

A Comparison of the Flow Behavior of Linear Polyethylene, Poly(butylene Terephthalate), and Poly(ethylene Terephthalate)

EDWIN BOUDREAUX, JR.* and JOHN A. CUCULO, *Fiber and Polymer Science Program, Department of Textile Chemistry, North Carolina State University, Raleigh, North Carolina 27650*

Synopsis

The viscous and elastic properties of linear high density polyethylene (HDPE), poly(butylene terephthalate) (PBT), and poly(ethylene terephthalate) (PET) are investigated using an Instron capillary rheometer and the Philippoff-Gaskins-Bagley analysis. The viscous properties studied are the shear viscosity and the constant shear rate activation energy and the elastic properties studied are the entrance pressure drop and the end correction. The variables are shear rate and temperature. The order of decreasing viscosity is HDPE > PET > PBT; the order of decreasing activation energy is PB > PET > HDPE; the order of decreasing entrance pressure drop is HDPE > PET > PBT; and the order of decreasing end correction is PBT > PET > HDPE. As temperature increases, both viscosity and entrance pressure drop decrease. The observed behavior is discussed in terms of the difference in number of terephthalic acid moieties in the polymer chains and in terms of oligomer plasticization.

INTRODUCTION

Polymer extrusion involves forcing a material to flow from an upstream reservoir into a capillary of smaller cross section. The material exists into either a downstream reservoir or as a free jet. If the pressure above the material is increased, the rate of flow through the capillary will also be increased. The most fundamental characterization of this process is a plot of pressure vs. flow rate. The exact shape of such a plot depends on features of the die geometry such as capillary length, capillary radius, and die entry angle, on extrusion temperature, and on the material being extruded. For polymeric materials the pressure drop for a given flow rate is not due to viscous dissipation alone, but includes contributions due to elastic dissipation, some of which may be recovered, and inertial dissipation, i.e., a change in the kinetic energy of the material. The elastic dissipation is responsible for such effects as excessive pressure losses, extrudate swelling, and melt fracture or elastic turbulence. Inertial dissipation is small compared to the other two components and is usually ignored in most treatments of flow behavior or rheology. The relative contributions of viscous and elastic dissipation to the total pressure drop cannot always be readily distinguished, and they, too, seem to change with features of the die geometry, extrusion temperature, and the material being extruded.

It is the purpose of this paper to present a broad based study of the flow of a series of polymers consisting of methylene chains which differ in number of terephthalic acid (TPA) moieties. The rheological behavior of the polymers

* Present Address: Owens-Corning Fiberglas Corp., Granville, OH.

should be determined to some extent by this difference. Emphasis will be placed on viscosity and elasticity as functions of shear rate and temperature. The effect of die entry angle on the rheological properties will not be discussed at this time. This topic will be the subject of a separate publication. This paper is part of a more extensive study of the rheological behavior of polymer melts.¹

EXPERIMENTAL

Materials

Three commercial polymers were selected for this study: a linear high density polyethylene (HDPE) and two polyesters. The polyethylene is DuPont's Alathon 7030. The two polyesters are poly(butylene terephthalate) (PBT) (VFR-4716A) and poly(ethylene terephthalate) (PET) (CTF-7202A). They were provided by the Goodyear Tire and Rubber Co., Akron, Ohio. All polymers are in chip form. A fairly detailed characterization of the three polymers is given in Table I. The data for the two polyesters were provided by the supplier. The polyethylene was characterized by Hare.² The polymers have relatively narrow molecular weight distributions. Furthermore, the two polyesters have approximately the same number average chain length; the number average chain length of the polyethylene is approximately twice that of the polyesters. Chemically the three polymers can be regarded as a series of methylene chains which vary in their TPA content; i.e., HDPE is a straight methylene chain, PBT is a methylene chain with TPA after every fourth methylene group, and PET has TPA after every second methylene group.

Equipment

The viscous and elastic properties of the three polymers were obtained with an Instron capillary rheometer. This instrument consists of an MCR capillary rheometer attached to a Model 1125 Instron testing machine. The rheometer is an electrically thermostatted stainless steel barrel in the bottom of which can be inserted one of a number of interchangeable capillary dies. Polymer melt in the barrel is driven through the capillary at preselected constant rates by a plunger coupled to the crosshead of the Instron testing machine. The force

TABLE I
Characterization of HDPE, PBT, and PET

Polymer	HDPE	PBT	PET
Intrinsic viscosity (IV) (dL/g)	0.93 ^a	0.815 ^b	0.720 ^b
M_n	28,000	22,800	24,400
Melt index (MI)	3	—	—
COOH (eq/10 ⁶ g)	—	36	20
Melting point (°C)	130	232.1	257.3
Viscosity (poise)			
250°C	—	1,850	—
290°C	—	1,000	4,600
Density (g/cm ³)	0.96	—	—

^a Decalin at 135°C.

^b 50/50 trifluoroacetic acid/dichloromethane at 30°C.

necessary to drive the polymer at a fixed speed is measured by a compression load cell and recorded on a strip chart recorder.

Two groups of three capillary dies were used for the rheological characterizations of the polymers. Each die has a nominal diameter of 0.0245 in. (6.223 mm) and a length to diameter ratio of either 5, 10, or 20. One group of dies has a flat or 180° entrance and the other has a 45° entrance which converges from the rheometer barrel diameter to the capillary diameter.

Procedure

In order to minimize hydrolytic degradation of the polymer during extrusion, the polyesters were dried under vacuum (<0.1 mm Hg) for exactly 24 h. The PBT chips were dried at 90°C, and the PET chips were dried at 140°C. Since HDPE is not subject to hydrolysis, drying prior to extrusion was unnecessary.

