Rheological Properties of Polypropylene/ High-Density Polyethylene Blend Melts. II. Dynamic Viscoelastic Properties

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SYNOPSIS

Three kinds of isotactic polypropylenes with different MFI were melt-blended with three kinds of high-density polyethylenes with different MFI using a screw extruder and the dynamic viscoelastic properties were studied. The storage moduli $G'(\omega)$ of the blends showed second plateaus and the dynamic viscosities $\eta'(\omega)$ of the blends showed two-step drops with increasing angular frequency ω. Such phenomenon was particularly notable for blend systems in which particles of lower viscosity were suspended in the disperse medium of higher viscosity and is considered to be the cause of abnormally large die swell.

INTRODUCTION

As for the melt rheology of isotactic polypropylene (PP)/high-density polyethylene (HDPE) blends, although many studies have been done on the steady-state flow properties as shown in the previous article,[1] a few studies[2,3] have been done on the viscoelastic properties. Plochocki[2] measured the relaxation spectra of PP/HDPE blends and found that the relaxation spectrum of a blend with an HDPE content of 25 wt % was lower than those of the other blends including the components and showed that any blending law could not be applied to the blends. Nishimura et al.[3] measured the dynamic viscoelastic properties of PP/HDPE blends and found abnormal behaviors in that the dynamic viscosities $\eta'(\omega)$ of blends with compositions of PP/HDPE = 20/80 and 40/60 were higher than those of the components at low angular frequencies ω and that the storage modulus $G'(\omega)$ of a blend with a composition of PP/HDPE = 20/80 was higher than those of the components at low ω. They conjectured from these results that PP and HDPE are partially compatible by the entanglements of molecular chains of the components.

In the present work, a new hypothesis on melt viscoelasticity of polymer blend, which has been proposed on the basis of new information obtained from the measurements of dynamic viscoelastic properties of PP/HDPE blend melts, will be reported.

EXPERIMENTAL

Samples

The same samples as used in the previous study[1] were used.

Dynamic Viscoelastic Properties

The storage modulus $G'(\omega)$ and dynamic viscosity $\eta'(\omega)$ were measured at 230°C under N_2 atmosphere with a concentric cylinder rheometer, Rheometer Almighty manufactured by Iwamoto Seisakusho Co., Ltd.

RESULTS AND DISCUSSION

Figures 1 (a)–(e) show the storage moduli $G'(\omega)$ and dynamic viscosities $\eta'(\omega)$ of PP/HDPE blends. Figure 1(a) is for the PPM/PEH system. As for

