Structural Characteristics, Rheological Properties, Extrusion, and Melt Spinning of 60/40 Poly (Hydroxybenzoic Acid-Coethylene Terephthalate) (PHB/PET)

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Synopsis

The rheological properties, extrusion, and melt spinning characteristics, and concomitant morphological features of 60/40 PHB/PET aromatic copolyester have been investigated. The material flows at temperatures above 190°C, but all crystallites may not melt completely until about 250°C. The material exhibits a yield stress value in shear flow. In fact, yield stress values were measured over a range of temperature from 190 to 260°C and estimated at higher temperatures. Extrudate swell measurements were also made in the same range. Significant extrudate swell does not occur until the fluid is at a temperature where the yield stress is approximately 1/50th of its maximum value. Extrudates are fibrillar in character and exhibit significant levels of crystalline orientation. The level of crystalline orientation in melt spun fibers does not vary significantly with drawdown ratio, since it is apparently developed to near its limiting extent during its flow through the die. All of these responses are similar to those observed in melt flow/processing studies of thermotropic liquid crystalline hydroxypropylcellulose.

INTRODUCTION

Liquid crystalline polymers are one of the most promising classes of polymeric materials. They have exhibited the ability to be prepared into both high modulus and tensile strength fibers and biaxially oriented films. This has been most widely shown in poly (p-phenylene terephthalamide) and other aromatic polyamides.[1-4]

In recent years attention has been drawn to thermotropic liquid crystalline polymers. Two important classes of materials, aromatic polyesters[5-18] and cellulose ethers,[19,20] exist. Most attention has been given to the organic synthesis and identification of phases in these systems, especially with the aromatic polyesters. The greatest effort on aromatic copolyesters has been given to the 60/40 poly (hydroxybenzoic acid-coethylene terephthalate) (PHB/PET) system.[5-7,10,12,13,15-18] Relatively little activity has been directed to melt flow and processing characteristics. Viscosity-shear rate data have been reported for PHB/PET[10,12] and other aromatic copolyesters[10] and for the cellulose ethers.[19,20] Both types of systems appear to exhibit unbounded viscosity increases at low shear rates. Extrudate swell has been found to

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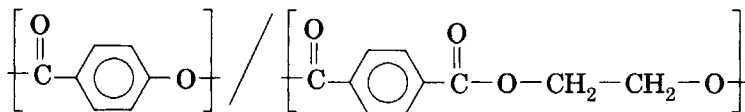
be almost completely absent for the aromatic copolyesters[12] and cellulose ethers.[20] Shimamura, White, and Fellers[19] have reported that extrudates of hydroxypropylcellulose (HPC) are highly oriented with fibrillated outer layers. Ethyl cellulose (EC) appears to have similar characteristics.[20] The level of orientation does not vary significantly in melt spun fibers. There have not been equivalent studies for aromatic copolyesters on samples prepared under known conditions. The flexural modulus and strength of injection molded aromatic polyester parts is found to be considerably greater in the machine than the transverse direction.[15,18] However, the situation is not clear.

In the present article we will first report on the structural characterization of a 60/40 PHB/PET sample and then describe its rheological properties. We will then treat extruded cylindrical filaments and structurally characterize them. In a·later part of the study, fibers are melt spun. The structure of these fibers is discussed as a function of spinning conditions. This article presents a much broader perspective of the structural characteristics of a thermotropic aromatic polyester during "melt" processing conditions than has been achieved in prior studies. This perspective arises from a comparison of the common structural and flow characteristics of PHB/PET, HPC, and EC.

EXPERIMENTAL

Materials

The material used in this study was prepared by the Tennessee Eastman Company from 60 mol % hydroxybenzoic acid and 40 mol % polyethylene terephthalate. It contains the units

$$\left[\begin{array}{c} O \\ \parallel \\ C-\langle\bigcirc\rangle-O \end{array}\right] \Big/ \left[\begin{array}{c} O \qquad\qquad O \\ \parallel \qquad\qquad \parallel \\ C-\langle\bigcirc\rangle-C-O-CH_2-CH_2-O \end{array}\right]$$

This is the same material as developed by Jackson and Kuhfuss[5] and investigated by many other researchers.

Polarized Light Microscopy

The polymer was investigated between glass slides on a Leitz Ortholux Microscope with a hot stage in the temperature range 20° to 450°C.

Differential Scanning Calorimetry (DSC)

The system was characterized using a Perkin-Elmer Differential Scanning Calorimetry between room temperature and 400°C. The temperature was increased at a rate of 4°C per min.

