

Studies on Fiber Formation of Thermotropic Copolyesters

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SYNOPSIS

Thermotropic copolyesters PET/60 PHB and PET/80 PHB fibers are melt spun at different extrusion temperatures and at different draw-down ratios. The flow behavior of PET/60 PHB is studied at different temperatures and shear rates. The melt of (PET/60 PHB) at temperatures above 265°C exhibit low viscosity and low activation energy of flow. The modulus and strength for both PET/60 PHB and PET/80 PHB fibers increase with the increase in extrusion temperature and draw-down ratio in the ranges studied. High birefringence, indicating the presence of mesophase is observed between 265 and 300°C on a hot stage polarizing microscope. X-ray diffraction patterns show that the molecular orientation increased with increasing draw-down ratio. Scanning electron microscopy of these fibers shows a well-developed highly oriented fibrillar structure. Superior mechanical performance of fibers spun at around 275°C are attributed to the presence of nematic mesophase in the polymer melt. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Thermotropic liquid crystalline copolymers exhibit a high degree of molecular orientation during processing in the melt state¹ and are able to maintain this orientation during solidification. Relatively rigid backbone molecules produce anisotropic or orthotropic structures capable of being formed into fibers of high stiffness and strength.

One of the first known Liquid Crystalline Polymers (LCPs), poly(ethylene terephthalate-co-*p*-oxybenzoate) (PET/PHB), supplied by Tennessee Eastman Co.²⁻⁴ has been the subject of many investigators.²⁻¹⁵ Sugiyama and co-workers¹¹ reported that the Hermans orientation factor of the fibers increased as the extrusion temperature increased from 230 to 270°C and then leveled off at about 290°C. Little change in the orientation was observed by increasing draw-down ratio [(V_f/V_0) , take-up speed/extrusion rate]. Similar observations were made by Muramatsu and Krigbaum¹⁵ using the LCP (PET/PHB) with intrinsic viscosity (IV) of 0.77. Recently, Cuculo and Chen¹⁶ also performed spinning of PET/60 PHB with different IVs at relatively

low to intermediate V_f/V_0 . They reported an increase in the tensile properties obtained by spinning at higher V_0 (while V_f/V_0 was kept constant) or at higher V_f/V_0 , and at relatively high extrusion temperatures.

In the present study, spinning of PET/60 PHB and PET/80 PHB is carried out at low to intermediate V_f/V_0 , and the effect of hot drawing on the properties of thermotropic copolyesters fibers has been investigated. The thermal and the tensile properties of the fiber are related to fiber structure developed under the given spinning conditions.

EXPERIMENTAL

Copolyester samples of poly(ethylene terephthalate) and *p*-hydroxybenzoic acid of different composition were supplied by the Mitsubishi Kasei Corp. The copolymers used were designated as PET/60 PHB and PET/80 PHB with intrinsic viscosities of 0.67 and 0.77 dl g⁻¹, respectively, measured in a mixture of phenol and tetrachloroethane (60 : 40, w/w) at 25°C. Polymer chips were dried overnight at 120°C in a vacuum oven prior to use.

Fiber spinning was carried out on a laboratory-made model, with a die having a diameter of 0.3 mm and a length of 5 mm. Filaments were collected using a take-up machine, placed at a distance of 2.5 m

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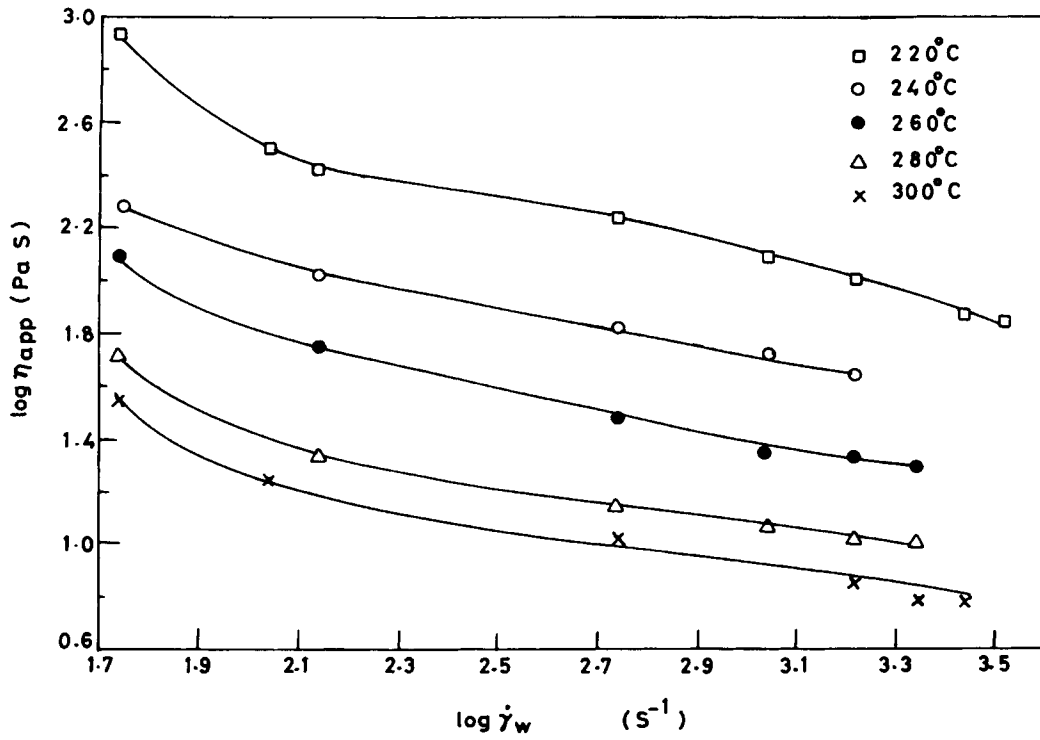


Figure 1 Logarithmic apparent melt viscosity vs. logarithmic corrected shear rate curves for PET/60 PHB copolyester.

