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Rheological Properties of Copolyester Liquid Crystalline Melts. I. Capillary Rheometry*

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Synopsis

Rheological properties of two copolyesters which exhibit liquid crystalline behavior in the melt state were determined using an Instron capillary rheometer. The two polymer melts with nematic liquid crystalline order consisted of copolymers of polyethylene terephthalate (PET) and 60 and 80 mole % of *p*-hydroxybenzoic acid (PHB). Data was also obtained on PET which was used as a control. Measurements included the temperature and shear rate dependence of viscosity, entrance pressure losses (ΔP_{ent}), and die swell (D_j/D). The viscosity of the liquid crystalline melts are as much as two orders of magnitude less than those of PET at temperatures at which they are ordinarily processed. The extrudate actually contracts at the lower end of processing temperatures but does increase to values greater than one with increasing temperature for the liquid crystalline polymers. Although the die swell data indicate that there is negligible elastic recovery at the capillary exit, values of the ratio of ΔP_{ent} to wall shear stress (τ_w) are considerably higher for liquid crystalline melts than for PET. Some explanation of these data is presented but more rheological measurements are needed before our understanding of these unique systems is complete.

INTRODUCTION

There is presently considerable interest in polymer systems with liquid crystalline order. The interest in these unique structured fluids stems from the production of ultrahigh strength and modulus fibers and plastics. At present fibers with exceptionable physical properties are produced commercially from lyotropic systems of poly-*p*-phenyleneterephthalamide (PPT) in sulfuric acid.^{1,2} The modulus of these fibers ranges from 600 to 1200 g/denier (this corresponds to 7.7

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$\times 10^{10}$ – 15×10^{10} Pa) and tensile strengths from 20 to 30 g/denier (2.57×10^9 – 3.85×10^9 Pa). For steel, these same material parameters range from 280 to 300 g/denier (19×10^{10} – 20.3×10^{10} Pa) for the modulus while the tensile strength values range from 3.0 to 4.5 g/denier (2.03×10^9 – 3.05×10^9 Pa). Hence, when compared on a weight basis man can now manufacture polymeric materials with physical properties exceeding those of steel.

Probably the most unique aspect of these fibers and plastics is the excellent physical properties found in the as-extruded filaments and as-injected molded specimens, i.e., no further processing is required to produce desirable physical properties. Similar findings have been reported for the spinning and injection molding of highly aromatic polyester melts with liquid crystalline behavior.³⁻⁵ In summary, a review of processing conditions seems to imply that the high degree of molecular orientation and physical properties of solid materials are the direct result of molecular orientation which is generated during melt or solution flow. Hence, the physical properties of solid materials produced from liquid crystalline polymers must be directly related to their flow behavior. For this reason, an in-depth understanding of their rheology is necessary.

Before reviewing existing studies concerned with the rheology of liquid crystalline polymeric systems, there are several terms which need defining. Lyotropic systems refer to liquid crystals which exist in solution. Liquid crystalline order has also been observed in polymer melts or undiluted polymers in which case we refer to the liquid crystalline melts as thermotropic. Fluids with liquid crystalline order are also referred to as mesophases because they are thought to be an intermediate phase between the crystalline and isotropic fluid phase and also as anisotropic fluids. There are three mesophases: nematic, cholesteric, and smectic. These are described in detail in several places.⁶⁻⁸ In this article our interest is in the nematic mesophase which seems to be formed by rodlike polymer chains.

Although we are primarily interested in thermotropic polymeric liquid crystals, we will look briefly at the rheology of lyotropic systems since there may be a similarity between rheological properties of lyotropic and thermotropic systems. The most distinguishing characteristic for lyotropic systems is the large drop in viscosity with the onset of liquid crystalline order.^{1,2,9,10} The onset of liquid crystalline order is a function of polymer molecular weight and concentration, temperature, and nature of the solvent. In addition to the

large decrease in viscosity, other material functions such as the primary normal stress difference (N_1) and the storage (G') and loss moduli (G'') decrease with the onset of liquid crystalline order.¹¹ The fluid elasticity, however, seems to increase with the degree of liquid crystallinity.¹¹

The existence of yield stresses in lyotropic systems has been reported by Papkov and co-workers⁹ and Aoki and co-workers.¹² The yield stresses, however, may be due to the formation of solid crystalline regions at high polymer concentration and low temperatures. Baird¹³ found that on heating lyotropic systems, the yield stresses disappeared and a Newtonian flow region was observed. The occurrence of yield stresses is an important phenomena since they can lead to plug flow during processing of these polymers.

There are only two reports in the literature pertaining to rheological measurements concerning properties other than viscosity.^{11,13} Baird¹¹ and Aoki and co-workers¹² measured the primary normal stress difference (N_1) and the dynamic oscillatory properties of solutions of poly-*p*-phenyleneterephthalamide (PPT) in 100% H₂SO₄. Baird compared data with two constitutive equations, one of which was developed for anisotropic fluids. Some agreement was found between data and theoretical predictions.

For thermotropic systems, there are only two reports pertaining to rheological properties.^{4,14} Jackson and Kuhfuss⁴ used a capillary rheometer to measure the viscosity of copolymers of polyethylene terephthalate (PET) modified with varying amounts of *p*-hydroxybenzoic acid (PHB). The viscosity of the compositions with liquid crystalline order was significantly lower than PET and other isotropic compositions. However, they measured only the apparent viscosity since they neither corrected their pressure measurements for end pressure losses nor the shear rate for nonparabolic velocity profiles. Wissbrun¹⁴ measured the rheological properties of similar copolymers using a Rheometrics Mechanical Spectrometer and a capillary rheometer. His major findings were that the anisotropic melts exhibited very long relaxation times and appeared to be highly elastic. Several flow anomalies were noted including rheopexy in some compositions, negative normal stresses, and negligible die swell. None of these phenomena, however, were studied in detail.

Although many types of rheological measurement are needed to fully characterize and understand these unique polymer fluids, the emphasis of the work presented here is on rheological properties de-

terminated from a capillary rheometer. In particular it is our purpose to measure not only the viscous properties but also die swell and entrance pressures of a thermotropic polymer system. In particular, results are reported for two thermotropic polymers consisting of 60 mole % PHB/PET and 80 mole % PHB/PET. Data are also reported for isotropic melts of PET.