HDPE was extruded at temperatures of 180°C, 200°C, and 220°C. For each extrusion the HDPE chips were loaded with the barrel at the desired extrusion temperature. The chips were allowed to melt for 5 min, then extrusion was begun. PBT was extruded at temperatures of 240°C, 250°C, and 260°C, and PET was extruded at temperatures of 265°C, 275°C, and 285°C. The PBT was loaded with the barrel at 265° under a nitrogen blanket; 5 min were allowed for melting; and then the rheometer temperature was lowered to the desired extrusion temperature. Upon attainment of thermal equilibrium, the extrusion was begun. The same procedure was followed for PET except that the chips were loaded with the barrel at 285°C.

It requires a considerable amount of time for the attainment of thermal equilibrium; the lower the extrusion temperature, the longer the time required. Since polyesters are subject to both hydrolytic and thermal degradation, the intrinsic viscosities of the extrudates from several runs at each extrusion temperature were measured in order to determine whether the properties changed with the length of the cool-down periods. In all cases, the average intrinsic viscosities remained within +5% of the values of the as-received chips. This is within the experimental limits of the intrinsic viscosity test method.

Data Analysis

The Instron capillary rheometer provides pressure–flow rate data. These data are converted by use of the Philippoff–Gaskis–Bagley (PGB) analysis.^{3–5} This analysis involves plotting the total pressure drop at a constant shear rate against the capillary length to radius ratio:

$$P_{\text{tot}} = 2\tau_{tw}L/R + 2\tau_{twe} \quad (1)$$

Linear plots are obtained. The slope is related to the shear stress, and the intercept is the entrance pressure drop. The shear stress divided by the shear rate is the shear viscosity and the entrance pressure drop divided by twice the shear stress is the end correction. Thus, the PGB analysis provides information about the viscous nature of the flow through consideration of the viscosity and about the elastic nature of the flow through consideration of the entrance pressure drop and the end correction. The variables are die entrance angle, shear rate, temperature, and polymer.

The shear stress obtained in this manner is the true or corrected shear stress. The apparent shear rate is given by

$$\dot{\gamma}_{\text{app}} = 4Q/\pi R^3 \quad (2)$$

where Q is the volumetric flow rate through a capillary with radius R . The shear rate was not corrected for changes in velocity profile due to pseudoplasticity. Criticisms of the PGB analysis and justification for its use are given elsewhere.¹ Viscosity and temperature can be related by an Arrhenius equation⁶ of the form

$$\eta_s = A \exp(E_{\dot{\gamma}}^a/RT) \quad (3)$$

where R is the gas constant, T the absolute temperature, and $E_{\dot{\gamma}}^a$ is the activation energy for the variation of viscosity with temperature at constant shear rate. The natural logarithmic transformation of Eq. (3) is

$$\ln \eta_s = \ln A + E_{\dot{\gamma}}^a/RT \quad (4)$$

which can be written

$$\ln \eta_s = a_0 + a_1(1000/T) \quad (5)$$

The slope of a linear least squares plot of $\ln \eta_s$ vs. $(1000/T)$ is a_1 . The activation energy is calculated from

$$E_{\dot{\gamma}}^a = (1000)Ra_1 \quad (6)$$

RHEOLOGICAL PROPERTIES

HDPE

Figures 1 and 2 show the change in viscosity with shear rate as a function of temperature for HDPE. Figure 1 contains the data collected with the flat entry dies, and Figure 2 contains data collected with the 45° entry dies. In all figures which follow, open points represent flow through a flat entrance and closed points represent flow through a 45° entrance. It can be seen that in both flat and 45° entrances HDPE is strongly pseudoplastic. There is some scatter in the curves at lower shear rates, but this seems to be typical of linear polyethylenes.⁷ At a given temperature and shear rate, the viscosity is lower for flow through a 45° die entrance than through a 180° entrance.

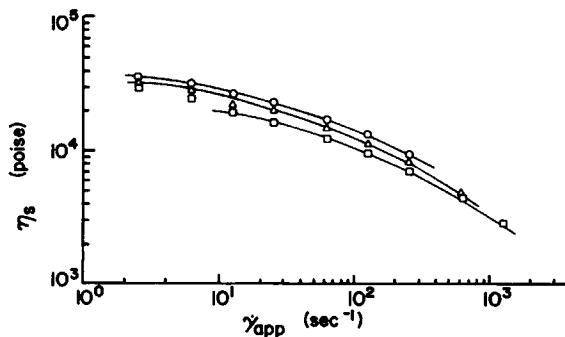


Fig. 1. Viscosity vs. apparent shear rate for HDPE with temperature as a parameter for flow through a 180° die entrance. (○) 180°C; (Δ) 200°C; (□) 220°C.

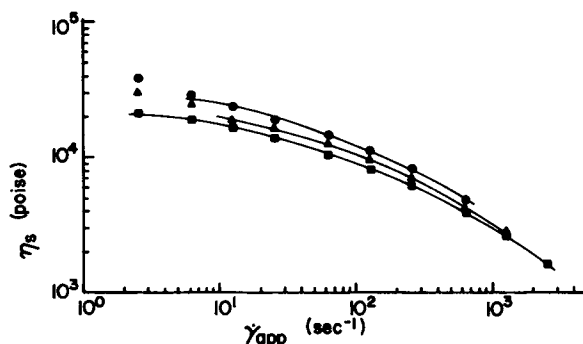


Fig. 2. Viscosity vs. apparent shear rate for HDPE with temperature as a parameter for flow through a 45° die entrance. (●) 180°C; (▲) 200°C; (■) 220°C.

The activation energies as a function of shear rate for the data in Figures 1 and 2 are listed in Table II. The column headings refer to the quantities defined in eqs. (5) and (6); r is the correlation coefficient for a linear least squares fit of eq. (5). There is a tendency for the activation energy to decrease as the shear rate increases. This is the usual trend.⁸ Table III lists activation energies for some Phillips Marlex high-density polyethylenes with the same density as Alathon 7030.⁹ The activation energies at constant shear rate agree well with those in Table II.