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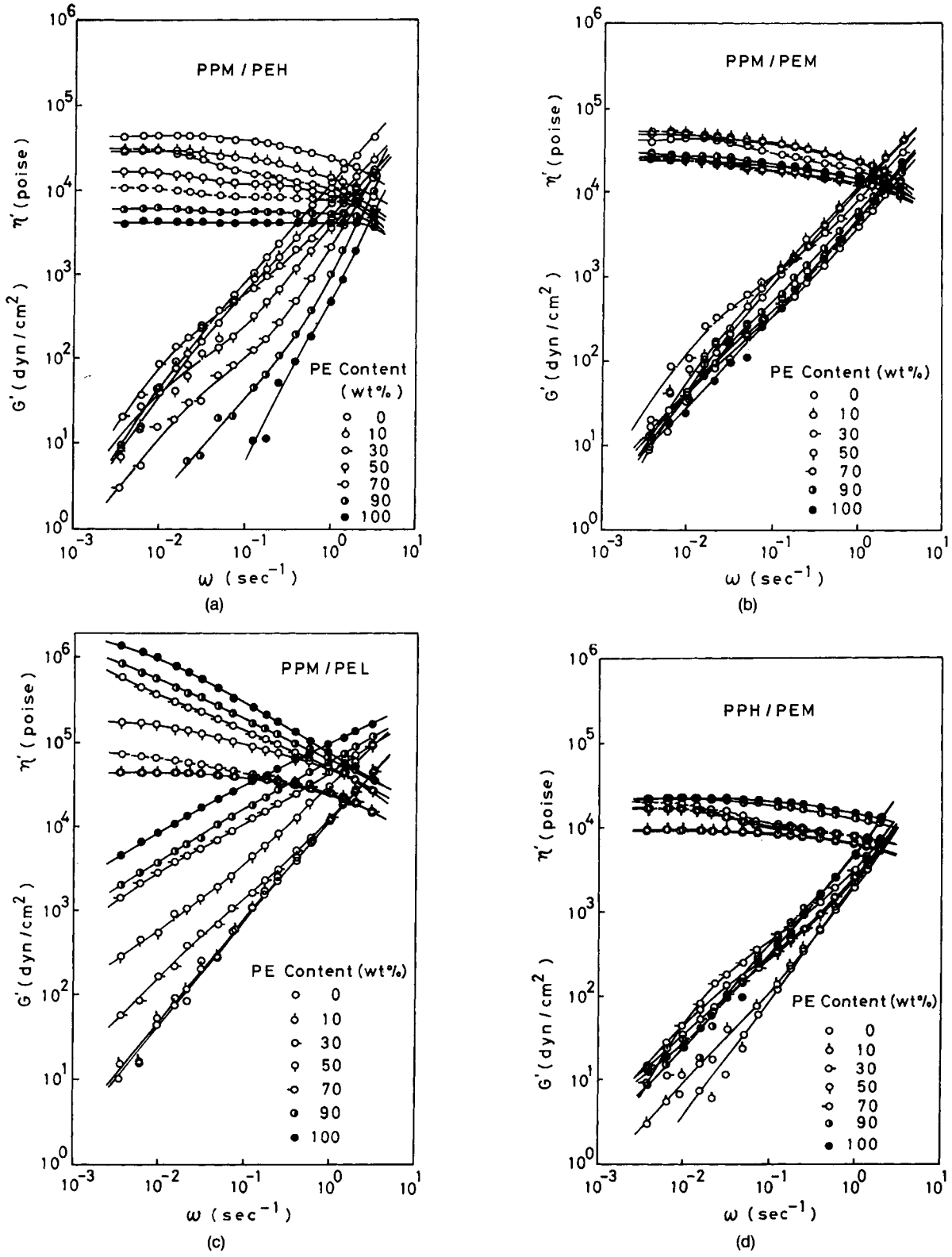

Figure 1 Storage moduli $G'(\omega)$ and dynamic viscosities $\eta'(\omega)$ of PP/HDPE blends. (a) PPM/PEH system, (b) PPM/PEM system, (c) PPM/PEL system, (d) PPH/PEM system, (e) PPL/PEM system.

