

# Rheological Properties of Ionically Crosslinked Poly(propylene)-Type Thermoplastic Elastomers

Mitsuyoshi Fujiyama, Kazuhiro Yamane, Kazuhiko Ayama, Hitoshi Inata

Tokuyama Research Laboratory, Tokuyama Corporation, 1-1, Harumi-cho, Tokuyama-shi, Yamaguchi-ken, 745-0024 Japan

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**ABSTRACT:** Maleic anhydride was grafted onto poly(propylene) (PP)-type thermoplastic elastomer PER by reactive processing with a screw extruder and a maleated PER (MPER) was prepared. With the intent of ionic crosslinking, metal compounds such as aluminum stearate (AlSt), magnesium stearate (MgSt), calcium stearate (CaSt), zinc stearate (ZnSt), potassium stearate (KSt), sodium stearate (NaSt), magnesium hydroxide (MH), zinc oxide (ZnO), and zinc sulfide (ZnS) were added to the MPER and melt-mixed with the screw extruder, and crosslinked compounds were obtained. The degree of crosslinking estimated from the gel fraction was in the order AlSt, MgSt, CaSt, ZnSt > NaSt, KSt > MH > ZnO, ZnS > MPER. The rheological properties, such as capillary flow properties and dynamic viscoelasticities, of the compounds were measured and their melt processabilities were evaluated. The viscosity increased with increasing the content of the metal compounds and the increase was higher at the lower shear rate. The increasing

effect of the viscosity at low shear rates was AlSt > MgSt > ZnSt > NaSt > KSt > MH > ZnO > ZnS > MPER. Namely, the viscosity increasing effect of the metal salt of stearic acid is the higher for the larger ionic charge and the viscosity increasing effects of other compounds are lower than those of the metal salts of stearic acid. Accordingly, by changing the kind and content of the metal compounds, the viscosity can be freely controlled. Considering also other rheological characteristics, these ionically crosslinked compounds are assumed to show ideal flow processabilities except for the extrudate appearance. To improve the appearance, it is necessary to dilute the compound with unmodified PER, PP, or fillers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2887–2897, 2002

**Key words:** poly(propylene); thermoplastics; elastomers; maleic anhydride; metal compounds; crosslinking; rheology

## INTRODUCTION

Poly(propylene) (PP)-type thermoplastic elastomer P. E. R. (manufactured by Tokuyama Corp., abbreviated as PER) is a reactor-type elastomer and a kind of block PP with much ethylene-propylene copolymer (EPR) part.<sup>1–3</sup> Although usual block PP contains 10–30 wt % EPR, PER contains 50–90 wt % EPR. Because PER contains so much EPR, many carboxyl groups, such as maleic anhydride, can be easily grafted.<sup>4</sup> In our previous paper,<sup>5</sup> maleic anhydride was grafted onto PER by reactive processing with a screw extruder, and a maleated PER (MPER) was prepared. With the intent of ionic crosslinking, magnesium 12-hydroxy stearate (MgStOH), zinc oxide (ZnO), and zinc sulfide (ZnS), and with the intent of covalent crosslinking, melamine as an amino compound and Epocizer and GRYCI-ALE as epoxy compounds, were added to the MPER in 5 weight parts (phr) and melt-mixed with a screw extruder and crosslinked compounds were obtained. The rheological properties,

such as capillary flow properties and dynamic viscoelasticities, of the compounds were measured and their melt processabilities were evaluated. In the cases of ZnO, ZnS, and melamine, a sufficient degree of crosslinking could not be obtained. In the cases of epoxy compounds, a fine extrudate could not be obtained because of excessive crosslinking. In the case of MgStOH, a moderately crosslinked compound could be obtained, which is suitable for extrusion processing in almost all aspects.

In the present study, to pursue further the ionically crosslinked MPER and obtain an ionically crosslinked compound with further superior flow processabilities, metal compounds aluminum stearate (AlSt), magnesium stearate (MgSt), calcium stearate (CaSt), zinc stearate (ZnSt), potassium stearate (KSt), sodium stearate (NaSt), magnesium hydroxide (MH), zinc oxide (ZnO), and zinc sulfide (ZnS) were added to the MPER and melt-mixed with a screw extruder and crosslinked compounds were obtained. For CaSt, KSt, NaSt, ZnO, and ZnS, the addition amount was fixed at 5 phr and for AlSt, MgSt, ZnSt and MH, the addition amount was varied. The rheological properties, such as capillary flow properties and dynamic viscoelasticities, of the compounds were measured and their melt processabilities were evaluated.

Correspondence to: M. Fujiyama (m-fujiyama@tokuyama.co.jp).

TABLE I  
Characteristics of Samples

Sample Code	MFI (g/10 min)	Gel Fraction (wt %)
MPER	21.9	11.5
ZnSt-1	9.8	23.6
ZnSt-3	7.0	30.4
ZnSt-5	2.7	43.3
MgSt-1	11.7	18.8
MgSt-3	5.4	29.4
MgSt-5	0.17	43.2
MgSt-7	0.06	71.4
AlSt-1	10.8	25.5
AlSt-3	3.0	29.9
AlSt-5	0.30	41.0
AlSt-7	0.03	59.0
MH-1	13.2	18.9
MH-3	12.7	23.1
MH-5	3.8	28.0
MH-10	0.95	32.2
MH-20	0.20	41.2
MH-30	0.13	54.5
MH-50	0.00	84.4
KSt-5	21.0	33.0
NaSt-5	7.3	34.0
CaSt-5	0.18	45.9
ZnO-5	12.4	26.0
ZnS-5	13.7	21.5

Many studies of the melt rheological properties of ionically crosslinked thermoplastics have been conducted for ionomers. If a polymer with carboxyl groups is neutralized with metal ions, the viscosity is increased and the increase of viscosity is the more notable at the lower shear rate and for the larger ionic charge.<sup>6–10</sup> For ionically crosslinked polymers, the absolute value of complex viscosity,  $|\eta^*(\omega)|$ , is lower than the steady-state viscosity,  $\eta(\dot{\gamma})$ , and Cox-Merz's empirical rule<sup>11</sup> does not hold.<sup>6,8</sup> The die swell is increased by the ionic crosslinking because of the substantial increase of molecular weight.<sup>8</sup> The elongational viscosity and its strain hardening increase with increasing the degree of ionic crosslinking and the increases are the more notable for the larger ionic charge.<sup>12,13</sup> In the melt viscoelasticity, the relaxation time at terminal zone is lengthened and the relaxation intensity is increased by the ionic crosslinking.<sup>6,7,9,10,14–16</sup> In the case of high ionic crosslinking, there is a case where the storage modulus  $G'$  is higher than the loss modulus  $G''$ .<sup>10,15</sup> These rheological characteristics of ionomers are regarded as due to the ion clusters (ion pockets).<sup>17</sup> The ion clusters are assumed to partially dissociate at 170–180 °C.<sup>16</sup>

## EXPERIMENTAL

### Samples

The characteristics of samples are shown in Table I. The raw MPER was prepared as follows: 100 phr

