The Effect of Heterogeneity on the Flow Behavior on High Density Polyethylene

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Synopsis

The effect of heterogeneity on the flow behavior of high density polyethylene (HDPE) has been studied by systematically homogenizing heterogeneous blends and observing the effect on the basic rheological parameters and on the extrudate surface appearance. Ample evidence is presented to show that heterogeneity causes substantial changes in the flow behavior although molecular parameters obtained through solution studies are unchanged. A simplified mathematical model which clearly illustrates the effects of the size of these flow units on the flow behavior is presented.

INTRODUCTION

It is widely known that the non-Newtonian steady state flow behavior of a polymer is determined by molecular properties such as the average molecular weight[1-3] and the molecular weight distribution (MWD).[4,5] Recent molecular entanglement theories,[6,7] notably that of Graessley,[8] allow us to calculate, to a good approximation, flow curves from molecular weight and molecular weight distribution data obtained by various techniques, including gel permeation chromatography (GPC). While more exact correlations, theoretical as well as experimental, between the molecular makeup and viscous response of melts or concentrated solutions are sought, an important effect on the viscoelastic behavior is often neglected; namely, the effect of large-scale heterogeneity or molecular aggregates. Mooney[9] suggested the existence of coherent masses containing many polymer molecules, in raw elastomers, which move and rotate essentially as rigid units. He has demonstrated the presence of these rheological units from the differences in the velocity of a color front under shear in a Mooney viscometer. More recently, Berens and Folt[10] observed pronounced differences in apparent viscosity, postextrusion swelling, and extrudate roughness, depending upon sample preparation and previous history for a number of poly(vinyl chloride) (PVC) samples. From fracture surface electron photomicrographs of molded or extruded PVC samples, they suggested that the melt flow of PVC under some conditions must involve the slippage of resin particles past one another, rather than a homogeneous deformation of the melt. Although there is some other published work along this line,[11-15] practically no reported data are available which systematically demon-

strate the effect of heterogeneity due to molecular aggregates or structural variations on a larger-than-molecular scale. We have varied the degree of heterogeneity by controlled shear work of bicomponent blends of high, medium, and low molecular weight polyethylene whole polymers. The effects of heterogeneity on viscoelastic properties are considered in terms of fundamental parameters such as the zero shear viscosity and the maximum relaxation time.

EXPERIMENTAL

Materials

The materials used in these experiments were three high density polyethylene (HDPE) homopolymers of densities 0.955–0.960 and melt indices of 0.08, 6.5, and 15.0, respectively. These materials are coded A, C, and B, respectively.

Instrumentation

The heterogeneous blends were homogenized in a Brabender Plasticorder[16] at 177°C under a nitrogen atmosphere. Roller blades were used in all cases. The high shear flow data were obtained on an Instron capillary rheometer[16] at 190°C using standard dies (90° entrance angle). The low shear data were taken on a Model R-17 Weissenberg rheogoniometer[16] at 190°C. A 2.5-cm, 4° cone and plate were used throughout this work. Three torsion bars were needed to cover the required shear rate range. These were 1.9×10^1, 2.1×10^2, and 2.1×10^3 dyne-cm/micron. The molecular parameters were obtained on a Waters Associates gel permeation chromatograph (GPC). The operating temperature was 135°C, and 1,2,4-trichlorobenzene was used as the solvent. Details of the operation and calibration procedure are discussed elsewhere.[24]

Blend Preparation

Heterogeneous Blend. This blend was prepared by physically mixing the components and stabilizer. All materials were ground to a maximum size of 50 mesh before mixing. The stabilizer used was Santonox, at a concentration of 0.6% by weight. After the materials were mixed, the blends were pressed into 0.125-in.-thick films at 175°C and then cut up into cubes of approximately 0.125 in. in size.

Blend Homogenization. The heterogeneous blend was homogenized to various degrees in a Plasticorder. The shear rate and time required depended on the particular blend (melt viscosity of the components) and has established from the torque–time history at a given rpm. The torque steadily increased as the material was homogenized and reached a steady state value when homogeneity was achieved. The time interval from the starting torque (measured right after melting) to the steady state torque

was established and later subdivided in order to obtain the various degrees of homogenization.

