

## Polystyrene/Poly(2,6-dimethyl-1,4-phenylene Oxide) 블렌드의 동적 복굴절과 점탄성

### 황 의 정

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## Dynamic Birefringence and Viscoelasticity of Polystyrene/Poly(2,6-dimethyl-1,4-phenylene Oxide) Blends

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### 요 약

PS/PPO 블렌드의 동적 탄성률,  $E^*(\omega)$ 와 동적 스트레인-광학계수,  $O^*(\omega)$ 을 유리전이 영역에서 동시에 측정하여, PS/PPO 3종류 조성 블렌드의  $E^*(\omega)$ 와  $O^*(\omega)$  완화거동을 조성 단일 중합체와 비교 고찰하였다. PS/PPO 블렌드의  $\alpha$ -분산 점탄성 거동은 조성에 관계없이 거의 유사하여, 조성 고분자가 상호 협동적으로 완화하는 것을 알 수 있었다. 그러나, 광학적 완화 스펙트럼,  $O^*(\omega)$ 는 정성적으로 명확히 다른 거동을 보였다. 단일 PS와 PPO의  $O^*(\omega)$ 는 전 영역에 걸쳐 상반된 부호를 나타냈으며, 두 고분자의 블렌드는 조성 고분자의 반대 부호의 상호 보상으로 인하여 복굴절이 감소하였다. 3종류 블렌드는 PPO의 조성이 증가함에 따라 상호 보상에 의해  $O^*(\omega)$ 의 부호가 순차적으로 변하여 반전하였으며, 저복굴절 PS/PPO 블렌드의 PS 조성이 65-80 wt% 범위 내에 있음을 추정할 수 있었다. 상이한 부호를 갖는 복굴절 특성으로 인하여 블렌드 내에서 각 성분 고분자의 완화 기여를 단순 가성법칙에 의해 정량적으로 계산하는 것이 가능하였다. 또한 PS/PPO 블렌드의 상용성을 광학적 부분 기여 파라미터를 사용하여 고찰하였다.

**Abstract**—The complex Young's modulus,  $E^*(\omega)$ , and the complex strain-optical coefficient,  $O^*(\omega)$ , of polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends were simultaneously measured and studied in the glass-to-rubber transition zone. The relaxation behaviors in  $E^*(\omega)$  and  $O^*(\omega)$  of three blends with different composition, were compared with each other in relation to the relaxation behaviors of constituents, PS and PPO. It was clarified that the PS/PPO blends seemed almost unique in the viscoelastic  $\alpha$ -relaxation dispersion without respect to the compositions, which implied that the dissimilar constituents relaxed cooperatively. But the optical relaxation spectra,  $O^*(\omega)$ , of the blends showed distinct difference in quality. The signs of  $O^*(\omega)$  of PS and PPO were opposite in the measured frequency range and blending of PS and PPO gave the reduction of birefringence coming from compensation of the birefringence of constituents. By increasing the incorporation of PPO in the blends, compensation of the opposite-signed birefringence of constituent polymers results in successive changes in sign of the  $O^*(\omega)$  of the blends. Hence, we can expect that the composition of birefringence free blend may be in the 65-80% of PS fraction in PS/PPO blend. The properties of the opposite-signed birefringence also made us possible to make a quantitative evaluation of the contribution of each constituent to the relaxation of the blends by simple additivity rule. Compatibility of the blends was discussed in light of fractional contribution parameter.

**Keywords:** Birefringence, Young's Modulus, Strain-optical Coefficient, Polystyrene, Poly(phenylene oxide), Fractional Contribution

### 1. Introduction

Recently, polymeric materials with far excellent optical properties have been required with the increasing use of optical polymers accompanying the progress in electronics and optical application area, e.g., optical discs and lenses [1,2]. Researches and developments for new optical polymers have been carried out for pursuing the up-grade of various other mechanical properties as well as optical properties. Amorphous polymers often exhibit the birefringence

arising from the orientation of polymer chains in the melt processing operations like injection molding or extrusion. In the glassy state after the processing, the chain orientation is solidified and gives rise to the residual stress and birefringence [3].

An orientational birefringence is determined by the intrinsic birefringence of the unit structure of molecular chain and its degree of orientation [4]. In case of substance for information storage in electronics, a birefringence becomes the source of errors when the information on sub-

stance are reproduced. Therefore, the birefringence-free state after processing operations is desired for the substance. In spite of the modern improved processing techniques to let down the birefringence, some molecular orientation is inevitable in melt-processed polymers. It is the reason why the development of new polymeric materials offering the low birefringence is required in addition to the improved processing techniques.

