

Rheological Properties of Ionically and Covalently Crosslinked Polypropylene-Type Thermoplastic Elastomers

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ABSTRACT: Maleic anhydride was grafted onto a polypropylene-type thermoplastic elastomer PER by reactive processing with a screw extruder, and a maleated PER (MPER) was prepared. Aiming at ionic crosslinking, magnesium 12-hydroxy stearate (MgStOH), zinc oxide (ZnO), and zinc sulfide (ZnS), and aiming at covalent crosslinking, melamine as an amino compound, and Epocizer and GRYCI-ALE as epoxy compounds, were added to the MPER, melt-mixed by use of the 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. The degree of crosslinking was in the order of epoxy compounds > MgStOH > melamine > ZnO, ZnS > MPER (blank). In the case of the compound with MgStOH of a moderately high degree of crosslinking, the non-Newtonian behavior is remarkable and the die swell ratio is low and suitable for extrusion. However, in the case of compounds with epoxy compounds of an excessive degree of crosslinking, fine extrudate cannot be obtained due to the lack of fusion and the control of degree of crosslinking is necessary. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 762–773, 2002

Key words: elastomers; reactive processing; ionomers; crosslinking; rheology

INTRODUCTION

It is well known that the thermal resistance, durability, abrasion resistance, chemical resistance, etc., of a thermoplastic resin are improved by crosslinking. Polypropylene (PP) is crosslinked by peroxides, azides, silanes, radiations, heat, ultraviolet, and ionic bonding, etc.^{1,2} Among these crosslinking methods, radiation crosslinking and silane crosslinking are commercially practiced. For the peroxide crosslinking and radiation crosslinking of PP, the addition of a multifunctional auxiliary is necessary since the chain scis-

sion at the β -site easily occurs for PP. In terms of an ionic crosslinking method of PP, two methods are known: one uses copolymers of propylene and acidic monomers, and the other uses PPs grafted with acidic monomers. Several patents^{3–5} concerned with the latter method have been applied for since the application of Rees' patent,⁶ part of which is concerned with ionomers. As examples in these patents, ionic crosslinking methods are shown in which polyethylenes (PEs) and PPs are grafted with carboxylic acids such as acrylic acid, fumaric acid, and maleic anhydride, and then the acids are neutralized with metal compounds such as sodium hydroxide and zinc acetate. Rees describes in his patent that ionomers show a remarkable non-Newtonian flow, which is caused by the dissociation of ionic bonds by the action of shear stress. Weiss and Agarwal⁷ studied the

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crystallinity, rheological properties, and mechanical properties of ionically crosslinked PPs prepared by grafting acrylic acid and then neutralizing with sodium hydroxide and zinc acetate. De et al.⁸⁻¹² recently ionically crosslinked maleated or sulfonated ethylene-propylene-dieneterpolymer (EPDM), PP, and high-density polyethylene (HDPE) with zinc oxide and zinc stearate, and studied the ionic crosslinking structure, mechanical properties, and rheological properties of the simple bodies and their blends. Concerned not with ionic crosslinking but with covalent crosslinking, Ishigure¹³ recently prepared covalently crosslinked PPs by melt-mixing a maleated PP with ethylene glycol, and studied the reaction behaviors, rheological properties, and morphology.

The polypropylene-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 a large ethylene-propylene copolymer (EPR) part.¹⁴⁻¹⁶ While the usual block PP contains 10-30 wt % of EPR, PER contains 50-90 wt % of EPR. Since PER contains much EPR, a good deal of carboxyl group such as maleic anhydride can be easily grafted.¹⁷ In the previous paper,¹⁸ the authors reported that a maleated PER (MPER) filled with magnesium hydroxide, a nonhalogen-type flame retardant, shows rheological properties as an ionically crosslinking thermoplastic elastomer. It is considered that the ionic crosslinking by maleic anhydride groups is possible by use not only of magnesium hydroxide but also of other metal compounds. Furthermore, covalent crosslinking is assumed to be possible by using compounds with more than two functional groups such as amino and epoxy groups that react with acid.

In the present study in order to research the crosslinker for MPER, magnesium 12-hydroxy stearate (MgStOH), zinc oxide (ZnO), and zinc sulfide (ZnS) were chosen for ionic crosslinking, and melamine as amino compound and Epocizer and GRYCI-ALE as epoxy compounds were chosen for covalent crosslinking. MPER was added with 5 weight parts (phr) of the crosslinkers, melt-mixed at 220°C by use of a screw extruder, and pelletized by a pelletizer. Rheological properties of the pellets were measured and the melt processability was evaluated.

