Melt Rheology of Ionomer Filled with Methyl Methacrylate–Grafted Perlite

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Synopsis

The shear viscosity, the shear compliance, and their shear rate dependence were determined by a Weissenberg rheogoniometer, and the effect of the grafted poly(methyl methacrylate) chains on the intensification of the interaction at the interface between the ionomer matrix and the filler was discussed. Results were as follows: (1) The relative viscosity of the ionomer filled with MMA-grafted perlite to the matrix ionomer and the yield stress increased with increase in the volume fraction of perlite, and these behaviors were more remarkable in the case of the perlite with larger quantity of grafted PMMA. (2) The effective thickness of the immobilized matrix layer on the filler surface in the Ziegel equation and the crowding factor in the Mooney equation showed larger values in the case of the filled systems of MMA-grafted perlite than in the case of the unmodified perlite. (3) At the same total volume fraction which was the sum of the quantities of the perlite and the grafted PMMA, the relative viscosity and the crowding factor showed respectively a maximum with the quantity of grafted PMMA. (4) The shear compliance of these filled systems decreased with perlite content. A little effect of the amount of grafted PMMA on the compliance was observed at the same volume fraction of perlite. According to these rheological properties, it could be concluded that the grafted PMMA chains were effective in increasing the interaction between the ionomer matrix and the perlite at their interface, particularly in the lower shear rate region.

INTRODUCTION

Recently, the importance of polymer composites has been recognized in industrial and commercial applications. Usually, various fillers are available for composites, but difficulty in the melt processing of such filled composites might increase.[1] Hence, a fundamental knowledge of the rheological properties of the filler-containing polymer melt would be required.

The effects of the content and the geometries of the fillers on the rheological properties of filled polymer melt were reported by Ziegel,[2] Mills,[1] Nazem,[3] White,[4] and many other workers. However, the effect of the extent of the interaction at the interface between the filler and the polymer matrix on their melt rheological properties seems not yet to be explained sufficiently.

Previously, we reported that the coupling of perlite with an ethylene–vinyl acetate copolymer increased the interaction with a high-density polyethylene matrix[5] owing to the partial compatibility through the common ethylene units.[6] We also reported that acetylation of cellulosic fillers intensified the interaction at the interface between the polyolefin matrix and the filler.[7] Therefore, if the coupling agent could be combined chemically with the filler, it is expected that the interaction at the interface between the matrix and the filler could further be increased.

In this paper, we have investigated a filled system of a methyl methacrylate-

0021-8995/79/0024-0975$01.00

grafted perlite and an ionomer matrix which may be compatible through the common methacrylate units. Shear viscosity and shear compliance were determined, and the effects of molecular interaction by the grafted poly(methyl methacrylate) chains with the ionomer were discussed, by means of the effects of filler content, amount of grafted PMMA, and the shear rate on the rheological properties of the ionomer melt filled with MMA-grafted perlite.

EXPERIMENTAL

Materials

The ionomer used as a matrix is Surlyn A 1555, which has a melt index of 10 g/10 min and a density of 0.94 g/cm^3.

The perlite has an apparent bulk density of 2.32 g/cm^3 and an average diameter of 5.5 micrometers.

Methyl methacrylate-grafted perlites were supplied by Professor Tadashi Yamaguchi of Tohoku University. The amounts of grafted poly(methyl methacrylate) of these samples were 3, 15, and 30 wt. %.

Blending

The matrix and the filler were mixed with a Banbury-type kneader, which had a charging volume of 25 cm^3, at 70 rpm and 160°C for 20 min.

Determination of Rheological Properties

The shear stress and the normal stress were measured at 190°C with a Weissenberg Rheogoniometer Model-R17, of which cone angle was 2° and the diameter was 50 mm.

The shear viscosity, the shear compliance, and their shear rate dependences were calculated.

From the observed values of the relative viscosity (η_r), the effective thickness of the immobilized layer on the surface of the perlite (ΔR) in the Ziegel[8] equation (1), and the crowding factor (S) in the Mooney[9] equation (2) were calculated:

$$\eta_r = 1 + 2.5\phi(1 + \Delta R/R_0)^3 \qquad (1)$$

$$\eta_r = \exp[2.5\phi/(1 - S\phi)] \qquad (2)$$

where ϕ and R_0 are the volume fraction and the radius of the filler particle, respectively.

