

Influence of Shearing History on the Properties of Polymer Melt. I.*

ZBIGNIEW K. WALCZAK,† *Phillips Petroleum Company, Research Center, Bartlesville, Oklahoma 74004*

Synopsis

Melt flow behavior was examined using "as polymerized," mechanically intact polypropylene, and the same polymer after pelletization in a screw extruder. In addition, the polymers were extruded through different capillaries and subsequently tested for melt flow characteristics. Significant differences in shear stress at a given shear rate and shear rate critical to the onset of extrudate roughness were found and compared with the previous shearing history. Both shearing intensity and mode of flow were found to impart long-lasting and short-term effects to the melt flow properties of the polymer. These differences were not explainable on the basis of changed molecular weights, since no significant differences were observed in the molecular weights as a result of the shearing treatments used in this study.

INTRODUCTION

It is widely believed that the mechanical perturbations a polymer has experienced influence its subsequent behavior in the melt. Such an opinion is frequently quoted in industry, but no systematic analytical treatment of this subject has been reported in the literature. Exploration of this phenomenon was undertaken to determine how extensive this influence may be, if indeed present, and possibly what kind of rules govern this process. Well-grounded knowledge of the influence of shear history on polymer melt would be very helpful in the standardization of processing conditions and would permit better reproducibility of product quality.

If any significant melt property changes related to the prior shearing history were present, it would be interesting to determine the morphologic alterations which occurred during shearing, their durability, and, most important, their points of origin. In this work it was attempted to perform such an initial exploration of the effects and causes.

EXPERIMENTAL

All of the experiments were performed at 240°C using an Instron rheometer with capillaries of 0.5-mm diameter and aspect ratios ranging from

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†Present address: M & T Chemicals Inc., Subsidiary of American Can Co., Research Laboratory, P.O. Box 1104, Rahway, New Jersey 07065.

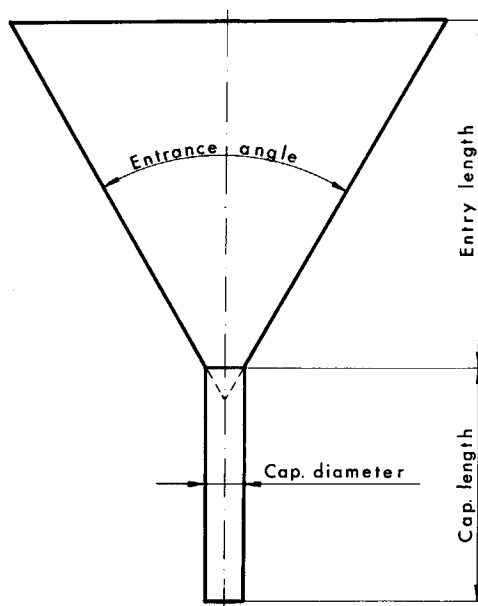


Fig. 1. Schematic representation of the geometry of a capillary for extrusion of polymer melt.

1 to 20. Besides conventional flat entry capillaries assumed in this work as having an entrance angle of either 180 or 0 degrees, 20- and 60-degree entrances were used. Figure 1 represents schematically the capillary geometry. To avoid more complex flow patterns, the entrance length varied with the entrance angle. The entrance length was 6.93 mm for a 60-degree-angle capillary; 22.69 mm for a 20-degree angle; and zero for the 180-degree angle. Polypropylene of medium-high molecular weight was selected as the polymer for these studies. Mechanically intact "as polymerized" polypropylene was selected as one of the samples (sample F). Stabilizers were introduced to the polymer by wetting it with the proper amount of a methanol solution of stabilizers and then evaporating the solvent under vacuum at room temperature. Polymer from the same polymerization batch as sample F was pelletized in a screw extruder under carefully controlled conditions to prevent degradation as far as possible. The same stabilizers were used. This pelletized sample was coded as sample P. Molecular weights of these two samples together with other polymers studied are given in Table I.

The relatively small differences between the molecular weights are probably within the limits of reproducibility of the methods of determination. Both samples, F and P, were then considered to be the same polymer with and without any "past" in the sense of shearing experience.

Both of the samples were extruded under several different volumetric flow rates through capillaries of various lengths and entrance angles. The

extrusion conditions along with the designation of the specimens obtained are given in Tables II through IV. It must be mentioned that one of the shear rates for each capillary length was chosen so as to be above the critical shear rate, that is, above the point where extrudate roughness begins.