Rheological Property Measurements

The copolymer was rheologically characterized in cone plate and capillary rheometers between 190 and 340°C. The cone-plate measurements were made in a Rheometrics Mechanical Spectrometer. A cone of radius 1.24 cm and cone angle of 0.1 radian were used. The cone-plate measurements were limited to low shear rates. Higher shear rate measurements were made in a Merz-Colwell Instron Capillary rheometer. Capillaries of diameter 0.074 cm and length-diameter ratios of 10, 30, 50, and 70 were used. Weissenberg corrections to the die wall shear rate and Bagley pressure drop corrections were made. The theory of rheological measurements in these instruments has been described in various monographs.[21,22] These are the same instruments as used in our earlier studies of rheological properties of the thermotropic liquid crystalline cellulose ethers.[19,20]

Extrusion/Melt Spinning

Filaments were extruded and melt spun from a Merz-Colwell Instron capillary rheometer with a die of diameter 0.074 cm and L/D ratio of 40. Measurements of extrudate swell (d/D) were made on the frozen extrudates collected using a fixed L/D 30 and fixed apparent shear rate ($\dot{\gamma}_{app}$) for temperatures ranging from 190° to 340°C.

Structural Measurements on Fibers

Wide angle x-ray scattering (WAXS) fiber patterns were measured using a Philips x-ray generator with nickel filtered Cu Kα radiation. An AMR high resolution scanning electron microscope (SEM) was used to make photomicrographs of extrudates.

STRUCTURAL CHARACTER OF QUIESCENT MATERIAL

Results

The 60/40 PHB/PET sample was investigated over the range of 20°–450°C. We show a plot of transmitted light intensity as a function of temperature in Figure 1. Light passes through all conditions and rises to a maximum at 350°C. The value of I/I_0 decays at temperatures above 400°C. These indicate an anisotropic structure in the rest state material.

In Figure 1, we also plot DSC traces for the 60/40 sample as a function of temperature up to 400°C. Four transition temperatures are noted at about 190, 250, 340 and 360°C.

Interpretation

The thermal transitions observed in the 60/40 PHB/PET copolymer have been interpreted by Meneczel and Wunderlich.[7] The transition at about 190°C corresponds to a glass transition, and that at 250°C to a melting of crystallites. Meneczel and Wunderlich detect a transition at about 70°C and interpret this as a second glass transition meaning the material contains two phases. The latter transition is for material richer in PET. The tran-
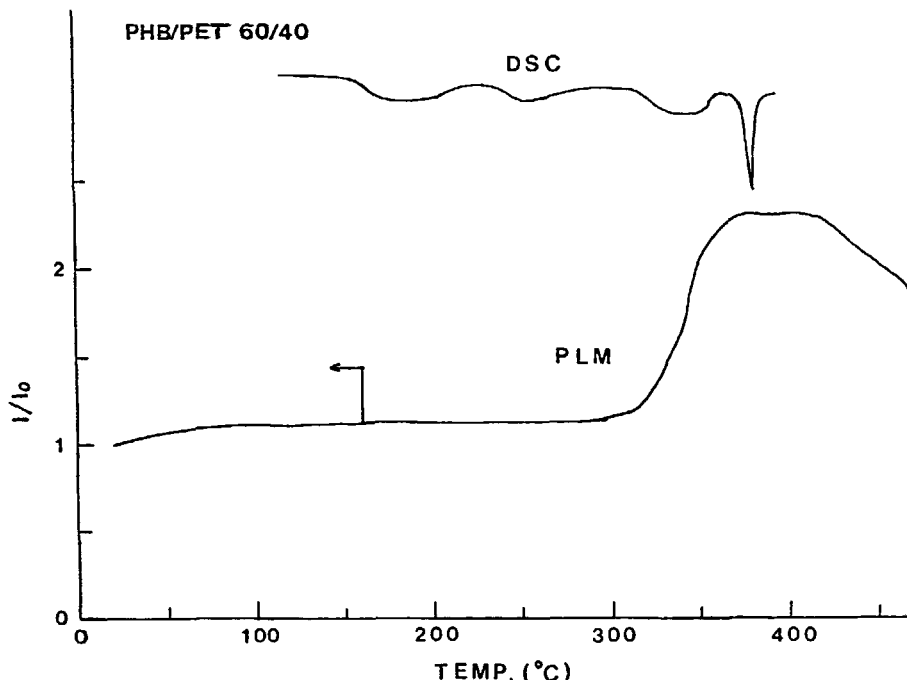
Fig. 1. PLM transmitted light intensity and Differential Scanning Calorimetry trace as a function of temperature for 60/40 PHB/PET copolyester.

sitions of 320–360°C correspond according to Viney and Windle[16] to the formation of a nematic phase, an isotropic phase and degradation. These authors consider the behavior at lower temperatures to indicate a single "smectic" phase, but Meneczel and Wunderlich's interpretation seems more likely.

RHEOLOGICAL PROPERTIES

Results

Shear viscosity-shear rate data for the 60/40 PHB/PET copolymer are shown in Figure 2 at temperatures of 190, 210, 240, 250, 260, 280, 300, 320, and 340°C. The viscosity decreases with increasing temperature from 190 to 260°C and then "groups together" in the range of 260 to 340°C. The data are unbounded at low shear rates in all experiments below 250°C. From 250 to 340°C the data trends at low shear rates are unclear.