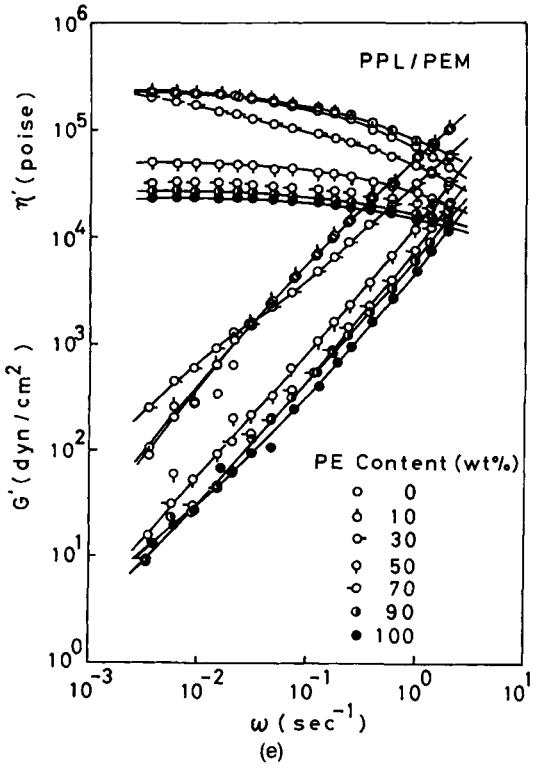

Figure 1 *(Continued from the previous page)*

the $G'(\omega)$'s of the blends, their slopes decrease at intermediate frequencies ω, and final relaxations occur after they pass through features of second plateaus. Such tendency is most notable for the sample with a PEH content of 30 wt % whose $G'(\omega)$ is higher than that of PPM at low ω. Corresponding to this, the $\eta'(\omega)$'s of the blends decrease in two steps with increasing ω and show two Newtonian regions. Similar results have been reported by Nishimura et al.[3] However, since their measurements were carried out at 180°C and the lower limit of ω was 0.1 s^{-1}, the final relaxation in $G'(\omega)$ and the second Newtonian region in $\eta'(\omega)$ were not observed. Chuang and Han[4] measured the steady-state shear viscosities η of polystyrene (PS)/poly(methylmethacrylate) (PMMA) blends and found that the η's of the samples with compositions of PS/PMMA = 70/30 and 30/70 showed two-step drops with increasing shear rate, and their η's were higher than those of the components at low shear rates. Levij and Maurer[5] found that the complex viscosities $|\eta^*|$ of ethylene–propylene block copolymer (block PP)/linear low-density polyethylene (LLDPE) blends showed a maximum at LLDPE contents of 30–40 wt % and that the maximum increased and the position of the maximum shifted toward higher LLDPE content with decreasing angular frequency. They explained

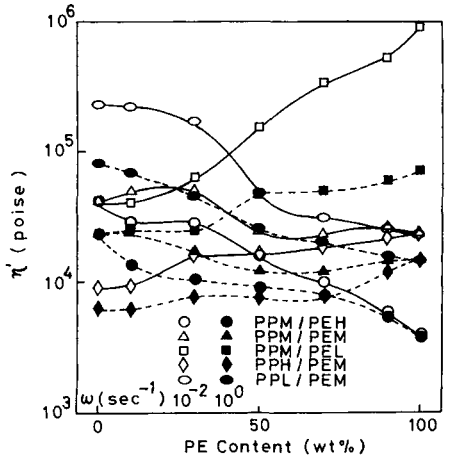

Figure 2 Dependence of dynamic viscosity η' on PE content.

this phenomenon using an extension of the spherical shell model of van der Poel.[6] Utracki et al.[7] obtained similar results to those of the present experiment for polycarbonate (PC)/LLDPE system, LLDPE/PP system,[8] and PS/LDPE system.[9] However, since the lower limit of ω was 0.01 s^{-1}, the final relaxation was not observed, and they suggested existence of the yield stress as in the case of particulate-filled polymer. Maeda and Masuda[10] observed similar results to those of the present experiment for a polyamide/styrene–acrylonitrile copolymer (PSAN)

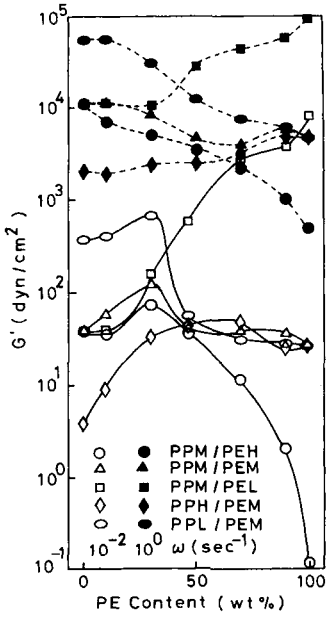

Figure 3 Dependence of storage modulus G' on PE content.

