

<연구논문>

PS/PP와 EPDM/PP 블렌드의 유변학적 거동에 미치는 계면의 영향

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Effects of Interface on the Rheological Behaviors of PS/PP and EPDM/PP Polymer Blends

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요 약

비상용성 고분자 블렌드계인 PS/PP와 EPDM/PP의 유변학적 거동에 미치는 계면의 영향을 알아보고, 그 실험 결과를 Park & Lee 모델과 비교하였다. PS/PP와 EPDM/PP 블렌드계에서의 계면에 의한 전단 응력과 법선 응력차에의 기여도는 κ 와 $\lambda(1-\mu)$, 두 개의 변수에 의해 잘 설명되었다. 특히, 계면의 탄성적인 효과와 관련있는 법선 응력차 항이 전단 응력 항보다 더 뚜렷하게 나타났다. 30PS/70PP 블렌드 조성에서는 블렌드의 유변학적 특성이 주로 연속상을 이루는 고분자의 의해 좌우된 반면에, 50PS/50PP 블렌드 조성에서는 계면에 의한 영향이 더 두드러지게 나타났다. 이것은 50/50 블렌드 조성에서 계면의 넓이가 증가한 것과 관계 있다. 그러나 EPDM/PP 블렌드계에서는 계면에 의한 응력 항들이 모두 PS/PP 블렌드계의 그것보다 매우 큰 값을 가졌지만, 그 상대적인 비를 나타내는 κ 값은 작았다. 이것은 블렌드를 구성하고 있는 순수한 성분의 법선응력차 값의 차이가 크기 때문이다. 또한, PS/PP 블렌드계에 대한 동적 계면장력을 Park & Lee 모델을 이용하여 예측해 보았다.

Abstract— Interfacial contribution on the rheological behaviors of immiscible polymer blends was analyzed for polystyrene (PS)/polypropylene (PP) and ethylene-propylene-diene rubber (EPDM)/PP blends at steady shear flow. The observed rheological behavior was compared with Park and Lee model. Both shear stress and normal stress difference due to the interfaces were well described by two parameters, κ and $\lambda(1-\mu)$. Especially, the normal stress difference terms which are related to elastic effect of the interfaces were more apparent than shear stress terms. In 30PS/70PP blends, the blend property was mainly determined by pure component's contribution. The interfacial contribution was more dominant at 50PS/50PP blends, which is due to the increased interfacial area. However, for EPDM/PP blends which has very elastic dispersion phase, the relative magnitude of interfacial contribution was small compared with pure component's contribution, even though it is still large compared with other blend systems. The blend properties were mainly determined by pure component's contribution when the original difference in first normal stress difference of pure components was too high. Park and Lee model was also successfully used to estimate the dynamic interfacial tension of PS/PP blend.

Keywords: Immiscible Polymer Blend, Steady Shear Viscosity, First Normal Stress Difference, Interfacial tension, Interface Contribution

1. Introduction

The rheological properties of polymer blends are very relevant with their industrial applications. However their rheology is too complex to fairly understand in detail yet. Blends properties would be influenced by various factors such as the component rheological characteristics, composition, interfacial tension, domain structure, etc. If the domain

structures can be deformed with external field, one should take into account the deformation, rupture and coalescence of dispersed domains under flow. Generally these blends will exhibit different rheological characteristics depending on the flow type adopted in the measurement due to the differences in structural change and the resulting domain structures[1,2]. If the relationship between rheological properties and domain structures of the blends can be elucidated, one can predict the rheological properties of the blends from the domain structures, or vice versa.

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Up to now, majority of the experimental works on immiscible polymer blends were focused on the response of two-phase polymeric mixtures to the linear oscillating flow [3-6]. Since small amplitude oscillatory flow does not alter the domain morphology much, it can be used to study the effect of morphology on the rheological behaviors in a nondestructive manner. One of the most remarkable results is the emergence of a pronounced elasticity at low frequencies, due to the interfacial contribution. In the literature, two distinct theoretical approaches have been proposed to successfully describe the behavior of blends under linear oscillatory flow. First, existing emulsion models can be adopted to account for two viscoelasticity of the components for blends with almost spherical dispersion morphology[4,7]. Second, a more generally applicable constitutive equation has been derived for materials with complex interfaces[8,9]. Under flow conditions, if break-up and coalescence processes are altering the rheology-morphology interrelationship a lot, then the rheological behavior can be better described by the latter.

A theory was developed by Doi and Ohta[8] in order to predict the rheology of two-phase Newtonian fluids with equal viscosities to predict that viscoelastic behavior arises as a consequence of the additional stresses generated due to interfacial contribution during flow. Takahashi *et al.*[5] considered two phase fluids under the steady shear flow and step-wise changes in shear rate to demonstrate the feasibility of Doi and Ohta theory. The steady shear flow measurements also revealed an enhanced elasticity of two-phase polymeric systems, manifesting mainly in the normal stress difference. In order to predict the rheology of a textured fluid consisting of an immiscible polymer blend, Lee and Park[9] have modified their approach for general applicability by including several terms which were previously neglected by them. Recently, more practical and simple analytic expression has been proposed by Park and Lee[10] which can predict the stresses arising from the viscoelastic nature of the neat polymers as well as the extra stresses arising as a consequence of interfacial contribution.

The objective of this paper is to see the effect of interfaces on the rheological behaviors of immiscible polymer blends experimentally to confirm the Park and Lee model. We investigated the rheological behavior for blends of polystyrene (PS) and polypropylene (PP), ethylene propylene diene monomer (EPDM) and polypropylene (PP) at steady shear flow and compared these results with theoretical prediction by Park and Lee[10]. The interfacial tension of PS/PP blend is also estimated in the frame of Park and Lee model.

