<td>Branched polyethylene</td>
<td>35.3</td>
<td>27.3</td>
</tr>
<tr>
<td>Linear polyethylene</td>
<td>35.6</td>
<td>28.1</td>
</tr>
<tr>
<td>Branched polyethylene</td>
<td>34.8</td>
<td>26.5</td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>42.8</td>
<td>30.0</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>29.4</td>
<td>22.1</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>40.7</td>
<td>32.1</td>
</tr>
<tr>
<td>Polybutene</td>
<td>34.0</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>36.5</td>
<td>28.6</td>
</tr>
<tr>
<td>Polytetrahydrofuran</td>
<td>31.9</td>
<td>24.6</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>41.1</td>
<td>32.0</td>
</tr>
<tr>
<td>Poly(n-butyl methacrylate)</td>
<td>31.2</td>
<td>24.1</td>
</tr>
<tr>
<td>Poly(i-butyl methacrylate)</td>
<td>30.5</td>
<td>23.3</td>
</tr>
</tbody>
</table>

b) Critical surface tension of wetting $\gamma_{cr}$ (at 20°C)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\gamma_{cr}$(mJ m$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>31-31.5</td>
<td>58, 59</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>30-35</td>
<td>60, 61</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>39</td>
<td>62</td>
</tr>
<tr>
<td>Polyacrylamide</td>
<td>35-40</td>
<td>61</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>35</td>
<td>63</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>33-44</td>
<td>64</td>
</tr>
</tbody>
</table>
### c) Contact angle measurements (at 20°C)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Surface tension (mJ m⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>43</td>
<td>60</td>
</tr>
<tr>
<td>Poly(dimethylsiloxane)</td>
<td>24</td>
<td>65</td>
</tr>
<tr>
<td>Poly(bisphenol-A carbonate)</td>
<td>45</td>
<td>24</td>
</tr>
</tbody>
</table>

### d) Estimation of surface tension mJ m⁻¹ (at 20°C)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>From the parachute</th>
<th>From the cohesive energy density</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>31.5</td>
<td>30</td>
<td>24</td>
</tr>
<tr>
<td>Poly-propylene</td>
<td>32.5</td>
<td>33</td>
<td>24</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>43</td>
<td>38</td>
<td>24</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>42.5</td>
<td></td>
<td>24</td>
</tr>
</tbody>
</table>

### e) Estimation of surface free energies from nucleation (mJ m⁻²)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Fold surface free energy</th>
<th>Lateral surface free energy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>90.5</td>
<td>14.2</td>
<td>66</td>
</tr>
</tbody>
</table>
2.5 DISCUSSION

Firstly, it must be emphasised that the interpretations of the scratch decay data is difficult due to the lack of experimental data on its kinetics. Lack of kinetics on scratch decay is primarily due to problems of effective temperature control at a fixed setting (see Section 2.2.4.2), and, hence, time and temperature had to be taken as (simultaneous) variables of an experiment. Under these circumstances it is essential to look at all possible surface transport phenomena (evaporation-condensation, volume diffusion, surface diffusion, and viscous flow) prior to interpretation of the data.

The process of evaporation and condensation can be eliminated without any doubts in this instance, due to the high molecular weight, \( \bar{M}_w = 24,000 \); see Appendix 2.3c) of the samples. Although the process of diffusion of polymer chains of relatively small molecular weights (up to 600) using the concept of 'reptation' \(^{28}\) has been reported in solid polyethylene \(^{29}\) it is unlikely that a polymer chain as bulky as poly(bisphenol-A carbonate) would diffuse. Furthermore, the molecular weight of the polymer, in this case, is above the entanglement molecular weight (see Section 3.4.5) and, it is very unlikely that diffusion is responsible for the movement of the polymer chains. The only other possibility is viscous flow.

The theory of scratch decay outlined in section 2.1.2 is for a multiple scratch rather than for a single one. Although single scratch decay theory has been developed \(^{49,50,67,68,69}\) and used \(^{47}\) for surface diffusion, volume diffusion and evaporation-condensation, it has not been extended to viscous flow and hence, the multiple scratch decay theory has been used in the experiments conducted in this work, thus making the results of the analysis approximate. However, it must be mentioned that Mullius \(^2\) has shown the variation of the central depth of a scratch in the two-dimensional case.
From the experiments conducted it is clear (see Figure 2.1) that uniform annealing of the 'v' shaped grooves occur only when the width of the groove is approximately below 50 µm, making it impossible to assess the change in shape of the groove (above a width of 50 µm) and account for this change in the evaluation of surface free energy. This problem is manifested in the surface free energy evaluations when the groove width is above 50 µm as seen in Table (2.1). One of the most important and widely criticized aspects of this method (see Section 1.2.3) is the relaxation of the stresses* around the groove on annealing (the stresses* are normally introduced on scratching the sample surface: see Section 2.2.2). However, in our experiments, the surface layer of the sample has been removed by chemical polishing, and hence, the removal of the said residual strains.** The question, does the surface change chemically during the process of chemical polishing may be asked. The GPC analysis of a PC specimen chemically thinned down to a thickness of several microns showed no appreciable change (see Appendix 2.3c(ii)). However, it is still possible that a chemical change may have occurred and a method to verify this is detailed in Section (2.7).

As described in Section 1.2.2, adsorption of impurities at relatively high temperatures (depending on the nature of the interface above the sample surface, in this instance air), and the anisotropy of the sample surface will effect the value of the surface free energy evaluated. The samples used in this experiment (see Section 2.2.2) are sections from extruded sheet and are obviously anisotropic, but may be assumed to have the same anisotropy for all practical purposes, as they have been obtained from a very small section of the sheet, the sample size being only 10 x 10 mm². However, it must be mentioned that (a) the anisotropy and (b) the variation of anisotropy in extruded PC is relatively small (see Appendix 4.2) in comparison with that of

* Molecular orientation may also be present.
** Relaxation of molecular orientation below the groove is negligible in extruded PC (see also Appendix 4.2).
injection moulded PC (see Section 4.6).

If the samples were annealed above the Tg the anisotropy of the samples could have been eliminated. However, it may be possible that some degree of embrittlement may occur during the annealing process. It is also possible that a slight variation of the interface (i.e. the gases in contact with the sample) may result in these experiments: a method of dealing with this problem is discussed in section (2.7).

On annealing the single scratches, widening of the grooves is expected, but, this is not observed in the experiments conducted in this work (see Figures 2.1a and 2.1b). This is probably due to the fact that annealing has not been conducted for a sufficiently long period of time to observe significant groove widening or that the transport phenomena assumed is not applicable; the former being the likely explanation.

One of the crucial requirements in the surface free energy evaluations is the estimation of viscosity at the annealing temperature using the WLF model (see Section 2.1.3). The validity of the WLF model used very much depends on the constants and the reference temperature used in the model. For all experiments two sets of conditions A, and B, have been used and two sets of surface free energy evaluations have been made. 'Condition A' uses the WLF constants obtained by fitting a large number of polymers while 'Condition B' uses the experimentally tested constants for polycarbonate (see Section 2.1.3).

As seen from Table 2.1 this surface free energy value evaluated using Condition B predicts a slightly higher surface free energy value than Condition A. Condition B is the more appropriate one for this evaluation although some degree of discrepancy may still arise due to the fact that (a) the molecular weight of the PC used in this work is different to that tested in condition B and the Tg is different,
although the latter has been corrected in the choice of the reference temperature, $T_s$.

One of the important requirements in the use of the WLF model is the knowledge of the viscosity of the polymer at a known temperature and its $T_g$. The model will thus inherit any errors that may occur in the $T_g$ and viscosity measurements. These measurements are discussed in Appendices 2.3(a) and 2.3(b).

As previously discussed (see Section 1.2.1) the measurement of surface free energy is one of considerable difficulty. Most values of these measurements available in the literature (see Table 2.2) are from critical surface tension of wetting$^{(70)}$, contact angle$^{(25,26)}$ and the pendant drop measurements$^{(30,31)}$. The problem of wetting the surface with a liquid would affect the surface of the polymer by crazing and, or plasticisation$^{(25,26)}$, depending on the type of wetting agent$^{(32,33,34)}$. The pendant drop method is also based on several assumptions such as (a) the empirical relationship between the molecular weight and surface free energy; (b) the extent of degradation and the effect of the gaseous phase on surface free energy being negligible. These assumptions are questionable, especially the latter, as the temperature at which the experiment is conducted would be very close to the melting point of the material.

Methods of calculating surface tension using (a) the 'parachor' (see Section 1.2.3) and more recently, using polarizabilities and dimagnetic susceptibilities of polymer constituent groups$^{(27)}$ have been used. These methods also have their own limitations and assumptions$^{(35,36)}$. 
Due to the intrinsic limitations of the nature of the experiment (previously discussed in this section) and those due to experimental error (see Section 2.6), it was not viable to estimate the extent of error in the values of surface free energy evaluated in this work. However, the following interpretation of the results (see Table 2.1) may be presented:

(i) Due to the anomalous change in shape of the grooves on annealing (of width above 47 μm), the estimations of the change in shape was not accurate; and secondly, the theory used did not account for this anomalous change. This is reflected in the spurious value of surface energy (groove width above 47 μm) as seen in Table (2.1) and thus may be disregarded.

(ii) The annealing temperature of experiment H₁ (see Table 2.1) was rather low (as shown in Figure 2.12) and hence the thermal decay of the groove was very small (0.05 μm). This value is comparable with the experimental error that may be generated in the interferometric technique (0.02 μm) itself, and hence the results of this experiment may be exceptionally inaccurate.

(iii) From the above it is clear that only the values of surface free energy evaluated in experiments H₂ and H₃ below a groove width of 50 μm may be considered. As an exact temperature value of the annealing process cannot be specified in experiment 'H₃' (see Figure 2.12) the value of surface free energy has to be mainly interpreted from experiment 'H₂' and would suggest a value of approximately 121 mJm⁻² at 174°C. * It is * using WLF condition 'B' (see Table 2.1).
interesting to observe that the effective (annealing is minimal below 150°C) average annealing temperature of experiment H₃ (see Figure 2.12) is approximately 174°C and that the average surface free energy value obtained is 118 mJm⁻² (using WLF condition 'B') in experiment H₃.

(iv) On comparison of the results from experiments II₁*, II₂ and H₃ it is clear that a significant variation of the surface free energy value calculated with each experiment (groove width below 50µm) occurs only in H₃. The rates of heating in experiments II₁* and II₂ are clearly different from that of H₃ (see Figure 2.12) and would suggest this as the cause for the discrepancy in the surface free energy values evaluated.

Finally, it must be mentioned that the value of surface free energy estimated for PC in this work (approximately 121 mJm⁻² at 174°C, see Table 2.1) is much higher than the values found in the literature for PC (45 mJm⁻² at room temperature) and other polymers (19 to 45 mJm⁻² at room temperature) as seen in Table 2.2. There are several limitations of the surface free energy evaluated in this work, and are previously discussed; however, it is worth re-emphasising the following:

(a) The surface free energy values evaluated in this work are much higher than that seen in the literature.**

(b) The kinetics of the scratch decay data is not available and the results may not necessarily follow the analysis adopted in this work.

(c) The analysis of the multiple scratch decay is approximated

* Experiment 'II₁' may be disregarded due to the high degree of experimental error; discussed previously.
** See page 48 point (i).
for a single scratch situation.

(d) Crack widening is not observed.

(e) The errors in measurement of the glass transition temperature, temperature, viscosity, and the limitations of the WLF model incorporate errors in the evaluation of surface free energy.

Thermal degradation on annealing, the effect of the polishing reagent on the polymer and the frozen-in stresses incorporated on the mechanical rulling may affect the surface free energy values evaluated. Appendix 2.3(c) clearly indicates that effect of thermal degradation and the effect of the chemical polishing are minimal and thus may be discounted in this instance. The chemical polishing of the samples prior to annealing eliminates any frozen-in stresses (which may relax on annealing, a limitation frequently highlighted in the literature\(^{44}\); also see Section 2.2.2).

2.6 EXPERIMENTAL ERRORS

Basically, three types of errors are seen in the annealing technique; firstly, those due to the change in nature of the polymer on annealing, secondly the limitations in the techniques of temperature control and measurement. The third problem is that of the limitation in accuracy of estimating the viscosity of the sample (at the annealing temperature).

Precise temperature control (see Section 2.2.4.2(a)) in annealing was rather difficult, but, any change of temperature was taken into account using a numerical integration (see Section 2.3.2) in the final surface free energy calculations; and hence, the error involved, if any, would be relatively small. Temperature measurement was a formidable task and its inaccuracies were minimised by the
methods described in Section 2.2.4.2(b). However, measurement errors of ± 0.1°C were unavoidable. The errors were manifested as either (a) a continuous error (for example due to a zero error in the volt meter) or (b) a random error (e.g. generated due to random inductive loads). The latter case of a random error usually integrates to zero (or approximately to zero) over a period of time and hence is not serious, in contrast to a continuous error which is normally manifested as a large (significant) experimental error.

The estimation of the viscosity at the annealing temperature depends on (i) the accuracy of the viscosity measurement made at 223°C (see Appendix 2.3a); (ii) the extrapolation technique used based on the WLF equation (see Section 2.1.3); (iii) the extent of thermal degradation of the polymer at 223°C and (iv) the accuracy of measurement of the glass transition temperature.

The extent of thermal degradation of the polymer on annealing and at the temperature of viscosity measurement is minimal (see Appendix 2.3c) and hence, does not affect the surface free energy evaluation.

Although it would be desirable to estimate quantitatively the error in the value of the surface free energy evaluated, it was not possible to do so, due to the nature of the errors (as previously described). In practice it is possible to estimate the extent of maximum error in temperature measurement, but the actual average error would be much smaller (due to the fact that the spurious voltages generated by inductive loads are random; as explained in Section 2.2.4.2(b)) and will have no bearing on the maximum error.

Finally, on the interferometric technique the measurements made could result in an inaccuracy of approximately ± 0.02 μm, which indeed would be trivial compared with other experimental errors and the limitations of the annealing technique itself (discussed in Section 2.5).
A change in the chemical nature of the surface, during sample preparation, may also occur; this problem as well as the model on which the surface free energy calculations are based have been discussed in Section 2.5.

2.7 FURTHER WORK

The development of the thermal decay technique for the measurement of surface free energy has triggered off several interesting areas of further work and are as follows:

(i) The experiments may be repeated at various annealing temperature using a rate of heating comparable with experiments H\textsubscript{1} and H\textsubscript{2} (see Figure 2.12) in order to estimate surface free energies at various temperatures.

(ii) The question of the change in surface (chemically) on chemical polishing could be answered by the examination of a chemically polished polycarbonate surface using 'Electron Spectroscopy for Chemical Applications' (ESCA), a relatively new technique for the study of chemical structure and bonding in the surface regions of polymers\textsuperscript{(40,41)}.

(iii) The experiments may be conducted in a vacuum or alternatively in an inert gas atmosphere and thus (a) being able to minimise the extent of thermal degradation and (b) being able to assess the influence of adsorption of different gases on the polymer surface and hence their effects on the surface free energy values evaluated.

(iv) It would be possible to observe the effect of
anisotropy on the surface free energy value calculated, using samples of different surface anisotropy.