Table III also shows that the activation energy at constant stress is greater than the activation energy at constant rate. Although this has been observed experimentally and is predicted theoretically,¹⁰ many papers fail to make the

TABLE II
Shear Flow Activation Energy Statistics for Alathon 7030 HDPE

Shear rate (s ⁻¹)	Flat entry			45° entry		
	r	a_0	$E_{\dot{\gamma}}^a$ (kcal/mol)	r	a_0	$E_{\dot{\gamma}}^a$ (kcal/mol)
12.75	0.999	6.09	3.69	0.994	5.93	3.71
25.5	0.991	5.75	3.88	0.989	5.99	3.48
63.75	0.989	5.50	3.83	0.994	5.38	3.80
127.5	0.998	5.29	3.78	0.998	5.41	3.52
255.0	0.996	5.37	3.42	0.998	5.55	3.11
637.5	—	—	—	0.998	5.84	2.38

TABLE III
Flow Properties of Some Phillips Marlex High-Density Polyethylenes of Density 0.96^a

Polymer	6002	6015	6035	6050
Melt index	0.25	1.44	3.76	4.66
Intrinsic viscosity ^b (dL/g)	2.52	1.92	1.73	1.60
$\overline{M}_w/\overline{M}_n$	14.9	14.3	—	12.1
Activation energy (kcal/mol)				
at 100 s ⁻¹	3.2	3.2	3.8	4.0
at 1000 psi (8.6 × 10 ⁵ dynes/cm ²)	5.9	7.6	6.9	6.7

^a See Ref. 9, p. 56.

^b Decalin at 120°C.

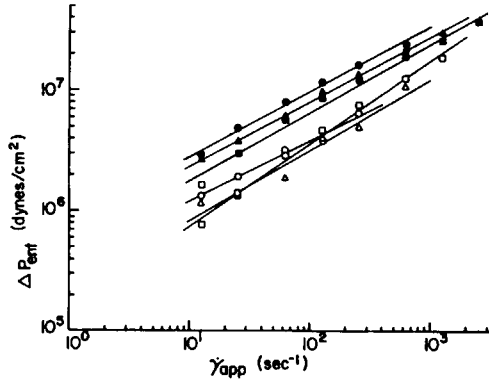


Fig. 3. Entrance pressure drop vs. apparent shear rate for HDPE with temperature as a parameter for flow through flat (open points) and 45° (closed points) die entrances. (●,○) 180°C; (▲,△) 200°C; (■,□) 220°C.

distinction when reporting activation energies. The activation energies in Table II show a slight dependence on die entry angle.

Figure 3 is a plot of entrance pressure drop vs. shear rate with temperature as a parameter for flow through flat and 45° entry dies. The plots are linear with the entrance pressure drop at constant temperature being greater for 45° entry flow. The slopes of all the plots except that for the flat entry at 220° are essentially equal. There is an increase in entrance pressure drop with decreasing temperature.

Figure 4 is a plot of end correction vs. apparent shear rate for HDPE with temperature as a parameter. Again, the end correction at a given temperature is greater for flow through a 45° entry. The change with temperature is not as clear as was observed with the entrance pressure drop. The end correction of HDPE has been observed to increase with decreasing temperature.⁷ It has been observed, however, that the end correction of HDPE increases as the die entry angle decreases.¹¹

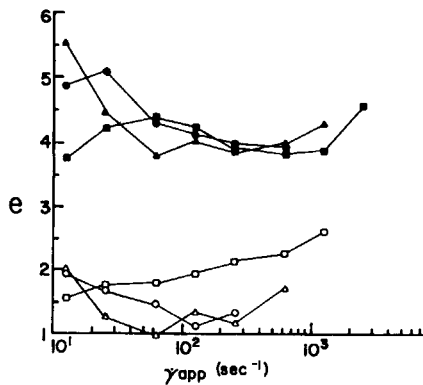


Fig. 4. End correction vs. apparent shear rate for HDPE with temperature as a parameter for flow through flat (open points) and 45° (closed points) die entrances. (●,○) 180°C; (▲,△) 200°C; (■,□) 220°C.

PBT

Figures 5 and 6 show the change in viscosity with shear rate as a function of temperature for PBT. Figure 5 presents data collected with flat entry dies, and Figure 6 presents data collected with 45° entry dies. Compared to HDPE, PBT is only mildly pseudoplastic. The viscosities are also approximately an order of magnitude lower. Again, for a given shear rate and temperature, the viscosity for flow through a 45° entrance is lower than that through a flat entrance. The activation energies for the data in Figures 5 and 6 are listed in Table IV. The shear activation energies show a fairly strong dependence on die entry geometry, particularly at lower shear rates. Figure 7 is a plot of entrance pressure drop vs. shear rate as a function of temperature for flow through flat and 45° entry dies. The data for a given entrance angle and temperature can be fitted to a straight line as shown. The entrance pressure drops are greater for flow through the 45° die entrance at constant shear rate and temperature. There is an increase in entrance pressure drop with decrease in temperature for 45° entrance data. The same trend is observed for the flat entry data, except for the 240°C plot. Not only are the entrance pressure drops lower, but the plot also exhibits considerably more scatter (although the correlation coefficient for a linear least squares fit is 0.95).