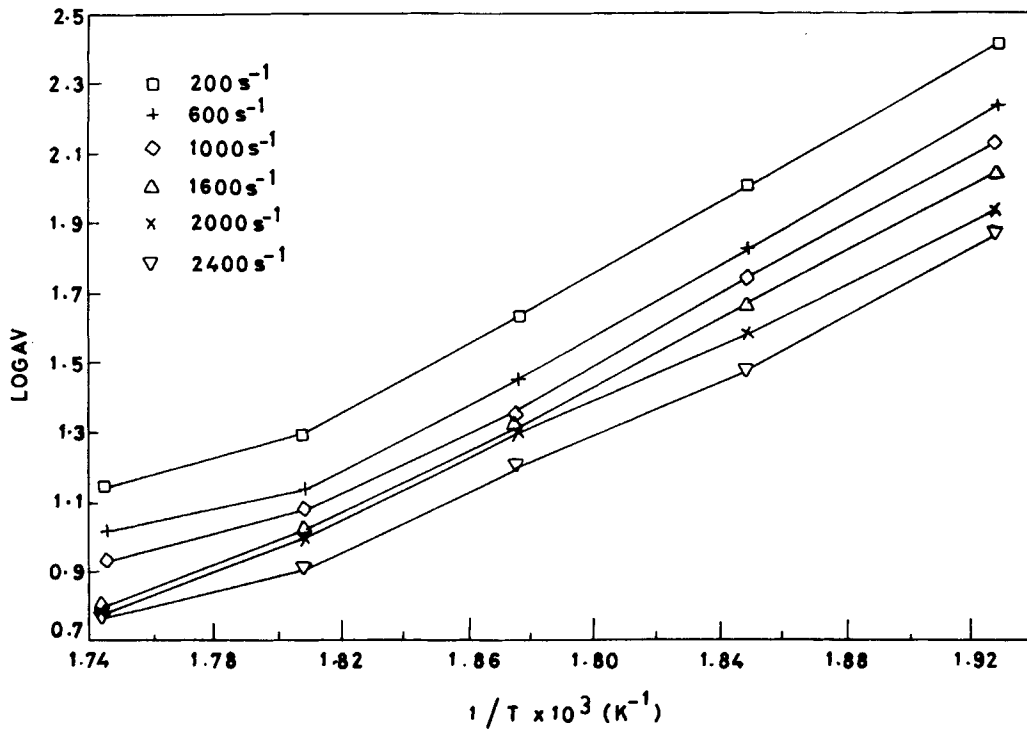


Figure 2 Logarithmic apparent melt viscosity vs. $1/T$ K for PET/60 PHB copolyester.

Table I Flow Activation Energy at Different Shear Rates for PET/60 PHB (220–300°C)

Shear rate (s ⁻¹)	200	600	1000	1600	2000
E_a (kJ/mol)	93.6	91.7	89.9	86.0	74.5

from the die exit. Filaments were quenched in air at room temperature and collected on bobbin. The spinning was performed with extrusion temperature and V_f/V_0 as variables.

Characterization Methods

The rheological properties of the copolyester melts were studied with a Rheograph 2000 rheometer using a capillary of 30 mm length with a length-to-diameter (L/D) ratio of 30. Most of the measurements were performed at temperatures in the range of 220–300°C.

The thermal transitions of the samples were investigated using a Perkin-Elmer differential scan-

