Rheological Properties of Mixtures of Molten Polymer and Fluorocarbon Blowing Agent. II. Mixtures of Polystyrene and Fluorocarbon Blowing Agent

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Synopsis

The viscosities of mixtures of polystyrene and fluorocarbon blowing agent were determined, using the experimental technique described in Paper I of this series. For the study, three commercial grades of polystyrene were used, together with the following fluorocarbon blowing agents, trichlorofluoromethane (FC-11), dichlorodifluoromethane (FC-12), and blends of FC-11 and FC-12. For each combination of polystyrene and blowing agent, blowing agent concentration and melt temperature were varied. We have found that, for all three polystyrenes used, a single correlation exists between the viscosity reduction factor (VRF) and the blowing agent concentration, in which VRF is defined as the ratio of the viscosity of polystyrene-blowing agent mixture to that of polystyrene homopolymer. The correlation was found to be independent of shear rate and temperature, and dependent upon only the type of fluorocarbon blowing agent. It was suggested that such a correlation be used in predicting the *bulk* viscosity of mixtures of polystyrene and fluorocarbon blowing agent, using information on the viscosity of polystyrene alone.

INTRODUCTION

Polystyrene is the most commonly used thermoplastic resin in producing low-density foam sheet for such usage as food packaging, disposable dinnerware, and insulation boardstock. The polystyrene foam sheet is manufactured by first injecting a physical blowing agent (e.g., fluorocarbons, pentane or hexane) into the polystyrene melt and then extruding the mixture of resin, nucleating agent, and blowing agent in an annular die. Upon exiting the die, the extruded tube is inflated in a manner similar to that in blown film extrusion operation, pulled over a sizing mandrel (usually an air- or water-cooled drum), slit into two sheets, and wound into rolls.[1,2] When the mixture of resin and blowing agent exits from the die lip, foaming occurs due to the expansion of the blowing agent. It is generally recognized that premature foaming in the die must be avoided in order to have foam sheets of good quality.

As in conventional blown film extrusion (or in any extrusion operations), in polystyrene foam extrusion operation one needs to know the viscosity of mixtures of polystyrene melt and blowing agent in order, for instance, to predict the pressure drops inside the die. During the past decade the market for extruded polystyrene foams has grown considerably; however, there is a scarcity of viscosity data, published in the literature, for mixtures of polystyrene melt and physical blowing agent. It is worth mentioning that, due to the greater fire hazard in the use of pentane or hexane, a strong trend seems to have been developed, in recent years, toward the use of fluorocarbons as blowing agents.[3]

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TABLE I
Summary of the Molecular Weights of Polystyrenes Used

Polymer	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
STYRON 678	5.31×10^4	2.29×10^5	4.31
Amoco R2	6.94×10^4	2.83×10^5	4.08
STYRON 685D	9.85×10^4	2.81×10^5	2.85

As part of our continuing effort on developing experimental techniques for determining the viscosities of mixtures of molten polymer and blowing agent, we very recently conducted an experimental study on measurements of viscosities of mixtures of polystyrene melt and fluorocarbon blowing agent.   In this paper we shall present the highlights of our findings.

EXPERIMENTAL

Materials

Three different grades of commercial polystyrene were used.   They are (1) Dow STYRON 678 (Dow Chemical Co.), (2) Amoco R2 (Amoco Chemical Co.), and (3) Dow STYRON 685D (Dow Chemical Co.).   The molecular weights of these resins were determined by the gel permeation chromatograph method (GPC), and they are given in Table I.   Figure 1 gives the molecular weight distribution curves of these resins.