Figure 8 is a plot of end correction vs. apparent shear rate for PBT as a function of temperature for flow through flat and 45° entry dies. At constant shear rate

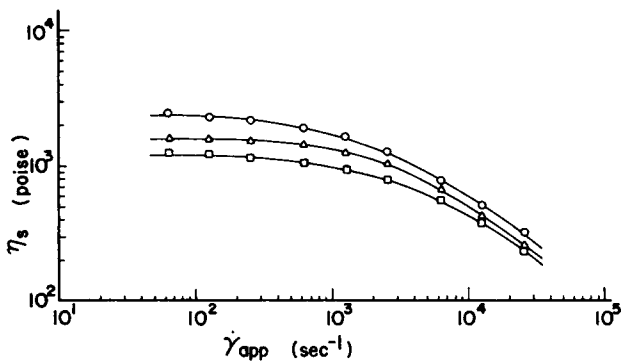
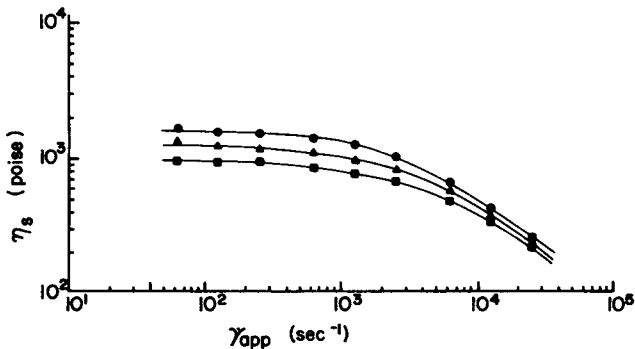


Fig. 5. Viscosity vs. apparent shear rate for PBT with temperature as a parameter for flow through a 180° die entrance. (O) 240°C; (Δ) 250°C; (\square) 260°C.



Figs. 6. Viscosity vs. apparent shear rate for PBT with temperature as a parameter for flow through a 45° die entrance. (\bullet) 240°C; (\blacktriangle) 250°C; (\blacksquare) 260°C.

TABLE IV
Shear Flow Activation Energy Statistics for PBT

Shear rate (s ⁻¹)	Flat entry			45° entry		
	<i>r</i>	<i>a</i> ₀	<i>E</i> _{γ̇^a} (kcal/mol)	<i>r</i>	<i>a</i> ₀	<i>E</i> _{γ̇^a} (kcal/mol)
63.75	0.986	-9.29	17.38	0.986	-6.32	14.00
255	0.999	-9.24	17.24	0.999	-5.89	13.47
637.5	0.999	-8.64	16.51	0.999	-6.60	14.13
1275	0.999	-7.38	15.05	0.999	-6.41	13.82
2550	0.997	-5.16	12.54	0.999	-4.60	11.77
6375	0.999	-1.84	8.66	0.999	-1.78	8.44
12750	0.997	-1.58	7.94	0.998	-0.46	6.65

and temperature, the end correction is greater for flow through the 45° die. There is also a definite dependence on temperature and shear rate. For a given entrance angle, the end correction decreases as the temperature decreases. There is also a distinct minimum which, for constant temperature shifts to a lower shear rate as the die entry angle increases, and for a constant entrance angle, shifts to lower shear rates as the temperature decreases.

Figure 9 repeats the 240°C data of Figure 7. In this figure the data are plotted to reflect both a linear least squares fit and the best smooth curve. Although the least squares fits are excellent, it is to be noted that the smooth curves are sigmoidal. Further, the inflection points of the curves, as drawn, coincide with the minima on the end-correction curves of Figure 8. Plotting the entrance pressure drops in this manner may be forcing a trend to the data, but it is intriguing to do so, especially upon comparing the entrance pressure drop and the end correction data.

PET

Figures 10 and 11 show the change in viscosity with shear rate as a function of temperature for PET. Figure 10 presents flat entry data, and Figure 11 presents 45° entry data. PET is only mildly pseudoplastic and the magnitudes of

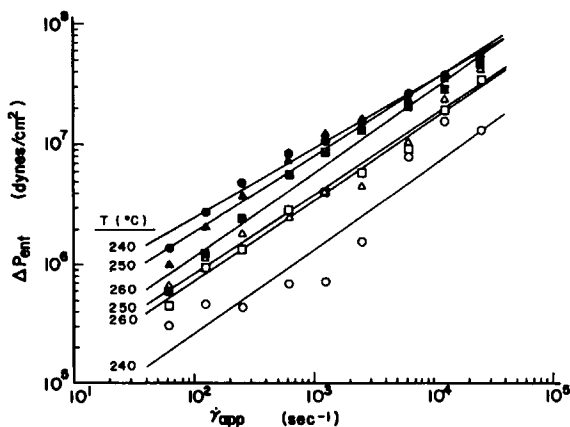


Fig. 7. Entrance pressure drop vs. apparent shear rate for PBT with temperature as a parameter for flow through flat (open points) and 45° (closed points) die entrances.

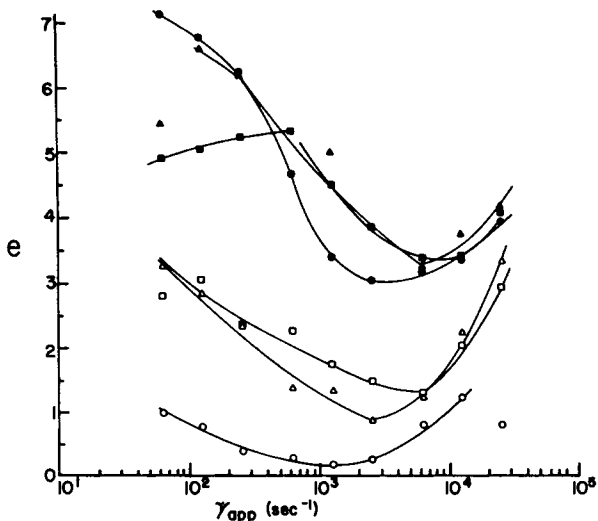


Fig. 8. End correction vs. apparent shear rate for PBT with temperature as a parameter for flow through flat (open points) and 45° (closed points) die entrances. (□, ■) 260°C; (△, ▲) 250°C; (○, ●) 240°C.

the viscosities lie between those of HDPE and PBT. At constant shear rate and temperature viscosity is lower for flow through a 45° die entrance. The last few points at the high shear rates deviate from the established trend. The increase in viscosity at higher shear rates is indicative of stress-induced crystallization.⁶ Further increases in shear rate resulted in either pressure oscillations on the force trace on the rheometer recorder or a rapid rise in extrusion force to the rheometer limit followed by the cessation of flow due to solidification of the melt in the rheometer barrel. Both phenomena have recently been discussed by Griswold and Cuculo.^{12,13} In their work the pressure oscillated about a mean level near 1400 atm. The oscillation phenomenon was independent of molecular weight but depended on capillary diameter. Their dies had a 90° entrance angle. In this work the oscillation phenomenon occurred at lower pressures and was dependent on die length. Also, it only occurred with the flat entry dies.

