

Effect of Mixing on Melt Flow Properties of High-Density Polyethylene

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Synopsis

An investigation has been made into the effect of mixing by a screw extruder upon the molecular characteristics and the melt flow properties of high-density polyethylene. The crosslinking between molecules predominates over the scission of a molecule at an early stage of mixing, but with further increase in the degree of mixing, this situation reverses itself to bring about the formation of branched polymers. Static flow and dynamic viscoelastic properties of molten high-density polyethylene change considerably with increase in the degree of mixing. The apparent viscosity drops rather sharply after mixing. The dynamic properties for the original resin show smaller frequency dependence of the viscosity and larger dependence of the rigidity than those for extrudates. The relaxation spectra become broader with increase in mixing. These may mainly be due to the change of the molecular characteristics of high-density polyethylene with mixing by an extruder.

INTRODUCTION

An examination of the various plastic processing techniques makes clear that the rheology of molten thermoplastics is useful in characterizing polymers. Usually, most polyethylene fabricators are faced with the problem of adding reproduced pellets to original pellets in order to save the cost of plastic materials. The reuse of scrap material may lead to problems in fabrication and end use properties owing to the physical and chemical changes associated with extrusion through an extruder.

Recently, Heitmiller et al.¹ have suggested that an observed increase in melt viscosity on extrusion could be attributed to improved mixing of polymer molecules of different molecular weights. More recently, Ford et al.² have studied the changes in flow properties of linear polyethylene when the resin is subjected to heating and mixing and suggested that both crosslinking and chain scission reactions occur during processing. In this paper, data for melt flow and dynamic viscoelastic behavior of high-density polyethylene are presented with special reference to the degree of mixing by a screw extruder.

EXPERIMENTAL

The sample of polyethylene used is a commercial Phillips-type ethylene-1-butene copolymer with a melt index of 0.30 g/10 min and density 0.947 g/cc. Samples to test the degree of mixing were prepared by extruding the original pellet through a screw extruder ($D = 40$ mm, $L/D = 18$, screw speed = 47 rpm, stock temperature = $233 \pm 2^\circ\text{C}$) into a water bath for several times.

The viscosity-average molecular weights \bar{M}_v of the polymer were determined from the intrinsic viscosity in Decalin at 135°C by the following equation given by Wesslau:³

$$[\eta] = 0.98 \times 10^{-3} \bar{M}_v^{0.63} \quad (1)$$

The corresponding number-average molecular weights \bar{M}_n were measured by means of a Dohrman Model M-100 high-speed membrane osmometer with Decalin, 102°C , as solvent.

The molecular weight distributions were determined from gel permeation chromatography elution curves. A Waters Associates Model 200 chromatograph was used. Column packings were rigid polystyrene gel of pore size 10^7 , 3×10^6 , and 10^4 Å. The eluant was trichlorobenzene at 130°C .

The number of total methyl branches was determined from the optical density at 1378 cm^{-1} by infrared spectrophotometry. The gel fractions were measured by the use of a modified Soxhlet-type extractor in *p*-xylene at 130°C . The degree of crystallinity was calculated by comparing the area of the respective endothermic peak with that of the peak of dotriacontane by means of a Shimadzu DT-10-type differential thermal analyzer.

The flow properties were measured over a wide range of the rate of shear from 10^{-3} to 10^3 sec^{-1} at temperatures of 190° to 239°C . Higher shear data were obtained with a constant pressure-type extrusion viscometer whose orifices had flat entries. The concentric cylinder-type rheometer⁴ was used to measure dynamic viscosity η' , dynamic rigidity G' , and apparent viscosity η_a in a region of lower shear rate. This rheometer is useful as a torsionally oscillating rheometer or a Couette-type viscometer by a minor change in the driving system. The angular frequencies and the rates of shear ranged from 10^{-2} to 10 sec^{-1} and from 10^{-3} to 10 sec^{-1} respectively.

RESULTS AND DISCUSSION

The molecular characterizations of high-density polyethylene resulting from different degrees of mixing are shown in Table I, which includes data for samples heat-treated at 235°C for 10 min without any shearing action. Both the viscosity-average and the number-average molecular weights increase slightly initially and then gradually decrease with increased mixing. The values of the sample molded in a compression press in which melting occurred (heat-treated sample) but without any significant shear

TABLE I
Molecular Characteristics of High-Density Polyethylene with
Different Degrees of Mixing

	$\bar{M}_v \times 10^{-5}$	$\bar{M}_n \times 10^{-3}$	Gel fraction, %	Density, g/cc	Degree of crystallization, %	Total no. of methyl groups, per 1000 carbon atoms
Base resin	1.3	8.3	3.1	0.947	86.7	3.2
Extrudate 1	1.4	8.9	4.2	0.945	85.2	5.4
Extrudate 2	1.2	7.9	3.0	0.942	81.0	8.5
Extrudate 3	1.0	6.6	2.1	0.944	81.4	7.9
Heat treated	1.3	8.0	3.0	0.947	85.8	3.5

were not so different from those of base resin. This was also the case for the gel fraction.