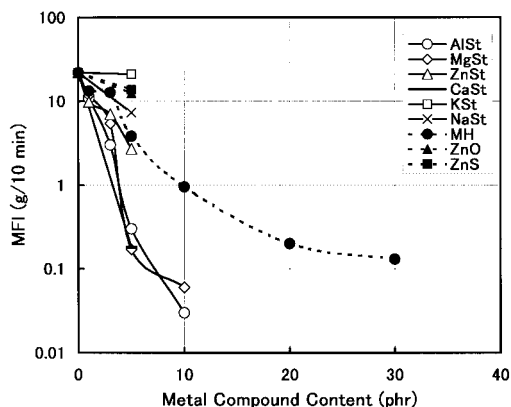
ultrahigh molecular weight PER was added with 4.5 phr maleic anhydride (MAH), 1.5 phr 1,3-bis (*t*-butylperoxyisobutyl) benzene as radical initiator, and 0.05 phr tetrakis [methylene (3,5-di-*t*-butyl-4-hydroxyphenyl) propionate] methane as antioxidant and thoroughly mixed in a Henschel mixer. The mixture was then melt-mixed with a 45 mm  $\phi$  corotating twin screw extruder PCM-45 type (Ikegai, Japan) at a maximum cylinder temperature of 210 °C and a screw rotation speed of 100 rpm and pelletized by strand-cutting with a pelletizer. The pellets were dried in a constant-temperature drying oven at 105 °C for 12 h, and an MPER with an MFI of 13.4 g/10 min and a grafted maleic anhydride content of 2.8 wt % was obtained. The crosslinking was carried out as follows: 100 phr of MPER and fixed amounts of the metal compound crosslinkers were thoroughly mixed in a tumbler, melt-mixed with the extruder at a maximum cylinder temperature of 220 °C and a screw rotation speed of 250 rpm, and pelletized by strand-cutting with the pelletizer. Aluminum stearate (AlSt), magnesium stearate (MgSt), calcium stearate (CaSt), zinc stearate (ZnSt), potassium stearate (KSt), sodium stearate (NaSt), magnesium hydroxide (MH), zinc oxide (ZnO), and zinc sulfide (ZnS) were used as metal compound crosslinkers. These metal compounds were all special grade reagents manufactured by Wako Pure Chemical Industries Ltd., Japan. For CaSt, KSt, NaSt, ZnO, and ZnS, the addition amount was fixed at 5 phr and for AlSt, MgSt, ZnSt, and MH, the addition amount was varied. The addition amount is represented by a figure following a hyphen after the metal compound abbreviation.

The melt flow index (MFI) and gel fraction in Table I were measured as follows: MFI was measured at 230 °C under a load of 2160 g according to the JIS K7210. Five grams of pellets were extracted with *p*-xylene for 6 h in a Soxhlet extractor. The insoluble part was dried in a vacuum drying oven at 70 °C for 6 h, and the percentage of the insoluble part was regarded as the gel fraction.

### Measurements

#### Capillary flow properties

Capillary flow properties were measured with a capillary rheometer Capirograph 1B type (Toyo Measurement Instruments Company, Ltd., Japan). The flow curve, die swell ratio, and melt fracture behaviors were measured at 210 °C with a die with a capillary length ( $L$ ) of 20 mm and a capillary diameter ( $D$ ) of 1 mm. The end correction coefficient  $\nu$  and entrance pressure loss  $P_0$  were measured at 210 °C with dies with a  $D$  of 1 mm and  $L$  values of 20, 10, and 5 mm. The change of elongational viscosity ( $\lambda$ ) with elongational strain rate ( $\dot{\epsilon}$ ) was calculated from  $P_0$  according to the Cogswell's method.<sup>18</sup>



**Figure 1** Dependence of melt flow index (MFI) on metal compound content.

### Dynamic viscoelasticity

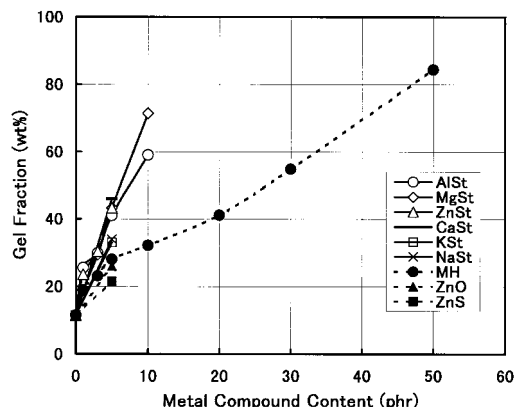
The storage modulus  $G'(\omega)$ , loss modulus  $G''(\omega)$  and absolute value of complex viscosity  $|\eta^*(\omega)|$  were measured at 210 °C under  $N_2$  atmosphere with a concentric cylinder rheometer (Rheometer Almighty, Iwamoto Seisakusho Company, Ltd., Japan).

## RESULTS AND DISCUSSION

### MFI and gel fraction

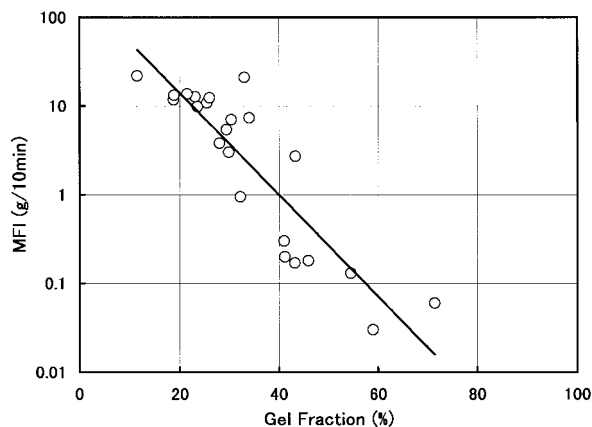
The dependence of MFI on metal compound content is shown in Figure 1. MFI decreases with increasing the metal compound content. The degree of the decrease is in the order AlSt, MgSt, CaSt > ZnSt > MH > NaSt > ZnO, ZnS > KSt, and the MFI decreasing effect is generally higher for the metal salts of stearic acid than for the other compounds. Among metal salts of stearic acid, the MFI decreasing effect is higher for the larger ionic charge. It is reported that if a polymer with carboxyl groups is neutralized with metal ions, the viscosity is increased and the increase of viscosity is the more notable at the low shear rate and for the larger ionic charge.<sup>6–10</sup> The present experimental results on MPERs ionically crosslinked with metal compounds agree with these reported results.

The dependence of gel fraction on metal compound content is shown in Figure 2. With increasing the content, the gel fraction increases, which is an inverse tendency of that of MFI except for KSt. Although KSt shows almost no effect of decreasing MFI, as shown in Figure 1, it contains a considerable gel fraction. This situation is assumed to be because KSt has a plasticizing or lubricating effect. The dissociation of ionic bondings at a high temperature of MFI measurement is also considered to be a cause. From these facts, it is seen that the MPERs ionically crosslinked with metal compounds in the present study consist of a crosslinked structure containing a gel fraction that is insoluble in solvent.