Figures 2–4 give plots of viscosity (η) and first normal stress difference ($\tau_{11} - \tau_{22}$) vs. shear rate ($\dot{\gamma}$) for the three polystyrene resins used.   The rheological properties were determined using the same experimental techniques as that described in Paper I of this series.[4]

As blowing agents, we used the following fluorocarbons: (1) trichlorofluoromethane (FC-11); (2) dichlorodifluoromethane (FC-12); (3) a blend of 50 wt % FC-11 and 50 wt % FC-12.   These fluorocarbon blowing agents were supplied to us by the Allied Chemical Co.
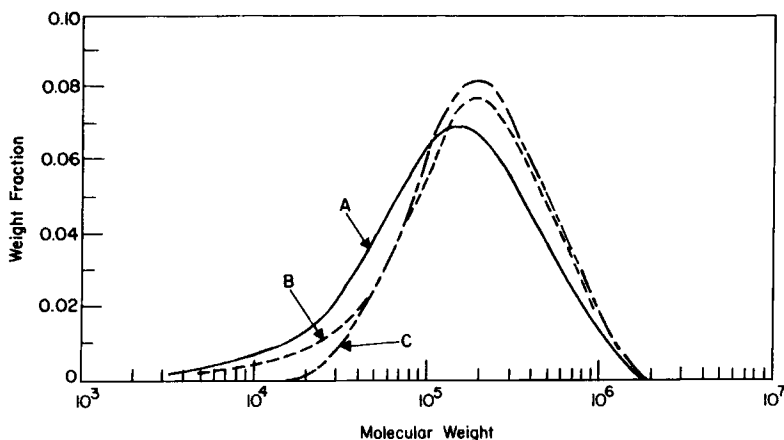

Fig. 1. Molecular weight distribution curves of three polystyrenes: (A) STYRON 678; (B) Amoco R2; (C) STYRON 685D.
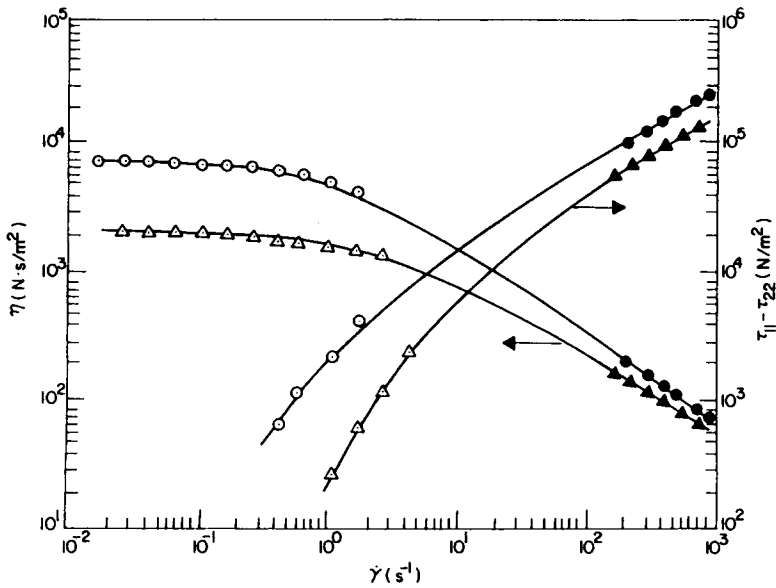
Fig. 2. Rheological properties of STYRON 678 at various temperatures (°C): (○,●) 200; (△,▲) 220.   Open symbols denote the cone-and-plate rheometer data, and closed symbols denote the capillary rheometer data.