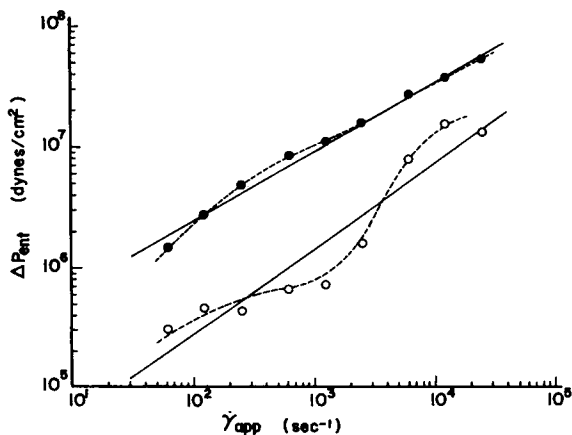


Fig. 9. Entrance pressure drop vs. apparent shear rate for PBT at 240°C comparing flow through flat (open points) and 45° (closed points) die entrances.

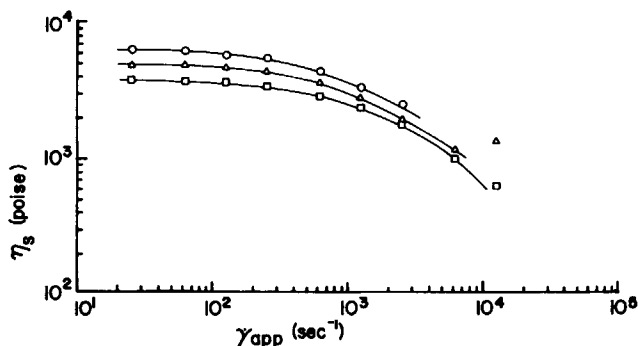


Fig. 10. Viscosity vs. apparent shear rate for PET with temperature as a parameter for flow through a 180° die entrance. (O) 265°C; (Δ) 275°C; (□) 285°C.

The activation energies for the data in Figures 10 and 11 are listed in Table V. The shear activation energy is observed to be a monotonic decreasing function of shear rate and is slightly dependent on die entrance angle. The die entrance angle dependence is more pronounced at lower shear rates. The values of the activation energies in the table agree well with other values reported in the literature.^{14,15} Gregory¹⁴ has noted that there is considerable scatter in the reported values of the shear activation energies of PET. In his own work the zero shear rate activation energy of PET was 13.5 kcal/mol. This value was independent of molecular weight. Hill and Cuculo¹⁵ reported a value of 16–17

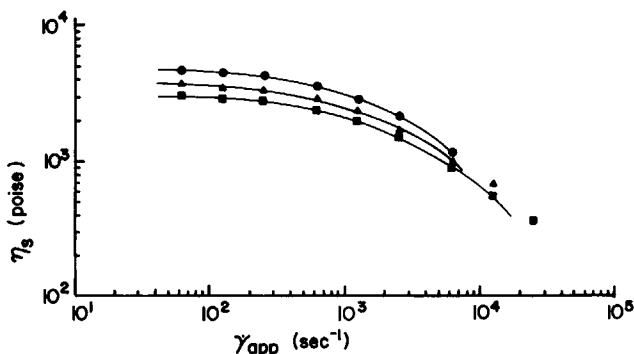


Fig. 11. Viscosity vs. apparent shear rate for PET with temperature as a parameter for flow through a 45° die entrance. (●) 265°C; (▲) 275°C; (■) 285°C.

TABLE V
Shear Flow Activation Energy Statistics for PET

Shear rate (s ⁻¹)	Flat entry			45° entry		
	<i>r</i>	<i>a</i> ₀	<i>E</i> _γ ^a (kcal/mol)	<i>r</i>	<i>a</i> ₀	<i>E</i> _γ ^a (kcal/mol)
63.75	0.998	-5.78	15.52	0.998	-4.01	13.33
255	0.998	-4.80	14.33	0.996	-4.03	13.25
637.5	0.997	-2.78	11.92	0.997	-3.09	12.05
1275	0.999	-1.48	10.24	0.998	-2.54	11.22
2550	0.989	-1.99	10.46	0.995	-2.27	10.59
6375	—	—	—	0.989	-5.38	13.46

kcal/mol for the zero shear rate activation energy of PET. The increase in activation energy at the higher shear rates in Table V corresponds to the increase in viscosity observed on the flow curves.

Figure 12 is a plot of entrance pressure drop vs. shear rate for PET as functions of temperature and die entrance angle. No attempt was made to fit the data to a straight line. At constant shear rate and temperature, the entrance pressure drop is greater for flow through a 45° entrance. Below 1000 s⁻¹ the entrance pressure drop increases with decreasing temperature for flow through the 45° entrance. The same is true for flow through the flat entrance below 100 s⁻¹. The behavior of the 45° entry curves is remarkably similar to die swell behavior. There is a maximum which decreases in magnitude and shifts to lower shear rates as the temperature decreases. Die swell maxima behave similarly.⁶ However, it is believed that the behavior in Figure 12 is controlled by flow crystallization effects rather than by changes in elastic response with shear rate. The decrease in entrance pressure drop just after a maximum corresponds to an increase in viscosity. As the extrusion temperature decreases, stress-induced crystallization occurs at lower shear rates. The shapes of the 275°C and 285°C curves are slightly sigmoidal.