**Figure 2** Dependence of gel fraction on metal compound content.

The relation between MFI and gel fraction is shown in Figure 3. In this figure, all results in Table I except for MH-50 with an MFI of  $\sim 0$  are plotted. Although the results show some scatter, there is an inverse proportionality on semilogarithmic plot. Narkis and Miltz<sup>19–20</sup> studied the flow properties of peroxide-crosslinked low-density polyethylenes (LDPEs) and high-density polyethylenes (HDPEs) and found that with increasing gel fraction, their viscosity and non-Newtonian behavior increase, the flow activation energy at a constant shear rate decreases, and the viscosity of the sol fraction decreases. They regarded the gels in the crosslinked polyethylenes (PEs) as a kind of filler, expressed the flow behaviors in a capillary by a Bingham plug flow, and quantitatively discussed the experimental results. According to their results for peroxide crosslinking, because a chain scission reaction occurs at the same time of crosslinking reaction, the viscosity of the sol fraction decreases with increasing the degree of crosslinking. Accordingly, the viscosity of the whole crosslinked compound abruptly increases at small gel fractions, slightly increases with increasing the gel fraction at gel fractions <50%, and



**Figure 3** Relation between melt flow index (MFI) and gel fraction.

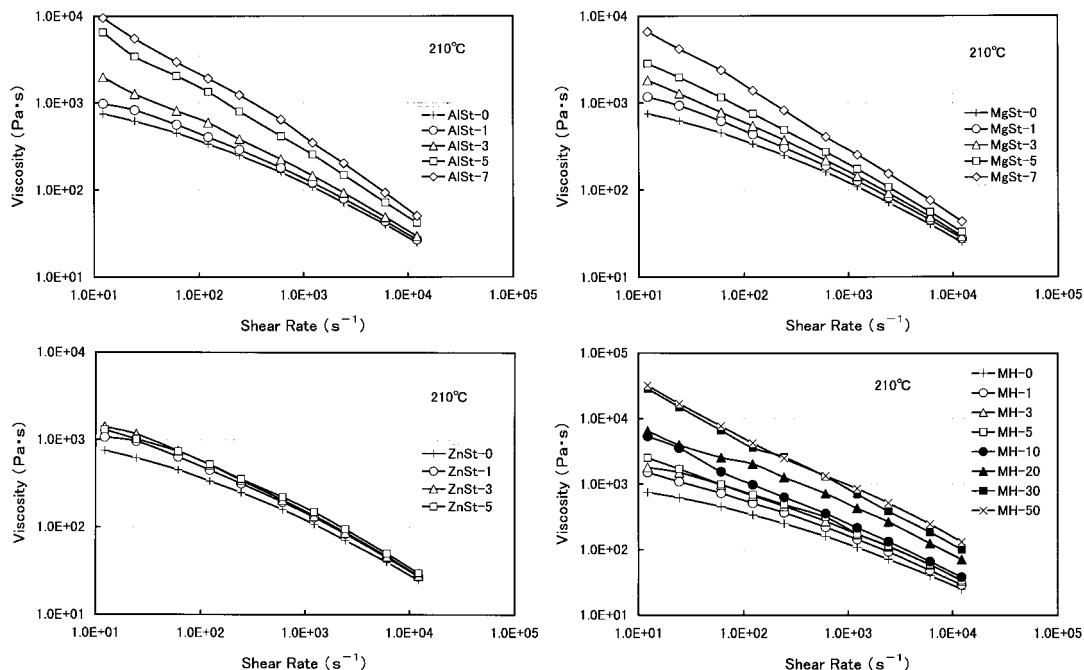


Figure 4 Flow curves for the (a) AlSt system, (b) MgSt system, (c) ZnSt system, and (d) MH system.

steeply increases at gel fractions  $>50\%$ . Fujiyama<sup>23</sup> showed that the logarithmically expressed viscosity of a peroxide-crosslinked LDPE increases abruptly at low gel fractions and increases linearly with increasing the gel fraction, which is similar to the experimental results on ionically crosslinked MPER. He also crosslinked a PP, using a liquid polybutadiene as an auxiliary, with a peroxide and showed that the viscosity first drops at low gel fractions and then increases with increasing the gel fraction, as in the case of the PE results of Narkis and Miltz<sup>19–22</sup> mentioned earlier. The viscosity increasing effect is at most 10-fold even with a gel fraction of  $\sim 80\%$  in the case of peroxide crosslinkings already mentioned. On the contrary, in the ionically crosslinked EPRs in the present experiment, the abnormal behaviors at low gel fractions could not be observed and the viscosity increasing effect at a gel fraction of  $\sim 80\%$  reaches  $10^3$ - to  $10^4$ -fold. This result is assumed to be because the viscosity reduction due to the decomposition of the sol fraction does not occur and only the gel fraction increases by the crosslinking reaction.

### Viscosity (flow curve)

The flow curves of the AlSt, MgSt, ZnSt, and MH series are shown in Figures 4a, 4b, 4c, and 4d, respectively. The AlSt series in Figure 4a and the MgSt series in Figure 4b show equivalent viscosity increasing effects; the viscosities increase with increasing the contents and the increase is the higher at the lower shear rate. Their viscosity increasing effect by an addition of 7 phr is  $\sim 10$ -fold at  $10 \text{ s}^{-1}$  and  $\sim 2$ -fold at  $10,000 \text{ s}^{-1}$ .

The viscosity increasing effect of the ZnSt series, shown in Figure 4c, is small and its content dependence is also small. Although the viscosity increasing effect of the MH series shown in Figure 4d is not so large as those of the AlSt and MgSt series, high loadings show the large effects. A small difference in the viscosity increasing effect by shear rate is also characteristic. This characteristic is assumed to be due to the viscosity increasing effect not only by ionic crosslinking but also by filling effect. The comparison of flow curve among metal compounds at a content of 5 phr is shown in Figure 5. These results show an almost inverse tendency of the MFI shown in Figure 1. The sample containing KSt shows abnormally lower viscosity than that of the base resin MPER, and KSt is assumed to have a plasticizing or lubricating effect.