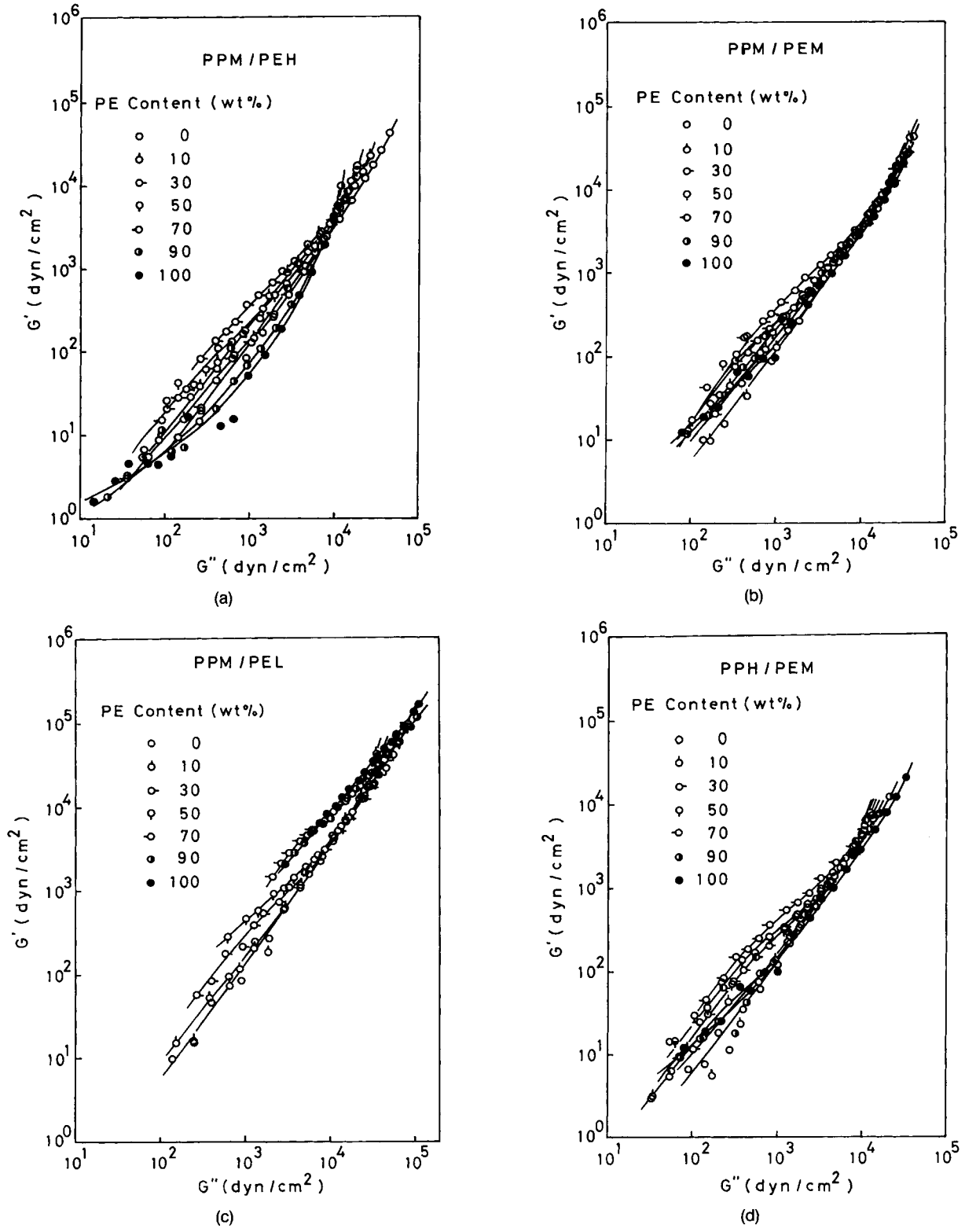

Figure 4 Log G'–log G'' plots of PP/HDPE blends. (a) PPM/PEH system, (b) PPM/PEM system, (c) PPM/PEL system, (d) PPH/PEM system, (e) PPL/PEM system.