It is seen from this table that both density and degree of crystallinity decrease but number of total methyl groups increases with extrusion through a screw extruder.

Figure 1 shows the molecular weight distributions of high-density polyethylene obtained from the gel permeation analysis. As the polymer is sheared, the lower molecular weight fraction decreases at first and then increases gradually. The fraction in the region of higher molecular weight seems to have a reverse tendency of that in the lower molecular weight region, which was also confirmed by the change in gel fraction described in Table I.

From these results it may be concluded that the crosslinking between molecules predominates slightly over the scission of a molecule at an early stage of mixing, but with further increase in the degree of mixing this situation reverses itself to bring about the formation of branched polymers.

Figure 2 shows the apparent flow curves of original resin in a higher shear rate region as a function of length-to-radius ratio, L/R , of a capillary at 239°C. For the data obtained from short capillary geometry, in the case of $L/R = 2.0$, the pressure loss in the barrel of an instrument could not be neglected. Hence, the pressure at a wall, P_w , was corrected by using the method of Metzger and Knox.⁵ With increase in L/R , the shear rate decreases at a constant pressure. Similar behavior was observed for all the samples studied at different temperatures.

On molding the pellet in a compression press in which melting occurs, but without any shear, there is very little change from the original resin, as shown in Figure 2. This indicates that the heat treatment does not affect the flow properties in the region of higher shear rate.

The corrected flow curves at various temperatures are shown in Figure 3 for the original resin sample in accordance with Bagley's method.⁶ Typical non-Newtonian flow curves are seen in the figure. Similar behavior was observed for the samples of various degrees of mixing.

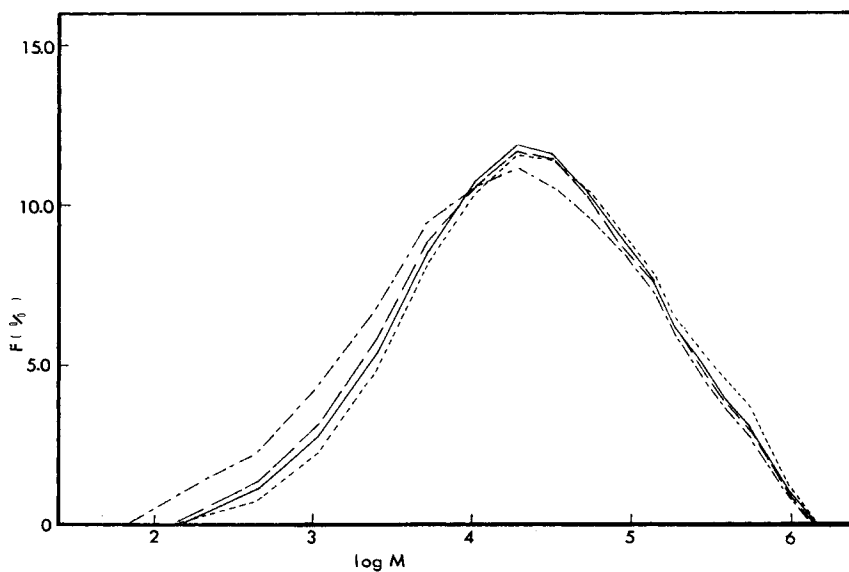


Fig. 1. Molecular weight distribution curves of high-density polyethylene with different degrees of mixing: (—) base resin; (----) extrudate 1; (-·-·-) extrudate 2; (- - -) extrudate 3.