Rheological properties of crosslinked thermoplastic polymers are reported for covalent crosslinkings such as peroxide crosslinking,¹⁹⁻³⁸ radiation crosslinking,^{1,27,39-45} silane crosslink-

ing,⁴⁶⁻⁴⁸ sulfur crosslinking,^{28,49} and other crosslinking,^{13,50,51} and for ionic crosslinking.^{7,8,11,12,52-73}

EXPERIMENTAL

Samples

Table I shows the characteristics of samples. The raw MPER was prepared as follows: To 100 phr ultrahigh molecular weight PER was added 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 by use of a 45 mm ϕ 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-cut with a pelletizer. The pellets were dried in a constant temperature drying oven at 105°C for 12 h and an MPER with a melt flow index (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 5 phr of the crosslinkers were thoroughly mixed in a tumbler, melt-mixed by use of the extruder at a maximum cylinder temperature of 220°C and a screw rotation speed of 250 rpm, and pelletized by strand-cut with the pelletizer. The crosslinker used for EP-1, Epocizer W-109EL, was manufactured by Japan Reichhold Chemicals, Inc., and was an epoxy compound with a viscosity (25°C, Gardner) of *U*, an acid value of 0.2, an iodine value of 3.5, and an oxirane oxygen of 9.1%. The crosslinker for EP-2, GLYSI-ALE PP-300P, was manufactured by Sanyo Chemical Industries, Ltd., and was an epoxy compound of glycidyl-etherificated polyether with a viscosity of 44 mPa s and an epoxy equivalent of 296 g/eq. Other crosslinkers were special grade reagents manufactured by Wako Pure Chemical Industries, Ltd.

The characteristic values of the crosslinked compounds were measured as follows: MFI was measured at 230°C under a load of 2160 g according to the JIS K7210. 5 g of pellets was 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 gel fraction. Other characteristics in Table I were measured with specimens injection-molded at a cylinder temperature of

Table I Recipes and Characteristics of Samples

Sample name	MPER	MgStOH	ZnO	ZnS	Melamine	EP-1	EP-2
MPER content (phr)	100	100	100	100	100	100	100
Crosslinking agent Name	—	Magnesium 12-hydroxy stearate	Zinc oxide	Zinc sulfide	Melamine	Epoxy compound	Epoxy compound
Grade name	—	Special grade reagent (Wako Pure Chemical Industries, Ltd. Osaka)	Special grade reagent (Wako Pure Chemical Industries, Ltd. Osaka)	Special grade reagent (Wako Pure Chemical Industries, Ltd. Osaka)	Special grade reagent (Wako Pure Chemical Industries, Ltd. Osaka)	Epocizer W-109EL	GLYCI-ALE PP-300P
Manufacturer	—	(Wako Pure Chemical Industries, Ltd. Osaka)	(Wako Pure Chemical Industries, Ltd. Osaka)	(Wako Pure Chemical Industries, Ltd. Osaka)	(Wako Pure Chemical Industries, Ltd. Osaka)	Japan Reichhold Chemicals, Inc. Tokyo	Sanyo Chemical Industries, Ltd. Tokyo
Content (phr)	—	5	5	5	5	5	5
Density (g/cm ³)	0.883	0.884	0.917	0.915	0.889	0.884	0.887
MFI (g/10 min)	13.4	0.06	12.4	13.7	3.15	<0.01	<0.01
Gel fraction (wt %)	11.5	51.6	26.0	21.5	25.3	58.2	41.3
Tensile strength (MPa)	6.8	11.1	7.4	7.8	9.6	12.7	10.7
Tensile elongation (%)	730	510	610	650	640	350	330
Flexural modulus (MPa)	16	22	19	21	19	22	21
Durometer hardness (JIS A)	65	72	67	68	74	70	68
Elongation set (%)	—	16	—	—	12	12	15
Compression set (%)	—	38	—	—	42	35	32

220°C and a mold temperature of 40°C by use of an injection molding machine J50E-P type (Nihon Seikoshu, Japan, clamping force: 50T). Tensile strength and elongation were measured according to the JIS K6301, flexural modulus according to the JIS K7203, durometer hardness according to the JIS K7215, tensile set and compression set according to the JIS K6301, respectively. Density was measured by use of an electronic gravimeter.

By addition of the crosslinkers, the MFI is lowered and the gel fraction is increased, which indicates an occurrence of crosslinking. With an increase of crosslinking, the tensile strength, modulus, and hardness increase, and the tensile elongation and permanent sets decrease. The degree of these tendencies is particularly remarkable for MgStOH, EP-1, and EP-2. The MFI is in the order of MPER > ZnO, ZnS > Melamine > MgStOH > EP-1, EP-2, and the gel fraction is the inverse order.

Measurements

Capillary Flow Properties

Capillary flow properties were measured with a capillary rheometer Capirograph 1B type (Toyo Measurement Instruments Co. Ltd., Japan). The flow curve, die swell ratio, and melt fracture behaviors were measured at temperatures of 190, 230, and 270°C by use of a die with a capillary length L of 20 mm and a capillary diameter D of 1 mm. The end correction coefficient ν and entrance pressure loss P_0 were measured at 230°C by use of dies with a diameter D of 1 mm and lengths L of 20, 10, and 5 mm. The change of elongational viscosity λ with elongational strain rate $\dot{\epsilon}$ was calculated from P_0 according to Cogswell's method.⁷⁴

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 Co., Ltd., Japan).