TABLE I
Identification of the Polymers Studied

Sample	$M_w \times 10^{-3}$ (L.S.)	$M_n \times 10^{-3}$ (Osm.)	$\frac{M_w}{M_n}$
F	376	66.3	5.67
P	389	66.0	5.89
A	440	66.8	6.59
B	359	38.7	9.28
C	396	69.4	5.71
D	401	58.0	6.91
E	490	43.0	11.40
G	410	95.0	4.32
H	969	267.0	3.63

TABLE II
Extrusion Conditions to Impart Shear History. Virgin Sample (F)

Sample	Uncorrected			
	Shear rate, sec ⁻¹	Shear stress, (dynes/cm ²) $\times 10^{-3}$	Aspect ratio L/D	$\left(\frac{\tau}{\dot{\gamma}^2}\right)_{\text{hist}}$
F ₁	250	1470	3	23.50
F ₂	500	2050	3	8.20
F ₃	1250	3199	3	2.05
F ₄	250	1033	9	16.53
F ₅	500	1240	9	4.96
F ₆	1250	1808	9	1.16
F ₇	250	817	20	13.07
F ₈	500	1066	20	4.26
F ₉	1250	1500	20	0.96

TABLE III
Extrusion Conditions to Impart Shear History. Pellet Sample (P)

Sample	Uncorrected				After extrusion	
	Shear rate, sec ⁻¹	Shear stress, (dynes/cm ²) $\times 10^{-3}$	Aspect ratio L/D	$\left(\frac{\tau}{\dot{\gamma}^2}\right)_{\text{hist}}$	$M_w \times 10^{-3}$ (L.S.)	$M_n \times 10^{-3}$ (Osm.)
P ₁	250	1592	3	25.47	—	—
P ₂	500	1915	3	7.66	381	63
P ₃	1500	3194	3	1.40	—	—
P ₄	250	818	20	13.09	347	63
P ₅	500	1052	20	4.21	369	64
P ₆	1500	1495	20	0.66	354	62

TABLE IV
Extrusion Conditions to Impart Shear History.
Virgin Sample (F), 20° Entry to Capillaries

Sample	Uncorrected			
	Shear rate, sec ⁻¹	Shear stress, (dynes/cm ²) × 10 ⁻³	Aspect ratio L/D	$\left(\frac{\tau}{\dot{\gamma}^2}\right)_{\text{hist}}$
F ₁₀	250	1705	3	28.22
F ₁₁	500	2207	3	9.13
F ₁₂	1500	3382	3	1.55
F ₁₃	250	1006	9	19.49
F ₁₄	500	1262	9	6.11
F ₁₅	1500	1820	9	0.98

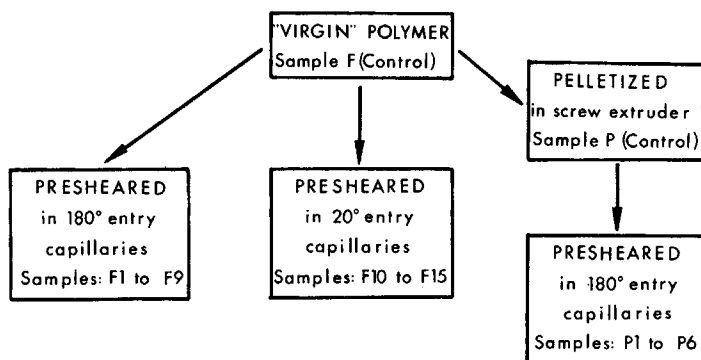


Fig. 2. General scheme of the genealogy of all the sheared samples studied in this work.

Particular care was exercised to prevent degradation during the pre-extrusions. Before a polymer became exposed to any heat, the adsorbed oxygen was removed by evacuating the polymer overnight under a slow nitrogen flow. Both loading of the rheometer and collection of the extrudate were performed under a nitrogen blanket. As may be concluded from Table III, the goal was achieved within the error limits for the molecular weight determinations.

A general scheme of the genealogy of all the samples is shown in Figure 2.

Using the same instrumentation and the same procedures, shear stress-shear rate relations were obtained for all the original and specially generated samples. Simultaneously critical shear rates were determined. The extent of die swell was measured by means of a photographic technique.

