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Alexandros D. Gotsis and Donald G. Baird

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Rheological Properties of Liquid Crystalline Copolyester Melts. II. Comparison of Capillary and Rotary Rheometer Results

ALEXANDROS D. GOTSIS and DONALD G. BAIRD,
Department of Chemical Engineering and Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-6496

Synopsis

In an earlier paper capillary rheometer results were presented for two liquid crystalline copolyesters consisting of 60 mole % and 80 mole % p-hydroxybenzoic acid (pHBA) and polyethyleneterephthalate (PET). In this paper obtained by means of cone-and-plate (CP) and parallel plate (PP) attachments of a Rheometrics Mechanical Spectrometer are compared with the capillary data. In particular, it is observed that over the range of conditions studied, viscosity data obtained in the CP and PP agree with those obtained by means of the capillary rheometer. Furthermore, there is no dependence of the viscosity on geometric or dimensional factors as is observed for low molecular weight liquid crystals under some conditions. Although the viscosity is still shear rate dependent for shear rates as low as 5×10^{-2} sec^{-1}, it is shown by stress relaxation experiments following the cessation of steady shear flow that no significant yield stresses exist. The primary normal stress difference (N_1) for the 60 mole % pHBA/PET copolyester is always positive under steady shear conditions but N_1 for the 80 mole % pHBA/PET system can be negative for certain temperatures and shear rates. Calculated values of the die swell using Tanner's theory and cone-and-plate data for the 60 mole % pHBA/PET system were considerably higher than the measured values while the agreement between the theory and measured values was quite good in the case of the 80 mole % system.

INTRODUCTION

In recent years there has been considerable interest in the processing of liquid crystalline polymer (LCP) melts (thermotropes) and solutions (lyotropes). This is because of the fact that extruded

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films and fibers and injection molded parts with exceptional physical properties can be produced directly from the fluid state without further mechanical processing.[1,2] It is apparent that the high degree of orientation found in the solid state must have been generated in the fluid state. Hence, the physical properties must be closely related to the texture and the structure generated during flow, which are themselves related to the rheological properties. In order to better understand the processing behavior of polymeric liquid crystalline fluids, it is important to understand their rheological properties.

Polymer liquid crystalline fluids have been observed to exhibit, on the one hand, shear flow properties which are similar to those of isotropic polymeric fluids. In particular, they are highly shear thinning and exhibit normal stresses. On the other hand, they may under some conditions exhibit a yield stress,[3] a negative primary normal stress difference,[4] and negligible die swell.[5] A more complete review of the phenomena exhibited by these fluids is given elsewhere.[6,7]

In an earlier paper,[8] we addressed the viscosity (η), entrance pressure losses, and die swell (D_e/D) of two liquid crystalline copolyesters consisting of 60 mole % and 80 mole % p-hydroxybenzoic acid (pHBA) and polyethyleneterephthalate (PET) and compared their properties with those of PET. This paper is a continuation of the earlier work and is concerned with the steady shear flow properties as determined by means of cone-and-plate (CP) and parallel plate (PP) rheometers. In particular, our goal is to compare viscosity (η) data obtained by means of the CP and PP apparatus with that obtained in the capillary rheometer, determine whether there is any dependence of viscosity on geometry or dimensions of the rheometers, determine the behavior of η at low and at high shear rates, and determine if there is a correlation between the observed die swell and measured values of N_1.

EXPERIMENTAL

Materials

Two liquid crystalline copolyesters were used in this study: 60 mole % pHBA/PET with an intrinsic viscosity (IV) of 0.74 dl/g and 80 mole % pHBA/PET, which was insoluble in any known

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solvent and thus its IV was not known. Also PET homopolymer was used (IV of 0.60 dl/g). All three polymers were supplied by Tennessee Eastman Kodak Co. and some of their physical properties are given in Refs. 1 and 2 along with details of the polymerization procedure. The polymers that were used in this study are similar to those used in the previous article.[8]

Rheological Measurements

Viscosity and normal force measurements were carried out in the cone-and-plate and the plate–plate attachments of a Rheometrics Mechanical Spectrometer. Cone angles of 0.1 and 0.04 rad and plate diameters of 25 and 50 mm were used. The distance between the truncated cone and the plate was set at 0.05 ± 0.004 mm while the gap between the plates was set at various widths of 0.125, 0.250, 0.50, and 1.00 mm. The experiments carried out in the CP or the PP could only be done up to shear rates ($\dot{\gamma}$) of about 400 s^{-1}. At shear rates above 400 s^{-1}, edge fracture occurred and the measurements were in doubt. Actually edge fracture occurred at shear rates as low as 50 s^{-1}. However, by flooding the free surface with excess melt which was contained in a surrounding ring and recording measurements as soon as steady state conditions were reached, one could obtain high shear rates.

To measure the viscosity at higher shear rates an Instron capillary rheometer was used. A capillary diameter of 0.354 mm (0.014 in) and length/diameter ratio of 107.60 was employed and because of this high ratio the entrance pressure loss at high shear rates was neglected. The wall shear rate was determined by using the well-known Rabinowitsch equation with the slope calculated by means of a central difference approximation at each point. At very high shear rates, this slope was zero (the material showed an infinite shear rate viscosity) and it was not necessary to use the Rabinowitsch correction.

The viscosity and the normal stress values were obtained from torque and normal force measurements by well-known methods as described in Ref. 9. The measurements of the normal thrust in the cone-and-plate lead directly to values of the primary normal stress difference (N_1), while in the plate–plate device one obtains values of $N_2 - N_1$, where N_2 is the secondary normal stress differ-

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ence. In our experiments, because no difference was found between measurements in the cone-and-plate and in the plate–plate, N_2 was considered to be negligible and measurements of the normal thrust were converted directly to N_1.

