Control of Wavelength Dispersion of Birefringence by Miscible Polymer Blends

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Introduction
The wavelength dispersion of birefringence (or retardation) is very important for optical use of polymer films. Birefringence free polymers have been used for applications such as lens and protect films. And retardation films have been widely used for applications such as liquid crystal display (LCD). In this study, miscibility between amorphous polymers was investigated and some kinds of miscible polymer blends which consist of polymers of positive and negative birefringence were found. For example, it was found that polybutylacrylonitrile (PBAN) which was known as optical polymer was miscible with poly(styrene-co-maleic anhydride) (SMA) and the blend showed a lower critical solution temperature (LCST) type phase diagram [1]. The wavelength dispersion of retardation in this polymer blend could be controlled by the blend composition and orientation of molecules by drawing. On the basis of these results, the retardation film which shows almost the same behavior as the ideal quarter wave film was obtained.

Experimental
NB is supplied from JSR Co. Ltd (ARTON). The blends of NB/SMA with 8wt% MA content were prepared by solvent-cast using toluene. Uniaxial drawing of the films was carried out by a drawing machine which equips a hot chamber. The strips were uniaxially drawn at constant draw rate (50mm·min⁻¹) and at the “equivalent” temperature (i.e. 20°C higher than each glass transition temperature). After drawing, strips were quenched under stress to room temperature. Retardation was measured with optical birefringence analyzer (KOBRA-31PR, Oji Scientific Instruments Inc.) at the wavelengths of 450–800 nm. We can directly obtain retardation as a function of wavelength. Wavelength dispersion (Re) is defined as Equation 1.

\[ 	ext{Re} = 	ext{d} \theta / \text{d} \lambda \]

Wavelength dispersion property of retardation was evaluated by numerical value itself and also by normalized retardation Re/Reₜₙ where the subscript 590 is a reference wavelength.

Results and discussion
The wavelength dispersion of retardation was investigated in detail with normalized retardation Re/Reₜₙ. Figure 1 shows the behavior with change of blend composition and that for the ideal quarter wave film was also shown [2]. The blends of NB/SMA 70/30 and 60/40 showed the larger retardation with longer wavelength, while the blends of 50/50 and 50/70 represented the smaller retardation with longer wavelength. The reversal of wavelength dispersion occurred between the composition 60/40 and 50/50, which was the consequence of change in birefringence sign between positive and negative.

By considering the positive birefringent composition (70/30, 60/40), the dispersion ratio was reasonably increased with increasing SMA8 content: whereas the negative birefringent composition (50/50, 30/70), the dispersion ratio was reasonably decreased with increasing SMA8 content. These results cannot be explained only by the change of graphical slope in Figure 1. Another reason is considered to be the change in birefringence value itself. When we compare two positive or negative birefringent graphs of the equal slope, the dispersion ratio for the lower birefringent one is larger because the influence of the slope upon the numerical value of retardation is relatively larger. We succeeded in controlling the wavelength dispersion (Re/Reₜₙ) by changing the blend composition, which resulted from not only the change of birefringence-wavelength slope but also the shift of numerical birefringence value. As a result, we can achieve the special wavelength dispersion by polymer blend that can never be achieved with single polymer; namely, larger retardation with the longer wavelength, or in other words, increasing normalized retardation with longer wavelength.

In order to discuss more detail by drawing, we chose the blend of NB/SMA=60/40 because this blend composition appeared to be the most suitable for the quarter-wave film as predicted from the result in Figure 1. Wavelength dispersion property, namely normalized retardation, was shown in Figure 2 (the dotted line is the property for ideal quarter-wave film), which clearly shows the change in wavelength dispersion with draw ratio. The graph of normalized retardation Re/Reₜₙ for 60/40 blend gradually approaches that for the ideal quarter-wave film by drawing; draw ratio of 3.3 seems to be the best for the ideal quarter-wave film. Thus, wavelength dispersion of retardation for pure polymer is characteristic of each polymer and independent of draw ratio, whereas that for the blends clearly changed with draw ratio. This is because the polymer chains of NB and SMA8 differently oriented in the blend, that is, the rich blend component seemed to be more oriented than the poor one.

Conclusions
Birefringence of the blend is a sum of positive birefringence of NB and negative birefringence of SMA8, and we can control the birefringence with blend composition and obtain the quarter wave film. In particular, the blend that contains approximately 55% of NB and 45% of SMA8 will be a birefringence free material. We also found a wide band birefringence free polymer blend which consists of olefin-maleinimide copolymer and SMA.

In consequence, by selecting optimum blend composition and drawing condition, one can obtain the polymer film which shows suitable wavelength dispersion of birefringence.

References

Figure 1. Changes in wavelength dispersion of normalized retardation with blend composition in NB/SMA blend. Draw ratio is constant (2.4).

Figure 2. Changes in wavelength dispersion of normalized retardation with draw ratio in NB/SMA (60/40) blend.