RESULTS AND DISCUSSION

In an attempt to interpret the results, a difficulty that became immediately apparent was to find a way to describe the shearing a polymer ex-

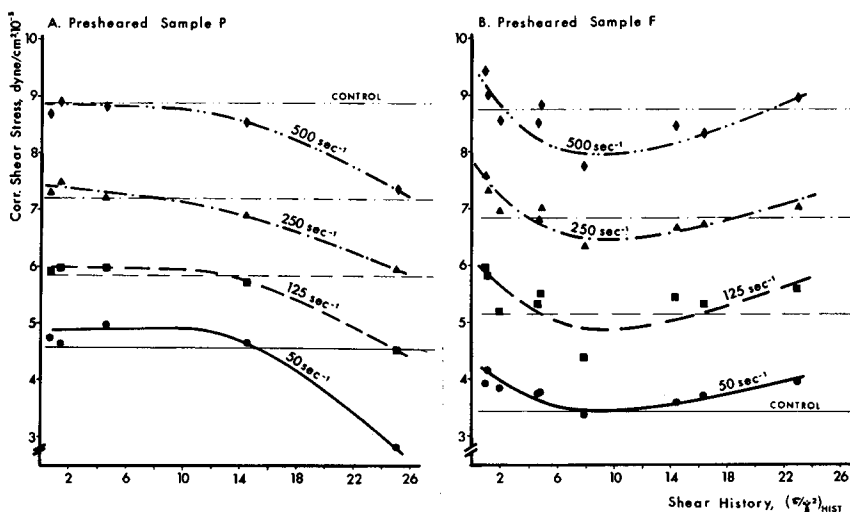


Fig. 3. Corrected shear stress vs. shear history. Shear rate given as parameter. Fine lines across the graph represent the corresponding data for unsheared control samples.

perienced. In a purely empirical way an expression consisting of Poiseuille flow parameters was composed:

$$\text{shear history} = \left(\frac{\tau}{\dot{\gamma}^2} \right)_{\text{hist}}$$

where $\tau = R\Delta P/2L$ (shear stress at wall) and $\dot{\gamma} = 4Q/\pi R^3$ (shear rate). In these expressions, Q is volumetric flow rate; R is radius of a capillary; L is capillary length; and ΔP is extrusion driving pressure. Use of this new parameter as a means of describing the shear history eliminates the necessity of handling the data for each capillary length separately, which would be the case if only shear rate or shear stress were used to describe the intensity of preshearing. The gentle shearing (slow extrusion) is represented by large values of $(\tau/\dot{\gamma}^2)_{\text{hist}}$, as the square of $\dot{\gamma}$ increases more rapidly than τ . Because of the strictly empirical character of this expression, and lacking any other theoretically justified parameter, the term $(\tau/\dot{\gamma}^2)_{\text{hist}}$ is considered a temporary "vehicle" only.

The formal similarity between the expression describing the shear history and the normal stress coefficient is assumed to be coincidental. This position was taken since no proper theoretical relationship between these two expressions could be found. It is speculated that both the shear history and the normal stress coefficient are connected in some way to changes of molecule conformation; however, this speculation is no justification for postulating any theories at this time.

Shear stress corrected for the entrance effects according to Bagley¹ is plotted in Figure 3 against the shear history term for the polymer P series and for the F set of samples. The four curves in each figure represent

different testing shear rates: 50, 125, 250, and 500 sec⁻¹. For comparison, corresponding data for the unsheared control samples are also presented as fine lines across the graphs. It is noted that there is a difference between the results obtained for the control samples and those specimens which were sheared before. The F polymer shows significantly lower shear stress than sample P (343,000 versus 456,000 dynes/cm²) for the shear rate of 50 reciprocal seconds. The differences decrease with increasing shear rate and practically disappear at 500 sec⁻¹.

The shear stress curves for series F go through a minimum. The position of the minimum in relation to the shear stress for the untreated sample changes with the shear rate of the test. Such a minimum may be considered to be an indication of at least two different competitive mechanisms which take place during the shearing process. On the other hand, the samples sheared in the mildest way, F₁, F₄, and F₇, show shear stress above that for the untreated sample. By extrapolating the curves to somewhat higher values of $(\tau/\dot{\gamma}^2)_{\text{hist}}$, one may conclude that the gentle shearing introduces very significant changes in the mechanically intact polymer. For the samples which were extensively sheared, higher shear stresses were obtained. These stresses were very close to those obtained for the sample P. The intact polymer, sample F, also showed a different slope in the plot of shear stress versus shear rate. This may be seen in Figure 3 as the difference in the relative level of the curves for the sheared polymers and the respective points for the control sample. As shown in Figure 3A, mild shearing has an even stronger effect on polymer which has been sheared before. This effect, however, is qualitatively opposite to that of the mechanically intact sample. Increasing shear, i.e., lower values of $(\tau/\dot{\gamma}^2)_{\text{hist}}$, tends to return the shear stress curve to the starting point, that is, to the values obtained for the control sample.

Figure 4 shows a comparison between the effect of preshearing sample F in flat entry capillaries and in the 20-degree entrance angle capillaries. The influence of the entrance geometry was found to be quite strong. Although the effects of mild shearing are virtually the same, irrespective of the entry geometry, with increasing intensity of preshearing the effects become vastly different for different entry geometries.