The shear viscosity-shear rate data of Figure 2 are replotted as a function of shear stress in Figure 3. Yield values in the range 100 to 20,000 pascal are indicated for the 190° to 250° data. These are plotted vs. temperature in Figure 4. Yield stresses were calculated via Casson plots ($\sigma^{1/2}$ vs. $\dot{\gamma}^{1/2}$).[23]

Interpretation

The same system has been studied in similar instruments over the narrower temperature range 210–240°C by Wissbrun.[10] His data indicate yield

values and are quantitatively similar to our own results at these two temperatures. Also it is to be noted that other thermotropic liquid crystalline polymers, notably cellulose ethers,[19,20] exhibit yield values in shear flow when they are in the liquid crystalline range. At higher temperatures in the isotropic range, the behavior of the cellulose ethers is Newtonian at low shear rates.

In a further attempt to characterize and understand the flow behavior we plot log $(\sigma_{12} - Y)$ vs. log $\dot{\gamma}$, see Figure 5. It is striking that PHB/PET, EC, and HPC all conform to a Herschel-Bulkley form,[24] i.e.,
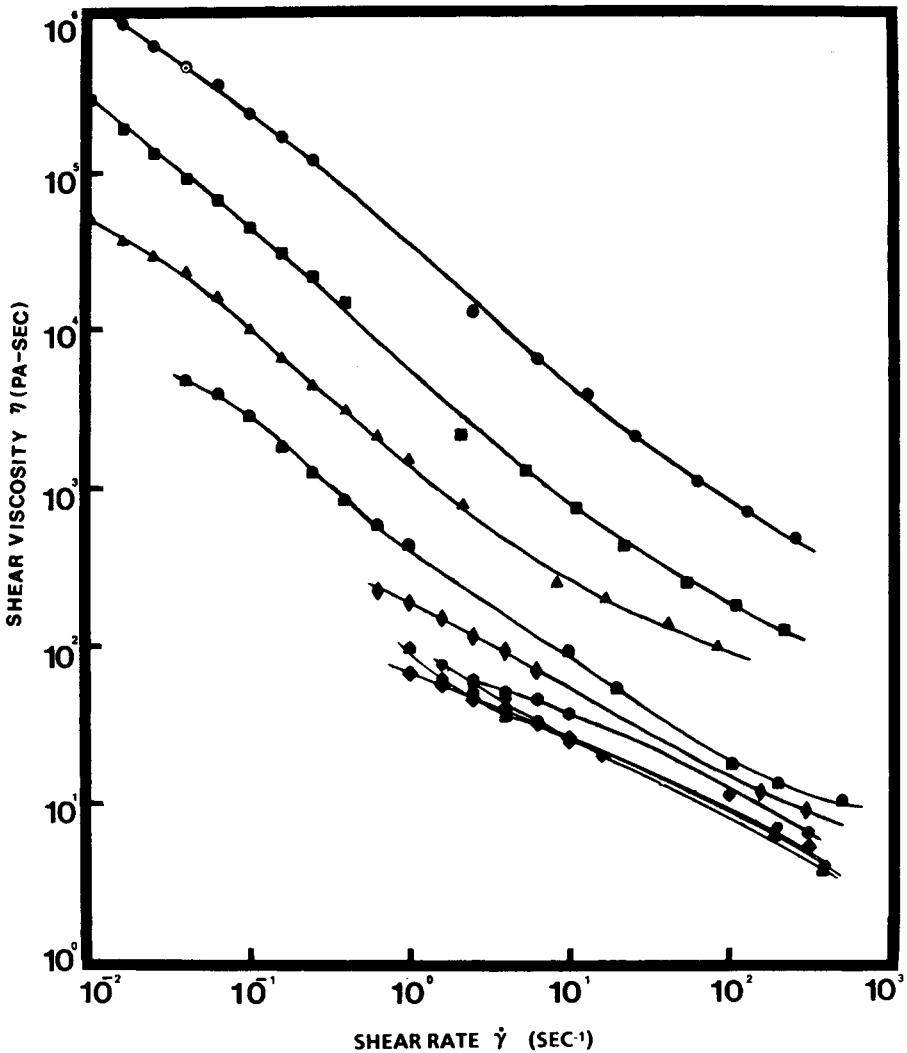
$$\sigma_{12} = Y + K\dot{\gamma}^n \qquad (1)$$

