

# Rheological Properties of Mixtures of Molten Polymer and Fluorocarbon Blowing Agent. I. Mixtures of Low-Density Polyethylene and Fluorocarbon Blowing Agent

CHANG DAE HAN and CHIN-YUAN MA, *Department of Chemical Engineering, Polytechnic Institute of New York, Brooklyn, New York 11201*

## Synopsis

The viscosities of mixtures of low-density polyethylene and fluorocarbon blowing agent were determined from the measurement of wall normal stress along the longitudinal axis of a capillary die. For the study, three different grades of commercial high-pressure low-density polyethylene were used, together with the following fluorocarbon blowing agents, dichlorodifluoromethane (FC-12), dichlorotetrafluoroethane (FC-114), and blends of FC-12 and FC-114. In the experiment, blowing agent concentration and melt temperature were varied for each combination of polymer and blowing agent employed. Analysis of the experimental data has led to a correlation between the viscosity reduction factor (VRF) and the blowing agent concentration, in which VRF is defined as the ratio of the viscosity of polymer-blowing agent mixture to that of the polymer alone. It was found that the correlation obtained is independent of shear rate and temperature and dependent upon only the type of fluorocarbon blowing agent. The practical significance of the correlation is discussed. We have shown that the entrance pressure drop obtained in the *absence* of phase separation in the entrance region may be used as a measure of the elastic properties of mixtures of fluorocarbon blowing agent and low-density polyethylene resin.

## INTRODUCTION

The use of physical blowing agents (e.g., fluorocarbons) in producing low-density polymeric foams has been practiced for over two decades in the plastics industry. Being soluble in a molten polymer under usual processing conditions, the physical blowing agent (e.g., fluorocarbons, pentane, hexane) is believed to have a profound influence on the rheological properties of the molten polymers.

Whereas extensive studies have been reported in the literature dealing with the rheological properties of homopolymers in the molten state, polymer blends, and filled polymers,<sup>1,2</sup> little has been reported in the literature dealing with the rheological properties of mixtures of molten polymer and physical blowing agent. This is understandable in view of the fact that the rotational type of rheometer, widely used in many research laboratories, is *not* suitable for such fluid systems. Being an *open* system, such a rheological instrument cannot prevent the escape of physical blowing agent (or volatile solvent) from the mixture at high temperature (say,  $T > 100^\circ\text{C}$ ). It is then clear that only a *closed* system (e.g., a capillary-type instrument) is suitable.

In the past, some investigators<sup>3-5</sup> measured the apparent viscosities of molten polymers containing gaseous components (e.g., nitrogen, carbon dioxide), using a plunger-type viscometer. As pointed out by Han,<sup>2,6</sup> rheological measurements

of mixtures of molten polymer and gaseous component, conducted with a plunger-type viscometer (e.g., an Instron viscometer) may be subject to serious criticism. This is because the plunger-type viscometer cannot guarantee that no foaming occurs inside the capillary, as the mixture approaches the exit plane of the die. When foaming (i.e., phase separation) occurs inside the die, the conventional method of data analysis, often practiced in analyzing the data for homopolymers obtained with a plunger-type viscometer, is not applicable.

Han and co-workers<sup>7</sup> measured wall normal stress in a slit die and observed linear pressure profiles when the extrusion rate was very high, but nonlinear pressure profiles, particularly as the melt approached the die exit, when the extrusion rate was below a certain critical value. Note that curvature of a pressure profile indicates that the usual assumption of fully developed flow in the die does *not* hold. By taking photographs, Han and Villamizar<sup>6</sup> have demonstrated that when gas bubbles were formed as a mixture of molten polymer and gaseous component flowed through a die, a nonlinear pressure profile was obtained inside the die. They pointed out that the use of a plunger-type capillary viscometer may not be suitable for determining the apparent viscosities of mixtures of molten polymer and gaseous component (or volatile solvent) when the formation and growth of gas bubbles occurs inside the die.

From visual observations made of bubble growth in a flow channel, together with pressure measurements along the die axis, Han and Villamizar<sup>6</sup> noted that the bubble inflation pressure, referred to as the critical pressure for bubble inflation, decreases with increasing melt extrusion temperature, and increases with increasing blowing agent concentration.

In an effort to prevent solvent vaporization in a polymer solution at elevated temperatures, Mendelson<sup>8</sup> attached a pressurized chamber to the exit of a plunger-type capillary viscometer, and used the measured pressure differential between the capillary entrance and exit to determine the apparent viscosity of concentrated polymer solutions containing volatile solvents. In his experiment, Mendelson first prepared polymer solutions in a glass jar by dissolving a polymer in a volatile solvent at room temperature, using continuous agitation for periods up to a week. He then charged a sample of the solution into the barrel of the viscometer, and finally extruded the polymer solution at elevated temperature into a pressurized chamber. From the point of view of sample preparation, such an experimental technique is extremely difficult, if not impossible, to apply to molten polymers containing a physical blowing agent.

Having recognized that the *bulk* rheological properties of a mixtures of molten polymer and physical blowing agent are of fundamental importance to the design of foam processing equipment and to a better control of foam extrusion processes, we have very recently launched a comprehensive research program, investigating the effects of fluorocarbon blowing agents on the rheological properties of molten polymers. In this paper we shall report the results of that portion of our study dealing with mixtures of low-density polyethylene and fluorocarbon blowing agent.

## EXPERIMENTAL

### Materials

Three different grades of commercial high-pressure low-density polyethylenes were used. They are: (1) Rexene 143 (El Paso Polyolefins Co.), (2) Dow PE510

TABLE I  
Summary of the Molecular Weights of Polyethylenes Used

Manufacturer	Sample code	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
El Paso Polyolefins	Rexene 143	2.00	1.41	7.0
Dow Chemical	PE510	1.39	1.12	8.1
Northern Petrochemical	PE952	2.02	3.70	18.3

(Dow Chemical Co.), and (3) Norchem PE952 (Northern Petrochemicals Co.). The average molecular weights of these resins, which were determined by the use of the gel permeation chromatograph (GPC), are given in Table I, and the molecular weight distribution curves are given in Figure 1.

The rheological properties of the three resins used are given in Figures 2–4. A cone-and-plate rheometer (Weissenberg rheogoniometer) was used for determining the viscosity  $\eta$  and first normal stress difference  $\tau_{11} - \tau_{22}$  at low shear rates (denoted by open symbols), and a capillary rheometer was used at high shear rates (denoted by closed symbols). The basic principles involved in determining the rheological properties given in Figures 2–4 are described in the literature.<sup>1,9</sup>

As blowing agents, the following fluorocarbons were used: (1) dichlorodifluoromethane (FC-12); (2) dichlorotetrafluoroethane (FC-114); and (3) a blend of 50 wt % FC-12 and 50 wt % FC-114. These fluorocarbon blowing agents were supplied to us by the Allied Chemical Co.

Various combinations of resin and blowing agent were used, and, for a given combination, the concentration of blowing agent and the melt extrusion temperature were varied. Table II gives a summary of the ranges of these processing variables that we investigated.