Apparatus and Experimental Procedure

The apparatus and experimental procedure employed are the same as that described in Paper I of this series.[4]   In the present study, however, the extrusion melt temperatures chosen were higher than those in the previous study that dealt
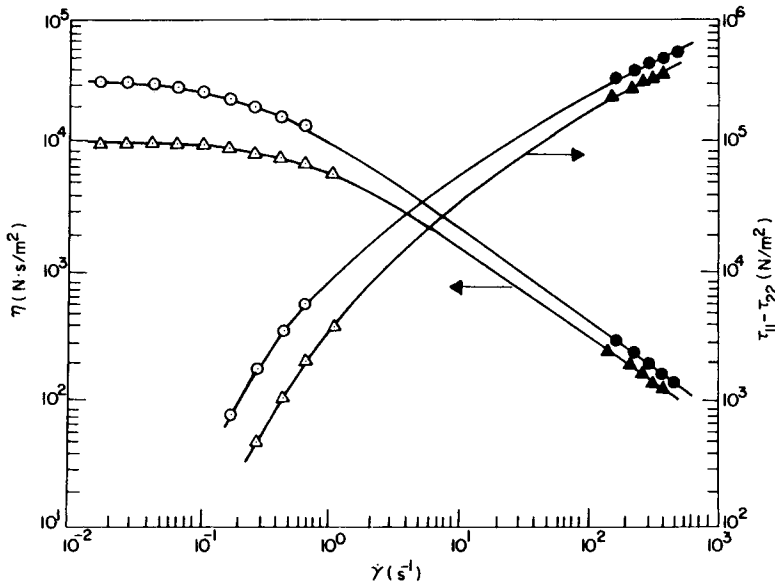
Fig. 3. Rheological properties of Amoco R2 at various melt temperatures.   Symbols are the same as in Figure 2.
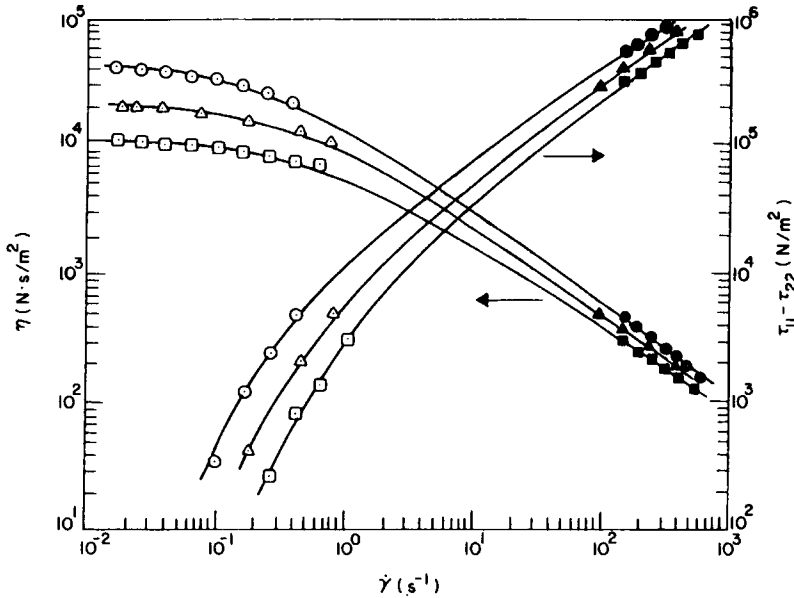
Fig. 4. Rheological properties of STYRON 685D at different temperatures (°C): (⊙,●) 200; (△,▲) 210; (▢,■) 220. Open symbols denote the cone-and-plate rheometer data, and closed symbols denote the capillary rheometer data.

with low-density polyethylene resins.[4]   This was primarily due to the fact that, as the temperature is decreased, the viscosity of polystyrene increases much more rapidly than does the viscosity of low-density polyethylene.   In other words, in order to take pressure measurements along the die axis at three different shear rates at least, the lowest temperatures at which we could take data with our apparatus were: (1) 160°C for both Amoco R2 and STYRON 685D and (2) 140°C for STYRON 678.   Table II gives a summary of the blowing agent concentrations and melt temperatures employed for each polymer.

RESULTS

Figure 5 gives plots of viscosity $\bar{\eta}$ vs. shear rate $\dot{\gamma}$ for mixtures of STYRON 678 and FC-11, STYRON 678 and FC-12, and STYRON 678 and FC-11/FC-12 blend

