Control of Wavelength Dispersion of Birefringence by Miscible Polymer Blends

*Keiichi Kuboyama, Takayuki Kuroda, Toshiaki Ougizawa**

Summary: Wavelength dispersion of birefringence in a miscible polymer blend of a polynorbornene and poly(styrene-*co*-maleic anhydride) was investigated. By adjusting the blend composition, the drawing ratio and the drawing temperature, the wavelength dispersion was controlled and the wide band quarter-wave film was obtained. From the results, the necessary conditions to control the dispersion for the wide-band quarter-wave film and wide-band birefringence-free material are discussed.

Keywords: miscible polymer blend; quarter-wave film; wavelength dispersion of birefringence; zero-birefringence

Introduction

Optical polymers are now being used extensively for versatile applications such as optical lens, optical disks and liquid crystal display (LCD) because of its lightweight, break-proof, moldability and optical characteristics as typified by high transparency and easiness to generate birefringence. In such applications, control of birefringence suitable for each application is important, that is, lowering of birefringence for optical lens and control of birefringence to suitable value for a retardation film in color LCD, that is, a wide-band quarter-wave film.

Industrially, a retardation film having larger retardation with longer wavelength plays an important role in optical displays such as LCD. But homopolymers usually show smaller retardation with longer wavelength (Re_A and Re_B in Figure 1). Therefore, the wide-band quarter-wave film is obtained by superposition of two films with different wavelength dispersion characteristic as drawing directions are not parallel, for example, orthogonal as shown in Figure 1 (its retardation is shown as $Re_{A\text{-}B}$ in Figure 1). Nonetheless, there are limitations in cost by bonding films, and then it is expected to make the quarter-wave film composed of a sheet of polymer.

There are some methods to control the birefringence of polymer materials, for example, copolymerization of monomer units with different sign of birefringence, blending of polymers or composition of a polymer and an inorganic or an organic material with positive and negative birefringence by which an effect similar to the superposition of two films is expected. Among them, polymer blend is a useful method because of its low cost and easiness in processing. There are some reports on control of birefringence by miscible polymer blend,[1,2] however, most of the reports are concerned in lowering of the birefringence only at a certain wavelength, for example, the center wavelength of visible light, 550 nm. However, control of the wavelength dispersion of birefringence in optical materials has become important in these years, because optical lens and films are used at wide wavelength region in visible light. Though there are a few reports on the wavelength dispersion of birefringence in polymer blends,[3–5] the detailed necessary conditions to control the

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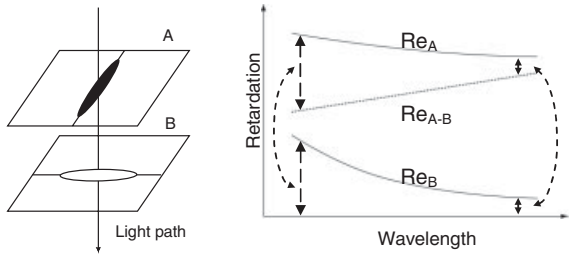

Figure 1.
Superposition of two films A and B and obtained wavelength dispersion of retardation.

wavelength dispersion was not necessarily understood. Thus, the conditions are discussed in this paper.

When birefringence of polymer material is controlled by polymer blend, miscibility between polymers is an important factor because immiscible polymer blends are not transparent because of light scattering due to phase-separated structure composed of polymers with different refractive indices. The miscibility between amorphous polymers has been investigated and some miscible polymer blends consisting of polymers with positive and negative birefringence were found. For example, it was found that a polynorbornene (NB) which was used 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.[6] In this paper, the method on how to control the wavelength dispersion of retardation are discussed for the NB/SMA blend.

Experimental Part

NB ($T_g = 162\,^{\circ}C$, Mw = 93,800) was supplied from JSR Co. Ltd.(ARTON). NB has positive birefringence, while SMA with 8 wt% of MA content ($T_g = 111\,^{\circ}C$, Mw = 310,000) has a negative one.

The blends of NB/SMA8 were prepared by solvent-cast using toluene. The blend films with several blend compositions were cut into strips of 30 mm length, 6 mm width and 150 μm thickness.

Uniaxial drawing of the films was carried out by a tensile machine which equips a hot chamber. The strips were uniaxially drawn at constant draw rate ($50\ mm \cdot min^{-1}$), and at the temperature which was $20\,^{\circ}C$ higher than each glass transition temperature. After the drawing, strips were quenched under stress to room temperature.