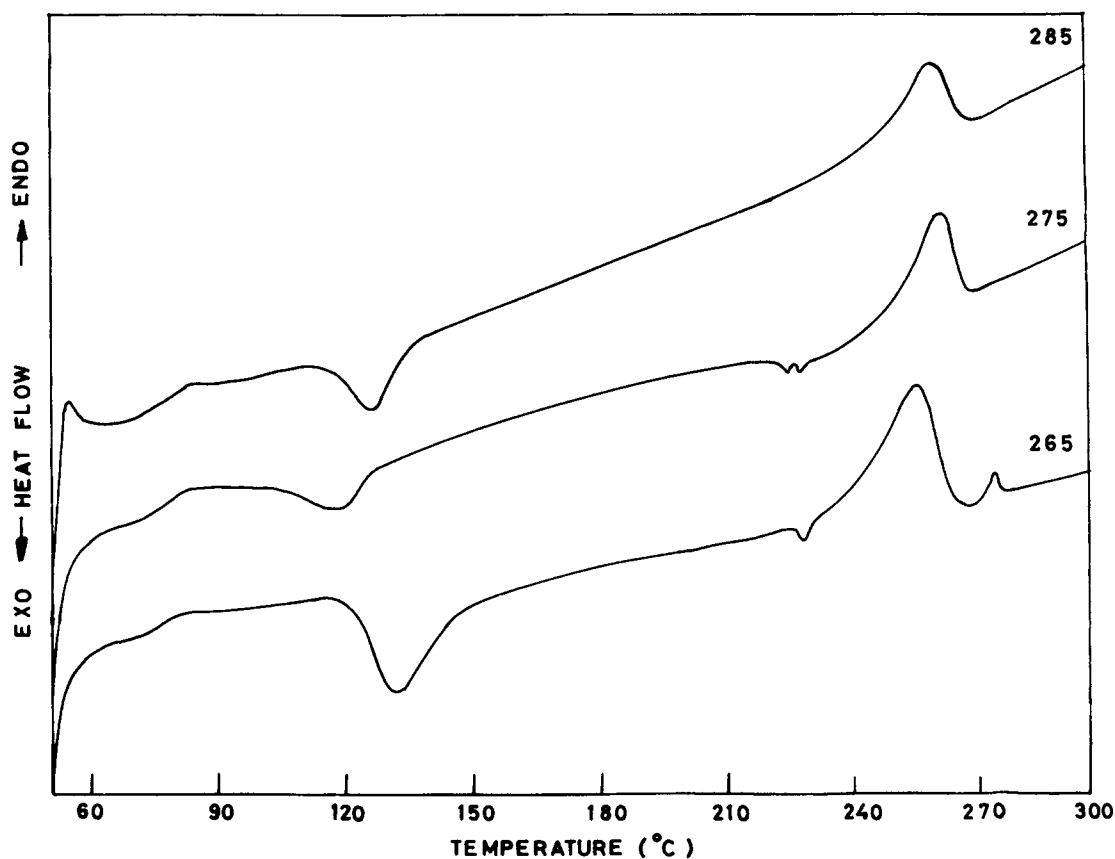
Table II Structural Viscosity Indices of Copolyester PET/60 PHB at Different Temperatures

$\dot{\gamma} = 1000 \text{ s}^{-1}$	T (°C)				
	220	240	260	280	300
Δn	1.4	1.1	0.8	0.7	0.8

ning calorimeter (Model DSC-7) at a heating rate of 20°C/min in a nitrogen atmosphere. Powdered samples of about 20 mg weight were used. For the evaluation of the transition enthalpies, indium and tin samples were used as reference standards and automatic baseline correction was used. Furthermore, using the software provided in the instrument, the thermograms were normalized to constant weight and recorded in all the cases.

A Mettler FP5 micro hot stage equipped with a polarizing microscope was employed to examine the texture of samples with temperature.

The change in length parallel to the filament axis

**Figure 3** DSC heating traces of as-spun PET/60 PHB fibers at different extrusion temperatures.

was measured on as-spun filaments. Samples were run in a thermomechanical analyzer (Perkin-Elmer) between 40 and 100°C at a scanning rate of 5°C/min.

Tensile tests were performed on an Instron machine, model 4112. All tests were carried out on single filaments using a gauge length of 50 mm and crosshead speed of 50 mm/min. The average of 20 readings were reported for each sample. The maximum standard deviation of both ultimate tensile strength and initial modulus was around 5%.

RESULTS AND DISCUSSION

Rheological Behavior

The logarithmic apparent melt viscosity ($\log \eta_a$) versus shear rate ($\dot{\gamma}$) curves are shown in Figure 1. A significant drop in melt viscosity is observed as the temperature increases from 220 to 300°C. The viscosity of PET/60 PHB at 220°C is about 10 times higher than that of the material at 300°C. The flow curves in the temperature range of 220–300°C are shear sensitive in the shear range of $10\text{--}10^3 \text{ s}^{-1}$. At

