

Rheogoniometry of Molten Blends of Polystyrene and Styrenic Ionomers

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Synopsis

The rheological properties of the molten blends between polystyrene (PS) and styrene-methacrylic acid copolymer (S-MAA) or its metallic salts were determined with a Weissenberg rheogoniometer, and the mixed structure and the processability were discussed. Results were as follows. (1) The viscosities of the salts increased and the compliances decreased with increasing density of ionic crosslinkings. (2) The viscosity of the molten blend between PS and S-MAA or its salt increased steeply even at lower shear rate and the Newtonian flow region was not observed. (3) This shear-sensitivity of viscosity in low shear rate region increased with increasing temperature. (4) The effect of temperature on the viscosity of these blends deviated from the simple Arrhenius plot. (5) Some network structures are suggested for the blends between PS and S-MAA salts but they may be broken eventually under high shear rate or at high temperature. Therefore, the mixed structures and the flow mechanisms of these molten blends seem to change with shear or temperature.

INTRODUCTION

This paper is concerned with the rheological properties of molten blends of polystyrene and styrenic ionomers, which may be partially compatible owing to the common polymerization unit of styrene.

Polystyrene is one of the popular plastics in general use, but its properties may be not always sufficient, and further modifications would be desirable for some applications.

Styrenic ionomers, e.g., ionically crosslinked copolymers of polystyrene and methacrylic acid, are unique polymers which can provide excellent thermal and mechanical properties similar to thermosetting polymers at room temperature and, simultaneously, good processability of thermoplastic polymers since the ionic crosslinkings are weakened at high temperature.^{1,2} Such ionomers have also been suggested as a matrix for asbestos reinforcement,³ owing to the ionic bonding ability.

Commercially, it would be more desirable to blend the filler with polystyrene using the ionomer as a coupling agent.

We have reported⁴ that the molten blends between polyethylene and ethylene-vinyl acetate copolymers show abnormal rheological behavior at low shear rate using a Weissenberg rheogoniometer, probably owing to the interaction in the partially compatible state through common ethylene units, and estimated the

size and distribution of the flow unit from the flow curves, based on Cross' modified equation.⁵

Thus, it is expected that the molten blends between polystyrene and styrenic ionomer would exhibit some unique rheological behavior and a special compatibility; and from another viewpoint the effects of ionic crosslinkings may be disclosed by dilution with polystyrene.

The purpose of this investigation is to determine the effect of a blended composition of polystyrene and styrene-methacrylic acid copolymers or its metallic salts on rheological properties with a Weissenberg rheogoniometer at different shear rate and temperature, and also to discuss the mixed structure and the processability.

THEORY

For the analysis of shear dependence of viscosity, we derived the following equation by modifying the Cross' and Bueche's equations which described the relation between the viscosity and the shear rate⁴:

$$\eta_0/\eta = 1 + (\tau\dot{\gamma})^m \quad (1)$$

where, η_0 is the zero-shear viscosity, η is the apparent viscosity, $\dot{\gamma}$ is the shear rate, and τ and m are parameters.

The reciprocal of the parameter τ corresponds to the shear rate at which η decreases to half of η_0 ; and so, the larger value of τ means that the non-Newtonian flow is apt to begin at the smaller shear rate. The larger value of the exponent m means a more severe shear thinning, which begins after the non-Newtonian flow occurs.

It was reported by Cross⁵ that the parameter τ , which corresponded to the characteristic relaxation time, was related to molecular weight and the exponent m depended on molecular weight distribution for the linear polymer solution.

For the polymer melts or the molten polymer blends, the assumption that τ and m were related to the size of the apparent flow unit and its distribution, respectively, was made similarly.⁴

EXPERIMENTAL

Materials

A general-purpose polystyrene (GPPS), a styrene-methacrylic acid copolymer (S-MAA), and its metallic salt, which were supplied by Central Research Laboratory of Mitsubishi Rayon, Ltd., were used in this study. Their compositions and properties are shown in Table I.

Blending

Both materials were dissolved separately in DMF at 130°C. After mixing the two solutions, the mixture was precipitated and washed with water. Then it was disintegrated in water by a Waring blender and dried at 50°C for two days. The dried mixture was homogenized and deaerated with a two-roll mill and finally processed into a sheet.