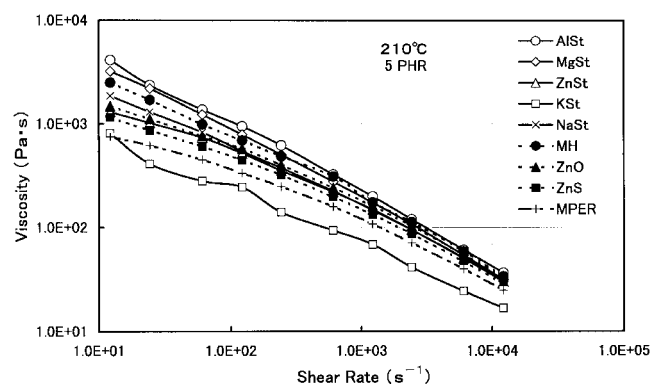
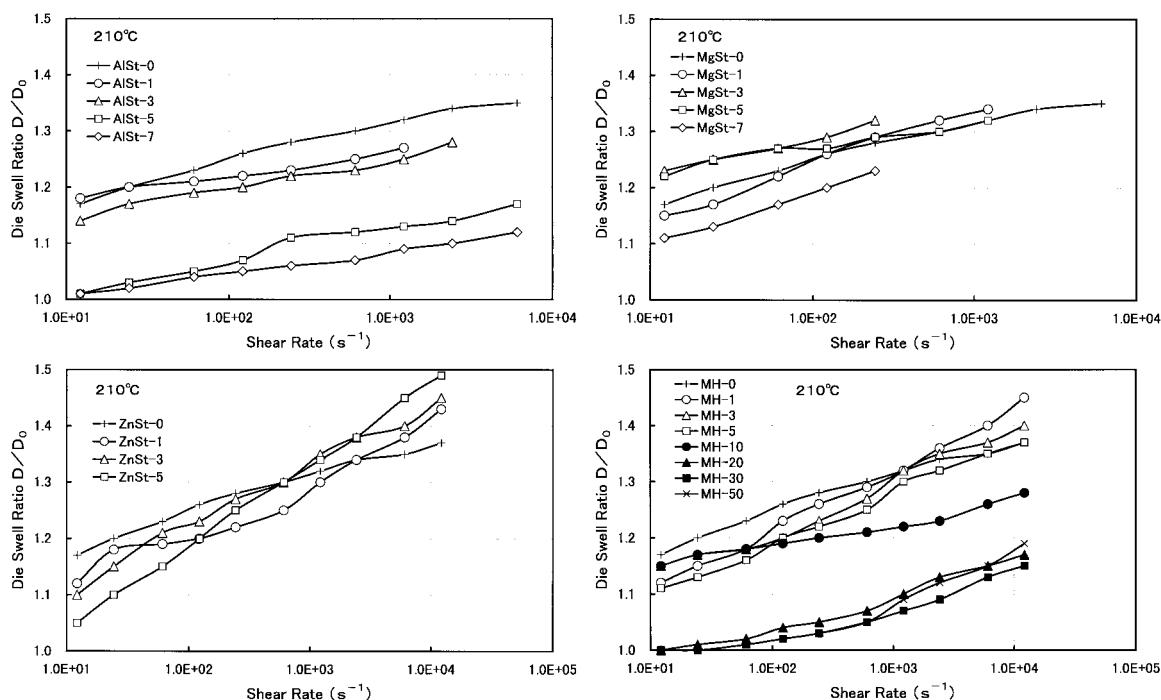


Figure 5 Comparison of flow curve among metal compounds.



**Figure 6** Change of die swell ratio,  $D/D_0$ , with shear rate for the (a) AlSt system, (b) MgSt system, (c) ZnSt system, and (d) MH system.

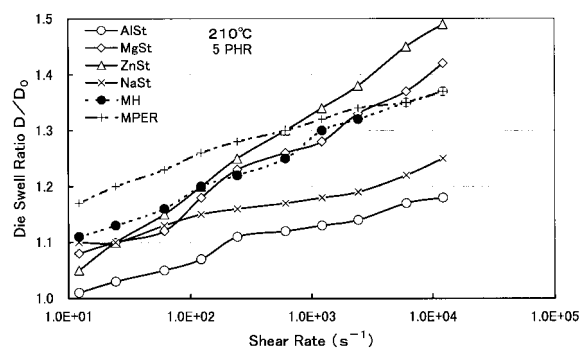
The fact that with increasing the degree of crosslinking the viscosity increases and the non-Newtonian behavior becomes notable is generally reported for peroxide-crosslinked various PEs,<sup>20,23–27</sup> peroxide-crosslinked PPs,<sup>23,28</sup> various radiation-crosslinked PEs,<sup>29–31</sup> radiation-crosslinked PPs,<sup>32,33</sup> various silane-crosslinked PEs,<sup>34</sup> and sulfur-crosslinked SBRs.<sup>35</sup> Accordingly, as for this point, it may be said that the ionically crosslinked MPEs in the present study show similar behaviors to those of general crosslinked polymers.

### Die swell

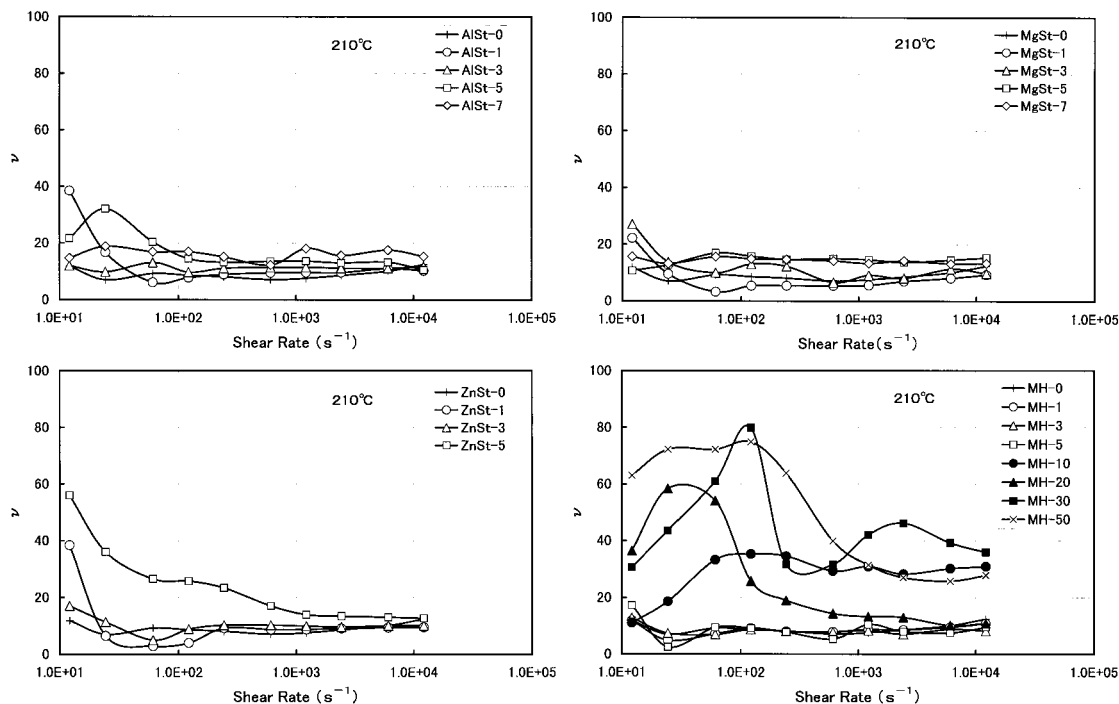
The changes in die swell ratio  $D/D_0$  with shear rate for the AlSt, MgSt, ZnSt, and MH series, are shown in Figures 6a, 6b, 6c, and 6d, respectively. The die swell ratio decreases with increasing the metal compound content for the AlSt series (Figure 6a) and for the MH series (Figure 6d). The decrease of die swell ratio is particularly notable at contents between 3 and 5 phr for the AlSt series and at contents between 10 and 20 phr for the MH series. The die swell ratio first increases and then decreases with increasing MgSt content (Figure 6b). For the ZnSt series (Figure 6c), the die swell ratio decreases at low shear rates and increases at high shear rates, and the shear rate change of the die swell ratio increases with increasing ZnSt content. A comparison of die swell ratio among metal compounds at a content of 5 phr is shown in Figure 7. By the addition of MgSt, ZnSt, or MH, the die swell ratio

tends to decrease at low shear rates and to increase at high shear rates. NaSt and AlSt show high die swell decreasing effects. The fact that NaSt shows a high die swell decreasing effect for its viscosity increasing effect is assumed to be due to the plasticizing or lubricating effect. Considering also the low viscosity of KSt-5 shown in Figure 5, it is assumed that univalent metal salts of stearic acid have a plasticizing or lubricating effect.