The sample preparation procedure was important for these materials because of the dependence of their rheological properties on the thermal and shear history of the sample[4] and the amount of moisture in the sample.[8] In this study, the samples were dried for 72 hr at 120°C under vacuum of -29 in Hg. To avoid overheating, the temperature in the heating chamber of the rheometer was raised very slowly and samples that were overheated more than 5°C above the desired temperature were discarded. The shear history of the samples could not be entirely controlled, because the pellets of the initial sample already carried some processing history. Also the squeezing flow that took place in setting the gap at its final position again contributed to some flow history in the sample. In order to minimize the differences in the shear history of the several samples, the exact procedure of loading the instrument was followed for each sample (i.e., the approximate number of pellets, the rate at which the sample was squeezed into place, and the time it was allowed to relax were the same for all samples). For each combination of copolyester, temperature, gap width, plate diameter and cone angle, at least three runs were made. More complete data can be found in Ref. 10.

RESULTS AND DISCUSSION

Viscosity

Most macromolecular fluids of sufficient polymer molecular weight exhibit viscosity dependent on shear rate. The copolyesters of pHBA/PET were also found to follow this general trend. In Figure 1 is shown the viscosity curve of the 60 mole % pHBA/PET copolyester at 275°C over a range of six decades of shear rate from 10^{-1} to 10^5 s^{-1}. The viscosity of this material is continuously shear thinning until a shear rate of about 5×10^4 s^{-1}. In the same figure is also shown the viscosity curve of PET for comparison. At the low shear rates the viscosity of the copolyester is about half the viscosity of the PET homopolymer. At higher $\dot{\gamma}$ the difference increases because the viscosity of PET is essentially

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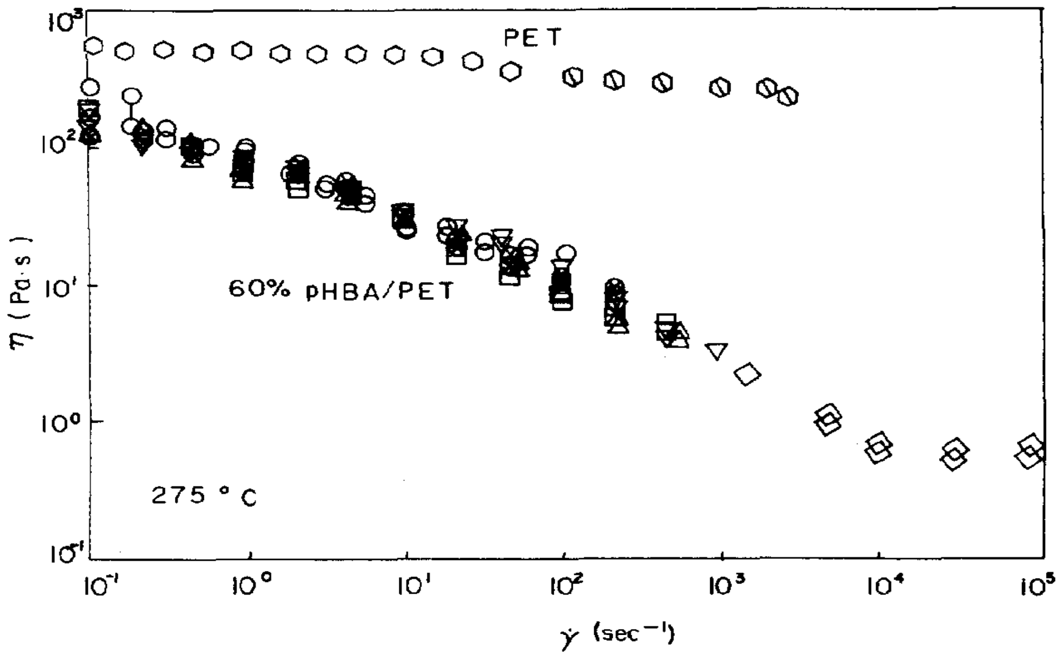

Fig. 1. Viscosity versus shear rate for 60 mole % pHBA/PET and for PET at 275°C using various rheometers. Multiple data points are used to indicate the repeatability of the measurements: 60 mole % pHBA/PET copolyester; CP (0.1 rad. cone, 25 mm dia.) ○; PP, 25 mm dia: 0.125 mm gap ⊗, 0.25 mm gap ▽, 0.50 mm gap △, 1.00 mm gap □; capillary rheometer (0.354 mm dia., L/D = 107.6) ◇; PET: CP ○, capillary rheometer ⊖.

constant up to shear rates of 100 s^{-1} and then it only slightly shear thins, while the copolyester starts to shear thin at shear rates lower than 0.1 s^{-1}. Measurements of η at shear rates lower than 0.1 s^{-1} were somewhat questionable because the torque at such shear rates was too low to be accurately measured. At high shear rates ($\dot{\gamma} > 5 \times 10^4\ s^{-1}$), the viscosity tends to level off to a value of 0.5 Pa·s (5 poise). At such shear rates, again, there is a degree of uncertainty in the accuracy of the data. There are several sources of error that are more important at high $\dot{\gamma}$. Such a source of error is the shear heating due to the extremely high stresses involved. In our experiments, at a shear rate of 80,000 s^{-1} and for adiabatic conditions, the temperature increase due to viscous dissipation in the capillary, is estimated to be of the order of 8°C. Of course, the conditions were not adiabatic and the actual increase is most likely even less. Further, a significant tempera-