Solution Blends. In order to confirm the homogeneity of the shear homogenized materials, we made several solution blends by dissolving the blend components in o-dichlorobenzene (ODCB) at 135°C under agitation. A concentration of 3% was used in all cases. After the polymer went into solution, it was precipitated in excess methanol by slowly and steadily pouring the solution into a large container under agitation. The precipitate was then filtered and dried at 60°C under vacuum until all of the solvent was removed.

The stabilizer was then added and the material was pressed into 0.125-in.-thick sheets.

Data Treatment

Entrance[17] as well as Rabinowitsch corrections[18] were performed on the high shear rate capillary flow data. The corrected data were plotted together with the low shear rate data obtained on the Weissenberg rheogoniometer.

The rheological parameters presented were obtained by computer-fitting the flow data to master curves of the following general form:

$$\ln (\eta/\eta_0) = [(\eta/\eta_0) - a] \ln [1 + (\dot{\gamma}\tau_0)^b]$$

where η_0 = zero shear viscosity; τ_0 = maximum relaxation time; a = flow curve shape factor; and $a \cdot b$ = constant. The use of this master curve for HDPE has been discussed by Sabia[22] and Nakajima and Wong.[4]

For a given flow curve shape factor a, η_0 and τ_0 are the shift factors.[19]

Extrudate Surface Photomicrographs

Extrudates were collected at a shear rate of 338 sec^{-1} and cooled slowly in ambient air. Photomicrographs were taken at a magnification of 40× using an optical microscope.

DISCUSSION

The steady state flow curves of the systematically homogenized blend of polymers A and B are shown in Figure 1. A quantitative description of these flow curves in terms of basic rheological and molecular parameters is given in Table I, together with the data for the blends of polymers A and C. These data clearly show that heterogeneity decreases the melt viscosity and the maximum relaxation time. Figure 2 shows that heterogeneities cause poor extrudate surface appearance. As the heterogeneous blend is systematically homogenized, the extrudate surface improves considerably. The effect of heterogeneity on the rheological response is best illustrated by the D factor[24] in Table I. This parameter is defined as follows:

$$D = \frac{\tau_0}{\eta_0} \times 10^6 \qquad (1)$$

SHIDA AND CANCIO

TABLE I
Quantitative Characterization of the Flow Curve

	Flow curve A	Rheological data			GPC data		
		η_0, poise	τ_0, sec	D^a	$M_n \times 10^4$	$M_w \times 10^5$	$M_z \times 10^6$
A–B Blend							
heterogeneous	2.50	2.1×10^4	0.012	0.57	1.77	0.831	0.461
homogenized 4 min	2.50	2.6×10^4	0.016	0.61	1.45	0.798	0.514
homogenized 6 min	2.50	4.0×10^4	0.029	0.74	—	—	—
homogenized 10 min	3.00	7.4×10^4	0.058	0.78	1.56	0.839	0.530
A–C Blend[b]							
heterogeneous	1.91	3.1×10^4	0.040	1.3	0.807	1.17	0.912
homogenized by one extrusion at 100 sec^{-1}	2.23	5.9×10^4	0.086	1.5	—	—	—
homogenized by two extrusions at 100 sec^{-1}	2.35	8.5×10^4	0.140	1.7	—	—	—
completely homogenized (5 min in Plasticorder)	2.50	3.2×10^5	0.909	2.8	1.01	1.23	1.00

[a] $D = \dfrac{\tau_0}{\eta_0} \times 10^6$.

[b] Due to limited amount of material, only the uncorrected high shear data were used to obtain the rheological parameters.