TABLE II
Summary of the Ranges of Processing Variables Investigated

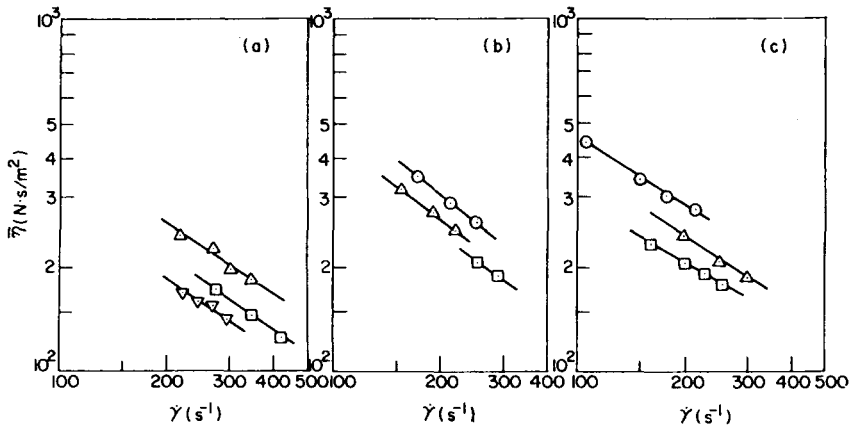| Blowing agent	Concn (wt %)	Temp (°C)
(a) STYRON 678		
FC-11	10; 15	150; 160; 170
FC-12	5; 10; 15	140; 150; 160
FC-11/FC-12	5; 10; 15	140; 150; 160; 170
(b) Amoco R2		
FC-12	10; 15	160; 170
FC-11/FC-12	10; 15	160; 170
(c) STYRON 685D		
FC-12	10; 15	160; 170
FC-11/FC-12	5; 10; 15	160; 170

Fig. 5. Viscosity vs. shear rate for mixtures of STYRON 678 and fluorocarbon blowing agent: (a) 10 wt % FC-11; (b) 10 wt % FC-12; (c) 10 wt % FC-11/FC-12 blend (50/50 by weight). (⊙) 140°C; (△) 150°C; (□) 160°C; (▽) 170°C.

(50/50 by weight) at various temperatures. It is seen in Figure 5 that $\bar{\eta}$ increases as the temperature decreases and that the type of blowing agent greatly influences the viscosity of the mixture. Figure 6 shows the effect of temperature on the viscosity of mixtures of STYRON 678 and FC-11/FC-12, mixtures of Amoco R2 and FC-11/FC-12, and mixtures of STYRON 685D and FC-11/FC-12. It is seen in Figure 6 that in all cases $\bar{\eta}$ increases as the temperature decreases and that the more viscous a polymer is, the greater the viscosity of the mixture (see Figs. 2–4 for the viscosities of the individual resins).

Figure 7 gives plots of $\bar{\eta}$ vs. $\dot{\gamma}$ for mixtures of STYRON 678 and FC-11/FC-12 at different levels of blowing agent concentration. Figures 8–10 give the effects of blowing agent concentration on the viscosities of various combinations of polystyrene and blowing agent. It is seen that $\bar{\eta}$ of the mixture decreases as the concentration of blowing agent increases.
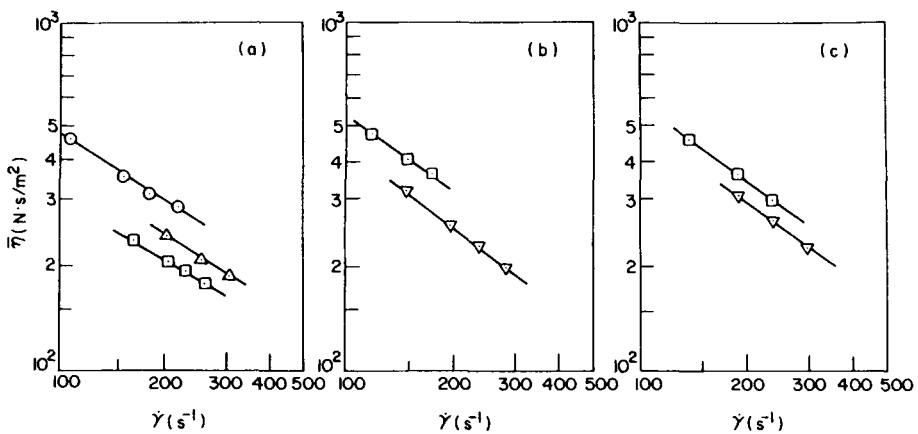

