Effect of thermal history on the morphology of thermotropic liquid crystalline copolyesters based on PET and PHB

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Morphological studies were carried out on thermotropic liquid crystalline copolyesters based on poly(ethylene terephthalate) (PET) and para-hydroxybenzoic acid (PHB), where PHB content varied from 30 mole percent up to 80 mole percent. The technique of chemical etching, using n-propylamine as the etchant, coupled with scanning electron microscopy was utilized to obtain structural information. Scanning electron microscopy results on chemically etched, compression moulded films show that selective chemical etching of the PET rich regions occur. This indicates that the morphology of the copolymers is hetergeneous in nature. Further support regarding a hetergeneous morphology was obtained by transmission electron microscopy. A morphological model has been proposed based on these results. The observance of non-equilibrium behaviour associated with amorphous PET regions (as seen from d.s.c. measurements) also strongly indicates the presence of a phase rich in PET and thus supports the non-homogeneous morphological model. Thermal analysis of these copolyesters suggests that the chain structure is non-random and this is an agreement with results published by Wunderlich *et al.* The glass transition temperature typically associated with PET is present and remains constant in all copolymers compositions where PET is the continuous phase. Further, the melting temperatures obtained experimentally are higher than the values predicted by theory for random copolymers and the melting endotherms are relatively narrow. These observations also indicate a non-random chain structure. Structural studies conducted on films compression molded at different temperatures show that morphological rearrangement occurs at higher temperatures with the formation of domains of the order of 10 microns.

(Keywords: liquid crystalline polymers; thermotropic; morphology; poly(ethylene terephthalate); para-hydroxybenzoic acid)

INTRODUCTION

Considerable research has been performed on polymeric systems that exhibit liquid crystalline or mesomorphic behaviour. Initially, the principal reason for this effort was that these materials might be developed as ultra-high strength and ultra-high modulus systems[1-10]. While these systems display liquid crystalline nature due to the rigid or semi-rigid polymeric backbone, there is also considerable interest in polymeric liquid crystals where the inducement of ordering extends from mesogenic side groups in contrast to that of the backbond[11-16,20]. These latter systems, however, are typically not investigated for the purpose of ultra-high strength nor modulus but have other possible unique applications, e.g. electro-optical, which are not to be considered in this paper. Our principal aim is to focus on the first type of polymeric liquid crystalline system and more specifically, on a series of copolyesters based on poly(ethylene terephthalate) (PET) and para-hydroxybenzoic acid (PHB).

The term liquid crystal refers to a state intermediate between the isotropic fluid and the three-dimensionally ordered crystalline state[2]. The first observation of this phenomenon was made by Ritizner in 1888[17] and the term liquid crystalline behaviour was introduced soon afterward by Lehmann[18]. A conventional view of liquid crystalline order is that it possesses many of the characteristic mechanical properties of fluids yet has a sufficient degree of molecular order so as to diffract X-rays according to Bragg's law. Hence, this texture is more rightly denoted as a mesophase[19]. Liquid crystalline order is commonly classified into one of the three general well known types of mesomorphic arrangements: nematic, smectic and cholesteric as shown in *Figure 1*. However, identification of these specific phases is not generally an easy task, particularly in macromolecular systems.

After the early work of Robinson and others[21-23] on lyotropic synthetic polypeptides, another group of lyotropic spinnable systems emerged, those based on the aromatic polyamides commercially known as the Aramides® and introduced by DuPont. Related efforts on lyotropic polymeric liquid crystalline systems were also promoted by workers at Monsanto but commercialization was never developed[1].

In 1976 Jackson and Kuhfuss[3] from Tennessee Eastman demonstrated that thermotropic liquid crystalline behaviour existed in copolymers based on poly(ethylene terephthalate) and para-hydroxybenzoic acid. In these copolymers, while PET has a flexible chain conformation, the polymer of PHB has a stiff rodlike conformation and upon polymerization promotes the develop-

ment of mesophase formation. These same workers have reported that processing of these systems can lead to highly anisotropic fluids whose melt viscosity behaves in a anomalous way when contrasted with conventional thermally processable flexible chain polymers. Specifically, *Figure 2(a)* shows that the melt viscosity starts to decrease approximately at a PHB value of 30 mole per cent due to the onset of liquid crystalline order with the lowest viscosity being present at about 60 mole per cent PHB. It is noted that the viscosity decreases by an order of magnitude over this composition range but that above this range, the viscosity again begins to increase. The latter rise is due to the presence of PHB crystallinity which does not totally melt at 275°C. The anisotropic nature of these materials following injection moulding and solidification is evident from the data presented in *Figure 2(b)* which was obtained on the 60 mole per cent PHB copolymer. The effect of specimen thickness on flexural modulus is clear in this figure. While injection moulding of flexible chain polymers often lead, under similar moulding conditions, to anisotropic materials caused by molecular orientation, the level of anisotropy is never of the magnitude observed for the mesophase systems described here.

Regarding the chain structure of these materials, it has been suspected that they are rather random in nature as is reported by McFarland et al. from Tennessee Eastman[4]. Specifically they have suggested that based on n.m.r. data, these liquid crystalline copolyesters have a completely random chain structure that is induced during the high temperature melt interchange reaction[4]. However, thermal studies performed by us and by Wunderlich et al.[25,26] strongly indicate that these materials may be somewhat non-random with respect to chain structure. It might be added here that recent morphological studies of Joseph et al.[24,29] on these same polymers also indirectly suggested possible non-random character of the chain structure. Further, morphological studies performed by Zachariades et al.[27,28] on the 80% PHB copolymer indicated heterogeneous morphology.

It is clear from the literature that while the area of liquid crystal polymers is of strong interest, there have been relatively few morphological studies carried out on polymer systems that display thermotropic behaviour and *more specifically*, how this texture may be altered by or correlated to thermal history and processability. The effect of processing conditions is of particular importance in view of the fact that it is well known that the texture of low molecular weight mesophase systems is very sensitive to deformation history[5]. The goal of this paper is to
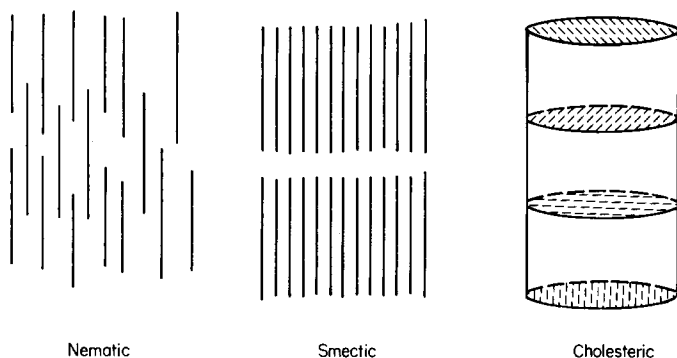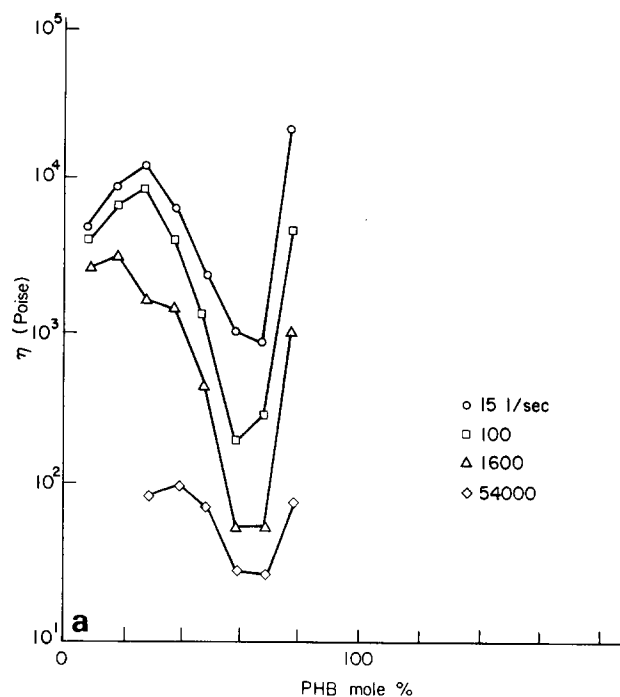

Figure 2(a)   Melt viscosity at 275°C of PET modified with different levels of p-hydroxybenzoic acid[3]
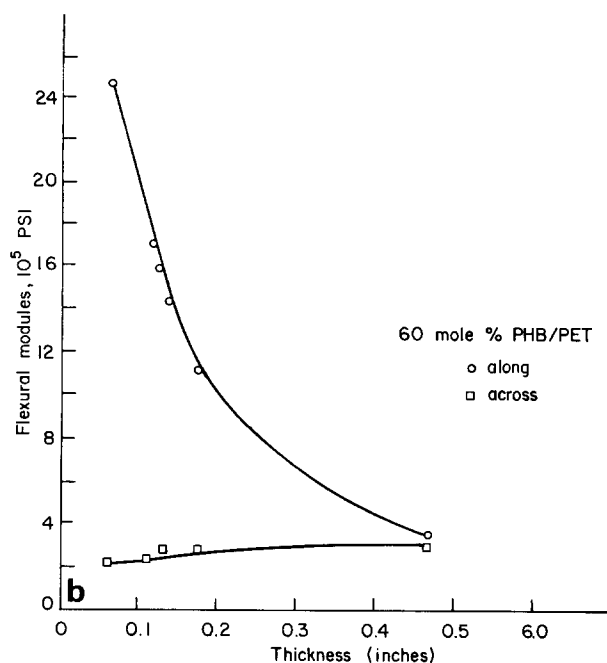

Figure 2(b)   Effect of specimen thickness on flexural modulus along the flow and across the flow direction for PET modified with 60% PHB[3]

provide some understanding on the effect of thermal history on the final bulk textures. The effect of processing conditions on the bulk morphology has also been investigated and appears in another publication[30].