In this study, we try to investigate the birefringence and viscoelasticity of the alloys of polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide). It is well-known that a general-purpose polystyrene is excellent in optical property (transparency). But it has a little deficiencies in some properties, for instance, a moderately low glass-transition temperature,  $T_g$ , and a high hygroscopic property. It contains a phenyl group with large optical anisotropy as a side group in the unit structure. Its birefringence caused by deformation is notably high and negative [5,6], i.e., the refractive index in extensional direction is smaller than that in the neutral direction. PPO is also fairly satisfactory in both the optical and mechanical properties. It also contains a phenyl group with large optical anisotropy as a main chain in the unit structure. Its birefringence is positive and large [7].

Recently, Hahn and Wendorf reported that the birefringence can be reduced even to zero by the blending of compatible pair of amorphous polymers without sacrificing their transparency [8]. Following the suggestions of Hahn's *et. al.*, we made the blends of PS/PPO and tested the optical and mechanical relaxations of them. As seen in our preceding studies [9,10], strain-induced birefringence also shows a relaxation phenomenon depending on the frequency. A blend of PS/PPO is known to show a good miscibility in the whole composition rendering excellent mechanical properties [1]. The pair is thus well proclaimed as the most successful representatives in the blend materials, and it is widely used in the electronics and automotive applications. We will concentrate on the points for the blend of PS/PPO such as: 1) the mechanical relaxation behavior, 2) the optical relaxation behavior, and 3) the variation of birefringence behavior as a measure of miscibility.

## 2. The Complex Strain-optical Coefficient and the Complex Young's Modulus

On application of a small strain to a material, a small stress is induced. The stress and the strain is related

through the linear viscoelasticity. In the same manner, a linear response relation can be constructed for the small strain and the induced birefringence [11,12]. Here we give only a few definitions relevant to later discussion. Notations for elongation are employed for simplicity. Generalization to other strains such as shear is straightforward. On application of a constant elongational strain,  $\epsilon_0$ , a tensile stress,  $\sigma(t)$ , and a birefringence,  $\Delta n(t)$ , is induced in the material. The latter is defined as the difference of the refractive indices for the lights polarized in the direction of elongation and the transverse directions, respectively. We can define the Young's modulus,  $E(t)$ , and the strain-optical coefficient,  $O(t)$ , in the stress relaxation process as follows:

$$E(t) = \sigma(t)/\epsilon_0, \quad O(t) = \Delta n(t)/\epsilon_0 \quad (1)$$

In an oscillatory deformation,  $\epsilon^*(t) = \epsilon_0 \exp(i\omega t)$ , the stress as well as the birefringence oscillates with the same angular frequency,  $\omega$ , and with phase shifts,  $\delta$  and  $\delta_B$ , respectively:

$$\sigma^*(t) = \sigma_0 \exp(i\omega t + \delta), \quad (2)$$

$$\Delta n^*(t) = \Delta n_0 \exp(i\omega t + \delta_B). \quad (3)$$

The complex Young's modulus,  $E^*(\omega)$ , and the complex strain-optical coefficient,  $O^*(\omega)$ , are defined from these quantities:

$$E^*(\omega) = E'(\omega) + iE''(\omega) = \sigma^*(t)/\epsilon^*(t), \quad (4)$$

$$O^*(\omega) = O'(\omega) + iO''(\omega) = \Delta n^*(t)/\epsilon^*(t). \quad (5)$$

The prime implies the real part of the complex quantity and the double prime implies the imaginary part.

## 3. Experimental

### 3.1. Materials

The blends used in this study were composed of a polystyrene (PS) (Torporax GP550-51, Mitsui Toatsu, Japan) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (G.E. Plastics, Japan) with various compositions. The molecular weight of homopolymer was measured by GPC and small angle light scattering. The weight average molecular weights,  $M_w$ , were  $2.7 \times 10^5$  and  $6.3 \times 10^4$  for PS and PPO, respectively. The blends were prepared by solution blending method, with compositions of PS/PPO as 80/20, 65/35, and 50/50 by weight. Hereafter they will be coded as PSPPO8020, PSPPO6535, and PSPPO5050, respectively.

### 3.2. Preparation of Specimens

A PPO was purified before making the blends. That is,

10 wt% PPO solution (thick yellowish) with a benzene solvent is dropped into a stirred excess methanol, and a precipitation of bulk PPO (thin yellowish) was obtained. The obtained PPO was submerged in a new excess methanol for a couple of days, and it was dried in a vacuum oven for five days. Above purification procedure was accomplished more than twice. Each pair of polymers with prescribed quantities was dissolved at 2 wt% of total polymer in a solvent. The solvent was a dichloromethane distilled to remove water. The solution was cast onto a 70°C hot-plate and a sheet of blend was obtained in a short time by evaporating the solvent. The sheet obtained above was well dried at 120°C under vacuum for 2 days before the film preparation.