Fig. 2.   Viscosity-shear rate data for the 60/40 PHB/PET copolyester; (●) 190°C; (■) 210°C; (▲) 240°C; (◖) 250°C; (◆) 260°C; (◉) 280°C; (◆) 300°C; (▼) 320°C; (▲) 340°C.
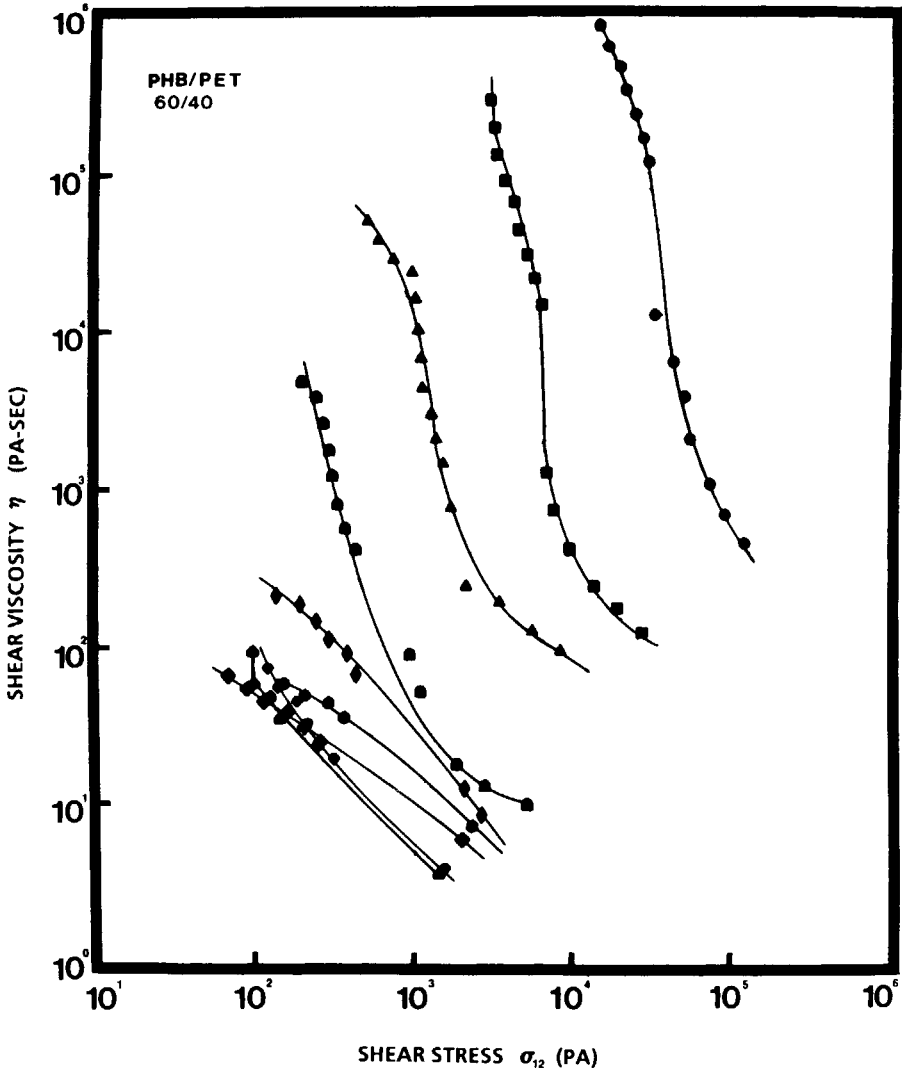
Fig. 3.   Viscosity-shear stress data for the 60/40 PHB/PET copolyester; (●) 190°C; (■) 210°C; (▲) 240°C; (■) 250°C; (◆) 260°C; (●) 280°C; (◆) 300°C; (▼) 320°C (■) 340°C.

with amazing precision. A least-square "goodness of fit" parameter is 0.98 or better. This is summarized in Table I. Thus the phenomenological shear behavior is that of a nonlinear Bingham fluid for these three materials.

EXTRUDATE SWELL

Results

A plot of extrudate swell (d/D) vs. temperature at constant shear rate is given in Figure 6. The coordinate axis is actually shear stress rather than temperature, but specific temperatures are clearly indicated. This shows that extrudate contraction occurs at temperatures below 260°C, whereas above 260°C the extrudate swell becomes greater than 1.0. Values above 1.15 only occur above 300°C.

Interpretation

Our results are consistent with the swell measurements made by Jerman and Baird[12] who also noted extrudate contraction below 260°C for this material. Suto, White, and Fellers[20] found very low swell values in HPC and EC extrudates in the liquid crystalline phase.