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ture increase would lead to a decrease of the viscosity and the high shear rate plateau would not exist as observed in Figure 1. For the same reason it is believed that neither shear degradation occurred in the flow even at the highest shear rates. The third source of error at high $\dot{\gamma}$ comes from the neglect of the inertia and this may be more significant. The Reynolds number was calculated at $\dot{\gamma} = 80{,}000\ \mathrm{s}^{-1}$ using the volumetric flow rate through the capillary and the value of the viscosity corresponding to the wall shear rate of that experiment. The value of 3.6 that was found, however, indicates that the flow was well inside the laminar region and such an error was not significant, even at the high shear rate limit of our measurements. Finally, the effect of the pressure on the viscosity is another source of potential error, since high pressures may increase the viscosity. This effect for our materials was investigated by studying the plots of the pressure drop versus L/D for a few high wall shear rates (Bagley plots were also used to calculate the entrance pressure loss). A significant increase of η with P will result in a deviation of the data from the straight line upwards at high L/D, where P is higher. For our data, however, only a slight curvature exists at high shear rates, a fact indicating that the effect of pressure on the viscosity is either very small or that it is compensated by the slight degree of viscous heating. Therefore, the authors believe that the viscosity curve of the materials in Figure 1 is rather accurate over the entire range of $\dot{\gamma}$ shown, including the high shear plateau. Finally, the values of the viscosity measured in this work agree with the results of Ref. 8 in general, but they cover a much larger range of shear rates.

The next question that we addressed is whether η is dependent on the dimensions or type of the rheometer. In the case of low molecular weight (MW) liquid crystals (LC), η is a function of the capillary diameter or plate gap setting if the rheometer surfaces are prepared to control the orientation of the surface layers.[11] Measurements in the cone-and-plate, the plate–plate geometries and the capillary rheometers were carried out to investigate the possibility of the existence of any effect such as that observed for low MW LC's. However, the only surface treatment given to the plates of the rheometer was due to the polishing of the surfaces in the tangential direction. Data are presented in Figure 1 for the CP, PP with three gap settings, and the capillary rheometer.

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Double points are presented for each method to show the extent of the scatter in the data. One sees here that the scatter of the data from each geometry overlaps the data from a different geometry or gap width. That is, all the data tend to fall on the same line within the limits of the accuracy of the measurements. The capillary data were obtained at slightly higher shear rates than was possible for the CP or PP, but they fall along the extrapolation of the data obtained by means of these apparatus. It is obvious, therefore, that there is no effect of the geometry or the gap width of the instrument on the measured values of the viscosity for these systems. However, in our experiments the surfaces of the plates were not treated other than the mechanical polishing in any specific way to control the orientation of the director as is assumed in the theories which predict the boundary layer effect.[12,13] Hence, although it is believed that such a boundary layer effect is of no significance in the case of LCP's more studies have to be done with surfaces treated to control director orientation.

Since our data cover such an extensive range of shear rates, they can be compared with the viscosity curve that was proposed by Onogi and Asada[14] to describe the viscosity of any liquid crystalline system. The above authors have proposed a flow curve consisting of three regions. In region I, as the shear rate goes to zero, the viscosity increases. In the intermediate region it is constant and at high shear rates (region III) it decreases with increasing $\dot{\gamma}$ and the curve is concave downwards. The increase of η at low shear rates has been thought to be associated with the existence of a yield stress (τ_o). However, measurements in the region of very low shear rates are very sensitive to the initial texture of the mesophase and depend considerably on the shear and the thermal history of the sample. So the behavior of the viscosity at such low shear rates is not very well defined and is usually difficult to measure. Our data at low shear rates do not show such an increase of the viscosity. The concavity of the curve is downwards and the viscosity tends to level off at low shear rates (lower than 0.1 s^{-1}). Although this could occur at $\dot{\gamma} < 0.1$ s^{-1}, the magnitude of any yield stress (τ_o) would be quite small. Furthermore, the plateau that the curve shows at very high shear rates is unlikely to be followed by another region of shear thinning at even higher shear rates.

Whether a yield stress is a common feature of LCP's seems to

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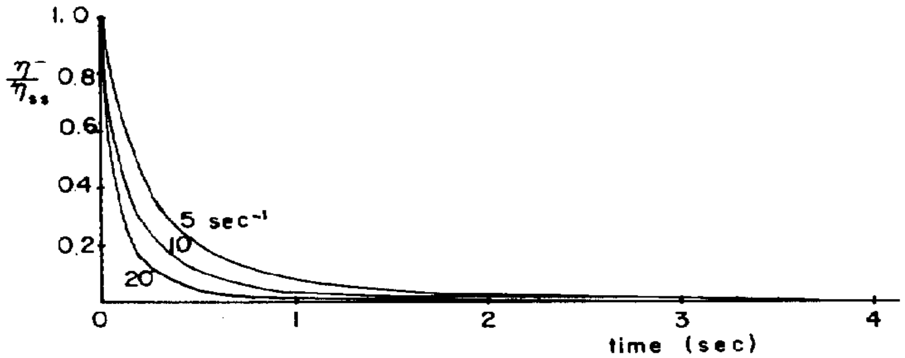

Fig. 2. Traces of stress relaxation following steady shear flow for 60 mole % pHBA/PET at 275°C for three shear rates.

still be a matter of debate.[3,6] In this case, the shear stress is of the order of 1 to 10 Pa at these lower $\dot{\gamma}$. Hence, if there was a yield stress it would be even lower and, therefore, insignificant. To further assess the existence of a yield stress, stress relaxation experiments were carried out and data is presented in Figure 2. Here we see that the shear stress relaxes completely to zero within the accuracy of the instrument. It is possible that a very weak structure exists which is easily destroyed, but at least in this case τ_0 would be insignificant.