### Apparatus

The apparatus consists of a plasticating extruder (Killion, 1-in. diameter, length-to-diameter ratio 24), a high-pressure diaphragm-type metering pump

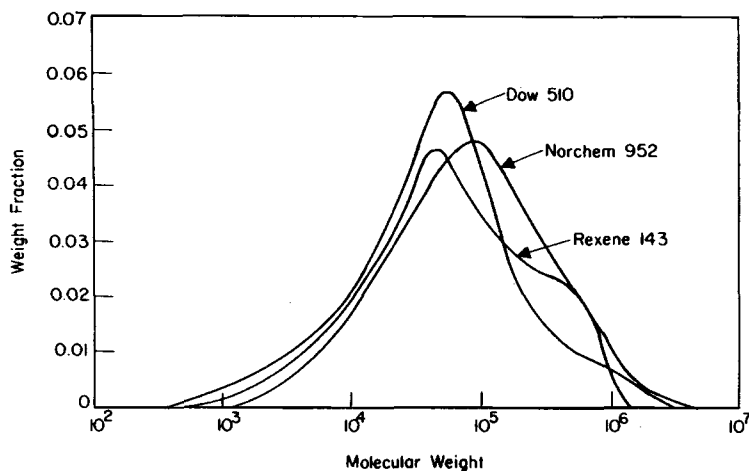


Fig. 1. Molecular weight distribution curves of three low-density polyethylenes: (a) Rexene PE 143; (b) Dow PE510; (c) Norchem PE952.

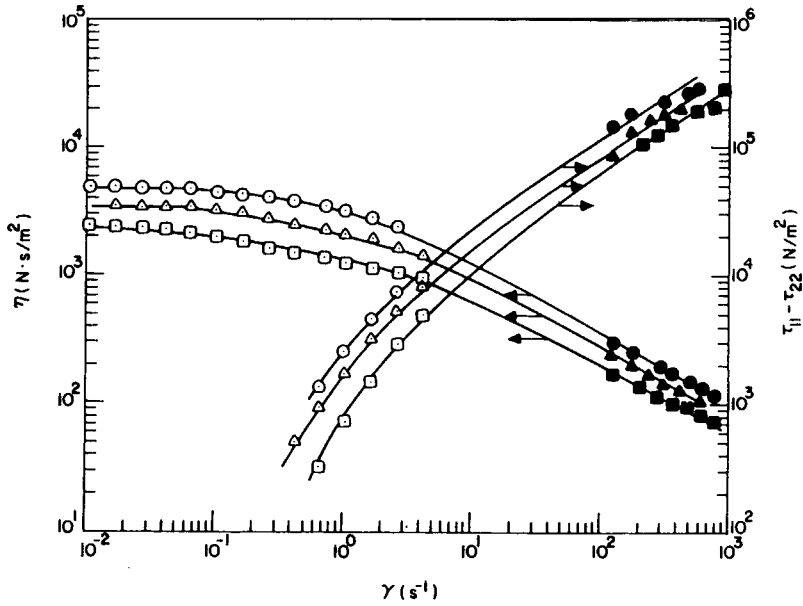


Fig. 2. Rheological properties of Rexene PE143 at various temperatures ( $^{\circ}\text{C}$ ): ( $\odot$ ,  $\bullet$ ) 180; ( $\triangle$ ,  $\blacktriangle$ ) 200; ( $\square$ ,  $\blacksquare$ ) 220. Open symbols denote the cone-and-plate rheometer data, and closed symbols denote the capillary rheometer data.

for the injection of blowing agent (discharge pressure 3,000 psi), two static mixers (Kenics Corp., 2.54 cm in diameter and eight motionless mixing elements) connected in series, a capillary die, and a pressure measuring device. A schematic layout of the process line is shown in Figure 5. The motionless mixers, as shown

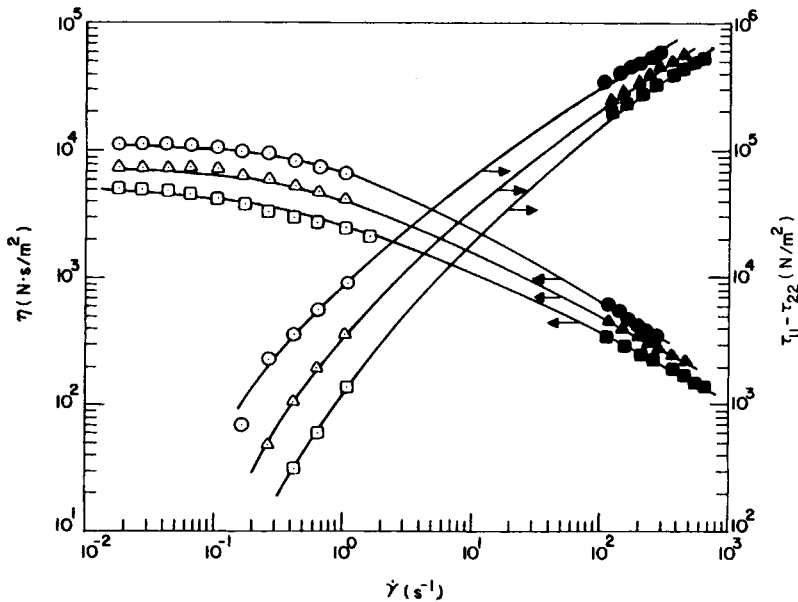


Fig. 3. Rheological properties of Dow PE510 at various temperatures. Symbols are the same as in Figure 2.

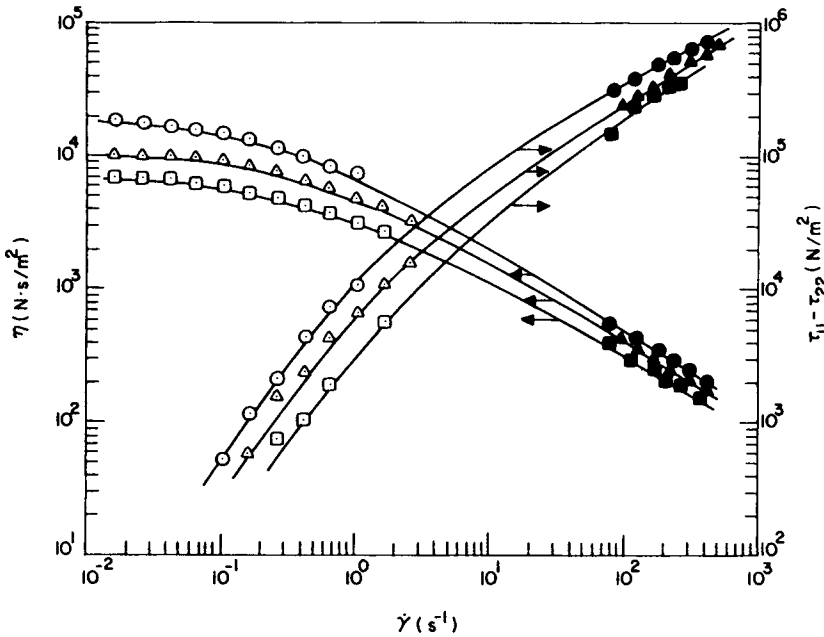


Fig. 4. Rheological properties of Norchem PE952 at various temperatures. Symbols are the same as in Figure 2.

in Figure 5, are placed between the extruder and the capillary die, in order to cool the mixture of molten polymer and blowing agent and to achieve a uniform melt temperature. In order to control the melt temperature in the static mixers, two hot-oil heat exchangers (Berg Industrial Co., Model BTU 10T-610-GO) were employed, one for each static mixer. The heat exchangers can cool, as well as heat, and are equipped with a proportional temperature controller.

The static mixer unit was inserted inside a large cylindrical chamber, so that the hot heat-transfer oil could be pumped through the annular space formed by the static mixer unit and the cylindrical chamber. The temperature of the heat-transfer oil was measured at the discharge end of the cylindrical chamber. The temperature and pressure of the melt stream were measured at the entrance of the first static mixer and at the end of the second.