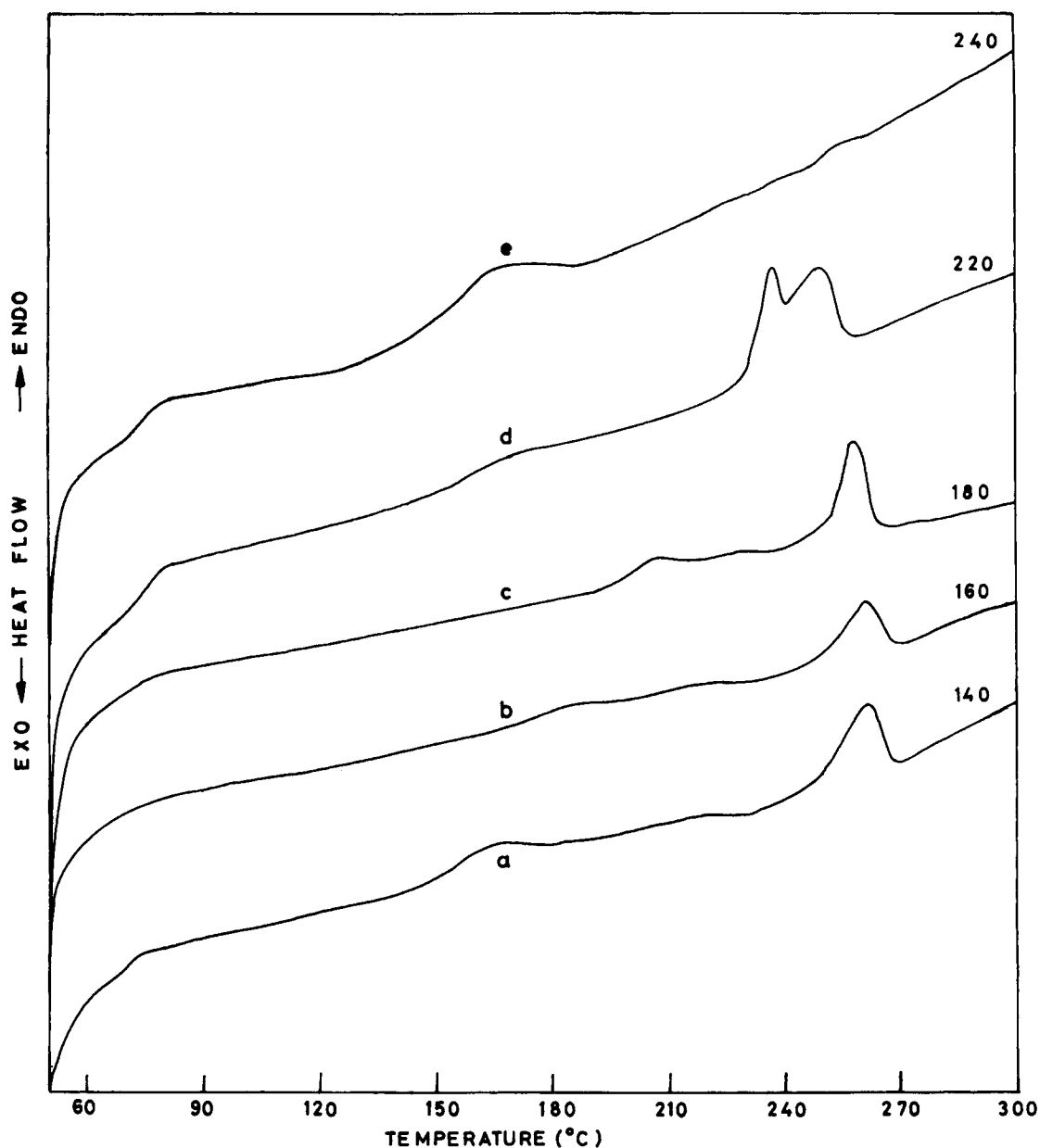


Figure 4 DSC heating traces of as-spun PET/60 PHB fibers annealed for 10 h at different temperatures.

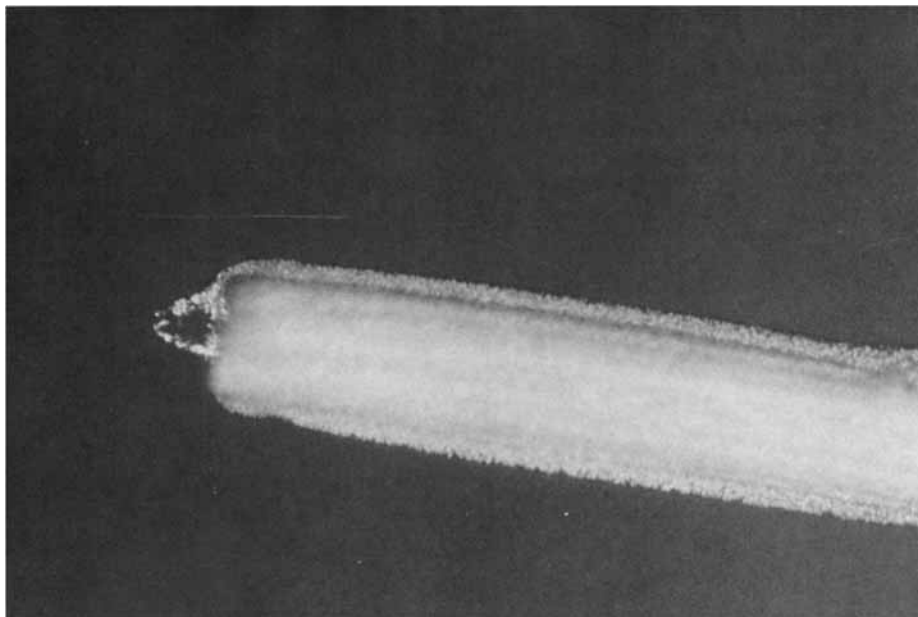


Figure 5 Optical micrograph of as-spun PET/60 PHB fiber at 275°C.

shear rates above 10^3 s^{-1} , the viscosity reaches its minimum value. When similar measurements were made with PET, the results were quite different. The PET polymer exhibits higher viscosity as compared to PET/60 PHB. When the temperature increases, there is only a small reduction in viscosity. It is evident that PET melt behaves almost as a Newtonian fluid.¹⁶

The viscosity is plotted against the inverse of the absolute temperature at fixed values of shear rate (Fig. 2). The calculated activation energy (E_a) values in the temperature range of 220–300°C are given in Table I. E_a is relatively high in the temperature range below 240°C and low above 280°C temperature. It decreases slightly as the shear rate increases. At temperature around 275°C a nematic liquid crys-