The dependence of the viscosity of the two LCP's on temperature is now examined. For the 60 mole % system (Figure 3) it is observed that η decreases as the temperature increases from 250°C to 260°C. However, as the temperature is increased from 260°C to 285°C, there is very little dependence of η on temperature. Similar behavior is observed for the 80 mole % system (see Figure 4) except that the temperature range is higher than that of the 60 mole % system and there is even less of a dependence of η on temperature. In fact, in the range of temperatures from 320°C to 338°C, the data are observed to fall within the error bands of the measurements.

There are several possible explanations for these results. One is that the polymers degrade at elevated temperatures and thereby give lower viscosities. However, on cooling the samples back to 250°C we find that, except at $\dot{\gamma} < 1\ \mathrm{s}^{-1}$, the flow curve is reproducible. Furthermore, the viscosity is stable for periods up to 30 min at the higher range of temperatures. Hence, we conclude that the

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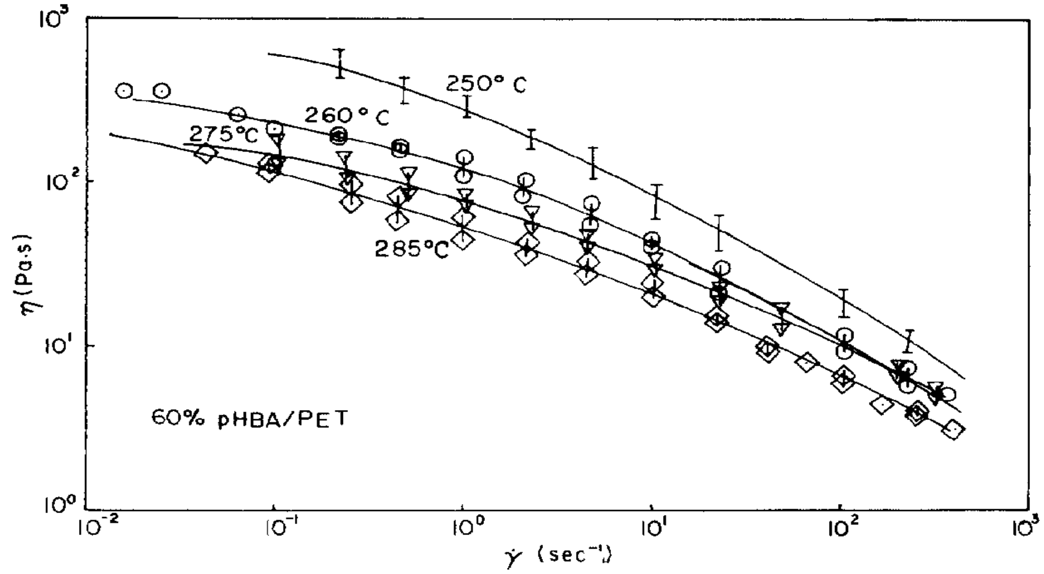

Fig. 3. Viscosity versus shear rate (CP data) for 60 mole % pHBA/PET at several temperatures. The line at 250°C represents the mean values of three runs and the bars represent the range of variation in the data. The lines at the other temperatures also represent mean values with the data points indicating the range of variation in the data.

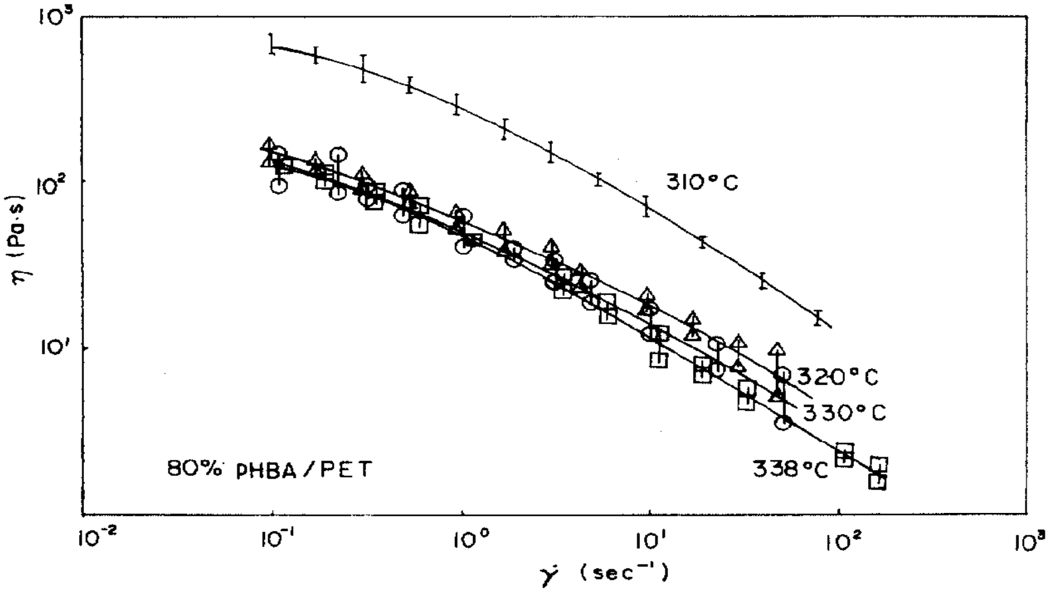

Fig. 4. Viscosity versus shear rate data (CP data) for 80 mole % pHBA/PET at various temperatures. See explanation in Figure 3 for lines and error bars.

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lack of temperature dependence of η is not due to degradation. A more likely explanation is that there is competition between an increase in viscosity due to the formation of isotropic regions and the decrease in η in the liquid crystalline state as the temperature is increased. This phenomenon is actually observed in the case of a lyotropic system.[15] Another possibility is the fact that the fluid may consist of domains whose size changes as the temperature is increased. The increase in domain size could lead to an increase in η, which negates the decrease in η due to the drop in viscosity of the isotropic regions. We should note that we have observed significant changes in the stress growth behavior of these polymers on heating them up to, say, 275°C and decreasing the temperature back to 260°C. In particular, although the steady-state viscosity is unchanged by the heat treatment, the stress growth behavior at 260°C is identical to that at 275°C (this is a topic which will be presented in a future paper and which can be found elsewhere[16]). Hence, there is evidence of a structural change in the fluid on heating.