TABLE I
Properties of Materials

Polymer	S/MAA, wt-%	Na or Zn contents, wt-%	MI, g/10 min		
			190°C	200°C	230°C
			2.16 kg ^a	30.6 kg ^a	
GPSS	100/0	0	3.5	—	—
S-MAA	85/15	0	—	8.3	73.5
S-MAA salts	85/15	Na 0.48	—	—	28.4
		Zn 0.42	—	5.1	—
		Zn 0.59	—	2.2	—
		Zn 2.1	—	—	0.6
		Zn 2.6	—	—	0.1

^a Load on plunger.

Determination of Rheological Properties

The shear stress and the normal stress were measured with a Weissenberg rheogoniometer (Model 17, 2° cone angle, 5 cm diameter). The shear viscosity, the shear compliance, and their shear and temperature dependence were calculated.

RESULTS

Rheological Properties of Each Component

Effect of Shear Rate. Figure 1 shows the flow curves of Na-crosslinked S-MAA salt. Similar flow curves were obtained for other materials. The effect of shear on the viscosity of each component could be expressed approximately by eq. (1). The compliance decreased with increase in shear rate.

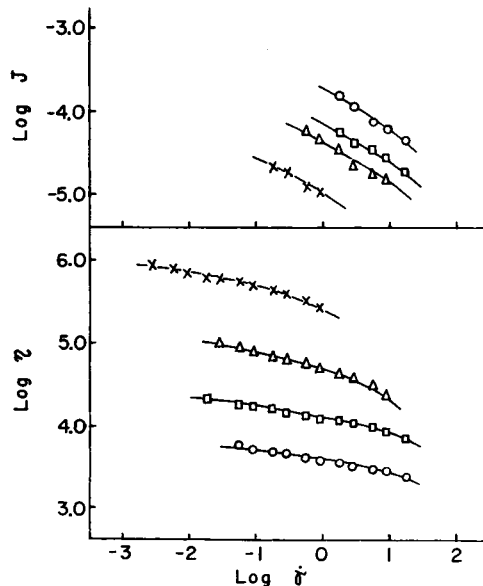


Fig. 1. Effects of shear rate on apparent viscosity and compliance of Na salt at various temperatures: (X) 200°C; (Δ) 220°C; (\square) 240°C; (O) 260°C.

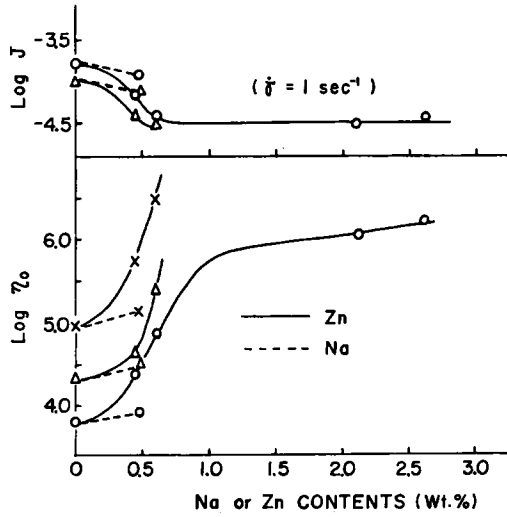


Fig. 2. Effects of metallic ion content on zero-shear viscosity and compliance at various temperatures: (X) 220°C; (Δ) 240°C; (O) 260°C.

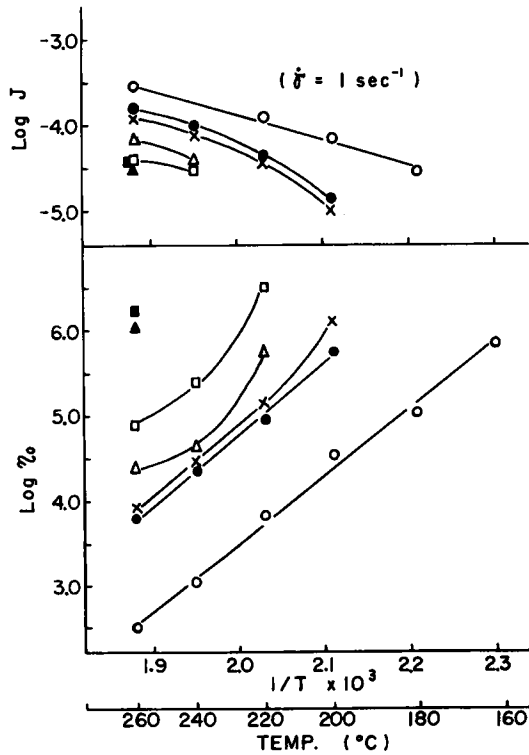


Fig. 3. Effects of temperature on zero-shear viscosity and compliance: (O) GPPS; (\bullet) S-MAA; (X) S-MAA salt (Na 0.48 wt-%); (Δ) S-MAA salt (Zn 0.42 wt-%); (\square) S-MAA salt (Zn 0.59 wt-%); (\blacktriangle) S-MAA salt (Zn 2.1 wt-%); (\blacksquare) S-MAA salt (Zn 2.6 wt-%).