It is essential to maintain a constant flow rate of blowing agent. For this, we

TABLE II  
Summary of the Ranges of Processing Variables Investigated

Blowing agent	Concentration (wt %)	Temp (°C)
(a) <i>Rexene 143</i>		
FC-12	10; 15; 20	110; 120; 140
FC-114	10; 15; 20	110; 120; 140
FC-12/FC-114	10; 15; 20	110; 120; 140
(b) <i>Dow PE510</i>		
FC-12	10; 15; 20	140; 150; 160
FC-114	10; 15; 20	120; 140; 160
(c) <i>Norchem PE952</i>		
FC-12	5; 10; 15; 20	130; 140; 150
FC-114	10; 15; 20	140; 150; 160

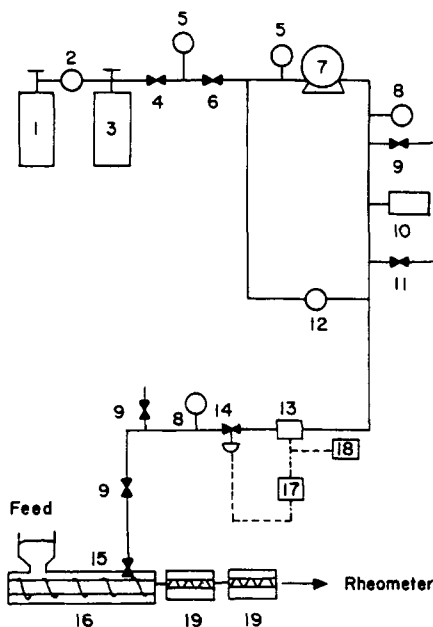


Fig. 5. Schematic of the process line: (1) nitrogen tank; (2) pressure regulator; (3) volatile liquid tank; (4) ball valve; (5) pressure gauge; (6) filter; (7) diaphragm pump; (8) pressure gauge; (9) bleed valve; (10) accumulator; (11) adjustable relief valve; (12) back pressure regulator; (13) flow meter; (14) control valve; (15) check valve; (16) screw extruder; (17) pneumatic controller; (18) pneumatic recorder; (19) static mixer with hot-oil temperature control unit. (—) Fluid, (---) pneumatic line.

used a flow control loop that monitors the flow rate of blowing agent and compares it to a set value. Any deviation sends a signal to a flow control valve that controls the flow at the set value. The accumulator in the system dampens any surge from the pump. The system maintains a constant flow rate regardless of suction pressure, pump and extruder pulsations, or back pressure.

The performance of the process was checked by continuously recording the die pressure, and the flow rate of blowing agent. The injection pressure of the blowing agent (1,000 ~ 2,000 psi) was also recorded and provided an indication of how uniform the feed of the extruder was.

### Experimental Procedure

Both the extruder (for resin) and pump (for blowing agent) were calibrated for each material before mixtures of resin and blowing agent were fed into the extrusion die. As the extruder speed was increased, the flow rate of blowing agent had to be increased accordingly in order to maintain the blowing agent concentration at its preset value.

A mixture of molten polymer and blowing agent was fed into the capillary die, in which melt pressure transducers were mounted along the longitudinal axis. On the basis of earlier investigations by Han,<sup>1,9</sup> measurements of axial pressure distributions permit us to determine the viscosities of mixtures of molten polymer

and blowing agent, as long as the pressure profiles are linear inside the die. The capillary die employed in this study has a length-to-diameter ( $L/D$ ) ratio of 20 ( $D = 3.175$  mm) and a reservoir-to-capillary diameter ( $D_R/D$ ) ratio of 16. The details of the design of the rheometer and its operating procedures are described in earlier publications by Han.<sup>9,10</sup> A commercial version of this rheometer is available from Seiscor Division, Seismograph Service Corp., Tulsa, Oklahoma.

In carrying out our experiments, melt temperature and flow rate were chosen such that a plot of the wall normal stresses along the die axis formed a straight line, ensuring that the viscosity of the molten polymer-blowing agent mixtures could be determined from the following expressions<sup>1,9</sup>:

$$\eta = \tau_w / \dot{\gamma} \quad (1)$$

in which

$$\tau_w = \left( -\frac{\partial p}{\partial z} \right) \frac{R}{2} \quad (2)$$

$$\dot{\gamma} = \left( \frac{3n+1}{4n} \right) \left( \frac{4Q}{\pi R^3} \right) \quad (3)$$

where  $-\partial p/\partial z$  is the pressure gradient,  $Q$  is the volumetric flow rate of the polymer-blowing agent mixture,  $R$  is the radius of the capillary, and  $n$  is a power-law index.

It should be emphasized that the method of viscosity measurement employed is valid as long as the pressure gradient ( $-\partial p/\partial z$ ) is constant.

## RESULTS

Figure 6 gives plots of wall normal stress profile along the die axis (commonly referred to as pressure profile) for Dow PE510 at 200°C. It is seen that the pressure profile is linear over the entire distance where the wall normal stress measurements were taken. However, as may be seen in Figure 7, when a mixture of Dow PE510 and FC-114 was extruded through the same die, the pressure profile is linear only over the distance where the first three pressure transducers are located. The last pressure transducer gives a pressure measurement that deviates from the linear pressure profile, indicating that the phase separation of the FC-114 begins as the liquid mixture approaches the die exit.

Where exactly the formation of gas bubbles occurs inside the die depends on the pressure and temperature (thus, the solubility of the blowing agent in the molten polymer), the blowing agent concentration, and the type (i.e., molecular structure) of blowing agent. Therefore, for a given combination of resin and blowing agent, there must exist a critical value of pressure at which the formation of gas bubbles begins, i.e., a critical pressure for bubble nucleation. In reference to Figure 7, if the extrusion rate were increased considerably, to the extent that the wall normal stress at the die exit plane (commonly referred to as "exit pressure," although it is a misnomer) exceeded the critical pressure for bubble nucleation, one would have obtained linear pressure profiles throughout the capillary die, including the exit plane. For the practical reason that our equipment could not be operated at sufficiently high pressures, we were not able to obtain

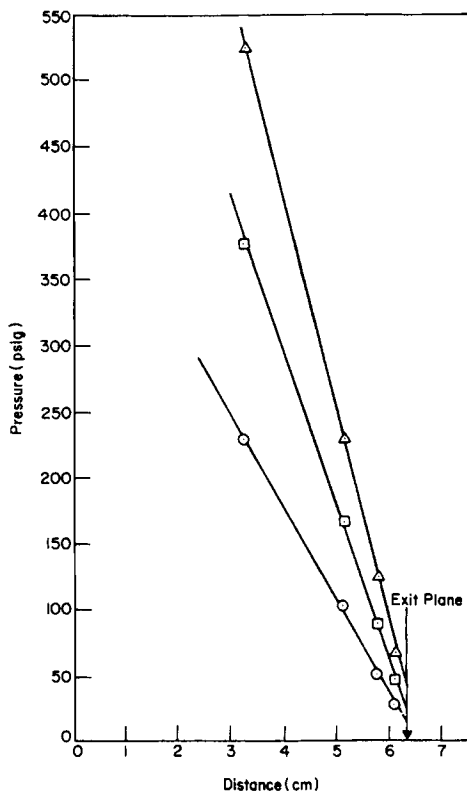


Fig. 6. Pressure profiles of Dow PE510 ( $T = 200^\circ\text{C}$ ) along the capillary die at various shear rates ( $\text{s}^{-1}$ ): (○) 57; (◻) 146; (◻) 359.

linear pressure profiles over the entire die length. If the critical pressure for bubble nucleation is very high, say above 500 psi, it will practically be impossible to prevent the nucleation of gas bubbles inside the die.