Finally, we compare the flow curves of the 60 mole % and 80 mole % systems. In general, they are quite similar in shape, and the viscosities are even similar in magnitude (we realize that the 80 mole % system is studied at much higher temperatures, but this is due to the high melting point of about 293°C). It seems that structural factors which account for the shear thinning characteristics must be common for both polymers. We further note that temperature seems to have no effect for either polymer in controlling the critical value of $\dot{\gamma}$ for which the fluids shear thin. That is, there appears to be no simple relation between temperature and the relaxation processes which go on within the fluid.

Normal Stresses, Elasticity, and Die Swell

In the previous paper[8] it was reported that the liquid crystalline copolyesters exhibited unique values of die swell. In particular, the 60 mole % copolyester actually contracted on leaving the die at a temperature of 260°C and die swell increased with increasing temperature. Similar results were reported for the 80 mole % copolyester. Because die swell is usually related to N_1, the question was raised as to whether these fluids also exhibited

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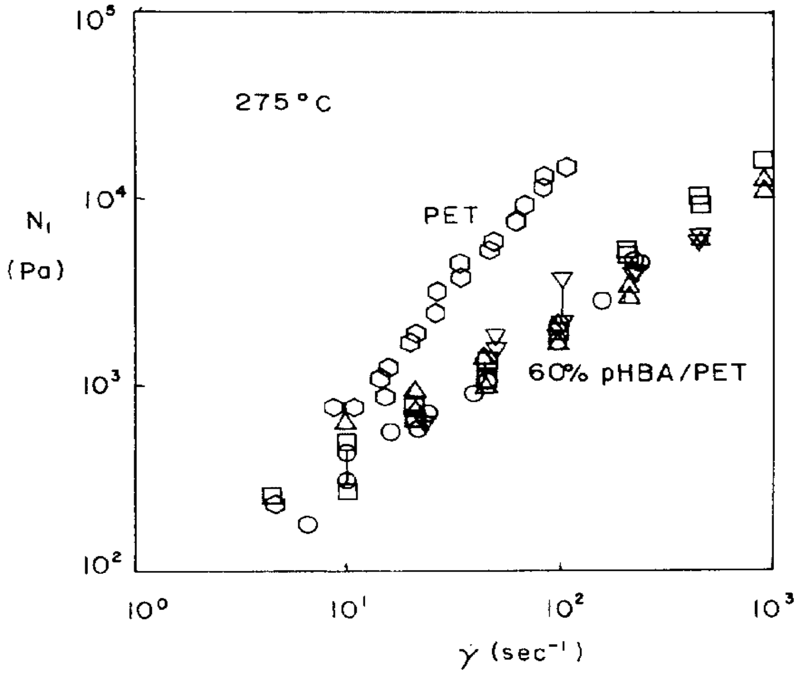

Fig. 5. Primary normal stress difference versus shear rate for 60 mole % pHBA/PET and PET at 275°C: CP ○; PP with 0.25 mm gap ▽; PP with 0.50 mm gap △; PP with 1.00 mm gap □; PET, CP ⬡.

unique values of N_1. In this section, we present values of N_1 and compare calculated values of die swell with the measured values.

The primary normal stress difference of the two pHBA/PET copolyesters and of PET homopolymer is shown in Figures 5 and 6. As can be seen there, the 60 mole % copolyester has significant (non-zero) values of N_1 (in our case a tensile stress is positive and hence $N_1 > 0$). Compared with values of PET, they are lower and they increase as $\dot{\gamma}^{1.0}$ instead of $\dot{\gamma}^{2.0}$ as is the case for PET. It is interesting to note here that this change of N_1 with $\dot{\gamma}^{1.0}$ agrees well with the predictions of the theories of anisotropic fluids proposed by Ericksen–Leslie[19] and Doi,[20] even though these two theories do not agree with the viscosity curve of the material. The 80 mole % copolyester shows a more complicated behavior in that the unusual phenomenon of negative N_1 values arise under certain conditions. This interesting phenomenon has been observed for a few materials, either in steady state (e.g., by Kiss and Por-

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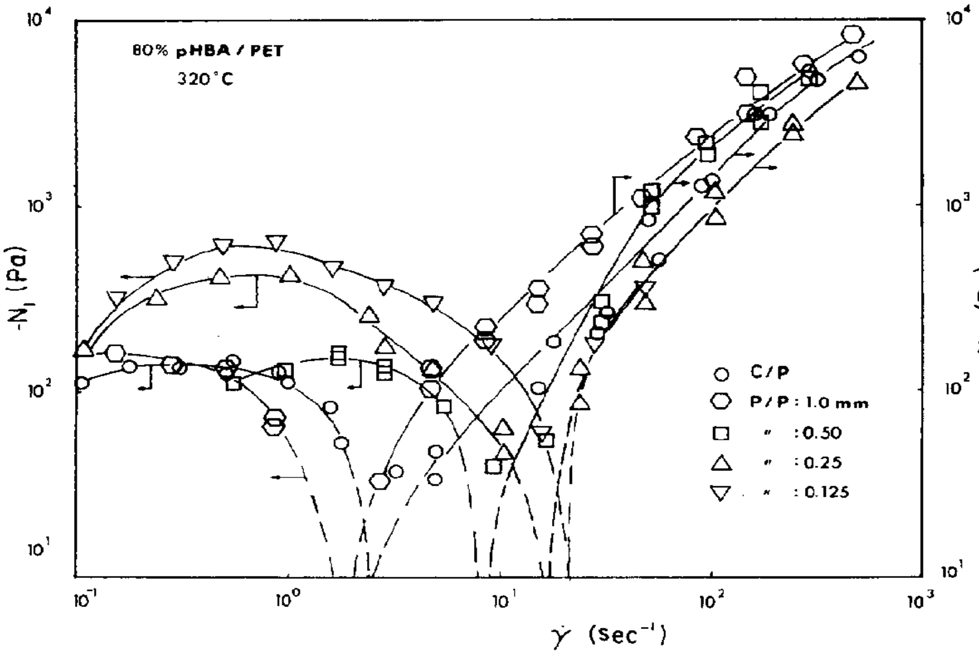

