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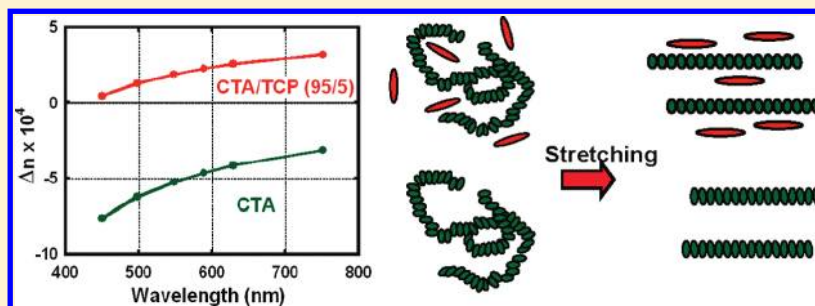
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Wavelength Dispersion of Orientation Birefringence for Cellulose Esters Containing Tricresyl Phosphate

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ABSTRACT:



Orientation birefringence and its wavelength dispersion are studied employing cellulose esters containing tricresyl phosphate (TCP) as a plasticizer. The addition of tricresyl phosphate (TCP) is found to increase the orientation birefringence of cellulose triacetate (CTA) and cellulose acetate propionate (CAP). In the case of CTA, which has negative birefringence with ordinary wavelength dispersion, the addition of TCP changes the sign of the birefringence to become positive. Moreover, it also provides extraordinary wavelength dispersion that is required for multiband retardation films. The origin of the phenomena is investigated by stress relaxation measurements and solvent treatment. It is found that after the removal of TCP from the stretched CTA/TCP film by methanol the film reverts to negative birefringence. This suggests that TCP molecules have positive birefringence associated with the polarizability anisotropy parallel to the long axis and are aligned to the stretching direction accompanying the chain orientation of CTA and CAP. However, as TCP is a liquidus compound with low molecular weight, the orientation relaxation will occur in a short time after stretching, leading to negative orientation birefringence with ordinary dispersion if not properly quenched.

INTRODUCTION

Cellulose esters, one of the biomass-derived materials, are useful optical materials and have been used in such application for many decades by virtue of their excellent transparency and high degree of heat resistance.^{1–3} For the same reason, currently, cellulose esters are being actively studied as a potential material for optical films such as polarizer protective films and retardation films in liquid crystal display (LCD) application. In order to be used in such application, it is necessary to control the birefringence of polymeric films to be suitable for their role in different parts in LCD assembly. For example, zero birefringence is needed for polarizer protective films, while birefringence must be controlled to a suitable value over a wide band of visible light for retardation films.^{4–7} In particular, retardation films with extraordinary wavelength dispersion of birefringence, in which the absolute value of birefringence increases with increasing wavelength, are required intensively these days although most polymers show ordinary dispersion of orientation birefringence.^{8–10}

By using the model of the statistical segment approach originated by Kuhn and Grun, orientation birefringence Δn of an oriented polymer can be expressed as¹¹

$$\Delta n = \frac{2\pi}{9} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} N_C (b_1 - b_2) \left[\frac{3\langle \cos^2 \theta \rangle - 1}{2} \right] \quad (1)$$

where \bar{n} is the average refractive index, N_C is the number of chains per unit volume, b_1 and b_2 are the polarizability parallel and perpendicular to the segment axis, and θ is the average angle that a segment makes with the stretching axis.

The bracketed term of $[3\langle \cos^2 \theta \rangle - 1]/2$ is identical to the Hermans orientation function,¹² which is commonly denoted as F . Thus, the orientation birefringence can also be written as

$$\Delta n = (\Delta^\circ n) F \quad (2)$$

where $\Delta^\circ n$ refers to the intrinsic birefringence. F is defined as the orientation birefringence of a perfectly oriented component.

Conventionally, extraordinary dispersion of birefringence is obtained by piling two or more polymer films having different wavelength dispersions, in which the fast axis of one film is set to be parallel to the slow axis of the other film. However, this technique leads to poor cost performance due to the complicated processing operation and results in a thick display. Thus, it is more favorable to use a single film having extraordinary dispersion of birefringence.

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Up to now, several methods have been proposed to control the birefringence in polymeric materials, such as polymer blending and copolymerization techniques. In a multicomponent system, the total orientation birefringence arising from different species Δn_T can be expressed by a simple addition of the birefringence from each component, as discussed by Stein et al.,¹³ and expressed by the relation

$$\Delta n_T = \Delta n_F + \sum_i \phi_i \Delta n_i \quad (3)$$

where i refers to the i th component, ϕ_i is the volume fraction, and Δn_F is the birefringence arising from form or deformation effects. In a polymer blending method, miscible polymer pairs showing intrinsic birefringence of different signs are mixed on a molecular scale are usually employed to avoid light scattering.

Uchiyama and Yatabe¹⁴ used the polymer blend technique to control the wavelength dispersion of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and atactic polystyrene (PS) blend. In the blend system, PS shows negative birefringence with strong wavelength dependence, whereas PPO exhibits a positive one with weak wavelength dependence. Although both polymers show ordinary wavelength dispersion, the blends at certain blend compositions show extraordinary wavelength dispersion as a summation of the contributions from both polymers.

Another study utilizing the polymer blend technique was performed by Kuboyama et al.⁵ They managed to control the wavelength dispersion of a miscible blend comprised of polynorbornene (NB) and poly(styrene-co-maleic anhydride) (SMA) by adjusting blend composition and stretching conditions. NB has positive birefringence with weak wavelength dispersion, while SMA has negative birefringence with strong wavelength dispersion. They found that the blend shows positive birefringence with extraordinary wavelength dispersion when the content of NB is 40 wt % and above.