We prepared the thin film of the blend by melt press. It was compression-molded into the film of about 500  $\mu\text{m}$  thickness at 250°C. The molded film was also dried under vacuum at temperatures 10°C below the  $T_g$  for 24 hr prior to the measurements.

### 3.3. Measurement

The apparatus for dynamic viscoelasticity and birefringence measurement is a combination of an oscillatory rheometer (Rheospectoler DVE 3, Rheology Co., Ltd.) and an optical system composed of a helium-neon gas laser, two Glan-Taylor polarizing prisms, a quarter wave plate and an optical detector [6,9]. The signal from the optical detector, of angular frequency  $\omega$  or  $2\omega$  depending on the construction of the optical system, is analyzed with a lock-in amplifier and taken into a computer [6]. The available frequency range, 1–130 Hz, is not determined by the limited capability of the optical system but by that of the rheometer with respect to the stable non-resonant oscillation. The measurements were performed at isothermal condition of several temperatures around  $T_g$ .

## 4. Results and Discussion

### 4.1. $E^*(\omega)$ and $O^*(\omega)$ of Constituent Polymers

Before comparing the properties of PS/PPO alloys, it is reasonable to describe the mechanical and optical properties of constituent homopolymers, PS and PPO. In Fig. 1, the master curves of the complex Young's modulus,  $E^*(\omega)$ , and the complex strain optical coefficient,  $O^*(\omega)$ , of PPO are displayed. The reference temperature,  $T_r$ , was as 225°C. The reference temperature was chosen according to the criterion taken throughout this study; the imaginary part,  $E''(\omega)$ , of  $E^*(\omega)$  must be  $10^8$  Pa at  $\omega = 10$  s<sup>-1</sup> at the

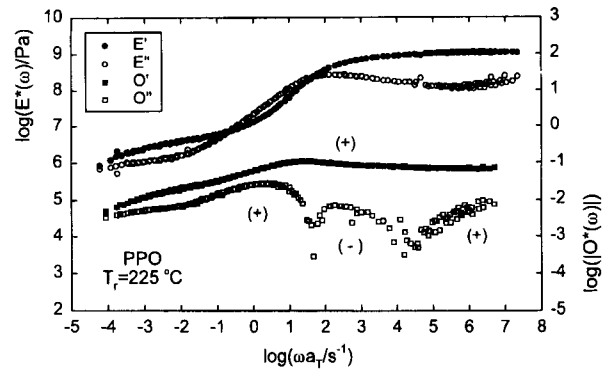


Fig. 1. Master curves of the complex Young's modulus and strain-optical coefficient of PPO constructed with time-temperature superposition principle. Reference temperature is 225°C.

reference temperature. We can see the typical behavior of amorphous polymers for  $E^*(\omega)$  in the glass-to-rubber transition zone. In contrast, the  $O^*(\omega)$  is complicated and inherent to the polymer. The  $O'(\omega)$  of PPO displays positive sign over the measured range, with delicate variations. With increasing the frequency, it increases slowly to the transition region, has a maximum near the frequency region where the  $E''(\omega)$  displays maximum, and decreases slackly in the glassy zone. On the other hand, the sign of  $O''(\omega)$  changed from positive to negative and then to positive again with increasing frequency. The negative  $O''(\omega)$  is observed in 2.5 decades of frequency, corresponding to a lower frequency part of the glassy zone. The two-fold changes of sign of  $O''(\omega)$  have been observed for poly(alkyl methacrylates) and is attributed to the  $\beta$ -relaxation [10]. Some sub-relaxation may be the origin of the positive zone at high frequencies in Fig. 1. The relatively poor superposition of  $E''(\omega)$  at high frequencies may represent the effect of the sub-relaxation.

We displayed the master curves of the  $E^*(\omega)$  and  $O^*(\omega)$  of PS in Fig. 2, and those of PPO, shown in Fig. 1, was also displayed by dotted line in the same frame for the direct comparison. Owing to the appropriate choices of  $T_r$ , 225°C and 116°C for PPO and PS, respectively, one can compare two polymers in the corresponding dispersion zones. In the master curves of  $E^*(\omega)$ , the difference at low frequencies is due to the difference in the rubbery plateau modulus,  $E'_N$ , between the PS and the PPO. The  $E'_N$  of PPO is higher than that of PS suggesting the low entanglement molecular weight,  $M_e$ , of PPO. The  $M_e$  of PS was estimated to be 12 times larger than that of PPO. In the glassy zone of high frequencies, the  $E^*(\omega)$  of PS is considerably higher than that of PPO. The decrease of the  $E''(\omega)$  for PPO becomes slow in the utmost high fre-