(v) Equation (2.17) may be rearranged so that the slope of a plot of $\log_{10}$ (decay rate) versus $\log_{10}$ (groove width, $\lambda$) may be obtained. If the slope is -1 then the transport phenomenon is confirmed to be viscous flow. (37, 38)

(vi) This method may be extended to other amorphous polymers.
APPENDIX 2.1

This appendix lists all computer programs used in this chapter, namely:

(a) SENERGY
(b) DATRST
(c) DATCAP
(d) DATLPT
(e) DATVDU

The development of these programs is discussed in Section 2.3.
55

10 PRINT "**ENERGY**"
11 REM
12 REM 'ENERGY' evaluates the surface free energy of
13 REM an amorphous polymer using a method of thermal
14 REM decay of surface profiles.
20 DIM F$(4) DIM T$ (42), C$ (4), D$ (8), C$ (3), D$ (3), D$ (8), R$ (30)
22 REM Lines 30-130 set the error jump and create and open
24 REM all the necessary files for use in subsequent parts
26 REM of the program.
30 F1"=, F3"=, F$, RST, 2
40 ERRSET 1160, XPY
50 INPUT 'FILE NAMES': F$
60 F4$=F$+F3$
70 CREATE F4$, 44
80 OFEN $3, F4$
90 OFEN $1, F$
100 READ e1, t$'
WRITE "3. D$
110 F2$=F4$+F1$
120 OFEN $2, F2$
130 READ "2,, $
140 REM Segment 140 to 490 is used to calibrate the
146 REM thermocouples using a PRT.
150 X'0\X1=0\X2=0\F=0
150 IF TYP(2)=0 OR TYP(2)=2 THEN 460
160 READ W2,T$
170 V4=VAL(T$(24.30))
172 REM Line 180 corrects any sign error of the thermocouple
174 REM output voltage if necessary.
180 IF SGN(D4)=-1 THEN D4=(D4*-1)
182 REM Line 190 divides the current resistance of the PRT
184 REM by the resistance of the PRT at a known temperature
186 REM and hence defines W2 as a reference.
190 W2=D4/247644
192 REM Lines 200-210 check the temperature of the oil bath
194 REM and indicates if it is not in the desired range.
200 IF W2<1.51 THEN 350
210 IF W2>=1.55 THEN 340
220 F'=F+1
222 REM Lines 230-330 calculate the temperature using
234 REM the PRT and its calibration constants.
230 IF W2<1.52 THEN 250
240 W1=2.6117*(W2-1.51)/.01+130.495
250 GOTO 360
260 IF W2<1.53 THEN 290
270 W1=2.6138*(W2-1.52)/.01+133.106
280 GOTO 360
290 IF W2<1.54 THEN 320
300 W1=2.6159*(W2-1.53)/.01+135.720
310 GOTO 360
320 W1=2.6180*(W2-1.54)/.01+138.336
330 GOTO 360
340 PRINT "Oil bath temperature above 140\C. ERRORS: GOT0 150"
350 PRINT "Oil bath temperature below 130\C. ERRORS: GOT0 150"
352 REM Lines 370-390 and 410-430 set the appropriate
354 REM thermocouple constants to convert voltage to
355 REM temperature difference between thermocouples
358 REM and the PRT.
360 D6=VAL(T$(36,42))\D1=VAL(T$(12,18))
370 IF SGN(D6)=1 THEN D6=(D6*-1)
380 IF D6>9999 THEN C=4000 ELSE C=40
390 IF D6<9999 THEN B=533000 ELSE B=533.10
400 A3=W1-(D6-B)/C
410 IF SGN(A3)=1 THEN A3=(A3*-1)
420 IF D1>9999 THEN C=4000 ELSE C=40
430 IF D1<9999 THEN B=533000 ELSE B=533н
440 A4=W1-(D1-B)/C
442 REM Lines 450-460 take the average of seven thermocouple
444 REM constants to give the mean constants A5 and A6 these
446 REM constants are used in all subsequent voltage to
448 REM temperature conversions.
540 \text{WRITE} $3, N, W
550 \text{V2}=\text{V1}10^((N(N1-N)/(P1N1-N)))
570 \text{PRINT} V2, V1 \text{GOTO} 600
560 \text{IF} D6(I)<W \text{THEN EXIT} 560
570 \text{IF} D6(I)<W \text{THEN} \text{IF} K=1 \text{THEN} 560
580 \text{IF} D6(I)<W \text{THEN} \text{EXIT} 560
590 \text{ REM Lines 820 calculates the inverse of the viscosity at }
600 \text{the appropriate temperature using the WLF equation.}
610 \text{R}(I) = (T(I+1)\text{-}T(I))/(\text{V2}\times10^(-M1(T(I)-N)/(P1T(I)-N)))
620 \text{IF} K+1 \text{THEN} \text{GOTO} 580
630 \text{NEXT} I
640 \text{REM Lines 850 executes a numerical integration using }
650 \text{Simpson's rule and lines 860-890 are the supporting }
660 \text{REM steps.}
670 R=\text{T(1)}\text{1/3}(T(I)-T(I))\text{1/3}(T(I)-T(I))
680 \text{IF} K=1 \text{THEN} \text{GOTO} 590
690 \text{NEXT} I
700 \text{REM Lines 900-1150 print the results of the calculations}
710 \text{REM on the computer terminal and builds a disk file with }
720 \text{REM extension RST of these results.}
730 \text{PRINT "Scan number",F(1)-1," and",F}
740 \text{WRITE 03,F(1)-1,F}
750 \text{FOR} P2=2 \text{TO} 3
760 \text{PRINT "\text{Scan number}1",F(P2)-T(I)6(I),"Channel1",C4(P2),"Channel2",C4(P2),"Channel3",C4(P2),"Temperature",T(I)6(P2)"}
770 \text{WRITE 03,T(I)6(P2),C4(P2),F(P2),C4(P2),F(P2)}
780 \text{PRINT "\text{Scan number}1",F(P2)-T(I)6(I),"Channel1",C4(P2),"Channel2",C4(P2),"Channel3",C4(P2),"Temperature",T(I)6(P2)"}
790 \text{WRITE 03,T(I)6(P2),C4(P2),F(P2),C4(P2),F(P2)}
57

960 WRITE #3, (F2), (C1(2)), (I1(F,1))
770 PRINT "NAME: "; (I1(2)); "LAB: "; (I1(2)); "CHANNEL: "; (I1(2)); "$A(S)"; "$B(S)"; "$C(S)"; "$D(S)"; "$E(S)"; "$F(S)"
980 WRITE #3, T(P2), C6(F2), T6(F2)
990 NEXT F2
1000 PRINT "Integral sum equals": S
1010 WRITE 13, S
1020 GOTO 570
1030 PRINT "Final value of integral sum is": S
1040 WRITE 13, S
1050 WRITE 13, S
1060 PRINT "Input number of times to lump:": A
1070 FOR I=1 TO A
1080 INPUT "Variables L, A1, A2, L": A1, A2
1090 E=P7/22*(LOG(A2)-LOG(A1))/G
1100 PRINT "Surface free energy equals": E; " ergs/cm^2!"
1110 PRINT "WAVELENGTH EQUALS": L; " CENTIMETERS!"
1120 WRITE 13, E, L
1130 NEXT I
1140 CLOSE 1
1150 END

1150 REM Lines 1160-1220 handle any errors that may occur.
1154 REM during program execution.
1156 IF Y=7 THEN 1180
1158 IF X=70 THEN 1190
1170 PRINT "FILE DOES NOT EXIST: GOTO 40"
1180 PRINT "FATAL ERROR IN LINE!": X
1190 DESTROY F4$
1200 PRINT "Previous result file destroyed!"
1210 ERRSET 1160+P+4
1220 GOTO 70

10 REM #DATAFST##
12 REM
14 REM Lines 70-190 read the data result file and
15 REM count the number of data items in that file.
16 REM for calculating the number of frames to print.
20 DIM F4(4), D$(30), F"0", F0, F1, F2=0
40 INPUT "Data file name: "; F$
50 F2+=4+F4+
60 ERRSET 8000+A+B
70 OPEN #1; F2
80 READ #1; D$
90 IF D=0 THEN 650
100 IF D=1 THEN 790
110 READ #1; I
120 IF I=100 THEN 150 REM End of data marker.
130 F=F4+1
140 GOTO 90
150 IF D=0 THEN 190
160 IF D=1 THEN 790
170 READ #1; I; F4+1
180 GOTO 150
190 CLOSE #1
192 REM Calculate the number of frames for print loop.
200 F=F4+4
210 K=INT(F/21)
220 J=INT(F/14)
230 OPEN #11; F2
240 READ #11; D$
242 REM Lines 250-390 print the frame results on a printer.
244 REM in formatted output. All headings are included here.
246 REM to save disk space. Lines 350-390 count the number
248 REM of frames per page up to 20.
250 F=F4+REM Page No.
260 PRINT 11
262 REM Line 270 prints the page header.
270 PRINT #11; TAB(12); "RESULT DATA FROM EXPERIMENT FILE "; F$
280 PRINT 11
290 IF D=0 THEN 650
100 IF G = 0 THEN GOTO 370
110 READ #1,N,W
120 PRINT #1,TAB(15),"Glass transition temperature:";N
130 PRINT #1,TAB(15),"Minimum temperature for starting integration:";W
140 READ #1,N2
150 PRINT #1,TAB(15),"Viscosity V2 equals:";N2;G=1
160 PRINT #1,GOTO 380
170 ! #1 \#1 \#1 ! #1 \#1 ! #1
180 FOR N=1 TO K
190 GOSUB 900
200 READ #1,F,F1
210 PRINT #1,TAB(15),"Scan number":F,"and":F1
220 FOR L=1 TO 2
230 GOSUB 900
240 READ #1,T,C,D
250 PRINT #1,TAB(15),"Time":T,TAB(31),"Noise level":D
260 FOR I=1 TO 2
270 GOSUB 900
280 READ #1,T,C,T1
290 PRINT #1,TAB(15),"Time":T,TAB(15),"Channel":C,TAB(47),"Temperature":T1
300 NEXT I
310 NEXT L
320 GOSUB 900
330 READ #1,S
340 PRINT #1,TAB(15),"Partial integral sum equals:";S
350 PRINT #1,TAB(15),"=0+1
360 IF 0=6 THEN EXIT 600
370 NEXT N
380 GOTO 610
390 REM Lines 600-630 decrement frame count and step the paper over to the next page.
400 PRINT#1\PRINT#1\PRINT#1\PRINT#1\PRINT#1\PRINT#1\=K-6\=0\GOTO 250
410 X=6-0
420 IF X>0 THEN GOSUB 830
430 GOTO 600
440 REM Lines 640-780 print final results to the printer.
450 GOSUB 900
460 READ #1,S
470 PRINT #1,TAB(15),"Final integral sum equals:";S
480 FOR M=1 TO J
490 GOSUB 900
500 PRINT S1
510 PRINT #1,TAB(15),"Surface free energy is wavelength loop:";M
520 READ #1,E,L,A1,A2
530 PRINT #1,TAB(15),"Surface free energy equals":E,"ergs/cm-2!1
540 PRINT #1,TAB(15),"Wavelength equals":L,"CENTIMETERS!1
550 PRINT #1,TAB(15),"Initial depth of crack":A1
560 PRINT #1,TAB(15),"Final depth of crack":A2
570 NEXT M
580 CLOSE #1\END
590 REM This subroutine moves the paper to the next page.
600 IF TYP(1)=0 THEN 780
610 IF TYP(1)=1 THEN 790
620 RETURN
630 REM This subroutine is for file type error checking.
640 IF TYP(1)=0 THEN 780
650 IF TYP(1)=1 THEN 790
660 RETURN
REM ***DATCAP***
10 DIM F$(4)
12 REM
14 REM Lines 30-50 set error jump and create file
16 REM on disk for the raw data.
20 INPUT *DATA FILENAME: *;F$
30 ERRSET 510;A,B
40 CREATE F$+40
50 OPEN #1,F$
60 INPUT *DATE: DAY MONTH YEAR.*;D$
70 WRITE #1,D$
80 IF INP(2)=83 THEN EXIT 180
90 FOR P=1 TO 25
 100 NEXT P
110 PRINT 'DO NOT TOUCH. EXPERIMENT IN PROGRESS.'
120 FOR I=1 TO 221
 130 INPUT I1, T$
 140 WRITE #1,TS
 150 IF INP(2)=83 THEN EXIT 270
 160 NEXT I
170 GOTO 190
180 PRINT *Data capture stopped with *"S" data readings:*
190 CLOSE #1,GOTO 270
200 PRINT 'Press key S: '
210 FOR I=1 TO 221
 220 FOR J=1 TO 500
  230 NEXT J
 240 PRINT CHR$(7).
 250 NEXT I
260 GOTO 210
270 FILL 10776.1
272 REM Lines 280-310 set up a disk file with extension .DS
274 REM for the calibration readings.
280 IF INP(2)=83 THEN EXIT 420
290 FOR I=1 TO 1000000
 300 NEXT I
320 PRINT 'Data capture stopped with *"S" data readings:*
330 CLOSE #1,GOTO 540
340 IF INP(2)=83 THEN EXIT 540
370 PRINT 'Press key S: '
380 FOR I=1 TO 1000000
 390 NEXT I
400 PRINT 'DO NOT TOUCH. EXPERIMENT IN PROGRESS.'
410 FOR I=1 TO 1000000
 420 NEXT I
430 PRINT 'FILE ALREADY EXISTS: *"S" data readings:*
440 CLOSE #1,GOTO 270
450 IF INP(2)=83 THEN EXIT 540
480 PRINT *Data capture stopped with *"S" data readings:*
490 NEXT I
520 PRINT 'DATA FILE ALREADY EXISTS: *"S" data readings:*
530 CLOSE #1,GOTO 540
540 END
10 REM ***DATNLPT***
12 REM Print raw captured data from disk to a printer.
14 REM Print raw captured data from disk to a printer.
16 REM Print raw captured data from disk to a printer.
20 DIM F$(8), T$(42), D$(30)
30 INPUT *DATA FILENAME: *F$
40 OPEN #1; F$
50 READ #1; D$
60 PRINT #1; TAB(20); *DATA TABLE FROM EXPERIMENT *F$,* ON *D$
70 FOR I=1 TO 22
80 IF TYP(1)=0 OR TYP(1)=2 THEN EXIT 120
90 READ #1; T$
100 PRINT #1, T$
110 PRINT #1; GOTO 60
120 CLOSE #1; END
10 REM ***DATNLPT***
12 REM Print raw captured data from disk to a printer.
14 REM Print raw captured data from disk to a printer.
16 REM Print raw captured data from disk to a printer.
20 DIM F$(8), T$(42), D$(30)
30 INPUT *DATA FILENAME: *F$
40 OPEN #1; F$
50 READ #1; D$
60 PRINT #1;
70 FOR I=1 TO 60
80 IF TYP(1)=0 OR TYP(1)=2 THEN EXIT 150
90 READ #1; T$
100 PRINT #1, T$
110 PRINT #1; GOTO 60
120 CLOSE #1; END
130 NEXT I
140 PRINT #1; GOTO 60
150 CLOSE #1; END
APPENDIX 2.2

EQUIPMENT USED FOR TEMPERATURE CONTROL, MEASUREMENT, ANALYSIS AND RECORDING

(a) Thermocouples:
Two types of thermocouples, manufactured by BICC\(^{(3)}\) were used and their details are as follows:

i) Type KSK2B10 is a nickel/chromium-nickel/aluminium thermocouple with a 1 mm diameter sheath (of Ti stabilised stainless steel) and a type IJ insulated hot junction with an 8 mm iso crimp-on seal.\(^{(3)}\)

ii) Type KSK4B20 consists of two independent nickel/chromium-nickel/aluminium thermocouples in a 2 mm diameter sheath (of Ti stabilised stainless steel) and an IJ type, separately insulated hot junction with an 8 mm iso crimp-on seal.\(^{(3)}\)

(b) Platinum Resistance Thermometer (PRT):
A type S1875A PRT manufactured by 'Tinsley' with a reproducibility of ± 0.001°C\(^{(14)}\) and calibrated (Class I) by the National Physical Laboratories (NPL)\(^{(8)}\) was used.

(c) Thermocouple Reference Chamber:
An 'ICELL MkII' 0°C Thermocouple reference chamber (with a ten channel marshalling system for Chromel-Alumel thermocouples) with a stability of ± 0.03°C at 0°C was
used as the reference cold junction of the thermocouples. (The circuit I of the marshalling system was used in this instance). (15)

(d) Temperature Controller and Thyristor:
A Eurotherm type (090-002-97-151-02-04-61-00) temperature controller (5) with an input millivolt range of 6 to 9.999 with standard Integral and Differential switching times was used in conjunction with a phase angle pulse thyristor type (031-080-06-42-00). (6)

(e) Chart Recorder:
An Oxford 3000 series (type FR2 HS with channel modules K927, S-381 and S-382) two channel chart recorder (16) was used as a back-up measurement instrument.