EXPERIMENTAL

Materials

Three polymers were used in this study: PET with an intrinsic viscosity (IV) of 0.60 dl/g, 60 mol % PHB/PET with an IV of 0.74 dl/g and 80 mol % PHB/PET. The last polymer was insoluble in any known solvent so that the IV could not be measured. The polymers were supplied by Tennessee Eastman Kodak Co., and polymerization procedures are given in the articles by Jackson and Kuhfuss⁴ and McFarlane and co-workers.⁵

Capillary Rheometry

All studies reported in this article were carried out using an Instron capillary rheometer (model 3211). Force readings and plunger speed were converted to pressure drop and apparent shear rate, respectively, using well-known methods. All measurements reported here were made using capillaries of 0.052 in. diameter and length to diameter ratios (L/D) of 20, 40, and 60. The entry angle was 90° in all cases. The pressure readings were then plotted as a function of L/D and extrapolated to $L/D = 0$ to determine the end correction pressures (P_{end}) according to procedures given by Bagley.¹⁵ Although more data is given elsewhere,¹⁶ the Bagley plots were linear over this range of L/D values. Values of P_{end} were repeatable to within $\pm 10\%$. The apparent shear rates ($\dot{\gamma}_{\text{app}}$) were converted to wall shear rates ($\dot{\gamma}_w$) using the Weissenberg-Rabinowitsch correction.¹⁷

The capillaries used in this study were different from the standard capillaries supplied with the Instron in that they protruded from the locking nut exposing the face of the capillary. The capillary portion protruding from the locking nut was heated by a band heater. The temperature of the capillary was controlled by a temperature controller to $\pm 1.0^\circ\text{C}$. The modified capillary design was necessary to facilitate measurements of die swell.

As shown later, die swell for the liquid crystalline polymers was less than 1 in some cases. So the method of measuring die swell had to be chosen with care. For data reported in this article, the melts were extruded directly into a silicone oil of density slightly less than the solid polymer. In this way the effect of the weight of the extrudate on drawing the filament was minimized. The diameter of the quenched filament was determined by using a photographic enlarger to project a silhouette of the extrudate on the floor. The silhouette, which represented a magnification of 30–40 times the filament diameter, was then measured. Quenching the extrudate immediately can lead to reduced die swell since the total expansion is in some cases not realized immediately on leaving the capillary.¹⁸ However, annealing quenched samples for 2 hr near the softening or melting point lead to no measurable increase in diameter. The quenching technique used here lead to results statistically equivalent to that obtained by photographing the extrudate directly as it emerged from the capillary.

Finally, great care had to be taken in handling these polymers because they rapidly degrade in the presence of moisture and heat leading to a reduction in viscosity. Small quantities of polymer sufficient to fill the rheometer barrel were dried under 25 in. of vacuum at 110°C for a period of 72 hr. On opening the drying oven nitrogen was bled over the samples. Still, even in loading the Instron barrel, sufficient moisture was available in the air in the barrel to degrade the polymers. For this reason, the Instron barrel was loaded while being flushed with dry nitrogen.

RESULTS

There is some question as to whether the polymers studied here are actually nematic liquid crystals. Similar to the observations reported by McFarlane and co-workers⁵ we find the copolyester melts to be turbid but of low viscosity. The PET melt is clear and has much higher viscosity than the copolyester at certain temperatures. Lyotropic cholesteric and nematic liquid crystals exhibit distinct birefringence patterns in the polarizing microscope.^{19,20} For example, cholesteric mesophases of poly- γ -benzyl-L-glutamate exhibit well-defined extinction bands with periodic spacing. Nematic mesophases of poly-*p*-phenyleneterephthamide (PPT) in sulfuric acid exhibit a few extinction bands, but the pattern looks more like microscopic

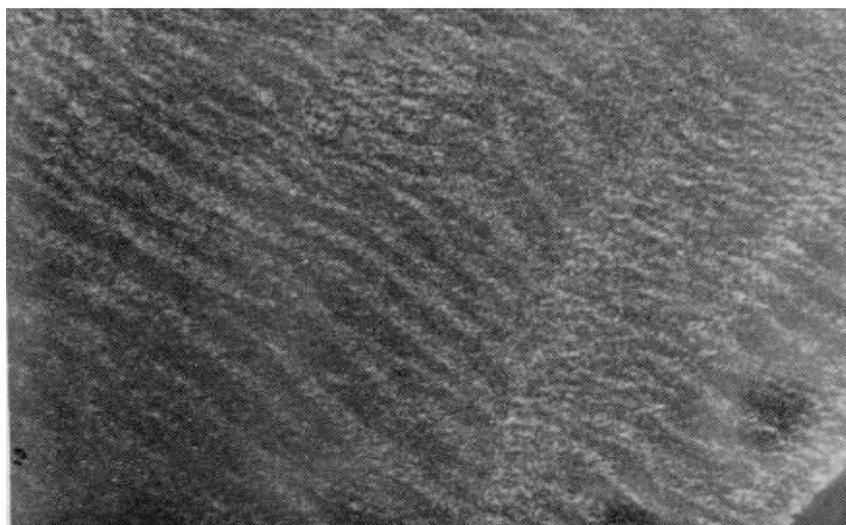


Fig. 1. Birefringence pattern of 60 mole % PHB/PET at 300°C, 120X.

domains.²⁰ In Figure 1 is presented a photograph of the birefringence pattern taken in a polarizing microscope of a thin liquid film of 60 mole % PHB/PET at 300°C. The pattern resembles to some degree that observed for lyotropic nematics.¹³ The microdomains of color are not crystalline regions, since, as shown later, the viscosity of this melt is only 1 Pa-sec. Other evidence for these melts exhibiting liquid