Therefore, in the use of a capillary (or slit) rheometer, it is essential to check the linearity of pressure profiles first, before one proceeds to determine the viscosities of mixtures of molten polymer and blowing agent. In the results presented below, we have checked the linearity of the pressure profiles of all experimental runs, and have used *only* the linear portion of the pressure profile in determining the viscosities. This implies that our results are valid only for the situation where the fluorocarbon blowing agent is dissolved completely in the molten polymer.

Figure 8 gives plots of viscosity ( $\bar{\eta}$ ) vs. shear rate ( $\dot{\gamma}$ ) for mixtures of Rexene PE143 and FC-114, demonstrating the effect of temperature on the viscosities of the mixtures at a given blowing agent concentration. Figure 9 gives the effect of melt temperature on the viscosities of mixtures of Rexene PE143 with FC-12, FC-114, and FC-12/FC-114 blend (50/50 by weight). Figure 10 gives the effect of melt temperature on the viscosities of mixtures of Dow PE510 with FC-12 and FC-114. Figure 11 gives the effect of melt temperature on the viscosities of mixtures of Norchem PE952 with FC-12 and FC-114. Two things are worth noting in Figures 8–11. First, in all the combinations of molten polymer and



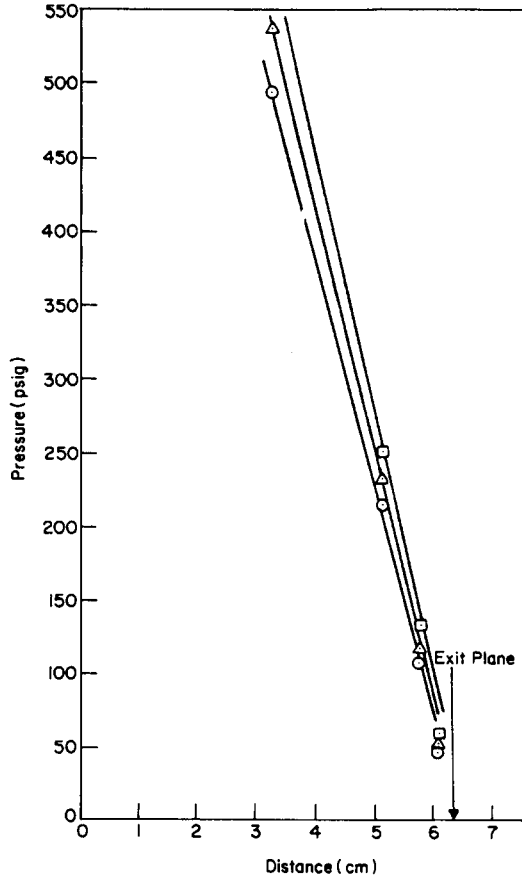


Fig. 7. Pressure profiles of a mixture of Dow PE510 and FC-114 (10 wt %) ( $T = 140^{\circ}\text{C}$ ) at various shear rates ( $\text{s}^{-1}$ ): (○) 112; (△) 134; (□) 154.

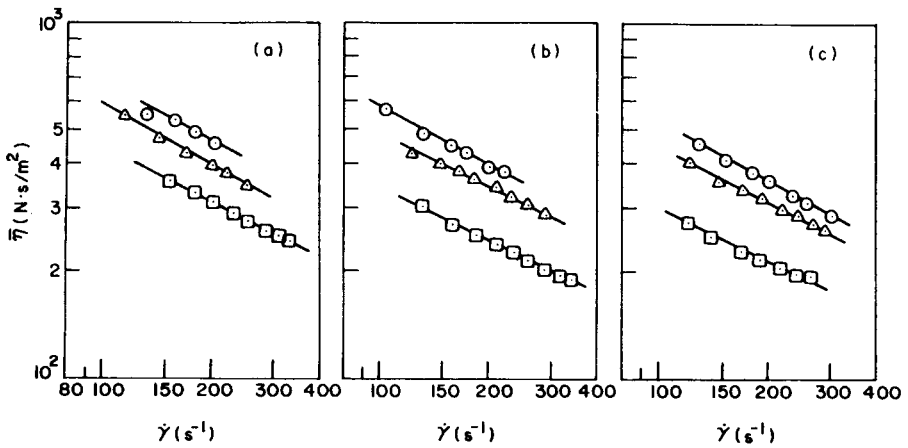


Fig. 8. Viscosity vs. shear rate for mixtures of Rexene PE143 and FC-114: (a) 10 wt % FC-114; (b) 15 wt % FC-114; (c) 20 wt % FC-114. (○)  $110^{\circ}\text{C}$ ; (△)  $120^{\circ}\text{C}$ ; (□)  $140^{\circ}\text{C}$ .

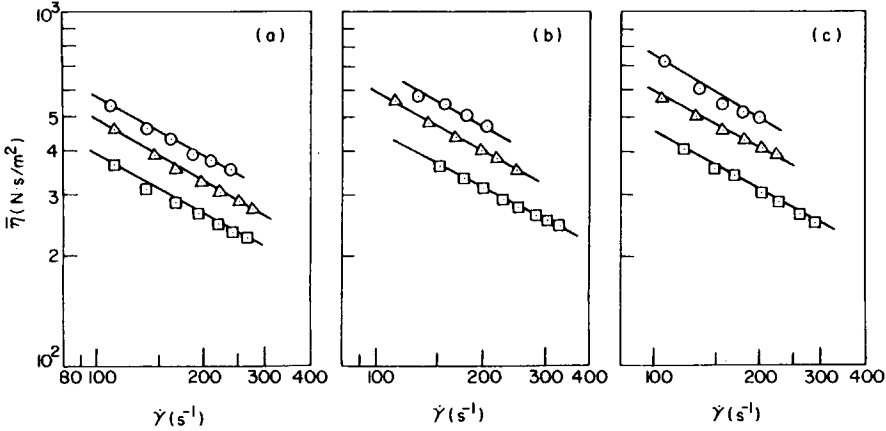


Fig. 9. Viscosity vs. shear rate for mixtures of Rexene PE143 and fluorocarbon blowing agent: (a) 10 wt % FC-12; (b) 10 wt % FC-114; (c) 10 wt % FC-12/FC-114 blend (50/50 by weight). (○) 110°C; (△) 120°C; (□) 140°C.

blowing agent used, the viscosity increases as the temperature decreases. Second, the type of fluorocarbon blowing agent greatly influences the viscosity.

Figure 12 gives plots of  $\bar{\eta}$  vs.  $\dot{\gamma}$  for the mixtures of Rexene PE143 and FC-114, demonstrating the effect of blowing agent concentration on the viscosities of the mixtures at a fixed melt temperature. Figures 13–15 gives the effects of blowing agent concentration and the type of fluorocarbon blowing agent on the viscosities of the mixtures of Rexene PE143 and FC-12 (or FC-114), mixtures of Dow PE510 and FC-12 (or FC-114), and mixtures of Norchem PE952 and FC-12 (or FC-114). It is clearly seen that in all cases the viscosity decreases as the concentration of blowing agent increases and that the type of blowing agent greatly influences the viscosity.