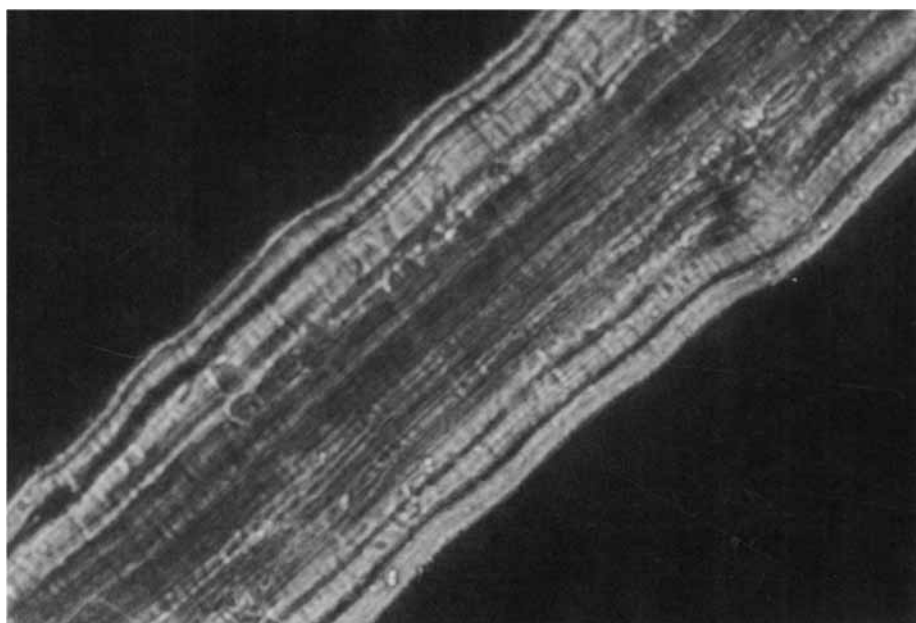


Figure 6 Optical micrograph of longitudinal section of as-spun PET/60 PHB fiber.

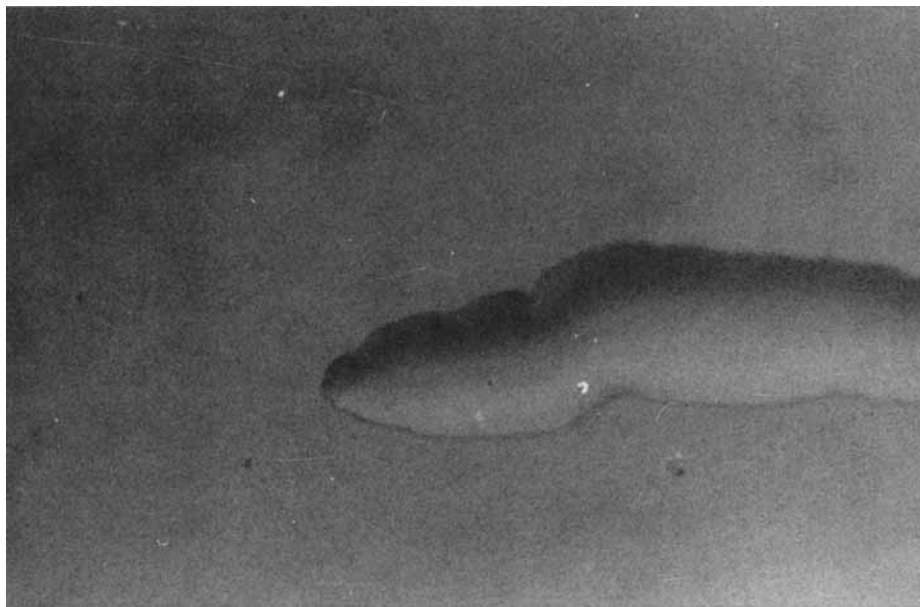


Figure 7 Optical micrograph of drawn PET fiber at 265°C.

talline state is observed in the melt with a highly oriented domain structure.¹⁷ During flow the domains act as the flow units, sliding smoothly over each other, thus dissipating less energy than randomly oriented and entangled molecules in isotropic fluids.

The structural viscosity index Δn indicates the degree of structurization of polymer melts, which has been calculated using the following equation¹⁷:

$$\Delta n = -[d \log \eta_a / d\dot{\gamma}^{1/2}] \times 10^2$$

The results of Δn are given in Table II. The experimental data indicate that better spinnability of the copolyester melts can be obtained at relatively higher temperatures around 280°C. Similar results have been reported by other investigators.^{8,16,17}

Thermal Behavior

Differential scanning calorimetry (DSC) curves of as-spun fibers of PET/60 PHB copolyester extruded at different temperatures are shown in Figure 3. In the heating cycle, three transitions, namely, T_g , crystallization temperature (T_c), and the melting temperature (T_m) associated with PET crystallites are shown. The DSC traces of as-spun fibers drawn at different draw-down ratios in the range of 55–415 depict the similar transitions as observed for the samples extruded in different extrusion temperatures. To obtain some insight into how crystallization occurs in the threadline, two observations are made from the DSC data. (i) As the extrusion temperature increases from 255 to 285°C, the enthalpy of melting due to PET component decreases. The

Table III Effect of Extrusion Temperature* on Mechanical Properties of As-spun Fibers of LC Copolyesters