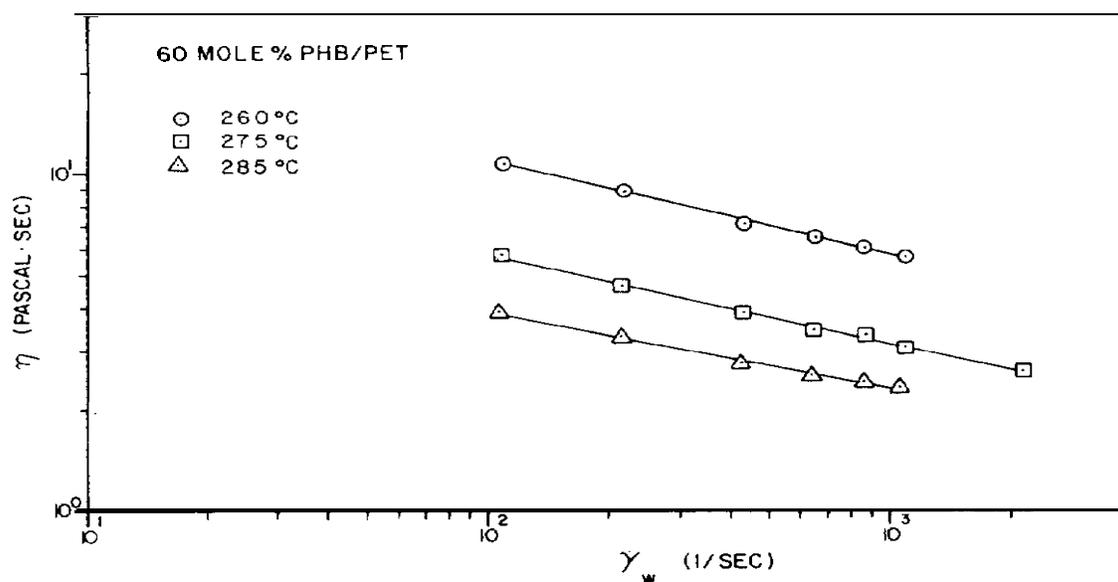


Fig. 2. Viscosity vs. wall shear rate for 60 mole % PHB/PET as a function of temperature.

crystalline order is given in the article by McFarlane and co-workers.⁵

From values of τ_w and $\dot{\gamma}_w$, the viscosity (η) was determined and results are presented in Figures 2–4. When compared at the same temperature (e.g., 285°C), the viscosity of the 60 mole % PHB/PET copolymer is two orders of magnitudes lower than that of PET. We also observe that η for the two copolymers is dependent on $\dot{\gamma}_w$, whereas it is nearly independent of $\dot{\gamma}_w$ for PET. Because of the shear dependence of η for the 80 mole % PHB copolymer, it actually becomes less than that for PET when compared at the same temperature. Finally, for the 80 mole % PHB/PET copolymer, the temperature of the melt must be considerably higher than that of the 60 mole % PHB/PET copolymer before η is similar in magnitude.

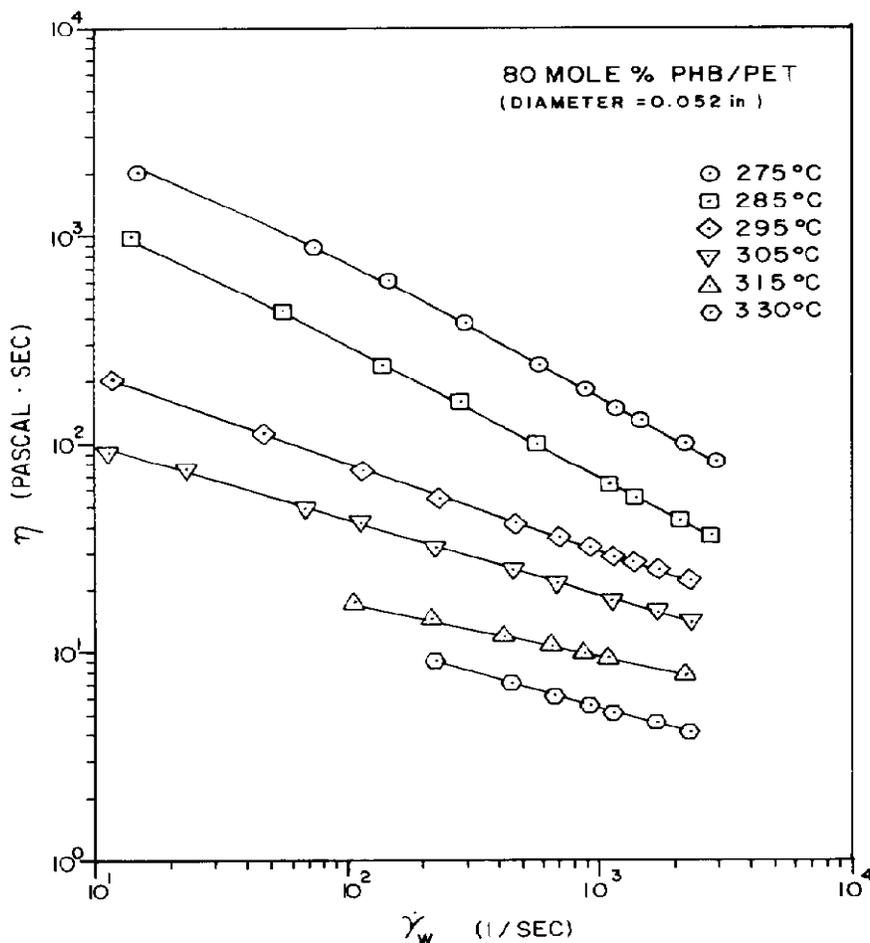


Fig. 3. Viscosity vs. wall shear rate for 80 mole % PHB/PET as a function of temperature.

Fluid elasticity has been associated with entrance pressure losses.^{15,16} Values of ΔP_{ent} vs. apparent shear rate ($\dot{\gamma}_{\text{app}}$) are presented in Figures 5–7. When compared at the same temperature values of ΔP_{ent} for the 80 mole % PHB/PET copolymer are considerably higher than those of PET and 60 mole % PHB/PET copolymer. Values of ΔP_{ent} for the 60 mole % PHB/PET copolymer are slightly lower than those of PET when compared at the same temperature. Finally, when η of the two copolymers is similar (i.e., at 275°C for the 60 mole % PHB/PET copolymer and 330°C for the 80 mole % PHB/PET copolymer) then ΔP_{ent} of the 80 mole % PHB/PET copolymer is significantly lower.