RESULTS AND DISCUSSION

Viscosity (Flow Curve)

Figure 1 exemplifies the flow curves of EP-1 sample at various temperatures. The viscosity de-

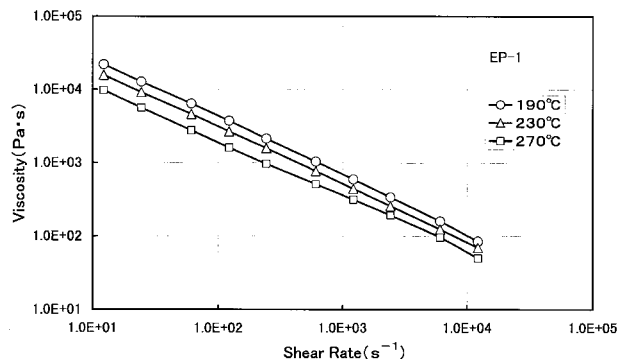


Figure 1 Flow curves of EP-1 at various temperatures.

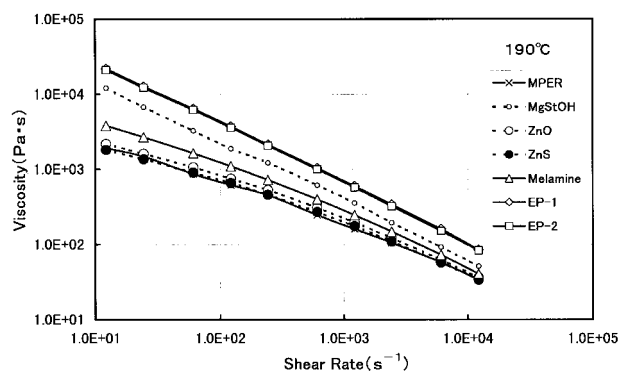
creases with increasing temperature and shear rate.

Figures 2(a)–(c) show the comparisons of flow curves of various samples at various temperatures. While the flow curves of samples with low viscosities and low degrees of crosslinking approach the Newtonian flow at low shear rates, those of samples with high viscosities and high degrees of crosslinking continue to increase also at low shear rates. The flow curves of MPER and ZnS samples with low viscosities turn to rise again at low shear rates at high temperature (270°C). Since the viscosity of ZnO sample increased with time at temperatures above 230°C, it could not be measured. This is assumed to be because the crosslinking reaction did not proceed sufficiently at the melt-mixing time. Accordingly, the flow curve of ZnO sample could be measured only at temperatures of 190 and 210°C. The viscosity is in the order of EP-1, EP-2 \gg MgStOH > Melamine > ZnO, ZnS, MPER, in the same order as that of the gel fraction and in almost inverse order of the MFI.

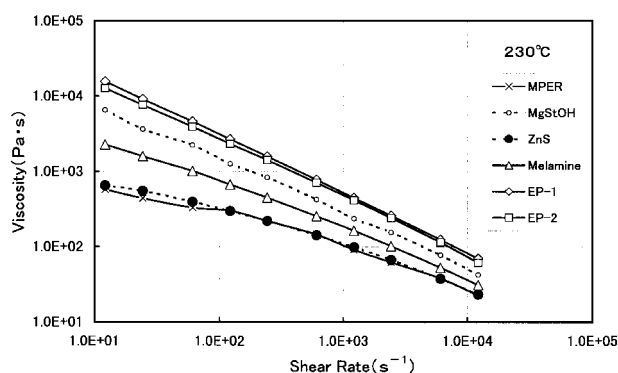
That with increasing the degree of crosslinking the viscosity increases and the non-Newtonian behavior becomes notable is generally reported for peroxide crosslinked various PEs,^{20,24–26,29,30} peroxide crosslinked PPs,^{29,34} radiation crosslinked various PEs,^{41–43} radiation crosslinked PPs,^{1,45} silane crosslinked various PEs,⁴⁸ and sulfur crosslinked styrene-butadiene rubbers (SBRs).⁴⁹ In accordance with this point, it may be said that the ionically and covalently crosslinked MPERs in the present study show similar behaviors to those of general crosslinked polymers.

The MgStOH sample with a considerably high degree of crosslinking did not give a smooth extrudate due to insufficient fusion. Although the

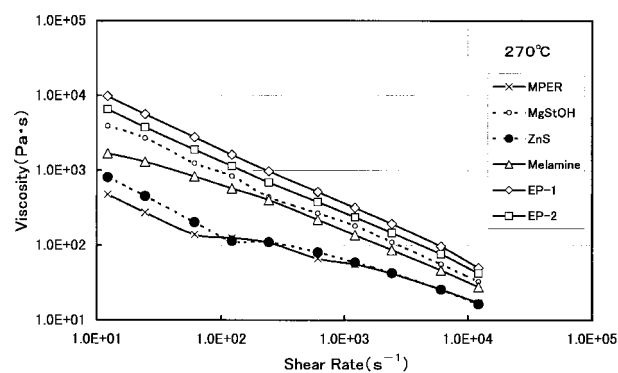
viscosity of MgStOH is similar to that of MP-MH, which is an ionically crosslinked compound by the filling of magnesium hydroxide (MH) in a previous study,¹⁸ the extrudate surface of the former is rough while that of the latter is smooth. Accordingly, it is assumed that the factor determining the extrudate nature is not the viscosity of whole



(a)



(b)



(c)

Figure 2 (a) Comparison of flow curves among samples at 190°C. (b) Comparison of flow curves among samples at 230°C. (c) Comparison of flow curves among samples at 270°C.