Although there is some point scatter in the presented plots, there seems to be little doubt that these changes are real. Table V shows the variability which can be produced in the rheological response of a single propylene polymer by shearing treatments conducted so that thermal and oxidative degradation is avoided. It is particularly noteworthy that the two preshear conditions represented produced increases in the shear stress required to maintain a given shear rate in a second extrusion. Furthermore, the direction of the changes in melt flow properties is opposite to what one would expect as a result of degradation, i.e., the more extensively presheared sample behaves as if it had higher molecular weight.

Another aspect which appears significant with regard to the rheological characterization of these polymers in the molten state is the variation of

TABLE V
Extremes of the Property Changes Caused by Shearing

Corrected shear stress, (dynes/cm ²) × 10 ⁻³				
"As polymerized"				
Shear rate, sec ⁻¹	Preextruded		Control	Pellets Control
	180° Capill., $\tau/\dot{\gamma}^2 = 1.16$	20° Capill., $\tau/\dot{\gamma}^2 = 0.98$		
50	442	248	343	456
125	600	367	513	580
250	759	482	682	718
500	917	574	876	886

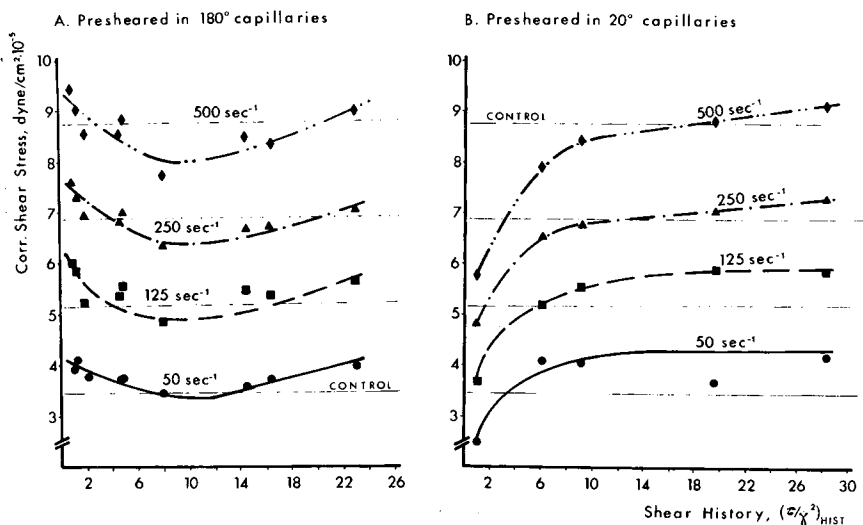


Fig. 4. Comparison of the influence of capillary entrance geometry on the effects of pre-shearing: (A) data for series F₁ to F₉; (B) data for series F₁₀ to F₁₆.

the slopes of the logarithmic plots of apparent melt viscosities *versus* corrected shear rates (using the Weissenberg-Rabinowitsch-Mooney equation²) with respect to prestress conditions (Fig. 5). Most of the individual rheological tests reported here lie between the extreme curves of Figure 5; a few points at the high shear rate end lie barely above the uppermost curve. The plot shows that extrapolation of viscosity would yield varying results for polymers which had experienced different shear histories, but have essentially the same molecular weight as determined by independent methods.

The influence of preshearing on the melt flow behavior may be called a long-term effect. The sheared polymer was allowed to swell after extrusion, crystallize, and then melted before test extrusion, and still the effects of shearing "survived" all of the opportunities for relaxation.

A number of polypropylene samples were extruded through capillaries of different entrance angles. The Bagley correction¹ applied to the shear stress should remove any differences caused by the entry geometry so that the extrapolated results would describe only flow in the straight portion

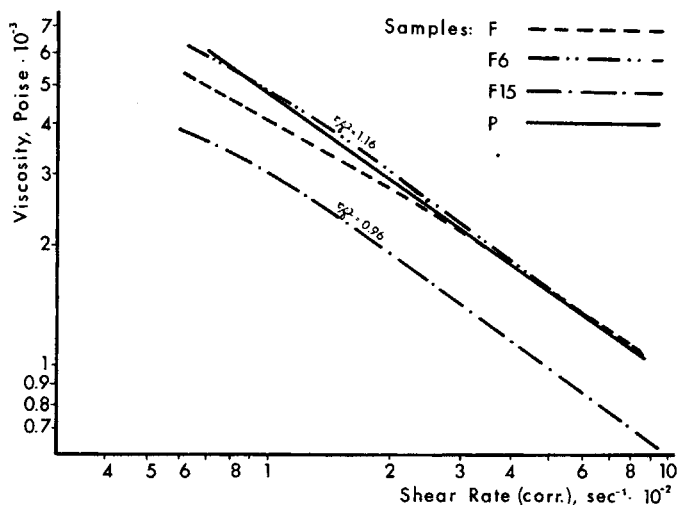


Fig. 5. Melt viscosity vs. shear rate for samples with different shearing history. Only the extremes are represented in this figure.