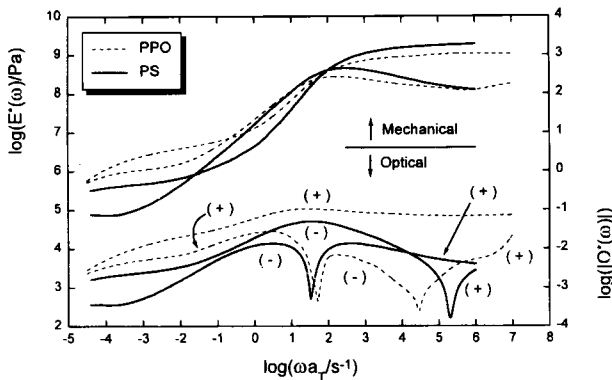


Fig. 2. Master curves of the complex Young's modulus and strain-optical coefficient of PS and PPO at respective reference temperature described in text.

quency region, which is probably due to the contribution of a sub-relaxation.

On the other hand, the strain-optical coefficient,  $O^*(\omega)$ , for two polymers may seem very different from each other. However, one can find a simple parallelism over a considerable range,  $\omega < 10^5 \text{ s}^{-1}$ . Here  $O'(\omega)$  does not change sign and has an extreme and  $O''(\omega)$  changes sign once for either of PS and PPO. A big difference is that the sign is opposite throughout and that the absolute value of the functions is higher for PPO. Thus, the blending of PS and PPO are expected to give the reduction of birefringence coming from compensation of the birefringence of constituents. In the transition zone, very delicate variations in the  $O^*(\omega)$  of the blends are expected owing to the inherent complexity in the  $O^*(\omega)$  of the both constituents.

4.2. Viscoelasticity and Miscibility of the Blends

It is very difficult for polymers with high molecular weight to make a miscible blend in the molecular level. However, in the case where there is a special interaction between the constituents, a miscible blend can be achieved [13]. Such a blend shows positive deviation behavior in the mechanical and thermal properties, i.e. they have improved properties rather than those of constituents [1]. The PS/PPO system has been known to carry such an interaction between the constituents [13]. It displays a good miscibility over the whole compositions. It is usually postulated as a confirmation of a good miscibility if only one single glass transition temperature was detected in the thermal measurement [1,13].

Fig. 3 displays the dynamic  $T_g$  which have been measured in the dynamic mechanical analysis. The  $T_g$  increases with increasing the content of PPO. It is well-known that

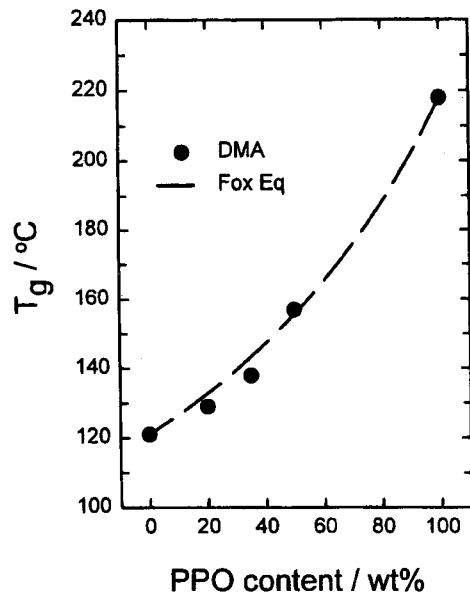


Fig. 3. The glass transition temperature with PPO content in the PS/PPO blend. Filled circle represents  $T_g$  measured by dynamic mechanical analysis. Broken line represents the calculated  $T_g$  evaluated by Fox equation [14].

the  $T_g$  of a compatible blend follows the empirical Fox relation [14]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{6}$$

where  $w_i$  is the weight fraction and  $T_{gi}$  is the glass transition temperature of homopolymer  $i$ . The broken line in Fig. 3 represents Eq. (6). The experimental values are well consistent with the line. This implies the pair of PS/PPO makes a compatible blend in the whole composition.

We display the master curves of  $E^*(\omega)$  and  $O^*(\omega)$  for the blends of PSPPO8020, PSPPO6535 and PSPPO5050 in Fig. 4, Fig. 5, and Fig. 6, respectively. The method for constructing the master curves were described previously. The reference temperatures,  $T_r$ 's, used in constructing the master curves of PSPPO8020, PSPPO6535 and PSPPO 5050 were 130°C, 146°C, and 155°C, respectively. These temperatures are nearly equal to the temperatures obtained by the Fox equation [13].