The wavelength dispersion of a copolymer as a function of monomer content was studied by Uchiyama and Yatabe⁸ using two monomers such as 2,2-bis(4-hydroxyphenyl)propane (BPA) and 9,9-bis(4-hydroxy-3-methylphenyl)fluorene (BMPF). The direction of the polarizability anisotropy of the former is perpendicular to that of the latter. They found that the wavelength dispersion of the oriented copolymer film could be controlled by the copolymerization ratio while the effect of the stretching condition was negligible.

Besides the polymer blend and copolymerization techniques, the addition of nonspherical materials having polarizability anisotropy is found to be effective to control the orientation birefringence. Utilizing this concept, Koike et al. added needle crystals whose polarizability anisotropy is opposite to that of a host polymer in order to develop a zero-birefringence polymer.¹⁵ The method is referred to as a birefringent crystal dopant method. Although the method can be applied in industry easily, fine fillers have to be dispersed homogeneously in order to avoid light scattering.

Yamaguchi et al. have demonstrated that some cellulose esters also show extraordinary wavelength dispersion of orientation birefringence.^{16,17} Using the relationship between the orientation function F and the dichroic ratio $D (= A_{||}/A_{\perp})$ as expressed by the equation

$$F = c \frac{D - 1}{D + 2} \quad (4)$$

where c is a correction for the inclination of the transition moment of the band from the molecular axis, they have measured

Table 1. Characteristics of Materials

sample	compositions, ^a wt %			molecular weights	
	acetyl	propionyl	hydroxyl	$M_n \times 10^5$	$M_w \times 10^5$
CTA	43.6 (2.96)	—	0.9	1.3	3.5
CAP	2.5 (0.19)	46.0 (2.58)	1.8	0.77	2.1

^aDegree of substitution in parentheses.

the infrared dichroic ratio of some cellulose esters and found that Δn is not proportional to $(D - 1)/(D + 2)$. The result indicates that the equation for orientation birefringence given in eq 2 is not completely applicable for cellulose esters. Thus, it is suggested that the orientation birefringence of cellulose esters is not determined by the orientation of the pyranose ring, i.e., main chain, but rather by the species and the amount of the ester groups. Furthermore, they found that acetyl group contributes to negative orientation birefringence, while propionyl and butyryl groups contribute to a positive one with weak wavelength dispersion. Combination of negative birefringence with strong wavelength dispersion originated from the acetyl group and positive birefringence with weak wavelength dispersion from the propionyl and butyryl groups enables some cellulose esters such as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) to exhibit extraordinary wavelength dispersion of orientation birefringence by having appropriate ester groups.

The effect of a plasticizer on the orientation birefringence has been studied by Yalcin et al. employing plasticized poly(vinyl chloride) (PVC).¹⁸ According to them, as birefringence is influenced by both stress and strain in the system, work is a useful parameter to correlate with birefringence. They found that work input into the materials during deformation generates master curves with birefringence. Furthermore, an addition of a plasticizer results in different values of work required to attain certain birefringence. While the stress–birefringence relationship was found to be affected by the presence of a plasticizer, the behavior was found to be nonlinear and shows multiple regimes during deformation.

In this study, a modification method of orientation birefringence by adding a liquid compound, tricresyl phosphate (TCP), which acts as a plasticizer, to cellulose esters is demonstrated. The experimental data in this paper suggest that the sign of orientation birefringence in some cellulose esters can be changed by an addition of a suitable plasticizer. Since the extraordinary wavelength dispersion can be achieved by this method without any difficulty, it will be significantly important information for the industrial application. Furthermore, the mechanism is also discussed from the viewpoint of molecular orientation.

EXPERIMENTAL SECTION

Materials. The polymeric materials used in this study were commercially available cellulose esters such as cellulose acetate propionate (CAP) and cellulose triacetate (CTA). CAP employed in this study was produced by Eastman Chemical, while CTA was produced by Acros Organics. The molecular characteristics are summarized in Table 1. The plasticizer used in this study was tricresyl phosphate (TCP) produced by Daihachi Chemical Industry.

Melt mixing of CAP with TCP was performed using a 60 cm³ batch-type internal mixer (Toyoseiki, Labo-Plastmill) at 200 °C. The rotational speed of the blades was 30 rpm, and the mixing time was 5 min. The obtained mixture was compressed into a flat sheet with a thickness

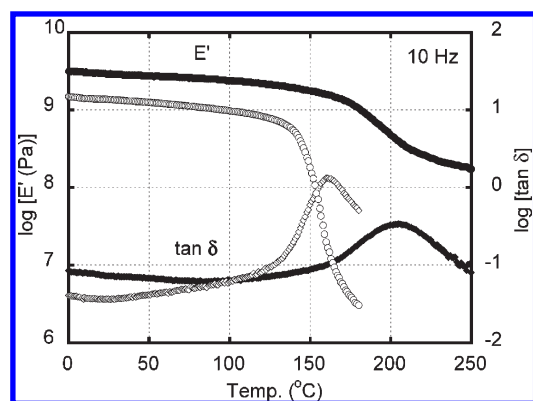


Figure 1. Temperature dependence of tensile storage modulus E' and loss tangent $\tan \delta$ for CAP (open circles) and CTA (closed circles) at 10 Hz.

of 200 μm by a compression-molding machine (Tester Sangyo, table type test press SA-303-I-S) for 5 min at 200 $^{\circ}\text{C}$ under 10 MPa and then subsequently plunged into an ice–water bath.

In the case of CTA, polymeric films were prepared using a solution cast method since melt processing is not applicable due to the severe thermal degradation of CTA.^{19,20} Both CTA and TCP were dissolved into chloroform and stirred for 24 h at room temperature before casting. The solution was poured onto a metal plate and left at room temperature for 48 h to allow the solvent to evaporate slowly in order to obtain a smooth thin film. The thickness of the films obtained was about 200 μm .