In contrast to the conventional flexible chain crystalline polymers, the morphological textures of polymeric liquid crystalline systems tend to be difficult to investigate by optical microscopy or some other related rheo-optical methods. This is due to the extremely high turbidity that these materials tend to display. The high turbidity is due to the high optical anisotropy that exists within these materials which may fluctuate in direction and degree over a scale very comparable with that of the wavelength

Figure 1   Three generalized forms of liquid crystalline order. (a) Nematic, (b) smectic, and (c) cholersteric

of light. Optical rotation effects, if present, can also influence optical anisotropy. In brief then, while use of such techniques as hot stage microscopy, small-angle light scattering, birefringence or linear dichroism have provided some information concerning changes in morphological texture that may occur with temperature for the thermotropic polymeric systems, they have not been particularly useful in terms of investigating processed materials due to a much higher degree of film or specimen thickness. Electron microscopy methods have also not been particularly revealing to date with regard to the nature and homogeneity of the textures that develop in these systems, although they have been utilized to some degree[27,49,50]. Our approach in this paper is to use a related method in conjunction with microscopy to help elucidate further detail concerning morphology. Specifically we have used selective chemical etching to preferentially degrade the PET component in an attempt to obtain information about the homogeneity of these materials.

Chemical etching techniques were first developed for the analysis of cellulose where the material was etched by acid hydrolysis in water and ethanol at 80°C to 100°C[31]. Then, using weight loss measurements and X-ray diffraction Baudisch et al.[32] obtained information about the crystal structure of native cellulose and regenerated cellulose. In the case of semi-crystalline polyolefins, the polymeric backbone is highly stable and a different approach is required for etching. It was first shown that oxidation with fuming nitric acid is selective enough to obtain information concerning differences in the amorphous and crystalline regions of crystalline polyolefins[33]. Many such studies have been carried out since that time to help elucidate the nature of chain folding, fold thickness and adjacent chain re-entry[34,35]. More recently Chu and Wilkes[36] as well as Adams[37] have utilized the technique of chemical etching to study the bulk morphology of semi-crystalline PET by using n-propyl amine as the etching reagent. These researchers used this etching reagent to preferentially degrade the amorphous PET regions and provide some information concerning the remaining crystalline substrate. Others have also utilized low molecular weight amines for studies of the morphology and degradation effects in PET[38]. In addition, use of aqueous ammonia has been applied to the PET/PHB copolymers in the recent work of Zachariades et al.[27]. Their goal was to selectively attack and remove PET as is the objective of our own work to be described. In the investigations presented here concerning the mesogenic PET–PHB copolyester, we will greatly depend upon the chemical etching technique with n-propyl amine. We have demonstrated, however, that other related amines can function in a similar manner. Specifically, the amine component has the capabilities of attacking the PET segments leading to chain sission whereas it does not seem to function as an etchant for PHB.

EXPERIMENTAL

Materials

The chemical structure of the PET/PHB copolyester systems used in this study is given in *Figure 3*. Values for m and n vary as the PHB content changes. For example, when $m=0.3$ and $n=0.7$, it would indicate a 30 mole% PHB–70 mole% PET material. Samples of these copolymers
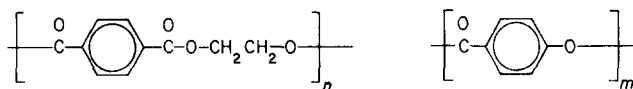
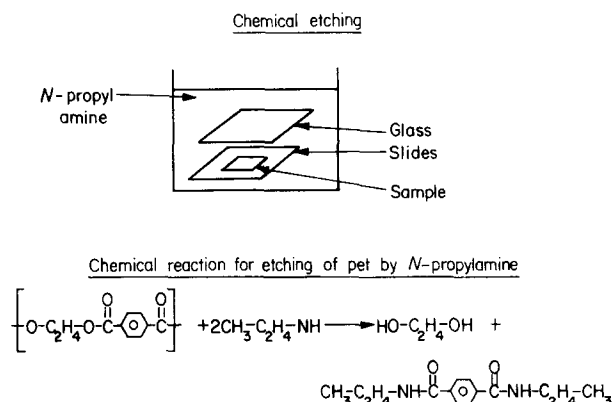**Figure 3** General chemical structure of the PET/PHB copolyesters studied

Figure 4 Schematic diagram for apparatus used for contact chemical etching and the chemical reaction for etching of PET by n-propylamine

with PHB content varying from 30 mole% to 80 mole% were obtained directly in powder or pellet form from Tennessee Eastman Company. Pure PET obtained from Tennessee Eastman and PHB obtained from Carborundum Company were also used as controls.

Details on the synthesis of the copolymeric materials are given in an earlier paper by Jackson et al. and therefore will not be repeated here[3]. To minimize hydrolysis by moisture sorption, all samples were heated in a vacuum oven at 100°C for approximately 72 h prior to being compression moulded into thin films. The 30 mole% PHB to 60 mole% PHB materials were moulded at three different temperatures, 235°C, 260°C and 285°C with the materials being held at the moulding temperature for a total time of approximately 10 min. This enabled the investigation of the effect of thermal history on the morphology. The 80 mole% PHB material required a higher temperature for flow and was compression moulded only at 285°C. The films were quenched in an ice-water bath upon removal from the press. The thickness of the films ranged from 4–7 ml. Solution cast films of the 60 mole% PHB material were also obtained. The pellets were dissolved in trifluoroacetic acid (TFA) at room temperature for apparoximately 12 h and cast in a Teflon mould at room temperature. In order to verify if degradation of the copolymer occurs in the presence of TFA, H^1 n.m.r. studies have been carried out on the copolymer/TFA solution. Initial results indicate that no noticeable degradation occurs when the copolymer is exposed to the solvent for approximately 12 h.

Procedures

Figure 4 shows schematically the apparatus used for the etching studies and was described earlier by Chu and Wilkes[36]. The sample is sandwiched between two glass slides, which in turn is placed inside a petri dish containing n-propyl amine. The petri dish is covered and due to the toxic nature of the amine fumes, is placed in a hood for the desired amount of time. Finally, the sample is removed, rinsed in cold water and dried. The stoichiometric equation which describes the chemical reaction of etching PET

by n-propylamine is also shown in *Figure 4*. The ester linkage in the PET molecule undergoes scission by aminolysis[36] and in the presence of excess amine, ethylene glycol and *N,N*-dipropylterephthalamide are formed. Also, these products are soluble in the presence of excess amine. The liquid crystalline copolyesters were etched by n-propylamine for approximately 2 h. In order to investigate the effect of etching time, similar compression moulded films were also etched for longer periods of time ($\simeq 28$ h). The lower PHB content films, i.e. $\leqslant 50$ mole% PHB, disintegrated but did not dissolve when etched for 28 h. No difference in etching behaviour was seen for the higher PHB content materials when etched for longer periods of time.

Techniques used for characterization

The morphological textures of the etched samples were studied using an ISI super III-A scanning electron microscope and a Zeiss polarizing microscope equipped with a Mettler hot stage. Wide-angle X-ray scattering studies were carried out on a Philips PW 1720 Table top X-ray generator system equipped with Warhus cameras using CuKα radiation. Scattering patterns were recorded photographically using a sample to film distance of 5.5 cm, 7.1 cm or 8.0 cm.

RESULTS AND DISCUSSION

Chemical etching and microscopy studies

As mentioned in the Introduction, one of the objectives of this investigation was to obtain morphological information on the PET/PHB copolyesters utilizing the technique of chemical etching. The purpose was to determine if PET rich regions could be etched out by the amine selectively, with etching being a means of detecting homogeneity. Scanning electron micrographs of the PET-/PHB copolyester films compression moulded at 235°C and chemically etched are given in *Figure 5(a)–(d)*. It is apparent from the micrographs that as PHB content increases, less material is etched out by the amine. Specifically, at a PHB content of 40 mole per cent, there appears to have been PET rich regions (regions that are etched away) that are approximately 10–20 microns in size, while in the 80% PHB material the regions that have
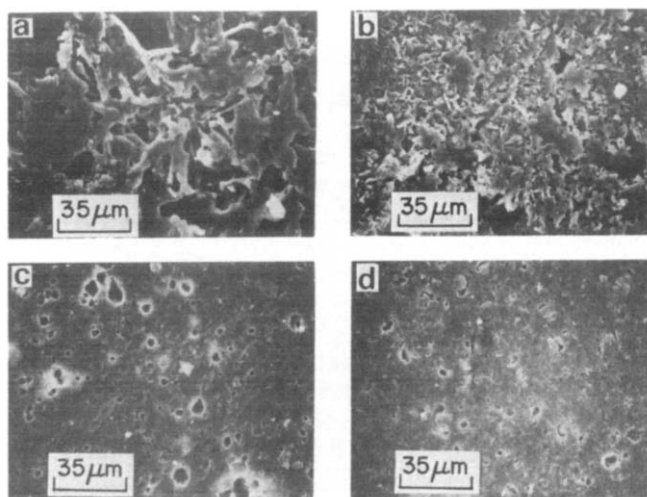
Figure 5 Scanning electron micrographs of PET/PHB copolyester films compression moulded at 235°C and etched in n-propylamine. (a) 40% PHB, etched 2 h; (b) 50% PHB, etched 2 h; (c) 60% PHB, etched 28 h; and (d) 80% PHB, etched 28 h
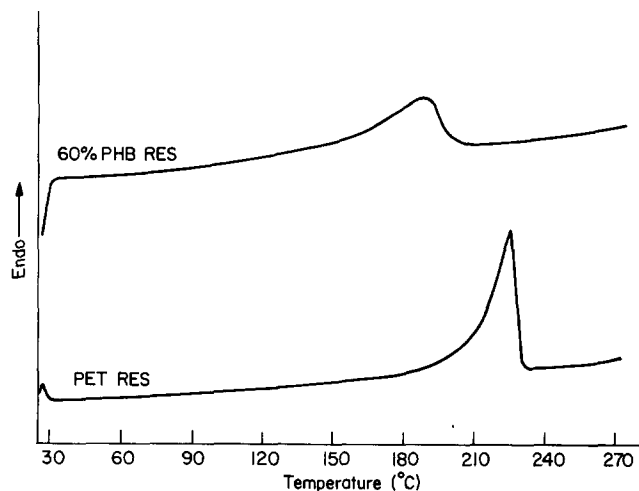
Figure 6 Differential scanning calorimetric scans of PET etched residue and 60% PHB etched residue

been etched out are fewer and are only the order of 3 to 6 microns in size. Qualitatively at least, the degree of etched volume is in line with PET content as it should be if selective etching occurs. However, it is clearly expected that small amounts of PHB will be etched out along with PET, even though no chemical reaction occurs with PHB during the time scale of the etching experiment. This latter point was verified by exposing pure PHB in a powder form to n-propylamine and it was observed by SEM that the powder did not undergo any etching after several hours. In order to verify if any PHB is removed by the amine during the etching of PET, the products of the etching reaction were analysed by d.s.c. The d.s.c. scans of the reaction products of pure PET and the 60 mole% PHB copolyester are given in *Figure 6*. It is evident that the melting temperature of *N,N*-dipropylterephthalamide is lowered in the 60 mole% PHB copolyester residue and is due to a diluent effect caused by the presence of some PHB segments. This helps confirm the speculation that small amounts of PHB are etched out during the reaction between PET and n-propylamine and also suggests the presence of regions that may be 'richer in PET' or 'richer in PHB'.