The trend of the extrudate swell data in Figure 6 parallels that of the plot of yield stress Y with temperature T in Figure 4. One can directly correlate the high yield stress regime to extrudate contraction, while normal extrudate swell occurs in the higher temperature regime. This correlation agrees with the suggestion of Jerman and Baird[12] that the presence of yield stresses inhibit the elastic recovery of the extrudate of liquid crystalline material. A similar phenomenon is observed in particle filled compounds.[25] This has been interpreted in some detail by White and Huang.[26]

EXTRUDATE STRUCTURE

Results

60/40 PHB/PET extrudates have been examined using scanning electron microscopy. Fracture surfaces prepared in liquid nitrogen for representative
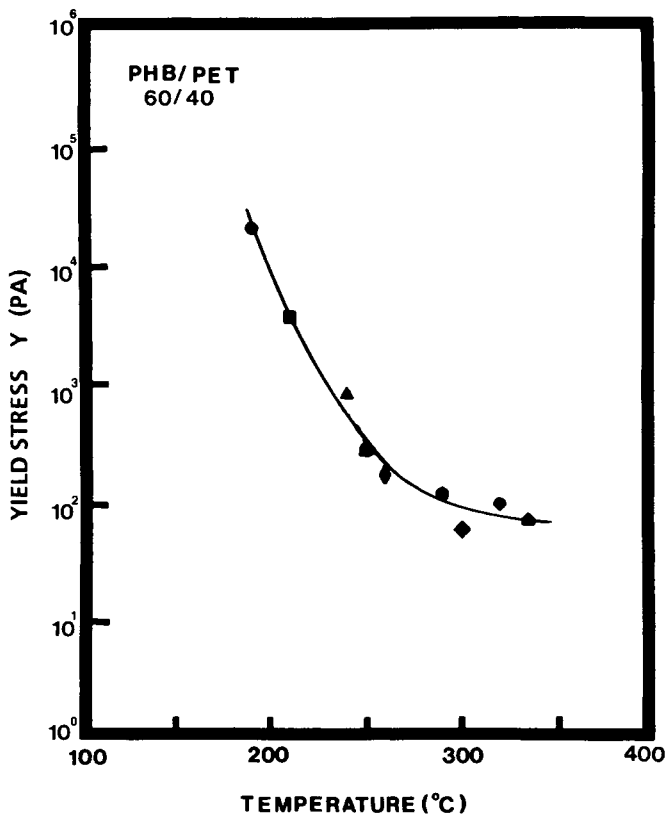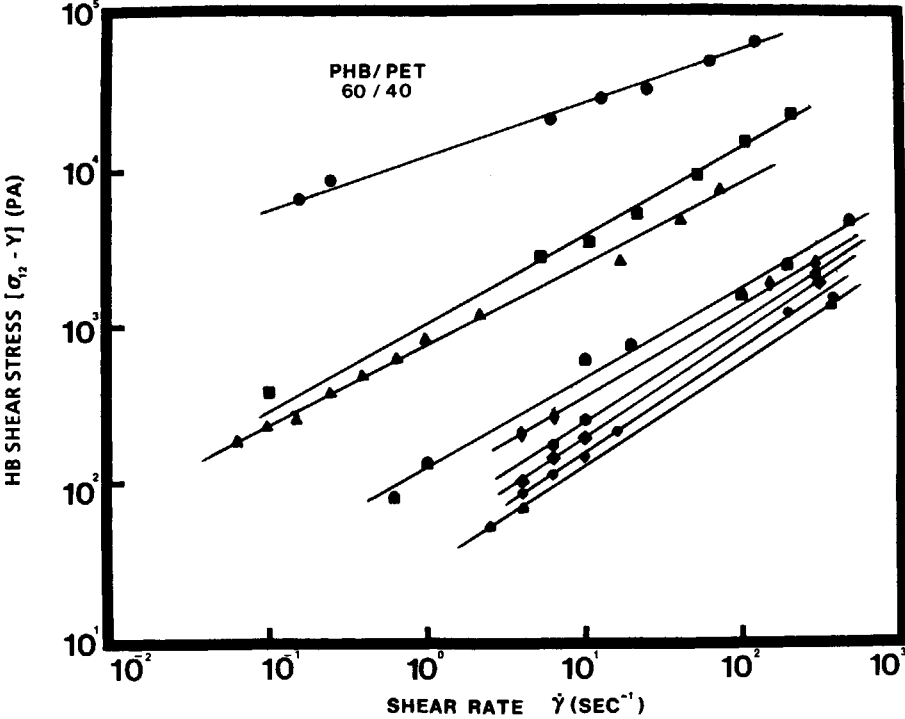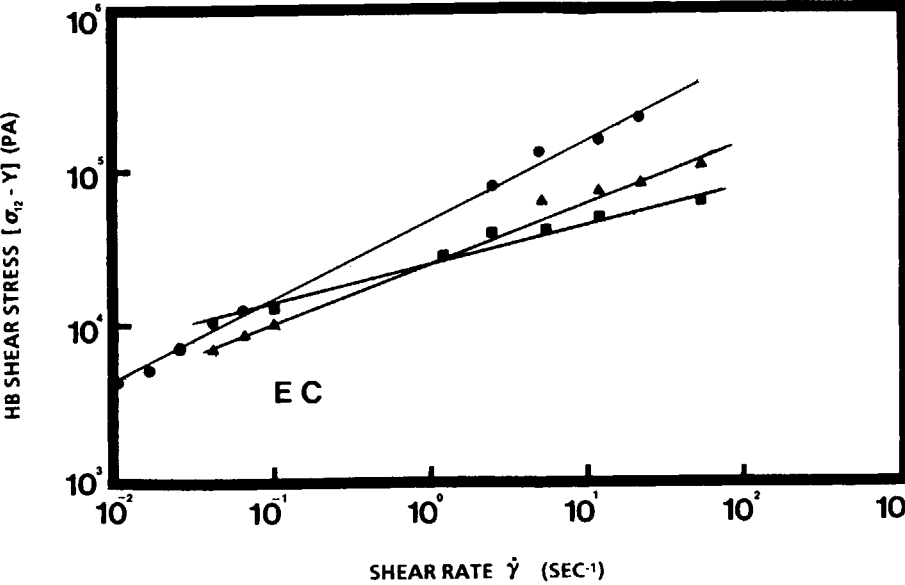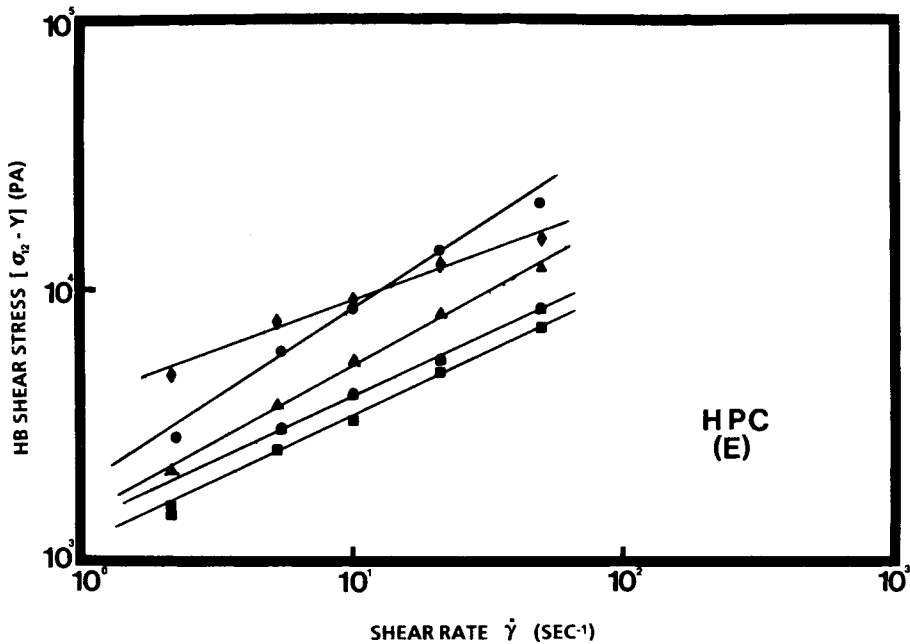

