

Birefringence control of solution-cast film of cellulose triacetate



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ABSTRACT

We controlled the optical anisotropy of a solution-cast film composed of cellulose triacetate (CTA) by adding ferrocene. Owing to the molecular orientation in the film plane of solution-cast films, which results from the normal stress applied during the solvent evaporation process, the average refractive index is usually higher in the plane of the film than in the thickness direction. We found that the addition of ferrocene, which is miscible with CTA, reduced the optical anisotropy by nematic interaction; i.e., ferrocene molecules are forcibly embedded into the film plane accompanying the CTA chains. Because the direction of anisotropic polarizability of ferrocene is perpendicular to the long axis of the molecule, the refractive index in the thickness direction is reduced. Furthermore, the stress-optical coefficient in the glassy state is reduced by the addition of ferrocene.

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1. Introduction

The control of the birefringence of optical retardation films is crucial for both conventional liquid-crystal displays and advanced systems including electroluminescent and 3D displays. Although there are three origins of birefringence, i.e., orientation birefringence, form birefringence, and photoelastic birefringence in the glassy state, most retardation films are produced by exploiting orientation birefringence [1–4]. Therefore, the wavelength dispersion of birefringence is determined by the molecular structure that defines the intrinsic birefringence. Furthermore, the degree of molecular orientation, as well as the intrinsic birefringence, decides the magnitude of the birefringence.

Recently, the addition of miscible low-molecular-weight compounds (LMCs) to polymers has been studied intensively as a means of controlling orientation birefringence [5–12]. The effect depends on the orientation of LMC molecules in the stretching direction of the aligned polymer chains: a mechanism known as nematic interaction. Nematic interaction was first proposed to explain the slow relaxation of a short chain surrounded by long chains in a polymer melt with broad molecular weight distribution [13–15]. Later, the phenomenon was confirmed even in miscible polymer blends [16,17]. LMCs are often miscible with polymers owing to the

contribution of mixing entropy; the addition of a polar liquid such as a plasticizer is important for controlling the magnitude and wavelength dispersion of birefringence. In nematic interaction, rod-shaped molecules always align with the flow/stretching direction by topological interaction with the surrounding polymer chains. The strength of the orientation correlation is believed to be dependent on size matching; i.e., strong orientation correlation is expected when the size of an LMC is comparable with the size of the polymer segments [12,17]. Furthermore, disk-shaped molecules tend to be embedded into a film plane when a polymer is stretched in one direction with a constant width, i.e., planar deformation [10].

Numerous studies on birefringence control have been conducted on various derivatives of cellulose, which is one of the most transparent biomass-based plastics, because nematic interaction with LMCs is often detected in such plastics [4–12]. Among the derivatives of cellulose, cellulose triacetate (CTA) is currently used as an optical film, especially as a polarizer-protective film, because it has marked transparency, high heat resistance, and relatively low birefringence. In general, CTA films are produced by solution casting because melt processing is impossible. In this study, we controlled the anisotropy in the refractive index of a solution-cast CTA film by the addition of an LMC.

2. Material and methods

2.1. Materials

We used commercially available CTA (LT-35; Daicel Corp.) in this

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study. The degree of substitution of the CTA was 2.96, and its number-average molecular weight (M_n ; evaluated by size exclusion chromatography with a polystyrene standard) was 7.60×10^4 Da. Ferrocene was purchased from Tokyo Chemical Industry (purity > 95%), and used without further purification. Fig. 1 represents the chemical structures of the raw materials.

2.2. Methods

CTA and ferrocene were dissolved in a mixture of chloroform and methanol (9/1, weight ratio), and stirred for 24 h at room temperature. The resulting solution was poured into a flat-bottomed glass petri dish and kept at room temperature to allow the solvent to evaporate. The obtained films were 100 μm thick. The films were dried in a vacuum oven at room temperature for 2 h to completely remove the solvent. They were then kept in a temperature- and humidity-controlled chamber (IG420; Yamato) at 25 $^\circ\text{C}$ and 50% relative humidity (RH) for at least one day before investigation.

3. Experimental

3.1. Measurements

We measured the temperature dependence of the oscillatory tensile modulus in the solid state between 0 and 250 $^\circ\text{C}$ in 5×20 mm rectangular specimens using a dynamic mechanical analyzer (E-4000; UBM). The frequency was 10 Hz and the heating rate was 2 $^\circ\text{C}/\text{min}$.