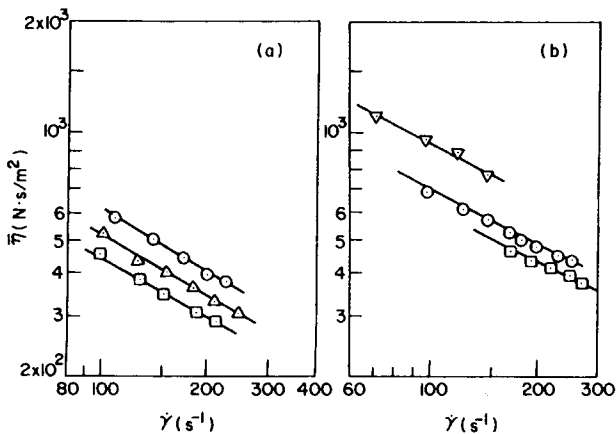


Fig. 10. Viscosity vs. shear rate for mixtures of Dow PE510 and fluorocarbon blowing agent: (a) 10 wt % FC-12; (b) 10 wt % FC-114. (▽) 120°C; (○) 140°C; (△) 150°C; (□) 160°C.

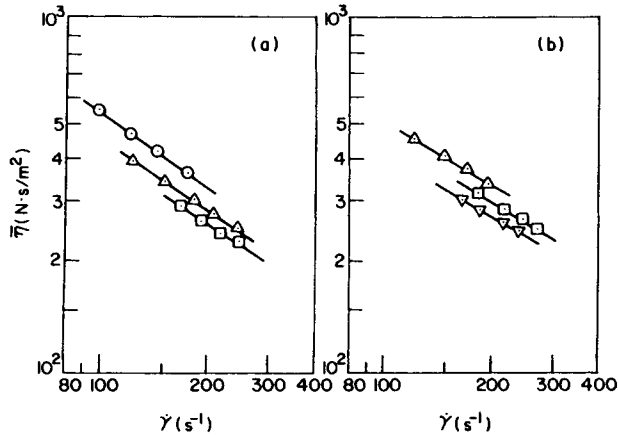


Fig. 11. Viscosity vs. shear rate for mixtures of Norchem PE952 and fluorocarbon blowing agent: (a) 10 wt % FC-12; (b) 10 wt % FC-114. (○) 130°C; (△) 140°C; (□) 150°C; (▽) 160°C.

## DISCUSSION

### The Effect of Temperature on Viscosity

As long as a blowing agent remains dissolved in a molten polymer over the range of temperatures studied, an increase in temperature decreases the viscosity of the mixture, as may be seen in Figures 8–11. However, the solubility of a blowing agent in a molten polymer depends on the pressure and temperature. As the temperature is increased, the solubility of fluorocarbon blowing agents

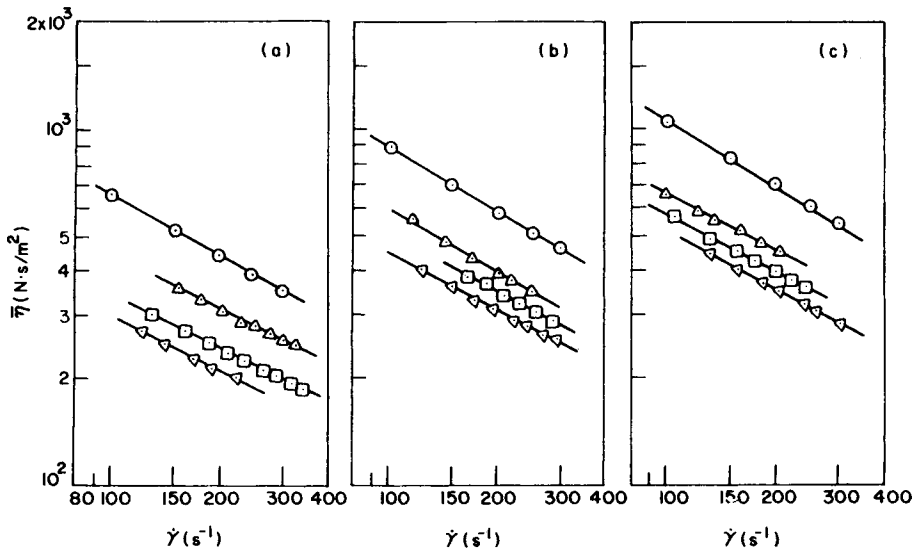


Fig. 12. Viscosity versus shear rate for mixtures of Rexene PE143 and FC-114: (a)  $T = 140^{\circ}\text{C}$ ; (b)  $T = 120^{\circ}\text{C}$ ; (c)  $T = 110^{\circ}\text{C}$ . (○) Virgin resin; (△) 10 wt % FC-114; (□) 15 wt % FC-114; (▽) 20 wt % FC-114.

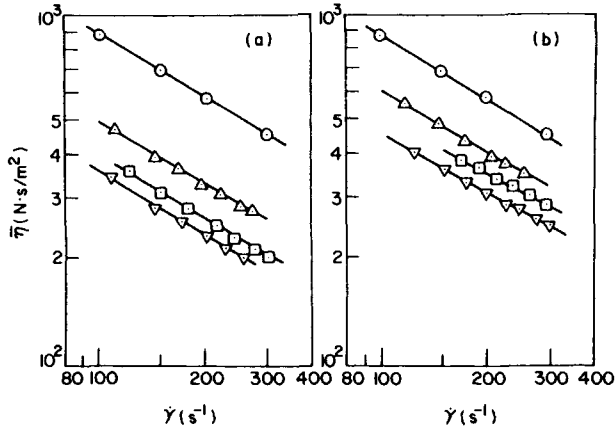


Fig. 13. Viscosity vs. shear rate for mixtures of Rexene PE143 and fluorocarbon blowing agent ( $T = 120^{\circ}\text{C}$ ): (a) FC-12; (b) FC-114. (○) Virgin resin; (Δ) 10 wt % FC; (◻) 15 wt % FC; (∇) 20 wt % FC.

will decrease and hence the blowing agent, once dissolved, tends to form a separate phase (i.e., forms gas bubbles) unless a higher pressure is exerted on the mixture. Since all the viscosity data presented above were obtained in the range of pressure readings that gave linear pressure profiles, it is safe to assume that, over the range of temperatures we employed, the mixtures of molten polymer and blowing agent formed homogeneous solutions.

From the point of view of foam extrusion, it is desirable to prevent the formation of gas bubbles in the die. The most effective method for achieving it is to choose a melt temperature at the extrusion die as low as possible. In doing so, one increases the solubility of blowing agent in the melt. On the other hand, there is a practical difficulty that limits how low a melt temperature we can use, because, as the temperature decreases, the viscosity increases and consequently increases the pressure drops in the die, as well as in the extruder, forcing one to

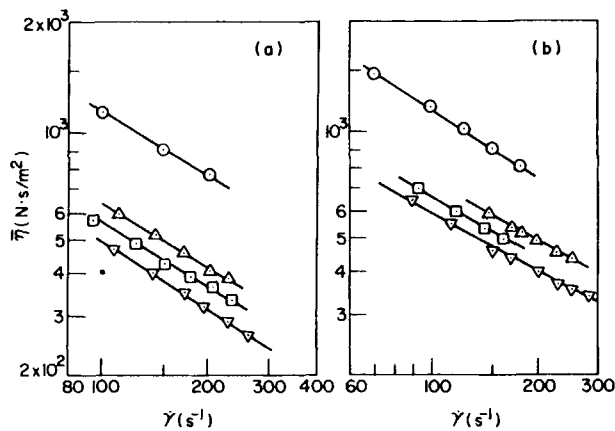


Fig. 14. Viscosity vs. shear rate for mixtures of Dow PE510 and fluorocarbon blowing agent ( $T = 140^{\circ}\text{C}$ ): (a) FC-12; (b) FC-114. (○) Virgin resin; (Δ) 10 wt % FC; (◻) 15 wt % FC; (∇) 20 wt % FC.