In the observation in Fig. 4, the  $E^*(\omega)$  of PSPPO8020 is qualitatively similar to those of PS and PPO. Only the  $E'_N$  are increased by piecemeal compared with PS. We cannot detect the inclusion of sub-relaxation in the high frequency zone. That is, it appears that the sub-relaxation of PPO does not affect the modulus of the blend in this composition. In case of PSPPO6535 in Fig. 5, the dynamic modulus seems to be invariable with respect to their con-

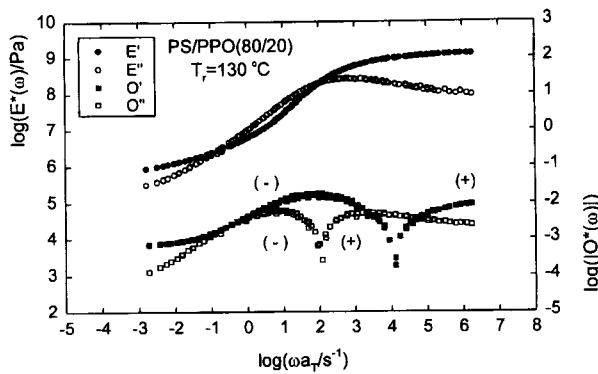


Fig. 4. Master curves of the complex Young's modulus and strain-optical coefficient of PS/PPO(80/20) constructed with time-temperature superposition principle. Reference temperature is 130°C.

stituents. But we can ascertain by referring to the high  $T_g$  that the glass transition temperature is elevated. In the low frequency region,  $E'_N$  is slightly increased owing to the high  $E'_N$  of PPO. Another discernible locus is the indication of sub-relaxation in the high frequency region. That is the rise of  $E''(\omega)$  with frequency, each of which was measured in the isothermal condition. For PS/PPO5050 in Fig. 6,  $T_r$  was further raised suggesting high  $T_g$ . We can perceive the intensity of sub-relaxation is strong compared with that of PS/PPO6535.

The characteristics of  $E^*(\omega)$  argued above will be condensed as follow: in the all compositions examined, the PS/PPO blends seem almost the same in the  $\alpha$ -relaxation distribution without respect to the compositions. It is not possible to evaluate separately the contribution of each constituent to the relaxation of the blend.

To probe the possible difference in another point of view, we showed the  $\tan\delta$  of the blends together with

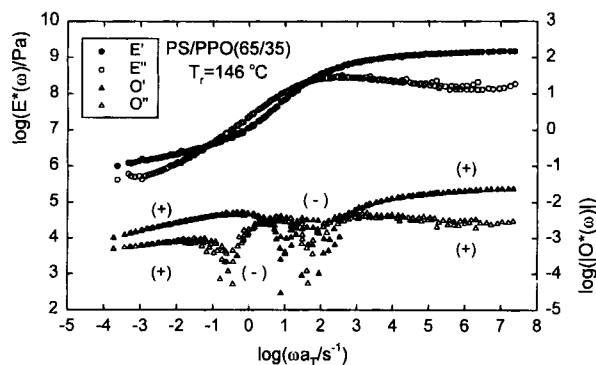


Fig. 5. Master curves of the complex Young's modulus and strain-optical coefficient of PS/PPO(65/35) constructed with time-temperature superposition principle. Reference temperature is 146°C.

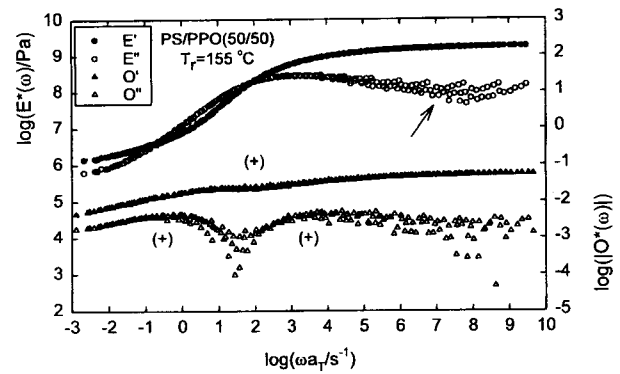


Fig. 6. Master curves of the complex Young's modulus and strain-optical coefficient of PS/PPO(50/50) constructed with time-temperature superposition principle. Reference temperature is 155°C.

those for PS and PPO homopolymers in Fig. 7. One can find the frequency dependence of  $\alpha$ -dispersion of five polymers are very similar to each other. The shapes of curves for the blends are very close to those for the constituent homopolymers. With increasing the fraction of PPO in the blends, a systematic inclusion of sub-relaxation are observed in the high frequency zone. That is, the differences in shapes of the three blends are hardly seen with compositions. Only in the glassy zone the mechanical relaxation behavior is affected by the presence of PPO.