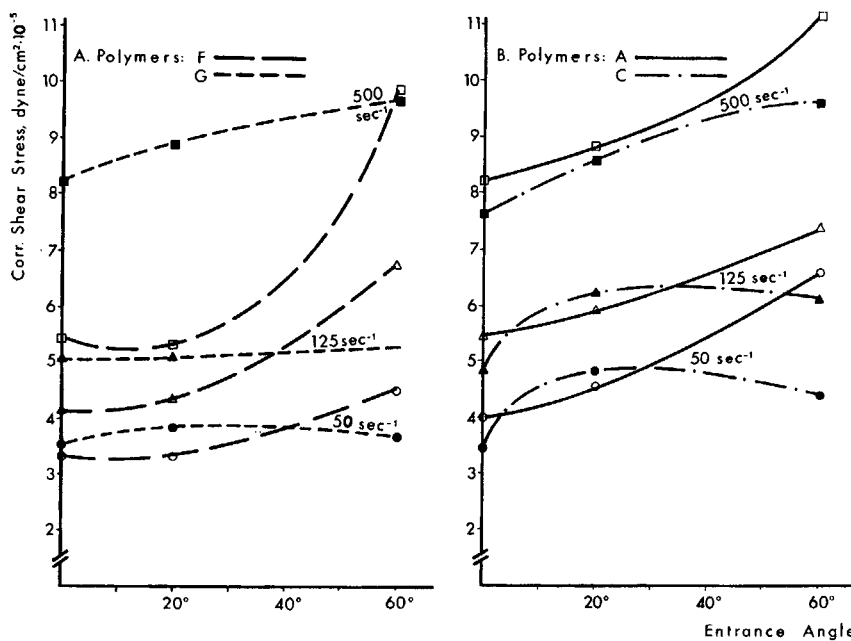


Fig. 6. Influence of entrance angle on corrected shear stress. Shear rate given as parameter.

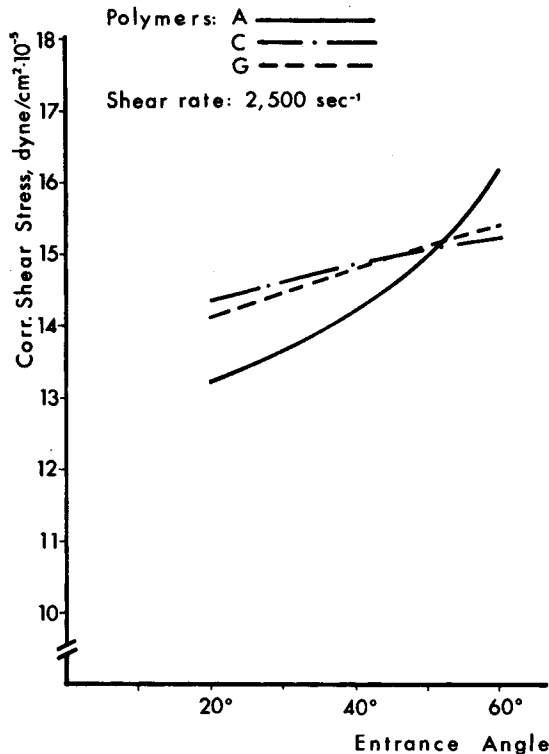


Fig. 7. Influence of entrance angle on corrected shear stress for those polymer samples which did not undergo melt fracture at 2500 sec⁻¹ shear rate.

of the capillaries, and as such, the corrected shear stress would be independent of the entrance geometry. The experimental results, as shown in Figure 6, make the validity of this assumption doubtful. Specifically, the entry geometry has an effect on the subsequent flow in the capillary, other parameters being constant. Moreover, different polymers react differently to the various modes of flow. Some portion of these short-term influences survives postextrusion relaxation and has longer-lasting effects, as shown by the differences caused by presheating in the 20-degree angle and in the flat-entry capillaries.

It may be important to mention that a certain similarity exists between the short- and long-term presheating effects; high shearing intensity tends to decrease the differences between the effects of different modes of flow (Fig. 7), and the polymer behavior becomes more uniform.