The die swell ratios of ionomers are higher than that of the base polymer without metal ions because of the apparent increase of molecular weight according to Weiss and Agarwal.<sup>8</sup> The ionomers are regarded as resins with low degrees of crosslinking. Contrary to this, Tang et al.<sup>25</sup> showed that the die swell ratio of a linear low-density polyethylene (LLDPE) crosslinked



**Figure 7** Comparison of change of die swell ratio,  $D/D_0$ , with shear rate among metal compounds.



**Figure 8** Change of end correction coefficient  $\nu$  with shear rate for the (a) AlSt system, (b) MgSt system, (c) ZnSt system, and (d) MH system.

with a peroxide of <0.8 wt % in a screw extruder decreases with increasing the peroxide content and hence with increasing the degree of crosslinking. Chung et al.<sup>36</sup> also reported that the die swell ratio of polypropylene (PP)/ethylene-propylene-dieneterpolymer (EPDM) thermoplastic vulcanizate (TPV) dynamically crosslinked with a phenolic resin decreases with increasing the degree of crosslinking. These peroxide-crosslinked compounds are regarded as resins with high degrees of crosslinking. From the results just presented, it is assumed that the die swell ratio of thermoplastic resin is increased by light crosslinking and is decreased by heavy crosslinking. For the ionically crosslinked MPERs in the present study, the competitive effect of the degree of crosslinking on die swell ratio just mentioned and/or other effects are assumed to give rise to differences in the effect of kind and content of metal compounds on die swell ratio and in the change of die swell ratio with shear rate.

### Extrudate appearance

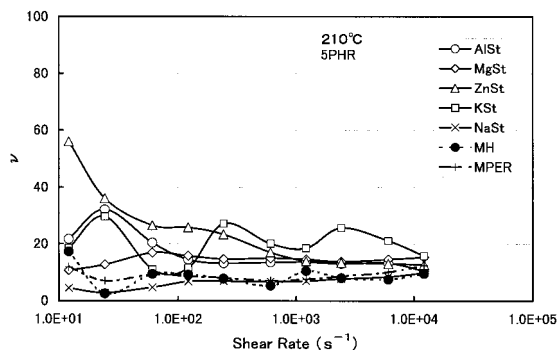
Although all the ionically crosslinked MPERs in the present study did not induce a melt fracture below maximum shear rate of  $1.2 \times 10^4 \text{ s}^{-1}$  of the present experiment, a smooth surface extrudate could not be obtained. Although the viscosities of MH-30 and MH-50 are higher than that of MP-MH, which is an ionically crosslinked compound produced by the filling of magnesium hydroxide (MH), in a previous study,<sup>37</sup> the extrudate surfaces of the former are rough

whereas that of the latter is smooth. Accordingly, it is assumed that the factor determining the extrudate nature is not the viscosity of whole compound but the viscosity of matrix resin itself. The composition of MP-MH is MPER 12.5 wt %, PER 12.5 wt %, PP 25 wt % and MH 50 wt %, and the content of MPER is 12.5 wt % of the whole and 25 wt % of the resin. Accordingly, the degree of crosslinking of the resin in MP-MH is assumed to be lower than those of the ionically crosslinked MPERs. Furthermore, it is also assumed that MH works as filler and increases not only the viscosity but also the smoothness of extrudate. Accordingly, it is necessary to dilute the compound for extrusion use with unmodified PER, PP, or fillers as well as to control the degree of crosslinking to improve the appearance of the extrudate. The addition of a lubricant may also be effective.

Otani<sup>38</sup> showed that an LLDPE crosslinked with peroxide does not flow by small segment groups as a movement unit but by large molecular groups. Accordingly, its extrudate shows a melt fracture-type irregular shape and has a rough surface. The ionically crosslinked compounds in the present study are assumed to be just in this aforementioned state.

### End correction coefficient

The changes in end correction coefficient  $\nu$  with shear rate for the AlSt, MgSt, ZnSt, and MH series, are shown in Figures 8a, 8b, 8c, and 8d, respectively. The  $\nu$  tends to increase with increasing metal compound



**Figure 9** Comparison of change of end correction coefficient  $\nu$  with shear rate among metal compounds.

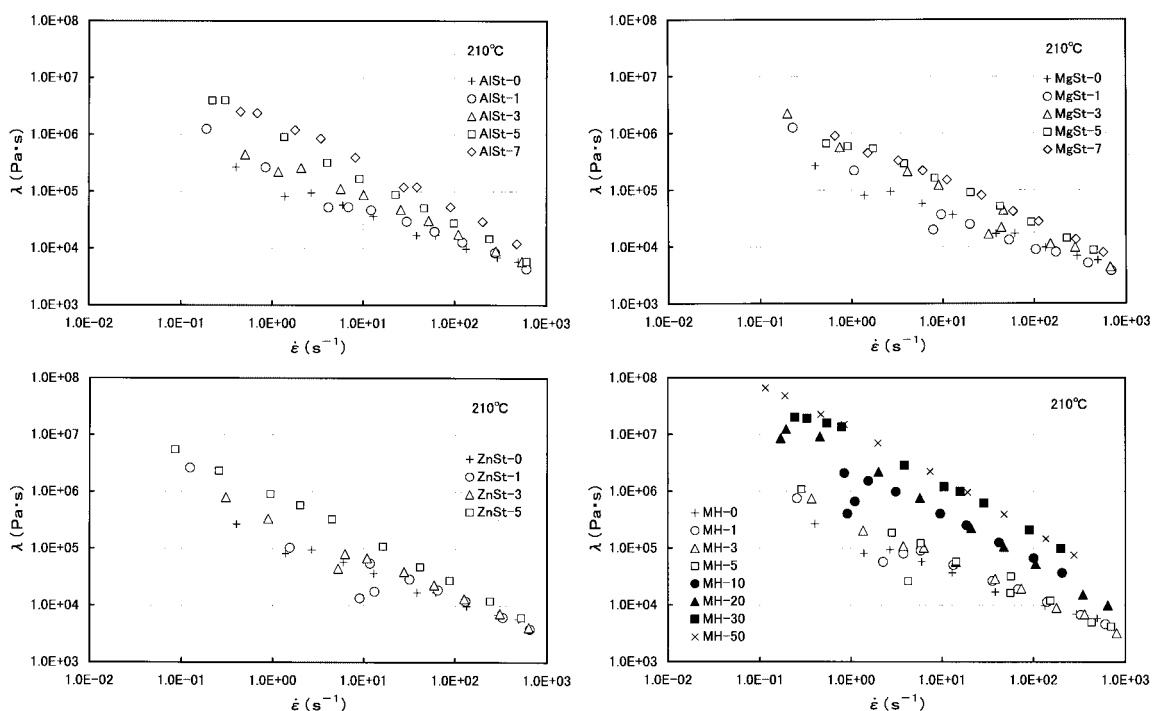
content for each metal compound. For the former three, the increases in  $\nu$  caused by the addition of the metal compounds at low shear rates are notable. For the MH series, the increase in  $\nu$  is particularly notable at contents  $>10$  phr. The  $\nu$  shows a maximum at shear rates of  $10\text{--}100\text{ s}^{-1}$ . A comparison of the end correction coefficient  $\nu$  among metal compounds at a content of 5 phr is shown in Figure 9. The  $\nu$  is increased by the addition of metal compounds and the increase is particularly notable for ZnSt and KSt. High  $\nu$  means that the pressure loss at the point where the shape of flow path changes by the contraction or divergence is larger than the pressure loss at the straight flow path.