RESULTS

Shear Viscosity

Effects of Shear. The flow curves of a filled system of ionomer/MMA-grafted (15 wt. %) perlite are shown in Figure 1. The flow curve of the matrix ionomer showed that the viscosity approached the definite value in the lower shear rate region, whereas the viscosity of the ionomer filled with the MMA-grafted perlite increased steeply even in the lower shear rate region. Figure 2 shows that the
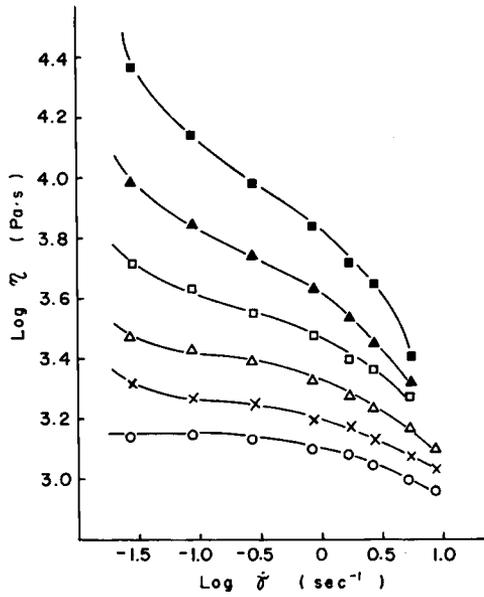
Fig. 1. Flow curves of ionomer filled with MMA-grafted (15 wt. %) perlite: (O) ionomer; ϕ perlite: (X) 0.04, ($\triangle$) 0.07, ($\square$) 0.11, ($\blacktriangle$) 0.15, ($\blacksquare$) 0.18; ϕ = volume fraction; T = 190°C.
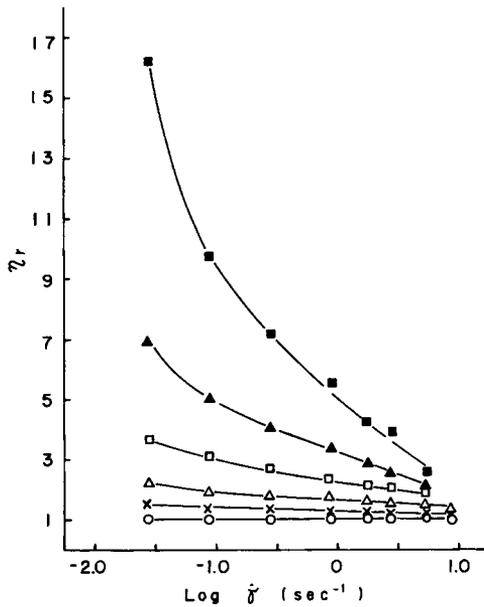
Fig. 2. Relationship between relative viscosity of ionomer filled with MMA-grafted (15 wt. %) perlite and shear rate: (O) ionomer; ϕ perlite: (X) 0.04, ($\triangle$) 0.07, ($\square$) 0.11, ($\blacktriangle$) 0.15, ($\blacksquare$) 0.18. T = 190°C.

relative viscosity of the filled ionomer to the unfilled ionomer matrix decreased with the shear rate. These behaviors were more significant in the case of the higher content of the MMA-grafted perlite. As shown in Figure 3, the ionomer filled with unmodified perlite also showed an increase in viscosity in the lower
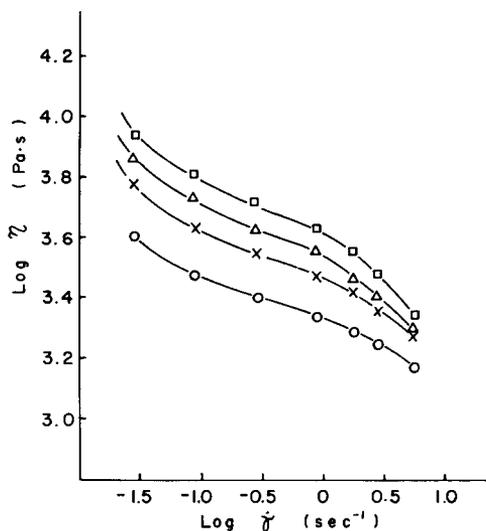
Fig. 3. Flow curves of ionomer filled with perlite containing different amounts of grafted PMMA. Grafted PMMA: (O) 0 wt. % (unmodified perlite), (×) 3 wt. %, (△) 15 wt. %, (□) 30 wt. %. ϕ (perlite) = 0.13; T = 190°C.

shear rate region, similarly to that observed in the dispersions of MMA-grafted perlite.