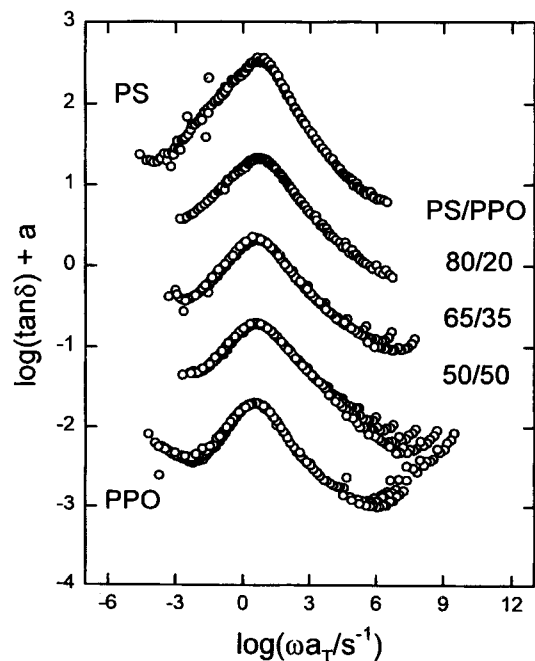


Fig. 7. Mechanical loss tangent of the blends and constituent homopolymers. The curves were shifted in the vertical direction to avoid the confluence.

### 4.3. Birefringence of the Blends

In the mechanical spectrum of the polymers and the blends,  $\alpha$ -dispersions were very similar to each other. In  $O^*(\omega)$  of the polymers in Fig. 4 through Fig. 6, we will explore the difference in the spectra.

In the master curve of  $O^*(\omega)$  in Fig. 4, the sign of  $O^*(\omega)$  changed from negative to positive with increasing frequency. This feature is very similar to that of PS in Fig. 2. But the absolute magnitude of  $O^*(\omega)$  was reduced to a half of PS homopolymer. Compared with the  $O^*(\omega)$  of PS, the sign inversion frequency of  $O^*(\omega)$  is little changed but the frequency of  $O''(\omega)$  is shifted 1/2 grade toward lower frequency region. This is attributed to the inclusion of a new different relaxation mechanism, as will be discussed in the next section.

On the other hand in Fig. 5, much noticeable change is seen in the  $O^*(\omega)$  spectrum. A remarkable change may be the sign in  $O^*(\omega)$  in the low frequency region. The signs of  $O'(\omega)$  and  $O''(\omega)$  are changed from negative to positive by incorporation of 35 wt% of PPO. Hence we can expect that the composition of birefringence free blend may be in the 65~80 wt% of PS fraction. Saito *et al.* [7] reported the birefringence free composition of PS/PPO was 71/29 by weight in the relaxation measurement. Next perceptible change in the  $O^*(\omega)$  is the reduction of birefringence in the transition zone. Compared with the  $O^*(\omega)$  of PS, the absolute value of  $O^*(\omega)$  of PSPPO6535 is lowered to 1/100. The sign in  $O^*(\omega)$  is negative over a very small region. The remarkable change happened in the relaxation mechanism inducing birefringence of the blend. That is, the effect of optical relaxation mechanism of PPO overrode the mechanism of PS in the blends.

In the optical properties of the PSPPO5050 in Fig. 6, the  $O'(\omega)$  displays positive sign in the whole reduced frequency range. It increases almost monotonously with frequency and levels off in the glassy zone. One may note a very shallow valley in the transition zone ( $\omega \cong 10^2 \text{ s}^{-1}$ ). The sign of  $O''(\omega)$  is also positive in the whole range and the valley observed in the transition zone is deep compared with  $O'(\omega)$ . In the glassy zone, severe scattering of data is observed arising from the inclusion of the sub-relaxation.

In brief, contrasting to the almost unique mechanical  $\alpha$ -relaxation independent of the compositions, the birefringence of the PS/PPO blends is clearly varied with compositions suggesting the possibility that the quantitative evaluation of the contribution of each constituent to the relaxation of the blend may be attainable.

### 4.4. Simulation of $O^*(\omega)$ and Inference of Miscibility of the Blends

For a more detailed comparison, the birefringences of the blends are plotted together in a frame in Fig. 8. Systematic changes in shapes from PS type to PPO are clearly seen with increasing the content of PPO. Birefringence usually depends on the degree of orientation of the optical anisotropic segments from the extensional direction. If there is a good miscibility between constituents of PS and PPO, the degree of orientation of the constituents would be similar in the blend under the dynamic deformation [15]. Conversely speaking, when the degrees of orientation of constituents are different in the blend, one would assess that the miscibility of the blends are not good.