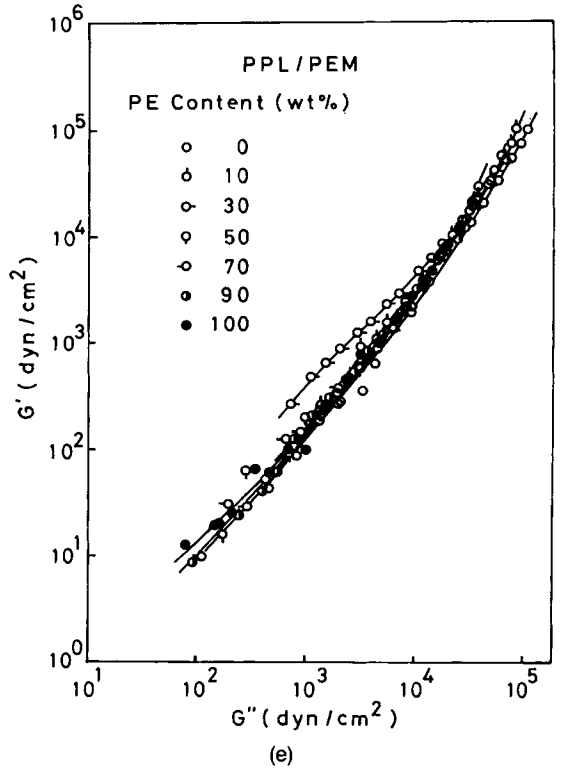

Figure 4 *(Continued from the previous page)*

blend with a composition of PA/PSAN = 75/25. However, since the lower limit of ω was about 0.1 s^{-1}, the final relaxation was not observed. Sholtz et al.[11] found that PP/PA blends with compositions of PP/PA = 60/40 and 40/60 showed higher $G'(\omega)$ than the components and conjectured that this phenomenon was originated from surface tension according to an emulsion model. Kitano et al.[12] found that a PC/HDPE blend with a composition of PC/HDPE = 25/75 showed higher $G'(\omega)$ than the components. However, since the lower limit of ω was 0.1 s^{-1}, the final relaxation was not observed. Iwakura and Tomita[13] observed similar results to the present experiment for HDPE/ethylenic ionomer blends and suggested the formation of a mixing structure differing from, for example, sea-island structure. They conjectured that the formation of such mixing structure was concerned with partial compatibility between common segments of the components and/or metal-ion crosslinkage.

Figure 1(b) is for the PPM/PEM system. Similar abnormal behavior to that of the PPM/PEH system is observed and is particularly notable for the sample with a PEM content of 30 wt %. The $G'(\omega)$'s and $\eta'(\omega)$'s of the samples with PEM contents of 10 and 30 wt % are higher than those of PPM at low ω. Figure 1(c) is for the PPM/PEL system. The abnormal behavior is weak and the final relaxation is not observed. Figure 1(d) is for the PPH/PEM system. In this case, the abnormal behavior is most notable for the sample with a PEM content of 70 wt %. Figure 1(e) is for the PPL/PEM system. The abnormal behavior appears notably for the sample with a PEM content of 70 wt %.

Figure 2 shows the dependence of η' on PE content. At a low angular frequency of 0.01 s^{-1}, the dependence curves upward at contents of lower viscosity component of 30 wt % and generally shows a tendency of positive deviation from logarithmic additivity. At a high angular frequency of 1 s^{-1}, this tendency weakens and a general tendency of negative deviation appears. Similar results have been obtained on $|\eta^*|$ of block PP/LLDPE system by Levij and Maurer[5] and on η of HDPE/ethylenic ionomer system by Iwakura and Tomita.[13]

Figure 3 shows the dependence of G' on PE content. As in the case of η', at a low frequency of 0.01 s^{-1}, the dependence curves upward at contents of lower viscosity component of 30 wt % and shows a tendency of positive deviation from additivity. Similar results have been obtained for the PA/PSAN system by Maeda and Masuda[10] and for HDPE/ethylenic ionomer system by Iwakura and Tomita.[13] Such tendency in G' is more notable than that in η'. At a high angular frequency of 1 s^{-1}, such tendency weakens, and a tendency of negative deviation strengthens at whole compositions.