Die swell was determined for all three polymers at various temperatures. Representative data for PET at 285°C is shown in Figure 8. As expected for flexible chain polymers, D_j/D increases with increasing $\dot{\gamma}_{\text{app}}$ and decreasing capillary length (L). Likewise, D_j/D decreases with increasing temperature. (Further data is available in Ref. 16). Data for 60 mole % PHB/PET at various temperatures is shown in Figure 9. At 260°C we see that the extrudate actually contracts but D_j/D increases with temperature becoming greater than 1.0 at 285°C. For the 80 mole % PHB/PET a composite of die swell values determined at various temperatures is presented in Figure 10.

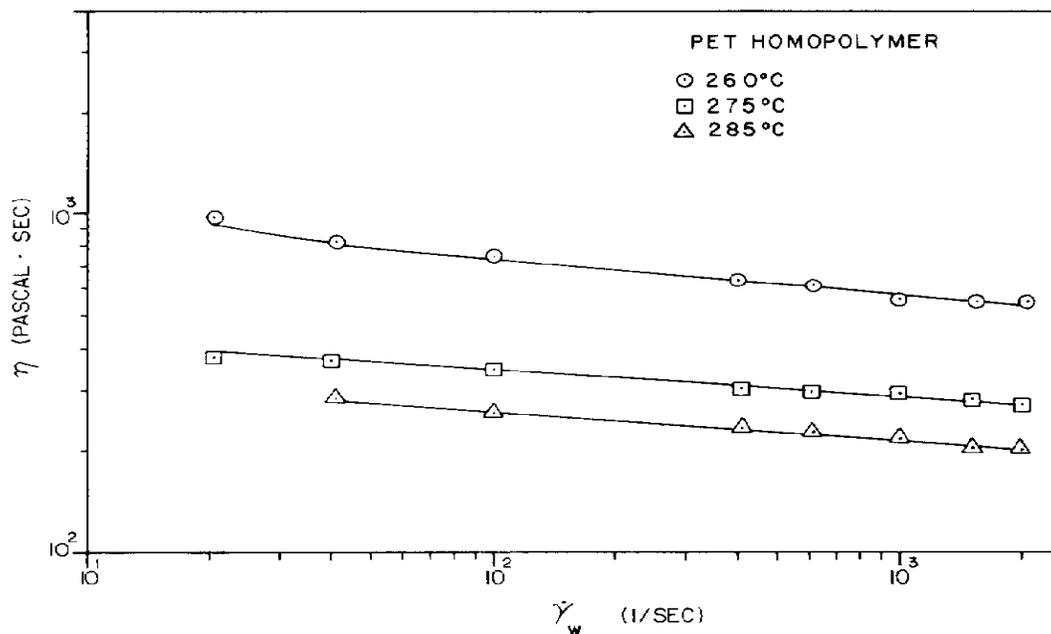


Fig. 4. Viscosity vs. wall shear rate for PET as a function of temperature.

Again at 275 and 285°C, the extrudate contracts but values of D_j/D increase with increasing temperature, reaching values similar to those for PET. Complete data is available elsewhere.¹⁶ Two further points are worth noting. First, even when the extrudate contracts, values of D_j/D increase with decreasing capillary length. Second, when values of D_j/D are less than 1, then D_j/D decreases with increasing $\dot{\gamma}_{app}$.

DISCUSSION

There seems to be overwhelming evidence that the two copolymer melts over some temperature range form nematic liquid crystals. Data given by McFarlane and co-workers⁵ supporting liquid crystalline behavior include formation of opaque quenched films, high-density amorphous solids, and wide-line NMR data. Our observa-

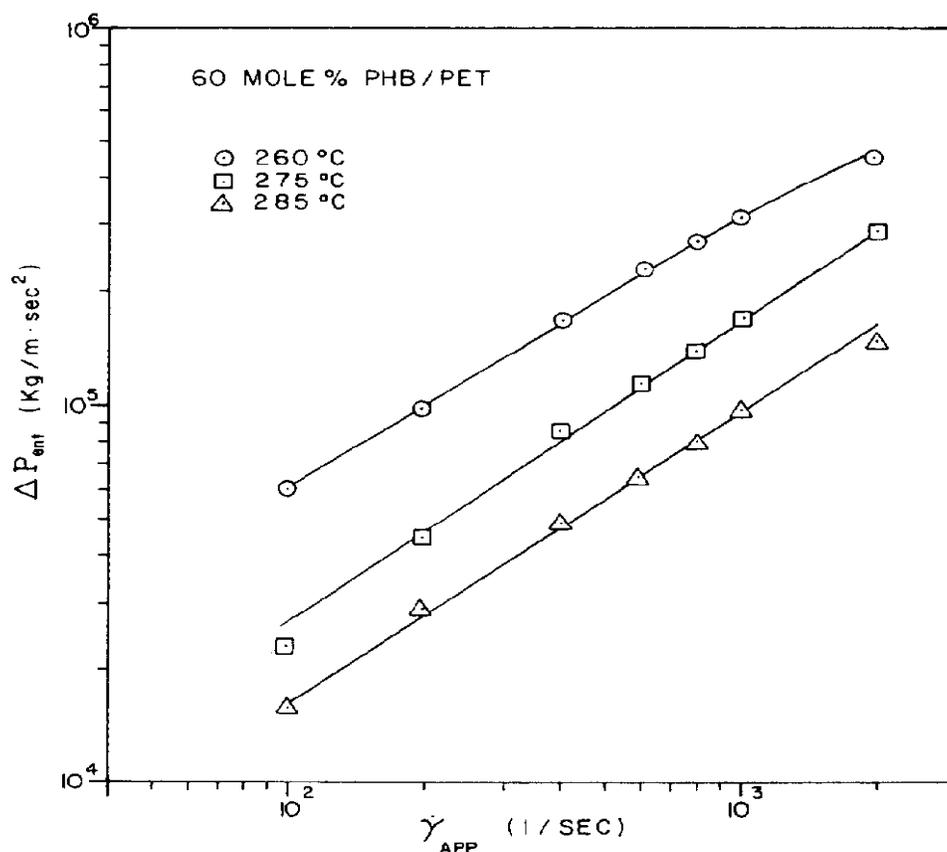


Fig. 5. Entrance pressure loss vs. apparent shear rate for 60 mole % PHB/PET.