The contribution of the birefringence of constituents may be assumed to be expressed by the following equation as a first approximation.

$$O^*(\omega a_T) = f_{PS} O^*_{PS}(\omega a_T) + (1 - f_{PS}) O^*_{PPO}(\omega a_T) \quad (7)$$

where  $f_{PS}$  is the fractional contribution of PS, and  $1 - f_{PS}$  is the fraction of PPO. By using the  $O^*(\omega)$  of PS and PPO homopolymers shown in Fig. 2, the estimation was performed by above equation. The results are plotted in Fig. 9. As can be seen, the characteristic birefringence, which

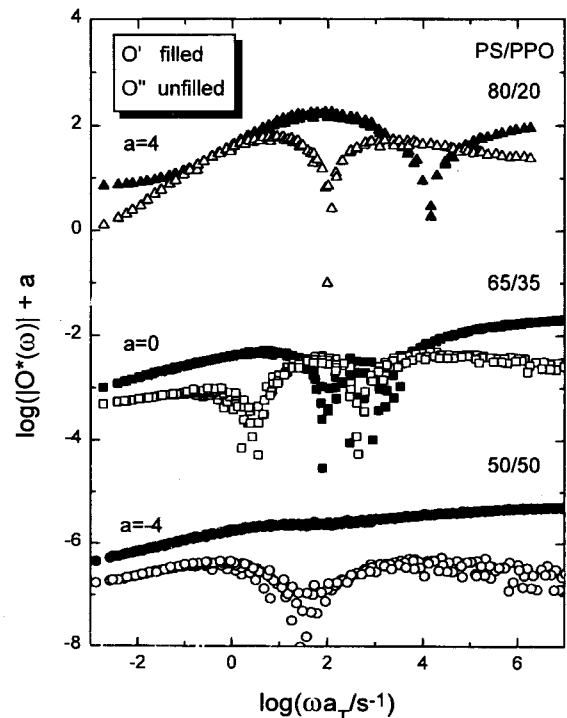


Fig. 8. Master plots of the complex strain-optical coefficient of PSPPO8020, PSPPO6535, and PSPPO5050 in a frame. The plots were shifted in the vertical direction to avoid the confluence.

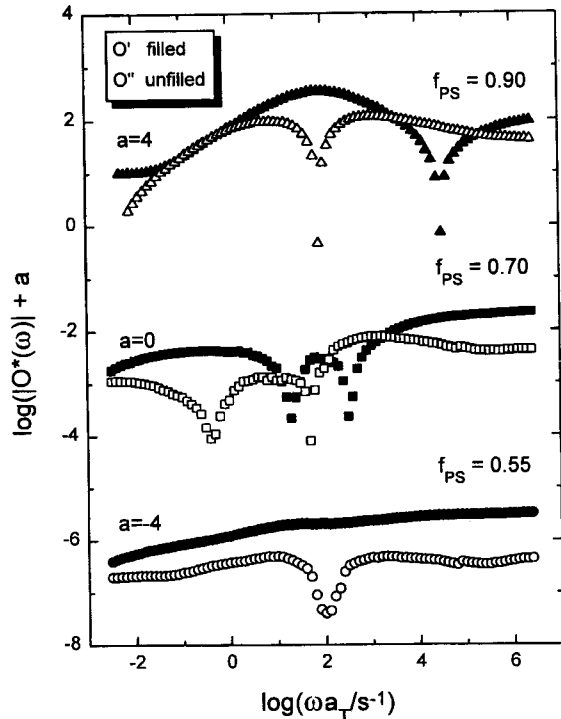


Fig. 9. Master plots of the complex strain-optical coefficient evaluated by simulating the PSPPO8020, PSPPO6535, and PSPPO 5050 with the first approximation of the Eq. (8). The plots were shifted in the vertical direction to avoid the confluence.

are qualitatively very similar to experimental results, could be simulated by varying the fractional contribution. The fractional contribution,  $f_{PS}$ , obtained in the simulation are 0.9, 0.7, 0.55 which correspond to PSPPO8020, PSPPO6535, and PSPPO5050, respectively. Their respective weight fractions are 0.8, 0.65, 0.5 and they can be assumed to be equivalent to volume fractions because the density of PS is nearly equal to that of PPO ( $\rho_{PS} = 1.05$ ,  $\rho_{PPO} = 1.07$ ).

In ideal mixing state of the blends, the degree of orientation of the two components will be similar, and the calculated contribution fraction must be equal to volume fraction. If there is a deviation from the ideal mixing state, two contribution fractions become dissimilar. From the above results, the ratios of contribution fractions to volume fractions are calculated as 1.13, 1.08, and 1.10 for PSPPO 8020, PSPPO6535, and PSPPO5050, respectively. The values are approximately equal to 1, suggesting nearly ideal mixing state of the blends. This result is consistent with the good miscibility inferred from the viscoelastic behaviors of the blends.