It has been reported that in non-Newtonian fluids, circumferential vortex-like flow disturbances may form around the capillary entry. The size and character of such turbulence, aside from being dependent on the volumetric flow rate, change with the entry angle for other than flat-entry capillaries. According to Gieskus³ and Schümmer,⁴ when using small entrance angles the geometry of the vortices is such that it may be expected

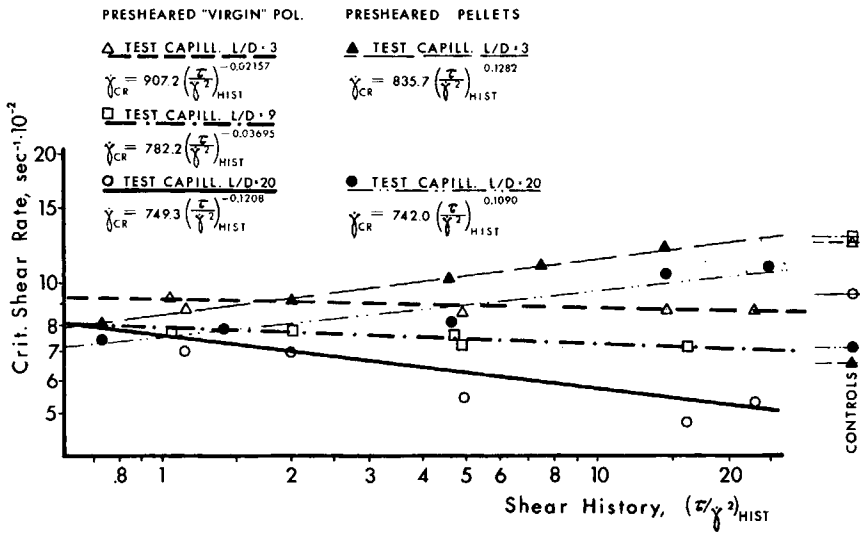


Fig. 8. Influence of shear history on critical shear rate.

to increase polymer shearing in comparison to that when flat-entry capillaries are used. The results reported here appear to be reasonably consistent with the data of Gieskus and Schümmer. Very extensive shearing tends to equalize the polymer behavior, with the general tendency of raising the shear stress at a given shear rate. This might also indicate that the entry vortices may be formed at sufficiently high flow rates and, for fluids as non-Newtonian as molten polypropylene, even in entrance cones as tight as 20 degrees.

It may also be speculated that the vortices not only introduce some turbulence into the flow, but also change the flow mode, e.g., vortex, screw-like, telescopic, or plug flow. In addition to the intensity of shearing effect, the flow mode may also be visualized as having an effect.

While the shearing history has an effect on the shear stress-shear rate relationship, this is not the only property affected. Shear rate critical to the onset of extrudate roughness shows an interesting behavior pattern in this respect (Fig. 8). The virgin sample behaves differently from the pelletized sample. In particular, an unexpected reversal of slope resulted from these measurements. The coefficients of the equation (shown in Fig. 8) appear to be in inverse proportion to the length of the capillary in which the critical shear rate was determined. No explanation for the inversion of signs of the exponential coefficients for the sets of "as polymerized" and pelletized series can be given at present. Another feature, equally difficult to explain, is the relationship between the critical shear rates of the control samples and their corresponding sheared derivatives. In order to alter the critical shear rate back to the level obtained with the original sample values, enormously large shear rates would be necessary. Extrapolation of the results show that these shear rates would be in the order of

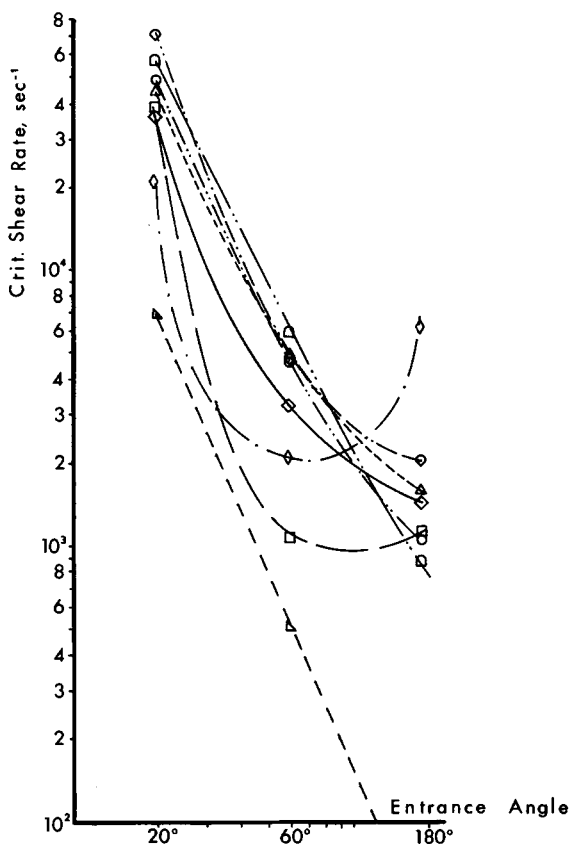


Fig. 9. Influence of capillary entrance angle on the level of critical shear rate. The polymers represented are: (○) sample A; (◇) sample B; (△) sample C; (◊) sample D; (□) sample E; (◻) sample F; (◑) sample G; (◒) sample H.