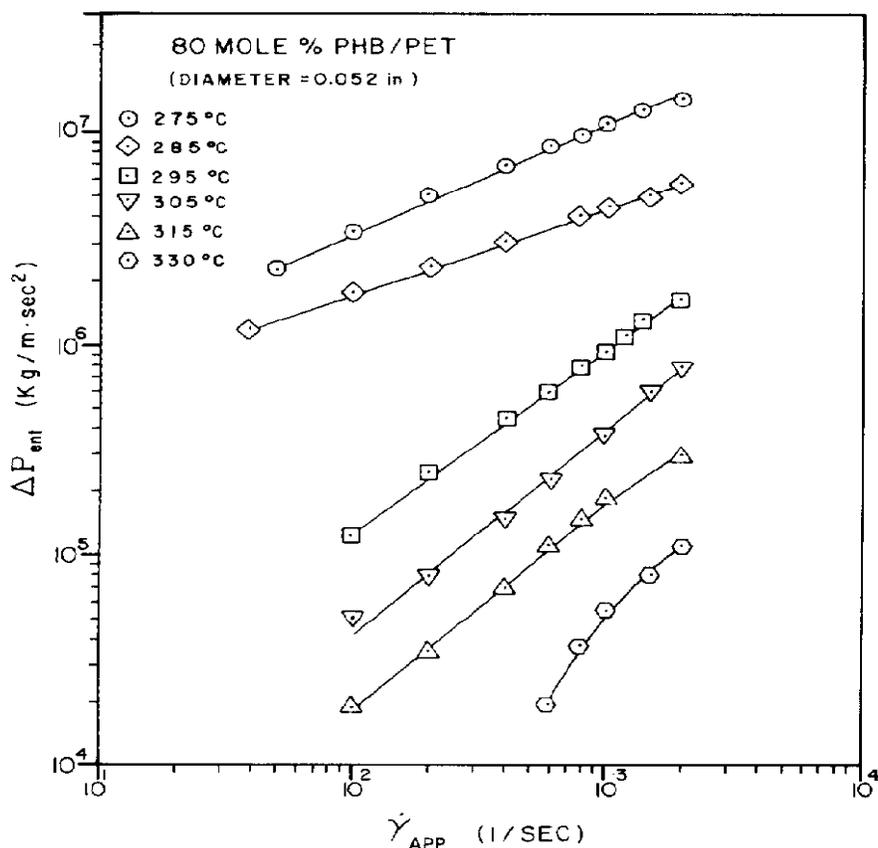


Fig. 6. Entrance pressure loss vs. apparent shear rate for 80 mole % PHB/PET.

tions of the melt in the polarizing microscope reveal that even though the melt viscosity is low, the liquid still transmits polarized light. These patterns are similar to those reported for lyotropic nematic liquid crystals.

As has been proposed for lyotropic nematics,^{10,13} the low viscosity of the 60 mole % PHB/PET copolymer may also be attributed to domains of rodlike molecules in which all molecules have a common orientation. During flow these domains act as the flow unit rather than the individual molecules. The molecules slide smoothly over each other dissipating less energy than randomly oriented and entangled molecules. This picture is similar to that proposed by Wissbrun.¹⁴

The 80 mole % PHB/PET copolymer exhibits much higher viscosity than the 60 mole % PHB/PET copolymer when compared at the same temperature. The 80 mole % PHB/PET copolymer, however, is

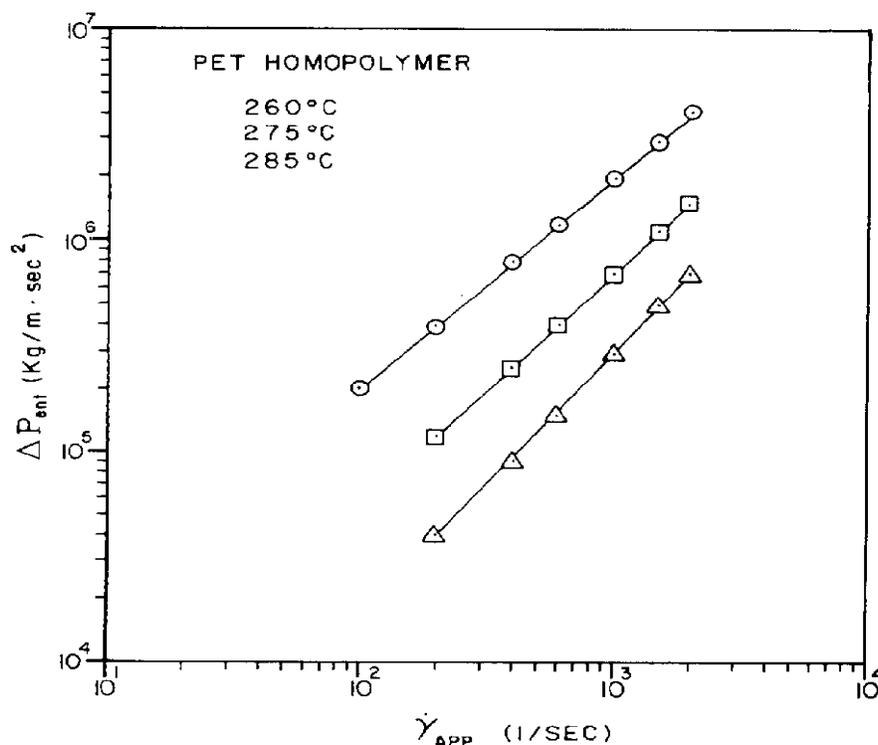


Fig. 7. Entrance pressure loss vs. apparent shear rate of PET.

known to exhibit a crystalline melting point at 293°C, whereas the 60 mole % PHB/PET copolymer exhibits neither a glass transition temperature or a melting point.⁴ Hence, the higher viscosity of the 80 mole % PHB/PET copolymer can be attributed to the solidlike regions below 293°C. Again, however, as the temperature is increased to 330°C, η becomes extremely low.