Subsequently, the films were hot-drawn using a dynamic mechanical analyzer (UBM, DVE-4) to prepare uniaxial oriented films at different temperatures. The initial distance between the clamps was 10 mm, and the stretching rate was 0.5 mm/s. The stress–strain data generated during the stretching were also collected. The samples were quenched by cold air blowing after holding the samples at the draw temperature for various times in the chamber.

Measurements. The temperature dependence of oscillatory tensile moduli in the solid state, such as storage modulus E' and loss tangent $\tan \delta$ were measured from -50 to 200 $^{\circ}\text{C}$ by a dynamic mechanical analyzer (UBM, E-4000) using rectangular specimens of 5 mm in width and 20 mm in length. The frequency and heating rate used were 10 Hz and 2 $^{\circ}\text{C}/\text{min}$, respectively.

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

The retardation of the drawn films was measured by an optical birefringence analyzer (Oji Scientific Instruments Inc., KOBRA-WPR). The measurements were performed as a function of the wavelength between 450 and 800 nm by changing color filters. Prior to the measurement, the drawn samples were placed in a temperature and humidity control chamber at 25 $^{\circ}\text{C}$ and 50% RH.

Infrared spectra was measured using Fourier-transform infrared spectrometer (JASCO, FT-IR 6100) at room temperature within the wavelength range of 4000–400 cm^{-1} . For TCP, which is in liquid form, a KBR plate was used to obtain the IR spectrum.

Thermal analysis was conducted by a differential scanning calorimeter (DSC) (Mettler, DSC820) under a nitrogen atmosphere. The samples were heated from room temperature to 300 $^{\circ}\text{C}$ at a heating rate 20 $^{\circ}\text{C}/\text{min}$. The amount of sample in an aluminum pan was about 10 mg in weight.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties. Figure 1 shows temperature dependence of the oscillatory tensile moduli for CTA and CAP. The storage modulus E' at low temperature, i.e., in the

Table 2. Thermal Properties of the Neat and Plasticized CAP and CTA

composition	T_m ($^{\circ}\text{C}$)	ΔH_f (J/g) ^a
CAP(100)	—	—
CAP/TCP (95/5)	—	—
CTA (100)	286	15.2
CTA/TCP (95/5)	279	14.3

^a ΔH_f is determined by subtracting the enthalpy of the cold crystallization from that of the melting for the system.

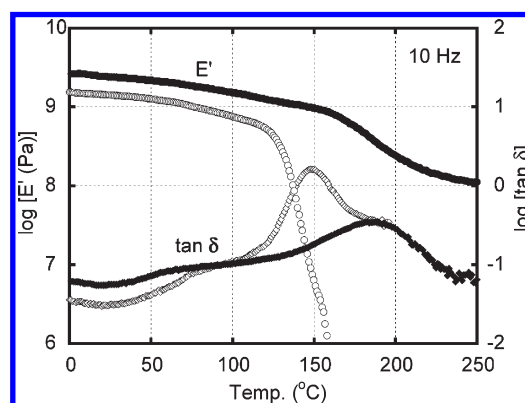


Figure 2. Temperature dependence of tensile storage modulus E' and loss tangent $\tan \delta$ for CAP/TCP (95/5) (open circles) and CTA/TCP (95/5) (closed circles) at 10 Hz.

glassy region of CTA, is higher than that of CAP. Furthermore, CTA also shows a higher glass transition temperature than CAP. In this study, glass transition temperature is defined as the peak of loss modulus E'' . It should be noted that an abrupt drop of E' , owing to the glass-to-rubber transition, is detected for CAP, whereas in CTA, E' decreases rather gradually. As a result, the peak of $\tan \delta$ for CTA is broader and its maximum value is lower.

The broad peak of $\tan \delta$ as observed in CTA is possibly due to the presence of a small amount of crystallites in CTA. The presence of crystallites affects the mobility of CTA chains, leading to a broad distribution of relaxation time. Because of the cross-linking effect of the crystallites, CTA shows a high value of E' even at 200 $^{\circ}\text{C}$. The melting point and the heat of fusion of both the CAP and CTA blends are summarized in Table 2. In the CAP/TCP blend, there is no melting peak observed, indicating that both pure and plasticized CAPs are fully amorphous.

Figure 2 shows the temperature dependence of the oscillatory tensile modulus for the blends containing TCP. CAP/TCP (95/5) shows an abrupt drop of E' as seen in pure CAP, although it occurs at a lower temperature. This is reasonable because TCP acts as a plasticizer and thus lowers the glass transition temperature of CAP. Furthermore, it should be noted that the peak value of $\tan \delta$ for the CAP/TCP (95/5) blend is higher than that of pure CAP, suggesting good miscibility between CAP and TCP.

As for CTA/TCP (95/5), addition of TCP lowers the peak temperature of $\tan \delta$, suggesting that TCP functions as a plasticizer. However, the miscibility with CTA seems to be poor in comparison with CAP because E' of the CTA/TCP (95/5) blend starts to decrease around 100 $^{\circ}\text{C}$. The decrease can be clearly observed by comparing E' of pure CTA and CTA/TCP (95/5). Correspondingly, $\tan \delta$ shows large values, larger than 0.1 in a wide temperature range. Furthermore, in the CTA/TCP

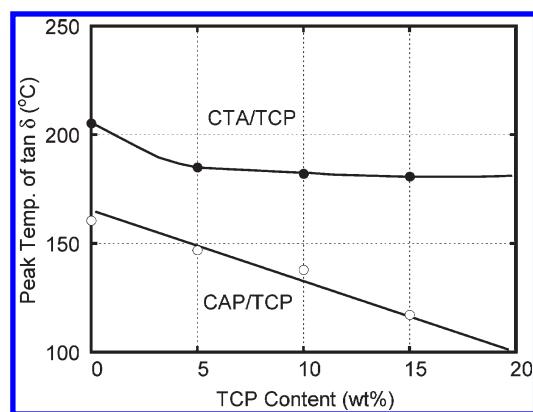


Figure 3. Relation between peak temperature of $\tan \delta$ and TCP content for CAP/TCP (open circles) and CTA/TCP (closed circles) blends.