#### 4.5. Temperature Dependence of $E^*(\omega)$ and $O^*(\omega)$

In Fig. 10 we displayed the temperature dependence of shift factors,  $a_T$ , which was obtained in constructing the

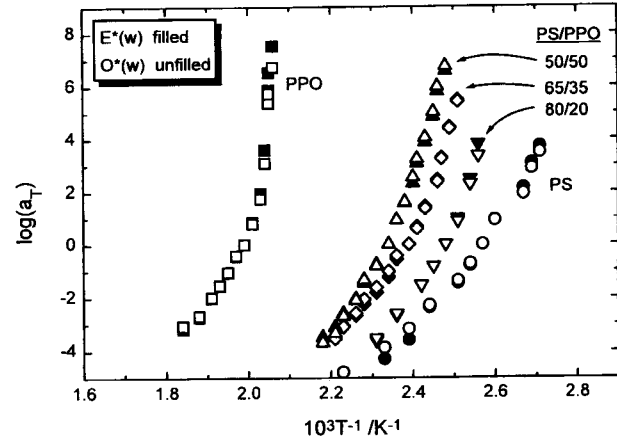


Fig. 10. Temperature dependence of shift factors evaluated on constructing the master plots of the complex Young's modulus and complex strain-optical coefficient of PS, PPO, PSPPO 8020, PSPPO6535, and PSPPO5050.

master curves of  $E^*(\omega)$  and  $O^*(\omega)$  of PS, PPO, PSPPO 8020, PSPPO6535, and PSPPO5050. We can obtain the activation energy for the homopolymers and the blends, assuming the temperature dependence of shift factors are expressed by following Arrhenius type equation

$$\ln a_T = \frac{\Delta H}{RT} + B \quad (8)$$

where  $\Delta H$  is the apparent activation energy,  $R$  is universal gas constant, and  $B$  is a constant. That is, the slope of the curves in Fig. 10 is equivalent to the activation energy of the polymer according to Eq. (8). We can see the curves of temperature dependence, however, are not straight line but  $\Delta H$  increases gradually with decreasing the temperature. This means they do not conduct in the way of Arrhenius type equation in the measured temperature range. However, it is possible to appraise the apparent  $\Delta H$  from the slopes in each temperature of the curves.

First, we make a comparison of the  $\Delta H$  of  $E^*(\omega)$  and  $O^*(\omega)$  for each polymer. As can be seen in Fig. 10,  $\Delta H$  of  $E^*(\omega)$  is larger than that of  $O^*(\omega)$  suggesting that the relaxation behavior of  $O^*(\omega)$  displays stronger temperature dependence rather than the  $E^*(\omega)$ .

On the other hand, the  $\Delta H$  of the blends increases with increasing the content of PPO in the blends. This may be considered as arising from the increased packing between molecular chains of constituents in the blend, or coming from the interaction of PS and PPO at a segmental level inducing a slow molecular relaxations in the blend rather than in the PS. Tsujita *et al.* [16] reported from the measurement of the thermal expansion of PS/PPO blends that

the density of the blend was larger than those of constituents.

### 5. Conclusion

We investigated the birefringence and viscoelasticity of the blends of PS and PPO. A blend of PS/PPO has a good miscibility in the whole composition rendering excellent mechanical properties. The birefringence of PPO was comparatively larger than that of PS. They displayed birefringences of opposite signs over the whole range except glassy zone. The  $O'(\omega)$  of PPO displayed positive sign in the measured region on the whole. The persistence of the positive sign in the glassy zone is probably due to the inclusion of a sub-relaxation. The proposition of a sub-relaxation was confirmed in the corresponding  $E''(\omega)$  spectrum.

In the all compositions, the PS/PPO blends seemed almost unique in the viscoelastic  $\alpha$ -relaxation dispersion without respect to the compositions. But the  $O^*(\omega)$ 's of the blends clearly varied with composition, and the quantitative evaluation of the contribution of each constituent to the relaxation of the blend was attained. The contribution of each constituent to the blends was simulated by the equation assuming a simple additivity. The fractional contribution,  $f_{ps}$ , obtained in the simulation was approximately equal to the respective weight fraction or volume fraction. The result was consistent with the nearly ideal mixing state of the blends estimated from the viscoelastic properties.

The temperature dependence of shift factors,  $a_T$ , was not expressed by an Arrhenius type equation. The activation energy,  $\Delta H$ , increased with decreasing temperature. This

was considered as arising from the increased packing between molecular chains of constituents in the blend or coming from the interaction of PS and PPO at a segmental level inducing a slow molecular relaxation in the blend rather than in the PS.

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