Birefringence and strain-induced crystallization of stretched cellulose acetate propionate films

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ABSTRACT

We have investigated the wavelength dependence of the birefringence (Δn) for cellulose acetate propionate (CAP) films stretched at various draw ratios (DRs) and strain rates (SRs) by comparing with the result of cellulose triacetate (CTA). CAP exhibits extraordinary wavelength dispersion of Δn although CTA shows ordinary dispersion, indicating that Δn of CAP is determined by the acetyl and propionyl groups. For CAP, the extraordinary dispersion becomes stronger at higher DR and SR. Thermal analysis suggests that hot stretching induces crystallization of CAP and the crystal size increases with increasing DR and SR. Furthermore, the two-dimensional X-ray diffraction patterns of CAP and CTA (a semicrystalline polymer) exhibit orientation of the induced crystal. These results mean that the acetyl orientation in CAP becomes stronger than the propionyl orientation. This conclusion is reasonable because the acetyl group is more tightly confined to the pyranose ring than the propionyl group.

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1. Introduction

When polymer films are stretched beyond the glass transition temperature (T_g), birefringence (Δn) is generated by chain orientation [1]. Here, Δn is defined as the difference of the two refractive indices $n_{//}$ and $n_\perp$ in the directions parallel and perpendicular to the stretching direction:

$$\Delta n = n_{//} - n_\perp \tag{1}$$

For most amorphous polymers, Δn is proportional to the tensile stress σ because the two properties are associated with the orientation of the chain segment [1]:

$$\Delta n = C\sigma, \tag{2}$$

where C is the stress-optical coefficient, which is determined from repeating units of the polymer. This relation is called the stress-optical rule (SOR). Because Δn is related to the polarizability anisotropy of the chain segment, general polymers with aromatic groups, such as polystyrene and polycarbonate, have high Δn values.

Using the model of the statistical segment approach introduced by Kuhn and Grun [2], Δn is determined by

$$\Delta n = \frac{2\pi}{9} \frac{(n+2)^2}{n} \frac{\rho N_A}{M_{seg}} \Delta\alpha \left[\frac{3\langle\cos^2\theta\rangle - 1}{2} \right], \tag{3}$$

where n, ρ, and N_A are the refractive index, density, and Avogadro's number, respectively. M_{seg} and $\Delta\alpha$ are the molecular weight and polarizability anisotropy of the chain segment for the oriented polymer, and θ is the average angle between the segment and the stretching direction. The term in brackets on the right-hand side of eq. (3) [($3\langle\cos^2\theta\rangle - 1$)/2] represents the orientation function F, and the following relation is obtained:

$$\Delta n = \Delta n^0 F \tag{4}$$

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$$\Delta n^0 = \frac{2\pi}{9} \frac{(n+2)^2}{n} \frac{\rho N_A}{M_{seg}} \Delta\alpha,$$

where Δn^0 is the intrinsic birefringence for the anisotropic molecule perfectly oriented in the stretching direction.

Cellulose derivatives are expected to be ecofriendly materials for various applications because of biomass resources [3–7]. In particular, cellulose esters have been investigated for application to optical films because of their attractive properties such as heat resistance and transparency [7–11]. Retardation films, which are optical films, have to be improved for optical devices such as stereo and organic electroluminescence displays. In addition, linear proportionality of the birefringence with the wavelength, which is called "extraordinary wavelength dispersion", is required for high-performance optical devices. However, for general polymers composed of a single component, the birefringence decreases with increasing wavelength (ordinary dispersion) because of the strong absorption in the ultraviolet region for polymers. In optical industries, extraordinary dispersion is produced by blending with other components [12–16], laminating films [17], and copolymerization [18–20].

Recently, Yamaguchi et al. found that cellulose acetate propionate (CAP, Fig. 1) shows extraordinary wavelength dispersion of the birefringence without any extra components [21]. As shown in Fig. 2, cellulose triacetate (CTA), which has only the acetyl group as a substitution group, exhibits ordinary dispersion. By comparing with the optical data of CTA, they found that the extraordinary dispersion of CAP originates from two different contributions: acetyl and propionyl groups. Furthermore, they explained the possibility of controlling the wavelength dependence by the stretching conditions, such as the draw ratio (DR) although the mechanism is still unknown. If the stretching conditions can control the wavelength dispersion of Δn, a new technique can be proposed to design an optical retardation film with ideal extraordinary dispersion. In this study, the wavelength dependence of the birefringence of stretched CAP films under various conditions was investigated based on the stress–strain curve, the birefringence, thermal analysis, and two-dimensional (2D) X-ray diffraction (XRD) experiments.