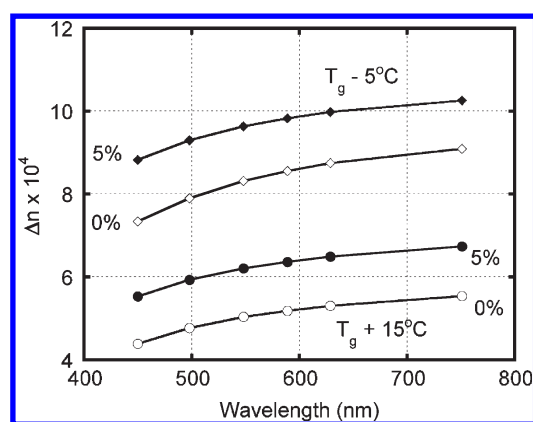


Figure 4. Wavelength dependence of orientation birefringence Δn for CAP (open symbols) and CAP/TCP (95/5) (closed symbols) stretched at stretching temperature above (circles) and below (diamonds) the glass transition temperature at a draw ratio of 1.5 (Hencky strain, $\epsilon \approx 0.41$).

blend, a decrease of E' in the glassy region is observed by the addition of TCP, whereas the CAP/TCP blend shows almost a same value of E' with that of pure CAP. In the CTA/TCP blend, addition of TCP increases the free volume, thus resulting in the decrease of storage modulus as observed here. The free volume fraction at the glassy state will also be different between the CAP/TCP and CTA/TCP blends.

The peak temperatures of $\tan \delta$ for the CAP/TCP and CTA/TCP blends are shown in Figure 3 as a function of TCP weight content. For the CAP/TCP blend, the peak temperature of $\tan \delta$ decreases almost linearly with the increase in TCP content. On the contrary, for the CTA/TCP blend, it decreases sharply at low TCP content and then shows only a minimal decrease beyond 5 wt %, indicating that TCP has limited miscibility with CTA. The results demonstrate that TCP has better miscibility with CAP than CTA.

Wavelength Dispersion of Orientation Birefringence. The wavelength dispersions of orientation birefringence of CAP and CAP/TCP (95/5) stretched at two different temperatures; T_{S1} and T_{S2} are shown in Figure 4. T_{S1} and T_{S2} refer to a temperature above and below the glass transition temperature, respectively. The stretching temperatures for both the CAP/TCP and CTA/TCP blends are shown in Table 3. These particular temperatures are selected so that samples can be stretched without rupture.

Table 3. T_g and Stretching Temperatures for CAP/TCP and CTA/TCP Blends

composition	T_g^a (°C)	T_{S1} (°C)	T_{S2} (°C)
CAP (100)	146	141	161
CAP/TCP (95/5)	129	124	144
CTA (100)	182	177	197
CTA/TCP (95/5)	165	160	180

^a T_g is determined from the peak of loss modulus E'' .

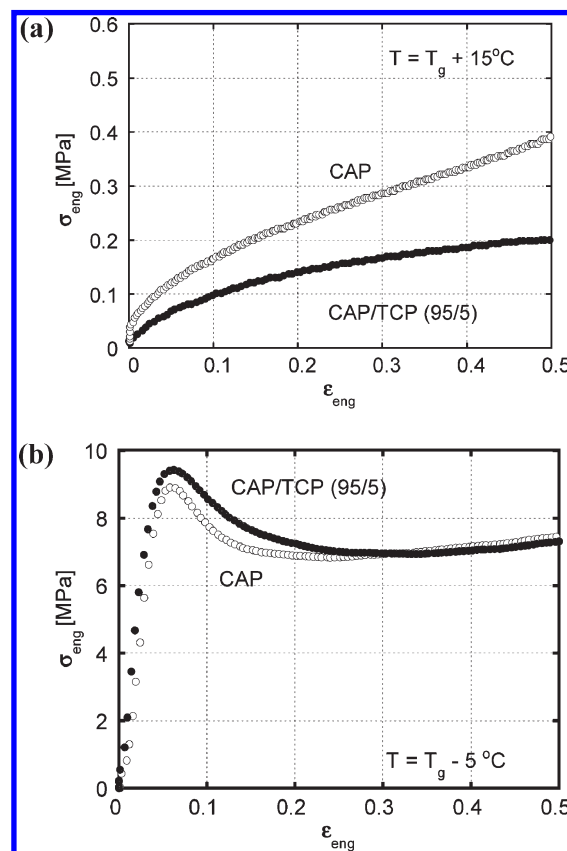


Figure 5. Stress–strain curves of CAP (open circles) and CAP/TCP (95/5) (closed circles) stretched at temperatures (a) above and (b) below the glass transition temperature.

The stress–strain curves of CAP and CAP/TCP stretched at temperatures above and below the glass transition temperature are shown in Figure 5. The curves for the samples stretched above the glass transition temperature show a rubber-like behavior. On the contrary, the samples stretched below the glass transition temperature show a yield point at around 0.05 of an engineering strain and can be stretched even at a constant engineering stress beyond the yield point.