2. Theoretical background

In the theory of Doi and Ohta[8], the rheology of two phases was focused on the interface and semi-phenomenological kinetic equations were derived which can describe the time evolution of interface area (Q) per unit volume and its anisotropy (q_{ij}) in a given flow field. The original theory of Doi and Ohta was modified in order to account for a mismatch in the viscosities of the polymers[9]. In short, the shear stress can be expressed as followings:

$$\sigma_{ij} = \left\{ 1 + \frac{6(\eta_i - \eta_m)}{10(\eta_i + \eta_m)} \phi \right\} \eta_m \dot{\gamma} - \alpha q_{ij} - P \delta_{ij} \quad (1)$$

Here, the interface contribution term can be calculated from the phenomenological time evolution equation of interface for a given flow field. The details can be found elsewhere[9]. The constitutive equation includes three different parameters, which come from time evolution equation of the interfaces. These fitting values can be obtained only after somewhat tedious calculations.

Recently, more compact constitutive equations which describe the interface contribution by two parameters have been suggested by Park and Lee[10] for steady shear flow. If we know the rheological properties of pure components, it is easy to predict the rheological behavior of immiscible blends with this model. To predict the interface contribution, a parameter, κ was introduced which means the ratio of extra normal stress difference to the extra shear stress due to the interfaces,

$$\kappa = \frac{N_{ex}}{\sigma_{ex}} = \frac{(q_{11} - q_{22})}{q_{12}} \quad (2)$$

As a result, two interfacial contributions can be expressed by two parameters. One is κ which is defined as the ratio of N_{ex} to σ_{ex} , and the other is $\lambda(1-\mu)$ which is defined as a parameter to describe overall relaxation of the interface. Detailed description of the parameters were reported elsewhere[9,10].

Let us consider the extra properties due to the interface in detail. These can be determined by the distribution of the unit normal vector n_i of the interface[13]. So, the extra shear stress and extra first normal stress difference can be represented by

$$\sigma_{ex} \propto \langle n_1 n_2 \rangle \quad (3)$$

$$N_{ex} \propto \langle n_1^2 - n_2^2 \rangle \quad (4)$$

where $\langle \rangle$ denotes the volume average. 1 is the direction parallel to the flow and 2 is the direction of vorticity in

case of simple shear flow. As shear rate increases, the drops are elongated and then ruptured. In the elongation process, n_i becomes nearly perpendicular to the flow direction when domains become long rods so that, $\langle n_1, n_2 \rangle$ becomes small, while $\langle n_1^2 - n_2^2 \rangle$ remains large. Consequently, the extra shear stress due to interfacial tension becomes very small, while the extra first normal stress difference becomes large. When the elongated rods are eventually ruptured to approach the steady ellipsoidal domains, $\langle n_1, n_2 \rangle$ and $\langle n_1^2 - n_2^2 \rangle$ becomes same in the magnitude and will not much change with various shear rates. Thus, the ratio κ may be assumed as a constant for the simplicity even though it would be dependent on the shear rate in reality. The extra shear and normal stress can be written as followings:

$$\sigma_{ex} = 12 \frac{\eta_m \dot{\gamma}}{\lambda(1-\mu)(6+\kappa^2)^2} \quad (5)$$

$$N_{ex} = 12 \frac{\kappa \eta_m \dot{\gamma}}{\lambda(1-\mu)(6+\kappa^2)^2} \quad (6)$$

With the aid of these quantities, one can obtain the full constitutive equation including interface contributions. For steady shear flow, the rheological properties of blends can be simply summarized as followings:

$$\frac{\eta_b}{\eta_m} = 1 + \frac{6(\eta_i - \eta_m)}{10(\eta_i + \eta_m)} \phi + \frac{\sigma_{ex}}{\sigma_m} \quad (7)$$

$$\frac{N_b}{N_m} = 1 + \frac{6(N_i - N_m)}{10(N_i + N_m)} \phi + \frac{N_{ex}}{N_m} \quad (8)$$

where η , σ , N and ϕ is the viscosity, shear stress, normal stress difference and volume fraction of inclusion phase, respectively. The subscript b, m, i and ex indicate the blend, matrix, inclusion phase and extra property due to the interfaces, respectively. The first term gives the matrix contribution, the second the mismatch of rheological properties between matrix and inclusion, and the third the extra properties by interface contribution.

In short, the rheological properties of blend over entire shear rate can be predicted by only two parameters, κ and $\lambda(1-\mu)$, in the model. With these parameters the interface contribution and its characteristics can be also interpreted in terms of blend morphology.

3. Experimental

3.1. Materials and preparation of blends

In order for systematic examination, experimental runs were focused on two aspects; one is the effect of the viscosity ratio on the blend rheology and second is the effect of

the elasticity of pure component. To see the viscosity effect, two grades of polypropylene (PP) with different molecular weight (MW=335,000 (PP1), 523,000 (PP2)) were blended with polystyrene (PS). On the other hand, polypropylene (PP2)/ethylene-propylene-diene monomer rubber (EPDM) system was chosen to see the elastic effect, which has very elastic domain in the visco-elastic matrix. Polystyrene (PS) was supplied by LG Chemical Co. and polypropylene (PP1, PP2) by SK Co.. The ethylene-propylene-diene monomer rubber was also from SK Co.. The rheological behaviors of pure components in steady shear flow are shown in Fig. 1. The samples were blended in