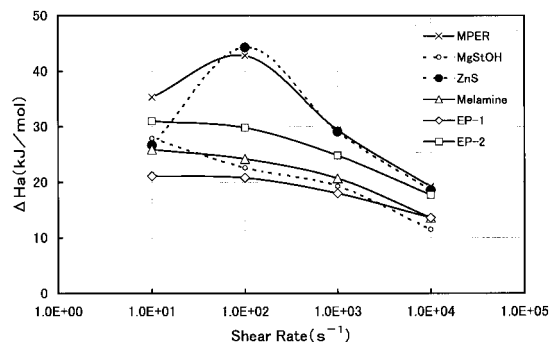


Figure 3 Comparison of flow activation energy ΔHa among samples.

compound but the viscosity of the 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 lower than that of MgStOH. Furthermore, it is also assumed that MH works as filler and increases not only the viscosity but also the smoothness of extrudate.

EP-1 and EP-2, which are assumed to be covalently crosslinked compounds with further enhanced crosslinkings, did not give a continuous extrudate and the extrudate crumbled into decay at high shear rates at low temperatures. Accordingly, the compound for extrusion use must be controlled in the degree of crosslinking.

Otani²³ showed that a linear low-density polyethylene (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 the surface is rough. The MgStOH sample with high degree of ionic crosslinking in the present study is assumed to be just in the above-mentioned state. It is also assumed that EP-1 and EP-2 with further high degrees of covalent crosslinking are in further enhanced states of the above-mentioned state.

Figure 3 shows the change of flow activation energy at constant shear rate, ΔHa , which is a measure of temperature dependence of viscosity, with shear rate. ΔHa 's of compounds with high degrees of crosslinking decrease with increasing shear rate. Compounds with low degrees of crosslinking such as MPER and ZnS show peaks around 10^2 s^{-1} and show high values of ΔHa . Although ΔHa does not always order in the order of degree of crosslinking, it generally decreases with increasing crosslinking.

That ΔH_a is decreased by crosslinking is reported for peroxide crosslinked PEs^{21,29,30} and X-ray crosslinked PE,⁴² and considered to be a general fact. Concerning this point, the crosslinked compounds in the present study also show similar behavior to those of other general crosslinked polymers.

A low flow activation energy of a polymer means small changes of viscosity and other rheological properties at temperature change, and hence means small changes of processing behaviors at the change of processing conditions (processing temperature). This finally means good stability at disturbances at processing. Accordingly, it may be said that the crosslinked compounds in the present study are stable at processing.

Die Swell

A phenomenon that the extrudate of a polymer melt swells at the die exit is called the die swell or Barus effect. Its cause is the recovery at the die exit of melt orientation, which has been formed at the die entrance where the polymer melt enters from a flow path with a larger cross section into the flow path with a smaller cross section. The die swell is generally evaluated by the ratio of the extrudate diameter D to the bore diameter of the die D_0 , D/D_0 , which is called die swell ratio or ME (Memory Effect) value. Owing to the die swell, the diameter of extrudate becomes larger than the bore diameter of rod die, the diameter and thickness of extrudate become larger than those of tube die, the side of extrudate swells and rounds in cases of profile dies such as triangular and cross-shaped dies. Accordingly, the die swell is an important technical factor in extrusion particularly in contour extrusion, and a polymer with a

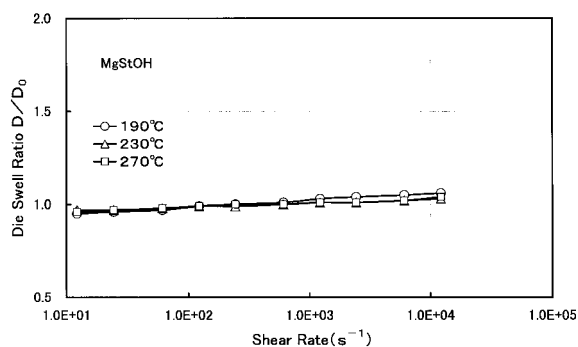
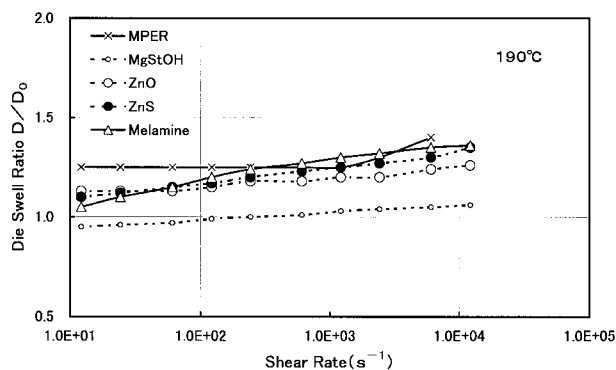
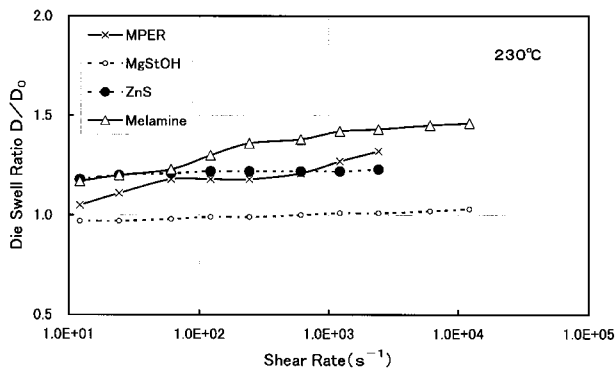


