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Development of microporous structure and its application to optical film for cellulose triacetate containing diisodecyl adipate

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ABSTRACT

Phase separation in plasticized cellulose triacetate (CTA) films is investigated to produce a microporous film that can be used in optical devices. Hot-stretched CTA films containing diisodecyl adipate (DIDA) show negative orientation birefringence similar to the hot-stretched pure CTA. After extracting DIDA from the stretched films by immersion into an organic solvent, however, the films exhibit positive birefringence. Moreover, the magnitude of the birefringence increases with the wavelength, known as extraordinary dispersion, which is an essential property in the preparation of an ideal quarter-wave plate. Numerous ellipsoidal pores with micro-scale were detected in the film after the immersion, indicating that DIDA were segregated and formed ellipsoidal domains in the CTA matrix during annealing and stretching. These results indicate that extraordinary wavelength dispersion is given by the combinations of orientation birefringence from CTA and form birefringence from micropores. Furthermore, it was found that annealing time and stretching condition affect the phase separation as well as the shape and size of pores.

1. Introduction

Porous materials have been studied intensively these days because of their application in the industry and their future potential of additional functions for various products (Silverstein, Cameron, & Hillmyer, 2011). In general, porous structure is responsible for some advantages such as increase in the surface area and penetration distance from one surface to another, besides weight saving. Therefore, microporous materials are used as absorbent, catalyst, and so on (Wakao & Smith, 1964; Arenas & Crocker, 2010). Especially, materials having pores with nano – micro scale are expected to expand the applications recently, because advanced functions attributed to pores have been discovered. As an example of their application in thermal insulation, it is desired that the pore size should be smaller than the mean free path of air, i.e., ca. 60 nm (Clyne, Golosnoy, Tan, & Markaki, 2006). Moreover, fine pores having appropriate size are also required for biomaterials such as vehicle for drug and gene delivery (Selvam et al., 2009). In the case of the Lithium ion battery, a separator has to have microporous structure, which should provide the self-shuttering function at high temperature (Love, 2011; Phulkerd, Hagihara, Nobukawa, Uchiyama, & Yamaguchi, 2013). These applications indicate that well-controlled micropores have a great potential to produce functional materials, and it is necessary to control the size and amount of micropores in order to be used in such applications.

There are several methods to produce porous materials: fiber bonding, solvent casting/particulate leaching, gas foaming, plastic deformation, and phase separation/emulsification (Mikos & Temenoff, 2000; Selvam et al., 2009; Phulkerd et al., 2013; Samthong et al., 2015). In the phase separation method, a component of dispersed phase is removed after separation to produce pores. Therefore, the miscibility is important to control the structure.

As well known, free energy of mixing ΔG_{mix} is expressed as,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (1)$$

where ΔH_{mix} is the mixing enthalpy and ΔS_{mix} is the mixing entropy. Eq. (1) demonstrates that the temperature and the interaction parameter which decides ΔH_{mix} are the basic parameters to be considered. These factors are important for the formation of pores. For example, phase separation should occur by spinodal decomposition in order to obtain large number of fine pores (Olmsted, Poon, McLeish, Terrill, & Ryan, 1998; Matsuba, Kaji, Nishida, Kanaya, & Imai, 1999). In addition, phase separation can occur by several factors other than temperature change and interaction of materials (Rangel-Nafaile, Metzner, & Wissbrun, 1984; Lee, Jung, Kang, & Lee,

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Table 1
Characteristics of samples.

	CTA	Plasticizer	
		DEP	DIDA
Solubility parameter ($(MPa)^{1/2}$)	19.4	20.7	17.0
Refractive index (−)	1.48	1.50	1.45

Table 2
Glass transition temperature and drawing temperature for the films.

	CTA	CTA/DEP	CTA/DIDA
T_g (°C)	195	151	192
T_{draw} (°C)	213	178	208

2004). Specifically, the orientation of polymer chains by stretching causes the phase separation originating from entropy loss of miscible system, i.e., the so-called flow-induced phase separation (Yanase et al., 1991). On the contrary, some polymer blends show flow-induced mixing by the reduction of concentration fluctuation (Mazich & Carr, 1983; Hindawi, Higgins, Galambos, & Weiss, 1990). In order to control the pore growth, the effect of these factors must be revealed.

Here, we focus on the mechanism of phase separation to produce the porous material. Cellulose triacetate (CTA), one of the general-purpose polymers for optical films, is used as a matrix polymer. Because CTA exhibits excellent transparency and heat resistance (Songsurang et al., 2012), the films are used for optical applications in industry. In this paper, the micropores in an oriented CTA film are provided using a plasticizer which has poor miscibility with CTA, and this film can be employed as a multi-band wave plate, one of the functional optical films required for an advanced display. In this study, the microporous structure using heat-induced and flow-induced phase separation is investigated.