Extrusion Temperature (°C)	PET/60 PHB			PET/80 PHB		
	Initial Modulus (GPa)	Strength (MPa)	Ext. (%)	Initial Modulus (GPa)	Strength (MPa)	Ext. (%)
255	6.98	131	4.25	20.8	250	1.2
265	7.34	137	4.95	21.5	256	1.4
275	8.55	148	5.51	22.3	268	1.5
285	8.63	150	6.75	23.6	274	1.7

* V_f/V_0 for PET/60 PHB is 196.6 (V_0 , 1.02 m/min). V_f/V_0 for PET/80 PHB is 189.2 (V_0 , 1.06 m/min).

decrease in enthalpy of fusion is presumably due to low quenching rate and also due to stiff PHB units, which hinder on-line PET crystal development. Therefore, the overall degree of crystallinity is lowered. (ii) As the draw-down ratio (V_f/V_0) increases, the melting endotherm becomes smaller.

The transitions shown in the DSC scans (Fig. 3) are essentially consistent with the results found in the literature.¹⁴⁻¹⁶ According to Wissburn,⁸ at temperature above 265°C all crystallites due to PET sequences in PET/60 PHB get melted, and a highly ordered liquid crystalline structure is fully developed. At the melt spinning temperature of 275°C, the situation is characterized by low shear viscosity, low activation energy, and high melt birefringence. In the spinning process, the semirigid molecular chains are readily oriented and, after solidification, a highly oriented fiber results.¹⁶ However, it should be noted that once the initial crystal nucleation from the mobile nematic melt has occurred, the crystals would immediately prevent the long rigid chain sliding longitudinally so that subsequent growth and perfection of crystal gets retarded.¹⁸ Furthermore, with the increase in the draw-down ratio (V_f/V_0), the alignment of the rods increases and also the orientation, but these rigid units resist the crystallization of PET chains, consequently leading to fewer or even a total lack of crystallites. As a result, the endothermic peak due to melting in the high draw-down filament becomes smaller and less obvious.

To substantiate this further the LCP fibers were annealed/held for 10 h at different temperatures (Fig. 4) in DSC pan, cooled immediately to room temperature, and then taken a second run. It is observed that annealing of the fibers in a DSC pan has a distinctive effect on the endotherm (Fig. 4). Samples annealed at temperature below 200°C, i.e.,

from 140 to 180°C exhibit a single melting endotherm around 260°C (curves *A* and *B* in Fig. 4), which corresponds to PET-like crystallites. In other words, when annealing temperature is below the T_g of PHB-rich domains, (T_{g2} in PET/PHB copolyester has been reported by various authors^{19,22,23} in the temperature range of 170–190°C), the PET-like crystallites are not very much affected by the annealing temperature. However, by raising the annealing temperature 220°C, and above the glass transition temperature, T_{g2} , a double melting peak (curve *D*) is observed. This should be due to: (a) crystalline–mesophase disordering in PHB-rich domains and (b) the melting of PET crystallites.

When annealing temperature is further increased to 240°C, a weak endotherm and a broadening of T_g are observed. At this temperature the PET-like crystallites melt and PHB-rich domains grow further.²⁴ Moreover, the sample was cooled immediately, therefore, the development of crystallinity is extremely small and hence, the melting endotherm almost disappears.

Hot-stage Optical Microscopy

The texture change with temperature of as-spun PET/60 PHB fiber was examined under a polarizing microscope. When an oriented fiber is viewed between crossed polars at 265°C, it is usually birefringent when positioned at 45° to the crossed polars. High birefringence became more evident on further heating to 275°C onward (Fig. 5). In Figure 6 a longitudinal section of PET/60 PHB fiber shows no apparent variation in brightness, when the fiber is rotated between the cross polars. Instead, randomly oriented domains (showing different colors in the polarizing microscope) are visible in all directions.

Table IV Effect of Draw-down Ratio (V_f/V_0)^a on Mechanical Properties of As-spun Fibers of LC Copolyesters

PET/60 PHB			PET/80 PHB		
Draw-down Ratio (V_f/V_0)	Initial Modulus (GPa)	Strength (MPa)	Draw-down Ratio (V_f/V_0)	Initial Modulus (GPa)	Strength (MPa)
55.6	6.1	133	—	—	—
72.5	6.6	136	—	—	—
106.3	7.4	139	102.6	21.6	252
196.6	8.5	148	189.2	22.3	268
373.6	10.9	158	361.2	25.8	310
415.5	12.0	175	400.3	26.7	315

^a Extrusion temperature for both LC copolyesters, 275°C.

This implies that the molecular chains are only locally oriented, i.e., chains are only oriented within each individual domains.²⁰

The melting behavior of PET fiber is quite different. As shown in Figure 7, a rapid shrinkage occurred as the temperature increased to 265°C, and the birefringence of the fiber disappeared as soon as the material melted completely.

Mechanical Properties

The initial modulus and tensile strength of as-spun fibers of copolyesters PET/60 PHB and PET/80 PHB, as a function of extrusion temperature, are shown in Table III. PET/60 PHB fibers were obtained at a V_f/V_0 of 196.6 (V_0 , 1.02 m/min), whereas fibers from PET/80 PHB were spun at a V_f/V_0 of 189.2 (V_0 , 1.06 m/min). It is seen that both the modulus and strength increases as the extrusion temperature increases from 255 to 285°C. The strength and modulus of the fibers of both the LCPs obtained at 245°C are very low because of inhomogeneity and frequent breakages in the fibers. Although the trend of change in the properties of both the copolyesters is the same, but the modulus and strength of the fibers of PET/80 PHB are higher than those of PET/60 PHB.