The behavior of the flat entry curves is similar although the sigmoidal shape is more pronounced. There is a discontinuity of sorts on the 275°C curve. The entrance pressure drop at 637.5 s⁻¹ had a negative value; i.e., the Bagley plot [eq. (1)] for that shear rate and temperature had a negative intercept. Since a negative intercept has no physical meaning, the point was omitted from the plot. The 1275 s⁻¹ point is very near the abscissa. The data for the 265°C curve were also limited because of negative values of the entrance pressure drop past 1000 s⁻¹. Negative entrance pressure drops occurred because the effects of flow crystallization are greater in longer dies for a given shear rate. This biases Bagley plots toward steeper slopes which result in higher viscosity (when the shear stress obtained from the slope is divided by the shear rate) and in negative intercepts (entrance pressure drops).

Figure 13 is a plot of end correction vs. shear rate for PET as a function of temperature and die entrance angle. At lower shear rates, the dependence on

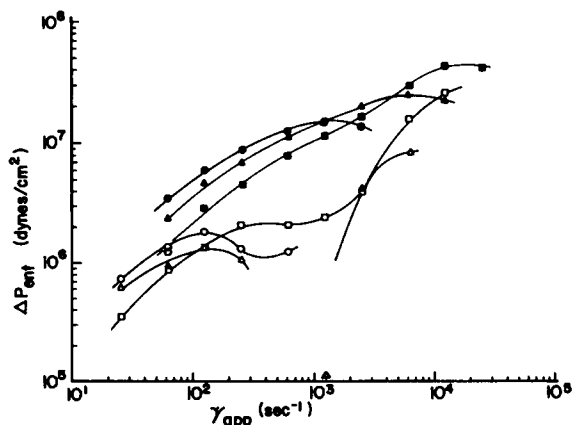


Fig. 12. Entrance pressure drop vs. apparent shear rate for PET with temperature as a parameter for flow through flat (open points) and 45° (closed points) die entrances. (■, □) 285°C; (▲, △) 275°C; (●, ○) 265°C.

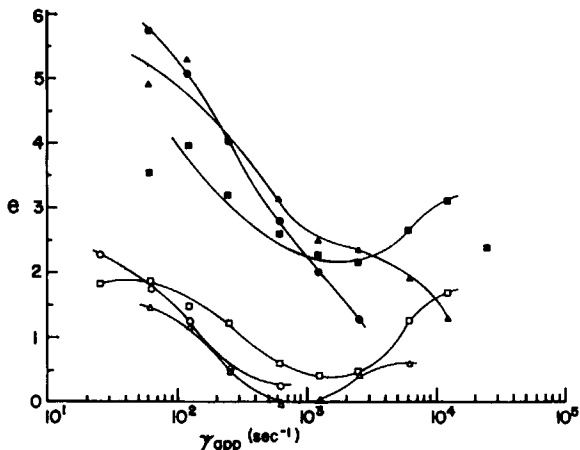


Fig. 13. End correction vs. apparent shear rate for PET with temperature as a parameter for flow through flat (open points) and 45° (closed points) die entrances. (■, □) 285°C, (▲, △) 275°C, (●, ○) 265°C.

temperature is the same as was observed with PBT. At higher shear rates the temperature dependence is more complicated. The shapes of the flat entry curves are similar to the shapes of the end correction curves in Figure 8 for PBT. The minima coincide roughly with the inflection points on the flat entry entrance pressure drop curves on Figure 12. The shear rate and temperature dependences of the 45° entry end correction curves are more complicated. The 285°C curve has a distinct minimum which is displaced to a slightly higher shear rate than the corresponding flat entry curve. The 275°C curve almost develops a minimum, but the 265°C curve decreases monotonically.

Gregory and Watson¹⁶ appear to be the only investigators to discuss end effect corrections to the shear stress of PET. They concluded that the end corrections for shear rates in the range of 50–24,000 s⁻¹ and for molecular weights in the range of 23,000–70,000 were negligible. Although the end corrections in this study are low, they do suggest that the flow behavior is a complicated function of shear rate and temperature.

DISCUSSION

Viscous Behavior

The change in viscosity with temperature is proportional to the flow activation energy. It has been widely demonstrated that flow activation energies of polymers are independent of molecular weight and molecular weight distribution.^{8,17-19} The implication of this is that the flow unit for viscous flow is smaller than the actual molecular length of the polymer.²⁰ Porter and Johnson⁸ have reported that the activation energy at constant stress is independent of stress while the activation energy at constant rate decreases with increasing shear rate. However, Brydson⁶ reports that the activation energy at constant stress increases with increasing shear stress. In this work, the constant rate activation energies of HDPE, PBT, and PET decreased with increasing shear rate. Combs et al.²¹ have noted that high values of activation energy are associated with increased sensitivity of melt viscosity to changes in temperature.

Tables II, IV, and V show that the order of decreasing sensitivity of viscosity to temperature is PBT > PET > HDPE. Comparison of Figures 1, 5, and 10 and Figures 2, 6, and 11 shows that the order of decreasing melt viscosity is reverse; i.e., HDPE > PET > PBT. Bueche²² has shown that melt viscosity is proportional to the entanglement density of the polymer. The viscosity increases as the entanglement density increases. Because of a greater degree of chain flexibility and a greater chain length, it is expected that HDPE should have a greater entanglement density than either PBT or PET. A large entanglement density requires a large change in temperature to cause a small change in viscosity. Therefore, of the three polymers, HDPE should have the highest viscosity and the lowest sensitivity to change in temperature, i.e., the lowest activation energy. On the basis of entanglements and flexibility, PBT is expected to have a higher viscosity and lower activation energy than PET. The observed reversal of order may reflect some mechanism other than entanglement density and chain flexibility. Recall that the molecular weights of the two polyesters are such that they have approximately the same number average chain length. For that chain length, the degree of polymerization (DP), or number of repeat units, of PBT is 103 and the DP of PET is 127. For the two polyesters, each repeat unit has one terephthalic acid moiety (TPA). Recently, Cruz et al.²³ have shown that the basis for miscibility in polyester-polycarbonate blends may be an $n-\pi$ complex formation between free electrons of the ester group and the aromatic ring. It is conceivable that the same type of interaction can occur between adjacent TPA moieties whether on the same or different molecules. It is reasonable then that the polyester with the greater TPA content may have a stronger overall dipole interaction. This stronger interaction would have the effect of increasing the resistance to flow, thus increasing the viscosity, and of decreasing the sensitivity to changes in temperature, thus lowering the activation energy.