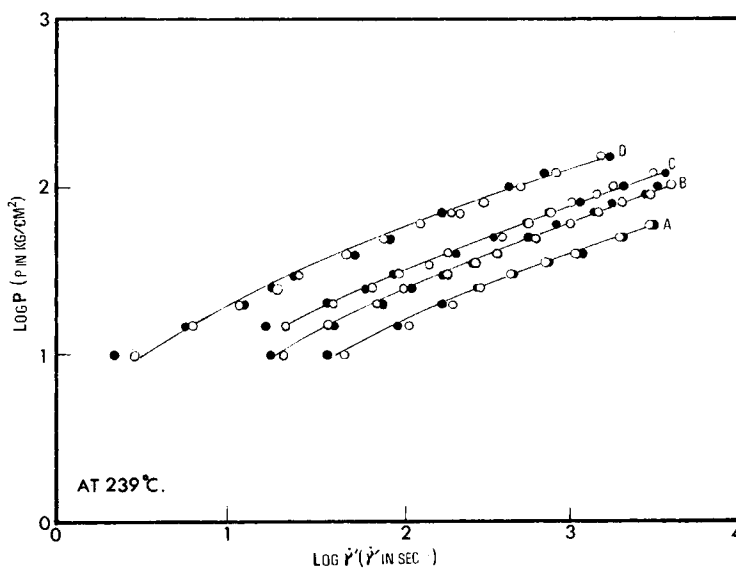


Fig. 2. Apparent flow curves of high-density polyethylene for various kinds of capillary geometry at 239°C: (O) base resin; (●) pellet (treated for 10 min in a compression mold at 235°C; (A) $L/R = 2.0$; (B) $L/R = 6.7$; (C) $L/R = 10$; (D) $L/R = 20$.

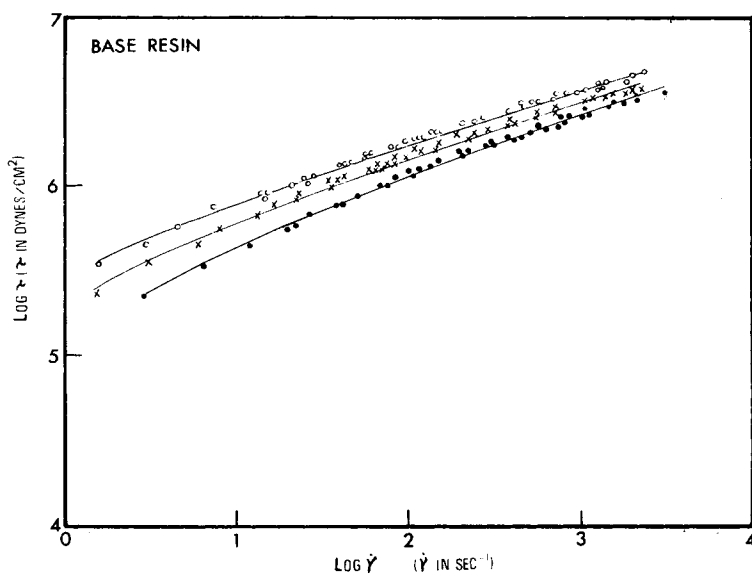


Fig. 3. Corrected flow curves at various temperatures for base resin: (O) 190°C; (X) 212°C; (●) 239°C.

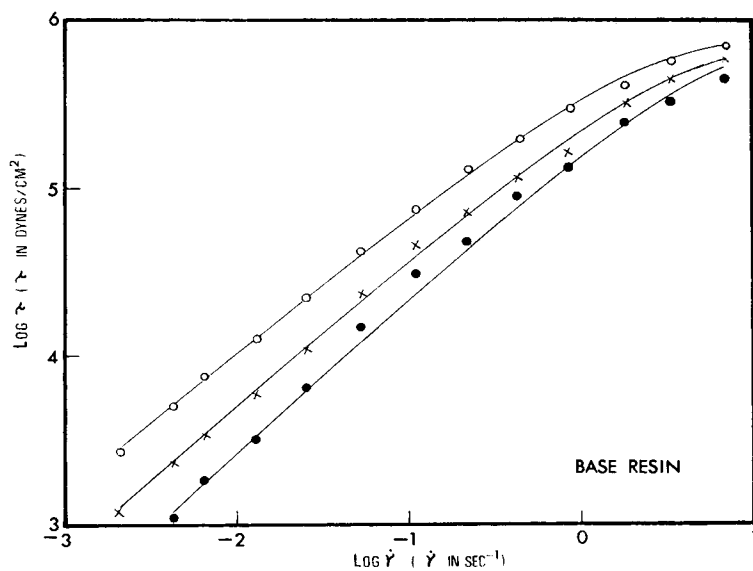


Fig. 4. Flow curves of base resin in the region of lower shear rate at various temperatures: (O) 190°C; (X) 212°C; (●) 239°C.