(f) Constant Temperature Oil Bath:
A "Thermomix-1480" type oil bath with very accurate temperature control (up to ± 0.05°C) supplied by F.T. Scientific Instruments Ltd (17) was used for calibration of the thermocouples against the PRT.

(g) The data logging system:
The basic system consisted of a 'Solartron' Analog Scanner, a data logger and a Digital Voltmeter (DVM) and are each described in detail below, while the output peripheral of the system is as in Section (h) of this Appendix.
An Analogue Series 3 Scanner (18,19) (which is basically an electronically controlled switch used to connect
several analogue signals to a common point) was used in conjunction with a 'Compact-33' data logger, (18,20) The Compact 33 was responsible for the selection of a particular analogue signal at pre-programmed time intervals; then digitalising the signal using the 7065 Solartron Microprocessor multimeter(18,21) and sending an appropriate signal in 'ASCI II' to the output peripheral. It should be mentioned that the Compact 33 was modified so that it could be programmed to make alternate measurements of voltage and resistance for the purpose of thermocouple calibration against the PRT.

(h) The Output Peripheral:
A 'Horizon, North Star' micro computer system with a 32k RAM and a dual floppy disk system(22) was used as the output peripheral.

(i) The Analysis and Recording of the data:
This was done by using the computer described in section (h) of this Appendix, in conjunction with (i) a Newbury CRT display terminal with a keyboard, (ii) a Decwriter, as a printer.
APPENDIX 2.3

SUPPLEMENTARY EXPERIMENTS

(a) **Viscosity Measurements**

The viscosity of polycarbonate was measured using a cone and plate viscometer (rheogoniometer) at the lowest possible temperature and the various shear rates. The apparent viscosity was calculated using the formula:

\[
\mu = \frac{t \alpha \Delta_T k_T}{94.25 d^3}
\]  

(2.25)

where

- \( t \) = seconds per revolution
- \( \alpha \) = cone angle (4°.8')
- \( \Delta_T \) = movement of transducer head
- \( k_T \) = torsion bar constant in dyne cm per thousandth of an inch movement of the transducer (5.7464 x 10^5)
- \( d \) = diameter of platens (2.5 cm)

Table (2.3) shows the variation of viscosity with shear rate at 223°C calculated using equation (2.25).
### Viscosity Measurements at 223°C

<table>
<thead>
<tr>
<th>Shear Rate (rev/sec)</th>
<th>Viscosity (μ) (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.98 x 10^-4</td>
<td>1.22 x 10^5*</td>
</tr>
<tr>
<td>6.25 x 10^-4</td>
<td>1.416 x 10^5</td>
</tr>
<tr>
<td>1.98 x 10^-3</td>
<td>1.466 x 10^5</td>
</tr>
<tr>
<td>6.25 x 10^-3</td>
<td>1.236 x 10^5</td>
</tr>
<tr>
<td>1.98 x 10^-3</td>
<td>1.141 x 10^5</td>
</tr>
</tbody>
</table>

Table (2.3)

To minimise thermal degradation viscosity measurement at the lowest possible temperature (223°C) was made and also as the measured viscosity is a function of the shear rate, the lowest shear rate (6.25 x 10^-4 rev/sec) which gave a reliable (steady) viscosity value of 1.42 x 10^5 poise (at 223°C) was used in the calculations of the surface energy (see Section 2.4).

The calculated viscosity value is comparable to that in the literature - of approximately 10^5 poise at 245°C (viscosity average molecular weight of 33,000). (45)

* The viscosity of 1.22 x 10^5 poise, at a shear rate of 1.98 x 10^-4 rev/sec was found to be too low (at 223°C) to obtain a steady reading and the measurement was not accurate probably due to slipping of platens on the polymer.
(b) Measurement of the Glass Transition Temperature (Tg)

The Tg of PC was measured using Differential Scanning Calorimetry (DSC) and the instrument used was a Perkin Elmer DSC-2. As the measured value of Tg will be dependent on the rate of heating (cooling) \(^{(71)}\), measurements at different rates conducted \(^{(13)}\) are as in Table (2.4). The Tg values in this table are those corrected using indium melting points. The definition of Tg is as in Figure (2.13). The rate of heating of 1.25° per min, (comparable to the heating rate in annealing experiments \(H_1, H_2\); see section 2.4), which gave a Tg of 140.5°C was chosen to be used in the WLF equation in Section 2.3.2. However, a Tg value of 149°C is reported in the literature \(^{(45,46)}\) and this discrepancy may be attributed to method, as well as the conditions of the method \(^{(71)}\), especially the rate of heating or cooling.

**MEASUREMENTS OF Tg AT VARIOUS HEATING/COOLING RATES**

<table>
<thead>
<tr>
<th>Rate of heating °C/min</th>
<th>Rate of cooling °C/min</th>
<th>Tg °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
<td>145</td>
</tr>
<tr>
<td>1.25</td>
<td></td>
<td>140.5</td>
</tr>
<tr>
<td>20*</td>
<td></td>
<td>146</td>
</tr>
</tbody>
</table>

* Sample first heated above Tg, cooled and reheated at 20°C/min.
(c) Degradation of Polycarbonate

Thermal Degradation

Two sets of experiments were conducted in order to assess the extent of thermal degradation in the annealing process. In the first experiment a set of samples were heated* to 196°C and held at that temperature for different lengths of time; in the second experiment the samples were held at various temperatures for half an hour (in each case). The samples were finally characterised by Gel permeation chromatography (GPC) using a Waters Associated Model 200. Four styragel columns of pore size between 700Å and 5 x 10^7 Å were used. The solvent was tetrahydrofuran; the concentration and flow rates were 0.2% (weight) and 1 ml/min, respectively. The chromatograms are analysed by drawing a base line and measuring the height of distribution at ml. intervals. The calibration of the chromatograms were derived from polystyrene standards and 'Mark-Houwink' constants were used for this conversion. In the formula \( \eta = KM^n \); \( \eta \) is the viscosity, \( M \) molecular weight, \( K \) and \( n \) 'Mark-Houwink' constants. \( K \) and \( n \) values used for polystyrene were taken as 0.120 x 10^{-3} and 0.710 respectively and for PC, 0.399 x 10^{-3} and 0.770 respectively.

The weight average molecular weight, \( \bar{M}_w \), and the number average molecular weight, \( \bar{M}_n \), were calculated as according to the equations given below:

\[
\bar{M}_w = \frac{\sum W_i M_i}{\sum W_i} \tag{2.26}
\]

\[
\bar{M}_n = \frac{\sum W_i}{\sum \frac{W_i}{M_i}} \tag{2.27}
\]

Table (2.5) summarises these results and the corresponding chromatograms are in Figures (2.14) to (2.26) and the calibration is in Figure (2.29).

* The heating was conducted in the experimental set up (for annealing) described in Section 2.2.4.
<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Time (hours)</th>
<th>Temperature °C</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_z$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
<th>$\bar{M}_z/\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.14</td>
<td>Unheated Sample</td>
<td></td>
<td>9,100</td>
<td>24,900</td>
<td>41,500</td>
<td>2.7</td>
<td>4.6</td>
</tr>
<tr>
<td>2.15</td>
<td>1.5</td>
<td>196</td>
<td>11,600</td>
<td>26,600</td>
<td>43,300</td>
<td>2.3</td>
<td>3.7</td>
</tr>
<tr>
<td>2.16</td>
<td>3.5</td>
<td>196</td>
<td>10,200</td>
<td>25,300</td>
<td>42,000</td>
<td>2.5</td>
<td>4.1</td>
</tr>
<tr>
<td>2.17</td>
<td>9.3</td>
<td>196</td>
<td>11,500</td>
<td>24,100</td>
<td>38,100</td>
<td>2.1</td>
<td>3.3</td>
</tr>
<tr>
<td>2.18</td>
<td>18</td>
<td>196</td>
<td>10,000</td>
<td>24,200</td>
<td>45,500</td>
<td>2.4</td>
<td>4.6</td>
</tr>
<tr>
<td>2.19</td>
<td>74</td>
<td>196</td>
<td>10,400</td>
<td>24,700</td>
<td>48,300</td>
<td>2.5</td>
<td>4.6</td>
</tr>
<tr>
<td>2.20</td>
<td>0.5</td>
<td>141</td>
<td>10,500</td>
<td>24,600</td>
<td>41,700</td>
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<td>4.0</td>
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<td>151</td>
<td>10,900</td>
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<td>161</td>
<td>11,200</td>
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<td>25,600</td>
<td>43,100</td>
<td>2.3</td>
<td>3.8</td>
</tr>
</tbody>
</table>

**TABLE (2.5)**

*GPC Analysis of Annealed Polycarbonate*
Kovarskaya et al\(^{(72,73,74)}\) have observed that below 240\(^\circ\)C thermo-
oxidative process of PC is insignificant and Davis and Golden\(^{(43)}\)
have reported that PC has a high thermal stability below 250\(^\circ\)C.
Kovarskaya\(^{(72)}\) has shown that thermal degradation can lead to chain
scission of the polymer. This was confirmed by a study of the
breakdown of the polymer in a sealed evacuated system\(^{(53)}\), but only
above 206\(^\circ\)C, while Bartosiewicz and Booth\(^{(42)}\) have reported that PC
film can undergo condensation and branching on annealing for several
hours at 200\(^\circ\)C under continuous evacuation.

Within experimental error of the GPC technique* no
significant change in \(\bar{M}_n, \bar{M}_w\) or \(\bar{M}_z/\bar{M}_n\) values are observed (see Table
2.5) and hence, degradation of PC is unlikely at 196\(^\circ\)C up to three
days. This is of course consistent with what might be expected from
the previously reviewed literature.

(ii) Chemical Degradation

A sample of PC 1mm thick, were chemically polished down to
0.16mm using a 5.8N KOH solution in 'Analar' Methanol. The polishing
technique is discussed in Section 3.2.4. The samples were then
characterised as indicated in Section (i) of this Appendix (the
chromatograms* are shown in Figures (2.27) and (2.28)) and its results
are as in Table (2.6).

As in the case of thermal degradation the results show no
degradation within the experimental error of the results.

\[\begin{array}{cccccc}
\text{Fig. No.} & \text{Sample Condition} & \bar{M}_n & \bar{M}_w & \bar{M}_z & \bar{M}_w/\bar{M}_n & \bar{M}_z/\bar{M}_n \\
4.27 & \text{Unpolished Sample} & 7,600 & 21,200 & 37,400 & 2.8 & 4.9 \\
4.28 & \text{Sample polished down to 0.16mm of thickness} & 7,300 & 23,200 & 50,800 & 3.2 & 7.0 \\
\end{array}\]

\text{TABLE (2.6)}

\text{GPC ANALYSIS OF CHEMICALLY POLISHED POLYCARBONATE}

* One of the major errors that occur in the GPC analysis is the problem
of drawing a suitable base line on which the chromatogram heights
depend, and hence the analysis.

** The calibration is in Figure (2.30).
REFERENCES


3. Publication No.779 JHL/SM/476 BICC Pyrotenex Limited, P.O.Box 1, Prescot, Merseyside, L34 552.


5. Eurotherm Bulletin 090D-2- Feb. 1974; 090W (Nov. 1974); Eurotherm Ltd., Worthing, Sussex, UK.


8. Class I calibration (reference number 120180) of type 5187 SA platinum resistance thermometer (identification number 231994) by the National Physical Laboratories (NPL) Teddington, Middlesex, England.


12. Private communication; A. Lovett, Department of Chemistry, Aston University, Gosta Green, Birmingham, UK.

13. Private communication; G.J. Howard, Department of Polymer and Fibre Science, UMIST, Manchester, M60 1QD.


Private communication; J. McConville, RAPRA, Shawbury, Shrewsbury, UK.


See reference 24, page 579.


64. E. Wolfram, Kolloid Z., 182, 75, 1962.
Before annealing

After annealing

Figure (2.1a) A typical set of interferograms of a single scratch groove (wave length 106 \( \mu \text{m} \)) obtained before and after annealing as in experiment 'H_2'.
Figure (2.1b) Typical sets of interferograms of single scratch grooves (wave length 70 \( \mu \text{m} \) and 47 \( \mu \text{m} \)) before and after annealing as in experiment 'H\textsubscript{2}'.
Figure (2.2)  A heating chamber used in conjunction with the second annealing rig.
(A - sample chamber, B - cavities for thermocouples).
Figure (2.3)  A heating chamber used in conjunction with the second annealing rig
(A - sample chamber, B - cavities for thermocouples, C - heating chamber lid)
The apparatus used for annealing PC (in an atmosphere of a desired gas or in a vacuum)

Figure 2.4
Figure (2.6) The final annealing rig (A - chart recorder, B - furnace and oil bath*, C - the 'PRT', D - temperature controller and thyristor, E - cold cell, F - the 'DVM', G - the data logger, H - the scanner, I - the computer, J - the thermocouples)
VIEW SHOWING CENTRAL CAVITY

CROSS SECTION OF HEATING CHAMBER

FIG (2:7)
Figure (2.9) Oil bath and furnace used in the final annealing.

A - furnace, B - oil bath, C - the 'PRT', D - the thermocouples.
Figure 2.10

Graphs showing temperature over time, with set values and steady deviations.
Figure 2.11 A sinusoidal surface profile described by the equation
\[ z = a \sin (\omega x) \]
Temperature Increase (or Decrease in the Cooling Schedule)

Figure 2.13 MEASUREMENT OF THE GLASS TRANSITION TEMPERATURE (Tg) USING DSC.
Figure (2.14)

Arbitrary Scale (v)

Elution Volume (ml)

50, 58, 66
Figure (2.21)
Figure (2.22)
Figure (2.23)
Figure (2.26)
Figure (2.27)

Elution Volume (ml)
Elution Volume (ml)

Figure (2.28)
Figure 2.9: Graph for chromatograms 2.14 to 2.26.
CALIBRATION GRAPH FOR CHROMATOGRAMS (SEC. TO SEC.)

FIGURE (2.30)

ELUTION VOLUME

Log (Polymer Molecular Weight)

0
1
2
3
4
5
6
7
CHAPTER III

CHEMICAL POLISHING, ETCHING AND THINNING OF POLYCARBONATE

3.1 THE THEORY OF CHEMICAL POLISHING

The theory of chemical polishing used by Lewis and Ward\(^9\) which is dependent on the presence of a viscous boundary layer is an adaptation of an electropolishing analysis developed by Wagner.\(^1\) The polishing action at the solid/fluid interface is analysed in terms of a concentration gradient of the attacking nucleophile in the viscous boundary layer. If it assumed that the rate of removal of solid is proportional to the concentration of the nucleophile, then the peaks in the surface are exposed to a higher rate of attack than the depressions, provided the boundary layer is much thicker than the surface roughness (see Figure 1.6). Consider a sine-wave profile surface of wave length 'a' and amplitude 'b'! Under steady state conditions the relevant diffusion equation is

\[
\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) = 0
\]  \hspace{1cm} (2.1)

where \(D\) is the diffusion coefficient.

- \(c\) is the concentration of the nucleophile
- \(x, y\) the coordinates parallel and perpendicular to the surface respectively.

A particular solution of (2.1) is

\[
c(x, y) = B[y - b \exp(-2\pi y/a) \sin(2\pi x/a)]
\]  \hspace{1cm} (2.2)
where $B$ is a constant and $a \gg b$.

Differentiating with respect to $y$ and evaluating $\frac{\partial C}{\partial y}$ at the surface $y = b \sin \left(\frac{2\pi x}{a}\right)$ gives

$$\left(\frac{\partial C}{\partial y}\right)_{y=b \sin \left(\frac{2\pi x}{a}\right)} = \left(\frac{\partial C}{\partial y}\right)_{av} \left[1 + \left(\frac{2\pi b}{a}\right) \sin \left(\frac{2\pi x}{a}\right)\right]$$  \hspace{1cm} (3.3)

if $a \gg b$ and $\delta \gg a$

where $\left(\frac{\partial C}{\partial y}\right)_{av}$ is the average value of the concentration gradient at the surface. If $y \gg a$, the concentration is constant and it is possible to define the boundary layer, $\delta$, in terms of the change in concentration gradient.