Fig. 6. Primary normal stress difference versus shear rate for 80 mole % pHBA/PET at 320°C: CP ○; PP, 0.125 mm gap ▽; pp, 0.25 mm gap △; PP, 0.50 mm gap □; PP, 1.00 mm gap ⬡.

ter[21] or in transient flows.[22,23] The negative values of N_1 of the 80 mole % pHBA/PET copolyester are discussed in more detail elsewhere.[10,16,17] It is sufficient here to say that, at temperatures below 330°C, the primary normal stress difference of the 80 mole % copolyester was found to be negative at low shear rates and it became positive at higher values passing through zero at some critical value of the shear rate. This value depended on the temperature and the gap width (see Figure 6). The magnitude of the negative values of N_1 was of the order of 10^3 to 10^2 Pa and decreased with temperature and gap width. At the shear rates where N_1 was positive, the magnitude of N_1 increased as $\dot{\gamma}^{1.0}$ as was the case for the 60 mole % copolyester. The 60 mole % copolyester did not show any measurable negative values of N_1 and N_1 did not depend on the gap setting.

Despite the fact that the negative part of N_1 in the case of the 80 mole % copolymer depended considerably on temperature, the positive part is almost independent of temperature. The change of N_1 with temperature is shown in Figures 7 and 8. For the 60 mole

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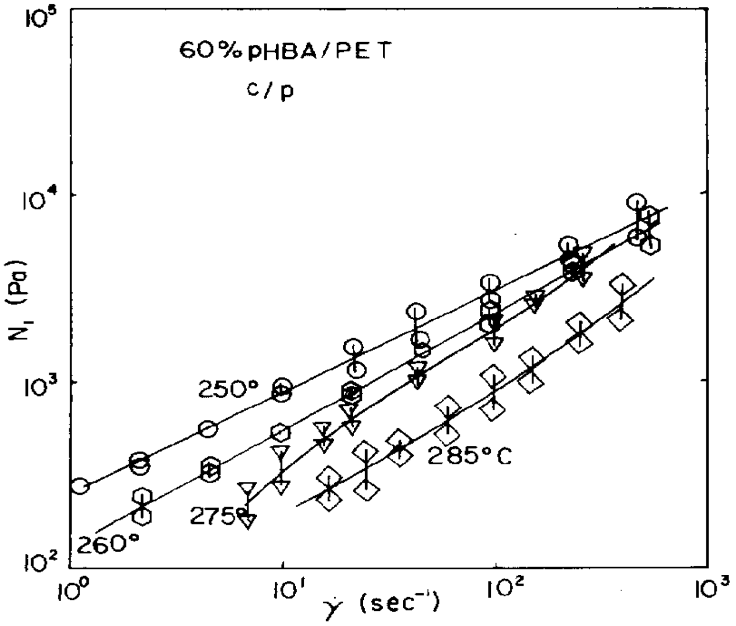

Fig. 7. Primary normal stress difference versus shear rate for 60 mole % pHBA/PET at various temperatures measured by means of a cone-and-plate.

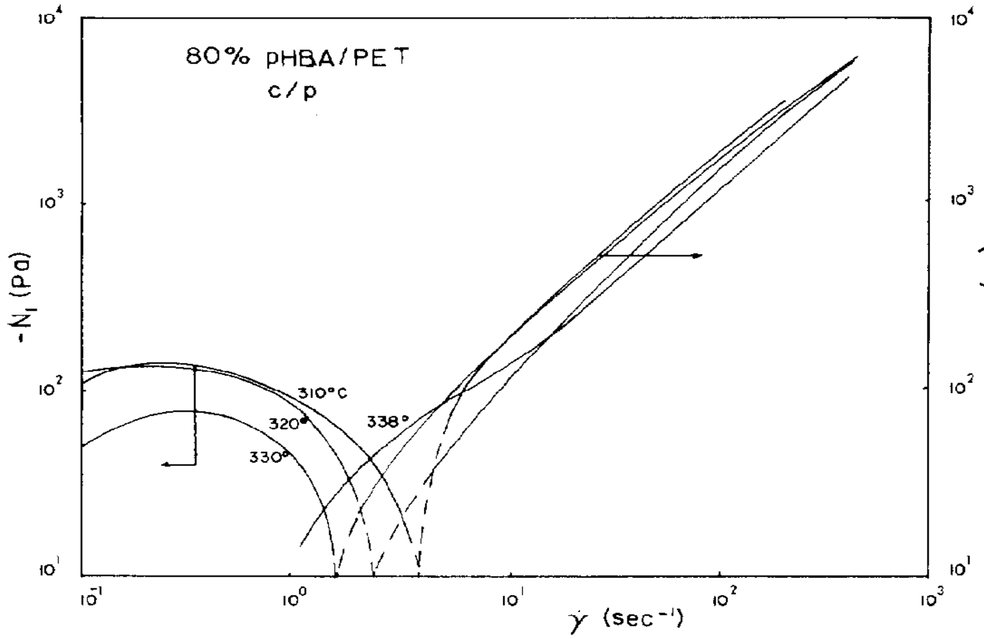

Fig. 8. Primary normal stress difference versus shear rate for 80 mole % pHBA/PET at various temperatures. Lines represent mean values for three runs. The data on the left side of the figure have negative values and the dashed lines show the extrapolation of the data from negative to positive values.