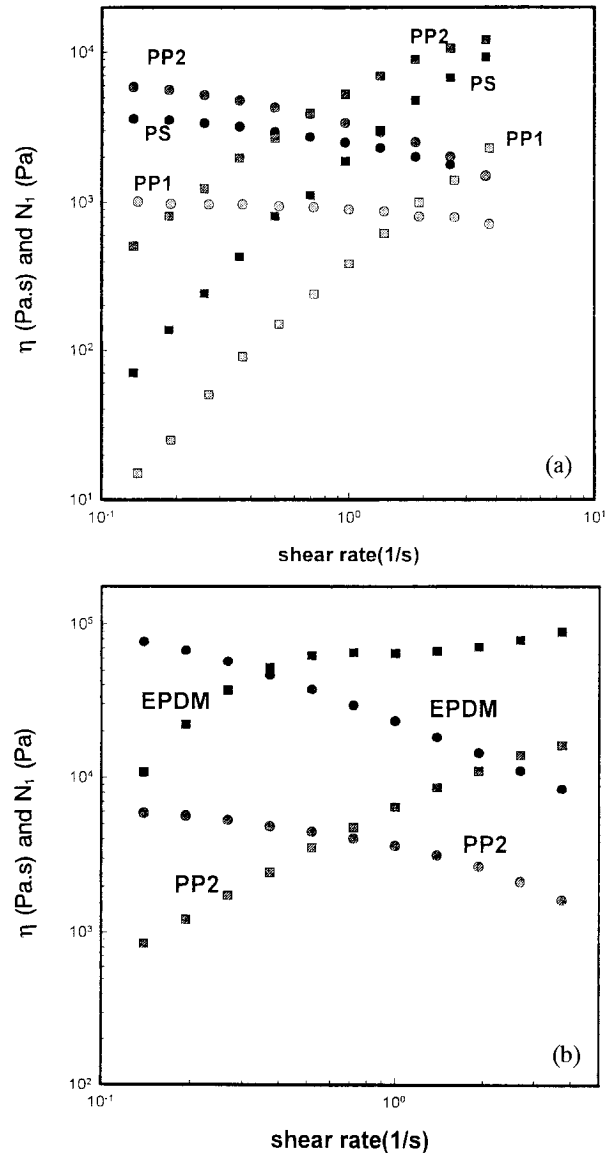
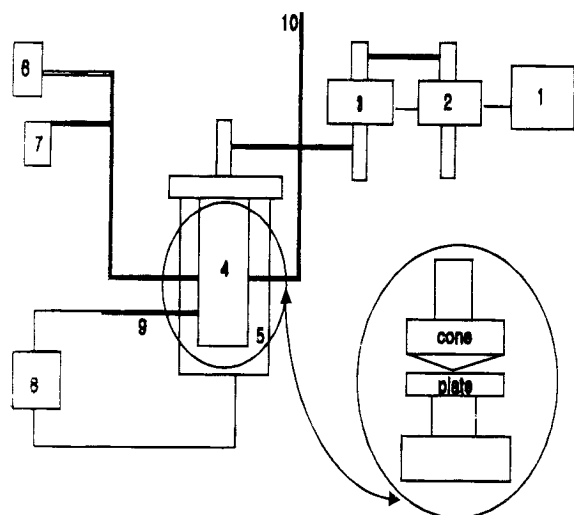


Fig. 1. Rheological behaviors of PS/PP and EPDM/PP at steady shear flow. (a) PS/PP, (b) EPDM/PP.



- | | |
|-----------------|--------------------------|
| 1. Compu-Motor | 6. Liquid N ₂ |
| 2. Motor-drive | 7. N ₂ gas |
| 3. Brake-Clutch | 8. Temp. controller |
| 4. Flow cell | 9. Thermocouple |
| 5. Heating band | 10. Ventillation |

Fig. 2. Schematic diagram of experimental system.

the twin-screw extruder at 205°C and 40 rpm. All blends were compression molded at 205°C and were dried at 80°C in the vacuum oven for 3 hours before any rheological measurements.

3.2. Method of investigation

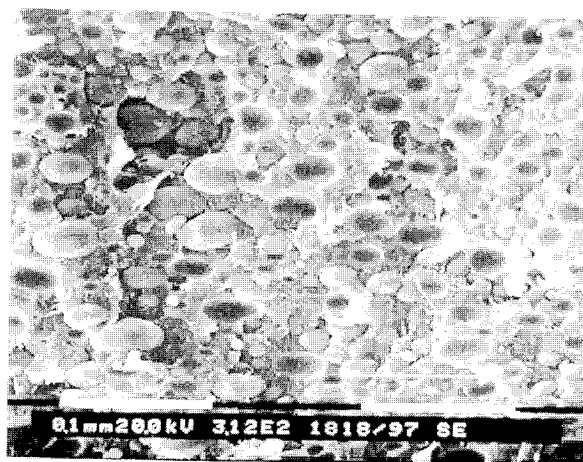
The rheological properties of PS/PP blends were measured by ARES (Advanced Rheometric Expansion System) in a cone and plate geometry with 25.0 mm diameter and 0.10 rad cone angle. For the EPDM/PP blends, ARES in a plate and plate geometry was used with 25.0 mm diameter and 1.5 mm gap size. In order to investigate the morphological evolution with shear rate, a separate quenching equipment which was shown in Fig. 2. was used. A special shearing device was designed with cone angle 4° and 25 mm cone-and-plate fixtures for this purpose. Constant shear rate experiments were carried out for the molten specimens which were quenched below melting temperature of both components so as to freeze the deformed and oriented domains of dispersion. Morphologies in these solidified specimens were investigated by SEM (Scanning Electron Microscopy).