Furthermore, the stress–strain curves of CAP and CAP/TCP stretched at temperatures below the glass transition temperature are almost similar, while those stretched at temperatures above the glass transition temperature show a large difference in the curves.

It is found that pure CAP shows positive orientation birefringence that increases with increasing wavelength, i.e., the so-called extraordinary wavelength dispersion of birefringence^{8–10} as shown in Figure 4. This is an anomalous optical anisotropy for

polymers as the orientation birefringence of polymers typically decreases with increasing wavelength as expressed by the Sellmeier equation¹⁰

$$\Delta n(\lambda) = A' + \frac{B'}{\lambda^2 - \lambda_{ab}^2} \quad (5)$$

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

Orientation birefringence of a stretched film can be defined as $\Delta n = n_{||} - n_{\perp}$, where $n_{||}$ and n_{\perp} are the refractive indices for the light polarized in the directions parallel and perpendicular to the stretching direction, respectively. The difference in the refractive indices is resulted by the polarizability anisotropy in the material. In the case of cellulose esters, the orientation birefringence is determined mainly by its ester groups, i.e., the acetyl and propionyl groups for CAP, as demonstrated in our previous papers.^{16,17} It was also clarified that the acetyl group has ordinary wavelength dispersion of birefringence with negative sign. Furthermore, it was assumed that the propionyl group has ordinary wavelength dispersion of birefringence with positive sign. Therefore, combination of birefringence from the acetyl and propionyl groups yields an extraordinary wavelength dispersion of orientation birefringence in CAP.

For the CAP/TCP blend, the orientation birefringence increases with the increase of TCP content for both stretching temperatures. The results are examined in relation with the stress–strain curves generated during the stretching process. The relationship between orientation birefringence and true stress, where the birefringence is generated when a polymer is deformed at a temperature sufficiently higher than glass transition temperature, is given as²¹

$$\Delta n = C\sigma \quad (6)$$

where C is the stress optical coefficient and depends only on the chemical structure of a material.

As seen in Figure 5a, the stress of plasticized CAP at a temperature above the glass transition temperature is lower than that of pure CAP. This result suggests that the degree of orientation of polymer chains, which is responsible for the stress, decreases by the addition of TCP. On the contrary, the orientation birefringence increases by the addition of TCP.

Another factor that influences the orientation birefringence in a system is the average refractive index as seen in eqs 1 and 2. Table 4 shows the mean refractive index of CAP and CAP/TCP and their respective value of $(\bar{n}^2 + 2)^2/\bar{n}$, which represents the contribution of the mean refractive index to intrinsic birefringence. It is found from the table that the difference between the mean refractive index of CAP and CAP/TCP is miniscule; i.e., its contribution is minimal and does not reflect the large increase in birefringence observed in this study. The result implies that the increase of birefringence in cellulose esters upon the addition of TCP is not influenced by the intrinsic birefringence but rather by the change of the optical anisotropy in the system.

Utilizing the relations given in the eqs 2 and 3, the total orientation birefringence Δn_T in the CAP/TCP blend can be expressed as

$$\Delta n_T = \phi \Delta n_{CAP} + (1 - \phi) \Delta n_{TCP} \quad (7)$$

where ϕ refers to the volume fraction of CAP. The change of orientation birefringence in CAP/TCP is believed to be associated with the polarizability anisotropy of TCP.

Table 4. Average Refractive Index for Neat CAP and CAP/TCP Blends

CAP/TCP composition	av refractive index \bar{n}	$(\bar{n}^2 + 2)^2/\bar{n}$
100/0	1.479	11.86
95/5	1.483	11.89
90/10	1.485	11.91

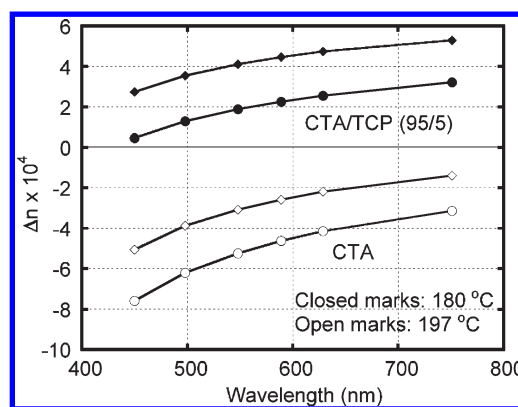


Figure 6. Wavelength dependence of orientation birefringence Δn for stretched films of CTA (open symbols) and CTA/TCP of (95/5) (closed symbols) stretched at temperatures above (circles) and below (diamonds) the glass transition temperature at a draw ratio of 1.5 ($\epsilon \approx 0.41$) and 1.4 ($\epsilon \approx 0.34$), respectively.

Upon stretching process, TCP molecules orient to the stretching direction accompanying the molecular orientation of CAP chains. Consequently, the oriented TCP molecules provide optical anisotropy, resulting in the increase in positive birefringence. A phenomenon in which low-mass compounds are forced to orient to the same direction by the alignment of polymer chains is called nematic interaction.^{22,23} Originally, nematic interaction was used to explain the orientation relaxation of a short chain in a polymer with broad molecular weight distribution. Urakawa et al.^{24–26} have further suggested that the nematic interaction is also detected in a miscible blend system when a low-mass compound has an appropriate size to move cooperatively with the chain segment of the host polymer.

The wavelength dispersion of orientation birefringence of the CTA/TCP blend stretched at temperatures above and below the glass transition temperature is shown in Figure 6. The stress–strain curves for the CTA/TCP blend stretched at temperatures above and below the glass transition temperature are shown in Figure 7. For the samples stretched below the glass transition temperature, the draw ratio used is 1.4 instead of 1.5 in order to avoid the rupture of the film.