It is proportional to the rheological average molecular weight (M_r) if Bueche's expression[20] for τ_0,

$$\tau_0 = \frac{12}{\pi^2} \frac{\eta_0 \cdot M_r}{\rho RT},$$

is substituted in eq. (1). Thus,

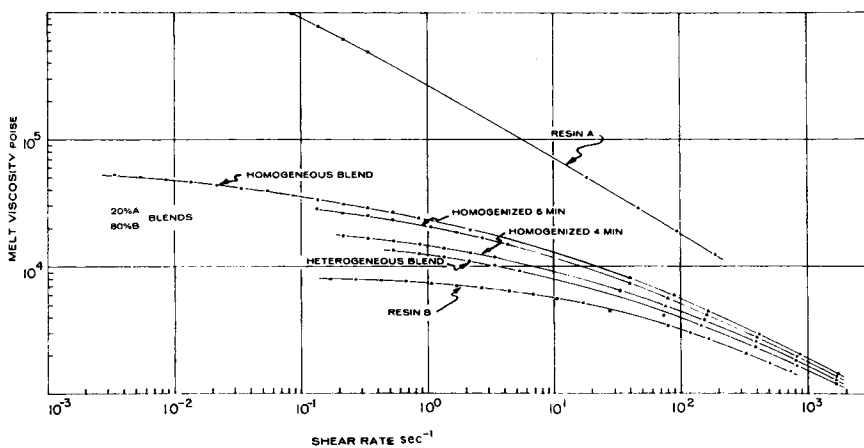$$D = C \cdot M_r, \tag{2}$$

Fig. 1. Effect of heterogeneity on flow behavior: (●) WRG data; (▲) Instron rheometer. 190°C test temperature.
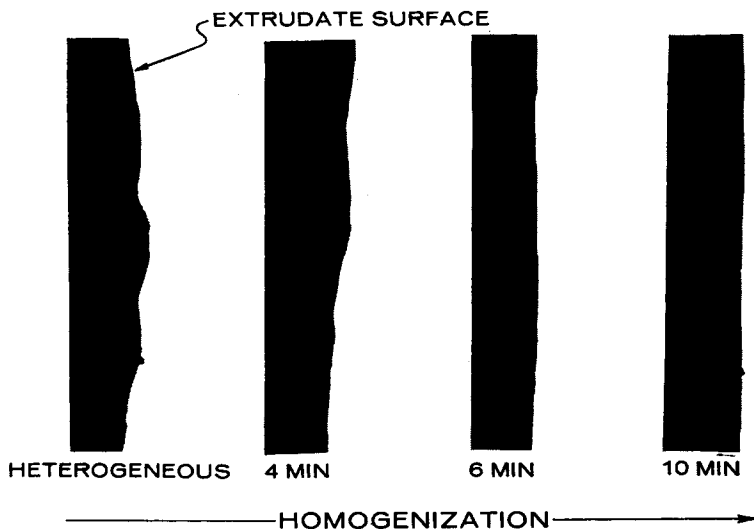

Fig. 2. Effect of heterogeneity on extrudate appearance. Extrusion conditions: shear rate, 338 sec⁻¹; temperature, 190°C; L/D ratio, 33.34; entrance angle, 90°.
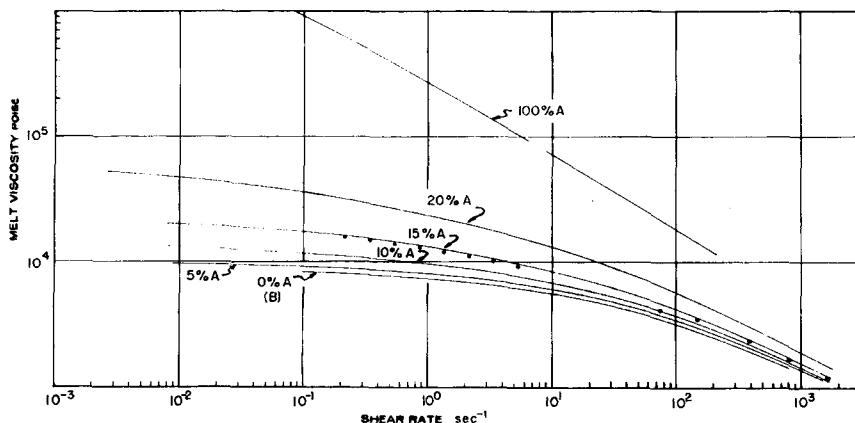
Fig. 3. Quantitative effect of heterogeneity on flow curve. Solid lines represent the flow curves of homogeneous blends of 5, 10, 15, and 20% A in B. Black circles represent flow curve of the heterogeneous blend of 20% A in B. Test temperature, 190°.

where C is a constant dependent on the density ρ, the gas constant R, and the absolute temperature T. Note that heterogeneity decreases the value of D.