50,000 to 1,000,000 sec^{-1} , which most probably would be well beyond the degradation point.

It is also worth stressing that the length of the capillary in which the critical shear rate is determined has a significant influence on the measured value. One may conclude that the occurrence of melt fracture has no effect on the long-range shear history. The history, on the other hand, influences the tendency of the polymer to melt fracture.

It is interesting to compare the long- and short-term effects of shearing history on the critical shear rate. In Figure 9, critical shear rates of various polymer samples are plotted against the entrance angle. In this case, representation of the flat-entry capillary as 180 degrees gave better correlation. Two polymers, B and F, deviate from the general trend by showing higher critical shear rates measured in the 180-degree entrance angle capillaries than in 60-degree capillaries. Both of the polymers were tested

as obtained from polymerization, without any mechanical treatment applied prior to the test.

In the case of long-lasting preshearing effects, quite intensive shearing [$(\tau/\dot{\gamma}^2)_{\text{hist}}$ equal to 0.96 or 0.66, which corresponds to $\dot{\gamma}$ of 1250 or 1500 sec^{-1}] changed the critical shear rate by some 15% to 30%. Differences of entrance geometry changed the critical shear rate by almost two orders of magnitude. Based on the studies of capillary entrance effects, Gieskus³ assumes variable asymmetry of the disturbance pattern near the entry as the cause of the melt flow instability. It has been shown above that the shearing history does affect the susceptibility of a polymer toward the formation of flow instabilities. On the other hand, unstable flow does not have noticeable long-lasting effects of the shearing history type which would deviate from the general pattern encompassing both regular and unstable flow. The relationship between the critical shear rate and capillary length is somewhat erratic, but the overall trend seems to indicate that, in long capillaries, the melt instability occurs at slightly lower shear rates. Thus, some of the morphologic configurations of the polymer chains which would favor high critical shear rate may have short relaxation times. Nevertheless, all of the effects that may be ascribed to shearing history are strongly overshadowed by the effect of the entrance geometry. This, in turn, would tend to confirm the hypothesis of Gieskus³ who claims that the existence of the melt flow instabilities of non-Newtonian fluids depends only on the flow pattern at the instant of entry to the capillary.

According to another point of view, melt fracture results from three different causes. With increasing shear rate, there first appears a surface roughness or just a dull appearance (sometimes called "shark skin"). This roughness originates in the exit of the capillary.⁵⁻¹⁰ In the intermediate region of shear rates, one encounters oscillatory flow which results from the flow velocity at the wall being other than zero (wall slip-page).^{8,10} At significantly higher shear rates, elastic flow turbulence occurs, which originates already at the entry to the capillary.^{3,4,8,10} The change of the polymer susceptibility to the melt flow instability as found in this work does not seem to be in disagreement with the interpretation of the phenomenon as just quoted.

Figure 10 represents the relationship between the extrudate die swell (expressed as the relative increase of the extrudate cross section area over the cross section area of the capillary) and capillary aspect ratio (length-over-diameter ratio). Extrusion shear rate is given as a parameter. The two polymers represented in Figure 10 are F and P. The large differences in the results appear to be self-explanatory. It must be stressed, however, that all of the other samples tested gave results which lie between the two extremes shown in Figure 10. Thus, there appears to be some parallel interrelationship between the die swelling and the apparent viscosity as presented in Figure 5.

In addition to the investigation of the polymer melt flow under shearing, a test was conducted to estimate the elongational (Trouton) viscosity in