4. Results and Discussions

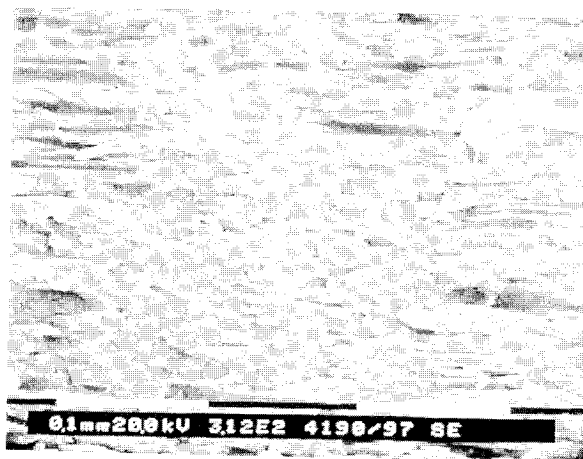
4.1. Morphology evolution with shear

Under steady shear flow, dispersed droplets were deformed

and elongated to the flow direction. Examples of their morphology change were shown in Fig. 3. For the 30PS/70PP blends, PS droplets were deformed a little in PP1 matrix, while PS droplets in PP2 matrix were deformed a lot and elongated long. The different shear effects on the morphology evolution were resulted from the fact that PP2 is more viscous than PS while PP1 is less viscous than PS. For the 50PS/50PP blends, the co-continuous structures were formed for both PS/PP1 and PS/PP2 blends. Their morphologies, which were elongated to the flow direction at steady shear rate are shown in Fig. 4. However, the rheological properties at higher shear rate, showed different behaviors for each blend. In PS/PP1 blends, the steady shear viscosity and first normal stress difference of blends approach to the properties of PP1. The rheological properties of PS/PP2, however, are close to the PS. Therefore it may be said that PP1 would act as a matrix in

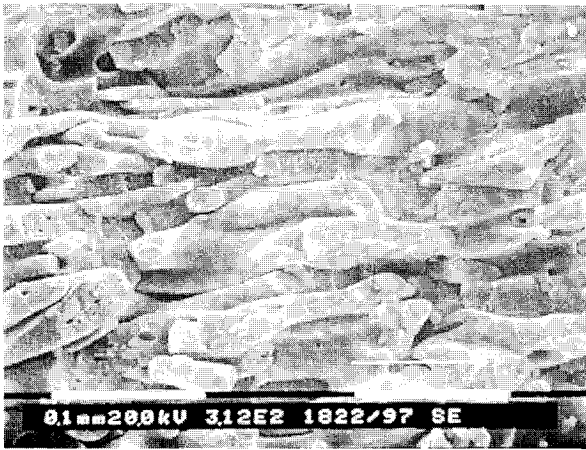


(a)



(b)

Fig. 3. Morphology of 30PS/70PP blends at shear rate 3(1/s) (Shear direction is shown as white arrow). (a) PS/PP1, (b) PS/PP2.



(a)



(b)

Fig. 4. Morphology of 50PS/50PP at shear rate 3(1/s) (Shear direction is shown as white arrow). (a) PS/PP1, (b) PS/PP2.

50PS/50PP1 blends whereas PS would behave as a matrix in 50PS/50PP2 blends.

Elastomer modified thermoplastics which are composed of EPDM and PP2 were prepared to see the effect of elastic domains on the interface contribution. Their structural changes under steady shear flow are shown in Fig. 5. In EPDM/PP2 blends, the dispersed EPDM domains were deformed little and retains their nearly spherical shape. Generally, when the very elastic domain can resist to the deformation and acts as a suspension of spherical particle, thus the morphology change will be very little.

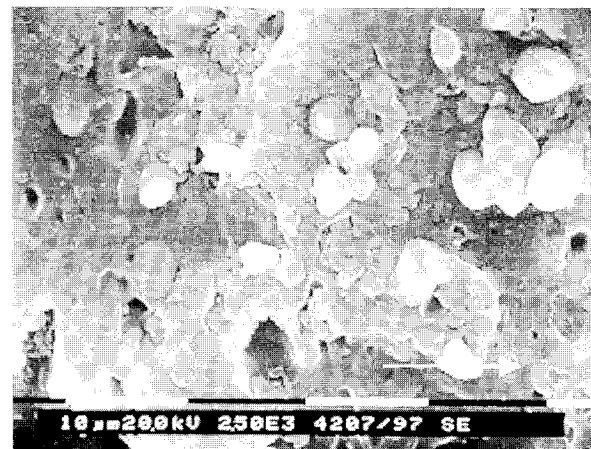
4.2. Steady shear flow characteristics

4.2.1. Measurement of Excess properties

To see the interface effect independently, extra properties were separated from the blend properties. Here, extra



(a)



(b)

Fig. 5. Morphology of EPDM/PP2 at shear rate 3(1/s) (Shear direction is shown as white arrow). (a) 30EPDM/70PP, (b) 50EPDM/50PP.

properties can be defined from the equation (9) and (10).

$$\sigma_{ex} = \eta_b \dot{\gamma} - \eta_m \dot{\gamma} \left[1 + \frac{6(\eta_i - \eta_m)}{10(\eta_i + \eta_m)} \phi \right] \quad (9)$$

$$N_{ex} = N_b - N_m \left[1 + \frac{6(N_i - N_m)}{10(N_i + N_m)} \phi \right] \quad (10)$$

Both of extra shear stress and extra normal stress difference terms were calculated for both blends at shear rate 0.72 s^{-1} . These experimental results including model parameters are listed in Table 1. As one can see in the Table 1, the extra normal stress differences are more distinguishably increased with volume fraction compared with extra shear stress in both PS/PP1 and PS/PP2 blends. Thus, the κ values were increased accordingly. We can also observe that the increased normal stress would deform dispersed domain easily, which results in small values

Table 1. Extra properties and fitting parameters for blends

Blend system	PS/PP1 30/70	PS/PP1 50/50	PS/PP2 30/70	PS/PP2 50/50	EPDM/PP2 30/70	EPDM/PP2 50/50
σ_{ex} (Pa)	36.09	38.07	338.40	201.33	1204.7	1788.5
$N_{1,ex}$ (Pa)	25.49	275.76	393.34	988.86	1270.2	1530.7
κ	0.71	7.20	1.16	4.91	1.05	0.86
$\lambda(1-\mu)$	5.25	0.06	1.74	0.12	0.57	0.43

of $\lambda(1-\mu)$.