Fig. 6. Viscosity vs. shear rate for: (a) mixtures of STYRON 678 and 10 wt % FC-11/FC-12 blend (50/50 by weight); (b) mixtures of Amoco R2 and 10 wt % FC-11/FC-12 blend (50/50 by weight); (c) mixtures of STYRON 685D and 10 wt % FC-11/FC-12 blend (50/50 by weight). (⊙) 140°C; (△) 150°C; (□) 160°C; (▽) 170°C.
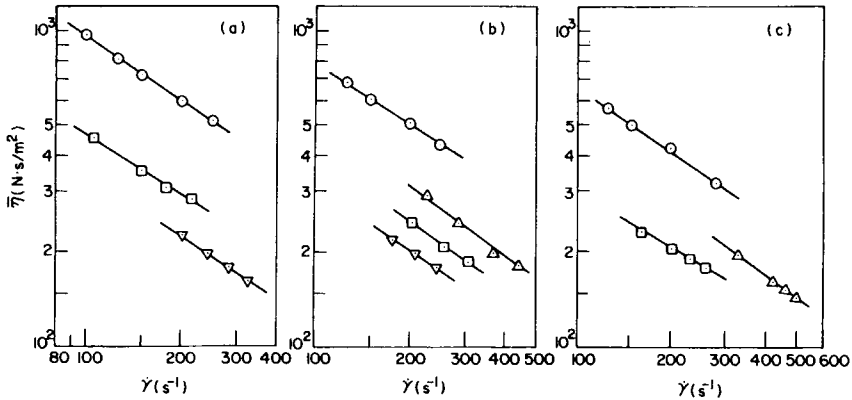
Fig. 7. Viscosity vs. shear rate for mixtures of STYRON 678 and FC-11/FC-12 blend at various temperatures (°C): (a) 140; (b) 150; (c) 160. (⊙) Virgin resin; (▲) 5 wt % FC; (▢) 10 wt % FC; (▽) 15 wt % FC.

DISCUSSION

It is seen in Figure 5 that the viscosities of the mixtures of STYRON 678 and FC-11 are lower than those of the mixtures of STYRON 678 and FC-12. This implies that FC-11 has a greater plasticizing effect on STYRON 678 than does FC-12. Note that FC-11 has a greater solubility in polystyrene than FC-12. It should be pointed out, however, that when a 50 wt % FC-11/50 wt % F-12 blend is mixed with STYRON 678, the viscosity of this mixture was not much different from the viscosity of the mixture of STYRON 678 and FC-11. The same conclusion may be reached for the other polystyrenes employed, Amoco R2 and STYRON 685D, as may be seen in Figures 9 and 10.

From the point of view of foam extrusion, the control of cell size is very important. Since FC-12 has much higher vapor pressure in polystyrene than FC-11, at a constant extrusion rate the formation of a gas bubble will occur more readily
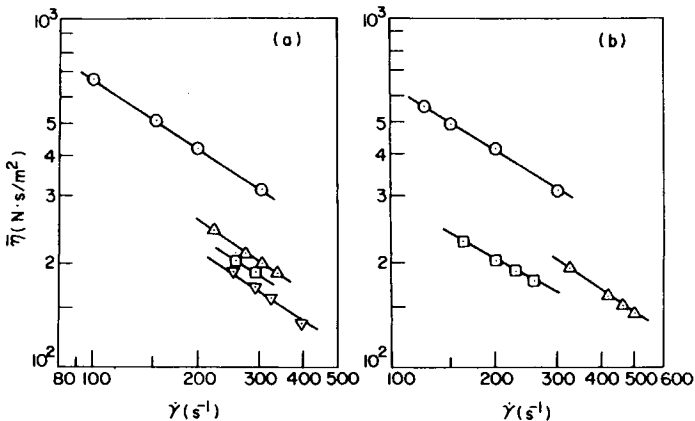

Fig. 8. Viscosity vs. shear rate for: (a) mixtures of STYRON 678 and FC-12 at 160°C; (b) mixtures of STYRON 678 and FC-11/FC-12 blend (50/50 by weight) at 160°C. (⊙) Virgin resin; (▲) 5 wt % FC; (▢) 10 wt % FC; (▽) 15 wt % FC.
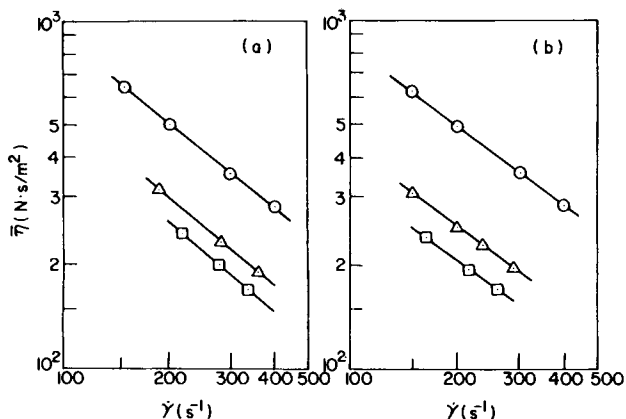
Fig. 9. Viscosity vs. shear rate for: (a) mixtures of Amoco R2 and FC-12 at 170°C; (b) mixtures of Amoco R2 and FC-11/FC-12 blend at 170°C. (⊙) Virgin resin; (△) 10 wt % FC; (□) 15 wt % FC.