The electron micrographs of the etched film surfaces clearly suggest a non-homogeneous morphological texture which indicates a two phase structure for these copolyester systems. Menzel and Wunderlich[25] from d.s.c. studies on the 60 mole% PHB copolymer synthesized at Tennessee Eastman Company concluded that it was non-random in chain structure, while Zachariades *et al.*[27] using transmission electron microscopy concluded that the 80 mole% PHB copolymer had a non-homogeneous morphology. Using the SEM results and the fact that the low PHB content films could be etched for long periods of time, the following conclusion can be made; at low PHB levels (i.e. $\leqslant 50$ mole% PHB), a PET rich phase is the continuous phase while at PHB levels equal to or greater than 60 mole%, it is the PHB rich phase that appears to form more of a continuous matrix. *Figure 7* shows first approximation morphological models that have been proposed earlier by the authors for two different levels of PHB[24]. They qualitatively account for the etching behaviour and SEM observations of these compression moulded films. A somewhat similar morphological model has been proposed by Asada *et al.*[39] that explains the rheological and rheo-optical properties of concentrated

poly(benzyl glutamate) in *m*-cresol. However, it should be pointed out that their system is lyotropic and homogeneous in nature with the domains representing regions of different orientation.

It has been observed by Baird[40] that the rheological properties of the 60 mole% PHB copolymer exhibited different behaviour when the experiment was performed at different temperatures. Hence, it was of interest to verify if the morphological texture of these liquid crystalline copolymers are altered by thermal history. In order to do that, SEM studies were carried out on 60 mole% PHB films compression moulded at 235°C, 260°C and 285°C, prior to and after chemical etching. As mentioned in the Introduction of this paper the 60 mole% PHB material had the most desirable properties in terms of processability and mechanical properties. Hence, more emphasis was placed on analysing this particular material in these studies. *Figure 8* shows the fracture surfaces of the 60 mole% PHB film moulded at 235°C, 260°C and 285°C at two different magnifications. It is clear that the fracture surface of the film moulded at 235°C is distinctly different than the fracture surfaces of the films moulded at the two higher temperatures. In the case of the film moulded at 235°C, a texture that appears to be relatively finer than the
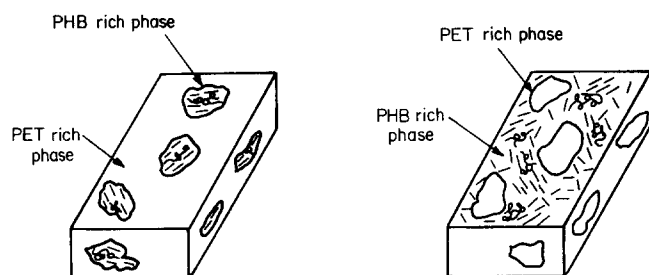
other two textures is observed. Also, a two phase texture appears to be present with one of the phases ranging from 2–10 microns in size (see arrows). Another view of this fracture surface (*Figure 9*) again shows the two phase structure with one of the phases of the order of 2–10 microns in size being present. It is strongly suggested that these regions are associated with partial PHB crystallinity as will be supported by WAXS and d.s.c. results to be discussed later. The fracture surfaces of the films moulded at 260°C and 285°C show textures that are more fibrous or sheet-like, and coarser than the 235°C film texture. It is also apparent that the 2–10 micron size structures that are seen in the film moulded at 235°C are not present in the films moulded at higher temperatures. The reason for this has been attributed to melting of the PHB rich regions which are also semi-crystalline in
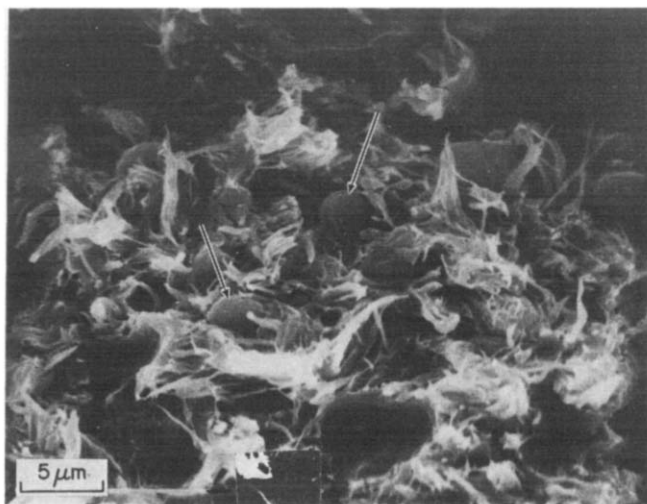

Figure 9 Scanning electron micrographs of the fracture surface of the 60 mole% PHB copolyester compression moulded at 235°C

Figure 7 Simplified molecular model at (a) low levels of PHB, (b) high levels of PHB, based on SEM studies of etched films
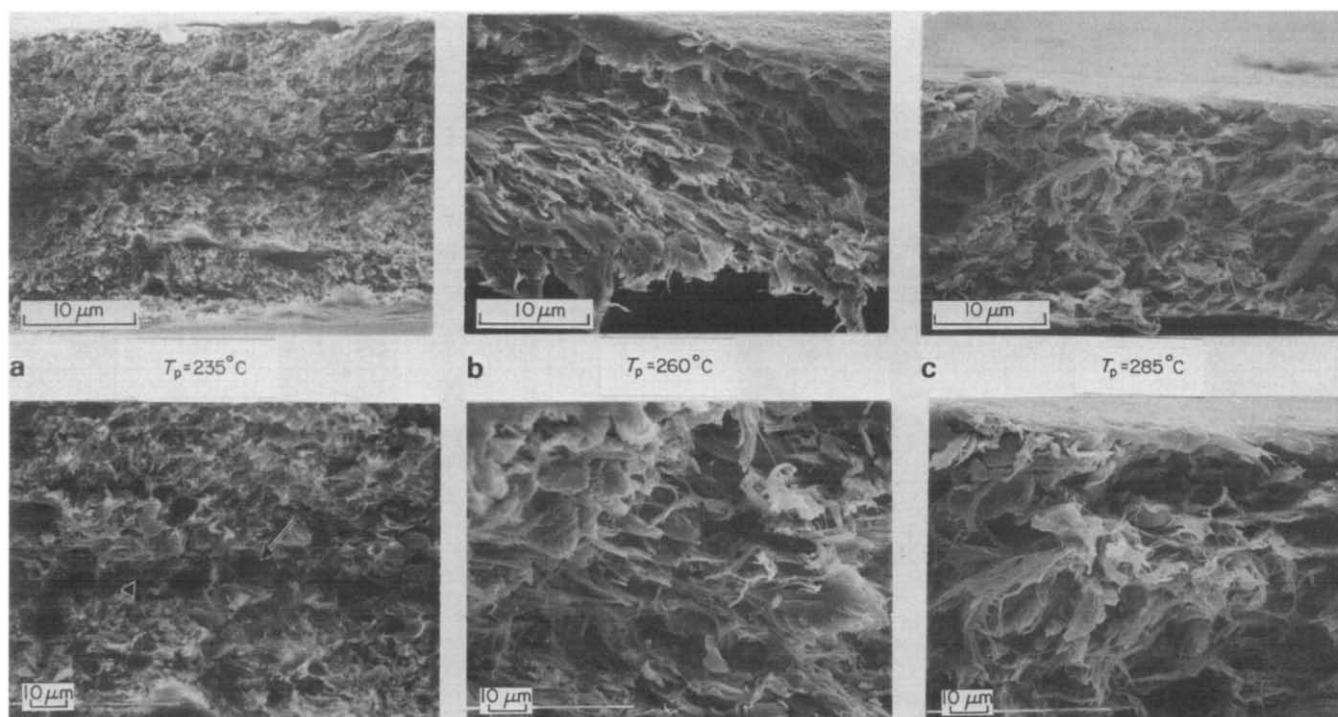

Figure 8 Scanning electron micrographs of the fracture surface of the 60 mole% PHB copolyester compression moulded at (a) 235°C, (b) 260°C, and (c) 285°C. Arrows indicate particulate structure
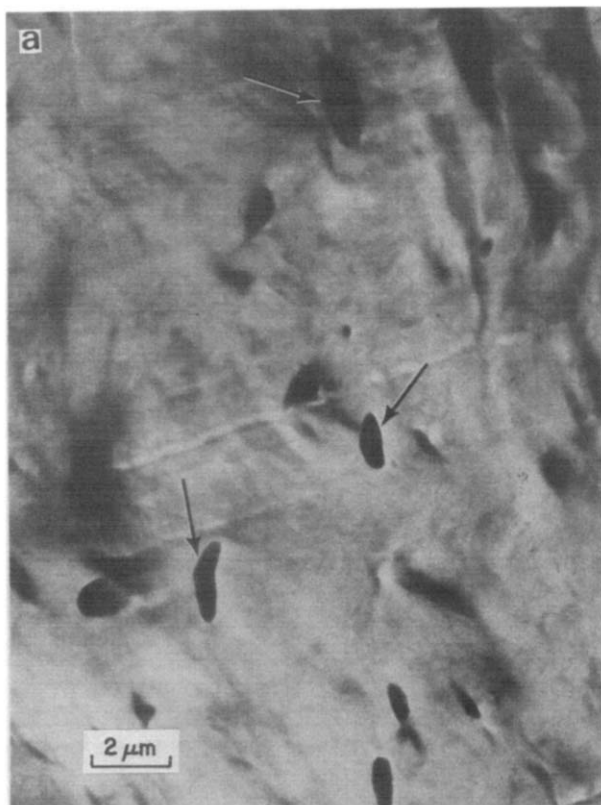
Figure 10(a) Transmission electron micrograph of 60 mole% PHB copolyester compression moulded at 235°C