However, for the EPDM/PP2 blends, both the extra normal stress difference and extra shear stress terms were very large and also increased a little with volume fraction. However, the ratio, κ remains almost same. It may be due to the very elastic dispersed domain which would not be

deformed much in the steady shear field.

4.2.2. Analysis of extra properties

Both experimental shear stress (shear viscosity) and normal stress difference were shown for PS/PP blends along with mixing rule term and interfacial contribution in Fig. 6. and Fig. 7. For the 30PS/70PP blends, the blend properties were mainly determined by the pure components contribution in both PS/PP1 and PS/PP2 blends. For simplicity, their results are shown only for the 30PS/70PP1 blend. The magnitude was slightly increased in PS/PP2 blends due to the more viscoelastic property of PP2. For the 50PS/50PP blends, the extra normal stress contribution

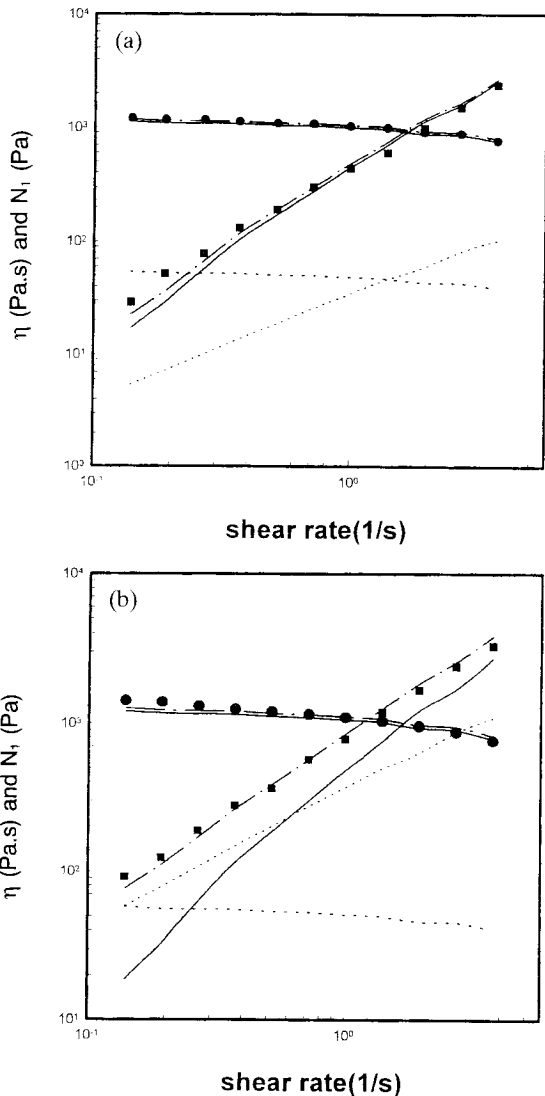


Fig. 6. Excess shear stress and normal stress contribution of PS/PP1 (■: experimental normal stress, ●: experimental shear viscosity) (dotted: interfacial contribution, solid: mixing rule, dash-dot: interfacial contribution+mixing rule). (a) 30PS/70PP, (b) 50PS/50PP.

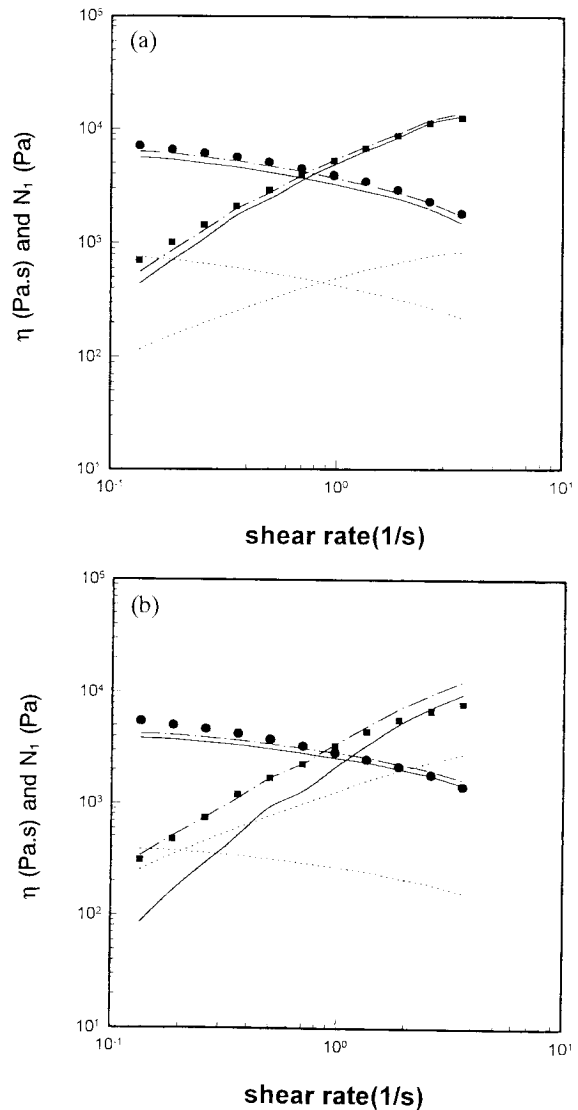


Fig. 7. Excess normal stress contribution of PS/PP2 (■: experimental normal stress, ●: experimental shear viscosity) (dotted: interfacial contribution, solid: mixing rule, dash-dot: interfacial contribution+mixing rule). (a) 30PS/70PP, (b) 50PS/50PP.