Our results show that for the copolymers the die swell is extremely temperature dependent. However, rather than decreasing with increasing temperature it increases. More interestingly, values of D_j/D are less than 1 at the lowest temperatures for which flow is possible. Various mechanisms can be proposed to account for the extrudate behavior. We first consider the extrudate contraction. One thought is that the density of the solid extrudate is considerably less than that of the melt. Hence, collecting the extrudate in silicone oil could quench and prevent it from expanding. However, photographs of the extrudate emerging from the capillary gave no statistical difference in the die swell values. Furthermore, die swell values for PET were similar to those reported for other flexible chain polymers in-

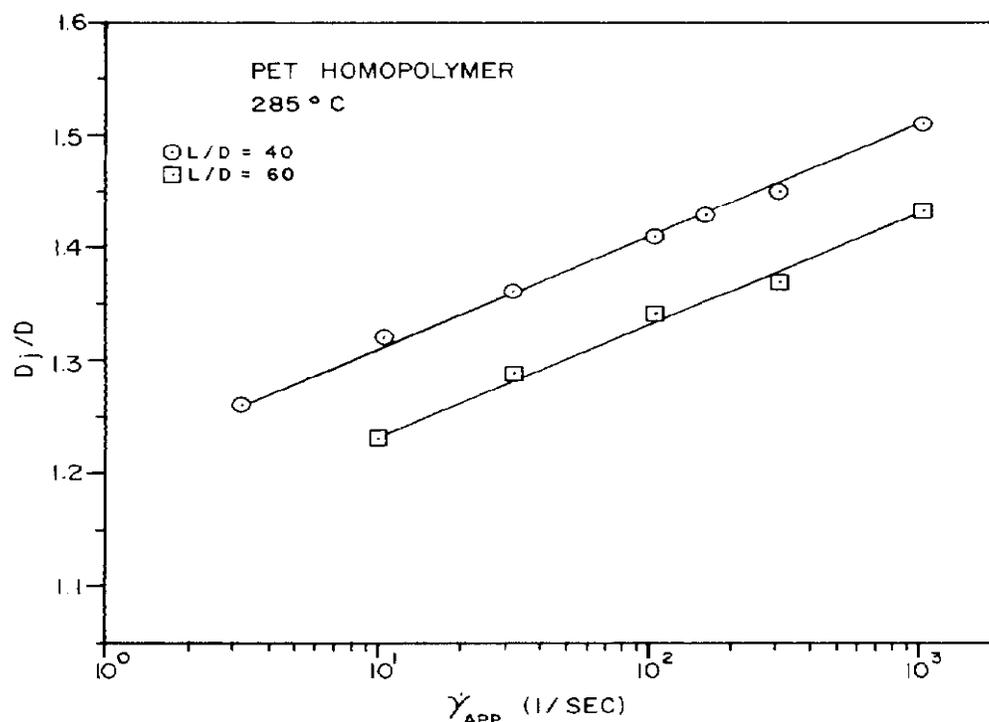


Fig. 8. Die swell vs. apparent shear rate for PET at 285°C. $L/D = 40$.

dicating that the quenching technique had no overriding effect on values. At a temperature of 285°C, values of D_j/D for the 60 mole % PHB/PET copolymer were greater than 1 while those for the 80 mole % PHB/PET sample were less than 1. Hence, if the quenching of the extrudate were responsible for the extrudate contraction then both polymers should show similar behavior since heat transfer would be the same. Finally, annealing the extrudates for 2 hr near their melting point lead to no significant increase in die swell.

Two other realistic mechanisms include yield stresses and negative normal stresses. Several researchers^{21,22} have reported that filled isotropic melts exhibited negligible die swell. These systems were also observed to exhibit yield stresses (τ_0). The lack of die swell could be attributed to the yield stresses which inhibit elastic recovery of the extrudate. Also, the shear field in the capillary is limited to a narrow region near the wall with the core of the melt passing through the capillary in plug flow. Hence, there will be a region in which elastic recovery will not occur. For lyotropic liquid crystals there is some evidence of yield stresses which occur at low temperatures as the result of crystalline regions but disappear at higher temperatures.¹³ For

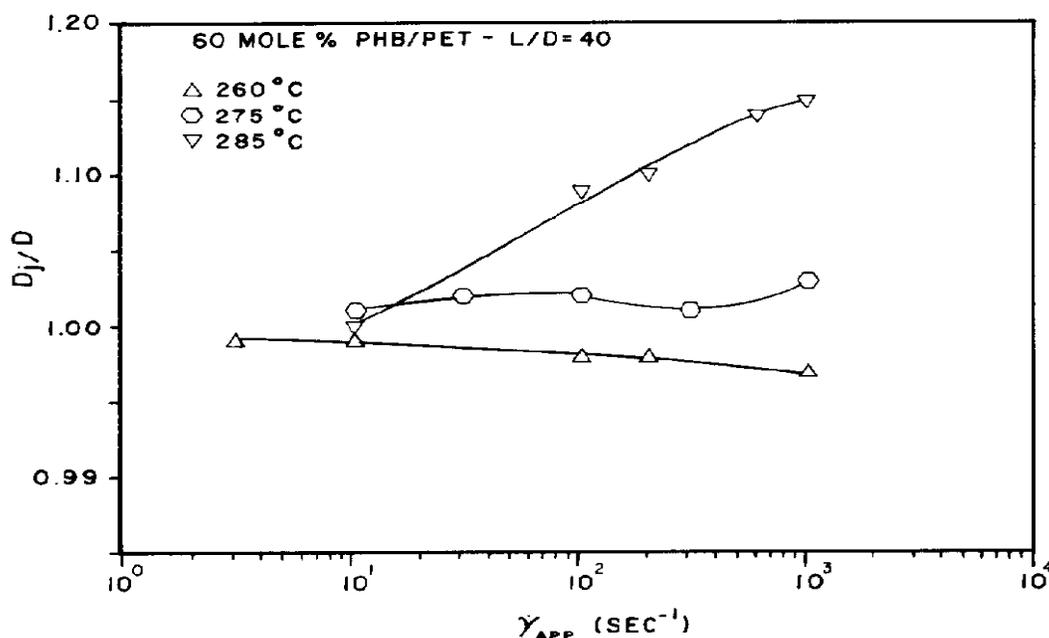


Fig. 9. Die swell vs. apparent shear rate for 60 mole % PHB/PET for various temperatures $L/D = 40$.

thermotropic systems, sufficient data at low shear rates is not available to determine the existence of yield stresses. However, if yield stresses do occur, they could account for all the behavior observed for the liquid crystalline copolymers. At low temperatures (e.g., at 285°C for the 80 mole % PHB/PET copolymer) sufficient crystalline regions exist to give rise to the formation of yield stresses (τ_0). As the temperature increases, the magnitude of τ_0 decreases, thus allowing some die swell to occur.