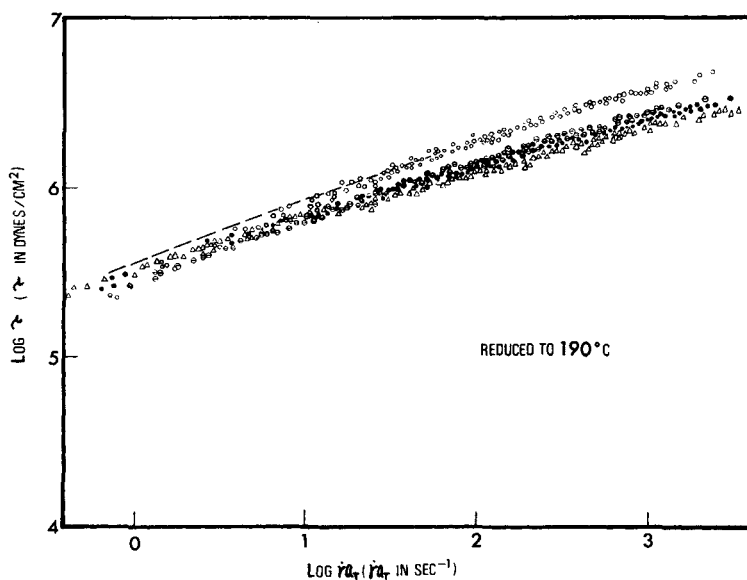


Fig. 5. Master flow curves of high-density polyethylene for various degrees of mixing at 190°C: (O) base resin; (Θ) extrudate 1; (●) extrudate 2; (Δ) extrudate 3; (---) heat-treated resin (235°C, 10 min).

Figure 4 shows the flow data of the original resin in the region of lower shear rate at various temperatures. Temperature dependence of flow curves for samples at a lower shear rate is almost similar to that observed at higher shear rate. The curves reveal Newtonian flow in the region of shear rate below 10^{-1} sec^{-1} .

The curves given in Figures 3 and 4 at various temperatures may be shifted along the $\log \dot{\gamma}$ axis to form a single composite curve, in accordance with the method of reduced variables. The reference temperature used here for all the samples of various degrees of mixing was 190°C. The resultant master curves shown in Figures 5 and 6 clearly illustrate the validity of the superposition method for each of the systems studied, Figure 5 referring to the region of higher shear rate and Figure 6, to that of lower shear rate, respectively. It is interesting to note that in the region of lower shear rate, $\dot{\gamma}$ becomes smaller at fixed shear stress with increase in mixing, but in the region of medium shear rate, the respective curves intersect with each other at about 0.3 sec^{-1} ; and with further increase in shear rate, $\dot{\gamma}$ becomes larger with mixing at constant shear stress.

The temperature dependences of the shift factor a_T obtained from both the flow curves in the region of lower and higher shear rates agreed with each other and were found to fit an Arrhenius-type equation of the form

$$a_T = A \exp[\Delta H/RT], \quad (2)$$

where T is absolute temperature, ΔH is the apparent activation energy, R is the gas constant, and A is a constant. The temperature dependence

of zero shear viscosity η_0 , calculated from Figure 4, was also found to fit an Arrhenius-type equation.

The apparent activation energies deduced from the superposition of flow curves and those for viscous flow are given in Table II for samples of various degrees of mixing. It is seen that both sets of data agree quite well with one another, suggesting that the superposition method used in the analysis of linear viscoelastic behavior is also applicable to the flow curves. The apparent activation energy for viscous flow, ΔH , of base resin is about 9.0 kcal/mole, which is slightly higher than the value of 6 to 7 kcal/mole reported for linear polyethylene.⁷ The value of ΔH is seen to increase with