Figure 10(b) Transmission electron micrograph of 60 mole% PHB copolyester compression moulded at 285°C

nature. The lack of PHB crystallinity at the higher moulding temperatures has been verified by WAXS and d.s.c. while the formation of new morphological textures has been verified by transmission electron microscopy. For example, the 60 mole% PHB material was compression moulded into films at three different temperatures, and analysed directly by TEM without utilizing any staining techniques. The TEM micrographs of the films moulded at 235°C and 285°C are given in Figure 10(a) and (b). The electron micrograph of the film moulded at 235°C shows dark regions that are approximately 1–2 microns in size. This clearly indicates the presence of a two phase structure. The dark phase associated with the structure of the material is shown by the arrows since other dark regions due to microtoming and due to 'curling' of the sample are also present. The electron micrograph of the film moulded at 285°C shows a distinctly different morphological structure. Domains that are approximately 10 microns in size with a slightly 'porous' looking texture are clearly apparent. Also, the one micron size dispersed phase that was observed in the film moulded at 235°C is no longer present. These micrographs suggest that when the 60 mole% PHB is exposed to higher temperatures (i.e. temperatures higher than, for example, 250°C), new morphological textures are formed. These observations strongly support hot stage optical microscopy results which will be discussed later. Specifically, when the 60 mole% PHB material is exposed to similar thermal conditions, the sizes of the domains that form at higher temperatures and seen by transmission electron microscopy are comparable in size to the structures seen by polarized optical microscopy techniques.

In order to understand the non-homogeneity of these liquid crystalline systems as a function of moulding temperature, chemical etching was performed on the 60 mole% PHB films compression moulded at three different temperatures using n-propylamine as the etchant. If selective etching of the PET rich regions occurred then structural differences due to varying moulding temperatures, if any existed, could hopefully be detected. The films were etched for approximately 2 h and the fracture surfaces analysed by SEM. The SEM micrographs of the fracture surfaces after etching are given in *Figure 11*. The film moulded at 235°C has a relatively fine texture, while a coarser structure is present in the films moulded at the higher temperatures. Also, the films moulded at 260°C and 285°C appear to have some layering effect with a 'swiss cheese-like' structure being present in each sheet. This layering effect is clearly apparent when the sample stage is tilted 45° to the electron beam in the SEM and the fracture surfaces then observed (see *Figure 12*). Again, at higher temperatures, melting of any remaining PHB rich semicrystalline regions occur. Upon flowing in the press, the overall material gives rise to a layered structure.

In summary of the already presented data, chemical etching in conjunction with SEM indicate that selective chemical etching of PET rich regions occurs when the PET/PHB copolyesters are exposed to n-propylamine. The SEM micrographs of the etched films show the presence of a heterogeneous morphology. The morphology of these PET/PHB copolyesters is visualized as being composed of a 'PET rich' continuous phase at lower PHB levels and a 'PHB rich' continuous phase at PHB levels equal to or greater than 60 mole%. The trans-
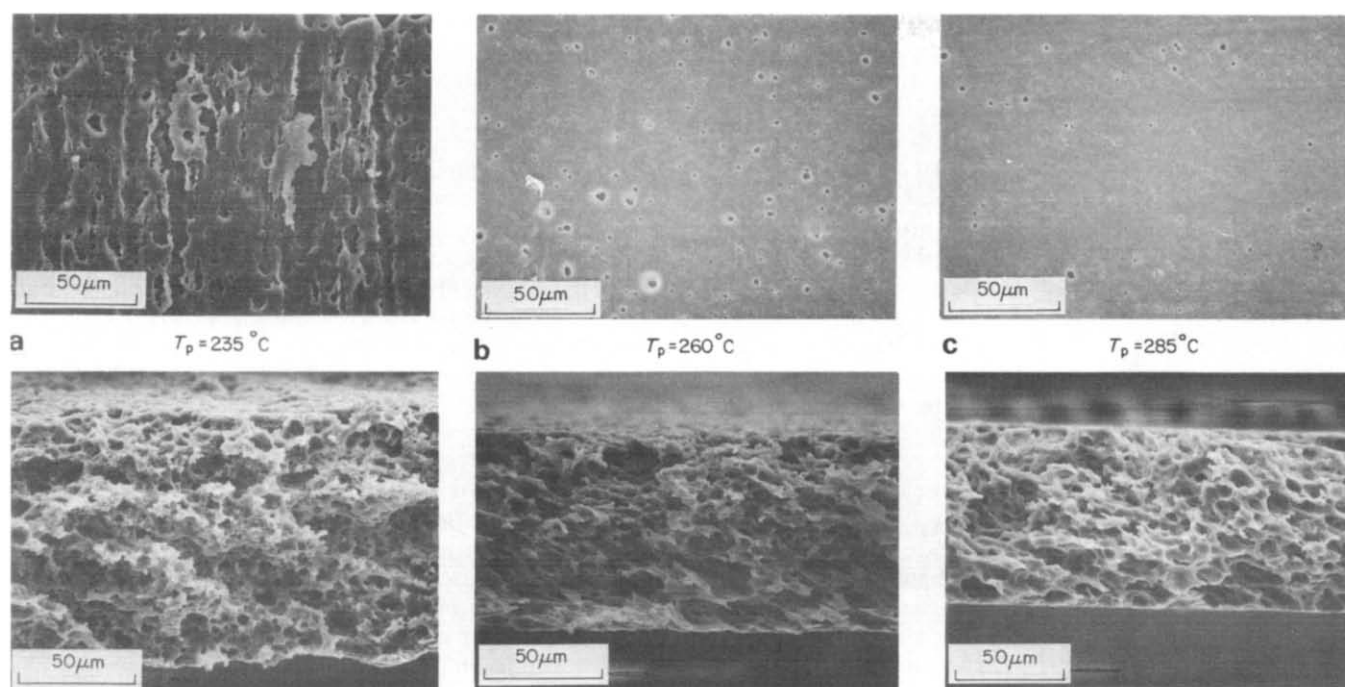
Figure 11 Scanning electron micrographs of the fracture surface of the 60 mole% PHB copolyester compression moulded at (a) 235°C, (b) 260°C, (c) and 285°C, and chemically etched
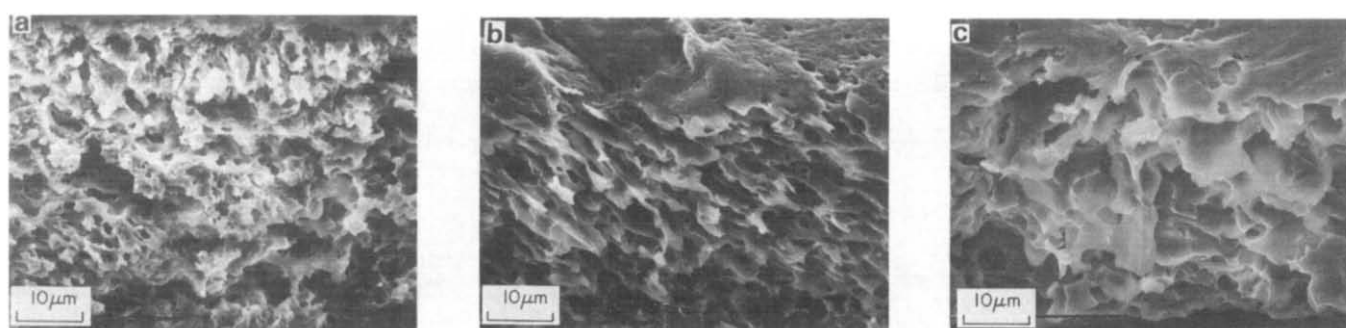

Figure 12 Scanning electron micrographs of the fracture surfaces of the 60 mole% PHB copolyester compression moulded at 235°C, 260°C, and 285°C and chemically etched. The sample stage was tilted 45° to the electron beam when viewing inside the SEM

mission electron microscopy results indicate the formation of new morphological textures with domains on the order of 10 nm, when higher moulding temperatures are used. At these higher moulding temperatures a layered or 'sheet-like' structure is produced as seen by scanning electron microscopy.

Optical microscopy studies

In order to study the morphological textures as a function of temperature, thin microtomed films of the 60 mole% PHB material were heated in a hot stage and observed through a polarizing optical microscope. Optical micrographs were obtained at different temperatures during the heating experiment and are given in *Figure 13*. The sample was heated at 10°/min from room temperature up to 250°C. It is evident that structural rearrangement occurs at about 220°C–225°C and upon further heating, a two phase structure is formed around 235°C. This two phase structure appears more distinct at 250°C. It is speculated that the regions that show more depolarization and have liquid crystalline textures are richer in PHB regions. The areas that appear totally dark are areas (see arrow) where no material is physically present due to separation upon heating. In order to confirm that
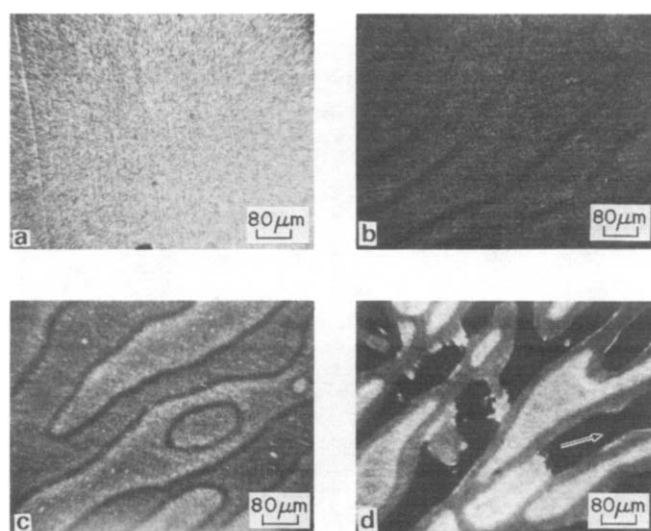

Figure 13 Polarized optical micrographs of a microtomed layer from a 60 mole% PHB injection moulded plaque, taken at different temperatures. (a) Room temp, (b) $T = 220°C$, (c) $T = 235°C$, (d) $T = 250°C$

the totally dark areas do not indeed contain any material, the sample was rotated and tilted between crossed-polars. No depolarization was observed in either case which confirms the absence of, for example, homeotropic textures in the totally dark regions. This sample was then cooled back to room temperature and when the two phase regions are observed under the optical microscope at a higher magnification, a nematic like texture similar to that observed by other researchers[41,42] in thermotropic liquid crystalline polymers becomes readily apparent. *Figure 14(a)* and *(b)* show polarized optical micrographs obtained at higher magnifications and two regions are observed: (i) an area in which a significant amount of depolarization is present (light region) and (ii) an area in which a relatively lower amount of depolarization is present (dark region). The lighter region shows the presence of a uniform liquid crystalline texture similar to that observed in other thermotropic systems. The dark outer regions are also uniform but do not possess the distinct texture that is seen in the lighter regions. This difference in texture in the light and dark areas is caused by a difference in anisotropy, possibly due to differences in the relative amounts of PHB present in each phase.