2. Experimental

2.1. Materials

Cellulose triacetate (CTA) (Daicel, LT-35) was employed as the matrix polymer. The degree of acetylation per a pyranose unit is 2.9. The weight-average M_w and the number-average molecular weights M_n were 1.3×10^5 and 3.5×10^5, determined by a gel permeation chromatography (Tosoh, HLC-8020) with TSK-GEL® GMHXL as a polystyrene standard. Commercially available plasticizers such as diethyl phthalate (DEP) and diisodecyl adipate (DIDA), which are involatile liquid, were used in this study without further purification. Both of them were produced by Daihachi Chemical Industry. The structure and properties of CTA and plasticizers are shown in Fig. 1 and Table 1. The values of refractive indices at 633 nm of the plasticizers are close to that of CTA at room temperature.

The solubility parameters calculated by the group contribution method (Grulke, 2003) indicate that DIDA has poor miscibility with CTA as compared with DEP.

2.2. Film preparation

The films were prepared by a solution-cast method. CTA and plasticizers with 10/1 weight ratio were dissolved into mixture solvent of dichloromethane and methanol with 9/1 weight ratio. It was confirmed that the solvent dissolves CTA rapidly. The solution containing 4 wt% of CTA was evaporated at room temperature to obtain the films with 70 μm thickness.

The films were uni-axially stretched at various strain rates of 0.01, 0.05, and $0.10\,\text{s}^{-1}$ by a tensile machine (UBM, DVE-3) with a temperature controller. The hot-stretching was performed after holding at the drawing temperature (T_{draw}) for 10 min. T_{draw}, shown in Table 2, was decided to obtain the same stress level for all samples. The hot-stretched films were immediately quenched by cold air blowing at a draw ratio of 1.5 to avoid relaxation of molecular orientation. Furthermore, the annealing treatment of non-stretched films was performed at 208 °C, i.e., T_{draw} for CTA/DIDA, for 1, 10, and 20 min to clarify the effect of thermal history on the morphology development.

The films were immersed into methanol for 6 h to remove plasticizers. Then, they were dried in vacuo at room temperature. The removal of plasticizers was confirmed from spectra of infrared absorption spectrometry (Perkin Elmer, Spectrum 100).

2.3. Measurements

Dynamic mechanical analysis (DMA) for the solution-cast films of CTA and plasticized CTA was performed to measure oscillatory tensile modulus at 10 Hz as a function of temperature using a dynamic mechanical analyzer (UBM, DVE-E4000) from −100 to 250 °C with a heating rate of $2\,°\text{C}\,\text{min}^{-1}$. The glass transition temperature T_g was estimated from a peak temperature of tensile loss modulus E'' and shown in Table 2.

The birefringence Δn of films was measured by an optical birefringence analyzer (Oji Scientific Instruments, KOBRA-WPR) as a function of wavelength by changing color filters. Prior to the measurement of birefringence, the films were kept in a humidic chamber (Yamato, IG420) at 25 °C and 50%RH for one night to avoid the moisture effect on the optical properties (Abd Manaf, Tsuji,

(a)

R= COCH₃

(b)   **(c)**
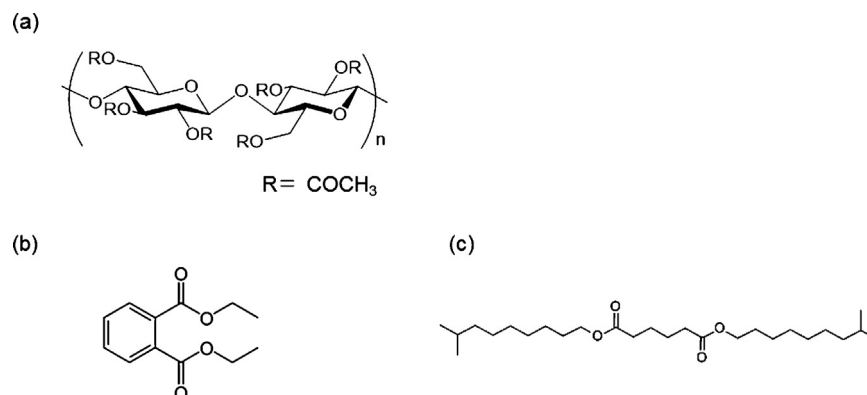
Fig. 1. Chemical structure of (a) CTA, (b) DEP, and (c) DIDA.