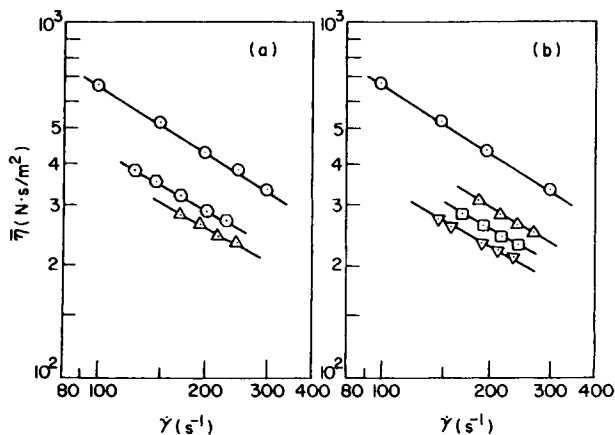


Fig. 15. Viscosity vs. shear rate for mixtures of Norchem PE952 and fluorocarbon blowing agent ( $T = 150^{\circ}\text{C}$ ): (a) FC-12; (b) FC-114. (○) Virgin resin; (⊙) 5 wt % FC; (Δ) 10 wt % FC; (◻) 15 wt % FC; (▽) 20 wt % FC.

reduce the throughput rate. In order to overcome this difficulty, one is tempted to increase the amount of blowing agent since an increase in blowing agent concentration decreases the viscosity of the mixture, as may be seen in Figures 12–15. However, as the amount of blowing agent is increased, there is a greater chance for the formation of gas bubbles, unless either a higher pressure is exerted on the mixture or the temperature is decreased further. Therefore, one must find an optimal processing condition in terms of temperature, pressure, and blowing agent concentration in order to achieve a successful foam extrusion operation.

It is worth mentioning that the molecular parameters of resins also dictate optimal extrusion conditions. When a resin is too viscous, the buildup of pressure in the processing equipment is so great that one cannot choose a die temperature as low as one would like. This was the reason why, in our study, the lowest melt temperature chosen for Dow PE510 and Norchem PE952 was  $140^{\circ}\text{C}$ , whereas we could bring the melt temperature down to  $110^{\circ}\text{C}$  with Rexene PE143 (see Figures 9–11). Figures 2–4 show the differences in melt viscosities of the three resins, Rexen PE143, Dow PE510, and Norchem PE952. It should be pointed out that we had a rather small extruder (25 mm in diameter), large pressure drops (about 1,000 psi) across the two static mixers, and large pressure drops in the die (about 1,000 psi). If we had either a large extruder that would have generated greater pressures at the extruder outlet or had two extruders in tandem, we are certain that we could have operated the die temperature as low as  $110^{\circ}\text{C}$  with Dow PE510 and Norchem PE952 also.

### The Effects of Type and Concentration of Blowing Agent on Viscosity

The decrease in the viscosity of molten polymer as the concentration of blowing agent was increased, seen in Figures 12–15, may be interpreted as caused by the blowing agent solubilizing (or plasticizing) the polyethylene molecules under the extrusion conditions. This interpretation, of course, assumes that the blowing agent is dissolved and distributed uniformly in the molten polymer. The extent to which a blowing agent reduces the viscosity of a molten polymer de-

depends on the molecular structure of the blowing agent, which in turn determines its solubility.

A close examination of Figures 9–11 and Figures 13–15 reveals that FC-12 reduces the viscosity more than does FC-114. This appears to imply that the solubility of FC-12 in low-density polyethylene melt is greater than that of FC-114. We are of the opinion that, once fluorocarbon blowing agents are dissolved in a molten polymer, the size of the fluorocarbon molecules may play an important role in plasticizing the large polymer molecules in the molten state under high pressure.

### Viscosity Reduction Factor

What would be of practical interest is to obtain a correlation between the extent of viscosity reduction and the concentration of blowing agent. For this, let us define the viscosity reduction factor (VRF) by

$$\text{VRF} = \frac{\text{viscosity of the mixture of molten polyethylene and blowing agent}}{\text{viscosity of the molten polyethylene}} \quad (4)$$

Using the viscosity data presented above, we have calculated VRF at various shear rates at a fixed melt temperature, for the various combinations of resin and blowing agent used in our experiments. Table III gives a summary of our calculations. The following observations may be made on Table III: (1) at a given blowing agent concentration, the value of VRF may be considered to be independent of shear rate and temperature; (2) for a given combination of resin and blowing agent, the value of VRF decreases as the blowing agent concentration increases; (3) the value of VRF varies with the molecular structure of blowing agent used; (4) the value of VRF is *little* sensitive to the grades of resin, i.e., their molecular weight and molecular weight distribution.

On the basis of the observations made above, we have calculated the average values of VRF at various blowing agent concentrations and for the different types of fluorocarbon blowing agent, and they are given in Table IV. Note that the values of VRF given in Table IV are independent of shear rate, temperature, and the molecular weights of the low-density polyethylenes used. In order to facilitate our discussion, Figure 16 gives plots of VRF vs. blowing agent concentration for different types of fluorocarbon blowing agent. The usefulness of Figure 16 (or Table IV) is that one can now predict the viscosities  $\bar{\eta}(\dot{\gamma}, T)$  of mixtures of low-density polyethylene and fluorocarbon (FC) blowing agent, using the following expression [see eq. (4)]:

$$\bar{\eta}(\dot{\gamma}, T) / \eta(\dot{\gamma}, T) = \text{VRF}(\text{FC concn; type of FC}) \quad (5)$$

or

$$\bar{\eta}(\dot{\gamma}, T) = \eta(\dot{\gamma}, T) \text{VRF}(\text{FC concn; type of FC}) \quad (6)$$

with information on the viscosities  $\eta(\dot{\gamma}, T)$  of virgin resin alone, at desired shear rates and temperatures. Such an experimental observation (i.e., Fig. 16) has practical significance, because one now does not have to take viscosity measurements of mixtures of low-density polyethylene and fluorocarbon blowing

TABLE III  
Summary of the Viscosity Reduction Factor Calculated for Various Combinations of  
Polyethylene and Fluorocarbon Blowing Agent