Fujiyama<sup>23</sup> measured the capillary flow properties of an LDPE and a PP covalently crosslinked with a peroxide and found that  $\nu$  is largely increased by light

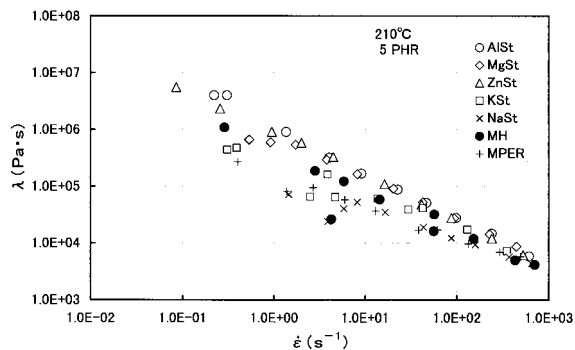
crosslinking and that the  $\nu$  values of samples with considerably high degrees of crosslinking are considerably high and scarcely change with shear rate, agreeing with the results of the present experiments. Inata et al.<sup>37</sup> showed that the  $\nu$  of an ionically crosslinked compound produced by the filling of MH, MP-MH, is considerably higher than that of an uncrosslinked compound, P-MH. Among the ionically crosslinked compounds in the present study, the increase of  $\nu$  is particularly notable at high MH contents in the MH series. The  $\nu$  of a polymer at constant shear rate has been reported to be decreased by the filling of particulates for a polychloroprene/glass beads system,<sup>39</sup> a natural rubber/carbon black system,<sup>40</sup> and a guayule rubber/carbon black system.<sup>41</sup> Accordingly, it is assumed for the MH series shown in Figure 8d there exists an increase in  $\nu$  caused by the ionic crosslinking effect that more than makes up for the decrease in  $\nu$  caused by the filling effect.

### Elongational viscosity

The changes of elongational viscosity  $\lambda$  with elongational strain rate  $\dot{\epsilon}$  for the AlSt, MgSt, ZnSt, and MH series are shown in Figures 10a, 10b, 10c, and 10d, respectively. The value of  $\lambda$  decreases with  $\dot{\epsilon}$  and shows a strain rate-softening behavior. The elongational viscosity tends to increase with increasing the metal compound content and almost corresponds to the shear viscosity, as shown in Figures 4 and 14



**Figure 10** Change of elongational viscosity  $\lambda$  with elongational strain rate  $\dot{\epsilon}$  for the (a) AlSt system, (b) MgSt system, (c) ZnSt system, and (d) MH system.



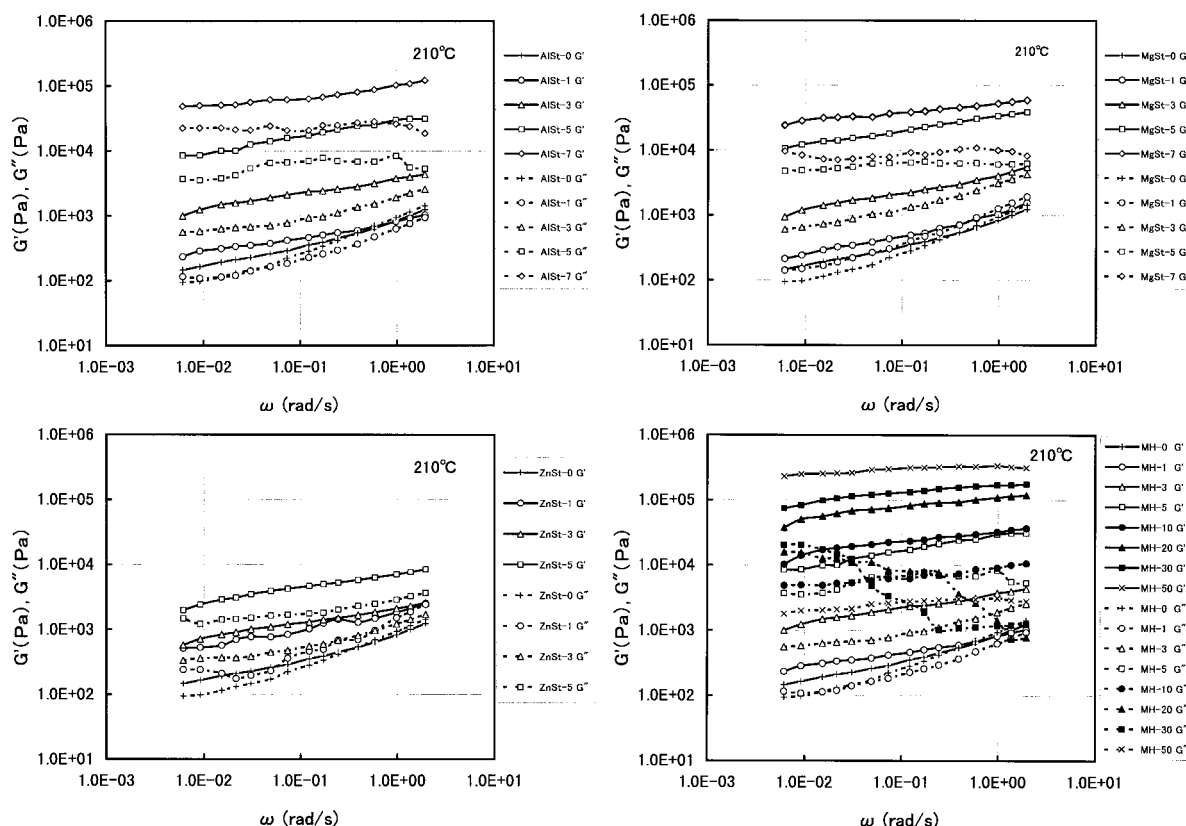
**Figure 11** Comparison of change of elongational viscosity  $\lambda$  with elongational strain rate  $\dot{\epsilon}$  among metal compounds.

(shown later). Namely, it may be said that a polymer with high shear viscosity also shows a high elongational viscosity. A comparison of elongational viscosity among the metal compounds at a content of 5 phr is shown in Figure 11. A compound with a high shear viscosity increasing effect also shows a high elongational viscosity increasing effect. From these results it may be said that the ionically crosslinked compounds in the present study are suitable for contour extrusion, big blow molding, pressure/vacuum forming, expansion molding, etc., because of their small drawdown.