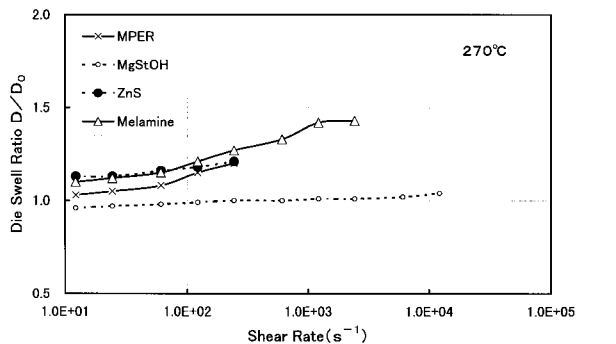
Figure 4 Change of die swell ratio D/D_0 of MgStOH with shear rate at various temperatures.



(a)



(b)



(c)

Figure 5 (a) Comparison of die swell ratio D/D_0 among samples at 190°C. (b) Comparison of die swell ratio D/D_0 among samples at 230°C. (c) Comparison of die swell ratio D/D_0 among samples at 270°C.

die swell ratio near unity gives extrudate with a shape true to the shape of the die cross section and is favorable.

Figure 4 shows change of die swell ratio D/D_0 with shear rate at various temperatures for MgStOH sample as an example. The die swell ratio is about 1.0 and very low. Its changes with temperature and shear rate are also very small and stable.

Figures 5(a)–(c) show comparisons of die swell ratio D/D_0 among samples whose extrudates could be taken at various temperatures. The die swell ratio generally decreases with increasing the degree of crosslinking. EP-1 and EP-2 samples whose continuous extrudate could not be obtained also show die swell ratios of about 1.0.

Although, according to Weiss and Agarwal,⁷ the die swell ratios of ionomers are higher than that of the base polymer without metal ions due to the apparent increase of molecular weight, the die swell ratios of ionically and covalently crosslinked compounds in the present study are decreased by high degree of crosslinking. This is assumed to be because the degrees of crosslinking of the highly crosslinked compounds are higher than those of the ionomers. Tang et al.²⁵ showed that the die swell ratio of an LLDPE crosslinked with a peroxide of below 0.8 wt % in a screw extruder decreases with increasing the peroxide content, which is the same tendency as that of the crosslinked compounds in the present study. Chung et al.⁵¹ also reported that the die swell ratio of PP/EPDM thermoplastic vulcanizate (TPV) dynamically crosslinked with a phenolic resin decreases with increasing the degree of crosslinking, agreeing with the present experimental results. From the above, it is assumed that the die swell ratio of thermoplastic resin is increased by light crosslinking and is decreased by heavy crosslinking. The die swell ratios of ZnS and Melamine samples with low degrees of crosslinking at 230 and 270°C in the present experiment are seen in a sense to be higher than that of the base resin MPER.

End Correction Coefficient

In the case where the shape of flow path in a processing machine changes by contraction or di-

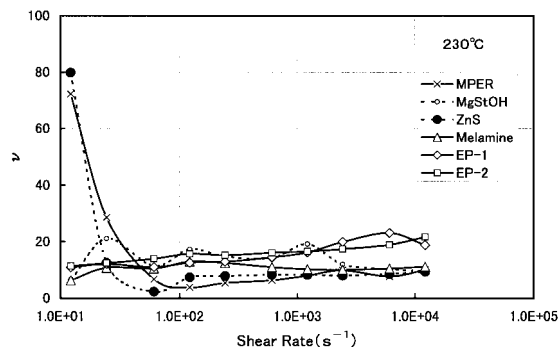


Figure 6 Comparison of end correction coefficient ν among samples.

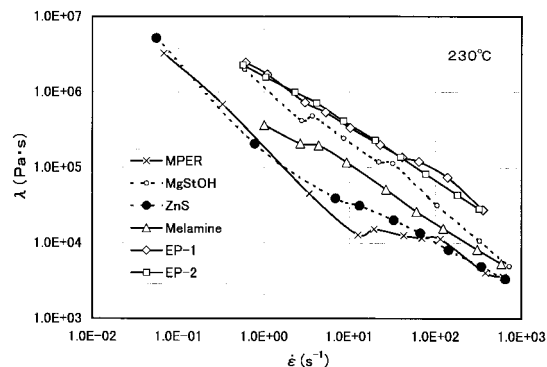


Figure 7 Comparison of elongational viscosity λ among samples.

vergence, a pressure drop occurs due to the change of flow lines. This is the entrance pressure loss P_0 and its nondimensional measure is the end correction coefficient ν . Namely, high ν means that the pressure loss at the point where the shape of flow path changes by the contraction or divergence is larger as opposed to the pressure loss at the straight flow path.