In order to verify if further molecular rearrangements occurs upon heating, the once heated and cooled sample was again heated in the hot stage at 10°C/min and observed under the optical microscope. When the material was heated up to a temperature of 290°C, the morphological texture shown in *Figure 15(a)* was observed. The two phase regions are still evident but are not

distinctly separated as in the micrographs obtained at 250°C. The material was now cooled down to room temperature and viewed under the optical microscope. The micrograph of this sample is shown in *Figure 15(b)* and again the two phase structure is present. However, as seen in this figure, there appears to be a new level of structure that has formed in the outer region and is superimposed on the already existing texture. Higher magnification optical micrographs of the two phase region are given in *Figure 16(a)* and *(b)* with *Figure 16(a)* representing the outer region and *Figure 16(b)* representing the lighter, inner region. It is clear from the micrograph of the outer region that domains in the 8–12 micron size range with liquid crystalline texture are present. These newly formed domains are in the same size range as those that are seen by TEM in the 60% PHB film compression moulded at 285°C and hence, lend support to the argument that at the higher moulding temperatures new morphological textures are formed. It should be recalled that in the 60% PHB film compression moulded at 235°C, it was not possible to detect any domains in the 8–12 micron size range using TEM. This agrees very well with the optical microscopy since the optical micrographs obtained at 235°C show the absence of domains that are approximately 10 microns in size. However, upon heating to 290°C, morphological rearrangement occurs giving rise to new textures. The optical micrograph of the inner region shown in *Figure 16(b)* shows a texture that is different to that present in the outer region. Again, this difference is presently speculated to be due to differences in the amounts of PHB present in each region.

It can be concluded from hot stage microscopy studies on the 60 mole% PHB thin films that molecular rearrangement begins to occur at temperatures in the range of 220°C–230°C. It is speculated that differences in depolarization that occur due to anisotropy differences are associated with the presence or absence of ordered PHB rich regions. Upon heating the material to higher temperatures, for example 275°C–285°C, further structural rearrangement occurs with domains in the 8–12 micron range with textures similar to nematic-like liquid crystalline systems being formed. These results are in good agreement with the TEM observations in compression moulded films of the same material, which indicate
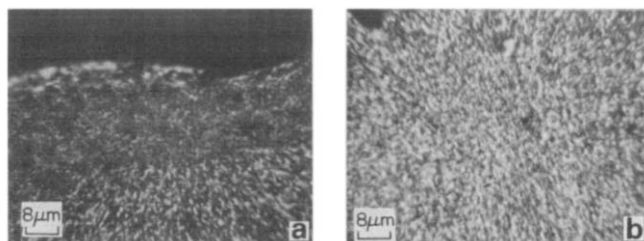

Figure 14(a) and (b) Higher magnification polarized micrographs obtained at room temperature of a microtomed layer from a 60 mole% PHB injection moulded plaque. The sample was heated to 250°C at 10°/min and allowed to cool back to room temperature
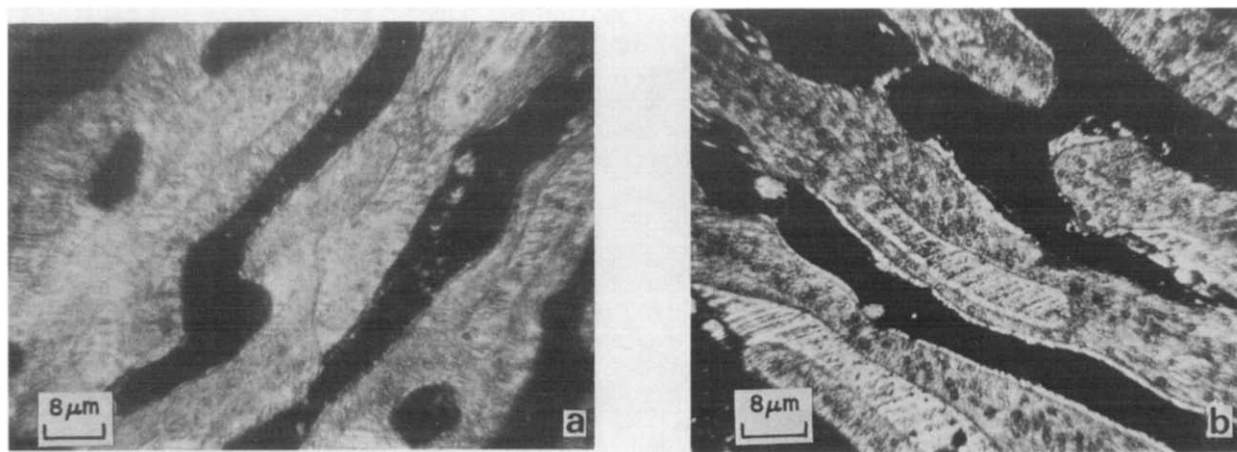
Figure 15 (a) Polarized optical micrograph of a microtomed layer from a 60 mole% injection moulded plaque obtained at 290°C. The material was heated to 250°C and cooled back to room temperature in the first heating cycle. (b) Polarized optical micrograph of a 60 mole% PHB microtomed layer that has been heated to 290°C the second time and cooled to room temperature. The material was heated to 250°C and cooled back to room temperature in the first heating cycle
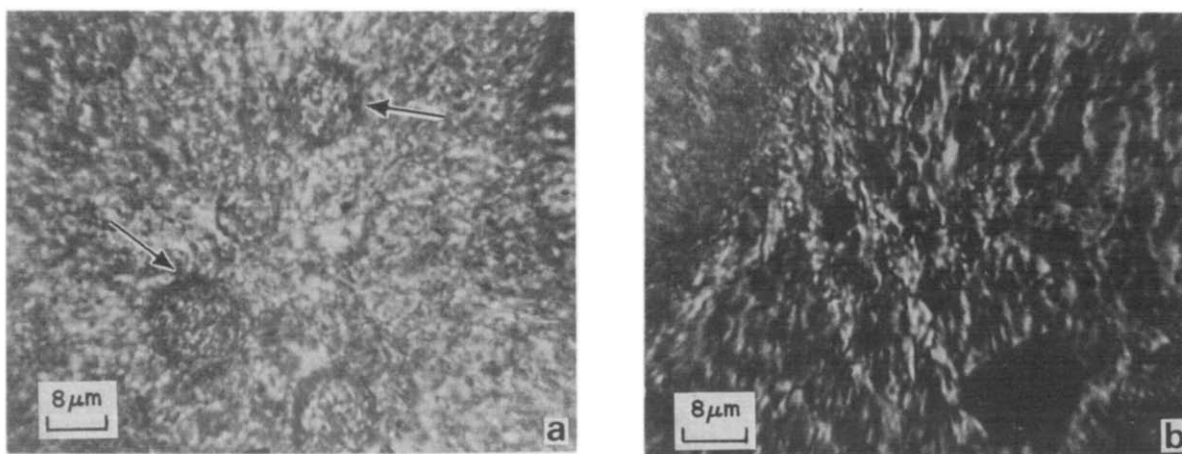
Figure 16 Higher magnification polarized optical micrographs of a 60 mole% PHB microtomed layer that has been heated to 290°C the second time and cooled to room temperature. In the first heating the material was heated to 250°C and cooled back to room temperature. (a) Outer region and (b) inner region
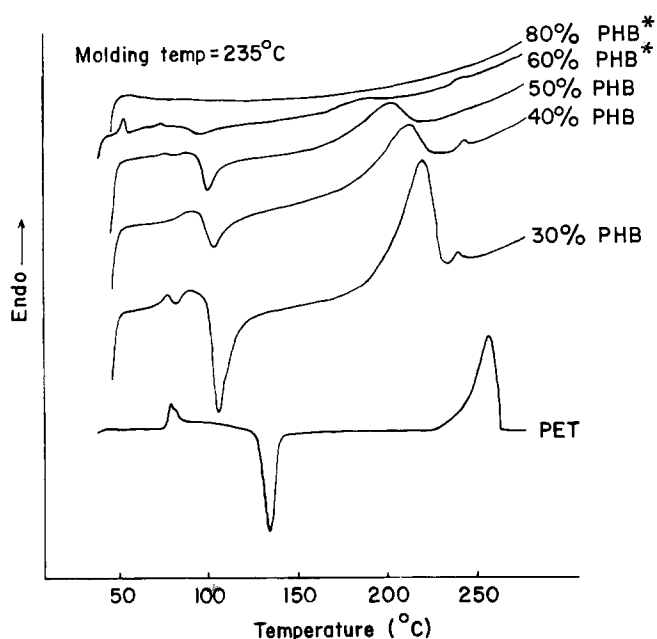

Figure 17 Differential scanning calorimetric scans of PET and the PET/PHB copolyester series. The 80% PHB material was moulded at 285°C while the rest of the copolyesters were moulded at 235°C. *means a high sensitivity was used during the experiment

that domain sizes on the order of 10 microns are formed when higher moulding temperatures are used.