Another explanation involves the possibility of negative primary normal stress differences (N_1). All theories of die swell relate D_j/D to N_1 . If D_j/D is less than or equal to 1, then one immediate conclusion is that N_1 is negative or negligible. Negative values of N_1 have been measured for a lyotropic liquid crystalline system²³ and for similar thermotropic copolymers at some temperatures.¹⁴ It may be that as the temperature increases the formation of isotropic regions begins leading to positive values of N_1 and hence values of D_j/D greater than 1.0. However, if isotropic regions form, then one might expect a rise in η which does not occur. Either, or a combination of both of these last two mechanisms, may be realistic for accounting for the observed die swell behavior. However, more rheological data is needed to establish the mechanism.

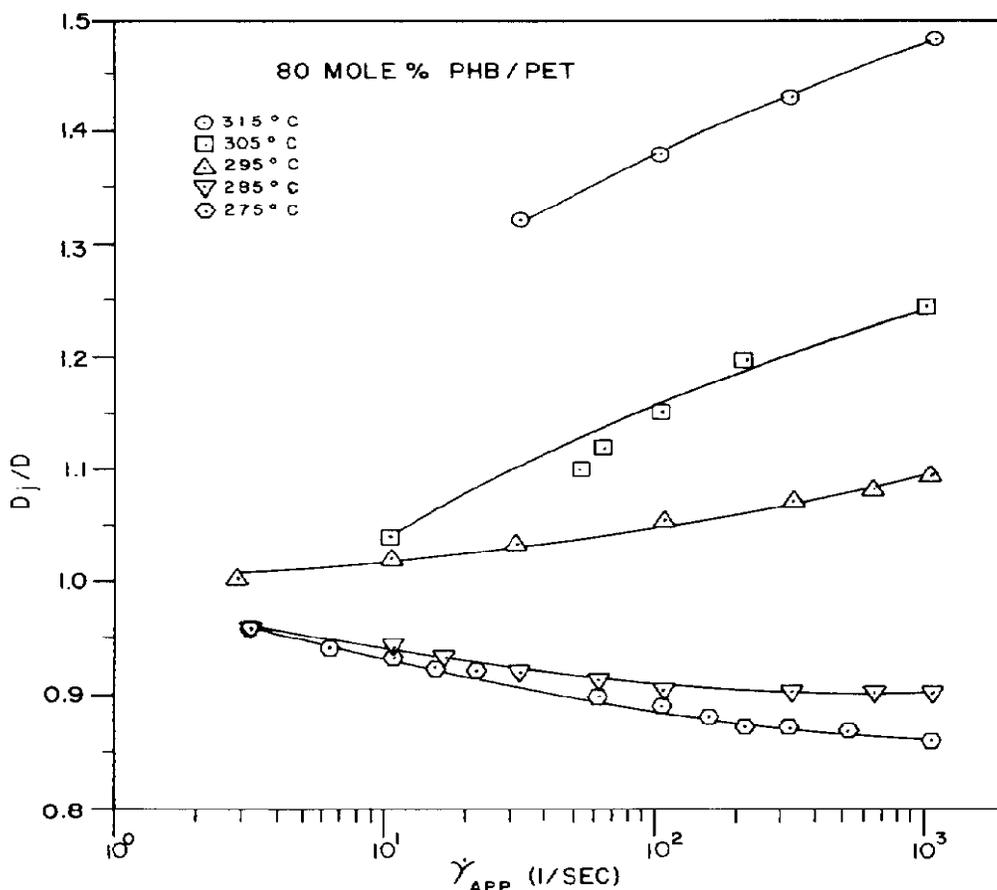


Fig. 10. Die swell vs. apparent shear rate for 80 mole % PHB/PET at various temperatures. $L/D = 40$.

For flexible chain isotropic polymer melts, entrance pressure losses have been associated with fluid elasticity and N_1 .^{15,18} Values of $\Delta P_{ent}/\tau_w$ are thought to represent the elasticity of a polymer melt.²⁰ It is therefore of interest to compare values of $\Delta P_{ent}/\tau_w$ for the three polymers and see if there is any correlation with die swell behavior. In Figure 11 values of $\Delta P_{ent}/\tau_w$ vs. $\dot{\gamma}_{app}$ are plotted for the three polymers at 275°C. At this temperature, values of D_j/D were less than 1 for the 80 mole % PHB/PET copolymer and slightly greater than 1 for the 60 mole % PHB/PET copolymer. For PET, values of D_j/D vary from 1.2 to 1.6. Yet, values of $\Delta P_{ent}/\tau_w$ are highest for the 80 mole % PHB/PET copolymer. In Figure 12 values of $\Delta P_{ent}/\tau_w$ are compared for the three polymers at temperatures where the die swell is similar. Again the liquid crystalline copolymers have higher values