Effects of Crosslinking Density. Figure 2 shows the effect of Na or Zn content in S-MAA salts on the zero-shear viscosity and the shear compliance. Even with small content of zinc ion, the viscosity increased and the compliance decreased steeply, then leveled off. The effect of crosslinking with sodium ion on the viscosity and on the compliance was not so considerable as that with zinc.

Effects of Temperature. As shown in Figure 3, plots of $\log \eta_0$ versus reciprocal of absolute temperature were approximated by straight lines for GPPS and S-MAA. However, in the case of salts, the plots did not follow straight lines but followed concave curves, and the apparent activation energy of flow increased gradually with decreasing temperature. The compliance at constant shear rate increased with increasing temperature remarkably in the case of S-MAA and its salts.

Rheological Properties of Blends

Effects of Shear Rate. As shown in Figures 4, 5, and 6 the blends between GPPS and S-MAA salts showed an abnormal increase in viscosity at low shear rate, although the single component exhibited the first Newtonian flow region at low shear rate.

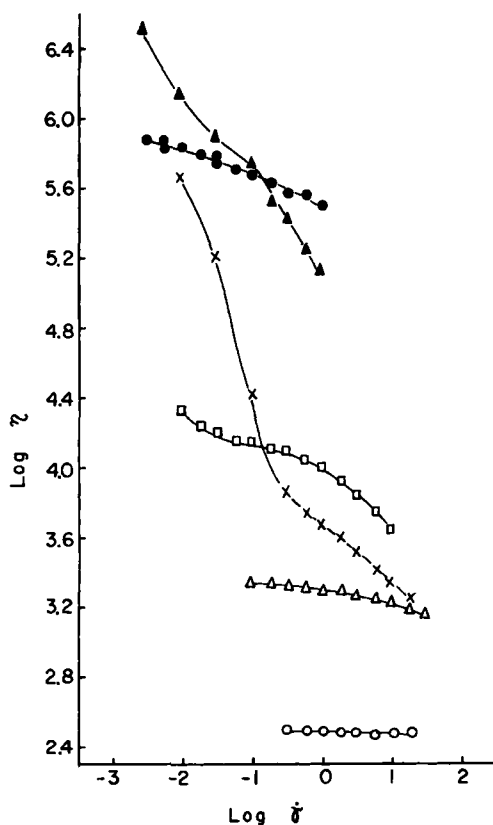


Fig. 4. Effects of shear rate on apparent viscosity of blends of GPPS and Zn-salt of S-MAA: (O) GPPS (A); (●) S-MAA salt (Zn 2.6 wt.%) (B); (Δ) A/B = 90/10 (wt-%); (◻) A/B = 70/30; (×) A/B = 50/50; (▲) A/B = 30/70; (■) A/B = 10/90.

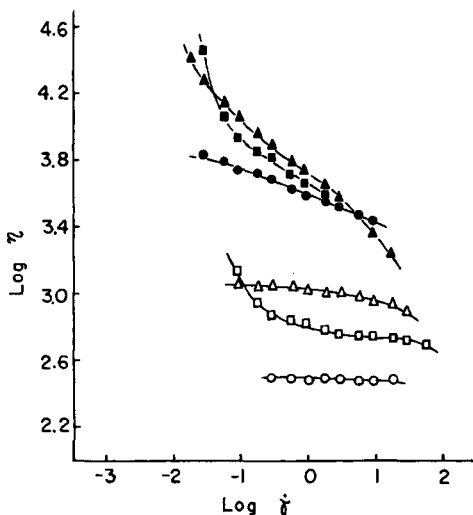


Fig. 5. Effects of shear rate on apparent viscosity of blends of GPPS and Na salt of S-MAA: (O) GPPS(A); (●) S-MAA salt (Na 0.48 wt-%) (B); (Δ) A/B = 90/10 (wt-%); (□) A/B = 70/30; (▲) A/B = 30/70; (■) A/B = 10/90.