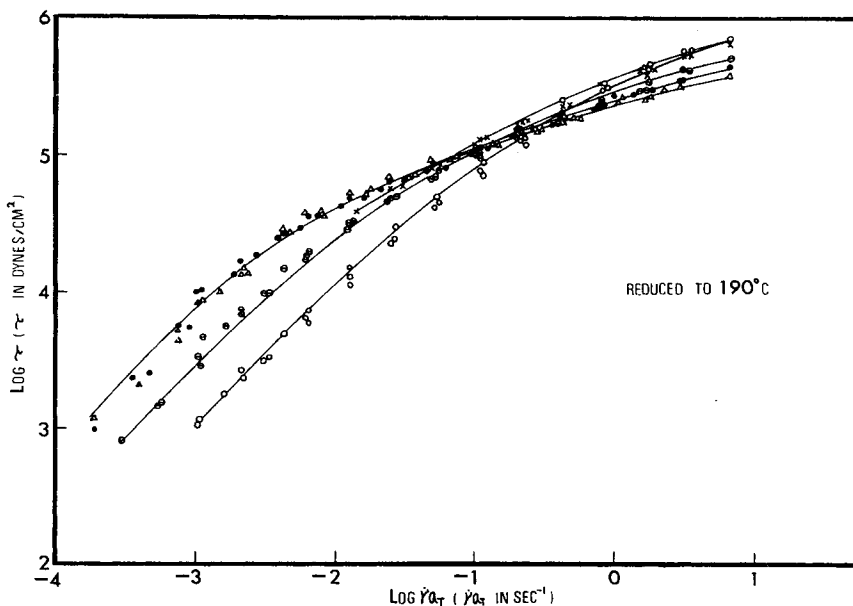


Fig. 6. Master flow curves of high-density polyethylene in the region of lower shear rate at 190°C: (O) base resin; (⊖) extrudate 1; (●) extrudate 2; (Δ) extrudate 3; (×) heat-treated resin (235°C, 10 min).

increase in resin mixing through a screw extruder. Recently, Porter et al.⁷ have discussed the effect of molecular weight and branching upon the activation energy for viscous flow of branched polyethylene. For linear polyethylene, ΔH is said to reach a characteristic value independent of molecular weight for all molecular weights above a lower limit of about 4000.

The molecular weight variation obtained for the samples shown in Table I could not account for the change in flow activation energy with mixing. Infrared studies, as shown in Table I, indicated that the total molar concentration of branches ranges from 3 to 9 per 1000 chain carbon atoms. Even if all of the branches were short, such concentrations are insufficient to account for the large values of ΔH observed for samples of different de-

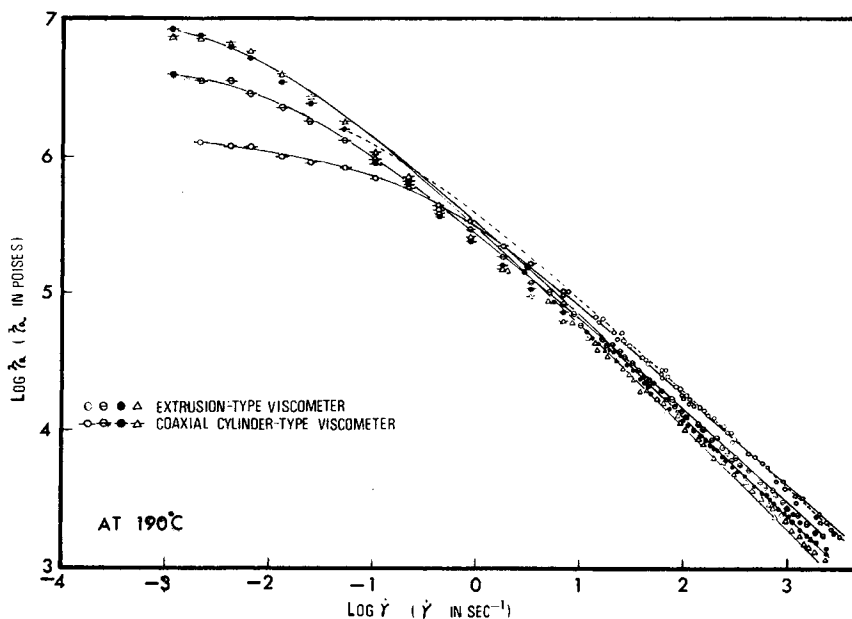


Fig. 7. Apparent viscosity of high-density polyethylene over the entire range of shear rate at 190°C: (O—O—) base resin; (⊖—⊖—) extrudate 1; (●—●—) extrudate 2; (Δ—Δ—) extrudate 3; (---) heat-treated sample (235°C, 10 min).

degrees of mixing. It is assumed that long-chain branches or permanent crosslinks may be responsible for the anomalous flow activation energy.

Figure 7 shows the apparent viscosity η_a versus shear rate over an entire range of shear rates for samples of different degrees of mixing at 190°C. It is seen from the figure that the viscosity-shear rate curves derived from a capillary extrusion viscometer agree with those obtained from a coaxial cylinder viscometer. In the region of lower shear rate, the viscosity increases with increase in mixing.