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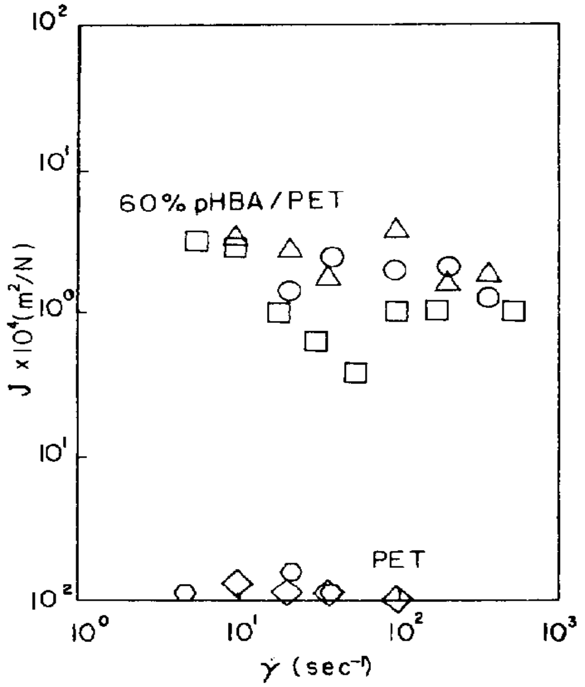

Fig. 9. Values of the compliance (J) vs. shear rate for 60 mole % pHBA/PET and PET at various temperatures. 60 mole % pHBA/PET at 260°C, ○; 275°C △, 285°C □; PET at 275°C ◇, 285°C ○ .

% system N_1 decreases at about the same rate with temperature as does the viscosity. It is actually rather remarkable that N_1 values followed the same dependence on temperature as did viscosity. This suggests a strong relation between the shear stress (σ) and N_1.

We next look at the relative elasticity of the two LCP's as determined by the compliance ($J = N_1/2\sigma^2$) and compare values with those for PET. In Figure 9 we have plotted values of J versus $\dot{\gamma}$ for 60 mole % pHBA/PET and PET. Here we see that values of J for the pHBA/PET copolymer are almost two orders of magnitude higher than the values for PET, while 80 mole % pHBA/PET has values of J similar to those for the 60 mole % system. Hence, although values of N_1 for PET are somewhat higher than those for pHBA, the values of J are considerably higher for the pHBA/PET copolymers.

On the other hand, the above results contradict the values of the die swell which, for the most part, are thought to be associ-

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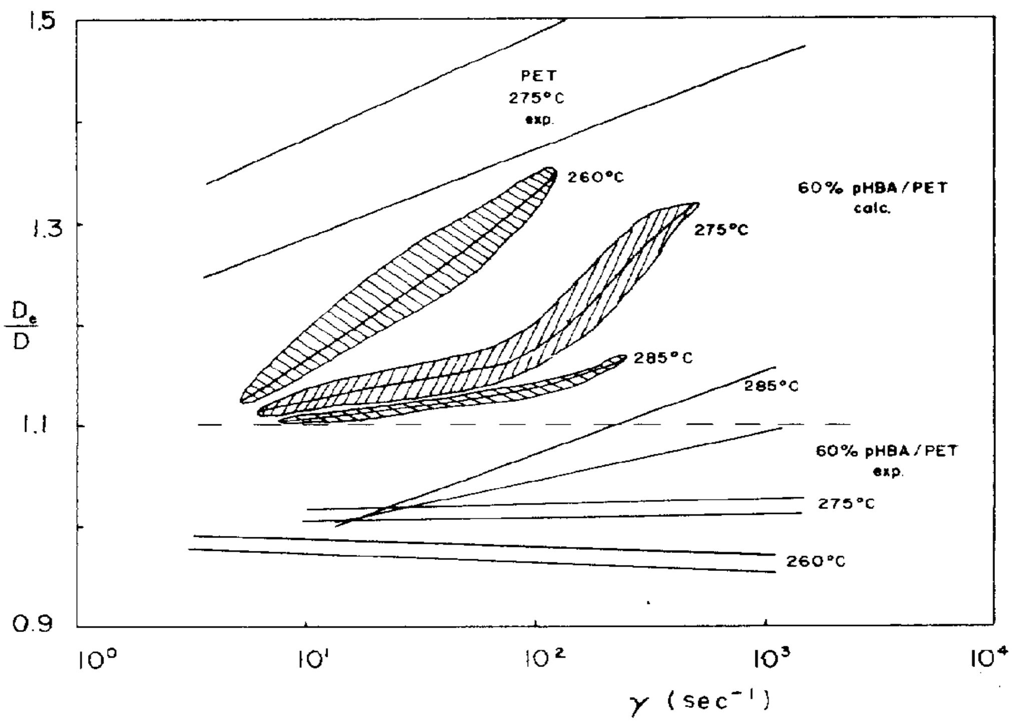

Fig. 10. Die swell behavior of 60 mole % pHBA/PET and PET. The shaded areas represent values of die swell calculated by means of Tanner's theory and CP data with the variation due to the variation in CP data. The solid lines represent experimental data taken from Ref. 5. In each case, the upper line represents data obtained by means of a capillary with $L/D = 40.0$ and the lower by means of a capillary with $L/D = 60.0$. The dashed line represents the lower Newtonian limit.