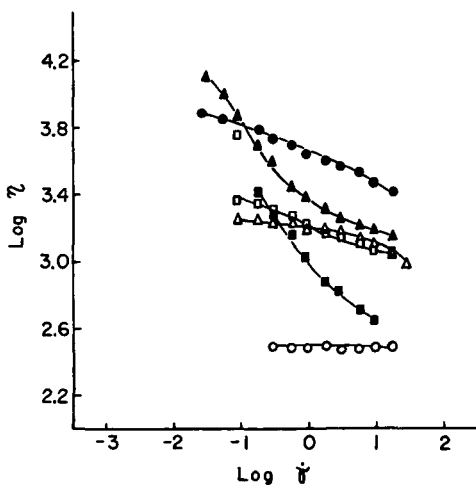


Fig. 6. Effects of shear rate on apparent viscosity of blends of GPPS and S-MAA: (O) GPPS(A); (●) S-MAA(B); (Δ) A/B = 90/10; (□) A/B = 70/30; (▲) A/B = 30/70; (■) A/B = 10/90 (wt-%).

The free methacrylic acid gave less considerable increase in viscosity at lower shear rate than its salts when the ionomers were blended with GPPS.

Effects of Temperature. As shown in Figure 7, it was observed that the abnormal behavior at lower shear rate region which was described above, was more remarkable at higher temperature.

Effects of Blended Composition. As shown in Figures 8, 9, and 10, the apparent viscosity of blends was not expressed by the simple additivity rule but showed maxima or minima irregularly against blended compositions, especially at lower shear rate. The plot of compliance at a constant shear rate versus blended compositions yielded S-shaped curves, as shown in Figures 8 and 9.

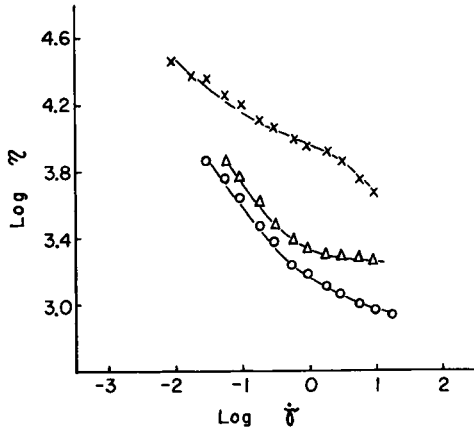


Fig. 7. Effects of shear rate on apparent viscosity of blend (GPPS/S-MAA = 30/70 wt-%) at various temperatures: (X) 220°C; (Δ) 240°C; (O) 260°C.

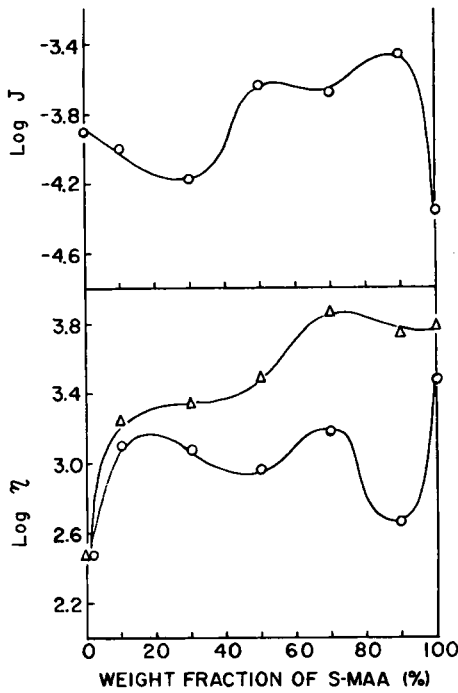


Fig. 8. Effects of blended composition of GPPS and S-MAA on apparent viscosity and compliance at a given shear rate: (Δ) $9 \times 10^{-2} \text{ sec}^{-1}$; (O) 9 sec^{-1} .

DISCUSSION

Mixed Structure

In the case of the zinc salt of S-MAA, the zero-shear viscosity and the parameter τ , which was related to the size of flow unit, increased and the compliance decreased steeply and approached to the equilibrium values even at the small content of zinc ions of about 1.0 wt-%, at 260°C, as shown in Figures 2 and 11.