Fig. 4.   Yield stress in shear flow as a function of temperature; (●) 190°C; (■) 210°C; (▲) 240°C; (◣) 250°C; (◆) 260°C; (◉) 280°C; (◆) 300°C; (▼) 320°C; (◢) 340°C.

(a)

(b)

(c)

Fig. 5. (a) Herschel-Bulkley plot for PHB/PET 60/40 system over temperature range of 190°–340°C; (●) 190°C; (■) 210°C; (▲) 240°C; (●) 250°C; (◆) 260°C; (●) 280°; (◆) 300°C; (▼) 320°C (●) 340°C. (b) Herschel-Bulkley plot for Ethyl Cellulose over temperature range 180°–200°C; (●) 180°C; (▲) 190°C; (■) 200°C. (c) Herschel-Bulkley plot for Hydroxypropyl cellulose (E) for temperature range 160°–200°C; (●) 160°C; (▲) 170°C; (●) 180°C; (■) 190°C; (◆) 200°C.

extrudates at temperatures from 230 to 280°C are shown in Figure 7. The extrudates may be seen to be fibrillar in character.

Wide angle x-ray patterns were made on the extrudates. These show considerable orientation, the level of which depends upon temperature. Hermans orientation factors[27] f_H defined by

$$f_H = \frac{3\,\overline{\cos^2\phi_{1c}} - 1}{2} \tag{2}$$

were determined. Here ϕ_{1c} is the average angle between the chain and the fiber axis. Methods of determining the value f_H for the 60/40 PHB/PET copolyester have been developed by Mitchel and Windle.[15] These have been applied here. In the range of temperatures from 260°–300°, f_H has magnitude of order 0.65. As the temperature and shear rate are lowered further, f_H decreases. This is summarized in Figure 8.

