



## Modification of orientation birefringence of cellulose ester by addition of poly(lactic acid)

Masayuki Yamaguchi\*, SoYoung Lee, Mohd Edeerozey Abd Manaf, Manami Tsuji, Tadashi Yokohara

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

### ARTICLE INFO

#### Article history:

Received 21 July 2010

Received in revised form 21 September 2010

Accepted 3 October 2010

Available online 28 October 2010

#### Keywords:

Birefringence

Amorphous polymers

Biopolymers

Blending

Dynamic mechanical analysis

### ABSTRACT

Effect of the addition of poly(lactic acid) (PLA) to cellulose acetate propionate (CAP) on the optical anisotropy is studied considering the morphology and molecular orientation. It is found that PLA is miscible with CAP when the amount of PLA is less than 3 wt.%. The dissolution of PLA chains having large intrinsic birefringence into CAP phase enhances the orientation birefringence of a stretched film, although the viscosity and thus the relaxation time of PLA is significantly shorter than those of CAP. The high level of orientation of PLA chains without relaxation is attained by the cooperative alignment with CAP chains. As a result, a retardation film having appropriate birefringence can be designed by polymer blends composed of biomass-based materials. When the amount of PLA is more than 3 wt.%, however, phase separation occurs. In the case of the blends with phase-separated morphology, the orientation birefringence is not greatly enhanced by blending PLA, because the molecular orientation of PLA in PLA phase relaxes immediately as compared with that of CAP.

© 2010 Elsevier Ltd. All rights reserved.

### 1. Introduction

Because of the rapid increase in the global market for liquid crystal display, high performance films are required to improve the contrast, view-angle, and cost-performance. In particular, the multi-band retardation films, in which absolute value of the orientation birefringence increases with increasing the wavelength of the visible light, are desired recently. This property is called as “extraordinary” wavelength dispersion [1–5]. Because the orientation birefringence of typical polymers decreases with increasing wavelength as expressed by Sellmeier relation (Eq. (1)) [5–8], various techniques are proposed to obtain films showing extraordinary dispersion.

$$\Delta n(\lambda) = A' + \frac{B'}{\lambda^2 - \lambda_{ab}^2} \quad (1)$$

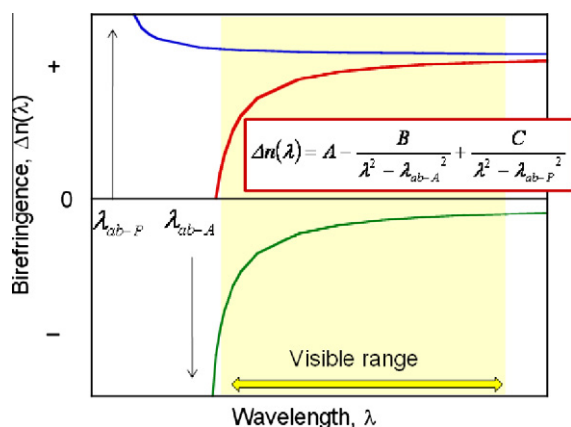
where  $\lambda_{ab}$  is the wavelength of a vibrational absorption peak in ultraviolet region, and  $A'$  and  $B'$  are the Sellmeier coefficients.

In case of cellulose esters,  $\lambda_{ab}$  of the ester groups which mainly determine the orientation birefringence is in the following order; acetyl > propionyl > butyryl [5]. Moreover, the sign of birefringence of the acetyl group is negative, whereas that of the propionyl and butyryl groups is positive [5,9]. Since the total value of the birefringence is provided by the sum of each component [10,11], it can be crudely expressed by the following relation for cellulose acetate propionate, CAP.

$$\Delta n(\lambda) = \Delta n_A(\lambda) + \Delta n_P(\lambda) = A - \frac{B}{\lambda^2 - \lambda_{ab-A}^2} + \frac{C}{\lambda^2 - \lambda_{ab-P}^2} \quad (2)$$

where  $\Delta n_A(\lambda)$  and  $\Delta n_P(\lambda)$  are the birefringences of the acetyl and propionyl groups, respectively,  $\lambda_{ab-A}$  and  $\lambda_{ab-P}$  are the wavelengths of the absorption peak for the acetyl and propionyl groups, respectively, and  $A$ ,  $B$ , and  $C$  are the positive values. As a result, CAP shows the extraordinary

\* Corresponding author. Tel.: +81 761 51 1621; fax: +81 761 51 1625.  
E-mail address: [m\\_yama@jaist.ac.jp](mailto:m_yama@jaist.ac.jp) (M. Yamaguchi).



**Fig. 1.** Schematic illustration of extraordinary dispersion of orientation birefringence for CAP; the blue and green lines represent the wavelength dispersion of propionyl and acetyl groups, respectively. The red line denotes the sum of them.

dispersion of positive birefringence in the visible wavelength as illustrated in Fig. 1, which was explained in detail in our preceding article [5].