Han et al.[4,14-24] recently used double-logarithmic plots of the storage modulus G' vs. the loss modulus G'' in order to study the dynamic viscoelastic properties of homopolymers, compatible polymer blends, and inhomogeneous polymer blends. They found that such plots were substantially independent of temperature and formed a curve approximated by a

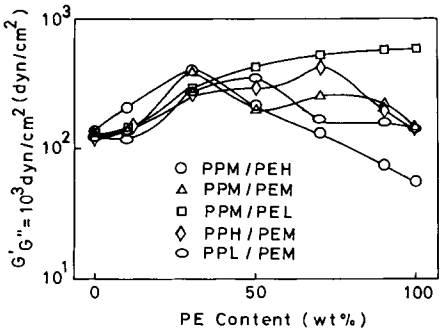

Figure 5 Dependence of storage modulus G' at loss modulus $G'' = 10^3$ dyn/cm^2 on PE content.

straight line for homopolymers and compatible polymer blends and were sensitive to the morphological state for inhomogeneous polymer blends as in the case of double-logarithmic plots of the first normal stress difference vs. the shear stress. They suggested that such plots could be used to evaluate the relative strength of elasticity to that of viscosity. Harrell and Nakajima[25] also independently used log G'–log G'' plots to study the influence of long-chain branching on the rheological properties of ethylene–propylene copolymers.

Figures 4(a)–(e) show the log G'–log G'' plots of PP/HDPE blends. Figure 4(a) is for the PPM/PEH system. Such plots change with the composition and show that PP and HDPE are incompatible. The samples with PEH contents of 10–70 wt % show higher G' than the components at low modulus range corresponding to low angular frequency range. Such tendency is most notable for the sample with a PEH content of 30 wt %. From these facts, it can be said that the blends, in particular the blends with a PEH content of 30 wt %, show notable elasticity. Figure 4(b) is for the PPM/PEM system. The samples with PEM contents of 30–90 wt % show higher G' than the components at low modulus range. This tendency is most notable for the sample with a PEM content of 30 wt %, and next comes the sample with a PEM content of 70 wt %. Figure 4(c) is for the PPM/PEL system. Although most of the blends locate between the components, the sample with a PEM content of 70 wt % shows slightly higher G' than PEL at low modulus range. Figure 4(d) is for the PPH/PEM system. The samples with PEM contents of 30–70 wt % show higher G' than the components at low modulus range. This tendency is most notable for the sample with a PEM content of 70 wt %. Figure 4(e) is for the PPL/PEM system. Although the plots of most of the samples ride on a curve, the sample with a PEM content of 30 wt % deviates from this curve and shows higher G' than the others.

Figure 5 shows the dependence of G' at $G'' = 10^3$ dyn/cm^2 on PE content. The dependence curves upward and shows positive deviations from logarithmic additivity. This deviation is particularly notable at compositions of a lower viscosity component content of 30 wt % and the dependence shows maxima. Since PPM and PEM have similar viscosities, although the former has a slightly higher viscosity than the latter, two peaks are observed at PEM contents of 30 and 70 wt % for PPM/PEM system. From these facts, it can be said that PP/HDPE blends show more notable elasticity than the components, and the elasticity is particularly notable at compositions of a lower viscosity component content of 30 wt %.

The dependence of die swell ratio on PE content, which is shown in Figure 10 of the previous study,[1] is analogous to the dependence of G' on PE content in Figure 5. Figure 6 shows the relations between the die swell ratio (D/D_0) at an apparent shear rate $\dot{\gamma}'_w = 10^2$ s^{-1} and G' at $G'' = 10^3$ dyn/cm^2. Semilogarithmic plots of both the quantities show linear relationships. Considering that G' is a measure of elasticity in small oscillating deformation and D/D_0 is a measure of elasticity in large steady-state deformation, it is interesting that there exists a positive correlation between them.