Interpretation

The magnitude of orientation in our extrudates is very similar to that reported by Mitchel and Windle[15] for their 60/40 PHB/PET. We want to

TABLE I
Parameter Fit for PHB/PET 60/40, Hydroxypropyl cellulose (HPC), and Ethyl cellulose
(EC) from Capillary and Cone Plate Rheometers. $\sigma_{12} = Y + K (\dot{\gamma})^n$

T(°C)	K (Pa)	n	Correlation or fit	Y (Pa)
HBA/PET				
60/40				
190	12,700	0.33	0.996	20,580
210	919	0.59	0.995	3,970
240	761	0.50	0.996	841
250	126	0.58	0.993	290
260	88	0.60	0.9990	180
280	56	0.64	0.9996	113
300	41	0.67	0.9998	61
320	34	0.66	0.994	100
340	29	0.65	0.99997	75
		mean (n)		
		0.61 ± 0.06		
HPC[20]				
(E)				
160	1,884	0.64	0.994	6,402
170	1,460	0.56	0.997	2,712
180	1,065	0.54	0.988	1,525
190	972	0.56	0.963	918
200	3,905	0.37	0.992	625
EC[20]				
180	48,041	0.52	0.998	5,880
190	26,782	0.39	0.988	3,872
200	24,948	0.28	0.976	3,106

compare these results with those on thermotropic liquid crystalline cellulose
ethers. Both Shimamura et al.[19] and Suto et al.[20] observe by SEM HPC
extrudates from liquid crystalline melts to be fibrillated and have a highly
oriented surface. Shimamura et al.[19] carried out WAXS measurements on
extrudates and found Hermans orientation factors of 0.6. These results are
very similar to the observations on 60/40 PHB/PET.

The behavior of Figure 8 showing f_H decreasing with decreasing temper-
ature and decreasing shear rate is significant. It may correspond to a re-
structuring of the liquid crystalline melt at lower temperatures. At these
low temperatures high shear rates and shear stresses are necessary to
develop permanent orientation.

The rheological behavior revealed by the yield values can perhaps be
helpful in thinking about these structural features. We may speculate that
the stresses acting near the wall and in the die entrance produce in liquid
crystalline melts the high orientation at the extrudate surface. Further-
more, shear flow is not occuring in the extrudate core but there is more of
a "plug-flow." This does not lead to orientation.

The low extrudate swell values observed in the previous section are prob-
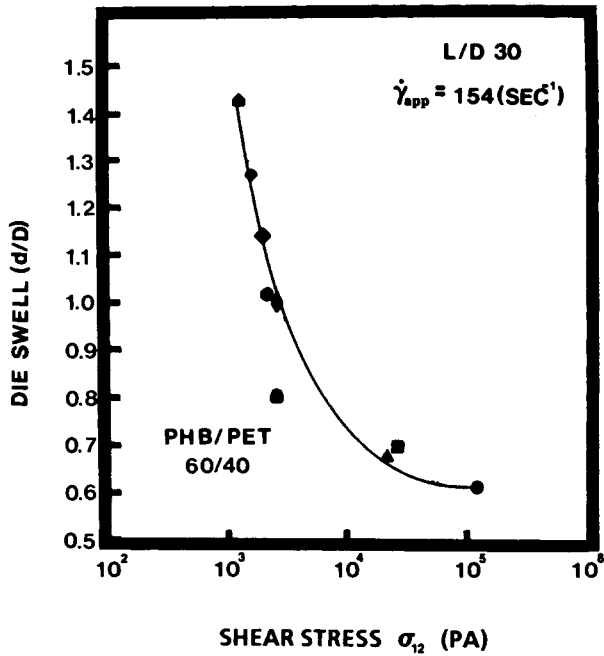ably interrelated with the failure of orientation to decay in the emerging
extrudates.