Figure 6 shows the comparison among samples of change of end correction coefficient ν with shear rate. The ν s of general resins tend to increase with increasing shear rate. Although the samples except for MPER and ZnS, which are assumed to crosslink lightly, show such tendency, ν s of MPER and ZnS increase largely at low shear rates. The ν s of samples with high degrees of crosslinking show high values in the wide shear rate range and scarcely change with shear rate.

Fujiyama²⁹ measured the capillary flow properties of a low-density polyethylene (LDPE) and a PP covalently crosslinked with a peroxide and found that ν is largely increased by light crosslinking and that ν s of samples with considerably high degrees of crosslinking show considerably high values and scarcely change with shear rate. It is assumed that MPER and ZnS, which are lightly crosslinked as shown later, correspond to the case of light crosslinking above and MgStOH, EP-1, and EP-2 correspond to the case of heavy crosslinking. Tang et al.²⁵ report that ν of an LLDPE covalently crosslinked with a peroxide decreases with increasing crosslinking, disagreeing with the present experimental results, whose reason is not known.

Elongational Viscosity

In polymer processing, there are many cases where an elongational flow participates: spinning,

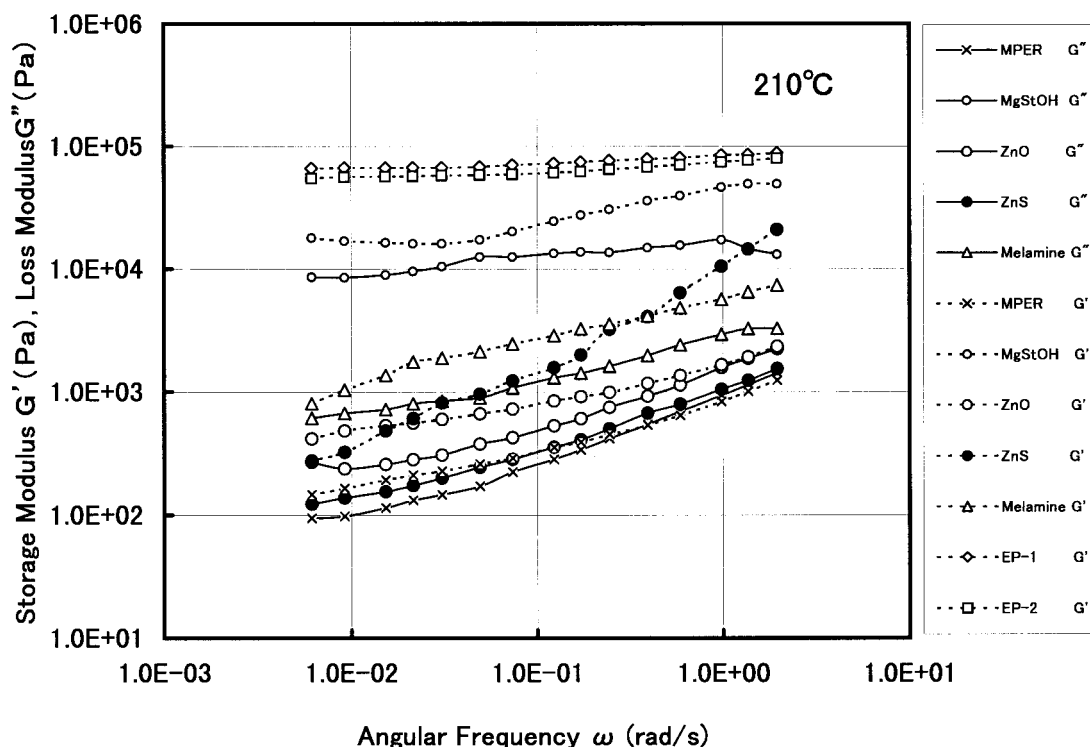


Figure 8 Comparison of storage modulus G' and loss modulus G'' among samples.

T-die cast film extrusion, extrusion lamination, inflation film extrusion, blow molding, pressure/vacuum forming, expansion molding, contraction flow into die, etc. Processabilities in such cases are usually evaluated by elongational viscosity. The elongational viscosity is measured under constant elongational stress and constant elongational strain rate, etc., and expressed against time, strain, strain rate, etc. In the present study, according to Cogswell's method,⁷⁴ the elongational viscosity as a function of elongational strain rate was calculated from the entrance pressure loss P_0 obtained by measurement of capillary flow properties.

Figure 7 shows the change of elongational viscosity λ with elongational strain rate $\dot{\epsilon}$. The λ decreases with $\dot{\epsilon}$ and shows a strain rate softening behavior. The elongational viscosity tends to be the higher as the degree of crosslinking is the higher and almost corresponds to the shear viscosity as shown in Figures 2(a)–(c) and Figure 9 shown later. Namely, it may be said that a polymer with high shear viscosity also shows a high elongational viscosity. MP-MH in the previous paper,¹⁸ which is a compound ionically crosslinked with MH, shows a similar elongational viscosity to that of MgStOH. From the above, it

may be said that the crosslinked compounds in the present study are suitable to contour extrusion, big blow molding, pressure/vacuum forming, expansion molding, etc., due to their small draw-down.