TABLE II
Apparent Activation Energy of Viscous Flow for High-Density Polyethylene with Different Degrees of Mixing

	ΔH , kcal/mole			
	Static measurement		Dynamic measurement	
	from ∂_0	from a_T	from a_T of $G'(\omega)$	from a_T of $G''(\omega)$
Base resin	9.5	9.0	9.4	9.5
Extrudate 1	14.5	12.5	14.1	15.0
Extrudate 2	15.7	15.2	16.0	15.7
Extrudate 3	15.4	14.9	15.8	15.7
Heat treated	—	8.8	9.7	10.1

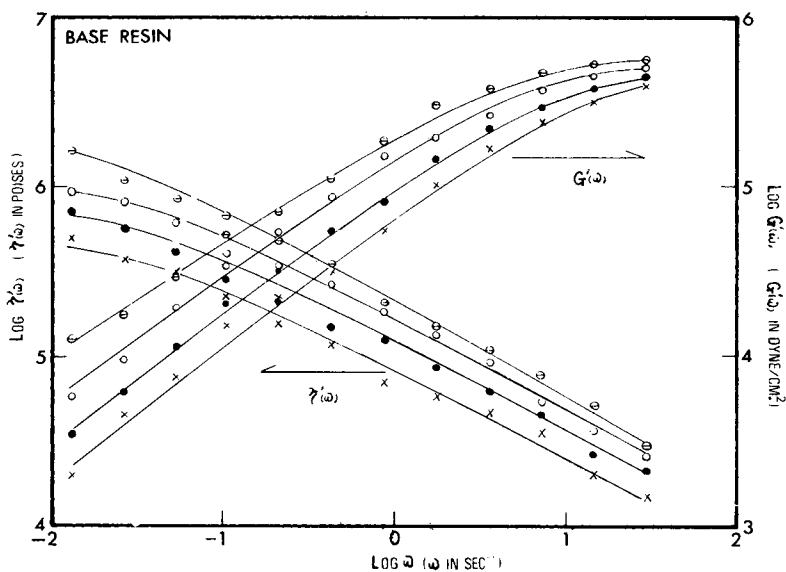


Fig. 8. Dynamic viscoelastic properties for base resin at various temperatures: (\ominus) 170°C; (\circ) 190°C; (\bullet) 212°C; (\times) 239°C.

Generally, the zero shear viscosity is proportional to 3.4 power of molecular weight above a certain critical molecular weight. As shown in Table I, the viscosity-average molecular weight increases slightly with increase in mixing, and such a minor change in molecular weight could not account for the larger increase in the zero shear viscosity observed in Figure 7.

The most interesting point is that with increase in mixing the shear rate for onset of non-Newtonian flow decreases and that an increase in the degree of non-Newtonian flow is observed. Recent papers^{8,9} have reported a reciprocal variation between the shear stress or shear rate for onset of non-Newtonian flow and \bar{M}_w , and an increase in the degree of non-Newtonian flow with increasing molecular weight. The variation of molecular weight cannot explain the shear dependence of melt viscosity on mixing, as in the case of zero shear viscosity. It is supposed that molecular weight distribution and chain branching or crosslink formation may be responsible.

The frequency dependence curves of dynamic viscosity $\eta'(\omega)$ and dynamic rigidity $G'(\omega)$ are shown in Figure 8 for original polyethylene resin at various temperatures. Marked dependence of $\eta'(\omega)$ and $G'(\omega)$ on frequency is seen from the figure, which is the expected feature from the linear viscoelastic body.

Recently, the dynamic viscosity $\eta'(\omega)$ was compared with the apparent viscosity η_a for melts of polyethylene,¹⁰ polystyrene,¹¹ poly(methyl methacrylate)¹² and poly(vinyl acetate),¹² concluding that the experimental results did not coincide with those predicted by several theories but agreed