The pure CTA shows negative birefringence that decreases with increasing wavelength. The negative orientation birefringence in CTA indicates that the direction of the polarizability anisotropy associated with the acetyl group is perpendicular to the main chain which aligns to the stretching direction. Upon the addition of TCP, the negative orientation birefringence of CTA does not increase instead changes drastically from negative to positive with extraordinary wavelength dispersion although the final stress applied on the plasticized CTA has almost a similar value to that for pure CTA, as shown in Figure 7a. The change also does not correspond to the degree of crystallization, of which the CTA and CTA/TCP blend show almost a similar amount of

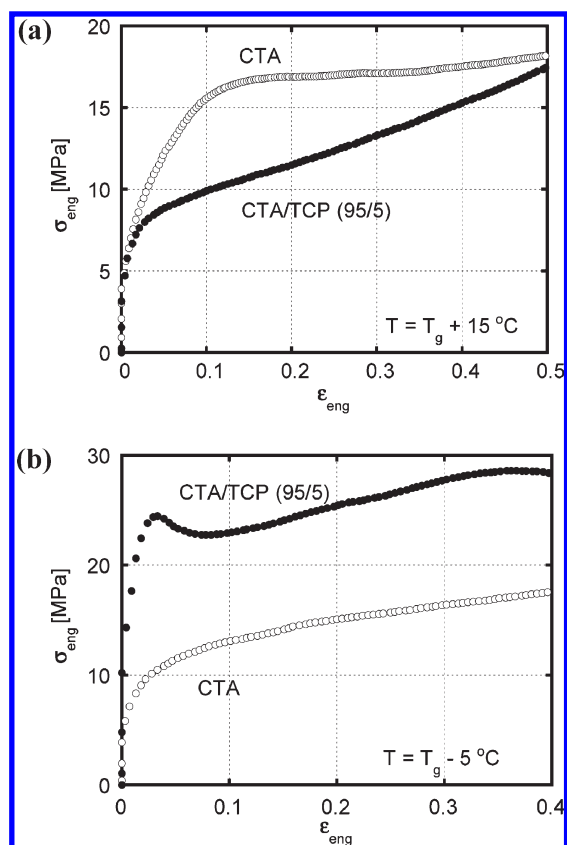


Figure 7. Stress–strain curves of CTA (open circles) and CTA/TCP (95/5) (closed circles) stretched at temperatures (a) above and (b) below the glass transition temperature at a draw ratio of 1.5 ($\epsilon \approx 0.41$) and 1.4 ($\epsilon \approx 0.34$), respectively.

crystallites as shown in Table 2. This demonstrates that the CTA crystallites have a negligible effect on the orientation birefringence of the CTA/TCP blend.

The drastic change of the sign in the CTA/TCP blend can be explained by the orientation of TCP molecules. As stretching takes place, TCP molecules orient to the stretching direction of the polymer chains. Since TCP shows polarizability anisotropy parallel to the stretching direction, the positive birefringence ascribed to the alignment of TCP molecules offsets the negative birefringence from the acetyl group in CTA. A small amount of TCP (5 wt %) is enough to change the sign of birefringence from negative into positive, suggesting that the polarizability anisotropy associated with TCP is stronger than that with the acetyl group in CTA.

Effects of TCP. In order to study the contribution of TCP to the orientation birefringence of CTA/TCP, drawn samples of the CTA/TCP (95/5) blend are immersed in methanol for 24 h to remove TCP, and the orientation birefringence is measured. After 24 h immersion, there is no considerable change in the dimension of the sample, suggesting that there is almost no alteration in degree of stretching upon the methanol immersion.

In order to confirm the removal of TCP by the methanol immersion, IR spectra analysis is carried out. It is found from IR spectra analysis there is a strong absorption peak around 780 cm^{-1} for the CTA/TCP blend, which is not detected in CTA but appears in TCP spectrum. As the vibrational peak around 780 cm^{-1} is associated with the vibrations of C–H bond

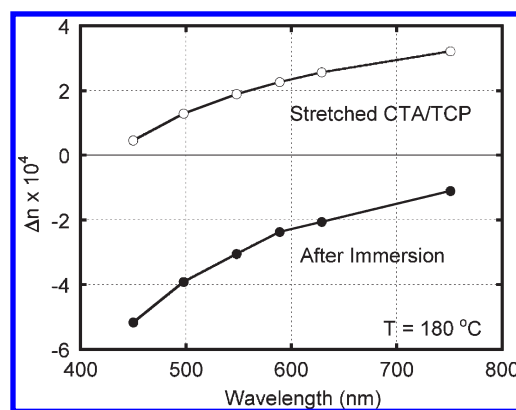


Figure 8. Orientation birefringence for CTA/TCP (95/5) (diamonds) at 589 nm wavelength before (open circles) and after (closed circles) methanol immersion.

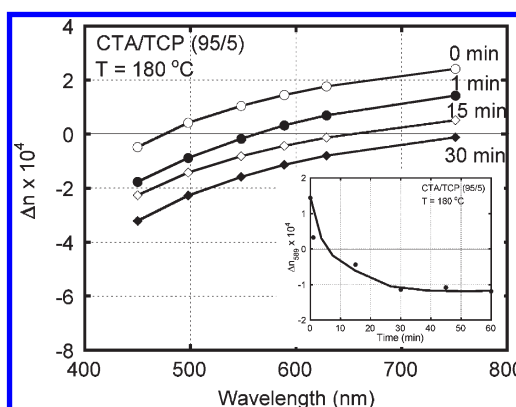


Figure 9. Wavelength dependence of orientation birefringence Δn for CTA/TCP (95/5) stretched at a draw ratio of 1.5 and then held in the chamber for 0 min (open circle), 1 min (closed circle), 15 min (open diamond), and 30 min (closed diamond) at the drawing temperature. The values at 589 nm are also plotted as a function of holding time.

in meta-disubstituted benzene, the peak is suggested to be resulted from TCP since CTA does not contain any benzene ring. After methanol immersion, there is no peak observed around 780 cm^{-1} , indicating that TCP has been completely removed.