Takahashi et al.⁶⁶ showed that the elongational viscosity and its strain-hardening of an ionomer increase with increasing the degree of ionic bonding, agreeing with the present experimental results. Isayev and Wan⁴⁹ showed that the entrance pressure loss P_0 of a sulfur crosslinked SBR increases with increasing the state-of-cure. Applying Cogswell's method⁷⁴ to their result as in the present study, λ increases with increasing the degree of crosslinking, agreeing with the present experimental results. Tang et al.²⁵ report that λ of an LLDPE covalently crosslinked with a peroxide decreases with increasing the degree of crosslinking. This is the inverse tendency of the present experimental results, whose reason is not known at the present time.

Dynamic Viscoelasticity

The dynamic viscoelasticities of a polymer melt are not only used for the evaluation of the pro-

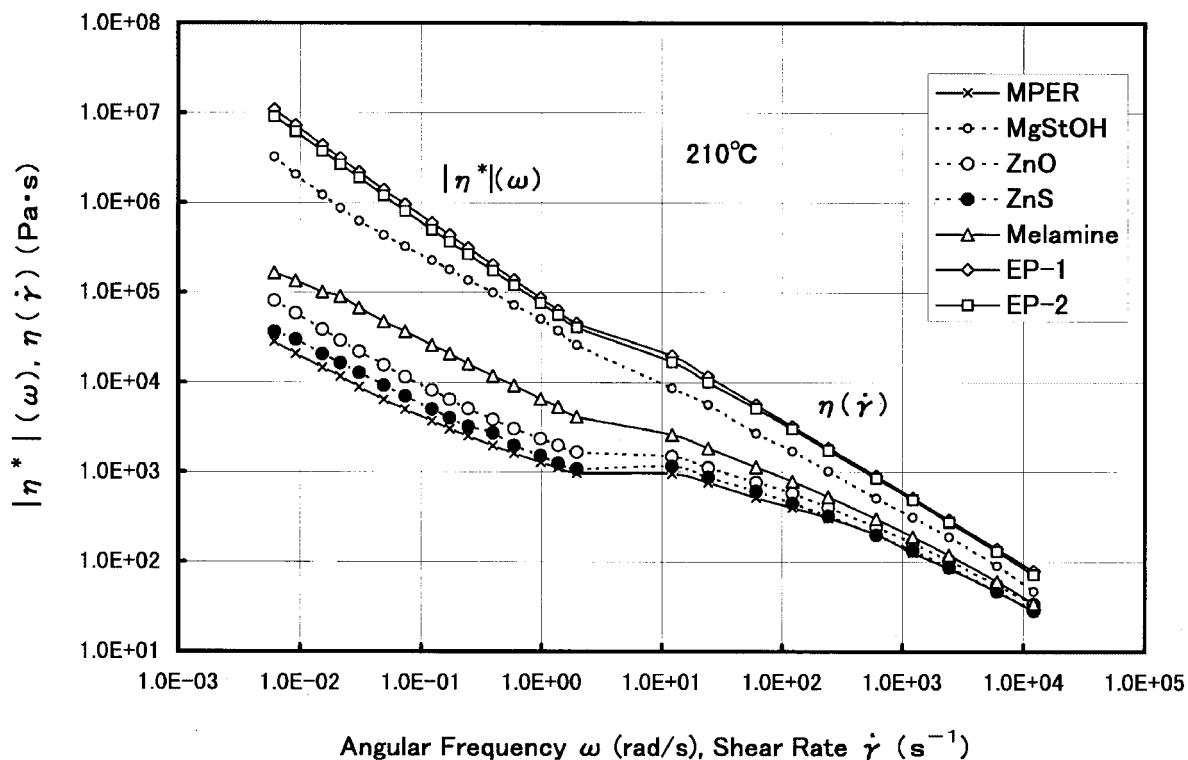


Figure 9 Comparison of flow curve in wide shear rate range among samples.

cessing behaviors at low deformation rates, but also are effective as a method for its rheological characterization. In the former case, according to Cox–Merz's empirical law,⁷⁵ since the change of the absolute value of complex viscosity $|\eta^*(\omega)|$ with angular frequency ω is an equivalent function of the change of steady state viscosity $\eta(\dot{\gamma})$ with shear rate $\dot{\gamma}$, $|\eta^*(\omega)|$ is often used to evaluate the flow behaviors at low shear rates.

Figure 8 shows the comparison of dynamic viscoelasticity among samples. The storage modulus tends to tail at low angular frequencies. This tendency is more notable for the sample with the higher degree of crosslinking, and with increasing crosslinking, the storage modulus approaches a plateau modulus independent of angular frequency. EP-1 and EP-2 with high degrees of crosslinking show plateau moduli attaining even to 10^5 Pa. Furthermore, the storage modulus G' is higher than the loss modulus G'' for all samples in all angular frequency range. This tendency is the more notable for the sample with the higher degree of crosslinking. Since Lissajous' figures of stress and strain of EP-1 and EP-2 with high degrees of covalent crosslinking show reversed rotations at high angular frequencies and strain-hardening type hystereses, the loss moduli G'' could not be measured.