ated with elastic recovery. In Figures 10 and 11 are shown experimental values of the die swell ratio as a function of $\dot{\gamma}$ for the two copolyesters for several temperatures. In these figures are also shown values of die swell of PET and those calculated by means of Tanner's equation[18] which is given below:

$$De/D = 0.1 + [1 + \tfrac{1}{2}(N_1/2\sigma)^2]^{1/6} \quad (1)$$

and using values of N_1 and σ measured by means of the cone-and-plate instrument at the same shear rate. It is obvious from this graph that PET shows much higher die swell than the copolyesters, in spite of the lower elasticity that was indicated above. Also, at the time of the publication of Jerman and Baird's work,[8] N_1 data for the copolyesters did not exist and the above calculations were not possible. Now one can see that, for the 60 mole %

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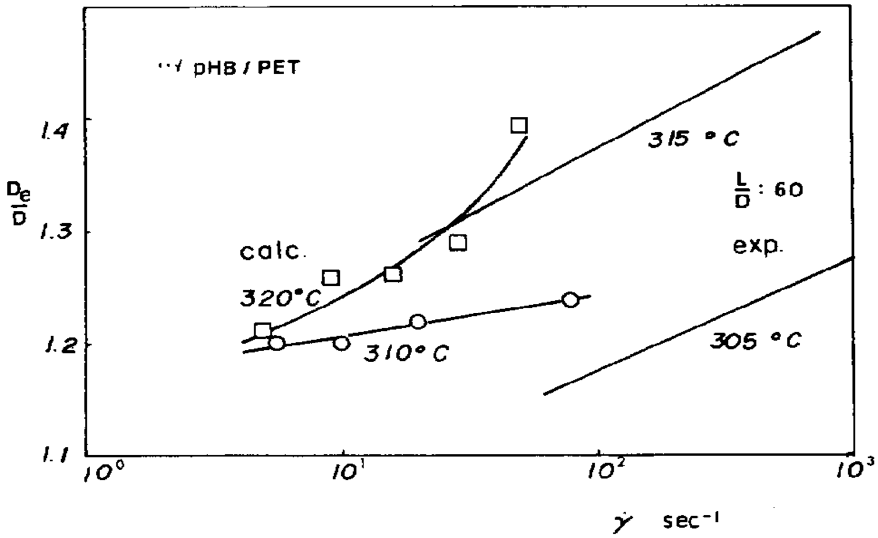

Fig. 11. Die swell data values for the 80 mole % pHBA/PET copolyester. The straight lines represent experimental data from Ref. 5 where as the points represent values calculated via Tanner's theory and cone-and-plate data.

copolyester, Tanner's theory predicts much higher die swell ratios for the same shear rate than were experimentally measured. Also, this equation has 1.1 as a lower limit, which by itself was higher than some data points. Surprisingly enough for the 80 mole % copolyester, the agreement is much better. For both cases this agreement improves as the temperature increases.

The die swell (D_e/D) values reported by Jerman and Baird[5] and by Wissbrun[4] were interesting in that for some conditions, values of D_e/D were even less than 1.0. In light of the significant degree of elasticity that is calculated from values of N_1 and σ, the lack of die swell in some cases is puzzling. Jerman and Baird[8] proposed two explanations which could account for the low die swell values. One explanation was based on the presence of a yield stress which could inhibit elastic recovery. Of course, the presence of a yield stress could affect die swell by another method also. For the case of large values of τ_0 the flow in the die would be almost that of plug flow and hence there would not even be any contribution to D_e/D due to the velocity profile rearrangement. Furthermore, there would be a large core region in which no deformation would occur. However, for the polymers used here there is no evidence of a yield stress. Furthermore, the flow

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curves change very little with temperature and hence the steady shear velocity profiles change very little with temperature. Hence, the stresses developed in the die and the recovery outside the die should change very little with temperature. The other explanation was based on the possibility of negative or negligible values of N_1. However, we have observed that the steady state values of the 60 mole % pHBA/PET system are always positive even for conditions when $D_e/D < 1.0$. The 80 mole % pHBA/PET system does exhibit negative steady state values of N_1 but D_e/D values are greater than 1.0 even when this occurs. Hence, neither of the above explanations can be used to account for the die swell behavior of the 60 mole % pHBA/PET system.

The question still remains then (assuming all the experimental observations are correct) as to the cause of the contraction, or at least lack of expansion, of the extrudate under certain conditions as it leaves the capillary. Obviously, we cannot account for the observed behavior via the rheological properties. One possible explanation may rest in the structure of the liquid crystalline fluids. It is believed that these fluids consist of domains whose size and shape may not change much during flow (i.e., nearly rigid domains). On cessation of flow there may be very little recovery of elastic energy. It is known that highly filled polymers exhibit considerably reduced values of die swell and LCP's may resemble filled polymers to some degree. In any event, additional studies involving optical examination of the extrudate must be carried out to help understand the die swell behavior.

CONCLUSIONS

Based on the results of this study we can draw the following conclusions. First, the viscosity of the 60 mole % pHBA/PET copolyester is highly shear thinning and lower than the PET homopolymer at the same temperature. The viscosity of the 80 mole % copolyester exhibits behavior similar to the 60 mole % system but it flows at higher temperatures. Second, there appears to be no geometric or size effect on the measurement of the viscosity. Third, there appears to be no yield stress exhibited by these copolyesters. Fourth, the normal stress of the 80 mole % pHBA/PET copolyester is negative under certain conditions. However, negative values of N_1 cannot explain the low die swell of these

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materials. Finally, the absence of die swell in combination with significant values of $N_1/2\sigma^2$ may mean that these parameters may not be an indication of elasticity in rod-like polymer systems.

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