The change in shape of the surface as a function of time may be considered in terms of a reference plane within the solid parallel to the surface

$$S = S_{av} + \eta$$  \hspace{1cm} (3.4)

where $\eta = b \sin \left(\frac{2\pi x}{a}\right)$ and $S$ is the distance of the reference plane from the surface. Change of $S$ with time is proportional to the concentration gradient given by equation (3.3). Hence

$$- \frac{ds}{dt} = - \left(\frac{dS_{av}}{dt}\right) \left[1 + \left(\frac{2\pi b}{a}\right) \sin \left(\frac{2\pi x}{a}\right)\right]$$  \hspace{1cm} (3.5)

from equations (3.5) and (3.4) we have

$$- \frac{dn}{dt} = - \left(\frac{dS_{av}}{dt}\right) \left(\frac{2\pi b}{a}\right) \sin \left(\frac{2\pi x}{a}\right)$$  \hspace{1cm} (3.6)

since $\frac{dn}{dt} = \left(\frac{db}{dt}\right) \sin \left(\frac{2\pi x}{a}\right)$ and the change of $S_{av}$ with time is just the rate of thinning $\frac{du}{dt}$, then equation (3.6) becomes $- \frac{db}{du} = \frac{2\pi b}{a}$ and on integration we have

$$\sin \left(\frac{b_0}{b}\right) = \frac{2\pi u}{a}$$  \hspace{1cm} (3.7)

where $b_0$ is the initial amplitude and $b$ the amplitude at time $t$.

Identifying 'a' with crack width and 'b' with crack depth, $u$ can
3.2.2 Preparation of the polishing and etching solution

'Analar' potassium hydroxide pellets were purified by washing with distilled water followed by 'Analar' methanol. The pellets were then dissolved in a 5 litre flask using the minimum amount of methanol. The highly viscous reagent was stored under a blanket of dry nitrogen to prevent absorption of water and carbon dioxide.

The normality of the reagent was determined by titration with 0.1 N hydrochloric acid using phenolphthalein as an indicator. Reagent of required normality was obtained by dilution with 'Analar' methanol and checking its normality by titration.

3.2.3 Interferometry

The amplitude of the profiles of the samples were monitored by obtaining interferograms.\(^{(4,5,6)}\) A Reichert Zetopan research microscope fitted with a Watsons 8 mm interference objective was used for this purpose (see Figure 3.2). A sodium lamp was the source of monochromatic light (of wave length \(589 \times 10^{-9} \text{ m}\)). Kodak tri-X pan 400 ASA film (exposure time six seconds) was used for recording the interference patterns.

3.2.4 The Etching and Polishing Procedure

All samples were washed in distilled water, then in 'Analar' methanol and finally dried in air. 25 cc of the polishing solution was thermostated in a water bath to the required temperature before introducing the sample. The samples were either held vertically (so that the surface containing the grooves were vertical) using forceps or were placed at the bottom of the vessel so that the surface of sample containing the grooves were in a horizontal plane (see Figure 3.12).
The temperature of the system was monitored by chromel-alumel thermocouple attached to a data-logging system described in Chapter 2. The tip of the thermocouple was placed as close as possible to grooves, and was assumed to measure the temperature of viscous layer. Interferograms of the grooves were obtained before and after each experiment as explained in Section 3.2.3.

3.2.5 Method of Sampling and Analysis of the Viscous Layer

Initially the viscous layer was allowed to build up to its maximum height by polishing a piece of polycarbonate in the horizontal position (see Figure 3.12) for a period in excess of 30 minutes in methanolic KOH (5.8 N) at 20°C.

A simple microscope modified to contain a syringe instead of the optical system (see Figure 3.3) was used to sample the viscous layer. The x-y movement of the sample was done by the microscope stage and the vertical (z) movement, by the main body of the microscope. The viscous layer was syringed at a height of about 1 mm above the sample (the height of the viscous layer being about 3 to 4 mm).

A 25 mm syringe with a gauge '12' stainless steel needle was used for this experiment. A known quantity of 5 N HCl was initially used in the syringe to retard the reaction in the viscous layer at the point of syringeing.

The substance in the syringe was transferred to a titration flask immediately after syringeing and was neutralised to completion using dilute HCl. The polycarbonate was extracted using tetrahydrofuran (THF) and finally the solid was obtained by evaporation of the THF at room temperature (to avoid any degradation of the polycarbonate) in a fume cupboard. The polymer was then analysed using Gel Permeation Chromatography (GPC). (8)
3.3 RESULTS

3.3.1 The Polishing, Etching and Thinning Results

The groove depth (d) of all samples was calculated using the formula \( d = n \frac{\lambda}{2} \), where \( n \) is the number of fringes from the planar surface to the root of the groove. The fringe number \( n \) was measured from enlarged prints taken from the original negatives. However, when \( d \) was above 7 μm (in the case of the 200 and 150 μm width grooves), the direct measurement of \( n \) was not possible due to the limitation of the interferometric technique; and hence, \( n \) had to be estimated by extrapolation of the slope of the fringes of the corresponding groove. This was based on the assumption that the slope of the groove was uniform, which indeed is justified by its method of preparation (see Section 3.2.1). Figure (3.8) shows a typical set of interferograms.

Three sets of experiments were conducted as detailed in Table (3.1) and their calculation (using equations 3.7 and 3.8) are given in Tables (3.2) to (3.4). An additional thinning experiment conducted is shown in Table (3.5).

The density \( \rho \) of the samples was measured to be 1.20 g cm\(^{-3}\) (this value compares very well with that found in the literature\(^{(7)}\)) and this value was used in all calculations. Graphs \( \ln \left( \frac{b_0}{b} \right) \) versus \( \nu' \) were drawn for each set of experiments. Figures (3.4) and (3.5) show the behaviour of polishing (etching) at two different temperatures for six different crack widths. Figure (3.6) shows the effect of the vertical and horizontal positions of the sample (see Figure 3.12), on polishing and etching; while, Figure (3.7) compares thinning \( \nu \) for all three sets of experiments. A set of 45 μm and 105 μm wide grooves (both single and multiple) ruled on a single sample and polished at 29.5°C in a 5.8 N methanolic KOH solution for 10 mins (sample held vertically; see Figure 3.12) indicated no significant difference between the
<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>See Table No.</th>
<th>See Figure No.</th>
<th>KOH Concentration</th>
<th>Temperature (°C)</th>
<th>Position of Groove</th>
<th>Groove Width in µm</th>
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<tr>
<td>1</td>
<td>3.2</td>
<td>3.4</td>
<td>5.8 N</td>
<td>20 ± 0.5</td>
<td>Vertical</td>
<td>25, 45, 70, 105, 150, 200</td>
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<td>2</td>
<td>3.3</td>
<td>3.5</td>
<td>5.8 N</td>
<td>29.5 ± 0.5</td>
<td>Vertical</td>
<td>25, 45, 70, 105, 150, 200</td>
</tr>
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<td>3.4</td>
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<td>5.8 N</td>
<td>20 ± 0.5</td>
<td>Horizontal</td>
<td>45</td>
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</table>

**TABLE (3.1) POLISHING, ETCHING AND THINNING EXPERIMENTS**

* see Figure (3.12)
<table>
<thead>
<tr>
<th>Time (t) (min)</th>
<th>u (µm)</th>
<th>b₀ (µm)</th>
<th>b (µm)</th>
<th>logₑ(b₀/b)</th>
<th>b₀ (µm)</th>
<th>b (µm)</th>
<th>logₑ(b₀/b)</th>
<th>b₀ (µm)</th>
<th>b (µm)</th>
<th>logₑ(b₀/b)</th>
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<td>0.03</td>
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<td>5.19</td>
<td>5.81</td>
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<td>7.57</td>
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<td>-0.06</td>
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<tr>
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<td>60.9</td>
<td>12.26</td>
<td>8.08</td>
<td>0.42</td>
<td>8.91</td>
<td>5.64</td>
<td>0.46</td>
<td>5.81</td>
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<td>0.58</td>
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<td>20</td>
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<td>1.41</td>
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<table>
<thead>
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<th>Time (t) (min)</th>
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<th>b₀ (µm)</th>
<th>b (µm)</th>
<th>logₑ(b₀/b)</th>
<th>b₀ (µm)</th>
<th>b (µm)</th>
<th>logₑ(b₀/b)</th>
<th>b₀ (µm)</th>
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<td>0.95</td>
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<td>0.74</td>
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<td>0.79</td>
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<tr>
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<td>102.9</td>
<td>3.31</td>
<td>0.66</td>
<td>1.61</td>
<td>2.28</td>
<td>0.36</td>
<td>1.81</td>
<td>1.02</td>
<td>0.13</td>
<td>2.06</td>
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**TABLE (3.2)**

POLISHING (ETCHING) RESULTS AT 20°C
FOR THE VERTICAL POSITION*

* See Figure (3.12)
<table>
<thead>
<tr>
<th>Time (t) (min)</th>
<th>u (µm)</th>
<th>( b_0 ) (µm)</th>
<th>b (µm)</th>
<th>( \log_e(b_0/b) )</th>
<th>( b_0 ) (µm)</th>
<th>b (µm)</th>
<th>( \log_e(b_0/b) )</th>
<th>( b_0 ) (µm)</th>
<th>b (µm)</th>
<th>( \log_e(b_0/b) )</th>
</tr>
</thead>
<tbody>
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<td>9.97</td>
<td>10.99</td>
<td>-0.10</td>
<td>6.43</td>
<td>7.90</td>
<td>-0.21</td>
<td>4.34</td>
<td>5.74</td>
<td>-0.28</td>
</tr>
<tr>
<td>2.0</td>
<td>39.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.89</td>
<td>5.57</td>
<td>0.06</td>
<td>4.69</td>
<td>4.44</td>
<td>0.05</td>
</tr>
<tr>
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<td>64.2</td>
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<td>5.76</td>
<td>3.51</td>
<td>0.50</td>
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<td>81.0</td>
<td>9.99</td>
<td>6.26</td>
<td>0.56</td>
<td>5.57</td>
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<td>1.08</td>
<td>8.34</td>
<td>2.56</td>
<td>1.18</td>
<td>4.37</td>
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<table>
<thead>
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<th>Time (t) (min)</th>
<th>u (µm)</th>
<th>( b_0 ) (µm)</th>
<th>b (µm)</th>
<th>( \log_e(b_0/b) )</th>
<th>( b_0 ) (µm)</th>
<th>b (µm)</th>
<th>( \log_e(b_0/b) )</th>
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<th>b (µm)</th>
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</tr>
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</tr>
<tr>
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<td>2.12</td>
<td>0.47</td>
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<tr>
<td>8.0</td>
<td>81.0</td>
<td>2.91</td>
<td>1.32</td>
<td>0.95</td>
<td>2.20</td>
<td>0.88</td>
<td>0.91</td>
<td>0.76</td>
<td>0.29</td>
<td>1.26</td>
</tr>
<tr>
<td>10.0</td>
<td>101.0</td>
<td>2.83</td>
<td>0.62</td>
<td>1.52</td>
<td>1.69</td>
<td>0.34</td>
<td>1.60*</td>
<td>0.92</td>
<td>0.13</td>
<td>1.95</td>
</tr>
</tbody>
</table>

**Table (3.3)**

Polishing (etching) results at 29.5°C for the vertical position**

* Results true for both single and multiple grooves

** See Figure (3.12)
### TABLE (3.4) POLISHING (ETCHING) RESULTS

AT 20°C FOR THE HORIZONTAL POSITION*

<table>
<thead>
<tr>
<th>Time (t) (min)</th>
<th>u (µm)</th>
<th>b₀ (µm)</th>
<th>b (µm)</th>
<th>logₑ(b₀/b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.8</td>
<td>1.25</td>
<td>1.14</td>
<td>0.09</td>
</tr>
<tr>
<td>2</td>
<td>25.1</td>
<td>1.32</td>
<td>1.10</td>
<td>0.17</td>
</tr>
<tr>
<td>4</td>
<td>30.6</td>
<td>1.16</td>
<td>0.78</td>
<td>0.40</td>
</tr>
<tr>
<td>6</td>
<td>44.9</td>
<td>1.11</td>
<td>0.48</td>
<td>0.84</td>
</tr>
<tr>
<td>10</td>
<td>70.5</td>
<td>1.37</td>
<td>0.38</td>
<td>1.28</td>
</tr>
</tbody>
</table>

* see Figure 3.12
<table>
<thead>
<tr>
<th>T°C</th>
<th>$\frac{1}{T} \times 10^{-3}$ (k)$^{-1}$</th>
<th>'u' in μm for 10 min</th>
<th>$\frac{du}{dt}$ μm s$^{-1}$</th>
<th>$ln \left( \frac{du}{dt} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.534</td>
<td>46.7</td>
<td>0.078</td>
<td>-2.553</td>
</tr>
<tr>
<td>20</td>
<td>3.413</td>
<td>68.0*</td>
<td>0.113</td>
<td>-2.177</td>
</tr>
<tr>
<td>25</td>
<td>3.356</td>
<td>83.7</td>
<td>0.140</td>
<td>-1.970</td>
</tr>
<tr>
<td>29.5</td>
<td>3.305</td>
<td>102.0*</td>
<td>0.170</td>
<td>-1.772</td>
</tr>
<tr>
<td>35</td>
<td>3.25</td>
<td>111.7</td>
<td>0.186</td>
<td>-1.681</td>
</tr>
<tr>
<td>15**</td>
<td>3.47</td>
<td>57</td>
<td>0.095</td>
<td>-2.354</td>
</tr>
</tbody>
</table>

**TABLE (3.5)**

VARIATION OF THINNING WITH TEMPERATURE FOR PC***

* The values obtained from graphs in Figure (3.7)

** The value obtained from the results of Lewis and Ward(9)

*** The experiment was conducted in the vertical position; see Figure (3.12)
polishing results of the single and the multiple scratches (see Table 3.3).

3.3.2 The Viscous Layer Analysis

The viscous layer was analysed by GPC. Figure (3.13) shows the chromatograms obtained on a high porosity column set while Figures (3.14) and (3.15) show those obtained on low porosity column sets. The conditions of this analysis are as in the chromatograms. The polishing time of this experiment was 45 minutes.

A polymer tail ranging from 5,500 to 330* can be seen on the high porosity column set in Figure (3.13), while on the low porosity column sets (Figures 3.14 and 3.15) the polymer tail is more spread out and is difficult to detect. The ultraviolet detector used in both low and high porosity column sets did not show any UV absorption in the expected range for PC(8). The experiment was repeated on different polishing times (60 and 75 minutes) on the high porosity column set but no effective change in the chromatograms was observed.

3.4 DISCUSSION

3.4.1 Introduction

\[ \ln \left( \frac{b_0}{b} \right) = \frac{2\pi u}{a} \]  
(3.7)

Equation (3.7) predicts a constant gradient of \( \frac{2\pi}{a} \) and a zero interrupt for a plot of \( \ln \left( \frac{b_0}{b} \right) \) versus \( u \), in contrast to the results obtained by Lewis(9), Ward(10) and Anderton(11) (see Figure 1.5 and 1.8). The

---

* Monodisperse Polystyrene samples were used to calibrate the columns and Polycarbonate molecular weights were calibrated using the formula

\[ M_{pc} = \left[ M_{ps}^{1.7} \left( \frac{1.4}{3.9} \right) \right]^{1/1.7} \]

where \( M_{pc} \) = molecular weight of polycarbonate

\( M_{ps} \) = molecular weight of polystyrene.

However, this conversion at low molecular weights is questionable. (12)

** Chromatograms were obtained using a I.R. detector.
above mentioned experimental results\((9,10,11)\) are consistent with the results obtained in this work as seen from Figures (3.4) to (3.6).

All experimental results clearly indicate, without exception, an initial negative gradient continuously increasing in value until a fixed positive value is reached. Hence, if the experiments were to obey equation (3.7) at all, it would be only after the point at which the slope attains its fixed positive value.