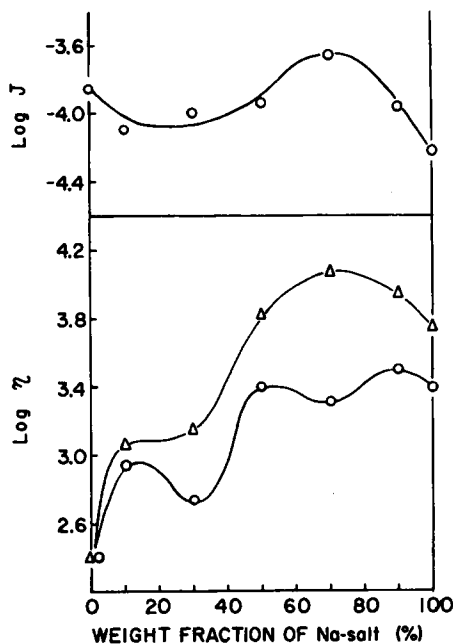


Fig. 9. Effects of blended composition of GPPS and S-MAA salt (Na 0.48 wt-%) on apparent viscosity and compliance at a given shear rate: (Δ) $9 \times 10^{-3} \text{ sec}^{-1}$; (\circ) 9 sec^{-1} .

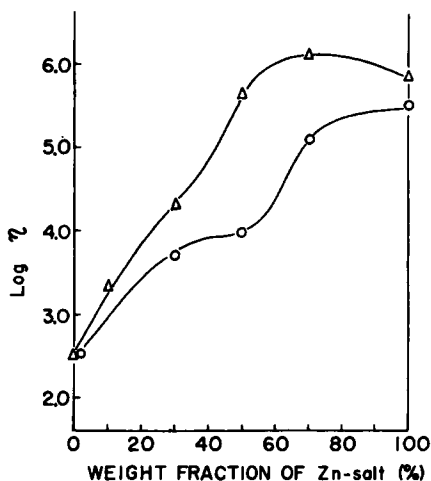


Fig. 10. Effects of blended composition of GPPS and S-MAA salt (Zn 2.6 wt-%) on apparent viscosity at a given shear rate: (Δ) $9 \times 10^{-3} \text{ sec}^{-1}$; (\circ) $9 \times 10^{-1} \text{ sec}^{-1}$.

Since the equivalent amount of zinc ions to the carboxyl groups in S-MAA copolymer is 6.4 wt-%, forming and breaking of the ionic crosslinkings seems to attain to equilibrium at about 15% of the possible crosslinkings by the carboxyl groups in S-MAA.

Considering that the zero-shear viscosity and the parameter τ decrease and the compliance increases with temperature, as shown in Figures 3 and 12, the network structure seems to loosen with temperature.

The parameter m , which is related with the homogeneity of flow units, scarcely changes with ion content or temperature, as shown in Figures 11 and 12, and it

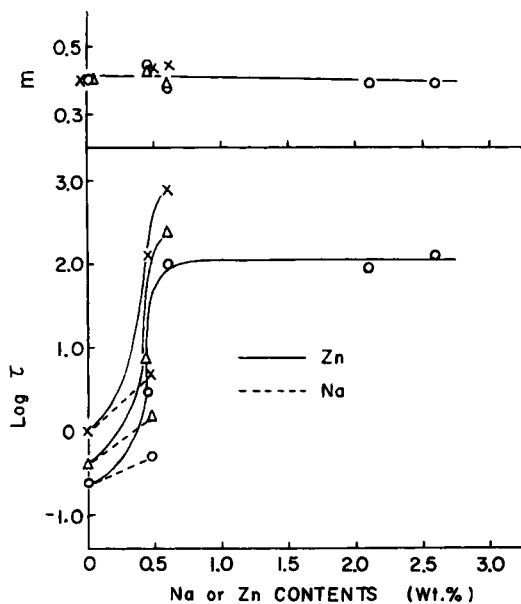


Fig. 11. Effects of metallic ion content on flow parameters in eq. (1) at various temperatures: (X) 220°C; (Δ) 240°C; (O) 260°C.

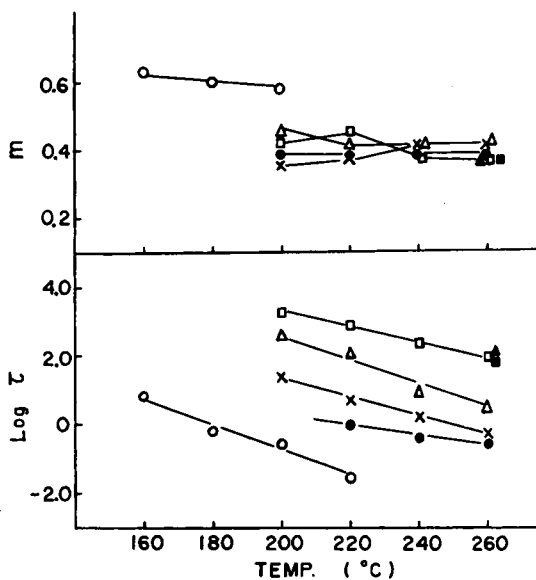


Fig. 12. Effect of temperature on flow parameters in eq. (1): (O) GPPS; (●) S-MAA; (X) S-MAA salt (Na 0.48 wt-%); (Δ) S-MAA salt (Zn 0.42 wt-%); (□) S-MAA salt (Zn 0.59 wt-%); (▲) S-MAA salt (Zn 2.1 wt-%); (■) S-MAA salt (Zn 2.6 wt-%).