becomes more significant than the pure components contribution at low shear rate. The tendency was similar in both PS/PP blends and it was shown only for 50PS/50PP2 blend in Fig. 7. The increased elastic effect was partly due to the increase of more elastic phase and partly due to the increase of the interface area. We can see that the relative magnitude of interfacial contributions on shear viscosity were small compared with pure components contributions for entire shear rate region.

For the EPDM/PP2 blends which has very elastic dispersion phase, the relative magnitude of the extra normal stress and extra shear viscosity contribution were small com-

pared with the pure component's contribution as shown in Fig. 8, though both the extra normal stress and extra shear stress terms were very large compared with other blend systems. It may be resulted from the fact that the original difference of two components in the first normal stress difference was too big. In other words, because the EPDM has very large elastic property, its contribution was more dominantly reflected on the overall blend properties than the interfacial ones.

4.2.3. Comparison of experimental data with theory

With two parameters listed in Table 1, which were obtained from experimental data, theoretical predictions of the steady shear viscosity and first normal stress difference of blends can be directly compared with ex-

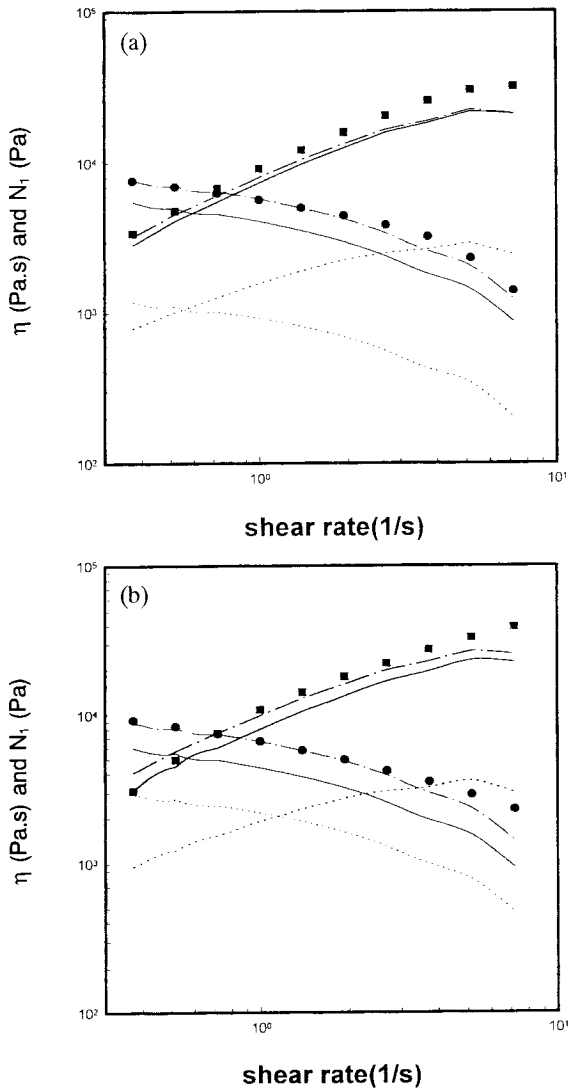


Fig. 8. Excess normal stress contribution of EPDM/PP2 (■: experimental normal stress, ●: experimental shear viscosity) (dotted: interfacial contribution, solid: mixing rule, dash-dot: interfacial contribution+mixing rule). (a) 30EPDM/70PP, (b) 50EPDM/50PP.

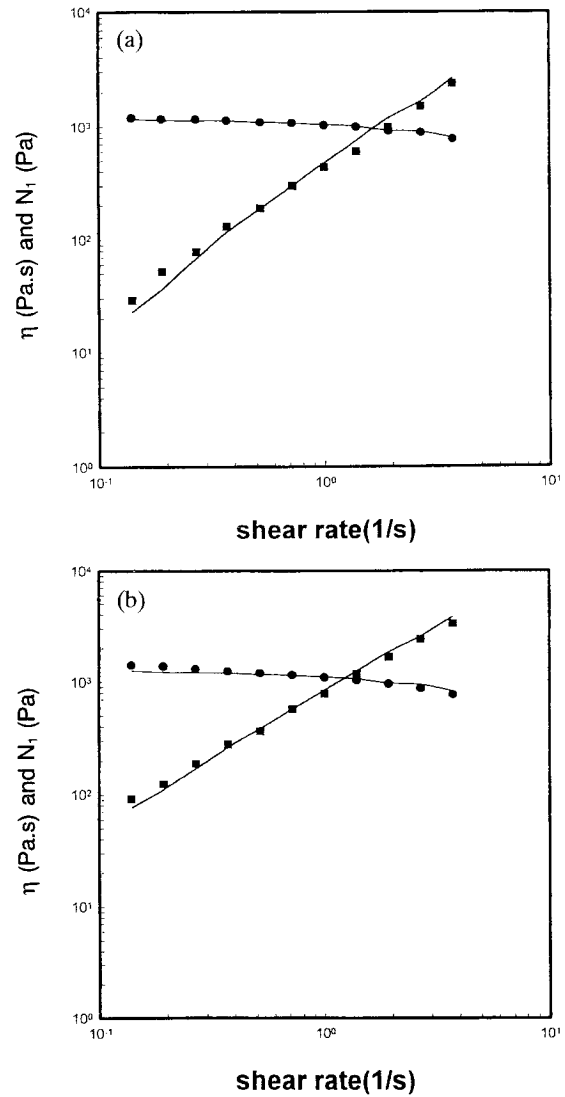


Fig. 9. Comparison of experimental data with theory for PS/PP1 (■: experimental normal stress, ●: experimental shear viscosity) (a) 30PS/70PP, (b) 50PS/50PP.

perimental data.