Retardation of the blend strips was measured by using the optical birefringence analyzer (KOBRA-31PR, Oji Scientific Instruments Inc.) at several wavelengths between 450 nm and 800 nm. Here, retardation (Re) is defined as Equation 1.

$$\mathrm{Re} = \Delta n \cdot d = \Delta n_0 \cdot f \cdot d, \qquad (1)$$

where Δn is birefringence, Δn_0 is intrinsic birefringence, f is orientation degree of polymer chain and d is thickness of sample.

Results and Discussion

Wavelength Dispersion of Birefringence of NB/SMA8 Blends

Figure 2 shows the wavelength dispersion of birefringence of the NB/SMA8 blends with different compositions. Both of the birefringence and the wavelength dispersion depended on the composition of the blend. From this figure, normalized retardation Re/Re_{590} (subscript of 590 is a wavelength) is plotted in Figure 3 in order to discuss in detail the wavelength dispersion, since it is difficult to compare the wavelength dispersion of birefringence between the blend compositions.[5] It is

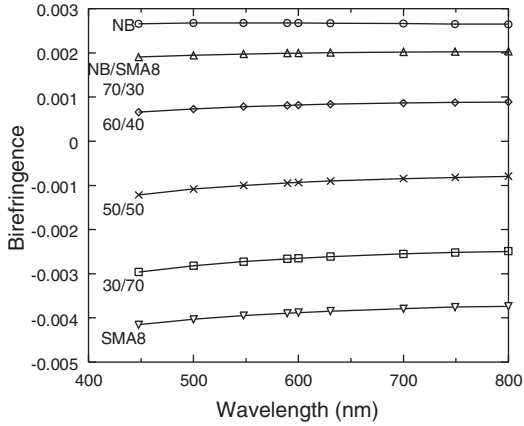

Figure 2.
Wavelength dispersion of birefringence of each NB/SMA8 blend. Draw ratio was fixed at 2.2.

easy to compare the wavelength dispersion in Figure 3 and we found that only the blends of NB/SMA8 = 70/30 and 60/40 showed larger retardation with longer wavelength, i.e., the reverse wavelength dispersion. The reversal of the slope of wavelength dispersion in normalized retardation occurred between the compositions of 60/40 and 50/50. This was the consequence of reversal in sign of birefringence between positive and negative as the wavelength dispersion of birefringence is going up of a right shoulder to either composition, as shown from the result of Figure 2.

In this manner, we were able to obtain the blend with the reverse wavelength dispersion which is difficult to be achieved with single homopolymer.

Orientation of Component Polymers in Blends

Blend composition dependence of the birefringence at 590 nm is shown in Figure 4. If the birefringence in the blend can be explained by the simple sum of

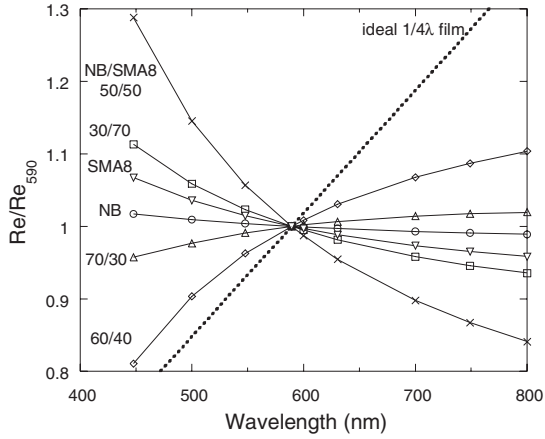

Figure 3.
Wavelength dispersion of normalized retardation in NB/SMA8 blends. Characteristic for ideal quarter-wave film is also shown for comparison. Draw ratio was fixed at 2.2.

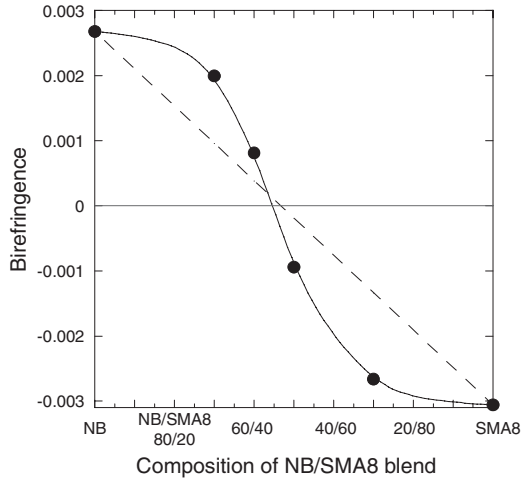

Figure 4.
Composition dependence of birefringence in NB/SMA8 blends at 590 nm at draw ratio of 2.2. Filled circles are experimental one and broken line is calculated value from Equation 2.