Thermal studies

Differential scanning calorimetric studies were carried out on the compression moulded films in order to obtain information on the thermal transitions of these systems and typical d.s.c. scans are shown in *Figure 17*. For a given material moulded at 235°C, for example, the 30 mole% PHB copolymer, the glass transition temperature (T_g), crystallization temperature (during heating) (T_c) and the melting temperature (T_m) associated with PET are present. The values of these parameters for the PET/PHB copolyester series are given in *Table 1*. As the amount of PHB is increased, no apparent change in the T_g corresponding to PET is observed. This clearly suggests the presence of non-random chain structure since if the system was completely random, one would expect an increase in the

T_g of PET due to the addition of stiff PHB units along the backbone. Similar results have also been reported by Menczel and Wunderlich[25] on the 60% PHB copolymer. In the lower PHB content systems for example, 30% PHB or 40% PHB, an endothermic peak is seen close to the glass transition region. This peak can be attributed to non-equilibrium behaviour of the amorphous PET regions and is similar to the results reported by Tant and Wilkes[41]. That is, when compression moulded films are rapidly quenched from the melt to below T_g, there is a decrease in molecular mobility due to the rapid increase in viscosity. Therefore, the molecules do not reach their equilibrium conformation with respect to temperature and are 'frozen' into a non-equilibrium state. Although the molecular mobility is significantly lower in the glassy state, when compared to the rubbery region, it is finite, and hence the molecules will approach the equilibrium state. This approach to the equilibrium state can be monitored by d.s.c. measurements, where the exotherm observed near the T_g can be correlated with the amount of recovery toward equilibrium. *The presence of non-equilibrium behaviour associated with amorphous PET regions also strongly indicates the presence of a phase rich in PET and supports the non-homogeneous morphological model mentioned earlier.*

In analysing the crystallization behaviour of these compression moulded and quenched films during the heating experiment in the d.s.c., two phenomena are observed. First, as PHB content increases it is apparent that the enthalpy of crystallization and hence, the degree of crystallization decreases systematically. This result is not surprising since the observed crystallization is due to PET and, as the PET content is lowered, the overall degree of crystallization is also lowered. It is observed, however, that as PHB content increases the onset of crystallization and the crystallization temperature (peak) decreases. It is known that (T_m-T_g) can be viewed as the 'window for crystallization' and as shown in *Table 1*, the corresponding (T_m-T_g) values also decrease. This is due to a surprisingly constant T_g value and the lowering of T_m. In other words, even though the 'window for crystallization', i.e. (T_m-T_g) decreases, PET crystallizes more readily at lower temperatures upon heating. Our tentative explanation for this behaviour is that PHB segments or PHB crystals may act as a nucleating agent for the crystallization of PET. Indirectly supporting this hypothesis are

Table 1 Differential scanning calorimetric results of PET/PHB copolyester series compression moulded at 235°C (initial heating experiment)

	T_g (°C)	T_c (°C)	T_m (°C)	$(T_m - T_g)$ (°C)	$(\Delta T)_c$ (°C)	ΔH_f (cal/g of sample)
100%PET	77	141	255	178	40	—
70%PET–30%PHB	81	106	218	137	52	10.4
60%PET–40%PHB	82	103	212	130	44	6.0
50%PET–50%PHB	82	100	203	121	38	4.6
40%PET–60%PHB	80	96	188	108	—	0.7

the recent results of Takayanagi *et al.*[42] who studied the influence of Aramid® filament surfaces on the crystallization of aliphatic nylons. They found that microfibrils of poly(*p*-phenylene terephthalamide) and poly(*p*-benzamide) accelerate the crystallization rate of nylon-6. Referring back to the same d.s.c. scans shown in *Figure 17*, it is observed that as PHB content increases there is a depression in the melting point from 255°C for pure PET to 188°C for 60% PHB. The values of T_m indicate that the melting is due to the PET regions with the incorporation of PHB segments causing a diluent effect. One observes, however, that the extent of broadening of the melting peak upon the incorporation of PHB is not anywhere near as pronounced as in other confirmed *random* copolymers. Specifically, it has been shown that even the random incorporation of approximately 6 mole% of a second comonomer causes a significant broadening of the melting peak[45]. However, in the case of the PET/PHB copolyesters, even the addition of 30 mole% PHB still provides a relatively sharp PET melting endotherm. In the 40 and 50 mole% PHB materials the melting peaks are slightly broadened, but not to the extent commonly observed in other copolymer systems. Again, this melting behaviour suggests that the PET/PHB copolyester materials are more non-random in chain nature.

In an attempt to use the melting information further in understanding the structure of these copolymers, the melting points obtained experimentally were compared with the values calculated by using the melting point–composition relationship developed by Flory for random copolymers[49]. The relationship is given by

$$1/T_m - 1/T_m^\circ = -R/\Delta H_{u_1} \ln x_1 \qquad (1)$$

where T_m and T_m° are the equilibrium melting temperatures of the copolymer and homopolymer respectively, R is the gas constant in energy units, ΔH_{u_1} is the heat of fusion of homopolymer 1 and x_1 is the mole fraction of comonomer 1 in the copolymer. A value of 265°C was used for T_m° of homopolymer PET, while 10.2 cal mol^{-1} was used for the ΔH_{u_1} of PET in the calculations[50]. *Figure 18* shows the experimental and calculated melting temperatures plotted as a function of PET mole fraction, x_{PET}. It is seen that the experimental melting values of the 40–60 mole% PHB materials are higher than the theoretical values. In general, the experimental melting temperature of a random copolymer is lower than the theoretical T_m. This is so because T_m predicted by theory represents melting of crystallites formed at the melting temperature. This is impossible to measure experimentally and hence, lower values are generally obtained. However, in the case of the PET/PHB copolymers the experimental melting points have higher values and therefore imply that these copolyesters are not completely random copolymers as first suggested by Jackson and Kuhfuss[3]. Specifically, the
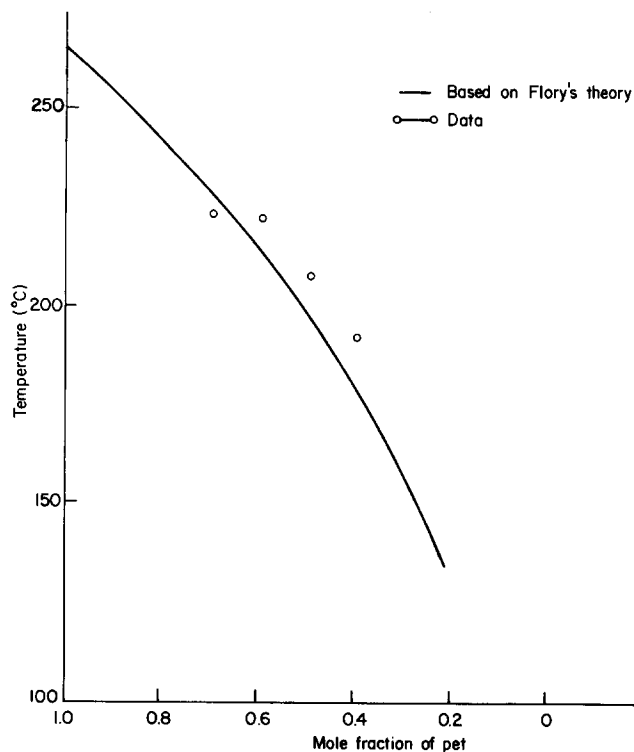
Figure 18 Plot of melting temperature *versus* mole percent of PET

melting points of the 40 mole% PHB to 60 mole% PHB systems have values higher than those calculated by Flory's theory which further suggests the non-random chain structure of these materials. It should also be pointed out that the experimental T_m values used in *Figure 18* are the endothermic peak temperatures. If the temperatures at the end of the melting endotherm had been used, the experimental T_m values plotted in *Figure 18* would be even higher which again indicates a non-random structure. A T_m° value of 275°C has also been used for melting of a random copolymer in Flory's equation to calculate T_m values of the copolymers. When these predicted values are compared with experimental values, again, the experimental values are higher than values predicted by theory. These results which suggest non-random chain structure lend additional support to the etching and electron microscopy observations where the presence of a two phase or heterogeneous morphology was indicated.

The areas under the endothermic peaks represent the heat of fusion and are proportional to the degree of crystallinity when normalized per mass of crystallizable material. The d.s.c. scans qualitatively show that the overall heat of fusion decreases as the amount of PHB is increased. This indicates that the amount of PET crystallinity is lowered as expected, assuming, of course that the ΔH_u for PET remains fixed. The d.s.c. scans of the

30 mole% PHB, 40 mole% PHB and 60 mole% PHB materials given in *Figure 13* show two endotherms; a large one, associated with the melting of PET and a smaller one at a slightly higher temperature. It is believed that the smaller endotherm is due to melting of a crystalline phase rich in PHB, that also contains low levels of PET. The presence of PHB crystallinity in the films moulded at 235°C has been verified by WAXS measurements and will be discussed later.

In order to erase previous thermal history, the compression moulded and quenched copolyester films were heated at 10°/min well past the melting temperature in the d.s.c. and then rapidly cooled. The heating experiment was again performed. The d.s.c. scans are shown in *Figure 19* and some of the values for parameters of interest obtained from the scans are tabulated in *Table 2*. It is also evident from these scans that the small endothermic peak near the glass transition region, due to the non-equilibrium behaviour of amorphous PET that was observed in the initial d.s.c. scans (*Figure 17*), is no longer present as expected.