The theory from which equation (3.7) is derived (see Section 3.1) assumes a viscous boundary layer above the sample surface. The viscous layer is formed by chain scission and dissolution of these chains in the polishing reagent. At the beginning of the experiment the viscous layer is absent and the attacking nucleophile (\(\text{OMe}^-\)) has direct access to the cracks, and hence, prominent etching is observed (see Figure 1.6). Subsequently, the degrading polymer chain fragments dissolve in the polishing reagent and start the formation of the viscous boundary layer, which in turn reduces the extent of etching. Further reaction results in build up of the viscous layer until it reaches a height \(\delta_2\) (see Figure 1.6) corresponding to a zero gradient in Figure (3.4); a situation of neither etching nor polishing, i.e. thinning. The layer continues to increase to a critical height \(\delta_3\), (above which the viscous layer is not physically stable) corresponding to a final constant gradient (see Figure 3.4) and a maximum polishing rate.

The change of etching to polishing may be explained using the model in Figure (3.9). The viscous layer contains a mixture of low molecular weight polymer fragments which further react with the nucleophiles (\(\text{OMe}^-\)) creating a concentration gradient of methoxy ions through the viscous layer. This leads to a higher concentration of methoxy ions at point B compared to point A in Figure (3.9), thus resulting in a faster rate of reaction at point B (with respect to
point A); i.e. polishing.

A constant polishing rate, $R_m^{**}$, as predicted by equation (3.7) is observed, once the viscous layer has built up to its critical height $d_2$ (see Figure 3.9), at which stage steady-state conditions are achieved. However, the predicted gradient of $2\pi/a$ (from equation 3.7) was not obtained as seen from Table 3.6 (the limitations of the proposed model of the polishing process are discussed in Section 3.5.1) and this result is consistent with that obtained by Lewis et al. (9,10,11).

3.4.2 The Mechanisms of the Polishing (Etching) Process

The polishing process is governed by a process of diffusion and chemical reactions. The nucleophiles (OME\textsuperscript{−}) diffuse from a polishing reagent through the viscous layer towards the PC surface while the PC chain fragments (oligomers) diffuse away from the solid PC surface. The reaction between the nucleophiles and the oligomers in the viscous layer result in local variations (such as temperature) in the viscous layer, thus affecting the process of diffusion.*

The expected sequence of chemical reactions are given in Figure (3.11) for the polishing process. Firstly, the diffusing methoxy ion reacts with a carbonyl group of a PC chain. For this reaction to occur, the oxygen atom of the methoxy ion has to diffuse sufficiently close (as well as approach it in such a way as to minimise steric hindrance: see Figure 3.11) to the carbon atom of the said carbonyl group, partially polarising it before reaction. Hence 'it is clear that steric hindrance, the electronegativity of the

---

* The model used in the analysis of the polishing process (in the work presented in this thesis and by previous workers (9,10,11) does not take these variations into consideration, and hence is a limitation in the analysis.

** $R_m = \frac{d (\ln (b_0/b))}{du}$
<table>
<thead>
<tr>
<th>Groove Width (µm)</th>
<th>Slopes of Polishing Curves (µm)$^{-1}$</th>
<th>From Fig. 3.4</th>
<th>From Fig. 3.5</th>
<th>From Vert.</th>
<th>From Horiz.</th>
<th>From Equation (3.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$3.8 \times 10^4$</td>
<td>$3.7 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
<td>$2.5 \times 10^5$</td>
</tr>
<tr>
<td>45</td>
<td>$3.0 \times 10^4$</td>
<td>$3.1 \times 10^4$</td>
<td>$2.9 \times 10^4$</td>
<td>$2.6 \times 10^4$</td>
<td></td>
<td>$1.4 \times 10^5$</td>
</tr>
<tr>
<td>70</td>
<td>$2.8 \times 10^4$</td>
<td>$2.7 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
<td>$9.0 \times 10^4$</td>
</tr>
<tr>
<td>105</td>
<td>$2.0 \times 10^4$</td>
<td>$2.1 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
<td>$6.0 \times 10^4$</td>
</tr>
<tr>
<td>150</td>
<td>$1.8 \times 10^4$</td>
<td>$1.8 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
<td>$4.2 \times 10^4$</td>
</tr>
<tr>
<td>200</td>
<td>$1.5 \times 10^4$</td>
<td>$1.2 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
<td>$3.1 \times 10^4$</td>
</tr>
</tbody>
</table>

**TABLE 3.6**

SLOPES OF LINES IN FIGURES (3.4), (3.5) and (3.6) AND THE EXPECTED GRADIENTS CALCULATED USING EQUATION 3.7.
nucleophile and the conformation of the PC chain are major factors that control the initiation step of this reaction.

Table (1.2) gives thinning rates of PC for different polishing reagents, and it is interesting to note the following:
(a) n-propylamine and isopropylamine have thinning rates of $23.5 \, \mu m \, (min)^{-1}$ and $2.8 \, \mu m \, (min)^{-1}$ respectively; (b) although n-butylamine and n-propylamine have similar electronegativity values\(^{(13)}\) the thinning rate of the latter is greater by a factor of three; (c) the electronegativity of tertiary-butylamine is much more (due to the positive inductive effect of the trimethyl group) than n-butylamine\(^{(13)}\) but the thinning rate of the former is zero compared to $9 \, \mu m \, (min)^{-1}$ of the latter. From the above observations it is clear that steric hindrance is a very important factor in the initiation step.

Finally the chain fragments that are released from the solid polymer must dissolve in the polishing reagent (as in the case of the reagent used in this work); a very important criterion for the formation of the viscous layer and hence the process of chemical polishing. The white insoluble precipitate observed after long polishing times, is probably due to the decarboxylation of the chain fragments, releasing $CO_2$, which in turn could react with $KOH$ to form an insoluble precipitate of $K_2CO_3$ (see Figure 3.11).

However, the viscous layer analysis conducted in section 3.3.2 did not show any UV absorption in the expected range for PC. This of course is inconsistent with the expected sequence of reactions in Figure 3.11, and here it is vital to (a) repeat the experiment and confirm the absence of UV absorption and (b) to conduct a comprehensive chemical analysis of the viscous layer and finally to identify the actual compounds in the viscous layer by comparison with model compounds.
3.4.3 The Effect of Temperature on Polishing, Etching and Thinning

The comparison of polishing (etching) curves in Figures (3.4) and (3.5) shows that temperature has apparently no significant effect on polishing nor etching. The observed changes are small and may be attributed to experimental error (see Section 3.5). However, the rate of thinning \( \frac{du}{dt} \) is clearly temperature dependent as seen from Figure (3.10).

The observations may be explained using the proposed model in Figure (3.9). A change in temperature will change the rate of diffusion of the nucleophile as well as the rate of chemical reactions occurring in the polishing process. If it were to be assumed that the activation energy of the process of diffusion is of the same order as that of the chemical reactions between the nucleophiles and the oligomers in the viscous layer, then the change in the concentration of the nucleophile through the viscous layer would be independent of temperature. Hence, in Figure (3.9), the nucleophile concentrations \( C_1 \) and \( C_2 \) corresponding to points A and B respectively, will be temperature independent. This would result in the ratio \( C_1/C_2 \) to be temperature independent, and hence the polishing curves (see Figures 3.4 to 3.6) would be independent of temperature. However, the rate of chemical reactions at the surface of the solid polymer will be temperature dependent (an increase in temperature will reduce the reaction time), but will not affect the polishing curves (i.e. \( \frac{d[\ln(b_0/b)]}{du} \) will be temperature independent).

This is clearly seen by the polishing curves in Figures (3.4) and (3.5), where no apparent change between the two sets of curves is observed with change in temperature; in contrast to the time scales of these experiments being 10 and 20 mins at 29.5°C and 20°C respectively. (see Tables 3.2 and 3.3). A typical Arrhenius plot law of \( \ln\left(\frac{du}{dt}\right) \) versus
(1/T) may be used to evaluate the activation energy (E) of the thinning process.

\[
\frac{du}{dt} = e^{E/RT}
\]  

(3.9)

where 'u' is amount of thinning observed in time 't'
'R' the ideal gas constant
'T' the temperature in degrees Kelvin

The plot of ln(du/dt) versus (1/T) is shown in Figure (3.10) and a value of 26.0 KJ (mol)^{-1} was calculated as the activation energy of the thinning process.

3.4.4 The Effect of the Height and the Rate of Formation of the Viscous Layer on the Polishing Process.

When the sample is held horizontally (see Figure 3.12) the viscous layer above the surface is expected to grow faster than when held in the vertical position (where the gravitational force would continuously remove the viscous layer). A rapid build-up of the viscous layer would reduce the extent (see Figure 3.6) as well as the time of etching (see Tables 3.2 and 3.4). However, it must be mentioned that the final rate of polishing \( R_m \) (where \( R_m = \frac{d\ln(b_0/b)}{du} \)) yields the same value of 2.7 x 10^{-2} for both vertical and horizontal positions. This indicates that the heights of the viscous layer in both positions (vertical and horizontal) are above a critical height* \( h_c \); the explanation for the same \( R_m \) for both positions. If the height of the viscous layer is below \( h_c \) then \( R_m \) is affected and this situation is seen in the Figures (1.9) and (1.10) where the stable height of the viscous layer is reduced by rotation (see Section 1.3.3).

* \( h_c \) corresponds to a critical height of the viscous layer, above which the ratio \( \frac{C_1}{C_2} \) (see Figure 3.9) which governs \( R_m \) does not change.
** For the 45 \( \mu \text{m} \) wide groove.
3.4.5 The Viscous Layer Analysis

The viscous layer analysis described in Section 3.3.2 indicates the presence of oligomers of molecular weights ranging from 5,500* to 330. This may be attributed to the persistent attack of methoxy ions on the oligomers and also due to the release of oligomers from the solid to the solvent. However, the solubility limit of PC in aqueous methanol was a limiting factor in the molecular weights that were observed in the viscous layer. The highest molecular weight observed in the viscous layer analysis may be associated with the molecular weight between entanglements (Me) of the solid polymer provided that the solubility limit of PC in aqueous methanol is above Me (in this instance above 5,500). An experiment to verify the solubility limit of PC in methanol is described in Section 3.6.2.

The methods for the observation of entanglement characteristics in the literature are by measurement of a rheological property** or by estimations usually based on the model of rubber elasticity(14,20). However, the information available in the literature on chain entanglements for PC is restricted to (a) determination of the melt viscosity over a molecular weight ($\bar{M}_w$) range of 13,000 to 80,000(22) and (b) estimations of Me based on tensile stress relaxation and creep data(23). The correlation in the former method had not been carried to low enough $\bar{M}_w$ for deviation***(23), and hence, only an upper limit value of characteristic entanglement molecular weight (Mc) of 13,0000 may be developed.

* N.B. Molecular weights of 5,500 and 330 for PC correspond to approximately 22 repeat units and a single repeat unit respectively.

** The rheological properties used include (a) low shear viscosity(15), (b) measurement of relaxation times using nuclear magnetic resonance (16,17), (c) viscoelasticity(18) and (d) high shear viscometry(19).

*** The abrupt change or break in a plot of viscosity versus molecular weight corresponds to 'Mc'.
According to the Bueche theory\(^{(21)}\) \(M_c = 2M_e\) and hence, an upper limit \(M_e\) value of 6,500 may be predicted. The latter method predicts an \('M_e'\) value of 2,400\(^{(22)}\) which is surprisingly low, for a stiff polymer chain like that of PC; and also in comparison with poly(methylmethacrylate) and polystyrene having \(M_e\) values of 6,100 and 30,000 respectively\(^{(24)}\).

The \(M_e\) value of 5,500 obtained from this work falls below the upper value of 6,500 and is also sufficiently large as that expected of a stiff polymer chain. However, a conclusion regarding the value of \(M_e\) is not possible without a more detailed examination of the system. Firstly, as previously mentioned the solubility limit of PC is methanol and secondly, the mechanisms of the polishing process should be further investigated.

3.5 DISCUSSION OF ERRORS

The errors involved are due to experimental limitations as well as the analysis of the polishing process, described in Section 3.1.

3.5.1 Limitations of the Analysis of the Polishing Process

Some of the limitations have been already discussed in Sections 3.4.1 and 3.4.2. Polishing a sample in the vertical position (under quasistatic experimental conditions) leads to slow streaming of the viscous layer under gravitational forces,\(^{(11)}\) which would undoubtedly cause local variations in the viscous layer; such variations are unaccounted for in the polishing analysis.

Lewis et al\(^{(9)}\) have shown that the concentration of KOH in the polishing reagent is a function of the polishing rate\(^*\), \(R_m\) (see Figure 1.5). This experimental observation is not accounted for in the polishing analysis (i.e. equation 3.7) and the reason for this variation may be explained as follows. A variation of the KOH

\[ R_m = \frac{d[n(b_0/b)]}{du} \]
concentration would alter the $\text{OMe}^-$ concentration, which in turn would alter the frequency of reaction of the oligomers with the nucleophiles; thus, changing the ratio $\frac{C_1}{C_2}$ (see Figure 3.9). As seen from Section 3.4.3 the ratio $\frac{C_1}{C_2}$ is a major factor that determines $R_m$.

As previously explained in sections (3.4.2) and (3.4.5), in the light of the evidence of the viscous layer analysis, the reaction mechanisms may be revised after further experiment (as suggested in sections 3.4.2 and 3.4.5) and hence, a more accurate model of the polishing (etching) process may be developed.

3.5.2 **Experimental Limitations of the Polishing (Etching) Process**

The major experimental limitation is that the etching phase occurs very rapidly if one or more of the following conditions are fulfilled:

(a) high KOH concentration  
(b) high temperature (above 20°C)  
(c) sample held horizontally.

thus reducing the number of experimental points that may be obtained in the etching phase. When situations (a) and (b) were combined only one experimental point (in the etching phase) was obtained as shown in Figure (3.4) and when situations (a) and (c) were combined it was not possible to obtain a single experimental point in the etching phase (see Figure 3.6). This clearly leads to limitations, such as the inability to predict the point at which polishing initially occurs.

3.5.3 **Errors in the Viscous Layer Analysis**

An error would occur in the sampling technique of the viscous layer (see Section 3.2.5) due to some degree of chain scission of the oligomers that may occur before the KOH could be neutralised. The accuracy of the GPC analysis is also restricted especially at the lower molecular weight range. (12)
3.6 CONCLUSION AND FURTHER WORK

3.6.1 Conclusion

The initial reaction of the polishing reagent with the bulk polymer creates an etching phase, and the subsequent build-up of the viscous layer formed by the dissolution of the polymer chains is responsible for the polishing phase. Equation 3.7, a direct result of the theory of chemical polishing, deviates from the experimental results and does not predict the effect of the nucleophile concentration on the polishing rate $R_m^*$. 

(a) The wider cracks have a lower rate of polishing than the narrow ones. 

(b) The rates of polishing and etching are independent of temperature but the rate of thinning increases with increase in temperature. 

(c) An activation energy of 26.0 KJ (mol)$^{-1}$ was calculated for the thinning process. 

(d) Holding the polishing surface in the horizontal position, dramatically decreases the etching phase at the expense of the polishing phase but does not affect the thinning nor the final polishing rates.*

3.6.2 Further Work

(a) The development of polishing and thinning reagents for other polymers would be interesting and useful especially in the examination of the structural detail in the bulk.

* Rate of polishing (etching), $R_m = \frac{d(n(b_0/b))}{t}$
state. Other polyesters such as poly(ethylene terephthalate) would be appropriate to study due to its sensitivity to hydrolysis. Development of a polishing reagent may be attempted by screening the polymer using a range of reagents.

(b) The investigation of the effect of lower temperatures on the process of polishing (etching) and thinning would undoubtedly further the understanding of these processes.

(c) It would be very interesting to pursue the analysis of the viscous layer at various KOH concentrations and at different time intervals from the start of the initial reaction; and secondly, to identify the actual compounds in the viscous layer by comparison with model compounds as suggested in Section 3.4.5.

(d) The phenomenon of chemical polishing of metals has been little studied from an analytical viewpoint (25) and future research in this area could be attempted using the methods discussed herein.