Shear rate (s <sup>-1</sup> )	FC concentration (wt %)		
	10	15	20
<i>(a) Rexene 143/FC-12 at 120°C</i>			
100	0.568	0.455	0.400
200	0.569	0.448	0.396
300	0.566	0.455	0.404
<i>(b) Rexene 143/FC-12 at 110°C</i>			
100	0.568	—	—
200	0.557	—	—
300	0.559	—	—
<i>(c) Rexene 143/FC-12 at 140°C</i>			
100	0.582	—	—
200	0.577	—	—
300	0.569	—	—
<i>(d) Rexene 143/FC-114 at 110°C</i>			
100	0.682	0.552	0.500
200	0.693	0.550	0.507
300	0.688	0.566	0.528
<i>(e) Rexene 143/FC-114 at 120°C</i>			
100	0.701	0.607	0.501
200	0.689	0.620	0.521
300	0.703	0.613	0.520
<i>(f) Rexene 143/FC-114 at 140°C</i>			
100	0.723	0.553	0.461
200	0.716	0.568	0.466
300	0.728	0.571	0.471
<i>(g) Dow PE510/FC-12 at 140°C</i>			
100	0.553	0.480	0.420
200	0.554	0.486	0.418
300	0.551	0.491	0.413
<i>(h) Dow PE510/FC-12 at 150°C</i>			
100	0.547	—	—
200	0.548	—	—
300	0.546	—	—
<i>(i) Dow PE510/FC-114 at 140°C</i>			
100	0.672	0.580	0.504
200	0.690	0.610	0.540
300	0.684	0.614	0.552
<i>(j) Norchem PE952/FC-12 at 130°C</i>			
100	0.600	0.500	0.433
150	0.578	0.500	0.422
250	0.580	0.500	0.430
<i>(k) Norchem PE952/FC-12 at 140°C</i>			
100	0.587	0.512	0.448
150	0.573	0.504	0.448
250	0.581	0.512	0.441
<i>(l) Norchem PE952/FC-114 at 150°C</i>			
125	0.694	0.593	0.525
200	0.693	0.602	0.522
300	0.691	0.602	0.529
<i>(m) Norchem PE952/FC-114 at 140°C</i>			
125	0.681	—	0.500
200	0.673	—	0.510
300	0.684	—	0.513

TABLE IV  
Average Value of the Viscosity Reduction Factor for Mixtures of Polyethylene and FC-12 and  
Mixtures of Polyethylene and FC-114

FC concn (wt %)	VRF ( $\bar{\eta}/\eta$ )
(a) FC-12	
10	0.567
15	0.487
20	0.423
(b) FC-114	
10	0.694
15	0.587
20	0.510

agent, as long as the viscosity information is available for the particular low-density polyethylene that one is interested in using.

### Entrance Pressure Drops

In the flow of mixtures of molten polymer and blowing agent, as pointed out above in reference to Figure 7, the extrapolation of wall normal stresses to the exit plane has *no* rheological significance when the pressure profile begins to *deviate* from linearity somewhere in the die. One may then raise the question of how one might find out the effect of a blowing agent on the elastic properties of a polymer melt, when completely dissolved in it. Such a question is very reasonable because we already have discussed above that fluorocarbon blowing agents reduce the viscosities of polyethylene melts.

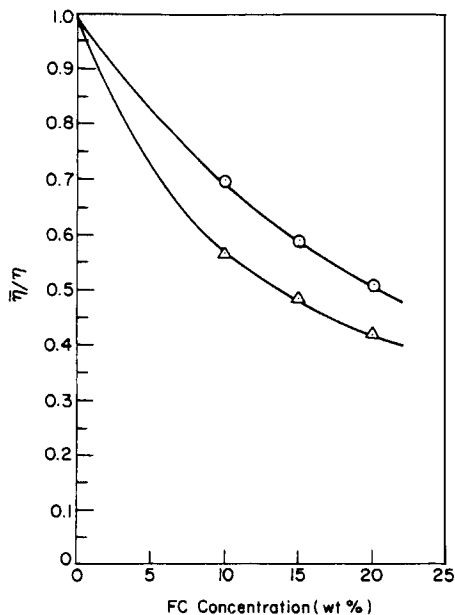


Fig. 16. Viscosity reduction factor vs. fluorocarbon blowing agent concentration: (○) FC-114; (△) FC-12.



In the past, much has been discussed about entrance pressure drops as a means of understanding the elastic nature of viscoelastic fluids.<sup>1,11-15</sup> In a recent paper, Han<sup>16</sup> has pointed out that, in dealing with multiphase polymeric systems (e.g., polymers containing particulates, heterogeneous polymer blends, polymers containing gas bubbles), an interpretation of entrance pressure drops becomes quite complex. This is because the state of dispersion (e.g., the orientation and shape of the discrete phase) keeps changing in the entrance region as a multiphase fluid enters the die entrance from a larger reservoir. Han<sup>16</sup> has therefore warned that the entrance pressure drops obtained in the flow of multiphase polymeric systems must *not* be used in determining the *elastic* effects of such fluids.

Figure 17 gives typical pressure profiles in the flow of a mixture of Rexene PE143 and FC-114 at 110°C. From such pressure profiles one can determine the entrance pressure drop.<sup>1</sup> Figure 18 gives plots of entrance pressure drop  $\Delta P_{\text{Ent}}$  vs. shear rate  $\dot{\gamma}$  for mixtures of Rexene PE143 and FC-114 at three different temperatures (110°C, 120°C, 140°C) and at different levels of FC-114 concentration. It is seen in Figure 18 that, at a given value of  $\dot{\gamma}$ ,  $\Delta P_{\text{Ent}}$  decreases

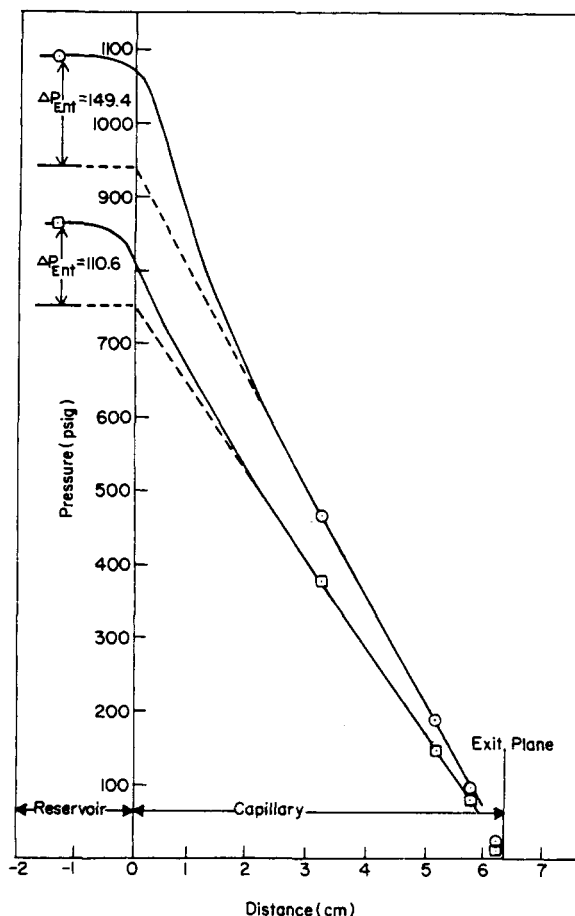


Fig. 17. Pressure profiles of a mixture ( $T = 110^\circ\text{C}$ ) of Rexene PE143 and FC-114 (20 wt %): (○)  $\dot{\gamma} = 260.3 \text{ s}^{-1}$ ; (◻)  $\dot{\gamma} = 156.8 \text{ s}^{-1}$ .