That with increasing degree of crosslinking the storage modulus increases and flattens is reported by Ishigure et al.¹³ for a maleated PP covalently crosslinked with ethylene glycol. It is also reported for peroxide crosslinked various PEs^{28,31,37} and ethylene–hexene–diene terpolymer,³⁸ electron beam crosslinked LLDPE,⁴⁴ silane crosslinked polybutadiene,⁴⁷ siloxane crosslinked polystyrene,⁵⁰ and PP/EPDM TPV dynamically crosslinked with a phenolic resin,⁵¹ and is considered to be a general fact. As for the rubbery plateau modulus, Pechhold et al.²⁷ report for the crosslinking of a polyisoprene that while it 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 found also for ionomers with high degrees of ionic bonding^{58,63} and covalently highly crosslinked polymers.^{31,51} From the facts such as the flattening of G' , and G' being higher than G'' , the samples in the present experiment are assumed to be crosslinked from lightly to heavily.

The rheological characteristic that ought to be considered first at the evaluation of flow processabilities of a polymer is the shear viscosity. The

shear viscosity is represented by the flow curve. In order to evaluate the flow processabilities in various processing methods, the viscosity at the corresponding shear rate range can be measured. For example, the mixing torque of screw extruder and the injection pressure of injection molding are evaluated by the shear viscosity at high shear rates, and the lower the value, the smaller the processing power. On the other hand, the drawdown after leaving a die at extrusion and blow molding and the drawdown at pressure/vacuum forming are evaluated by the viscosity at low shear rates.

Figure 9 shows flow curves in a wide shear rate range that were obtained 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 law⁷⁵ and 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 degree of crosslinking and the viscosity enhancement is the higher at the lower shear rate. Namely, it may be said that the viscosity shows a very high value at low shear rates under which a drawdown of a shaped molten article occurs and it is not so high at high shear rates that a molten resin encounters at extrusion and injection molding. The viscosity enhancing effect is in the order of EP-1, EP-2 > MgStOH > Melamine > ZnO > ZnS > MPER, is in the same order as that of the gel fraction and is in almost inverse order of the MFI. The viscosity of MP-MH, which is an ionically crosslinked compound by the filling of MH in a previous study,¹⁸ is similar to that of MgStOH. That the viscosity is increased by the crosslinking and the increase is more notable at lower shear rate is generally reported for peroxide crosslinked various PEs,^{20,24–26,29–33,36,37} peroxide crosslinked PPs,^{29,34} peroxide or sulfur crosslinked PP/EPDM,²⁸ radiation crosslinked various PEs,^{41–43} radiation crosslinked PPs,^{1,45} silane crosslinked various PEs,^{46,48} siloxane crosslinked PE,⁵⁰ sulfur crosslinked SBRs,⁴⁹ and PP/EPDM TPV dynamically crosslinked with a phenolic resin,⁵¹ and is considered to be a general fact. In according with this point, it may be said that the ionically and covalently crosslinked MPERs in the present study show similar behaviors to those of general crosslinked polymers.

From the above, it may be said that the crosslinked compounds in the present study are suitable to contour extrusion, big blow molding, pressure/vacuum forming, expansion molding, etc., due to their small drawdown.

CONCLUSIONS

Maleic anhydride was grafted onto a polypropylene-type thermoplastic elastomer PER by reactive processing with a screw extruder and a MPER was prepared. Aiming at ionic crosslinking, MgStOH, ZnO, and ZnS, and aiming at covalent crosslinking, melamine as amino compound and Epocizer and GRYCI-ALE as epoxy compounds, were added to the MPER, melt-mixed by use of the 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.

The viscosities of the crosslinked compounds continue to increase straightly even at low shear rates. Therefore, they show very high values at low shear rates under which a drawdown of shaped molten article occurs. However, they scarcely differ from those of usual resins at high shear rates that a molten resin encounters at extrusion and injection molding. Although the changes of viscosities with shear rate are large, the changes with temperature are very small. The die swell ratios of compounds with high degrees of crosslinking are near unity and the extrudates scarcely swell after leaving a die. The changes of die swell ratios with temperature and shear rate are very small, and the extrudates are stable at disturbances. The compounds with high degrees of crosslinking do not give continuous extrudates and the extrudates crumble into decay at high shear rates at low temperatures due to the insufficient fusion. The elongational viscosities are very high. The dynamic viscoelasticities show rubbery plateau moduli attaining to 10^5 Pa.

The degree of these behaviors is in the order of epoxy compounds > MgStOH > Melamine > ZnO, ZnS > MPER (blank), and the crosslinking efficiency may also be regarded as in this order.

Since too enhanced crosslinking does not give a smooth extrudate due to the insufficient fusion, it is necessary to control the degree of crosslinking by adjusting the MPER content (dilution by un-

modified PER and/or PP) and the amount of crosslinkers.

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