(e) To determine the solubility limit of PC oligomers in 'Aqueous' methanol using a range of molecular weights in order to verify the Me value evaluated in the viscous layer analysis (see section 3.4.5). The PC samples of different molecular weights may be obtained by thermal degradation of PC, subsequently checked by GPC.
REFERENCES

8. C. Booth, Department of Chemistry, University of Manchester, Manchester, private communication.


Figure (3.1) Mechanical scratcher used for ruling grooves
Figure (3.2) Reichert zetopan microscope fitted with a Watsons 8 mm interference objective
FIG (3:3)

EXPERIMENTAL SET UP USED FOR SYRINGING THE VISCOS LAYER
Figure 3.4 Polishing and etching of six cracks in 5.8 N methanolic KOH at 29.5°C (cracks of the sample held vertically).
Figure 3.5  Polishing and etching of six cracks in 5.8 N metanolic KOH at 20°C (cracks of the sample held vertically).
Figure 3.6 Polishing and etching of a vertically and a horizontally held crack (λ = 45 μm) in 5.8 N methanolic KOH at 20°C.
Figure 3.7 Thinning curves for polycarbonate in methanolic KOH at two different temperatures and crack positions.
A typical set of interferograms of single scratch grooves (of wave length 45 and 25 μm) before and after chemical polishing in the vertical position (see Figure 3.12) for 20 minutes at 20°C in a 5.8 N methanolic KOH solution.
A typical set of interferograms of a single scratch groove (wave length 25 μm) before and after chemical polishing in the vertical position (see Figure 3.12) for 45 seconds at 29.5°C in a 5.8 N methanolic KOH solution.
Figure (3.8c) A typical set of interferograms of a multiple scratch groove (of wave length 105 μm) before and after chemical polishing in the vertical position (see Figure 3.12) for 10 minutes at 29.5°C in a 5.8 N methanolic KOH solution.
Figure 3.9 The concentration gradient of the methoxy ions through the viscous boundary layer.
Figure 3.10 An arrhenius law type plot for the thinning of polycarbonate.

Data point obtained from the results of Lewis and Ward (9)
Polishing Reaction Sequence

(1) Equilibrium of KOH and Methanol

\[ \text{KOH} + \text{MeOH} \rightleftharpoons \text{K}^+ + \text{OMe}^- + \text{H}_2\text{O} \]

(2) Random Chain Scission

(3) Decarboxylation

\[ \text{CO}_2 + 2\text{KOH} \rightarrow \text{K}_2\text{CO}_3 \]
FIGURE (3.1k)

(a) Sample held Horizontally

(b) Sample held vertically
2 ml of injection
1 ml/min flow

Columns:
- $7 \times 10^5 - 5 \times 10^4 \AA$
- $1.5 \times 10^5 - 7 \times 10^4 \AA$
- $10^4 \AA$
- $500 - 2000 \AA$
- $150 - 350 \AA$

Elution Volume (ml) "The corresponding PC molecular weights are shown in brackets"
2ml of injection
1ml/min flow

Columns
700 - 2000 Å
500 - 2000 Å
200 - 500 Å
150 - 350 Å
50 - 80 Å

Figure (3.14) "The corresponding $^{12}$C molecular weights are shown in brackets."
2 ml injection
1 ml/min flow

Columns
700 - 2000 Å
500 - 2000 Å
200 - 500 Å
150 - 350 Å
50 - 80 Å

Elution Volume (ml)

Figure (3.15)
CHAPTER IV

MOLECULAR ORIENTATION AND RESIDUAL STRESSES
IN INJECTION MOLDED POLYCARBONATE

4.1 INTRODUCTION

The catastrophic failure of injection moulded polycarbonate miners' lamps under severe environmental conditions of the pit, is thought to be due mainly to 'Molecular Orientation' and 'Residual Stress'. (1,29) The work presented in this work is an attempt to understand the fundamental nature of the above mentioned problems using a combination of techniques (including 'Photoelastic Strain Analysis'), and in so doing contribute to the solution of the immediate industrial problem of mould design and processing conditions. (1) Birefringence measurements of PC crash helmet visors were also conducted and is present in Appendix (4.2).

4.2 PHOTOELASTIC TECHNIQUES

4.2.1 The use of a Polariscope in Experimental Strain Analysis

A 'Plane Polariscope' (see Figure 4.1) consists of a polarizer, and analyser and a light source. When a polarised beam (P) propagates through the thickness (t) of a material, where x and y are the

* The concepts of molecular orientation and residual stress have been explained in Section 1.4.1.
directions of principal strain at the point 'O' (under consideration),
the light vector splits and two orthogonal polarised beams are propagated
in the 'x' and 'y' directions.

Hence the relative retardation of the two beams (δ) =

\[ C \left( \frac{t}{V_x} - \frac{t}{V_y} \right) = t(n_x - n_y) \]  \hspace{1cm} (4.1)

where \( V_x \) is the velocity and \( n_x \) the refractive index in the X direction,
while \( V_y \) is the velocity and \( n_y \) the refractive index in the Y direction
(see Figure 4.1). \( C \) is the velocity of light in a vacuum and \( t \) the
thickness of the material. The relative change in the refractive
index is proportional to the difference in the principal strains\(^{12,13}\)
according to Brewster's law and hence

\[ (n_x - n_y) = (\epsilon_x - \epsilon_y) \]

where \( \epsilon_x \) and \( \epsilon_y \) are the strains along X and Y direction respectively.

\[ (n_x - n_y) = k (\epsilon_x - \epsilon_y) \]  \hspace{1cm} (4.2)

where \( k \) is the strain optical coefficient. Hence from equations (4.1)
and (4.2) we have

\[ \epsilon_x - \epsilon_y = \frac{\delta}{tk} \]  \hspace{1cm} (4.3)

The intensity of the emerging light (I) can be calculated to be

\[ I = a^2 \sin^2 2(\beta - \alpha) \sin^2 \left( \frac{\pi \delta}{\lambda} \right) \]  \hspace{1cm} (4.4)

where \( \lambda \) is the wave length of the light used and \( \alpha \) and \( \beta \) are the angles
shown in Figure (4.1).

The directions of principal strains may be measured by using the
fact that the light intensity is zero when \( \beta - \alpha = 0 \) (i.e. at a point
when the direction of one of the principal strains coincides with the
direction of polarization of incident light). The locus of such points are known as 'Isoclinics'. At any point on an isoclinic the principal strains have the same inclination $\phi$ to an arbitrary axis. Two orthogonal sets of curves (for a 2-dimensional case) known as 'Isotatics' may be drawn (which gives the directions of principal strains at every point on the model) using a set of isoclinics obtained by varying the setting of the polariser and analyser, (by steps of 15° say) from 0 to 90° from an arbitrary axis.\(^{(2,3,4)}\)

Figure (4.2) shows the effect of the introduction of crossed quarterwave plates between the polariser and analyser thus, changing it from a plane polariscope to an 'Circular Polariscope'. The emergent light intensity ($I_1$) of a circular polariscope is independent of the directions of the principal strains and may be given as follows:

$$I_1 = a^2 \sin^2 \left(\frac{\pi \delta}{\lambda}\right)$$

From equation (4.5) it is clear that when the light intensity ($I_1$) is zero

$$\delta = n\lambda$$

where $n$ is an integer. From equations (4.3) and (4.6)

$$\varepsilon_x - \varepsilon_y = \frac{n\lambda}{tk}$$

$n$ may be obtained by a method of compensation or by the colour of the fringe (if white light is used), as described in Section 4.2.2 These fringes are obtained by using a circular polariscope which gives the magnitude of the difference in principal strains and are said to be

* If white light is used then it is best to use the wavelength as 5750 Å which defines the colour of the first fringe order. Any change of wavelength in this particular region is very sensitive to the human eye and hence is advantageous in identification of the fringe order.
'Isochromatics'. The difference principal stresses may be obtained by using Hook's Law and equation (4.7) (assuming that the stresses are within the elastic limit). The principal stresses $\sigma_x$ and $\sigma_y$ may be separated at a free surface using the fact that the stress perpendicular to a free surface is zero. Oblique incidence measurements may be used (2,4) for the separation of $\varepsilon_x$ and $\varepsilon_y$ at a point not on a free surface.

4.2.2 Measurement of Optical Retardation by Compensation

The approximate optical retardations can be measured by the colour sequence of the isochromatics (2,3). Table (4.1) lists the colours corresponding to particular optical retardations. More accurate measurements may be done using a reflection polariscope (5) and (a) the Tardy method of compensation; (b) using a Babinet* compensator. (5)

4.2.2.1 Tardy Compensation

Initially the crossed polariser and the analyser are aligned with the direction of the principal strains at the required point P, (as explained in Section 4.2.1) by rotating the analyser and polariser with respect to the sample ensuring that an isoclinic passes through P. The angle of rotation gives the directions of principal strains (2,4). Then the quarter wave plates are introduced as shown in Figure (4.2). Clockwise rotation of the analyser (by an angle $\alpha$ with respect to the polariser) will move a fringe to the position $P$ and the fractional fringe order will be $\frac{\alpha}{180}$. From equation (4.7) we have

$$\varepsilon_x - \varepsilon_y = \frac{n\lambda}{2tk} \tag{4.8}$$

* A Babinet compensator may also be used in transmission.

** In reflection the light passes through the specimen twice and hence a factor of two is incorporated in equation (4.8).
<table>
<thead>
<tr>
<th>Retardation (10⁻⁷ m)</th>
<th>Colour Observed</th>
<th>Fringe Order (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Black</td>
<td>0</td>
</tr>
<tr>
<td>3.05</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>4.57</td>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>5.77</td>
<td>1st Fringe</td>
<td>1</td>
</tr>
<tr>
<td>6.35</td>
<td>Blue-Green</td>
<td></td>
</tr>
<tr>
<td>8.89</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>10.16</td>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>11.53</td>
<td>2nd Fringe</td>
<td>2</td>
</tr>
<tr>
<td>12.70</td>
<td>Green</td>
<td></td>
</tr>
<tr>
<td>14.48</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>16.00</td>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>17.30</td>
<td>3rd Fringe</td>
<td>3</td>
</tr>
<tr>
<td>18.54</td>
<td>Green</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE (4.1)**

THE COLOUR SEQUENCE ASSOCIATED WITH

OPTICAL RETARDATION (⁴)
The fringe order \( n = n' + n_f \) 

\[ n' = \text{the integral fringe order at the point of measurement on rotating the analyser dial} \]

\[ n_f = \text{fractional order by which the analyser is rotated} \left( \frac{\alpha}{180} \right) \text{ where } \alpha \text{ is the angle of rotation.} \]

If the lower fringe order moves to the point of measurement \( n_f \) is taken to be positive and if the higher fringe order moves to the point of measurement \( n_f \) is taken to be negative. [In both cases the analyser is rotated clockwise.]

Hence using equations (4.8) and (4.9) \( \epsilon_x - \epsilon_y \) can be found

4.2.2.2 Null Balance Method

The same procedure as in the Tardy compensation method is followed up to the point of inserting the quarter wave plates. (See Section 4.2.2.1.) Then the Babinet compensator is introduced so that it is in line with one of the principal strains in order that the photoelastic signal at the required point may be nullified by the addition of an identical signal in the opposite direction. (5) The added signal can be obtained from the calibration curve of the compensator. As the compensator can add a photoelastic signal only in one direction it may be that the added signal is in the same direction as \( (\epsilon_x - \epsilon_y) \) in which case the compensator has to be rotated by \( 90^\circ \) to reverse the direction. This method may also be used in transmission.

4.3 RESIDUAL STRESS MEASUREMENT TECHNIQUES

4.3.1 Layer Removal Technique

Successive removal of surface layers and observation of bending of the sample is a well established technique for the measurement of
residual stress. \(6,7,11\) A strip of material (bar shaped) may be cut from the original sample as shown in Figure (4.20), and the surface layers (BCEH) may be successively removed by chemical polishing (see Section 4.4.2). The corresponding curvature is measured by placing the sample on a flat surface and observing the elevation at its mid point using a travelling microscope.

The bending moment \(M\) due to the removal of a layer of thickness \(t\) may be written as

\[
M = \frac{T}{2} \sigma_x b t
\]  

(4.10)

where \(\sigma_x\) is the stress in the direction \(BC\) (see Figure 4.20)

- \(b\) the width of the sample
- \(\frac{T}{2}\) the distance from the neutral axis of the sample to the centre of force (due to the removed layer)

Now

\[
2\theta = \frac{ML}{EI}
\]  

(4.11)

where \(E\) is the modulus of the material

\[
I = \frac{T^3b}{12}
\]

length of the arc

and \(2\theta\) the angle of the arc.

From equations (4.10) and (4.11) we have

\[
\sigma_x = \frac{ET^2P}{6t}
\]  

(4.12)

where \(P = \frac{1}{R}\) = the curvature.

However, it must be mentioned that this model has several limitations and the following are assumed.

(a) The stresses vary only through the thickness of the specimen but not in the plane of the specimen.

(b) Successive uniform layers are removed so that no additional
stresses are introduced to the specimen.

(c) The stress distribution across the thickness is symmetrical and only half the thickness needs to be removed: the modulus of the material is a constant.

(d) The specimen bends to form an arc of a circle, after layer removal.

(e) The effect of the transverse stress was not taken into account in this model.

A more accurate model for the same purpose is available. (11)

4.3.2 Scratching and Cutting Technique

If the surface of a specimen (containing residual stress) is scratched then a free surface is created thus releasing the residual stress (perpendicular to the free surface). If the isochromatics of such a specimen (see Section 4.2.1) were to be observed, a change in the fringe pattern around the vicinity of the scratch corresponding to the release in residual stress would be observed. However, it must be mentioned that cutting stresses also contribute to a similar change in fringe pattern but, the extent of such a contribution may be assessed by repeating the experiment on a similar specimen with minimal residual stress.

The same may be repeated, cutting a specimen through its thickness (rather than scratching), but the change of the isochromatics will show only the average release of the residual stress through the thickness of the sample. In most instances the release in average residual stress through the thickness of the specimen is zero, although residual stresses may exist (generally compressive at the surface and tensile at the middle) and hence, such an experiment would reveal minimal information.

Finally it is worth mentioning that simple experiments to that mentioned in this section would be very useful from an industrial point
of view for quick and easy results (although less informative) for the much desired quick feedback in the manufacturing processes.

4.4 POLISHING OF POLYCARBONATE

Mechanical sectioning of polycarbonate results in cutting stresses (see Figures 4.24 and 4.25) and hence the polishing technique described in Section (3.24) was modified for the removal of surface layers of the battery boxes in order to carry out through thickness birefringence measurements.

4.4.1 Polishing of All Surfaces

Figure (4.3) shows the apparatus used for polishing. To obtain uniform thinning of the sample it is necessary to obtain a uniform viscous layer above the sample surface (see Chapter 3). This was done by regulating the flow pattern of the polishing reagent,* which depends on several aspects such as the shape of (a) the sample, (b) the vessel, (c) brake plates, (d) stirrer as well as the speed of stirring. The shape and the size of the equipment (relative to the sample) used is as in Figure (4.3) and 50 rpm was the speed of stirring. It was also important to check the basicity of the solution regularly to ensure that the polishing process was not reduced significantly; and this was done by titrating a sample of the reagent with 0.1 N HCl. A fresh polishing solution was used if its normality fell below 4.0.

4.4.2 Polishing of a Selective Surface

In order to assess the extent of residual stress it was necessary

* The basicity of the polishing reagent initially used was approximately 4.5 N.
to polish a single surface.

This was done by coating a section of a battery box on all its sides, except one, with a 'silastic 9161 RTV rubber' and using the polishing reagent as described in Section 3.2.4. For relatively short periods of time (less than two hours), the coating was found to be generally resistant to the polishing reagent.

4.5 EXPERIMENTAL METHODS AND RESULTS

Two sets of injection moulded PC battery boxes* were used for all experimental work in this section whose moulding conditions are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Box 'L'</th>
<th>Box 'H'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Temperature</td>
<td>290°C</td>
<td>290°C</td>
</tr>
<tr>
<td>Cavity Temperature</td>
<td>60°C</td>
<td>90°C</td>
</tr>
<tr>
<td>Mould Temperature</td>
<td>70°C</td>
<td>100°C</td>
</tr>
</tbody>
</table>

Figure (4.4) shows an injection moulded battery box and the numbering in the diagram was used as a means of identification before cutting the moulding for the experiments. The cutting was done using a band-saw with a sharp blade to minimise cutting stresses. The belt loops in part 'l' (see Figure 4.4) of both boxes (i.e. L and H as previously defined in this section) were cut so as to obtain a flat specimen (before any experiments were conducted).