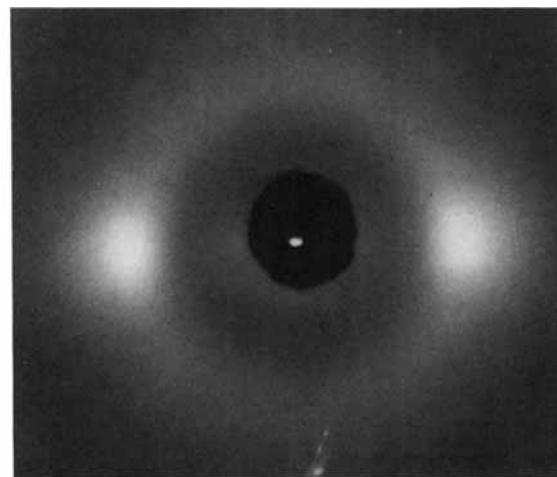
Table IV shows the initial modulus and tensile strength of as-spun fibers of PET/60 PHB and PET/80 PHB copolyesters as a function of V_f/V_0 . It is shown that the modulus and strength tend to increase with increasing V_f/V_0 . Our results appear to be consistent with those reported by Cuculo et al.,¹⁶ who reported that the high orientation and superior mechanical performance are due to the presence of the nematic mesophase in the polymer melt. The improvement in initial modulus and strength is due to the fact that the chains are nearly fully extended and parallel at higher extrusion temperature and higher draw-down ratio. At higher draw-down ratio (V_f/V_0) the orientation becomes better and the lateral packing of the chains improve.

Thermo-Mechanical Analysis (TMA) studies of as-spun filaments of PET/60 PHB polymer records extension as the temperature increases. This shows that the filaments still have drawing capacity. The thermal expansion coefficient obtained on heating this fiber (V_f/V_0 , 56.6) is 4.3×10^{-4} . The change in thermal coefficient may be attributed to the local rearrangement of noncrystalline chain configuration with rise in temperature. The thermal coefficient value is, however, larger in comparison to wholly aromatic copolyesters. This might be because of high fluctuations of the noncrystalline chains perpendic-

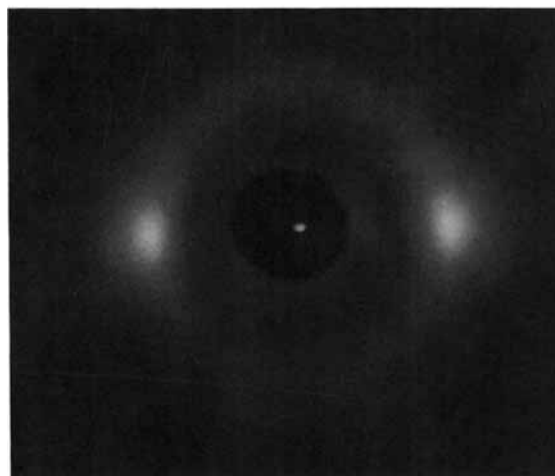
ular to the chain axis at the temperatures above T_g due to their high flexibility.

X-ray Diffraction

Figure 8 shows the Wide Angle X-ray Scattering (WAXS) patterns of PET/60 PHB fibers extruded



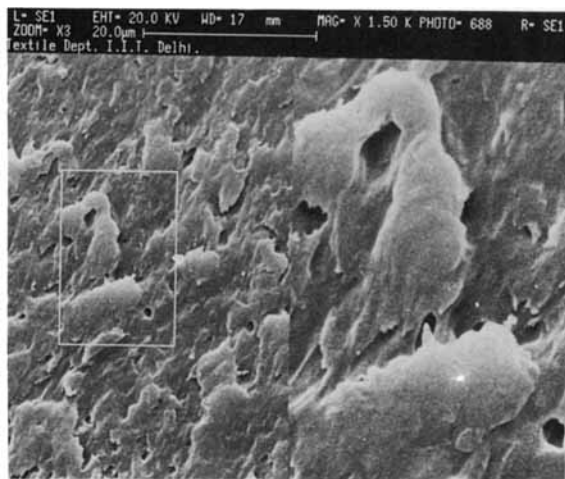
(a)



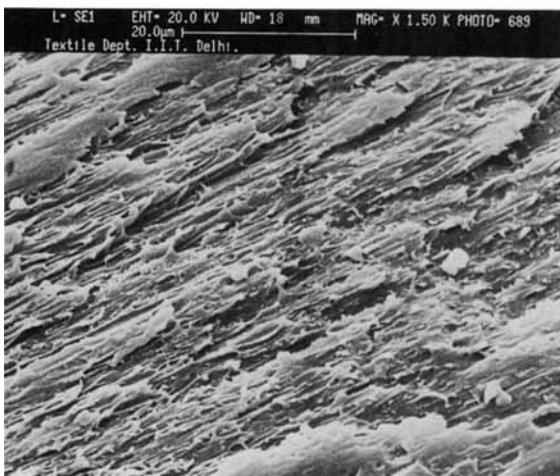
(b)

Figure 8 WAXS patterns of as-spun PET/60 PHB filaments. Filaments with the extrusion ratio of (a) 55.6 and (b) 373.6 were spun at 275°C.