Orientation birefringence of CTA/TCP (95/5) before and after the methanol immersion is shown in Figure 8. After methanol immersion, the positive orientation birefringence of the CTA/TCP blend decreases and approaches that of pure CTA. The removal of TCP is reflected in the change of the orientation birefringence from positive values to negative values. The result suggests that the positive birefringence in the CTA/TCP blend is largely attributed to the orientation of TCP.

Effects of Stress Relaxation. The uniaxially drawn CTA/TCP was kept in the chamber at the drawing temperature for 0, 1, 15, 30, 45, and 60 min to study the effect of the stress relaxation on the orientation birefringence. For pure CTA kept at the drawing temperature for 30 min or longer, there is no significant decrease in the magnitude of birefringence, suggesting that stress relaxation is negligible. Figure 9 shows the wavelength dispersion of orientation birefringence for the stretched CTA/TCP (95/5) blend with various holding times.

As seen in the figure, CTA/TCP with 0 min holding time, i.e., immediately cooled after the hot-drawing procedure, shows the

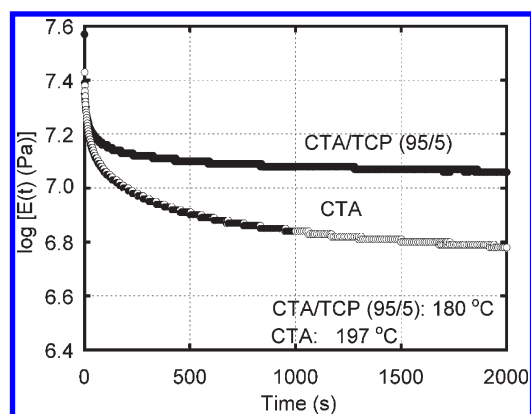


Figure 10. Tensile relaxation modulus of CTA (open circles) and CTA/TCP (95/5) composition (closed circles), upon being stretched at a draw ratio of 1.5 ($\epsilon \approx 0.41$) and held in a chamber at the drawing temperature.

highest value of birefringence. After the film was held in the chamber at its drawing temperature, the orientation birefringence decreases and subsequently becomes a negative value. Furthermore, there is no further decrease of orientation birefringence for the 45 and 60 min holding times. The shift of the orientation birefringence from positive to negative indicates that the overall polarizability anisotropy in the sample has changed from parallel to perpendicular to the stretching direction after being held at high temperature. The decrease of orientation birefringence to approach the birefringence of CTA suggests that the change of the overall optical anisotropy observed here is mainly attributed to the relaxation from pseudoaffine orientation of TCP molecules.^{27,28} Furthermore, it should be noted that the birefringence at long wavelength shows positive values even after 15 min. Considering that CTA kept in a chamber at the drawing temperature for the same period of time does not show a positive birefringence, it suggests that at this condition TCP molecules still orient to the stretching direction to some degrees.

In order to clarify the phenomenon, the tensile relaxation moduli at their drawing temperatures are shown in Figure 10 for the CTA and CTA/TCP (95/5) blend. As seen in the figure, the relaxation modulus for both compositions drops sharply after the drawing stops. Subsequently, it shows a gradual decrease, indicating a very slow relaxation takes place. The decrease is slow in the CTA/TCP (95/5) blend compared to the pure CTA. The results suggest that relaxation dwindles down as the time increases and that the CTA/TCP blend has a longer relaxation time than the pure CTA. In comparison to pure CTA, the CTA/TCP (95/5) blend has a broader peak width of $\tan \delta$ which is apparent in Figure 2, indicating a broad distribution of relaxation time ascribed to T_g . Consequently, the CTA/TCP (95/5) blend has a longer relaxation time, leading to a slow decay of relaxation modulus.

The relation between the orientation birefringence and the relaxation modulus of the CTA/TCP (95/5) blend with 0, 1, 15, and 30 min holding time is shown in Figure 11. The orientation birefringence is found to decrease with decreasing relaxation modulus. However, it shows a rather obvious decrease with time, compared to the gradual decreases shown by the relaxation modulus. The result indicates that while the orientation birefringence correlates with the degree of orientation relaxation in the system, the relation is not directly proportional. A huge decrease

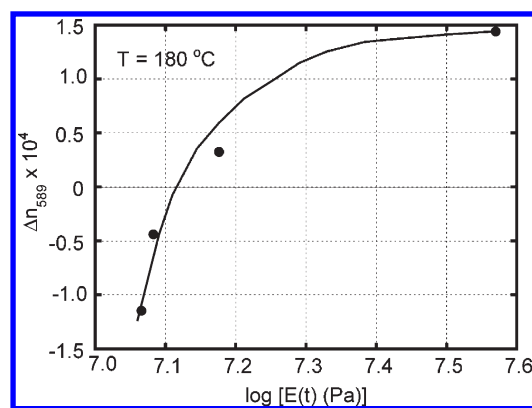


Figure 11. Relation between orientation birefringence at 589 nm and tensile relaxation modulus $E(t)$ of CTA/TCP (95/5) held in a chamber for 0, 1, 15, and 30 min at the drawing temperature.

in orientation birefringence can be observed even at 1 min holding time since TCP, being a low molecular weight compound, has a short relaxation time.