The GPC data (Table I) show that, as expected, heterogeneity has no effect on the molecular parameters. This is a consequence of the fact that molecular aggregates disappear in dilute solution (such as used for GPC). From a rheological standpoint, the apparent effect of heterogeneity is a reduction in the average molecular weight (lower D, lower η_0).

This is further substantiated in Figure 3, which shows that the flow curve of a heterogeneous blend of 20% A in B is equivalent to the flow curve of a 15% homogeneous blend of A and B. In other words, this is equivalent to reducing the concentration of the high molecular weight component by 25%. To make sure that the blends shown in Figure 3 were homogeneous, we determined the flow curve of solution blends at 10% and 20% concentrations. These flow curves matched the flow curves shown in Figure 3 reasonably well.

In order to illustrate the effect of molecular aggregates (flow units) on the flow behavior, let us consider the following simplified model. First, let us assume that all of the molecules of the high molecular weight polymer A exist as aggregates, i.e., no loose or individual molecule of A is present in the system. The aggregates are also assumed to be spherical in shape with an effective average radius R. The molecular contributions to viscous dissipation by polymer A come only from the fraction of A molecules at or near the surface of the sphere where effective entanglements with polymer B molecules are possible. Similarly, with Bueche's shielding factor,[20] the fraction of A molecules entangled with B molecules at any radial position r within the flow unit is expressed as

$$f(r) = \exp\left\{-K(R-r)\right\} \qquad (3)$$

where K is a parameter that indicates the degree of penetration of polymer B molecules into the flow unit. Figure 4 shows the dependence of $f(r)$ on K. Since B molecules are also large, diffusion of these molecules into the flow unit is very slow. Hence, the effective entanglements between A and
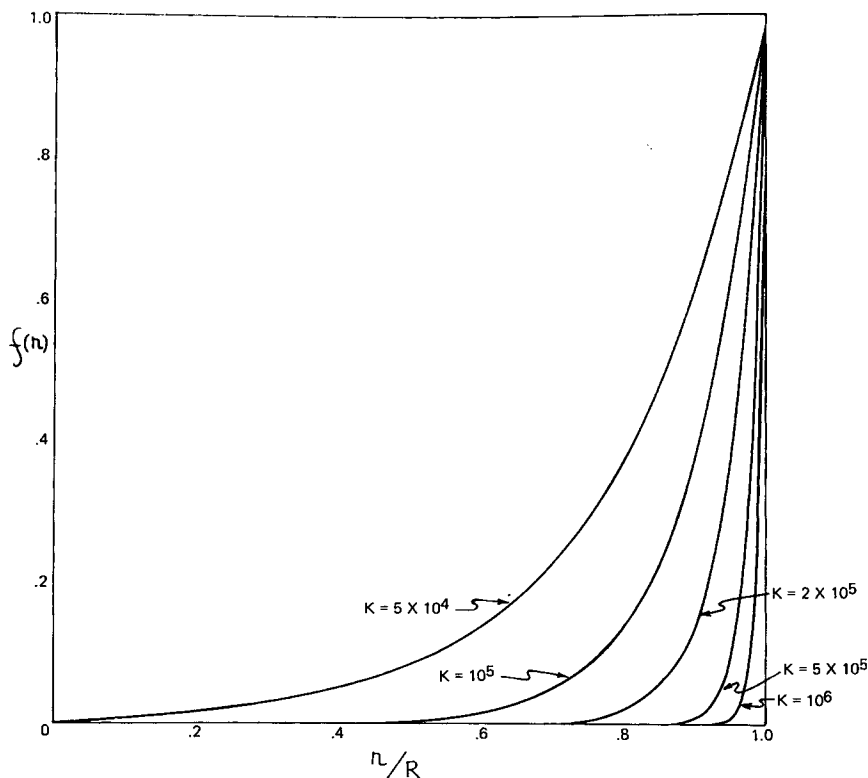

Fig. 4. Dependence of $f(r)$ on K.