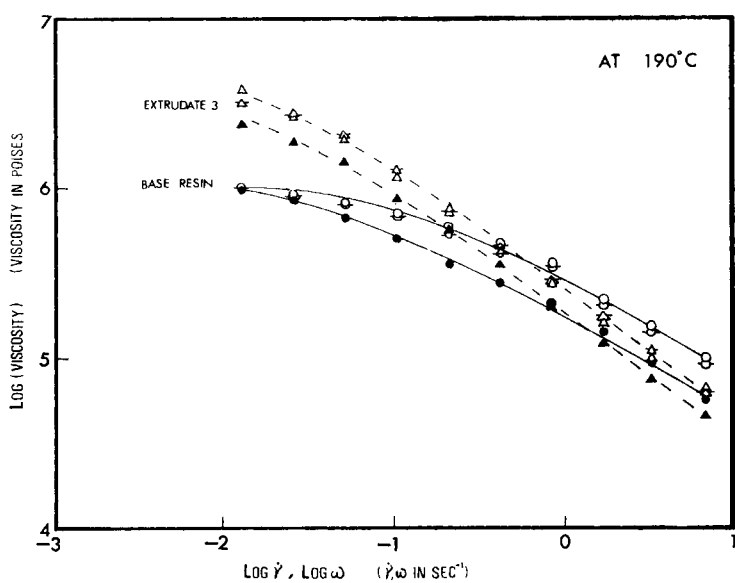


Fig. 9. Comparisons of apparent viscosity with dynamic viscosity and absolute value of complex viscosity for high-density polyethylene at 190°C: (O Δ) apparent viscosity; (\bullet) dynamic viscosity; (-O- Δ -) absolute value of complex viscosity.

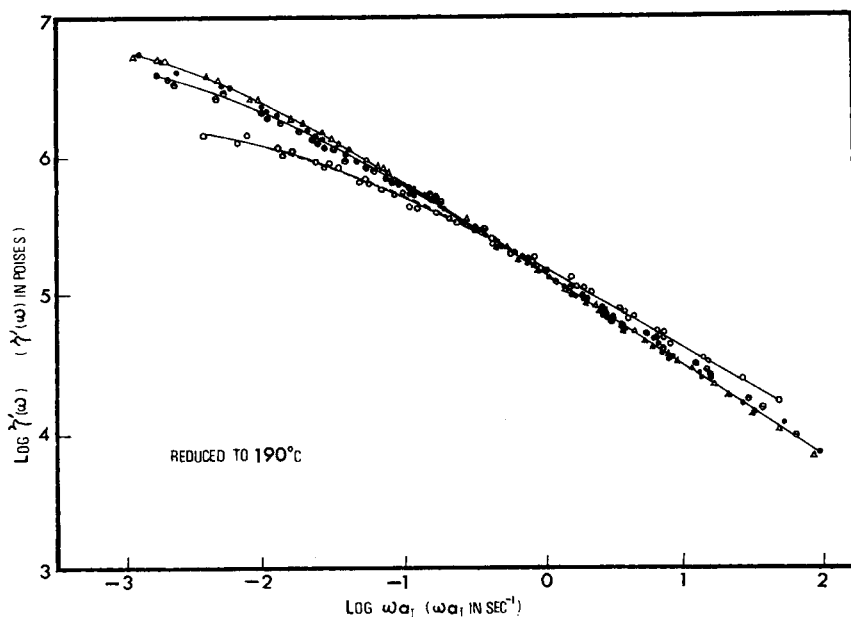


Fig. 10. Master curves of dynamic viscosity of high-density polyethylene for different degrees of mixing at 190°C: (O) base resin; (\ominus) extrudate 1; (\bullet) extrudate 2; (Δ) extrudate 3; (- - -) heat-treated resin (235°C, 10 min).

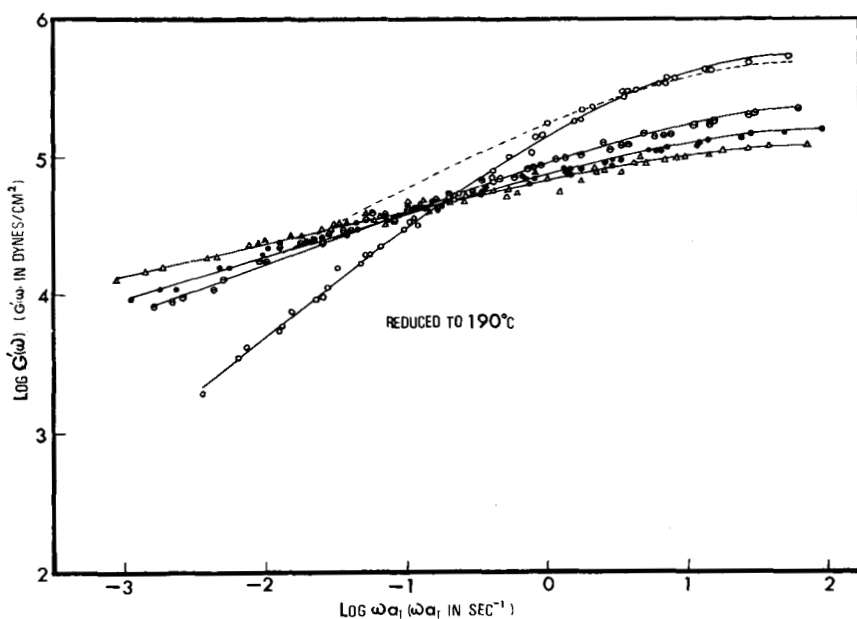


Fig. 11. Master curves of dynamic rigidity of high-density polyethylene for different degrees of mixing at 190°C: (O) base resin; (⊖) extrudate 1; (●) extrudate 2; (Δ) extrudate 3; (----) heat-treated resin (235°C, 10 min).