Effect of Filler Content. Figure 4 shows that the relative viscosities of ionomers containing MMA-grafted perlites increased with increasing volume fraction of perlite, and this behavior was more remarkable in the case of the perlite with the larger amount of grafted PMMA. Figure 5 shows the relation
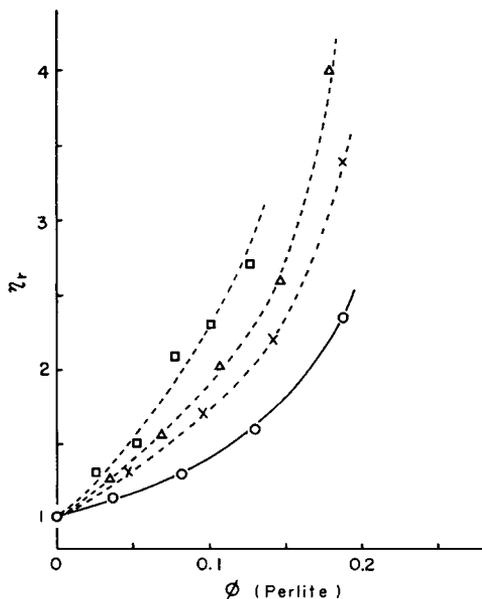
Fig. 4. Relationship between relative viscosity and volume fraction of perlite. Grafted PMMA: (O) 0 wt. % (unmodified perlite), (X) 3 wt. %, (△) 15 wt. %, (□) 30 wt. %. $\dot{\gamma}$ = 2.84 sec^{-1}; T = 190°C.
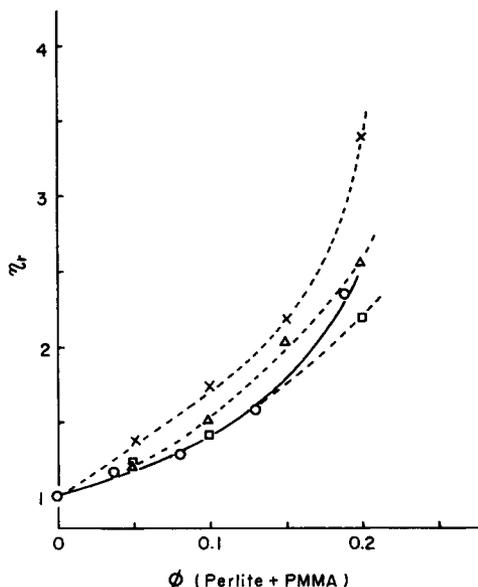
Fig. 5. Relationship between relative viscosity and total volume fraction of perlite and grafted PMMA. Grafted-PMMA: (O) 0 wt. % (unmodified perlite), (X) 3 wt. %, (△) 15 wt. %, (□) 30 wt. %. $\dot{\gamma} = 2.84 \, \text{sec}^{-1}$; $T = 190°C$.

between the relative viscosity and the total volume fraction which was the sum of the quantities of the perlite and the grafted PMMA. The extent of the increase in relative viscosity with the total volume fraction of the MMA-grafted perlite depended on the amount of grafted PMMA.

Effect of PMMA Amount Grafted. Figure 6 shows that, at the same volume fraction of the perlite, the relative viscosity increased with the amount of grafted PMMA. The effective thickness of the immobilized layer (ΔR) on the perlite surface which was calculated from the Ziegel equation (1) increased similarly, corresponding to the behavior of the relative viscosity. But the value of ΔR was larger than the thickness of the grafted PMMA layer, which is shown by the dotted line in Figure 6. At the same total volume fraction of the grafted perlite, the relative viscosity shows a maximum toward the amount of the grafted PMMA at approximately 3 wt. %, as shown in Figure 7. Figure 7 also shows that the values of the crowding factor in the Mooney equation[9] shows a maximum toward the amount of grafted PMMA, almost correspondingly to the maximum of the relative viscosity. The yield stress, which was obtained from the Casson plot,[10] increased with the amount of grafted PMMA, at the same volume fraction of perlite, as shown in Figure 8.