Although $n-\pi$ complex formation is a plausible explanation for the orders of viscosity and activation energy of PBT and PET, another explanation can be advanced. A study of the effect of drying time and drying temperature before extrusion showed that the apparent viscosities of the polyesters were possibly functions of oligomer content.¹ The experimental results suggested that oligomer content influences the behavior of PBT to a greater extent than PET. It is possible that the oligomers function as a plasticizer. Then, if PBT is plasticized to a greater extent than PET, the viscosity would be lower and more sensitive to changes in temperature. For this particular study, there is no real basis to prefer one explanation over the other.

Elastic Behavior

If viscoelasticity is described by a simple Maxwell model, then the elastic response of a polymer system will be given by a Hooke's law relation of the form.

$$\tau_{tw} = GS_R \quad (7)$$

where G is the shear modulus of elasticity and S_R is the recoverable shear strain. A similar relation describes elasticity due to tensile deformation. The modulus is directly proportional to the absolute temperature and inversely proportional to the molecular weight between entanglements. For the purpose of the following

discussion, elasticity will be defined in terms of the recoverable shear strain. For a given stress, the material that exhibits the larger recoverable shear strain will be considered the more elastic material. Obviously, any event that alters the modulus will affect the elastic response of the polymer. Although the Hooke's law relation is strictly valid only for small deformations, it can be applied to large deformation processes by considering the effect of the process on the modulus.

In the PGB analysis as set forth in eq. (1), the entrance pressure drop is shown to be twice the product of the shear stress at the wall and the end correction. Philippoff and Gaskins³ first showed that the end correction is proportional to the recoverable elastic shear strain. Lodge²⁴ has shown that the product of the shear stress and the recoverable elastic shear strain is proportional to the first normal stress difference. Therefore, the first normal stress difference is directly related to the capillary entrance pressure drop. Since the first normal stress difference is a direct consequence of polymer elasticity,²⁴ this suggests, then, that as a first approximation one should be able to rank the elasticity of various polymers on the basis of the entrance pressure drop.

Figures 3, 7, and 12 show the entrance pressure drops of HDPE, PBT, and PET, respectively. The order of decreasing entrance pressure drop is roughly HDPE > PET > PBT. This is the same order observed for the decrease in melt viscosity. On the basis of entanglements and their effect on the modulus, the order of decreasing elasticity should essentially be opposite the order of decreasing entrance pressure drop. Again, the reversal of the order of PBT and PET may be due either to greater dipole interaction in PET or oligomer plasticization in PBT. Increase dipole interaction would increase the shear modulus of PET, thus causing a decrease in apparent elasticity. On the other hand, plasticization decreases the coherence or modulus of the fluid and produces an increase in apparent elasticity. Therefore, the overall ranking of the elasticity may be expected to be PBT > PET > HDPE.

The die entry angle dependence of the entrance pressure drop is opposite of what would be expected on the basis of other measures of elasticity. Observations of die swell²⁵ and melt fracture^{26,27} indicate a decrease in elastic response with decreasing die entry angle. However, it is observed in this work and elsewhere^{28,29} that entrance pressure drop increases as die entry angle decreases. Han²⁹ has argued that the increase in entrance pressure drop with a decrease in die entrance angle may be due to an increased viscous interaction between the walls of the entrance region of the die and the flow patterns of the polymer. For a given polymer and die entry angle, the entrance pressure drop has a tendency to increase with decreasing temperature with the exception of the 240°C curve of PBT in Figure 7. Polymer elasticity is generally observed to increase with decreasing temperature. For example, at constant shear rate, die swell increases with decreasing temperature up to the point of melt fracture.^{6,29} Although the entrance pressure drop can be correlated with elasticity based on the temperature dependence, the other observations suggest that the behavior of the entrance pressure drop correlates more strongly with viscous response rather than elastic response. It is concluded, therefore, that the entrance pressure drop perhaps should not be considered as an independent rheological measure of elasticity for the purpose of ranking polymers.

White³⁰ has pointed out that the Weissenberg number physically represents

the amount of recoverable shear strain in a fluid. Therefore, the Weissenberg number specifies the ratio of the elastic to viscous forces; i.e., the ratio of the first normal stress difference to the shear stress. As pointed out above, the first normal stress difference is directly related to the entrance pressure drop. The Weissenberg number, then, is more or less equivalent to $\Delta P_{\text{ent}}/\tau_{\text{tw}}$ or to the end correction as used in this study.³¹ This suggests that elasticity should correlate better with end correction than entrance pressure drop. Figures 4, 8, and 13 show the end corrections of HDPE, PBT, and PET, respectively, as functions of die entry angle, shear rate, and temperature. The order of decreasing end correction is roughly PBT > PET > HDPE. As was brought out earlier, this is the expected order of decreasing elasticity in these polymers. The figures also show that there is a general tendency for the end correction to increase with decreasing die entrance angle. The die angle dependence may reflect the enhanced viscous interaction between the walls of the entrance region of the die and the polymer flow patterns mentioned above. There is too much scatter in the end correction data to specify the trend with temperature. However, for most polymer systems, the end correction is observed to increase with decreasing temperature.⁷

The shear rate dependence of the end correction curves is more complicated, particularly for the two polyesters. The end correction of HDPE is observed to increase with shear rate^{11,29} and that is the general tendency observed in Figure 4. This is indicative of an increase in elasticity with shear rate, at least up to the point of melt fracture. The end correction curves of the two polyesters exhibit distinct minima which shift to higher shear rates as the temperature increases or the die entry angle decreases. This behavior is somewhat analogous to die swell behavior.