The crystallization temperature and the onset of crystallization decrease with an increase in PHB content and as speculated earlier is due to a nucleating effect caused by PHB. However, when T_c values for the initial scan and rescan are compared for a given material, for example the

30 mole% PHB system, there is an increase in T_c when heated the second time. It is observed that there is no significant change in the corresponding 'window of crystallization', i.e. (T_m-T_g) values. In terms of a nucleating agent effect, these data would now suggest a decrease in nucleating agent. Based on the molecular model proposed for these copolyester systems as well as optical and transmission electron microscopy results, this hypothesis may be reasonable. Specifically, our data suggest that these PET/PHB copolyesters are non-random in chain structure. This leads to regions that are richer in PET or in PHB which occur on more of a macroscopic scale. However, the thermal history of a given material also influences the nature of the final morphological state as might be expected. It is these thermally induced changes which clearly appear to alter the ability of the PHB to nucleate the crystallization of PET. Hence, an increase in crystallization temperature is observed in the rescan. However, when T_c of the rescan for any copolymer is compared with the T_c or pure PET, the T_c of the rescan is still lower, thereby indicating some partial nucleation influence on PET. Referring back to the melting endotherms, the values of T_m decrease as the PHB content increases which is similar to the observation for the initial d.s.c. heating experiment. It is also evident that for a given material, there is no significant change in T_m for the initial d.s.c. scan or the rescan. The small endothermic peak that is seen past the main melting peak in the initial d.s.c. scan is no longer present and appears as a shoulder at a lower temperature. It is believed that this behaviour is caused by melting of the PHB semi-crystalline regions and the consequent morphological rearrangement in the melt during the initial d.s.c. scan.

In order to investigate the effect of different moulding temperatures on the thermal transitions and to verify if the morphological changes observed by electron microscopy can also be detected by thermal analysis, d.s.c. measurements were performed on similar PET/PHB films moulded at 235°C, 260°C and 285°C. The various parameters obtained from the scans are summarized in *Tables 1*, *3* and *4*. The following observations were made in the d.s.c. scans of the films moulded at 260°C and 285°C:

(i) a small endotherm in the PET glass transition region is present in the lower PHB content films,

(ii) the glass transition temperature remains approximately unchanged as PHB content is varied,

(iii) an exothermic peak due to crystallization of PET is present with the peak temperature decreasing as the amount of PHB is increased,

(iv) an endothermic peak associated with melting of PET is observed and the peak temperature is lowered with an increase in PHB content.

These observations were also made in the films moulded at 235°C as discussed earlier. Specifically, the reader should recall that the small endotherm in the PET glass
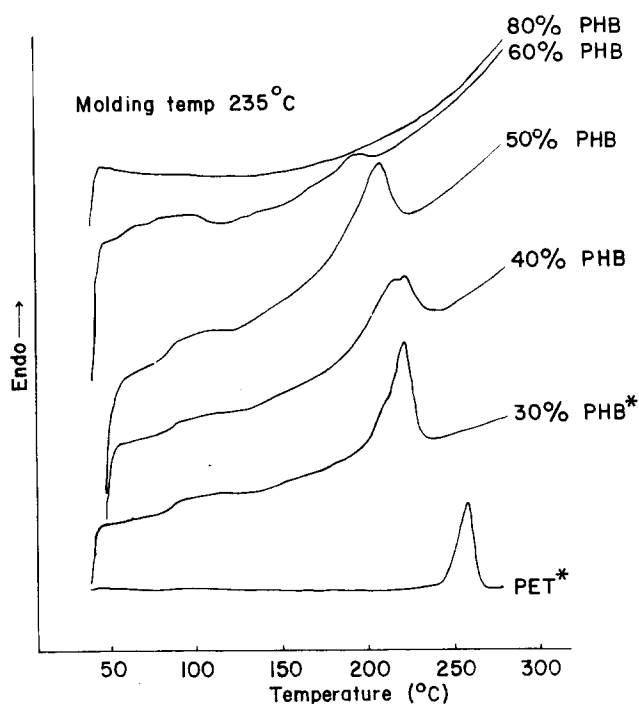

Figure 19 Differential scanning calorimetric scans of PET and the PET/PHB copolyester series that has been heated to 280°C in the d.s.c. cooled back to room temperature and then rescanned at 10°/min

Table 2 Differential scanning calorimetric results of PET/PHB copolyester series compression moulded at 235° C (second heating experiment)

	T_g (°C)	T_c (°C)	T_m (°C)	(T_m-T_g) (°C)	$(\Delta T)_c$ (°C)	ΔH_f (cal/g of sample)
100%PET	78	—	254	176	—	—
70%PET–30%PHB	81	128	218	137	46	9.6
60%PET–40%PHB	82	125	213	131	40	4.4
50%PET–50%PHB	82	119	205	123	42	2.5
40%PET–60%PHB	80	114	192	112	—	0.4

Table 3 Differential scanning calorimetric results of PET/PHB copolyester series compression moulded at 260°C (initial heating experiment)

|	T_g (°C)	T_c (°C)	T_m (°C)	$(T_m - T_g)$ (°C)	$(\Delta T)_c$ (°C)	ΔH_f (cal/g of sample)
100%PET	78	141	255	178	40	—
70%PET–30%PHB	83	105	214	131	47	7.2
60%PET–40%PHB	84	106	211	127	50	5.4
50%PET–50%PHB	78	101	203	125	34	3.0
40%PET–60%PHB	—	95	189	—	34	0.6

Table 4 Differential scanning calorimetric results of PET/PHB copolyester series compression moulded at 285°C (initial heating experiment)

	T_g (°C)	T_c (°C)	T_m (°C)	$(T_m - T_g)$ (°C)	(ΔT_c) (°C)	ΔH_f (cal/g of sample)
100%PET	78	141	255	178	40	—
70%PET–30%PHB	81	106	211	130	40	7.3
60%PET–40%PHB	79	107	209	130	38	5.8
50%PET–50%PHB	80	101	201	121	48	3.4
40%PET–60%PHB	—	93	186	—	32	1.0
20%PET–80%PHB	—	—	301, 340	—	—	0.9, 1.1

transition region was attributed to the physical ageing behaviour of the amorphous PET regions. It was also speculated that the decrease in crystallization temperature of PET is due to a nucleation effect caused by the presence of PHB while the decrease in PET melting temperature is due to a diluent effect produced due to the incorporation of PHB. When the values of T_g, T_c and T_m associated with PET are compared for the films moulded at the three different temperatures, no significant changes are observed. ·

There is one observation seen in the d.s.c. scans that indeed can be attributed to differences in moulding temperature. Specifically, a small endothermic peak past the major endotherm that is seen in the lower PHB content films moulded at 235°C is not present in the films moulded at 260°C or 285°C. An example of this is shown in *Figure 20* where the d.s.c. scans of the 30 mole% PHB material moulded at three different temperatures are plotted. It was speculated earlier that the second endotherm was due to melting a PHB rich semicrystalline phase. Apparently this PHB rich semicrystalline phase melts upon moulding at higher temperatures and does not re-crystallize when quenched below room temperature or during the heating experiment in the d.s.c. Hence, a second endotherm is not observed in films moulded at 260°C and 285°C. However, it is expected that under appropriate cooling conditions crystallization of PHB might well occur.

In order to *eliminate all previous thermal history*, the films moulded at 235°C, 260°C and 285°C were heated well past their melting temperature in the d.s.c. and cooled down to room temperature. The same d.s.c. heating experiment was then performed as those given above. The observations made in the film moulded at 235°C (discussed earlier) were also made in the films compression moulded at 260°C and 285°C. It is interesting to note that even though a second melting endotherm is not observed in the initial d.s.c. scans for the 260°C and 285°C films, they do exhibit a shoulder near the melting peak when reheated. This shoulder was also present in the film moulded at 235°C and was attributed to rearrangement in the melt. The above conclusion is supported by TEM results that have already been discussed, where it was found that at the higher moulding temperatures, a
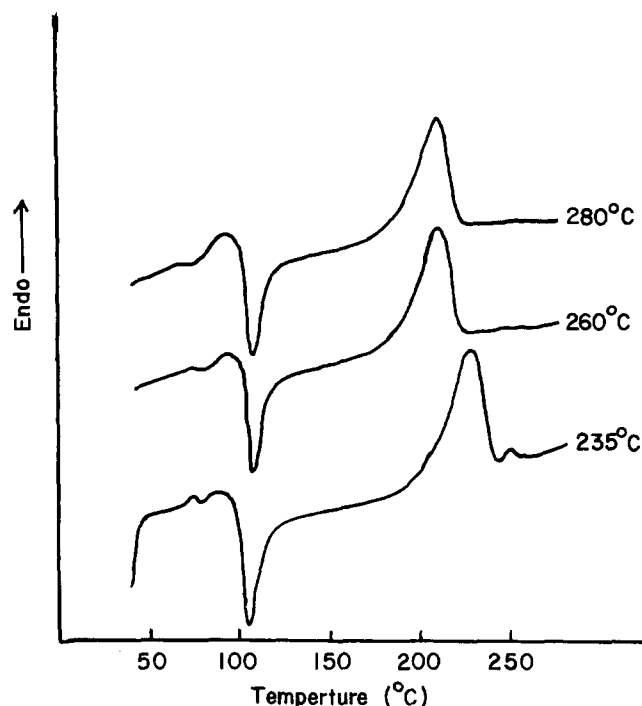
Figure 20 Differential scanning calorimetric scans of the 30% PHB copolyester compression moulded at 235°C, 260°C and 285°C

different morphological texture is formed with domains on the order of 10 microns in size being present.