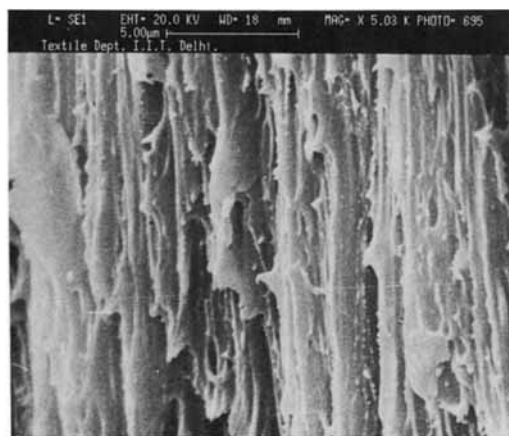
at different draw-down ratio (V_f/V_0). With the increase in draw-down ratio, the size of the diffraction arc in the azimuthal direction decreases, indicating an increased orientation. The strong reflection observed at a d -spacing value of 4.54 Å corresponds to the reflection observed in crystalline PHB. This indicates the presence of PHB crystallites in these as-spun filaments. This has been observed by Viola



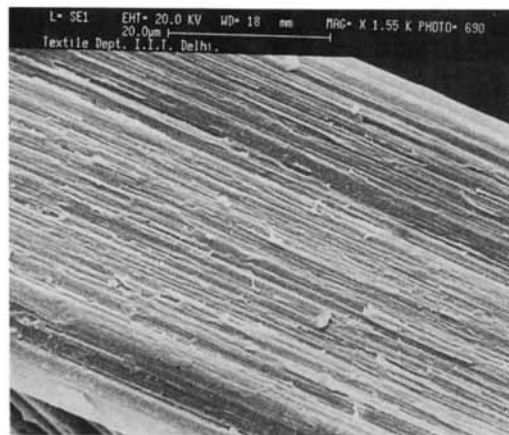
(a)



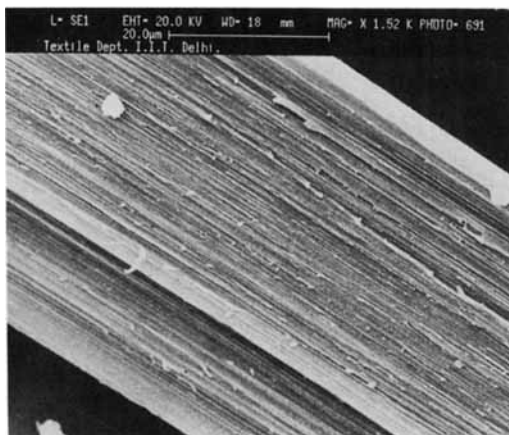
(b)



(a)



(b)



(c)

Figure 9 SEM photomicrographs of free-fall extrudates of as-spun PET/60 PHB fibers at different extrusion (a) 255°C and (b) 275°C. The fibers were chopped parallel to the flow direction at room temperature.

Figure 10 SEM photomicrograph of as-spun PET/60 PHB fibers at different draw-down ratios: (a) 55.6, (b) 196.6, (c) 373.6.

et al. and Muramatsu et al.¹³ Itoyama et al.²¹ reported that up to an extension ratio (α) of 10, orientation index (π) increased monotonically with α , while above this value, π asymptotically increases and eventually reaches a plateau with increasing α . These results show that a high level of chain orientation in liquid crystalline states does not necessarily bring about higher crystallite orientation during subsequent solidification processes. This may presumably be related to the bent structure of the copolyester.

Scanning Electron Microscopy

Figure 9 shows photomicrographs of free-fall extrudates of PET/60 PHB copolyester during spinning at 255 and 275°C. The extrudates were cut near the center with a hand-held razor blade, and the upper half was peeled off. The extrudate obtained at 255°C appears to be poorly oriented and has a nonfibrillar structure while extrudate obtained at 275°C is fairly oriented. It seems that some domains are deformed and begin to form fibrils while some others are still in a semispherical shape.

Figure 10 shows the as-spun PET/60 PHB fibers obtained at different draw-down ratios (V_f/V_0). The fiber spun at a higher V_f/V_0 is more highly oriented; it consists of well-developed fibrils, in comparison to the fibers spun at lower V_f/V_0 .

CONCLUSIONS

1. Rheological measurements show that the viscosity decreases as the temperature increases. The flow activation energies ΔE_a are 93.6 to 74.5 kJ/mol over the shear rate of 200 to 2000 s⁻¹ and temperatures between 220 and 300°C.
2. DSC results reveal that as the extrusion temperature increases, the enthalpy of melting decreases. Similar behavior is observed when draw-down ratio is increased.
3. The fiber strength and modulus are significantly improved at higher extrusion temperature and at higher draw-down ratio. The maximum initial moduli for PET/60 PHB and PET/80 PHB copolyesters are 12 and 26.7 GPa, respectively.
4. SEM studies reveal that the fibers spun at temperatures above 265°C have a well-developed, highly oriented fibrillar structure.

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