Die swell increases with shear rate up to a limit which is near the critical shear rate for the onset of melt fracture; beyond this, die swell decreases. The maximum swelling ratio shifts to higher shear rates as the die entry angle decreases.³² At constant shear rate the maximum swelling ratio decreases as the die entry angle decreases.²⁹ The behavior of the minima in Figures 8 and 13 parallels the behavior of the die swell maxima.

That the end correction curves exhibit minima seems to suggest that the elasticity first decreases and then increases. Although the end correction can be related to polymer elasticity through consideration of the Weissenberg number and by analogy with die swell behavior, the appearance of minima may be due to another mechanism. Since the extrusion temperatures of the polyesters were fairly close to the solidification temperatures, there is a possibility that incipient crystallization effects alter the fluid properties. These effects would be more important at lower temperatures and in flat entry dies where elongational deformation is greater for a given shear rate.^{27,33} This would explain the shifts in the minima with changes in temperature and die entry angle. Incipient crystallization would be expected to increase the viscosity of the fluid. In addition it would also lead to a decrease in elastic response. Crystal nuclei, at first approximation, may function as temporary crosslinks which would increase the modulus. The minima may be due to the effect of stress on the crosslinks. The increase in viscosity and modulus would tend to decrease the end correction. This may be more important at lower shear rates. At higher shear rates the crystallite crosslinks are broken, thus producing an increased elastic response. Eventually, however, a point would be reached at which crystallization effects

would again dominate. This coincides with the onset of massive stress induced crystallization. This appears to be the case at higher shear rates for the 240°C flat entry PBT data in Figure 8 and for all the data in Figure 13.

Since 240°C is very near the solidification temperature of PBT, crystallization effects may account for the anomalous behavior of the flat entry plot in Figure 7. If crystallization is more important in longer dies, then Bagley plots would have steeper slopes and smaller intercepts. The most severe crystallization would be associated with the lowest temperatures. Crystallization effects, then, may be responsible for the drastic decrease in entrance pressure drop in going from 250°C to 240°C.

SUMMARY

The rheological properties of linear high density polyethylene (HDPE), poly(butylene terephthalate) (PBT), and poly(ethylene terephthalate) (PET) were investigated. The three polymers have narrow molecular weight distributions, and their molecular weights are such that they have essentially the same number average chain lengths. The polymers can be regarded as a series of methylene chains which differ in content of terephthalic acid moieties. The specific rheological properties investigated were the melt viscosity, the entrance pressure drop, and the end correction. The variables were die entry angle, shear rate, and temperature. The following results and conclusions were drawn from the study.

The shear viscosity of the three polymers decreased with increasing shear rate and increased with decreasing temperatures. The flow curves of PET show evidence of flow induced crystallization. The order of decreasing viscosity was roughly HDPE > PET > PBT. The viscosity were lower for flow through dies with 45° entry angles. The order of decreasing activation energy at constant shear rate was PBT > PET > HDPE. The activation energies decreased with increasing shear rate and with decreasing die entry angle. The activation energy was related to the sensitivity of the melt viscosity to changes in temperature. The larger the activation energy, the more sensitive the polymer is to changes in temperature. Although PBT is more flexible than PET and is expected, therefore, to have a greater entanglement density, the ranking of the two polyesters is reversed. It was suggested that the reversal of the expected order was due either to increased polar interaction in PET due to a greater number of terephthalic acid moieties in the polymer chain, or to increased plasticization in PBT due to oligomer content.

The entrance pressure drop was related to polymer elasticity. The order of decreasing entrance pressure drop was the same as the order of decreasing viscosity; i.e., HDPE > PET > PBT. The entrance pressure drop was observed to increase with decreasing temperature and with decreasing die entry angle. The increase with decreasing temperature is a decidedly elastic response since elasticity is observed to increase with decreasing temperature. The increase with decreasing die entry angle was briefly suggested to be due to an increased viscous interaction between the flow patterns of the polymer and the convergent walls of the die entrance. It was concluded that the entrance pressure drop should not be considered an independent measure of elasticity for the purpose of ranking polymers. The end correction, on the other hand, was shown to be

a fairly accurate gauge of elasticity. The end correction was shown to be equivalent to the Weissenberg number; i.e., the ratio of elastic to viscous forces in flow. The end correction increased with decreasing die entry angle. The end correction of the polymers decreased in the order PBT > PET > HDPE. Again the order of the two polyesters was expected to be reversed.

Usually the end correction increases with shear rate. The end correction curves of both polyesters exhibited distinct minima which shifted to higher shear rates as the temperature increased or the die entry angle decreased. The minima coincided with inflection points on the entrance pressure drop plots. The behavior of the minima was shown to be analogous to the behavior of die swell maxima. Since the extrusion temperatures were close to the solidification temperatures of the polyesters, it was proposed that the appearance of minima was due to changes in the microscopic structure of the polymers caused by the effects of incipient crystallization. Nascent nuclei would cause the viscosity to increase, thus causing a decrease in the end correction. At the same time, it was speculated that the nuclei function as temporary crosslinks which alter the elastic network. An increase in shear rate would cause an increased elastic strain as the crosslinks are broken, thus, causing the end correction to increase. The minimum in an end correction curve, then, reflects the relative importance of the two competing responses. At higher shear rates the end correction decreases again. This decrease was thought to be due to the onset of stress induced crystallization. These effects are not important at the usual fiber forming extrusion temperatures. However, they may be important in other forming processes which occur at temperatures closer to the solidification temperature of the polymer, i.e., injection molding or cold forming.

The work covered in this report was supported by The Goodyear Tire and Rubber Co. and the National Science Foundation (Polymers Program—Grant DMR 75-14231). Dr. V. M. Nadkarni of Owens-Corning Fiberglas Corp. made helpful comments concerning the preparation of this manuscript.

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Received March 31, 1981

Accepted July 8, 1981