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* The battery boxes were test moulded in clear lexan 161, the highest molecular weight grade of PC for injection moulding. The samples chosen were those moulded at the highest and lowest mould/cavity temperature of a much larger set of test specimens. (8)
4.5.1 Through Thickness Birefringence Measurements

Parts 2 and 3 of both types of mouldings (see Figure 4.4) were used to obtain the through thickness birefringence measurements (in transmission) using plane polarised monochromatic (Sodium D) light (see Section 4.2.1). The chemical milling was done as in Section 4.4.1 (i.e. removal of all surface layers). Figures (4.5) and (4.6) show the sequence of birefringence measurements with progressive chemical milling.

A similar experiment was done on part '1' of both lamps (see Figure 4.4) using circularly polarised white light and its results are as in Figures (4.7) to (4.14). Figures (4.7) to (4.10) compare the optical retardations of part 1* of both lamps while figures (4.11) to (4.14) compare the optical retardations (at a magnification of '4') in the shaded area of part 1* of both lamps L and H as shown in Figure (4.15). In addition to these experiments the optical retardations were measured at specific points on the sample (the numbering in Figure (4.15) indicates these points) using either a Babinet compensator (see Section 4.2.2.2) or a reflection polariscope (Tardy compensation; see Section 4.2.2.1), and the results are shown in Figures (4.16) to (4.19).

4.5.2 Birefringence Measurements Perpendicular to the Direction of Through Thickness

The sample used for this experiment was cut from part '1' (see Figure 4.4) of box L as shown in Figure (4.15)**. Sides EFGH and ABCD were mechanically polished leaving the skin of the moulding unaltered on both sides. The optical retardation of the sample was measured in the

* The part numbers are defined in Figure (4.4) and Figure (4.15) shows a detailed diagram of part '1' in this instance.
** The sample used is defined by the section marked BCEH in Figure (4.15) and is redrawn in detail Figure (4.20).
*** See Figure (4.20).
direction shown in Figure (4.20) using circularly polarised white light at a magnification of seven (the sample thickness being 2.93 mm), and the results are as in Figure (4.21). The same experiment was repeated at a magnification of 25, using a modified Reichert Zetopan microscope, and its results are as in Figure (4.22).

The graph in Figure (4.23) is a general representation of the optical retardation from skin to skin of the moulding (i.e. from X to Y; see Figure 4.20). The direction of optical retardation was obtained by inserting an optically stressed photoelastic material between the polariser and analyser and observing the change in the fringe pattern.

4.5.3 Residual Stress Measurements by Cutting or Scratching

The isochromatics of a section of part '2' for both mouldings were obtained as described in Section (4.3.2). Figures (4.24) and (4.25) show the fringe patterns obtained for both mouldings, on scratching the surface to a depth of 0.5 ± .2 mm and also by cutting.

4.5.4 Residual Stress Measurements Using the Layer Removal Technique

Two strips of the moulding (marked A'B'C'D' in Figure 4.15) were cut from part '2' of both boxes L and H. The residual stress* ($\sigma_x$) in the direction B'C' (see Figure 4.15) was calculated as detailed in Section 4.3.1. Figure (4.26) shows the variation of stress from the surface to approximately half its thickness for both mouldings.

* Tensile modulus of the polycarbonate battery box was measured to be $(2.5 \pm 0.3) \times 10^{-6}$ Nm$^{-2}$ (variation within the battery box) and a value of $2.5 \times 10^6$ Nm$^{-2}$ was used for the calculation of residual stress.

** The part number is defined in Figure (4.4) and the section PQRS in Figure (4.15) defines the sample used in this instance.

*** See Figure (4.4).
4.6 DISCUSSION

4.6.1 Through Thickness Birefringence Measurements

The study of melt flow in mould filling is a fundamental step in understanding the problem of molecular orientation and residual stress in injection mouldings. There are two regimes of mould filling\(^{(31)}\), the more common being an expanding polymer melt front which completely fills the mould as shown in Figure (4.35a). Tadmor developed a semi-quantitative model\(^{(32)}\) to explain the complex molecular orientation observed in amorphous polymers based on the said expanding front type filling. In the second, and the less common type of mould filling, the melt tissues as a jet and shoots across the mould (see Figure 4.35b\(^{(31)}\)) and this mechanism of jetting has been investigated by Oda, White and Clark\(^{(33)}\). The existence of these two regimes greatly complicates the question of the influence of moulding conditions and mould design on orientation in the moulded parts.

In the case of the battery boxes it is very likely that an advancing melt front radiates from the points of injection at the base of the battery box (as shown in Figure 4.4) and continues to advance along the mould on sides 1, 2, 3, 4 and 5 (as marked in Figure 4.4) and finally filling the belt loops. However, it must be mentioned that since the initial direction of melt flow in the mould would be perpendicular to the direction of injection (see Figure 4.4) the analysis of the melt flow pattern becomes very complicated.
The sequence of photographs seen in Figures (4.7) to (4.14) are the isochromatics of samples from lamps L and H with progressive removal of all surface layers by chemical polishing. It is clear that the isochromatics seen in Figures (4.7) and (4.11) (i.e. after the first polish) is due to the difference in principal strains ($\varepsilon_x - \varepsilon_y$) in the XY plane (see Figure 4.15) averaged over almost its original thickness in contrast to the isochromatics in Figures (4.10) and (4.14) (i.e. after the final polish) being only due to the difference in principal strains (in the XY plane) averaged over the centre of the sample. From these photographs and the graphs in Figures (4.16) to (4.19) it can be observed that:

(a) In general, the sample from box L resulted in a higher ($\varepsilon_x - \varepsilon_y$) value than the sample from box H for all through thickness measurements of the samples.

(b) The change in ($\varepsilon_x - \varepsilon_y$) with progressive polishing is dependent on the position at which the measurement was made, and this is confirmed by the fact that similar shapes of curves are obtained at similar positions for both L and H samples in Figures (4.17) to (4.19). Hence it may be inferred that the geometry of the mould (and possibly the position of the gate) is the major factor affecting the ($\varepsilon_x - \varepsilon_y$) values of all layers through the thickness of the specimen.

(c) Figures (4.11) to (4.14) show the position of the belt loop at which the polymer melt in the mould
would have moved in the \( z \) direction (see Figure 4.15), and hence, as expected a complicated fringe pattern is observed.

(d) It is very difficult to interpret the edges of the moulding as they were not of uniform thickness in addition to the complicated flow pattern of the polymer melt (at an edge) would have on \((\varepsilon_x - \varepsilon_y)\).

(e) The fringe pattern of the through thickness measurements due to the combination of isoclinics and isochromatics are shown in Figures (4.5) and (4.6). Analysis of this fringe pattern is very difficult as monochromatic light was used (and not white light).

However, the change of the fringe pattern due to the isoclinics and the isochromatics (see Figures 4.5 and 4.6) when compared with the fringe pattern due to the isochromatics only in Figures (4.7) to (4.10) indicate a possibility that the isoclinics change in through thickness measurements. Hence, it is likely that the directions of principal strains in the \( XY \) plane varies through the thickness of the sample. It must be mentioned that for more positive evidence of this, it is essential to conduct through thickness measurements using plane polarised white light as described in Section 4.2.1 and thus, obtain sets of isostatic lines.

4.6.2 Birefringence Measurement Perpendicular to the Through Thickness Measurements

In this experiment both principal strains observed were in a plane orthogonal to the direction of melt flow; one of the principal strains being in the \( EF \) direction and the other in the \( FG \) direction (see Figure 4.20). As seen from Figure 4.23, high negative
birefringence \((8 \times 10^{-4} \text{ metres per metre})\) at the skin of the moulding rapidly increasing to zero, and further increasing at a lower rate to approximately \(8 \times 10^{-4} \text{ metres per metre}\) at the centre of the specimen, was observed. Kamal and Tan\(^{(34)}\) conducted a similar experiment on injection moulded polystyrene which showed maximum birefringence at the surface rapidly decreasing towards the centre; with the exception of the sample nearest to the point of injection where a relative maximum (a skin effect) was observed\(^{(34)}\). However, it must be mentioned that the polystyrene moulding was a flat plate with the point of injection in line with samples examined, in contrast, to the complex shape and position of the samples examined in this study (see Figure (4.4) and (4.15)). Such a change in shape may affect the melt flow pattern and hence the photoelastic signal observed. Furthermore, the moulding conditions and the type of polymer used in these two instances are different, and hence, add to the reasons for the different birefringent patterns observed.

For more conclusive results further investigation such as measurement of birefringence (a) at different parts of the moulding in the same direction (i.e. YZ direction as indicated in Figure 4.15) and also in the XZ direction (see Figure 4.15) would be desirable. Birefringence observed in the XZ direction of the sample would be indicative of the melt flow pattern of the moulding, which indeed would be very useful in relating to the final interpretation of the photoelastic analysis. A similar experiment conducted\(^{(34)}\) on polystyrene indicated fountain flow\(^{(32)}\) as well as a skin effect.

### 4.6.3 Residual Stress Measurements by Cutting or Scratching

Cutting or scratching a material will create a free surface and the principal stresses perpendicular to the surface will be zero, thus releasing residual stress (if any). The release of residual stresses will result in a change of the strains (if stresses are sufficiently
large) and hence the photoelastic signal. However, cutting nor scratching does not affect strains due to molecular orientation (see Section 1.4) and any change observed in the photoelastic signal (on scratching or cutting) may be associated with a release in residual stress.

From the results in Section 4.5.3 it is clear that:

(a) The average residual stress (averaged over the thickness) of both mouldings is very small.

(b) The above observation is also true for the surface layer (0.5 ± 0.2 mm) of both mouldings.

(c) The changes in the photoelastic signal seen may be attributed to both release in residual strains as well as the residual strains introduced by the process of mechanical cutting or scratching, thus making the results less conclusive.

A similar experiment has been conducted by Broutmann and Krishnakumar(35,36) where residual stresses of quenched polycarbonate sheet has been investigated. In this instance saw-cuts were made normal to the sheet surface, and birefringence was observed in a direction perpendicular to the through thickness direction. The saw-cut would release one of the principal stresses (if present) and hence the corresponding principal strain thus leading to a change in the photoelastic signal observed. Broutmann observed a significant change in the photoelastic signal after the saw-cut in the quenched sample, and insignificant change in the 'as-extruded' sample(35,36). From this experiment he was able to determine residual stress induced on quenching polycarbonate. More information on the residual stresses of the injection moulded PC battery boxes can be undoubtedly obtained by making similar saw-cuts and observing the birefringence in the same direction as that in Broutmann's experiments.
4.6.4 Residual Stress Measurements Using the Layer Removal Technique

Cinematographic records of stress-induced birefringence in glass during quenching has shown a tensile surface layer and a compressive mid-plane at the initial stages of tempering gradually changing into a permanent compressive surface layer balanced by interior tension \(^{(37)}\). The reason for this may be explained as follows. During the initial stages of quenching the surface cools more rapidly than the interior resulting in tensile stresses at the surface and compressive stresses in the mid-plane. Furthermore, the temperature difference between the surface and the mid-plane attains a maximum, and hence, the interior cools more rapidly than the surface until isothermal conditions are established. Since hot glass relax, initially induced stress, relaxes much more compared to that induced subsequently (at a lower temperature), thus resulting in a final stage of permanent compression at the surface balanced by interior tension. A theory for calculating stresses produced in glass by Lee et al \(^{(38)}\) (taking into account the above mentioned viscoelastic properties of glass) was experimentally found to be in good agreement after minor modification to the numerical formulation of the theory \(^{(39)}\).

Broutmann's measurements on quenched polycarbonate \(^{(16)}\) confirm the above mentioned theory and this model is generally accepted \(^{(11,14,15)}\). Beaumont and Russell \(^{(40)}\) observed a similar (i.e. compressive stresses at the surface and a tensile stress at the centre of the moulding) stress distribution in injection moulded Nylon 6. The magnitude of the residual stress was also found to be inversely proportional to the mould temperature (within the appropriate temperature range).

The results in our experiments show an initial compressive layer followed by a tensile layer and the repetition of a similar set of (compressive and tensile) layers prior to the midpoint of the specimen. This result is inconsistent with the previously mentioned theories of residual stresses, Broutmann's experiments \(^{(16)}\), and Beaumont's \(^{(40)}\) measurements on injection mouldings. This suggests that the oscillations observed in Figure 4.26 are experimental artefacts.
The likely explanation for this anomaly lies in the layer removal technique, of chemical polishing (see Section 4.4.2). In certain circumstances, the surface of the specimens, supposedly protected by the rubber coating, was found to be polished to some extent, thus removing the outside compressive layer and leading to the oscillations observed in Figure 4.26.

4.6.5 Problems of Injection Moulding Polycarbonate

The quality of an injection moulded part is very much governed by the processing conditions and the mould design, and this fact cannot be sufficiently emphasised. Injection of the polymer melt into cold moulds (sometimes in order to increase the rate of production and sometimes to prevent the moulding sticking to the core or mould surface), the poor design of the mould (stress concentrations that can be easily avoided, inappropriate wall thickness, etc.) coupled with totally inadequate methods of testing (e.g. the drop test of a lead acid battery from a height of two meters onto a concrete base\(^{(17)}\)) were the major reasons for the poor quality of the final product. The use of the appropriate molecular weight (and distribution), proper pre-moulding preparation of the polymer, ensuring the quality of the surface of the mould and the critical wall thickness of the moulding are some of the other important aspects, among many others, \(^{(23,24,30)}\) that should be taken into consideration in injection moulding.

Birefringe due to orientation of polymer chains in a preferred direction is often confused in the literature\(^{(20,21)}\) with birefringe due to residual stress. Residual stress could be considered as local, elastic (energy) stress that exists in a solid body in the absence of external forces, and may be released by cutting in contrast to molecular orientation* which is not affected by cutting.

* In photoelastic analysis the difference in principal strains are measured, and in a situation of molecular orientation (the strain in the direction of orientation is different from the transverse direction and so are the refractive indices) a photoelastic signal is observed. A situation of residual stress also results in a photoelastic signal.
In our experiments attempts were made to separate orientation from stress, by releasing the residual stress. From the results of Section 4.6.3 it appears that the stresses are minimal in the surface layer, while section 4.6.4 indicates the presence of an appreciable degree of residual stress through the thickness of the moulding. Unfortunately problems with the layer removal technique (developed in this work) did not allow an accurate analysis of residual stress. However, using the maximum** stress value of $4.3 \times 10^6$ N m$^{-2}$ of the cold moulding 'L' (see Figure 4.26) a change in optical retardation of $2.9 \times 10^{-4}$ per unit thickness is predicted using a stress optical coefficient of $7 \times 10^{-11}$ m$^2$ N$^{-1}$ (see Appendix 4.1). Figure 4.18 shows optical retardations as high as $12 \times 10^{-4}$ and (in the light of the above mentioned evidence on the maximum residual stress values) this may be explained as being predominantly due to a situation of molecular orientation.

From these observations it appears that the birefringence seen is due to a combination of residual stress as well as molecular orientation. However as emphasised on several occasions it is necessary to conduct more accurate residual stress measurements as indicated in Sections 4.6.3 and 4.6.4 for a more positive conclusion on the situation of residual stress and molecular orientation.

As discussed in Section 4.6.1 birefringence dramatically increases in a very complex manner at the position of the belt loops, an area at which the melt flow would have changed its direction by 90°, thus

** These values must be treated with caution due to experimental artefacts explained in Section 4.6.4.
leading to a complex flow pattern and to a change in molecular orientation. On observing Figures (4.7) to (4.10) it is clear that the area near the lower end of the belt loop (the shaded area in Figure 4.15) shows higher optical retardation than the end above it. Figure (4.4) shows that the lower end of the belt loop is closer to the point of injection of the polymer melt than to the upper end. If it were to be assumed that the cooling rates, and hence, the residual stress levels at both ends of the belt loop are similar, the observed difference in optical retardation at the two ends of the belt loops (see Figures 4.7 to 4.10) may be predominantly attributed to molecular orientation.