with FC-12 than with FC-11. Being more soluble in polystyrene, FC-11 tends to give larger cell sizes than FC-12, because bubbles will grow by the diffusion of dissolved FC-11. Therefore, as a practical means of controlling cell size, the foam extrusion industry frequently uses mixtures of FC-11 and FC-12 in producing extruded polystyrene foams. It is worth mentioning that, in order to obtain a fine-cell structure with FC-11, citric acid/sodium bicarbonate is often used as a nucleating agent.

Similarly to what we have done in Paper I of this series (4), in which we dealt with mixtures of low-density polyethylene and fluorocarbon blowing agent, we have calculated the viscosity reduction factor (VRF), defined as

$$\text{VRF} = \frac{\text{viscosity of the mixture of polystyrene and blowing agent}}{\text{viscosity of polystyrene melt}} \quad (1)$$

using the viscosity data presented in Figures 5–10. Table III gives a summary
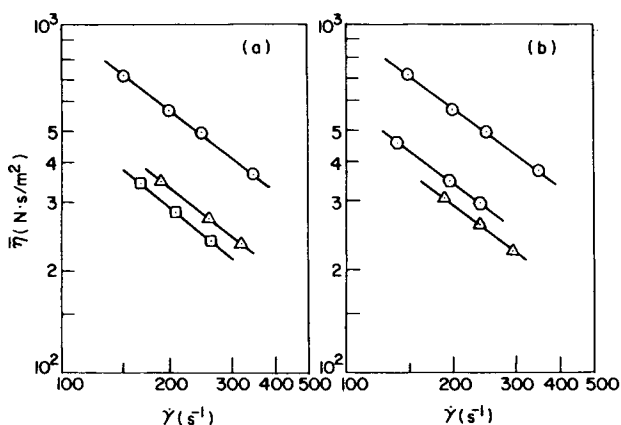

Fig. 10. Viscosity vs. shear rate for: (a) mixtures of STYRON 685D and FC-12 at 170°C; (b) mixtures of STYRON 685D and FC-11/FC-12 blend at 170°C. (⊙) Virgin resin; (⊙) 5 wt % FC; (△) 10 wt % FC; (□) 15 wt % FC.

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

Shear rate	FC concentration (wt %)			
(s^{-1})	5	10	15	20
(a) STYRON 678/FC-11 at 150°C				
200	—	0.500	0.400	0.320
300	—	0.512	0.407	0.328
400	—	0.515	0.390	0.318
(b) STYRON 678/FC-11 at 160°C				
200	—	0.506	—	—
300	—	0.500	—	—
400	—	0.500	—	—
(c) STYRON 678/FC-11 at 170°C				
200	—	0.500	—	—
300	—	0.509	—	—
400	—	0.500	—	—
(d) STYRON 678/FC-12 at 160°C				
200	0.660	0.597	0.524	—
300	0.661	0.596	0.523	—
400	0.653	0.596	0.500	—
(e) STYRON 678/FC-12 at 140°C				
200	—	0.555	—	—
300	—	0.544	—	—
400	—	0.541	—	—
(f) STYRON 678/FC-12 at 150°C				
200	—	0.571	—	—
300	—	0.567	—	—
400	—	0.568	—	—
(g) Amoco R2/FC-12 at 170°C				
200	—	0.610	0.509	—
300	—	0.597	0.513	—
400	—	0.596	0.508	—
(h) Amoco R2/FC-12 at 160°C				
200	—	—	0.525	—
300	—	—	0.527	—
400	—	—	0.530	—
(i) STYRON 685D/FC-12 at 170°C				
150	—	0.608	0.520	—
250	—	0.581	0.520	—
350	—	0.593	0.492	—