For the PS/PP blend system, the steady shear viscosity and first normal stress difference are well predicted by Park and Lee model as shown in Fig. 9 and Fig. 10. For the EPDM/PP2 blends, the comparison of experimental data with theory is shown in Fig. 11. The model also predicts well the steady shear flow characteristics of EPDM/PP blends except of discrepancy at high shear rate. The small discrepancy of experimental data with theoretical prediction may be due to the fact that the original difference in normal stress differences of pure components was too big.

4.3. Prediction of interfacial tension

Interfacial tension of PS/PP blend can be estimated by Park & Lee model by analyzing the morphology with shear rate. As mentioned previously, the interface contribution which is related to morphology of blends can be predicted by κ and $\lambda(1-\mu)$. And Q and q_{ij} which represent the blend morphology, can also be expressed by the parameters. Especially, the Q , which represents the interfacial area per unit volume could be expressed like equation (11).

$$Q = \frac{12 \cdot \dot{\gamma} \eta_m}{\alpha \cdot \lambda(1-\mu)} \cdot \frac{1}{\kappa \cdot (\kappa^2 + 6)} \tag{11}$$

The right hand side of equation (11) indicates that the drop morphology is determined by the counterbalance

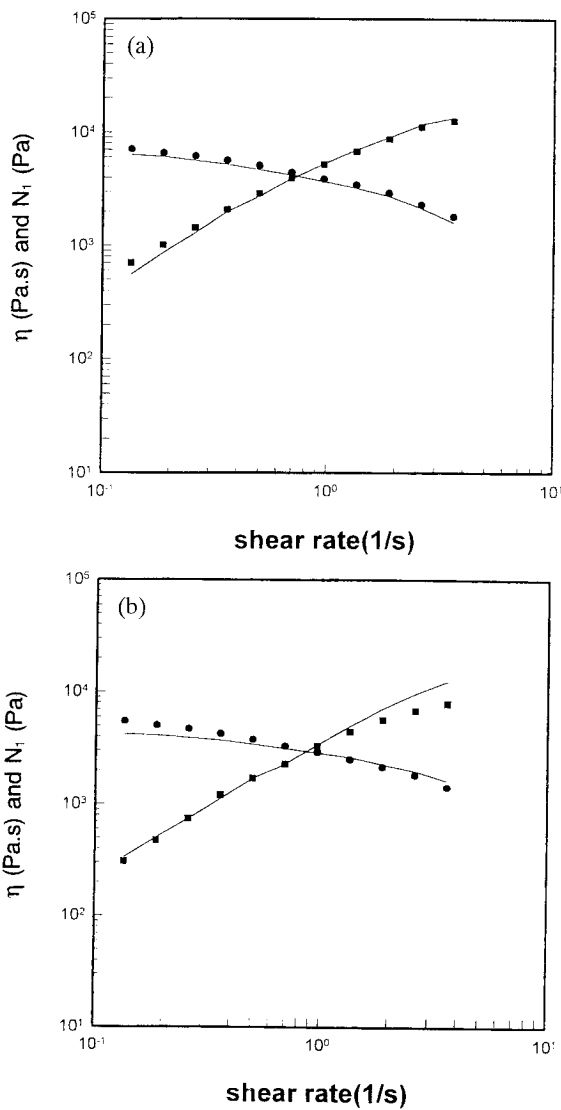


Fig. 10. Comparison of experimental data with theory for PS/PP2 (■: experimental normal stress, ●: experimental shear viscosity) (a) 30PS/70PP, (b) 50PS/50PP.