A similar set of PC battery boxes with its moulding conditions as that of box L and H, defined in Section 4.5, had shown a remarkable lowering of impact strength and a higher degree of crazing (when exposed to solvents during welding) in the cold moulding. This fact may be attributed to the high degree of molecular orientation and residual stress observed in the cold moulding. The failure rate of PC miners' lamps in a Lancashire Colliery* is shown in Figure 4.27: the drop in failure rate observed since 1976 is associated with the change in design and moulding conditions (primarily, increasing the mould cavity temperatures). The failure curve covers general battery designs. The drop in failure rate coincided with the introduction of a PC cell similar in design to that studied herein and moulded using condition 'H' as defined in Section 4.5.

Finally it is interesting to consider residual stress and molecular orientation as entropy effects due to configurational changes in macromolecules and a parallel may be drawn to that of rubber elasticity. However unlike rubber, a glassy polymer does not undergo configurational changes unless sufficiently large deformations are imposed.

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* The severe environmental conditions of this relatively deep pit of 1000 m to which the lamps are exposed includes (a) steep seams (between 1 in 5 and 1 in 2 gradients for inbye/outbye and along seams) of 1.7 m in height; (b) mechanised longwall coalface with ripper. The importance of a reliable and robust lamp is further justified by the fact that there are only eight miners in an average shift work on a 200m to 300m long face.
on it. Orientation parallel to the direction of tensile stress leads to an increase in yield stress\(^{(25,26)}\) and during the post-yield deformation of a glassy polymer strain stiffening (i.e. orientation) occurs. This could be explained as the process of straightening the macromolecules and this becomes more and more difficult (i.e. stiffening). These effects have been represented by models.\(^{(27,28)}\)

It can be suggested that the optical retardation observed may be associated as residual stress or molecular orientation or both depending on the treatment given to the polymer.

The questions (a) has the term 'stress' in residual stress the same meaning as the word stress used generally, (b) does molecular orientation affect residual stress and vice versa, lead to the basic philosophy of the problem, i.e. can molecular orientation be treated separately from residual stress? Although this question is of some difficulty I would like to suggest not: molecular orientation and residual stress being a basic manifestation of change in molecular configuration when the polymer changes from a liquid state to a solid state.

4.7 SUMMARY

Molecular orientation and residual stress are critically dependent on mould temperature, cold moulding leading to a high degree of molecular orientation and residual stress, and hence undesirable properties (i.e. low impact strength, crazing etc.). The high birefringence observed appeared to be predominantly due to molecular orientation although an appreciable degree of residual stress was observed. A change in direction of the melt flow in the mould was found to cause a considerable extent of molecular orientation, thus reflecting the importance of mould design. The
of vital importance to use the correct processing conditions, mould
design etc. in injection moulding of PC, coupled with adequate
mechanical testing (e.g. impact strength), and photoelastic analysis
of test mouldings in order to ensure the quality of the final product.
These aspects are often overlooked by the manufacturers, sometimes
leading to disastrous consequences.

4.8 FURTHER WORK

(i) A surface coating more resistant to the polishing reagent
could be developed and residual stress measurements using
the layer removal technique as described in Section 4.3
may be conducted. In the above experiment it would be
interesting to measure optical retardations in the
through thickness direction (a) after the removal of
each layer; (b) after the removal of each layer and on
applying force in order to straighten the sample (the
sample would most probably be curved due to the removal
of the compressive surface layer); thus, introducing
an equivalent amount of stress as that the sample
would have experienced by the removed layer.

(ii) More conclusive measurements on (a) birefringence
perpendicular to the through thickness direction and
(b) residual stress measurements by cutting or scratching
described in Sections 4.6.2 and 4.6.3 respectively.

(iii) To conduct solvent crazing experiments (a) using different
parts of a moulding; (b) using mouldings of different
moulding conditions.
APPENDIX 4.1

DETERMINATION OF THE STRESS-OPTICAL COEFFICIENT

Although a tensile or compression test seems convenient for measuring the stress-optical coefficient, difficulties of ensuring precise axial load may arise\(^{(9)}\) and hence a simple disc in diametrical compression was used.\(^{(2)}\)

The change in optical retardation on loading was measured using circularly polarised white light and a Babinet compensator as described in Section 4.2.2.2. A plot of the fringe order versus force, gave a gradient of 0.01476 fringes per Newton. For diametrical compression

\[
(\Delta \sigma) = \frac{8P}{\pi dt} \quad (4.13)
\]

where \(\Delta \sigma\) is the difference in principal stresses due to the loading \((P)\)

\(d\) is the diameter of the disc

and \(t\) the thickness\(^{(2)}\).

Now optical retardation

\[
(R) = (\Delta \sigma) c t \quad (4.14)
\]

where 'c' is the stress optical coefficient. From equations (4.13) and (4.14)

\[
R = \frac{8P}{\pi d c} \quad (4.15)
\]

i.e.

\[
n = \frac{c8}{\pi d \lambda} P \quad (4.16)
\]

where \(R = n\lambda\)
d was measured to be 0.03 m

λ was taken to be 575 x 10^{-9} m

and using equation (4.12)

c was calculated to be 7 x 10^{-11} m^2 N^{-1}.

This value corresponds very closely to that observed previously (8 x 10^{-11} m^2 N^{-1} when λ = 589 x 10^{-9} m). (10)
APPENDIX 4.2

PHOTOELASTIC ANALYSIS OF CRASH HELMET VISORS

Six motorcycle crash helmet visors made of extruded Poly(bisphenol-A carbonate) sheet were used in this investigation and their physical properties are as in Table (4.2). It was observed that some visors (see Table 4.2) contained assembly stresses due to the rivets. The surface of all visors were scratched to different extents as shown in Table (4.2). Figures (4.28) to (4.30) show the visors photographed in white light and Figures (4.31) to (4.33) show the isochromatics of the six PC visors, obtained by using circularly polarised white light in transmission (see Sections 4.2.1 and 4.2.2). More accurate measurements of optical retardation were done by using a Babinet Compensator (see Section 4.2.2.2) and its results are as in Table (4.2)*. The visors were also bent to the same extent as they would be in actual use with a crash helmet and optical retardations were measured. These results are tabled in the columns labelled 'stressed' in Table (4.2).

The edges of the visors were found to be rough and the surface roughness was estimated using interferometry (see Section 3.2.3). Interferograms of the edges of visors are shown in Figure (4.34) and the surface roughness varied up to 6 μm.

The poor quality of the visors is due probably to a combination of reasons: (a) molecular orientation and residual stress; (b) stress concentrations at the edges of the moulding and this is due to damage during the normal use of the visor; (c) assembly stresses due

* Analysis of the birefringence data must be treated with caution, due to the complications of surface coatings and self colour of the visors.
## OPTICAL RETARDATION IN POLYCARBONATE VISORS

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Colour and Type of Visor</th>
<th>Surface Condition</th>
<th>Assembly Stress due to Rivets</th>
<th>Maximum Retardation (meters/mm) x 10^-7 Unstressed</th>
<th>Maximum Retardation (meters/mm) x 10^-7 Near Rivets Unstressed</th>
<th>Maximum Retardation (meters/mm) x 10^-7 Near Rivets Stressed*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Transparent, Everoak Casquette Standard Lexan</td>
<td>D</td>
<td>Minimal Assembly Stress</td>
<td>4.61</td>
<td>7.73</td>
<td>5.38</td>
</tr>
<tr>
<td>2</td>
<td>Smoked, Unmarked</td>
<td>E</td>
<td>Minimal Assembly Stress</td>
<td>5.81</td>
<td>5.83</td>
<td>7.74</td>
</tr>
<tr>
<td>3</td>
<td>Transparent, Everoak Casquette MR 400 Coated Mar Resistant</td>
<td>B</td>
<td>Minimal Assembly Stress</td>
<td></td>
<td>Very high optical retardation ranging for 15 x 10^-7 to 30 x 10^-7 meters/mm</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Yellow, Griffin Shatterproof</td>
<td>C</td>
<td>Assembly Stress Present</td>
<td>4.28</td>
<td>9.03</td>
<td>2.6</td>
</tr>
<tr>
<td>5</td>
<td>Black Unmarked</td>
<td>F</td>
<td>Assembly Stress Present</td>
<td>2.96</td>
<td>3.48</td>
<td>3.40</td>
</tr>
</tbody>
</table>

* The term 'stressed' refers to a situation when the visors are bent, as when used in conjunction with a crash helmet.
to the rivets; (d) the effect of various crazing agents that may come into contact with the surface during use. However, it must be mentioned that the visors that were surface coated reduced the effects due to (b) and (d), to some extent but may have caused different problems.

It is clearly necessary to investigate further the problem (e.g. photoelastic measurements perpendicular to the through thickness direction etc.) before a conclusive analysis could be attempted.
REFERENCES

1. 'Investigations of impact strength of polycarbonate Miners battery boxes; (Summary report for the National Coal Board (Scotland), September 1978), P.R. Lewis, The Dept. of Material Science, The Open University, Walton Hall, Milton Keynes.


8. Private communication, The Technical Director, Oldham and Son Ltd., Denton, Manchester.


15. J.R. White, Fourth International Conference on Deformation, Yield and Fracture of Polymers, April 1979, 8.1.


22. Private communication, Dr P. Lewis, Department of Materials Science, The Open University, Walton Hall, Milton Keynes.


When a polarized beam (P) propagates through a transparent plastic of thickness, t, where x and y are the directions of principal strains at the point under consideration, the light vector splits and two polarized beams are propagated in planes "x" and "y".

Figure (4.1) (After photoelastic inc., 4)
Adding quarter-wave plates in the path of light propagation, transforms the instrument into a "Circular Polariscope". The emerging light intensity is now independent of the direction of principal stresses:

\[ I = a^2 \sin^2 \frac{\delta}{\lambda} \]  
(See Figure 3)

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**CIRCULAR POLARISCOPE**

Figure (4.2)  (After photoelastic inc., 4)
CONSTRUCTION OF POLISHING TANK

STAINLESS STEEL BAFFLE

GLASS TANK

SPECIMEN

CIRCULATION HOLES

FLOW PATTERN IN TANK

FIGURE (4.3)
Figure 4.4 The definition of the part numbers and the expected 'simple mould filling'.
(The melt flow may tend to be more complex at the belt loops, along edges and on part 5 of the moulding)
Figure (4.5) A sequence of birefringence photographs with progressive chemical milling of part '2' (see Figure 4.4) of both mouldings H and L using monochromatic plane polarized light in transmission
Figure (4.7) Birefringence photographs of part 'l' (see Figure 4.4) of both mouldings 'H' and 'L' obtained using circularly polarized white light in transmission after chemically milling by 0.2 mm
Figure (4.8) Birefringence photographs of part '1' (see Figure 4.4) of both mouldings 'H' and 'L' obtained using circularly polarized white light in transmission after chemically milling by 0.4 mm
(a) sample box injected into 60/70°C mould with (b) 0.43 mm (c) 1.3 mm (d) 1.8 mm removed by chemical milling

Figure (4.6) A sequence of birefringence photographs with progressive chemical milling of part '3' (see Figure 4.4) of moulding 'L' using monochromatic plane polarized light in transmission.
Figure (4.10) Birefringence photographs of part '1' (see Figure 4.4) of both mouldings 'H' and 'L', obtained using circularly polarized white light in transmission after chemically milling by 1.7 mm.
Figure (4.11) Birefringence photographs of the shaded area in part* '1' of both mouldings H and L obtained at a magnification of four using circularly polarized white light in transmission after chemically milling by 0.2 mm

* Part numbers are as in Figure (4.4) and Figure (4.15) shows a detailed diagram of part '1'
Figure (4.12) Birefringence photographs of the shaded area in part* '1' of both mouldings H and L obtained at a magnification of four using circularly polarized white light in transmission after chemically milling by 0.4 mm

* Part numbers are as in Figure (4.4) and Figure (4.15) shows a detailed diagram of part '1'
Figure (4.13) Birefringence photographs of the shaded area in part* '1' of both mouldings H and L obtained at a magnification of three using circularly polarized white light in transmission after chemically milling by 1.2 mm

* Part numbers are as in Figure (4.4) and Figure (4.15) shows a detailed diagram of part '1'
Figure (4.14) Birefringence photographs of the shaded area in part* '1' of both mouldings H and L obtained at a magnification of five using circularly polarized white light in transmission after chemically milling by 1.7 mm

* Part numbers are as in Figure (4.4) and Figure (4.15) shows a detailed diagram of part '1'
Figure (4.15) A detailed diagram of part '1' as defined in Figure (4.4) which notes the following:

(a) The numbering is to identify specific points at which optical retardations were made (see Figures 4.16 to 4.19)

(b) The oval shapes shown are the areas in which the belt loops were connected to the lamp (see Figure 4.4)

(c) The shaded area was used to measure optical retardation as in Figures (4.11) to (4.14)

(d) The areas marked A'B'C'D' and BCEH were cut and used for "residual stress measurements" and "optical retardation measurements in the through thickness direction" respectively.
The graphs show the changes in optical retardation on progressive chemical milling of the mouldings. The specific points at which the measurements were conducted are labelled either 'L' or 'H' followed by one or two digits (e.g. L₁, H₁). The digit defines the position of measurement as in Figure (4.15) while L or H defines the moulding conditions of the sample as in Section 4.5.
The graphs show the changes in optical retardation on progressive chemical milling of the mouldings. The specific points at which the measurements were conducted are labelled either 'L' or 'H' followed by one or two digits (e.g. \( L_1, H_2 \)). The digit defines the position of measurement as in Figure (4.15) while 'L' or 'H' defines the moulding conditions of the sample as in Section 4.5.
The graphs show the changes in optical retardation on progressive chemical milling of the mouldings. The specific points at which the measurements were conducted are labelled either 'L' or 'H' followed by one or two digits (e.g. L1, H12). The digit defines the position of measurement as in Figure (4.15) while L or H defines the moulding conditions of the sample as in Section 4.5.

FIGURE (4.18)
The graphs show the changes in optical retardation on progressive chemical milling of the mouldings. The specific points at which the measurements were conducted are labelled either 'L' or 'H' followed by one or two digits (e.g. L₁, H₁₂). The digit defines the position of measurement as in Figure (4.15) while L or H defines the moulding conditions of the sample as in Section 4.5.
Figure (4.21) Optical retardation measured* as indicated in Figure (4.20) at a magnification of seven

Figure (4.22) Optical retardation measured* as indicated in Figure (4.20) at a magnification of twenty five

* The sample used is the section BCEH as defined in Figure (4.15) of the moulding 'L' (as defined in Section 4.5)
Birefringence measurement perpendicular to the direction of through thickness (as shown in Figure 4.20) for the moulding 'L' (defined in Section 4.5)
Figure (4.24) The change in isochromatics on cutting and scratching of the sample 'PQRS' as defined in Figure 4.15* for the moulding 'H'**

Figure (4.25) The change in isochromatics on cutting and scratching of the sample 'PQRS' as defined in Figure 4.15* for the moulding 'L'**

* Figure 4.15 is taken as the detailed diagram of part '2' (part number defined in Figure 4.4) in this instance.
** See Section 4.5.
Change in residual stress of both mouldings through its thickness (see Section 4.5.4)
Figure (4.27) The failure rate of PC miners' lamps in a Lancashire Colliery from 1973 to 1978 (after Lewis; 1,22)
Figure (4.28) Visors 1* and 2* photographed in white light

* Sample numbers are defined in Table 4.2.
Figure (4.29) Visors 3* and 4* photographed in white light

* Sample numbers are defined in Table 4.2
Figure (4.30) Visors 5* and 6* photographed in white light

* Sample numbers are defined in Table 4.2
Figure (4.31) Isochromatics of Visors 1* and 2*

* Sample numbers are defined in Table 4.2
Sample 3*

Figure (4.32) Isochromatics of Visors 3* and 4*

* Sample numbers are defined in Table 4.2
Figure (4.33) Isochromatics of Visors 5* and 6*

* Sample numbers are defined in Table 4.2
Figure (4.34) Interferograms of the edges of Visor 1*

* Table 4.2 defines the numbering of the visors
Figure 4.35(a)  SIMPLE MOULD FILLING

Figure 4.35(b)  JETTING IN MOULD FILLING