of the calculations. The following conclusions may be reached from Table III:
(1) the same value of VRF is obtained, regardless of the shear rate, the temper-
ature, and the molecular weight of the polystyrene; (2) the value of VRF decreases
as the concentration of blowing agent increases; (3) the value of VRF decreases
more with FC-11 than with F-12. On the basis of the above observations, the
average values of VRF were computed and are given in Table IV. In order to
facilitate our discussion, plots of VRF versus blowing agent concentration are
given in Figure 11.

As we have suggested in Paper I of this series,[4] Figure 11 may be used in pre-
dicting the viscosities of mixtures of polystyrene melt and fluorocarbon blowing
agent, knowing only the viscosity of the polystyrene melt at the desired shear
rate and temperature. In other words, one now need not take viscosity mea-

TABLE IV
Average Value of the Viscosity Reduction Factor for Mixtures of Polystyrene and FC-11 and
Mixtures of Polystyrene and FC-12

FC concn (wt %)	VRF ($\bar{\eta}/\eta$)
(a) FC-11	
10	0.504
15	0.399
20	0.322
(b) FC-12	
5	0.658
10	0.581
15	0.515

surements of mixtures of polystyrene and FC-11 or mixtures of polystyrene and FC-12, because one has the following empirical correlation:

$$\bar{\eta}(\dot{\gamma},T) = \eta(\dot{\gamma},T) \, VRF(FC \; concn; \; type \; of \; FC) \qquad (2)$$

in which $\bar{\eta}(\dot{\gamma},T)$ is the desired viscosity of the mixture and $\eta(\dot{\gamma},T)$ is the viscosity of the polystyrene melt. The value of VRF may be read off the curves of Figure 11.

CONCLUDING REMARKS

In this paper, we have presented experimental data on the viscosities of mixtures of polystyrene melt and fluorocarbon blowing agent, at various levels of blowing agent concentration and at various melt temperatures. The experimental data permitted us to obtain a correlation between the extent of viscosity
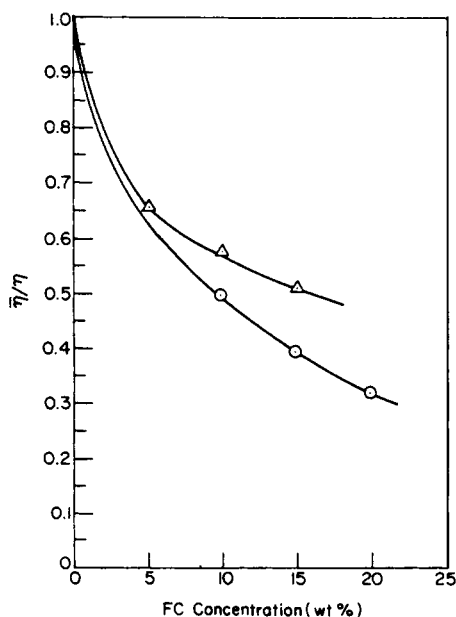

Fig. 11. Viscosity reduction factor vs. blowing agent concentration: (⊙) FC-11; (△) FC-12.

reduction in the presence of fluorocarbon blowing agent and the concentration of blowing agent. The salient feature of the correlation lies in that it is independent of (or only slightly sensitive to) shear rate, temperature, and molecular weight of polystyrene resin and dependent only on the type of the fluorocarbon blowing agent (FC-11 or FC-12). In view of the fact that in industry either FC-11 or FC-12 (or blends of FC-11 and FC-12) are used in polystyrene foam extrusion operation, the experimental correlation reported in this paper will permit one to predict viscosities of polystyrene containing either FC-11 or FC-12 (or blends of the two), knowing the viscosity of polystyrene alone.

In our future publications we shall report on the effects of die geometry, the type of blowing agent, and the type of nucleating agent on the foaming characteristics of extruded polystyrene foams, namely the foam density and the cell morphology.

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