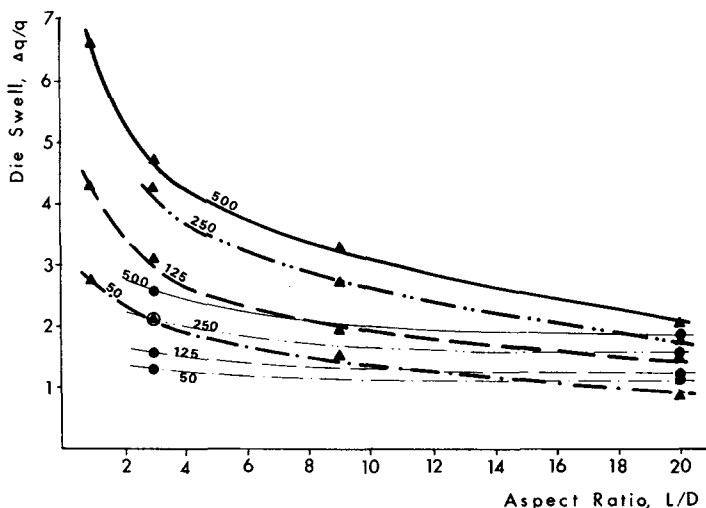


Fig. 10. Relation between die swell (Barus effect) and capillary aspect ratio (length over diameter). The die swell is given as the relative increase of the extrudate cross section area over the cross section area of the capillary. Parameter: shear rate; (\blacktriangle) sample F; (\bullet) sample P.

relation to shear in the capillary extruding the material just prior to its extension. The experiment was performed using a melt spinning machine. The polymer was extruded at 1700 and 9500 sec^{-1} shear rate and was subsequently elongated. By selecting a proper combination of entrance angle and capillary diameter, while retaining the same aspect ratio, conditions were selected so that at the same volumetric flow rate the same diameter of extrudate was obtained from two different capillaries. This procedure assured the same extension and cooling conditions with the same extrudate take-up (winding) velocity. The tension measurements showed that the elongational viscosity at the same extension rate was 2.4 times larger with the higher shear rate in the extruding capillary. It is true that besides the shear rate, entrance geometry was also changed. Nevertheless, the effect of shear history, as generated by one means or another, seems dramatic enough.

CONCLUSIONS

In this paper it was shown that shearing history influences the polymer flow properties to a measurable and significant degree. The effects of shear history may also be found in, and correlated with, some features of the solid-state structure of a crystallizing polymer.¹¹

It has been reported by many authors that when a polymer solution or melt is sheared at a constant shearing rate in a rotational viscometer, the resulting shear stress is not constant. With polymer solutions, particularly at medium and high concentrations, the shear stress raises with time to reach a certain maximum and then decreases, finally leveling off

at an equilibrium value.¹²⁻¹⁵ The type of solvent may have some quantitative influence, though qualitatively the phenomenon remains the same.¹² For molten polystyrene,¹⁶ the time dependence of shear stress is very similar for shear rates higher than 0.1 reciprocal seconds. Polymer sheared at lower rates gives shear stress rising with time to some equilibrium value, but without going through a maximum. Formation of molecular aggregates has been suggested as the reason for the observed time dependence of shear stress.¹²⁻¹⁶ These phenomena are reversible with time. A polymer solution or melt which has been sheared until it reached equilibrium shear stress may be left to recover at the same experimental conditions. When sheared again, the sample may again show a maximum occurring at the same time interval from the beginning of the experiment. The magnitude of this maximum, however, depends on the length of recovery time. A complete recovery to the same level of maximum shear stress as in the first shearing run is obtainable.¹³⁻¹⁶

As reported elsewhere, differences in the shear treatment also lead to differences in the morphology of the subsequently crystallized specimen. The different morphologies, in turn, lead to different mechanical properties of the solidified polymers.^{17,18}

The results presented in this paper seem to be analogous to the observations just described. Also, a similar explanation may be offered to account for the changes of melt flow properties induced by preshearing. Naturally, one must account for the differences in the principles of the experiments conducted in a capillary and rotational viscometers, and for the different behavior of solutions versus melts. Molecular weight might also be suspected to play some role in determining the magnitude of the effects caused by shearing history. Changes of the supermolecular structure of the melt may be assumed to be the reason, but several additional points should be stressed. Changes in the supermolecular structure introduced by preshearing appear to be relatively permanent. Neither swelling of the extrudate under relatively slow cooling nor a 30-min heating period before testing is sufficient for the polymer to fully recover its original properties. Not only is the intensity of the preshearing an important factor but the mode, or pattern, of flow has significant influence on the resulting melt properties. It was found to be almost impossible, at least within the series of experiments reported here, to restore all of the melt properties to their original values. This indicates that the macromolecules are able to form a very large range of structures differing by the degree of entanglements, strength, etc. The shape of the curves describing the shear stress changes versus the intensity of preshearing suggests that the large variety of different structures may be realized via several different mechanisms. Currently available methods of analysis of polymer morphology in a noncrystalline state do not appear to be sufficient for thorough experimental evaluation of all possible structures. The present state of molecular rheological theories seems to require further refinement before such a complex problem can be resolved.¹⁹⁻²⁴

In view of the findings presented here, the effectiveness of Bagley's entrance correction¹ appears to need reexamination or refinement.

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