Although CAP shows the extraordinary wavelength dispersion of the orientation birefringence, the magnitude of the birefringence is not high, leading to thick films to satisfy the required retardation, i.e., the product of the birefringence and thickness. Therefore, the birefringence enhancer is desired in the industry.

Up to now, some polymers such as poly(methylmethacrylate) PMMA [13], poly(epichlorohydrin) (PECH) [12,13], and poly(vinyl acetate) (PVAc) [12,14] were employed to modify the optical anisotropy for CAP. However, PMMA, PECH, and PVAc show negative orientation birefringence. Therefore, they can be used to erase the orientation birefringence of CAP, not to enhance the birefringence. On the contrary, poly(lactic acid) PLA shows positive intrinsic birefringence whose value is significantly larger than that of CAP [15]. Furthermore, PLA is miscible with PMMA and PVAc [16,17], which are miscible with CAP [12–14]. Therefore, PLA could be miscible with CAP at specific condition. At the best of our knowledge, however, only a research group of Tatsushima et al. studied the miscibility between PLA and cellulose esters [18]. According to them, PLA is immiscible with cellulose acetate butyrate, CAB, although they did not study the miscibility with CAP in detail. Further, the optical anisotropy has not been reported for the blends. In this study, the effect of the addition of PLA on the orientation birefringence is discussed considering the miscibility between them.

## 2. Experimental

### 2.1. Materials

Materials employed in this study were commercially available CAP (Eastman Chemical, CAP-482-20) and PLA (Mitsui Chemical, Lacea H280). The degree of substitution

of the acetyl group for CAP is 0.19 and that of the propionyl group is 2.58. The optical purity of PLA is 10%.

The molecular weights of the samples were evaluated using a gel permeation chromatograph (Tosoh, HLC-8020) with TSK-GEL<sup>®</sup> GMHXL; chloroform was employed as the eluant and its flow rate was 1.0 ml/min. The temperature was maintained at 40 °C and the sample concentration was 1.0 mg/ml. The number- and weight-average molecular weights are  $M_n = 7.7 \times 10^4$  and  $M_w = 2.1 \times 10^5$  for CAP and  $M_n = 2.5 \times 10^5$  and  $M_w = 3.6 \times 10^5$  for PLA as a polystyrene standard.

CAP and PLA were melt-mixed at various blend ratios by an internal batch mixer (Toyoseiki, Labo-Plastmil) at 220 °C. The blade rotation speed was 40 rpm and the mixing time was 5 min.

The obtained samples were compressed into flat sheets by a compression-molding machine for 5 min at 220 °C under 10 MPa and subsequently quenched by another compression-molding machine in which the temperature was controlled at 20 °C.

The uniaxial oriented films were prepared by hot-drawing operation using a dynamic mechanical analyzer (UBM, S1000-DVE3, Mukou, Kyoto, Japan) at the temperature where the tensile storage modulus is 10 MPa at 10 Hz. The initial distance between the clamps was 10 mm and the stretching rate was 0.5 mm/s. Therefore, the engineering strain rate was  $0.05 \text{ s}^{-1}$ . The drawn sample was quenched by blowing cold air in order to avoid relaxation of molecular orientation.

### 2.2. Measurements

The frequency dependence of the oscillatory shear moduli in the molten state, such as storage modulus  $G'$  and loss modulus  $G''$ , was measured by a cone-and-plate rheometer (UBM, MR-500) at various temperatures under a nitrogen atmosphere. A parallel plate geometry was employed at the measurements of CAP at low temperatures.

The temperature dependence of the oscillatory tensile moduli in the solid state, such as storage modulus  $E'$  and loss modulus  $E''$ , was measured from –100 to 180 °C using a dynamic mechanical analyzer (UBM, E-4000). The frequency and heating rate were 10 Hz and 2 °C/min, respectively. The rectangular specimen, in which the width is 5.0 mm and the length is 20 mm, was employed.

The refractive index of the polymer films was evaluated by an Abbe refractometer (Atago, NRA 1T) at room temperature employing  $\alpha$ -bromonaphthalene as a contact liquid.

The birefringence of the drawn films was measured at room temperature by an optical birefringence analyzer (Oji Scientific Instruments, KOBRA-WPR) as a function of wavelength by changing color filters. The diagram of the measurement was illustrated in our previous paper [5].

The optical transparency of the films was evaluated at room temperature by a haze machine (Toyoseiki, Direct Reading Haze Meter). The thickness of the films was 200  $\mu\text{m}$ . Haze is defined as the percentage of total transmitted light passing through the specimen that is scattered from the incident beam by more than 2.5 degree; it is often employed as a measure of the turbidity of a film specimen.

Download English Version:

<https://daneshyari.com/en/article/1400707>

Download Persian Version:

<https://daneshyari.com/article/1400707>

[Daneshyari.com](https://daneshyari.com)