Fig. 6. Die Swell as a function of shear stress over the temperature range of 190°–340°C and fixed *L/D* 30 and fixed apparent shear rate ($\dot{\gamma}$ = 154 second^{-1}) (●) 190°C; (■) 210°C; (▲) 240°C; (●) 250°C; (◆) 260°C; (●) 280°C; (◆) 300°C; (▼) 320°C; (▲) 340°C.
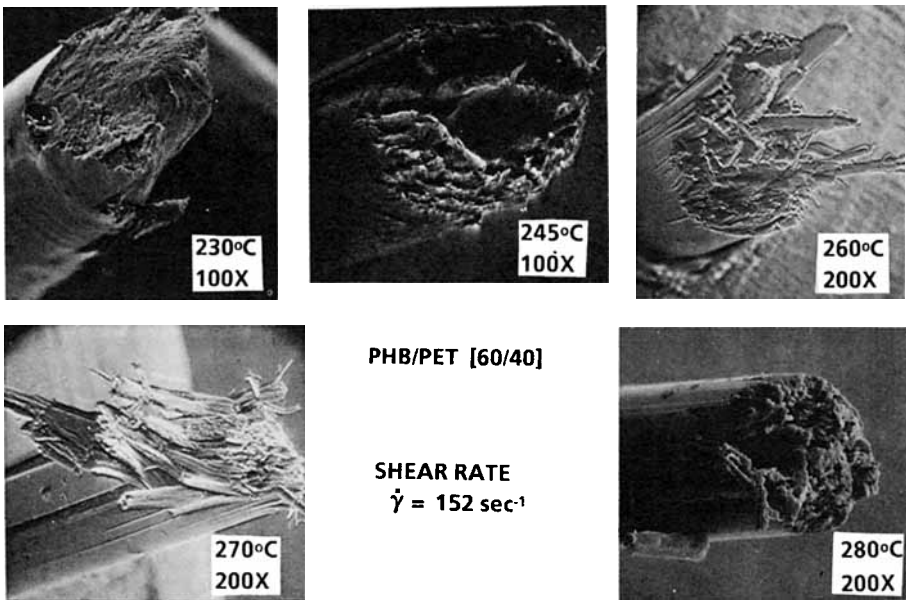

Fig. 7. SEM photomicrographs for a 60/40 PHB/PET copolyester extrudate $\dot{\gamma}_w$ = 152 second^{-1}, T = 230°, 245°, 260°, 270°, and 280°.

TEMPERATURE DEPENDENCE
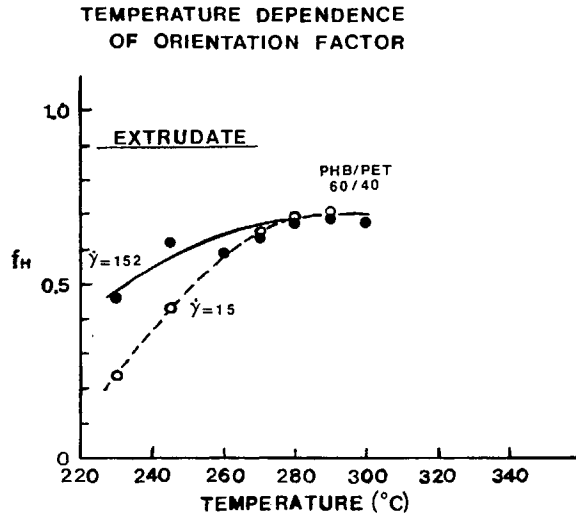OF ORIENTATION FACTOR

Fig. 8. Temperature dependence of the Hermans orientation factor, f_H for 60/40 PHB/PET extrudates.

MELT SPUN FIBERS

Results

The WAXS characteristics of melt spun fibers have been investigated. Little change in orientation was observed as a function of drawdown ratio. This is expressed in Figure 9 as the Hermans orientation factor as a function of drawdown ratio.

Interpretation

These observations on 60/40 PHB/PET correspond to those by Shimamura et al.[19] on melt spun HPC fibers. There is little variation in orientation
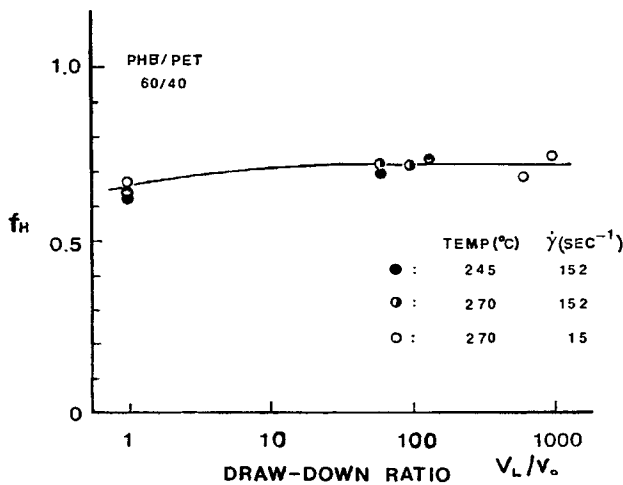

Fig. 9. Hermans orientation factor f_H of 60/40 PHB/PET function of drawdown ratio V_L/V_0.

of HPC filaments as a function of spinline drawdown ratio. Almost all of the orientation appears to be developed in the capillary. Shimamura et al.[19] concluded that only the central core of the filaments increased in orientation during spinning.

CONCLUSIONS

There seems to be a great similarity in the rheological and "melt" processing characteristics of the thermotropic liquid crystals at least between the 60/40 PHB/PET and cellulose ethers. Yield values are observed during shear flow rheological measurements. The structure developed in flow is retained in the melt following deformation. This results in low extrudate swell and fibrillated oriented extrudates. Drawing down the extrudates of such polymers on a rapidly rotating takeup roll results in only minor increases in orientation. We interpret these similarities in behavior to arise from the structure developed during flow in the die.

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