Shear Compliance

Figures 9 and 10 show that the compliance of the ionomer filled with the MMA-grafted perlite decreases with the shear rate and with the content of the perlite. A small effect of the grafted PMMA amount on the compliance was observed at the same volume fraction of perlite, as shown in Figure 10.
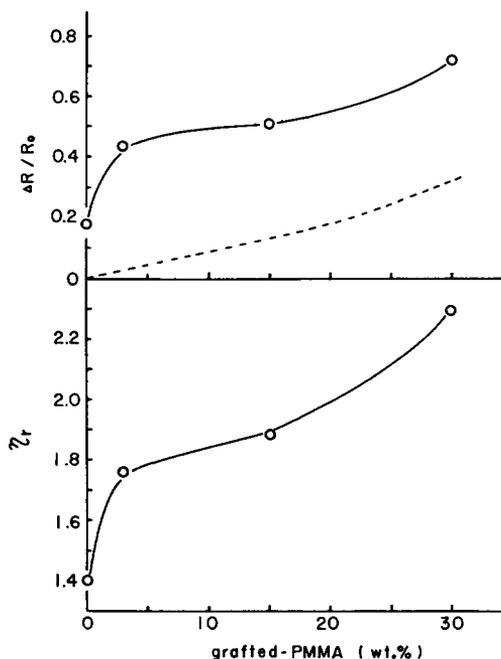
Fig. 6. Relationship between relative viscosity, effective thickness of layer on perlite surface (ΔR) in the Ziegel equation (1), and amount of grafted-PMMA. Dotted line is the thickness of grafted PMMA layer. ϕ (perlite) = 0.1; $\dot{\gamma}$ = 2.84 sec^{-1}; T = 190°C.

DISCUSSION

Effect of Filling

The increases in the relative viscosity and in the yield stress with increase in amount of grafted PMMA at a constant volume fraction of perlite suggest that the accumulated volume fraction of the flowing particle unit was increased by the fixed layer of grafted PMMA chains. Even if these values were compared at the same total volume fraction which was the sum of the quantities of the perlite and the grafted PMMA, the relative viscosities of the filled system with MMA-grafted perlite showed higher values than that of the filled system with unmodified perlite.

These data suggested that the total volume fraction of the flowing particle unit increased not only by the grafted PMMA layer but also by the matrix layer fixed on the surface of the MMA-grafted perlite, owing to the interaction with the grafted PMMA chains. Such increases in the accumulated volume fraction of the flowing unit which consisted of the perlite particle, the grafted PMMA layer, and the immobilized matrix layer could be confirmed also by the results of the increases in the effective thickness (ΔR) in the Ziegel equation[8] (1) and in the crowding factor (S) in the Mooney[9] equation (2).

These layers which attached to the perlite surface might be affected with shear, since the viscosity and the crowding factor in the Mooney equation depended remarkably on the shear rate. Also, the higher compliance in the system containing MMA-grafted perlite might be attributed to the flexibility of longer grafted chains. Therefore, it would be desirable to estimate the effect of the
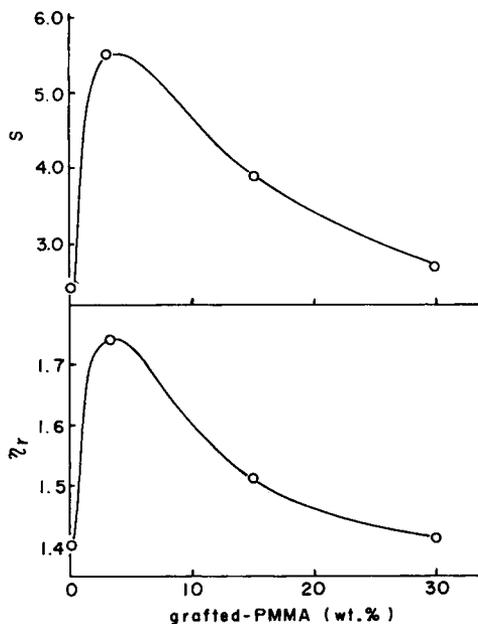
Fig. 7. Relationship between relative viscosity, crowding factor in the Mooney equation (2), and amount of grafted PMMA. $\dot{\gamma} = 2.84\ \text{sec}^{-1}$; ϕ (perlite + PMMA) = 0.1; T = 190°C.
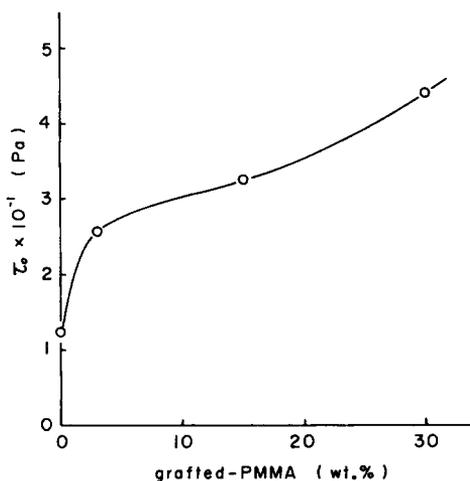
Fig. 8. Relationship between yield stress and amount of grafted PMMA. ϕ (perlite) = 0.13; T = 190°C.

deformation at the interface layer attached to the perlite surface on the rheological properties of the filled systems.