The birefringence was measured using an optical birefringence analyzer (KOBRA-WPR; Oji Scientific Instruments) at room temperature. The out-of-plane birefringence was calculated from the retardation in the thickness direction, determined by retardation measurements at an oblique incident angle of 40 $^\circ$, divided by the film thickness measured using a digital micrometer. The in-plane birefringence was also evaluated using the analyzer. Both measurements were performed as a function of the wavelength between 450 and 800 nm by changing the color filters. The average refractive index was measured using an Abbe refractometer (DR-M2; Atago) as a function of wavelength at room temperature.

Simultaneous measurements of stress and birefringence were performed at room temperature using a uniaxial tensile machine (S1000-DVE3; UBM) and a polarized laser beam (632.8 nm) (L5-LPH-121; Melles Griot). Optical retardation was calculated using light intensities in crossed-nicol and parallel-nicol states. The stretching speed was 0.1 mm/s and the initial distance between the clamps was 10 mm. The details of the measurements are described in our previous paper [5].

4. Theory/calculation

Although a solution-cast film is usually free from birefringence in the film plane, i.e., in-plane birefringence, the refractive index in

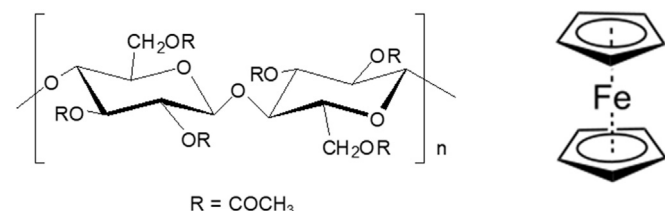


Fig. 1. Chemical structure of (left) CTA and (right) ferrocene.

the film thickness direction is generally different from the average value in the film plane. This can be attributed to the molecular orientation in the film plane caused by the stress developed during the evaporation of the solvent, which is called “out-of-plane birefringence Δn_{th} ”, and is defined by the following equation:

$$\Delta n_{th} = \frac{n_x + n_y}{2} - n_z \quad (1)$$

where n_x and n_y are the refractive indices in the film plane, and n_z is the refractive index in the direction normal to the film plane.

In general, out-of-plane birefringence is not desirable in protective films, and should be reduced. Although decreased molecular weight and prolonged evaporation speed effectively reduce out-of-plane birefringence, they are not recommended in industry. Therefore, we attempted to reduce out-of-plane birefringence by adding an LMC.

As with most polymer films, CTA films have positive out-of-plane birefringence, because n_x and n_y are larger than n_z . According to Songsurang et al., nematic interaction is also expected in solution-cast films [10]. A disk-shaped LMC tends to be embedded in the film plane. However, disk-shaped LMCs usually have a large refractive index in the disk plane compared with the normal direction. An increase in the refractive index in the film plane also occurs when using a rod-shaped LMC. Therefore, the out-of-plane birefringence is usually increased by the addition of a conventional LMC. In this study, we used ferrocene, i.e., bis-(η^5 -cyclopentadienyl) iron, as the LMC because the anisotropic direction of polarizability of CTA is perpendicular to its long molecular axis [18,19]. The concept of this study is illustrated in Fig. 2.

5. Results and discussion

5.1. Solvent evaporation rate

Out-of-birefringence is determined by the competition between the normal stress induced by solvent removal and the orientation relaxation caused by Brownian motion [20]; therefore, the effect of ferrocene on the solvent evaporation rate should be considered. A glass plate carrying approximately 1 mL of the solution was placed on a chemical balance to evaluate the weight change during the evaporation process. The experimental results are shown in Fig. 3. It is obvious that the addition of ferrocene does not affect the evaporation rate, which indicates that the orientation of the CTA chains is barely affected by ferrocene. Songsurang [9] reported a similar result: the addition of tricresyl phosphate does not affect the evaporation rate of the CTA solution or the orientation of the CTA chains in the film plane.

5.2. Dynamic mechanical properties

Fig. 4 illustrates the temperature dependence of the tensile storage modulus E' and the loss modulus E'' at 10 Hz for CTA and CTA/ferrocene (95/5). The storage modulus drops off sharply at approximately 200 $^\circ\text{C}$ for pure CTA. The storage modulus increases slightly with temperature at approximately 205 $^\circ\text{C}$. This can be attributed to the cold-crystallization of CTA. Because the solution-cast film has a low degree of crystallinity, it exhibits crystallization beyond the glass transition temperature T_g . As a result, the modulus beyond 210 $^\circ\text{C}$ is significantly higher than typical values in the rubbery region, although the transparency is hardly affected by crystallization. The crystalline structure plays an important role in the hot-stretching process used to produce retardation films [21–23].

The peak temperatures in the E'' curve ascribed to T_g are 199 $^\circ\text{C}$

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