birefringence of each pure polymer as in Equation 2, it would behave as the dashed line in Figure 4.

$$\Delta n_{NB/SMA8} = \phi_{NB}\Delta n_{NB} + \phi_{SMA8}\Delta n_{SMA8}, \quad (2)$$

where ϕ is volume fraction and Δn is the birefringence of a pure polymer. In Equation 2, it is assumed that the birefringence of each component polymer in the blend is a constant value independent of the blend composition, however, the birefringence in the blend did not agree with the dashed line in Figure 4. The result suggests that contribution of the birefringence of each polymer within the blend changes depending on the composition.

The birefringence can be expressed as $f \cdot \Delta n_0$ and then the birefringence in the blend can be expressed as follows:

$$\Delta n_{NB/SMA8} = \phi_{NB} \cdot f_{NB} \cdot \Delta n_{0,NB} + \phi_{SMA8} \cdot f_{SMA8} \cdot \Delta n_{0,SMA8}. \quad (3)$$

From the equation, it is suggested that the polymer chains of NB and SMA8 are oriented differently in the blend depending on the blend composition. As shown in Figure 4, the birefringence in the NB rich blends was higher than the dashed line and that in the SMA8 rich blends was lower than the dashed line. This suggests that the rich component oriented more than the less component within the blend.

In order to discuss in more detail the effect of drawing on the birefringence of the blend, wavelength dispersion characteristic of the blend of 60/40 is shown in Figure 5 (the dashed line is the characteristic for the ideal wide band quarter-wave film).

By using Equation 3, the normalized retardation of the blend can be expressed as follows:

$$\frac{\mathrm{Re}}{\mathrm{Re}_{590}} = \frac{\phi_{NB} \cdot f_{NB} \cdot \Delta n_{0,NB} + \phi_{SMA8} \cdot f_{SMA8} \cdot \Delta n_{0,SMA8}}{\phi_{NB} \cdot f_{NB} \cdot \Delta n_{0,NB,590} + \phi_{SMA8} \cdot f_{SMA8} \cdot \Delta n_{0,SMA8,590}}. \quad (4)$$

If $f_{NB} = f_{SMA8}$, Equation 4 can be simplified to Equation 5 and then the normalized retardation of the blend must depend only on the composition.

$$\frac{\mathrm{Re}}{\mathrm{Re}_{590}} = \frac{\phi_{NB} \cdot \Delta n_{0,NB} + \phi_{SMA8} \cdot \Delta n_{0,SMA8}}{\phi_{NB} \cdot \Delta n_{0,NB,590} + \phi_{SMA8} \cdot \Delta n_{0,SMA8,590}} \quad (when\ f_{NB} = f_{SMA8}). \quad (5)$$

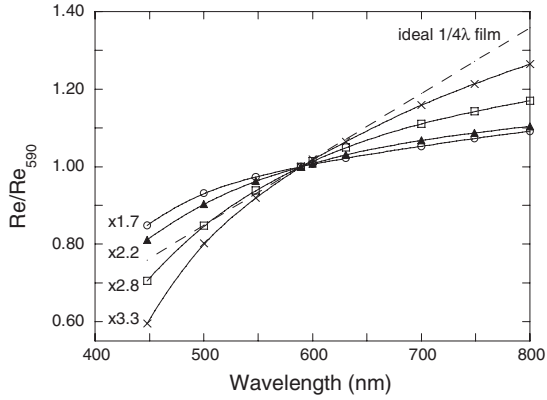

Figure 5.
Changes in wavelength dispersion of normalized retardation with draw ratio in NB/SMA8 (60/40) blend.

However, the normalized retardation also depended on the draw ratio as shown in Figure 5. It indicates that the ratio of orientation degree of component polymers f_{NB}/f_{SMA8} in the blend also changed depending on the draw ratio. Moreover, the change in wavelength dispersion with drawing temperature was also observed and it means that the ratio of orientation degree of component polymers is also changed by the drawing temperature.

The slope of the wavelength dispersion of normalized retardation was larger with the higher draw ratio and then we realized the wavelength dispersion similar with the ideal wide-band quarter-wave film at the draw ratio of 3.3.