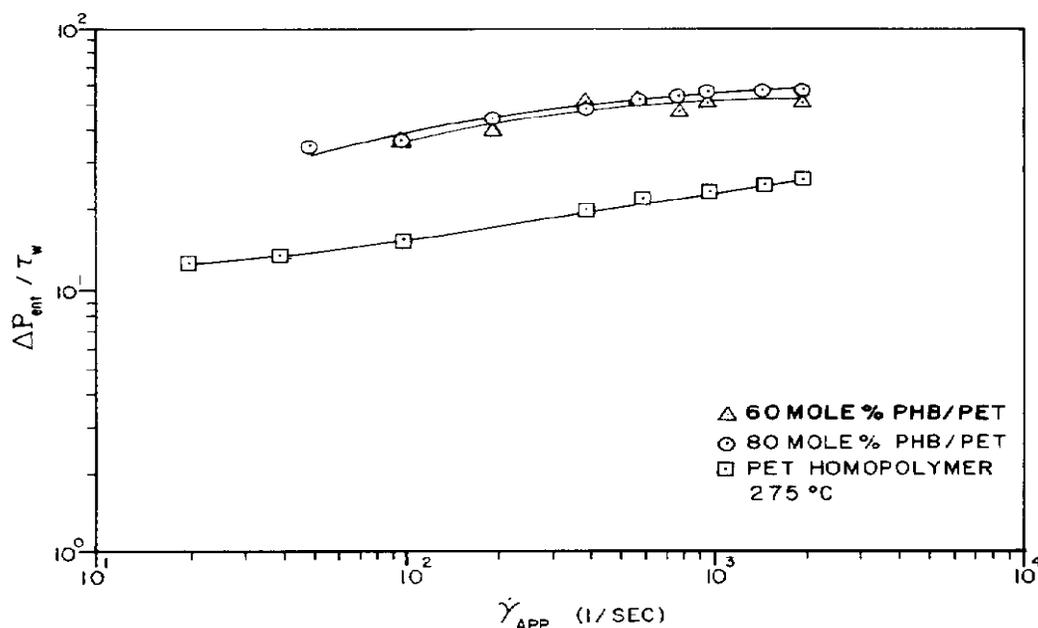


Fig. 11. Values of $\Delta P_{ent}/\tau_w$ vs. apparent shear rate for PET, 60 mole % PHB/PET and 80 mole % PHB/PET at 275°C.

of $\Delta P_{ent}/\tau_w$. One conclusion that can be drawn is that large amounts of energy are used in the entrance of the capillary to orient the domains of rigid chain molecules. Because the relaxation times are extremely long, the energy is not recovered at the exit of the capillary. Hence, there is very little recovery at the exit of the capillary. There is some support of this idea since as-extruded fibers and injection molded plates have a high degree of molecular orientation.^{3,4}

FURTHER DISCUSSION

Kuhfuss and Jackson⁴ report a number of interesting data relating physical properties of injection molded test specimens to processing conditions. For example, they observed that the tensile strength of the test specimens depended on the thickness of the mold and the fill rate. Furthermore, the test specimens were highly anisotropic with the highest physical properties along the flow directions. Finally, at a given fill rate the optimum physical properties depended on the molding temperature. These data imply that the excellent physical properties (e.g., tensile strength and modulus) arise from molecular orientation of the rodlike molecules during melt flow.

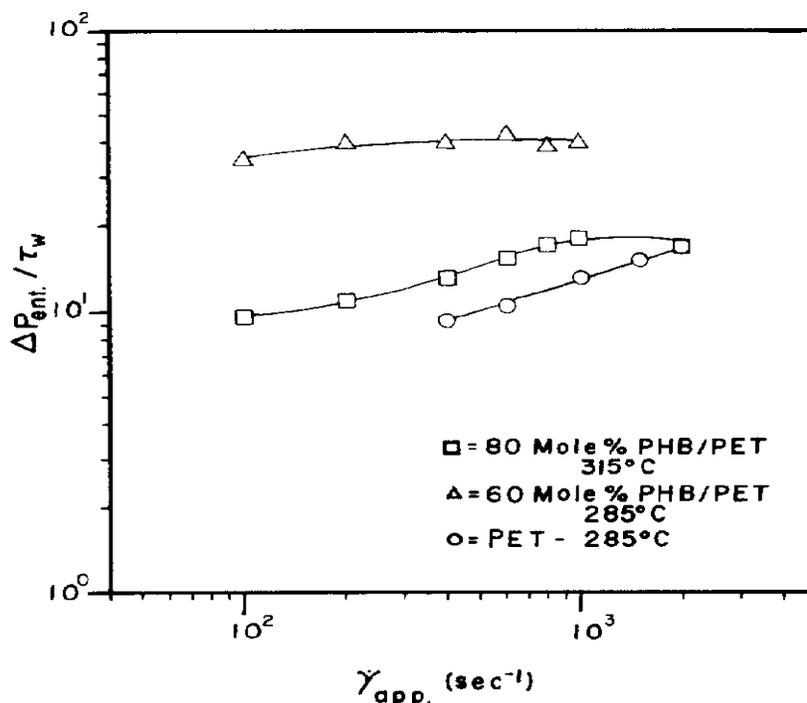


Fig. 12. Values of $\Delta P_{ent}/\tau_w$ vs. apparent shear rate for PET, 60 mole % PHB/PET and 80 mole % PHB/PET compared at temperatures where die swell is similar for the three polymers.

One question which arises is whether there are any keys in the rheological behavior suggestive of processing conditions which would lead to the optimum physical properties. Because of lack of sufficient data we can only speculate at this time. According to the data of Kuhfuss and Jackson⁴ the optimum physical properties for a 60 mole % PHB/PET copolymer occur someplace between 260 to 280°C. From our data we see that in this temperature range the melt viscosity is very low (less than 10 Pa·sec) and die swell is becoming greater than or equal to 1. It may be that the disappearance of yield stresses allows nearly complete orientation of the molecules during mold filling. Similar results were reported for 80 mole % PHB/PET but the temperature range for the optimum physical properties was between 340 and 400°C which is higher than the range of temperatures used here. This higher temperature range for the 80 mole % PHB/PET copolymer may be due to the existence of high temperature melting crystallites.

CONCLUSIONS

A number of interesting rheological properties were observed for these liquid crystalline melts. In particular we find that

(1) the melt viscosity of the copolyesters is considerably lower than that of PET at processing temperatures;

(2) contraction of the extrudate occurs at the lowest temperatures for which flow is possible but with increasing temperature die swell increases to values greater than one; and

(3) there is no correlation between the values of $\Delta P_{ent}/\tau_w$, which is considered a measure of fluid elasticity for flexible chain polymers, and die swell.

Further rheological studies are needed to understand the flow behavior of these unique polymer systems. The next article in this series will be concerned with possible boundary layer orientation of the molecules during flow through a capillary.

We would like to thank Dr. Wissbrun of Celanese for pointing out the importance of minimizing the exposure of polyesters to ambient air and for suggesting handling procedures. We gratefully acknowledge Tennessee Eastman Kodak Co. for supplying the polymers used in this work. Part of this research was supported by the Army Research Office under ARO Grant No. DAAG29-80-K-0093.

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