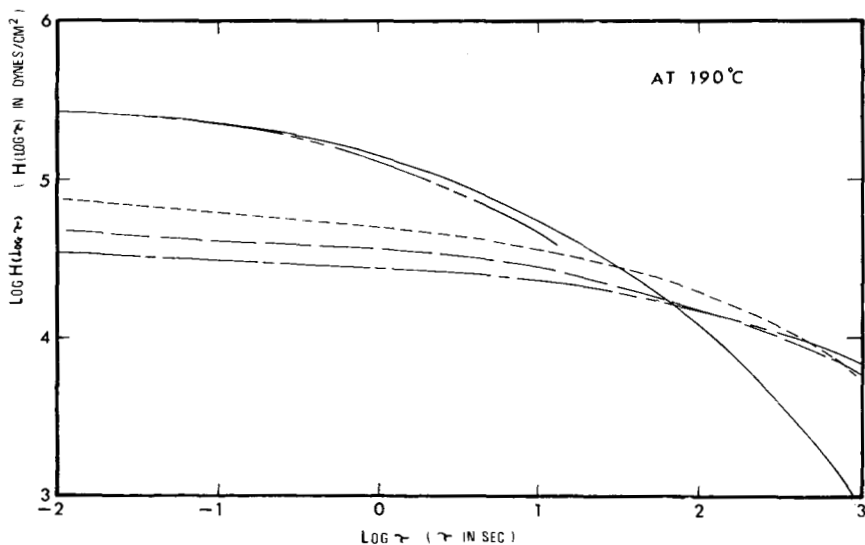


Fig. 12. Relaxation spectra of high-density polyethylene for different degrees of mixing at 190°C: (—) base resin; (----) extrudate 1; (—) extrudate 2; (----) extrudate 3; (-·-·-) heat-treated resin.

with the empirical law of Cox and Merz.¹³ A similar comparison has been attempted for the polyethylene samples of different degrees of mixing.

Figure 9 shows the results of comparison at 190°C. Here, solid lines refer to the results from the original resin and broken lines, to those of the extrudate mixed three times. As seen from the figure, the apparent viscosity η_a , plotted against the rate of shear $\dot{\gamma}$, coincides with the absolute value of complex viscosity $|\eta^*|$, plotted against the angular frequency ω , in the lower regions of $\dot{\gamma}$ and ω in accordance with the empirical law by Cox and Merz.¹³ In this case the elastic effect seems to be included in the apparent viscosity.

The frequency dependence curves of rigidity loss, $G''(\omega)$, calculated from the dynamic viscosity, and the dynamic rigidity for all the samples can be superposed to give master curves according to the procedure of time-temperature superposition without any correction for temperature and density. The reference temperature of the superposition is chosen as 190°C. The values of the shift factors $\log a_T$ derived from the dynamic properties are the same as those obtained from steady flow curves, and the apparent activation energy for the relaxation process coincide with that for viscous flow (Table II).

Figures 10 and 11 show the master curves of $\eta'(\omega)$ and $G'(\omega)$ of high-density polyethylene for various degrees of mixing, respectively. As is seen from these figures, the data for the original resin show smaller dependence of viscosity and larger dependence of rigidity upon frequency, and the original resin has lower viscosity and rigidity at low frequencies than the extrudates.

The difference between the original resin and the extrudates is apparent in the relaxation spectra shown in Figure 12. This figure shows the relaxation spectra $H(\log \tau)$ of high-density polyethylene for different degrees of mixing at 190°C. The spectra become broader with increase in mixing by an extruder. Similar behavior has been observed by Onogi et al.¹² for blends of two fractions having the bimodal distribution of molecular weight for polystyrene and for poly(methyl methacrylate), or for linear and branched fractions of poly(vinyl acetate). Such an abnormal behavior with mixing may be caused by the broadening of molecular weight distribution due to crosslinking or scission of molecules, or to the branching between the molecules.

The exact relation between the rheological properties of polymer melts and the molecular weight distribution and chain branching is not clear to us. In order to clarify the effect of mixing on melt viscosities of polyethylene, we must await more extensive data for rheological properties of polymer melts having different molecular weight distribution and chain branching.

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