Necessary Condition for Controlling Wavelength Dispersion of Retardation

As mentioned above, it was found that the NB/SMA8 blend was a suitable material to achieve the reverse wavelength dispersion such as the quarter-wave film; nevertheless, not all the polymer blends show such a reverse dispersion. The birefringence of the blend is thought as weighting sum of those of blend components. In order to control the wavelength dispersion by the polymer blend, the slope of the dispersion of normalized retardation in the component polymers is one of the most important factors for obtaining the reverse dispersion. The wavelength dispersion of normalized retardation of pure NB and SMA8 is shown in Figure 6. Each dispersion of pure polymer almost overlapped on a master curve. The normalized retardation of a polymer is expressed as follows:

$$\frac{\mathrm{Re}}{\mathrm{Re}_{590}} = \frac{\Delta n_0 \cdot f \cdot d}{\Delta n_{0,590} \cdot f \cdot d} = \frac{\Delta n}{\Delta n_{590}}. \qquad (6)$$

It is clear from the equation that it consists only of intrinsic birefringence and then the value is inherent for each material independent of orientation degree and thickness.

In Figure 6, the slope of wavelength dispersion of normalized retardation in NB was relatively smaller than that in SMA8. In

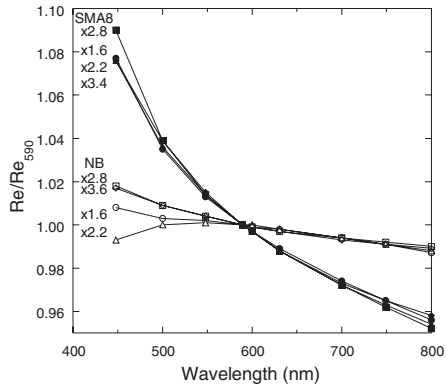

Figure 6.
Wavelength dispersion of normalized retardation of pure NB and SMA8 at several draw ratios.

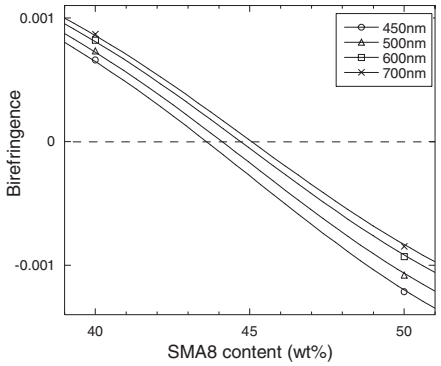

Figure 7.
Composition dependence of birefringence in NB/SMA8 blends at each wavelength.

the blend of them, by weighting sum of the birefringence of them, it can be easily figured out that there will be blend compositions with positive birefringence and wavelength dispersion of positive slope as typified by the blend of 60/40 and 70/30 (NB/SMA8) as shown in Figure 2. Moreover, in order to obtain larger slope of the reverse dispersion, one of the component polymers of which the slope of the dispersion is smaller should have larger magnitude of birefringence than another component polymer.

On the other hand, it is necessary to consider whether it is possible to obtain zero-birefringence at all the wavelength in the visible light by using the NB/SMA8 blend. It seems that the blend with the composition between 50/50 and 60/40 takes zero-birefringence at appropriate wavelength as shown in Figure 2. The composition dependence of birefringence in the polymer at some wavelength around zero-birefringence is shown in Figure 7. In this figure, the composition expected to give zero-birefringence depends on the wavelength and there is no composition where the NB/SMA8 blend shows zero-birefringence at all the wavelength. This suggests that the NB/SMA8 blend is not suitable for the wide-band birefringence-free material, while it is a suitable material for the reverse wavelength dispersion such as the wide-band quarter-wave film.

From the discussion, it is considered that the normalized dispersions of component polymers must have the same slope of wavelength dispersion of normalized retardation to obtain the wide-band zero-birefringence. In fact, we found the wide-band birefringence-free polymer blend which almost fulfill such the condition.[7]

Conclusions

Birefringence of the polymer blend is the weighting sum of positive birefringence of NB and negative birefringence of SMA8, and we could control the birefringence with the blend composition, the drawing ratio and the drawing temperature, and then obtained the wide-band quarter-wave film.

In order to control the wavelength dispersion of birefringence by polymer blend, two polymers must have birefringence of opposite sign to each other. It was also revealed that the slope of wavelength dispersion of normalized retardation was an important factor to control the wavelength dispersion. Moreover, the wide-band birefringence-free material was also obtained by the polymer blend.

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

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