In summary of the thermal analysis studies, the d.s.c. results on films moulded at 235°C show that while the T_g remains unchanged with the addition of PHB, the values of T_c and T_m corresponding to PET are lowered. The lowering of T_c is speculated to be due to a nucleating effect caused by the PHB moieties, while the decrease in T_m is caused by a partial diluent effect. It was also observed that PHB crystallinity was present in the 235°C films while at moulding temperatures of 260°C and 285°C, this was not the case. These studies indicate that morphological rearrangement occurs at higher temperatures which is in agreement with the microscopy results. Rheological studies also show different behaviour at 250°C and 275°C
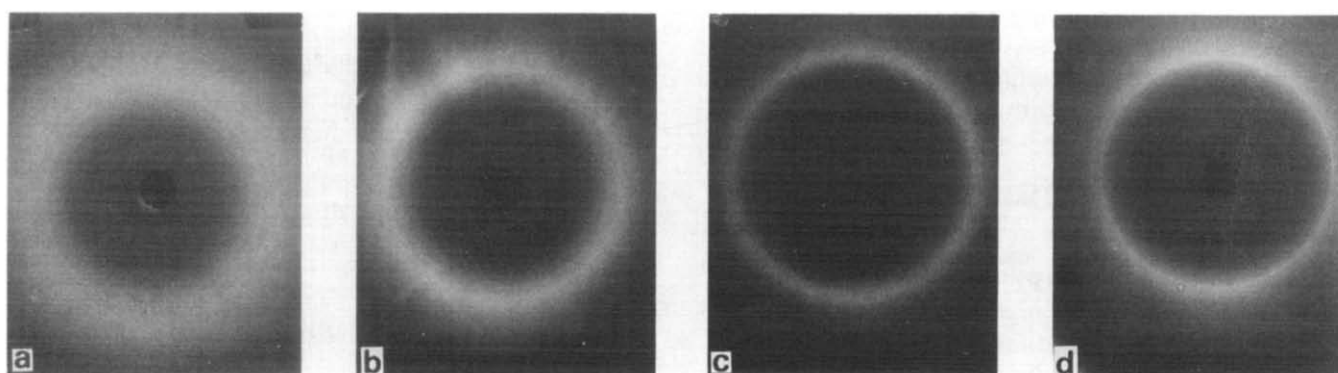
Figure 21 Wide-angle X-ray scattering patterns of PET/PHB copolymer films compression moulded at 235°C and quenched. (a) 30% PHB, (b) 40% PHB, (c) 50% PHB, and (d) 60% PHB
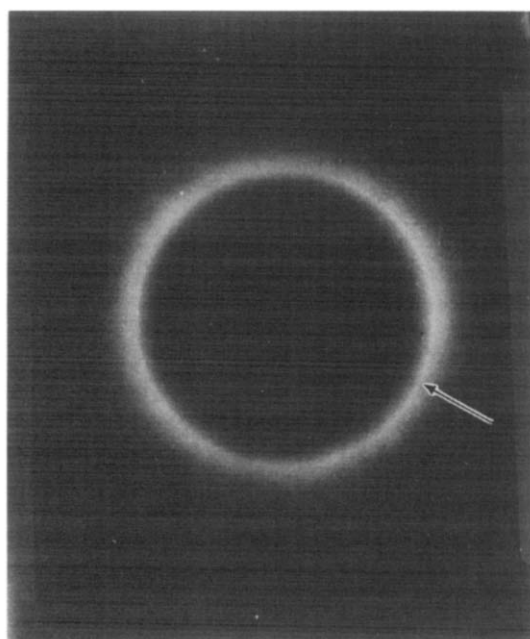

Figure 22 Wide-angle X-ray scattering pattern of 60% PHB film compression moulded at 235°C and quenched

Table 5 Comparison of d-spacings of 60mole%PHB compression moulded at 235°C with d-spacings of semi-crystalline PET and PHB

60%PHB–40%PET (Å)	PET (Å)	PHB [a] (Å)
4.54	5.54	6.25
4.44	5.02	4.53
3.88	4.20	3.72
3.28	3.88	9.12
—	3.43	2.58
—	2.75	—

[a] From ref. 47

which is related to the rearrangement occurring at higher temperatures. When the experimental melting points are used in conjunction with calculated values obtained by using Flory's equation for melting of a random copolymer, the results imply that the PET/PHB copolymers are non-random in structure. This is further supported by the relatively narrow melting endotherms at 30 to 50 mole% PHB levels.

Wide-angle X-ray scattering studies

The reader recalls from the d.s.c. data that the PET-/PHB copolyesters showed two melting endotherms (see *Figure 17*). It was speculated that the second (small) endotherm is due to PHB crystallinity. In an attempt to verify this and also to obtain further structural information on these liquid crystalline copolymers, WAXS measurements were made. Scattering patterns of the PET/PHB films moulded at 235°C and quenched are given in *Figure 21*. They appear to be diffuse in general with the presence of a few distinct but relatively weak rings. The overall diffuseness of the scattering patterns indicates the lack of crystallinity, and this result is not surprising since the films had been quenched immediately upon removal from the film press. However, as the amount of PHB is increased, the overall diffuseness of the scattering patterns decreases. This is believed to be due to greater order that is present in the higher PHB content materials. Rheological measurements and mechanical property studies on injection moulded plaques performed by the Tennessee Eastman researchers have also shown that ordering of the molecules under flow increases as the level of PHB is increased. Although their results were obtained on materials that had been sheared as opposed to compression moulded films, they indirectly support the explanation of the WAXS results. From *Figure 21*, it is noted that the scattering pattern of the 60 mole%PHB is the least diffuse and also indicates the presence of a fairly distinct ring, indicating some level of crystallinity. In order to understand the origin of this ring, the WAXS pattern of the 60 mole% PHB film was obtained using a longer exposure time to the X-ray beam. A different sample to film distance was also used in this experiment. The scattering pattern is shown in *Figure 22* and a sharp, distinct ring is observed (see arrow). The d-spacings calculated from the WAXS pattern are given in *Table 5* along with the d-spacings for pure PET and pure PHB, for comparison purposes. The spacings for PET were obtained experimentally from a well annealed, semi-crystalline, isotropic sample. The values for PHB were taken from ref. 45 in which the d-spacings for pure PHB were calculated theoretically and also obtained experimentally. When the d-spacings of the 60 mole% PHB are compared with those of pure PET and pure PHB, it is evident that the strong reflection observed at 4.54 Å corresponds to that seen in crystalline PHB. This clearly indicates the presence of a small amount of PHB crystallinity in the initial pressed (235°C), quenched film. The 3.88 Å and 3.28 Å reflections are very close to those

observed for PET and these extremely weak reflections indicate very little PET crystallinity. Similar WAXS measurements have been performed by Acierno et al. on the 60 mole% PHB copolyester in the fibre form and upon annealing at 240°C for 70 h, only d-spacings very close to those of pure PHB were obtained[48] thereby indirectly supporting our interpretations above.

Differential scanning calorimetric results indicated that PHB crystallinity was present only in the PET/PHB copolymers moulded at 235°C (the second endothermic peak) and not in the films moulded at 260°C or 285°C. The lack of PHB crystallinity in the films moulded at higher temperatures was attributed to melting of the PHB crystals during the moulding operation. In order to verify this with WAXS measurements, the WAXS patterns of the 60 mole% PHB material compression moulded at 235°C, 260°C and 285°C were obtained. The film moulded at 235°C shows two additional rings that are not present in the scattering patterns of films moulded at 260°C and 285°C. These two rings correspond to d-spacings of 3.84 Å and 4.54 Å and the d-spacings of the 60 mole% PHB material moulded at three different temperatures are compared in *Figure 23*. Of the two additional d-spacings present in the film moulded at 235°C, the 4.54 Å spacing is clearly due to PHB while the 3.84 Å spacing corresponds to the 3.88 Å d-spacing present in PET. It is also observed in the scattering pattern that the ring corresponding to a d-spacing of 4.54 Å is strong while the ring corresponding to the d-spacing of 3.88 Å is weak. This latter observation shows that very little PET crystallinity is present in the 60 mole% PHB material as expected. The WAXS results therefore indicate the presence of PHB crystallinity in the 60 mole% PHB material compression moulded at 235°C, while the films moulded at 260°C and 285°C do not show evidence of PHB crystallinity. This confirms the earlier speculation that the PHB crystals do not completely melt at the moulding temperature of 235°C. However, at 260°C and 285°C, complete melting of the PHB crystals apparently occurs for at least the 60 mole% PHB system.
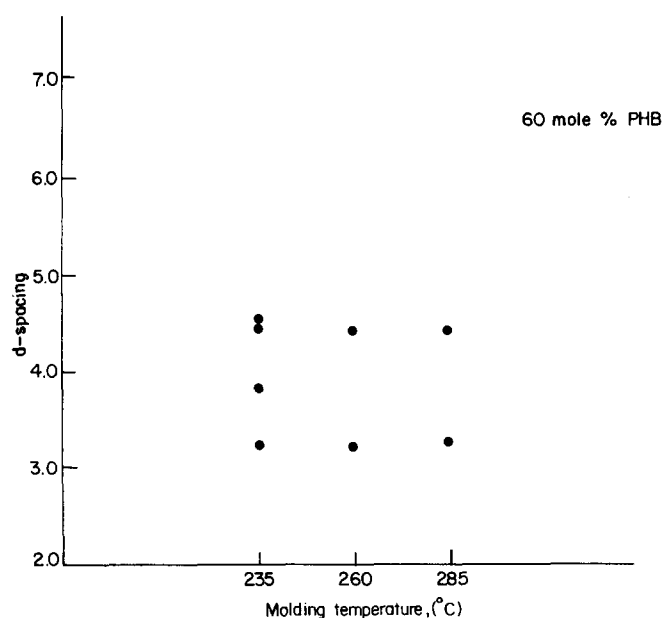
CONCLUSIONS

(1) The technique of selective chemical etching is feasible to study the morphological textures of PET/PHB liquid crystalline copolyesters. Specifically, using an appropriate amine, PET rich regions can be selectively etched away within the time scale of etching.

(2) Chemical etching studies in conjunction with scanning electron microscopy on thermally pressed, quenched films show that at low PHB levels, a PET rich phase is the continuous phase. In the higher PHB content films (i.e. 60 mole% PHB), it is the PHB rich phase that is the continuous phase and PET is the dispersed phase. These studies indicate that the morphology of the thermotropic copolyester system is more non-homogeneous in nature. This is further supported by d.s.c. results where the presence of non-equilibrium behaviour associated with PET indicates that a PET phase or PET rich phase exists.

(3) Transmission electron microscopy studies on the 60 mole% PHB copolyesters shows that at the lower moulding temperatures (235°C) a non-homogeneous structure is present. One of the phases is in the same size range as that seen in the corresponding SEM micrographs and is speculated to be due to PHB rich regions that are semicrystalline. At higher moulding temperatures, a new morphological texture is formed and domains in the 10 micron size range are present. These results also show that the system is non-homogeneous on a larger scale.

(4) Differential scanning calorimetric studies show that the glass transition temperature of the copolymer remains unchanged and the melting endotherms are relatively narrow upon the addition of PHB. This suggests that the chain structure of the PET/PHB copolymers are non-random. This conclusion is further supported by comparing the experimental melting points of the copolymers with corresponding values predicted by theory for random copolymers which shows that the experimental values are higher.

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Figure 23 Plot of d-spacing values for 60 mole% PHB copolyester moulded at 235°C, 260°C, and 285°C

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