CONCLUSION

Wavelength dispersion of orientation birefringence for cellulose acetate propionate (CAP) and cellulose triacetate (CTA) containing a small amount of tricresyl phosphate (TCP) is studied. Dynamic mechanical spectra indicate that CAP shows better miscibility with TCP than CTA, although TCP acts as a good plasticizer as far as the amount is lower than 10 wt %. It is found that an uniaxially drawn film of CAP shows an extraordinary dispersion of orientation birefringence, which increases further upon the addition of TCP, having positive sign of intrinsic birefringence. On the other hand, CTA shows an ordinary dispersion of negative birefringence, and the addition of TCP is found to drastically change its orientation birefringence to positive birefringence with extraordinary dispersion. This is attributed to the orientation of TCP molecules upon stretching process. It has also been found that when a stretched sample of the CTA/TCP blend is held in the chamber at the drawing temperature for a certain period of time, its birefringence return from positive back to negative, which is presumably due to the prompt relaxation from pseudoaffine orientation of TCP molecules. Finally, the stretched samples of the CTA/TCP blend were immersed in methanol to remove the TCP in order to evaluate its effect on the orientation birefringence. Upon TCP removal, orientation birefringence changes from positive to negative values, proving that the positive orientation birefringence observed in CTA/TCP blend is largely attributed to the orientation of TCP molecules.

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REFERENCES

- (1) Edgar, K. J.; Buchanan, C. M.; Debenham, J. S.; Rundquist, P. A.; Seiler, B. D.; Shelton, M. C.; Tindall, D. *Prog. Polym. Sci.* **2001**, *26*, 1605–1688.
- (2) Yamaguchi, M. In *Cellulose: Structure and Properties, Derivatives and Industrial Uses*; Lejeune, A., Deprez, T., Eds.; Nova Science Publishers, Inc.: New York, 2010; pp 325–340.
- (3) Sata, H.; Murayama, M.; Shimamoto, S. *Macromol. Symp.* **2004**, *208*, 323–333.
- (4) Yamaguchi, M.; Masuzawa, K. *Eur. Polym. J.* **2007**, *43*, 3277–3282.
- (5) Kuboyama, K.; Kuroda, T.; Ougizawa, T. *Macromol. Symp.* **2007**, *249–250*, 641–646.
- (6) Ohkita, H.; Tagaya, A.; Koike, Y. *Macromolecules* **2004**, *37*, 8342–8348.
- (7) Kim, J. C.; Watanabe, T.; Miyata, S. *Jpn. J. Appl. Phys.* **1997**, *36*, 232–238.
- (8) Uchiyama, A.; Yatabe, T. *Jpn. J. Appl. Phys.* **2003**, *42*, 6941–6945.
- (9) Yamaguchi, M.; Lee, S. Y.; Abd Manaf, M. E.; Tsuji, M.; Yokohara, T. *Eur. Polym. J.* **2010**, *46*, 2269–2274.
- (10) Harding, G. F. In *Optical Properties of Polymers*; Meeten, G. H., Ed.; Applied and Science: London, 1986; pp 63–98.
- (11) Wilkes, G. L.; Stein, R. S. In *Structure and Properties of Oriented Polymers*; Ward, I. M., Ed.; Chapman & Hall: London, 1975; pp 44–90.
- (12) Hermans, P. H.; Platzek, P. *Kolloid Z.* **1939**, *88*, 68–72.
- (13) Stein, R. S.; Onogi, S.; Sasaguri, K.; Keedy, D. A. *J. Appl. Phys.* **1963**, *34*, 80–89.
- (14) Uchiyama, A.; Yatabe, T. *Jpn. J. Appl. Phys.* **2003**, *42*, 3503–3507.
- (15) Koike, Y.; Yamazaki, K.; Ohkita, H.; Tagaya, A. *Macromol. Symp.* **2006**, *235*, 64–70.
- (16) Yamaguchi, M.; Okada, K.; Abd Manaf, M. E.; Shiroyama, Y.; Iwasaki, T.; Okamoto, K. *Macromolecules* **2009**, *42*, 9034–9040.
- (17) Yamaguchi, M.; Iwasaki, T.; Okada, K.; Okamoto, K. *Acta Mater.* **2009**, *57*, 823–829.
- (18) Yalcin, B.; Cakmak, M. *J. Polym. Sci., Polym. Phys.* **2005**, *43*, 724–742.
- (19) Charles, K. J.; Buchanan, C. M.; Debenham, J. S.; Rundquist, P. A.; Seiler, B. D.; Shelton, M. C.; Tindall, D. *Prog. Polym. Sci.* **2001**, *26*, 1605–1688.
- (20) Zugenmaier, P. *Macromol. Symp.* **2004**, *208*, 81–166.
- (21) Treloar, L. R. G. In *The Physics of Rubber Elasticity*; Clarendon Press: Oxford, UK, 1975; pp 174–210.
- (22) Doi, M.; Watanabe, H. *Macromolecules* **1991**, *24*, 740–744.
- (23) Merrill, W. W.; Tirrell, M.; Tassin, J. F.; Monnerie, L. *Macromolecules* **1989**, *22*, 896–908.
- (24) Urakawa, O.; Ohta, E.; Hori, H.; Adachi, K. *J. Polym. Sci., Polym. Phys.* **2006**, *44*, 967–974.
- (25) Nobukawa, S.; Urakawa, O.; Shikata, T.; Inoue, T. *Macromolecules* **2010**, *43*, 6099–6105.
- (26) Urakawa, O.; Nobukawa, S.; Shikata, T.; Inoue, T. *Nihon Reologi Gakkaishi* **2010**, *38*, 41–46.
- (27) Owen, A. J. *Colloid Polym. Sci.* **1988**, *266*, 311–315.
- (28) Pucci, A.; Ruggeri, G.; Moretto, L.; Bronco, S. *Polym. Adv. Technol.* **2002**, *13*, 737–743.