2. Materials and methods

2.1. Materials

The CAP sample was produced by Eastman Chemical Company (Kingsport, TN, USA). The sample was obtained in the powdered state. The weight- and number-average molecular weights (M_w and M_n) of CAP were determined by gel-permeation chromatography (GPC, HLC-8020 Tosoh, Japan) to be 2.1×10^5 and 7.7×10^4, respectively. The degrees of substitution of the acetyl and propionyl groups per pyranose unit of CAP are 0.19 and 2.58, respectively. To avoid the effect of water on the physical properties, the CAP powder was dried in vacuo at 80 °C for 2 h prior to melt compression. After
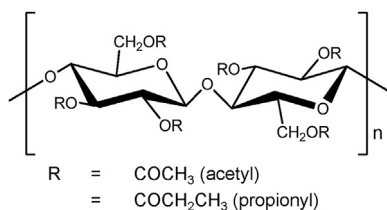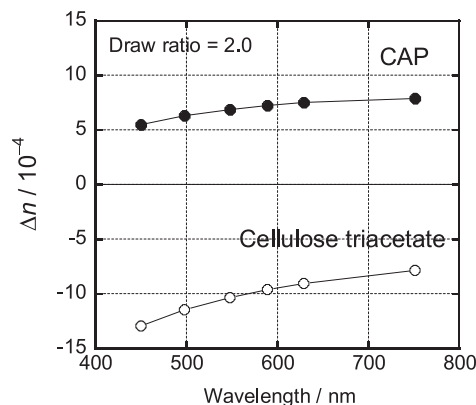

Fig. 2. Wavelength dependence of stretched CAP and CTA films.

being kept in a vacuum oven at room temperature for at least for one day, the blend samples were compressed into sheets with a thickness of 200 μm at 200 °C for 5 min under 10 MPa by a compression-molding machine (Table-type-test press SA-303-I-S, Tester Sangyo, Japan) and then cooled at 25 °C for 5 min.

To compare the crystallization effect, CTA was also used. The sample characterization and preparation have been reported in our previous paper [9].

2.2. Methods

Dynamic mechanical analysis (DMA) was performed to measure the tensile storage and loss moduli (E' and E'') at 10 Hz as a function of temperature from 25 to 250 °C with a heating rate of 2 °C min^{-1} using a tensile oscillatory rheometer (DVE-E4000, UBM, Japan).

Hot-stretching tests were performed at various conditions (DRs and SRs) using a tensile drawing machine (DVE-3, UBM, Japan). The stretching temperatures (T_d) were chosen to be 163 and 215 °C for CAP and CTA, respectively, as explained in our previous papers [9,21]. For CAP, T_d was determined from the DMA data, where $E' = 10$ MPa at 10 Hz. For CTA, T_d was selected from the plateau region of E' (>100 MPa) beyond T_g in the DMA data. The stretched films were immediately quenched with cold air after stretching to avoid relaxation of the molecular orientation.

The stretched samples were kept in a humidic chamber (IG420, Yamato, Japan) at 25 °C and 50% relative humidity for one day to prevent the moisture effect on the optical properties, as previously reported [22]. The birefringence was measured as a function of wavelength using an optical birefringence analyzer (KOBRA-WPR, Oji Scientific Instruments, Japan). The details of the optical system are described in our previous paper [21].

Thermal analysis was performed using a differential scanning calorimeter (DSC-822e, Mettler Tolede, Greifensee, Switzerland) under a nitrogen atmosphere to avoid thermal-oxidative degradation. The approximately 10 mg sample was placed in an aluminum pan. The first heating curve was recorded at a heating rate of 10 °C min^{-1}.

To investigate the anisotropic crystalline structure, 2D wide-angle XRD patterns were recorded using a graphite mono-chromatized CuKα radiation beam focused via a 0.3 mm pinhole collimator with a flat 20×20 cm^2 imaging plate (IP) detector with 1900×1900 pixels (R-AXIS IIc, Rigaku, Japan). A small piece of the sample with edge sizes less than 1 mm was mounted with a sample–IP distance of 10 cm. The exposure was performed with 7 min per shot in the geometrical condition by directing the X-ray beam in the normal direction to the film plane.

R   =   COCH$_3$ (acetyl)
      =   COCH$_2$CH$_3$ (propionyl)

Fig. 1. Chemical structure of CAP.