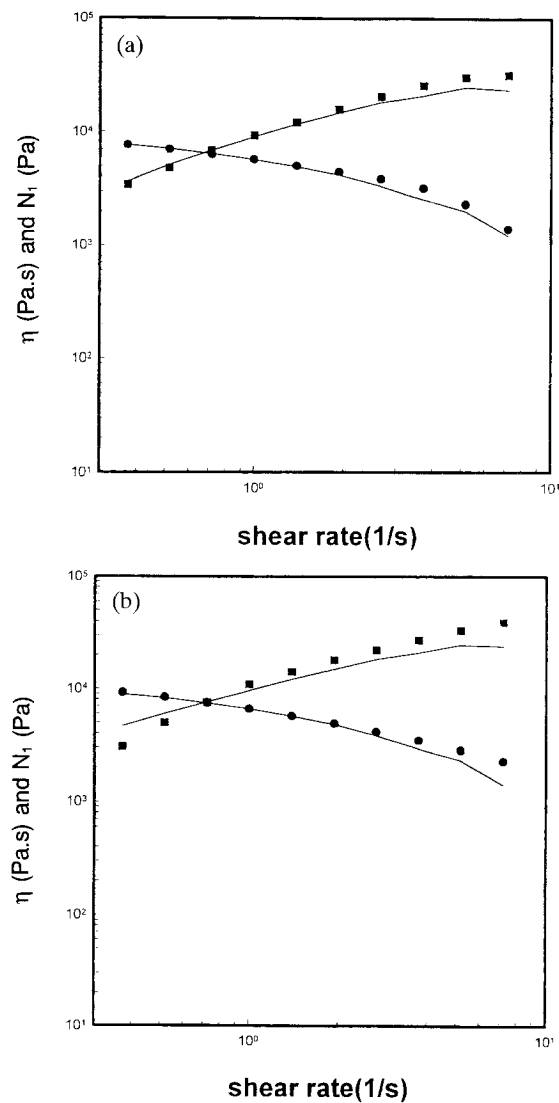


Fig. 11. Comparison of experimental data with theory for EPDM/PP2 (■: experimental normal stress, ●: experimental shear viscosity) (a) 30EPDM/70PP, (b) 50EPDM/50PP.

between viscous force and interfacial tension.

For ellipsoidal shapes, the Q can be defined as following equation (12).

$$Q = \frac{\phi \cdot \sum 4\pi \cdot a_i \cdot b_i}{\sum_i \frac{4\pi}{3} \cdot a_i \cdot b_i^2} \quad (12)$$

Here, a_i is the long semi axis of ellipsoidal droplet of type i and b_i is the short semi axis of ellipsoidal droplet of type i .

The morphology of ellipsoidal droplet was observed in the PS/PP1 blends as shown in the Fig. 3. The size distributions of a_i and b_i for the blend are shown in Fig 12. Here, n is the number of droplet of type i . And the interfacial area per unit volume was calculated by equation (12). The parameters for the calculation of interfacial tension of PS/PP1 blend are summarized in the Table 2.

The interfacial tension of PS/PP1 blends calculated by equation (11) is 3.47 (m N/m). The experimental data re-

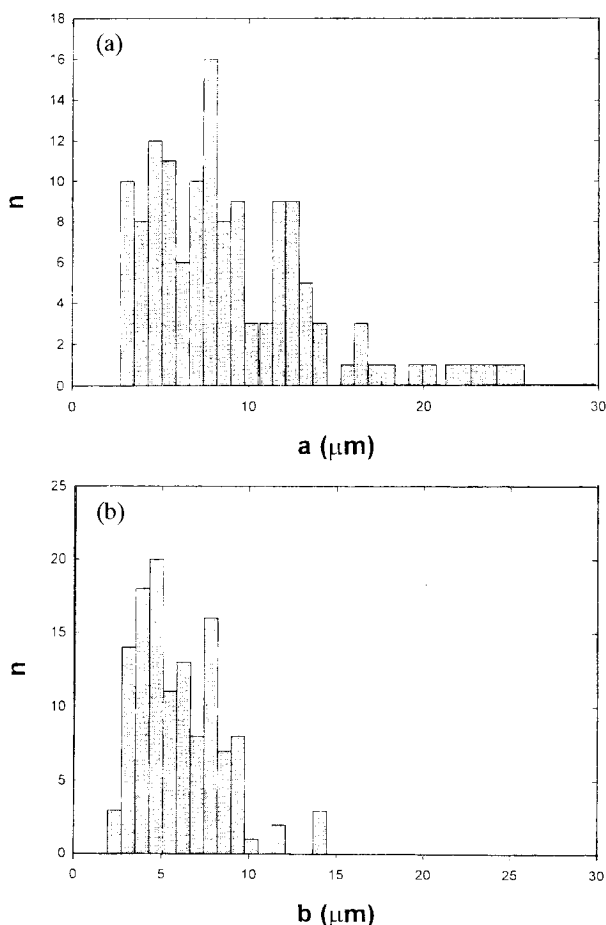


Fig. 12. Drop size distributions of 30PS/70PP1 blend at shear rate 3(1/s) (a) long semi axis, (b) short semi axis.

Table 2. Experimental parameters for the PS/PP1 blend system

Parameters	Values
$\lambda(1-\mu)$	5.25
κ	0.71
Q (1/ μm)	112.32
$\dot{\gamma}$ (1/s)	3
η_m (Pa.s)	768.52

ported in the literature for PS/PP blend ranges in 5.0~5.1 (m N/m)[12,13]. It can be said that the estimated value is quite reasonable if we consider that it is the dynamic interfacial tension while the literature value is the static one. Thus, it may be concluded that Park and Lee model can be used to estimate the interfacial tension between immiscible polymer blends. It was difficult to define the shape of domains for the PS/PP2 due to long elongated form. The dispersion morphology of EPDM/PP2 blend was also not apparent enough to define the shape exactly. Therefore estimation of interfacial tension was excluded for these blends. Further research should be done in order to estimate the interfacial tension in the blends with the complex morphology.

5. Conclusion

Interface contribution defined as extra terms has been well explained in both PS/PP and EPDM/PP blends with the Park and Lee model. Especially, the extra normal stress difference terms related to elastic effect are more apparent than extra shear stress terms. In 30PS/70PP blends, the blend property is mainly determined by pure component's contribution. On the other hand, the interface contribution is more dominant at 50PS/50PP blends, which may be reflected by the increased interfacial area with volume fraction.

However, for EPDM/PP blends which has very elastic dispersion phase, the relative magnitude of interface contribution is small compared with pure component contribution, even though it is still large compared with other blend systems. The blend properties are mainly determined by the pure components contribution because the original difference in first normal stress difference of pure components is too high, which is also the reason of the discrepancy between experimental results and theoretical predictions of rheological behavior.

Interfacial tension of PS/PP1 blend can be also estimated by Park and Lee model and successfully compared with literature data.

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