Takahashi et al.<sup>12</sup> showed that the elongational viscosity and its strain-hardening of an ionomer increase with increasing the degree of ionic bonding, which is in agreement with the present experimental results. Isayev and Wan<sup>35</sup> showed that the entrance pressure loss  $P_0$  of a sulfur-crosslinked styrene-butadiene rubber (SBR) increases with increasing the state-of-cure. Applying Cogwell's method<sup>18</sup> to their result as in the present study,  $\lambda$  increases with increasing the degree of crosslinking, which is a trend that is in agreement with the present experimental results. The elongational viscosity  $\lambda$  and its strain rate-softening increase with increasing filler content because of the effect of particulate filling on the change of elongational viscosity  $\lambda$  with elongational strain rate  $\dot{\epsilon}$ , for the HDPE/glass fiber system,<sup>42</sup> the PP/glass fiber system,<sup>43,44</sup> the polystyrene/carbon black, titanium dioxide, and calcium carbonate systems,<sup>45,46</sup> the HDPE/mica system,<sup>47</sup> and the polystyrene/carbon black system.<sup>48</sup> That  $\lambda$  largely increases with increasing MH content in the MH series, shown in Figure 10d, is assumed to be due to a synergism of crosslinking and filling effects by MH.

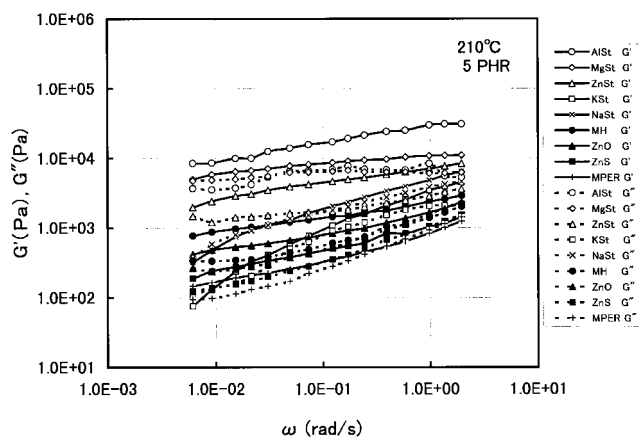
**Dynamic viscoelasticity**

The dynamic viscoelasticities [storage modulus  $G'(\omega)$ , loss modulus  $G''(\omega)$ ] of the AlSt, MgSt, ZnSt, and MH



**Figure 12** Change of storage modulus  $G'$  and loss modulus  $G''$  with angular frequency  $\omega$  for the (a) AlSt system, (b) MgSt system, (c) ZnSt system, and (d) MH system.





**Figure 13** Comparison of change of storage modulus  $G'$  and loss modulus  $G''$  with angular frequency  $\omega$  among metal compounds.

series, are shown in Figures 12a, 12b, 12c, and 12d, respectively. For all the samples, the dynamic viscoelasticities increase with increasing metal compound content. The changes of both  $G'$  and  $G''$  with angular frequency  $\omega$  are small and show rubber elasticity. This tendency is the more notable at the higher metal compound content. Furthermore,  $G'$  tends to be higher than  $G''$  for all the samples including the base resin MPER, and this tendency increases with increasing the metal compound content. The fact that  $G'$  drops at high  $\omega$  at MH contents  $>5$  phr, shown in Figure 12d, is assumed to be due to the hardening-type hysteresis effect. A comparison of dynamic viscoelasticities among metal compounds is shown in Figure 13. A metal compound with a higher viscosity increasing effect also shows a higher increasing effect of dynamic viscoelasticities. The KSt and NaSt series show steep slopes of  $G'$  at low  $\omega$ , which also indicates they have a plasticizing or lubricating effect.

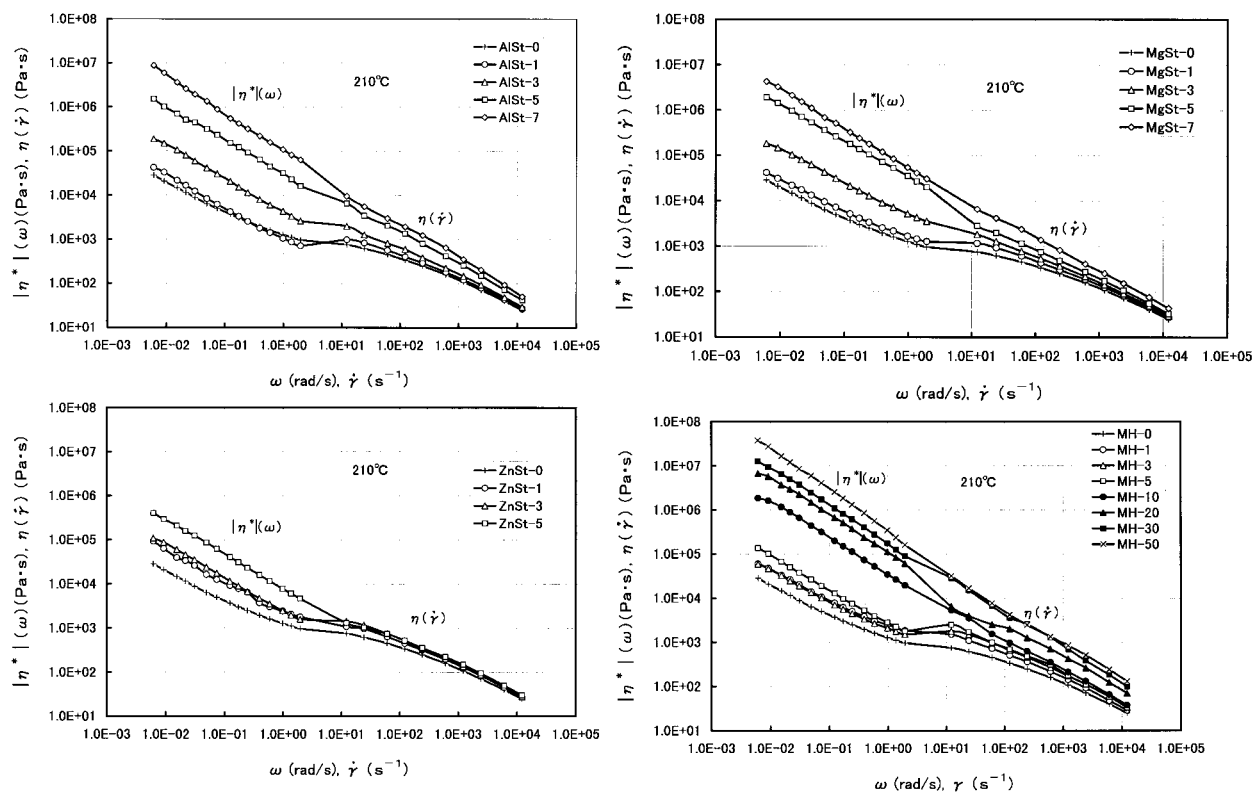
Increasing the degree of crosslinking results in an increase and flattening of the storage modulus of a maleated PP that is covalently crosslinked with ethylene glycol according to Ishigure et al.<sup>49</sup> This relationship is also reported for various peroxide-crosslinked PEs,<sup>50–52</sup> ethylene-hexene-diene terpolymer,<sup>53</sup> electron beam-crosslinked LLDPE,<sup>54</sup> silane-crosslinked polybutadiene,<sup>55</sup> siloxane-crosslinked polystyrene,<sup>56</sup> and PP/EPDM TPV dynamically crosslinked with a phenolic resin,<sup>36</sup> and is therefore considered to be a general fact. As for the rubbery plateau modulus, Pechhold et al.<sup>57</sup> report that although the crosslinking of a polyisoprene continues to increase with increasing the radiation dose in the case of electron beam crosslinking, it tends to level off above a peroxide content in the case of peroxide crosslinking. The tendency that the storage modulus  $G'$  is higher than the loss modulus  $G''$  is also found for ionomers with high degrees of ionic bonding<sup>15,58</sup> and covalently highly

crosslinked polymers.<sup>36,51</sup> From facts such as the flattening of  $G'$  and  $G'$  being higher than  $G''$ , the ionically crosslinked compounds in the present experiment are assumed to be crosslinked from lightly to heavily.