B molecules occur only at or near the surface. Then the total number of effective A molecules is as follows:

$$N' = \frac{4\pi}{\bar{N}_w V_0} \int_0^R r^2 \cdot f(r) \cdot dr = \frac{4\pi}{\bar{N}_w V_0} \int_0^R r^2 \cdot \exp\left\{-K(R-r)\right\} \cdot dr \quad (4)$$

where $\bar{N}_w$ is the weight-average degree of polymerization, and V_0 is the volume of the monomer unit at 190°C. If all the A molecules were homogeneously mixed with B molecules, then all of these would be effectively entangled. The number of effective A molecules would then be

$$N = \frac{4\pi R^3}{3\bar{N}_w V_0}. \quad (5)$$

From eqs. (4) and (5) we can calculate the fraction of A molecules available for effective entanglements when they exist as spherical aggregates of average radius R:

$$\frac{N'}{N} = \frac{3}{KR}\left(1 - \frac{2}{KR} + \frac{2}{K^2R^2} - \frac{2}{K^3R^3}\,e^{-KR}\right) \tag{6}$$

Figure 5 shows the dependence of N'/N on the aggregate radius for three values of the parameter K. The radius R is considered in such a way as to include the concentration effect at the boundary of the flow unit.

We have shown that in our case the effect of heterogeneity on the flow curve is equivalent to reducing the concentration of the high molecular weight component by 25%. This means that about 25% of polymer A
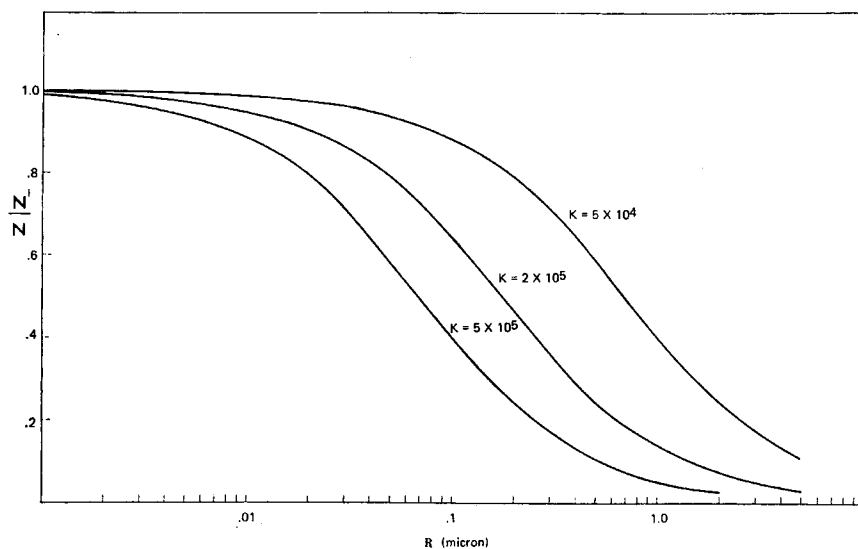

Fig. 5. Dependence of the molecular entanglement fraction on aggregate size.

molecules do not participate in effective entanglements. Figure 4 clearly illustrates that as the shielding parameters K increases, the thickness of the molecular entangling layer decreases, and Figure 5 demonstrates that for a given value of K the fraction of effective polymer A molecules in the entangling layer increases as the flow unit radius decreases. As the heterogeneous blend is shear homogenized, the aggregates are broken down into many smaller ones (Fig. 2). Therefore, the total number of entanglements and the melt viscosity increase.

The model is undoubtedly oversimplified. The shape of the aggregates is not spherical but rather a highly eccentric ellipsoid with rough surfaces. Also, certain loose A molecules exist in the system. However, the model does show qualitatively the effect of aggregate size on the flow behavior.

CONCLUSIONS

Through a systematic homogenization of heterogeneous blends of high density polyethylenes we have shown that heterogeneity decreases the zero shear viscosity, decreases the maximum relaxation time, and significantly affects the surface appearance of extrudates. We have shown that the effect of heterogeneity is equivalent to the effect of reducing the concentration of the high molecular weight component of the blend. Furthermore, we have proposed a simplified qualitative model to explain our results.

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