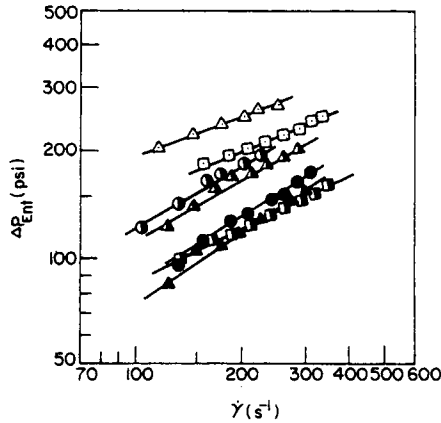


Fig. 18. Entrance pressure drop vs. shear rate for mixtures of Rexene PE143 and FC-114: ( $\Delta$ )  $T = 120^\circ\text{C}$ , 10 wt % FC; ( $\square$ )  $T = 140^\circ\text{C}$ , 10 wt % FC; ( $\bullet$ )  $T = 110^\circ\text{C}$ , 15 wt % FC; ( $\blacktriangle$ )  $T = 120^\circ\text{C}$ , 15 wt % FC; ( $\blacksquare$ )  $T = 140^\circ\text{C}$ , 15 wt % FC; ( $\bullet$ )  $T = 110^\circ\text{C}$ , 20 wt % FC; ( $\blacktriangle$ )  $T = 120^\circ\text{C}$ , 20 wt % FC.

as temperature increases and, also, as FC-114 concentration increases. However, when  $\Delta P_{\text{Ent}}$  is plotted against shear stress  $\tau_w$ , one obtains a correlation that becomes independent of temperature, as may be seen in Figure 19.

The correlation shown in Figure 19 has important rheological implications. First, it is safe to assume that no foaming occurred in the entrance region, because if foaming occurred one would not expect to obtain such a correlation. Moreover, from the information on the solubility of FC-114 in polyethylene, the phase separation of FC-114 from the mixture of Rexene PE143 and FC-114 is most unlikely to occur at the pressure (above 600 psi) that existed in the entrance region (see Fig. 17). In other words, the correlation given in Figure 19 represents a truly homogeneous, single-phase system. Second, the values of  $\Delta P_{\text{Ent}}$  given in Figure 19 may be interpreted as representing the elastic behavior of the mixtures, because the correlation between  $\Delta P_{\text{Ent}}$  vs.  $\tau_w$  is independent of temperature. This interpretation is based on the experimental observation that, with few exceptions so far, the elastic parameters, such as normal stress difference,

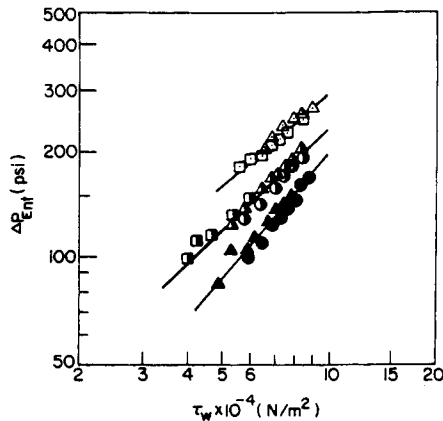


Fig. 19. Entrance pressure drop vs. shear stress for mixtures of Rexene PE143 and FC-114. Symbols are the same as in Figure 18.

extrudate swell ratio, exit pressure, recoverable shear strain, and steady-state shear compliance, give rise to correlations that become independent of temperature when they are plotted against *shear stress*, instead of against shear rate.<sup>1,2</sup>

It can then be concluded from Figure 19 that, as the concentration of fluorocarbon blowing agent FC-114 is increased, the elastic property of the mixture of Rexene PE143 and FC-114 is decreased.

### CONCLUDING REMARKS

In this paper we have demonstrated the usefulness of the capillary/slit rheometer in determining the rheological properties of mixtures of fluorocarbon blowing agent and molten low-density polyethylene. The same experimental technique should be applicable to other types of thermoplastic resins as well. Although useful in determining the rheological properties of homopolymers at *low* shear rates, the rotational-type of rheometer (e.g., the Rheometrics Mechanical Spectrometer; the Weissenberg rheogoniometer) is *not* capable of handling fluid systems containing volatile solvents or gaseous components, because such a rheological instrument, being an *open* system, cannot prevent the escape of the physical blowing agent or the volatile solvent from the mixture at high temperature (say,  $T > 100^{\circ}\text{C}$ ). It is then clear that only a *closed* system (i.e., a capillary-type instrument) is suitable.

We have obtained a correlation between the extent of viscosity reduction (referred to as viscosity reduction factor, VRF) and blowing agent concentration. For low-density polyethylene resins, such a correlation is found to be independent of (or only slightly sensitive to) shear rate, temperature, and molecular weight, and dependent only upon the type of blowing agent employed. We have suggested how such a correlation may be used in predicting the viscosities of mixtures of fluorocarbon blowing agent and low-density polyethylene, when one wishes to use low-density polyethylenes other than those employed in our study.

We have shown, also, that the entrance pressure drop obtained in the *absence* of phase separation in the entrance region may be used as a measure of the elastic properties of mixtures of fluorocarbon blowing agent and low-density polyethylene resin.

So far, no theory has been developed which permits us to predict the viscosities of mixtures of molten polymer and physical blowing agent. Considering the size of polymer molecules, which generally exhibit non-Newtonian behavior, the existing theories<sup>17-19</sup> dealing with the viscosity of Newtonian liquid mixtures are *not* applicable to predicting the viscosities of mixtures of molten polymer and fluorocarbon blowing agent. This seems to be an area of research worth pursuing.

This study was supported in part by the National Science Foundation under Grant CPE-7910171 and the Owens-Illinois Corp., for which the authors are very grateful. We also wish to thank the Allied Chemical Co. for supplying us with the fluorocarbon blowing agents used in the present investigation.

### References

1. C. D. Han, *Rheology in Polymer Processing*, Academic, New York, 1976.
2. C. D. Han, *Multiphase Flow in Polymer Processing*, Academic, New York, 1981.
3. L. L. Blyler and T. K. Kwei, *J. Polym. Sci., Part C*, No. 35, 165 (1976).

4. D. M. Bigg, J. R. Preston, and D. Brenner, *Polym. Eng. Sci.*, **16**, 706 (1976).
5. Y. Oyanagi and J. L. White, *J. Appl. Polym. Sci.*, **23**, 1013 (1979).
6. C. D. Han and C. A. Villamizar, *Polym. Eng. Sci.*, **18**, 687 (1978).
7. C. D. Han, Y. W. Kim, and K. D. Malhorta, *J. Appl. Polym. Sci.*, **20**, 1583 (1976).
8. R. A. Mendelson, *J. Rheol.*, **23**, 545 (1979); **24**, 765 (1980).
9. C. D. Han, *Trans. Soc. Rheol.*, **18**, 163 (1974).
10. C. D. Han, *J. Appl. Polym. Sci.*, **15**, 2567 (1971).
11. E. B. Bagley, *J. Appl. Phys.*, **28**, 624 (1957).
12. W. Philippoff and F. H. Gaskins, *Trans. Soc. Rheol.*, **2**, 263 (1958).
13. H. L. LaNieve and D. C. Bogue, *J. Appl. Polym. Sci.*, **12**, 353 (1968).
14. C. D. Han and M. Charles, *Trans. Soc. Rheol.*, **15**, 37 (1971).
15. T. F. Ballenger and J. L. White, *J. Appl. Polym. Sci.*, **15**, 1989 (1971).
16. C. D. Han, *Polym. Eng. Rev.*, **1**, 363 (1981).
17. L. Grunberg and A. H. Nissan, *Nature (London)*, **164A**, 799 (1949).
18. A. S. Teja and P. Rice, *Ind. Eng. Chem. Fundam.*, **20**, 77 (1981).
19. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, 1977, Chap. 9.

Received August 17, 1982

Accepted October 4, 1982