Summarizing these results, for PP/HDPE blends in which a lower viscosity component is dispersed as the disperse phase, the storage modulus $G'(\omega)$ enters the terminal region after passing through a second plateau, the dynamic viscosity $\eta'(\omega)$ drops in two steps with increasing angular frequency, and the viscosity and elasticity, in particular the elasticity, notably increase at low angular frequencies. Seven cases where the second plateau appears on the storage modulus $G'(\omega)$ have so far been known as shown in Table I. They are bimodal molecular weight distribution polymers, particulate-filled polymers, graft copolymers, block copolymers, crosslinked polymers, ionomers, and liquid crystalline polymers. Incompatible (partially compatible) polymer blends have appeared as the eighth case. Table I, which compares the eight types of second plateaus, shows that polymer blend shows different behaviors from other types. The fact that the poly-

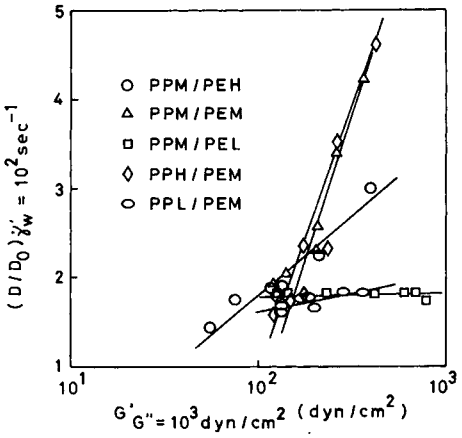

Figure 6 Relations between die swell ratio D/D_0 at apparent shear rate $\dot{\gamma}'_w = 10^2$ s^{-1} and storage modulus G' at loss modulus $G'' = 10^3$ dyn/cm^2.

Table I Comparison Among Eight Types of Second Plateaus

Type	Minor Component	Terminal Relaxation	Die Swell	Cause of Second Plateau
Incompatible polymer blend	Low viscosity	Observable	Increase	Deformable particles in medium
Bimodal MWD polymer	High viscosity	Observable	Increase	Bimodal relaxation time distribution
Particle-filled polymer	—	Inobservable	Decrease	Network structure of particles
Graft copolymer	—	Inobservable	Decrease	Network structure of particles
Block copolymer	—	Inobservable	?	Domain structure
Crosslinked polymer	—	Inobservable	Decrease	Network structure of molecular chains
Ionomer	—	Observable	Increase	Ionic network structure
Liquid crystalline polymer	—	Inobservable	Decrease	Domain structure

mer blend shows the second plateau is conjectured to be because particles with a lower viscosity and higher deformability are suspended in the disperse medium with a higher viscosity and lower deformability. However, the reason the viscosity and elasticity, in particular the elasticity, are notable in such a case is not obvious at the present time and more studies are needed.

Han and Kim[26] found that HDPE was spherically dispersed in PS medium in HDPE/PS blends with compositions of HDPE/PS = 25/75 and 50/50 and that in these cases the shear viscosity and first normal stress difference were minimum and maximum, respectively. They explained this phenomenon by assuming that HDPE particles were deformed during flow and stored recoverable elastic energy. However, considering that while their results were obtained under large steady-state deformations our results were obtained under a small oscillating deformation and that while the viscosity decreased and the elasticity increased in their results both the viscosity and elasticity increased in our results, our results cannot be explained by the theory of Han and Kim. Sholtz et al.[11] found that PP/PA blends with compositions of PP/PA = 60/40 and 40/60 showed higher G' than the components and conjectured that this phenomenon originated from surface tension according to an emulsion model. However, since the loss modulus G'', which is the viscosity component, hardly changes according to their theory based on surface tension, the increase of η' in the present experiment cannot be explained by their theory.

CONCLUSIONS

Three kinds of isotactic polypropylenes with different MFI were melt-blended with three kinds of high-density polyethylenes with different MFI using a screw extruder and the dynamic viscoelastic properties wee studied. The slopes of storage moduli $G'(\omega)$ of the blends decrease at intermediate angular frequencies ω, and the final relaxations occur after the $G'(\omega)$'s pass through features of second plateaus. Corresponding to this, the dynamic viscosities $\eta'(\omega)$ of the blends drop in two steps with increasing ω and show two Newtonian regions. This phenomenon is particularly notable for the blends with compositions of a lower viscosity component content of 30 wt % and is considered to be the cause of abnormally large die swell. The reason such abnormal behavior appears in the blend system in which particles of a lower viscosity component are suspended in the medium of a higher viscosity component is not obvious at the present time and more studies are needed.

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