Flow curves of the AlSt, MgSt, ZnSt, and MH series, are shown in Figures 14a, 14b, 14c, and 14d, respectively. These curves were determined in a wide shear rate range as the absolute values of complex viscosities  $|\eta^*(\omega)|$  from dynamic viscoelasticities and as the steady state viscosities  $\eta(\dot{\gamma})$  from capillary flow properties. That the absolute value of complex viscosity  $|\eta^*(\omega)|$  and the steady state viscosity  $\eta(\dot{\gamma})$  are equivalent functions is known as the Cox-Merz's empirical law,<sup>11</sup> which is widely applied to evaluate the flow properties of polymer melts. The viscosity continues to increase with decreasing shear rate for all the samples. This tendency is the more notable for the sample with the higher content of metal compound and with the higher degree of crosslinking, and the viscosity enhancement is higher at the lower shear rate. The viscosities of samples with low metal compound contents tend to show a Newtonian flow behavior and after that they return to a non-Newtonian flow behavior with decreasing shear rate. A comparison of flow curve in wide shear rate range among metal compounds at a metal compound content of 5 phr is shown in Figure 15. Although the viscosity increases straightly with decreasing shear rate for the series of metal salts of stearic acid, it shows a slump of Newtonian flow tendency at intermediate shear rates for the series of other metal compounds. The viscosity increasing effect at low shear rates is in the order AlSt  $>$  MgSt  $>$  ZnSt  $>$  NaSt  $>$  KSt  $>$  MH  $>$  ZnO  $>$  ZnS  $>$  MPER. Namely, the viscosity increasing effect of the metal salt of stearic acid is higher for the larger ionic charge and the viscosity increasing effects of other compounds are lower than those of the metal salts of stearic acid.

That the viscosity is increased by the crosslinking and the increase is more notable at lower shear rate is generally reported for various peroxide-crosslinked PEs,<sup>20,23–27,51,52,58–60</sup> peroxide-crosslinked PPs,<sup>23,38</sup> peroxide- or sulfur-crosslinked PP/EPDM,<sup>50</sup> various radiation-crosslinked PEs,<sup>29–31</sup> radiation-crosslinked PPs,<sup>32,33</sup> various silane-crosslinked PEs,<sup>34,61</sup> siloxane-crosslinked PE,<sup>56</sup> sulfur-crosslinked SBRs,<sup>35</sup> and PP/EPDM TPV dynamically crosslinked with a phenolic resin,<sup>36</sup> and is therefore considered to be a general fact. Accordingly, as for this point, it may be said that the ionically crosslinked MPERs in the present study show similar behaviors to those of general crosslinked polymers.

According to the results just presented, it may be said that the ionically crosslinked compounds show very high viscosities at low shear rates under which a drawdown of shaped molten article occurs. However, the viscosities scarcely differ from those of usual res-



**Figure 14** Change of absolute value of complex viscosity,  $|\eta^*(\omega)|$ , and steady-state viscosity,  $\eta(\dot{\gamma})$ , with angular frequency,  $\omega$ , and shear rate  $\dot{\gamma}$  for the (a) AlSt system, (b) MgSt system, (c) ZnSt system, and (d) MH system.

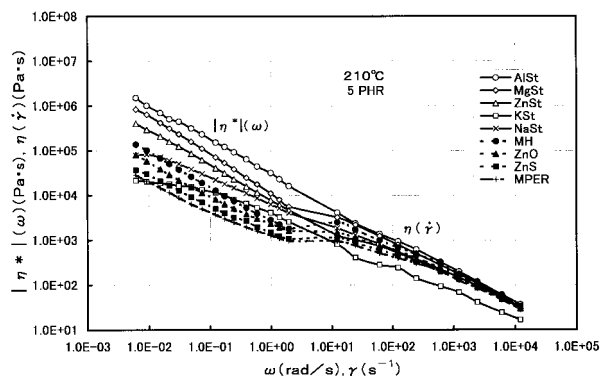
ins at high shear rates that a molten resin encounters at extrusion and injection molding. Accordingly, it is assumed that the ionically crosslinked compounds in the present study are suitable for contour extrusion, big blow molding, pressure/vacuum forming, expansion molding, etc., because of their small drawdown.

## CONCLUSIONS

To study the ionic crosslinking of maleated PER (MPER), metal compounds aluminum stearate (AlSt),

magnesium stearate (MgSt), calcium stearate (CaSt), zinc stearate (ZnSt), potassium stearate (KSt), sodium stearate (NaSt), magnesium hydroxide (MH), zinc oxide (ZnO), and zinc sulfide (ZnS) were melt-mixed into the MPER, and crosslinked compounds were obtained. The rheological properties of the compounds were measured and their melt processabilities were evaluated.

1. The shear viscosity increases with increasing metal compound content and the increase is higher at the lower shear rate. The viscosity increasing effect of metal salts of stearic acid is higher for the larger ionic charge. Although the KSt compound shows a higher viscosity than MPER at low shear rates, it shows a lower viscosity than MPER at high shear rates of actual processing. The viscosity increasing effects of other compounds are lower than those of the metal salts of stearic acid.
2. The elongational viscosity shows similar behaviors to the shear viscosity.
3. The die swell ratio monotonously decreases with increasing the metal compound content for the AlSt and MH series. It first increases and then decreases with increasing MgSt content and scarcely depends on ZnSt content. Compared at a metal compound content of 5 phr, the die swell



**Figure 15** Comparison of change of absolute value of complex viscosity,  $|\eta^*(\omega)|$ , and steady-state viscosity,  $\eta(\dot{\gamma})$ , with angular frequency  $\omega$  and shear rate  $\dot{\gamma}$  among metal compounds.

ratio is in the order MPER, ZnSt, MgSt, MH > NaSt > AlSt.

4. The changes of dynamic viscoelastic moduli with angular frequency are easy and the compounds show rubber elasticity. This tendency is more notable at the higher metal compound content and for the higher degree of crosslinking. There are cases where the Lissajous's figures of stress and strain show reverse rotations at high angular frequencies at high MH contents and the viscosity component could not be measured. This phenomenon is assumed to be due to strain-hardening-type hysteresis and is more notable at the higher MH content and angular frequency.
5. The extrudate surfaces of the ionically crosslinked compounds are not as smooth as that of unmodified PER or PP.
6. The degree of ionic crosslinking can be freely controlled by adjusting the kind and content of metal compound.

From these results, we assume that these ionically crosslinked compounds show ideal flow processabilities except for extrudate appearance. To improve the appearance, it is necessary to dilute the compound with unmodified PER, PP, or fillers. Furthermore, to make more clear the characteristics of flow processabilities of the ionically crosslinked compounds in the present study, a comparison of the rheological properties of the compounds in the present study with those of other thermoplastic elastomers is still necessary.

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