Effect of Coupling

In previous papers[5,7] it was reported that impregnating the filler with a copolymer which contained the common units to the matrix polymer was effective in increasing the coupling effect, owing to interaction through the common units.[6,11] Furthermore, if the coupling layer is combined with the covalent bonds to the filler surface, the coupling effect would be more excellent.
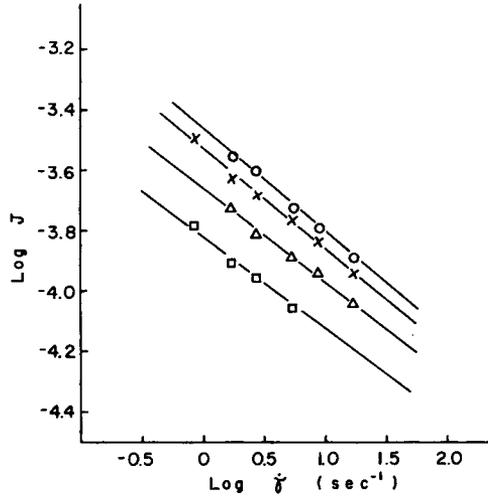
Fig. 9. Relationship between shear compliance of ionomer filled with MMA-grafted (15 wt. %) perlite and shear rate: (O) ionomer; ϕ perlite: (×) 0.04, (△) 0.07, (□) 0.11. $T = 190°C$.
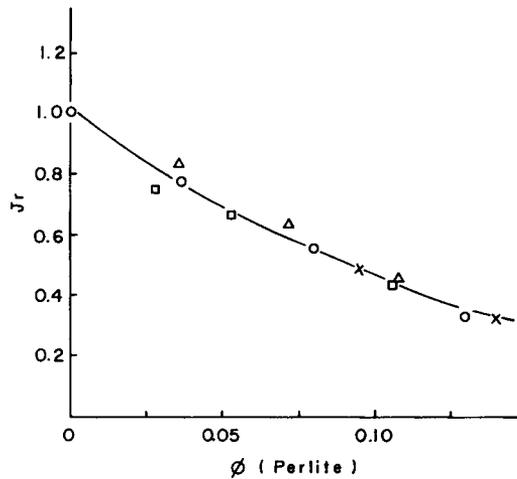
Fig. 10. Relationship between relative shear compliance and volume fraction of perlite.   Grafted PMMA: (O) 0 wt. % (unmodified perlite), (×) 3 wt. %, (△) 15 wt. %, (□) 30 wt. %. $\dot{\gamma} = 2.84\ \mathrm{sec}^{-1}$; $T = 190°C$.

In this paper the results of the rheological properties suggested that PMMA chains bonded with covalency on the perlite surface and the PMMA chains interacted with the matrix ionomer strongly due to partial compatibility through the common methacrylate units.   Therefore, a remarkable coupling effect could be observed in this filled system.

These interactions between the matrix ionomer and the grafted filler surface might be increased by control of the length and frequency of the grafted chains.

Application to Processing

From the viewpoint of polymer processing, the yield stresses of these filled polymer melts would be advantageous in the dimensional stability in some processing. And since the high melt viscosities of these filled systems reduce steeply with shear rate in the higher shear rate region, the practical flowability in the processing of composites might not decrease so precipitously. For instance, in the case of parison in extrusion blow molding, the high yield stress can be effective for improving of draw-down and folding[12] because the viscosity increases steeply at the low shear state after extrusion from the parison die.

In injection molding, the dimensional stability of the product even at comparatively high temperatures, due to the high yield point, would allow reduction of the cooling-time necessary for ejection without deformation, and consequently the productivity could be increased.

In the case of extrusion, the shear rate is very high generally. Consequently, the viscosity of the filled polymer decreases remarkably during the flow in the channel of the screw, and the power consumption will increase less considerably.

CONCLUSIONS

According to the rheological behavior of the ionomer melt filled with MMA-grafted perlite, it can be concluded that the grafted PMMA chains were effective in increasing the interaction at the interface between the ionomer matrix and the filler, probably due to the partial compatibility through their common methacrylate units, particularly in the lower shear rate region.

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