seems that the distribution of apparent flow units changes scarcely with ion content or temperature. In the case of the sodium salt, the ionic crosslinkings are weak and are broken with temperature so easily that a rheological behavior similar to S-MAA without crosslinking is observed at high temperature.

When these S-MAA salts were diluted with low-viscosity GPPS, the number of the ionic groups per unit volume of the blend should decrease; but, on the con-

trary, the apparent viscosity of the blend increased at some blended compositions, as shown in Figures 9 and 10. This suggests that the rheological property of this blend would be affected not only by the ionic crosslinkings but also by other factors such as the interaction between two components, the texture of mixed structure, or the size of domain.

In our previous paper,⁴ it was observed that the zero-shear viscosity of the molten blend of polyethylene and ethylene-vinyl acetate copolymer deviated from the simple additivity rule and showed maxima or minima against the blended composition, and it was presumed that such abnormal behavior might be due to the interaction by the partial compatibility through ethylene groups which are common to both components.

An abnormal increase in the apparent viscosity at lower shear rate was also reported in the case of SBS block copolymer by Arnold and Meier.⁶ For the explanation of such abnormal behavior, they⁶ proposed a mixed structure in which the separated PS phase formed domains and the domains were connected to each other by polybutadiene chains.

Since the maxima or minima of the apparent viscosity against the blended composition, the abnormal increase in the apparent viscosity at lower shear rate, and the change of activation energy of flow with temperature were observed also in the blends of GPPS and S-MAA salts, the mixed structure of these blends might consist of the domains of the styrene phase which was formed by mutual compatibility through the common styrene units and the ionically crosslinked methacrylic acid units which connected the domains. These structures would be broken at higher shear rate and at higher temperature.

Processability

Because of the considerable shear-thinning property of the molten blends of GPPS and S-MAA salt, the flow in channels approaches a plug flow which resembles a uniform distribution of flow rate. Therefore, the rearrangement of velocity profile after extrusion could be reduced. The steep increase in the apparent viscosity at lower shear rate may be advantageous to reduce the draw-down and the folding at the parison extrusion for the blow molding.

Since, in the case of blends of GPPS and S-MAA salts, the relaxation time, which is calculated from viscosity and compliance, increases, the Deborah number⁷ also increases, and this may result in frozen strain of the products in injection molding.

Furthermore, the mixed structure of the blend changes with shear or temperature so irregularly that it may result in heterogeneity of the products, according to change in processing condition. Therefore, the operating conditions might be controlled precisely for processing of these blends.

CONCLUSIONS

1. Crosslinking of S-MAA copolymers with metallic ions increases the viscosity and the apparent activation energy of flow and decreases the compliance. When such an ionomer is blended with GPPS, an abnormal increase in viscosity at lower shear rate is observed.
2. Some structures of domains with common styrene units and networks with ionic crosslinkings could be suggested for the blends of S-MAA salts and GPPS, and they would change with temperature.

3. Due to the sensitive effects of temperature and shear rate on rheological characteristics of the blends of GPPS and styrenic ionomers, processing conditions should be carefully controlled.

References

1. V. I. Bukhgalter, F. F. Meshcherova, et al., *Int. Chem. Eng.*, **8**, 104 (1968).
2. F. Ide, T. Kodama, et al., *Kobunshi Kagaku*, **26**, 873 (1969).
3. E. A. Noga and R. T. Woodhams, *SPE J.*, **26**, 23 (1970).
4. T. Fujimura and K. Iwakura, *Int. Chem. Eng.*, **10**, 683 (1970).
5. M. M. Cross, *J. Appl. Polym. Sci.*, **13**, 765 (1969).
6. K. R. Arnord and D. J. Meier, *J. Appl. Polym. Sci.*, **14**, 423 (1970).
7. O. Pawelski, *Rheol. Acta*, **2**, 273 (1962).

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