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Description	

**Modification of Orientation Birefringence of Cellulose Ester  
by Addition of Poly(Lactic Acid)**

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**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 retardant 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.

**Key words:** Birefringence; Amorphous Polymers; Biopolymers; Blending;

Dynamic Mechanical Analysis

## 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.<sup>1-5</sup> Because the orientation birefringence of typical polymers decreases with increasing wavelength as expressed by Sellmeier relation (eq. (1)),<sup>5-8</sup> 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.<sup>5</sup> Moreover, the sign of birefringence of the acetyl group is negative, whereas that of the propionyl and butyryl groups is positive.<sup>5,9</sup> Since the total value of the birefringence is provided by the sum of each component,<sup>10,11</sup> 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 dispersion of positive birefringence in the visible wavelength as illustrated in Figure 1, which was explained in detail in our preceding article.<sup>5</sup>

[Figure 1]

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,<sup>13</sup> poly(epichlorohydrin) (PECH),<sup>12,13</sup> and poly(vinyl acetate) (PVAc)<sup>12,14</sup> 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.<sup>15</sup> Furthermore, PLA is miscible with PMMA and PVAc,<sup>16,17</sup> which are miscible with CAP.<sup>12-14</sup> 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.<sup>18</sup> 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.

## EXPERIMENTAL

### *Materials*

Materials employed in this study were commercially available CAP (Eastman Chemical, CAP-482-20) and PLA (Mitsui Chemical, Lacea 280). 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® 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 vs. a polystyrene standard 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 (Labo-Plastmil, Toyoseiki, Japan) 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, DVE-4) 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.

### ***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  $180 \text{ }^\circ\text{C}$  using a dynamic mechanical analyzer (UBM, E-4000). The frequency and heating rate used were 10 Hz and  $2 \text{ }^\circ\text{C}/\text{min}$ , 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.<sup>5</sup>

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.

## RESULTS AND DISCUSSION

### *Viscoelastic Properties of CAP, PLA, and the Blends*

The master curves of frequency dependence of the oscillatory shear modulus for the individual pure components are shown in Figure 2. The reference temperature was 163 °C, *i.e.*, the stretching temperature. It is demonstrated that the time-temperature superposition principle is applicable for both CAP and PLA, demonstrating that both polymers are fully amorphous in this temperature range. Although the melting point of a conventional poly(L-lactic acid) is around 175 °C, the low level of the optical purity prohibits the crystallization even at 163 °C.

[Figure 2]

As seen in the figure, PLA shows the typical viscoelastic properties in the terminal (flow) region, whereas CAP shows rubbery plateau in the high frequency region. Since the applied strain rate is  $0.05 \text{ s}^{-1}$  at the hot-drawing operation, the stretching is performed at the end of rubbery region of CAP.



The weight-average relaxation time  $\tau_w$  of a viscoelastic liquid is derived by the following relation;

$$\tau_w \equiv \frac{\int \tau^2 H(\tau) d \ln \tau}{\int \tau H(\tau) d \ln \tau} = \eta_0 J_e^0 \quad (3)$$

where  $H(\tau)$  the relaxation spectrum,  $\eta_0$  the zero-shear viscosity, and  $J_e^0$  the steady-state shear compliance. The rheological terminal parameters,  $\eta_0$  and  $J_e^0$  are defined as;

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (4)$$

$$J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'}{G''^2} \quad (5)$$

The relaxation time of PLA at 163 °C can be calculated by the master curves using equations (4) and (5) and found to be approximately 0.045 s. In case of CAP, the parameters in the terminal zone cannot be determined from Figure 2(a). However, the relaxation time will be longer than 1000 s, because  $\eta_0$  is around  $10^7$  [Pa s] and  $J_e^0$  is larger than  $10^{-4}$  [Pa<sup>-1</sup>]. As a result, the average relaxation time of PLA is considerably shorter than that of CAP at this temperature.

The temperature dependence of the oscillatory tensile modulus for CAP, PLA, and CAP/PLA (90/10) are shown in Figure 3. In case of PLA, the storage modulus falls off sharply around at 60 °C due to the glass-to-rubber transition.

[Figure 3]

It is found that  $E'$  at low temperature of PLA is higher than that of CAP. Furthermore, the peak of  $E''$  is detected around 60 °C for the blend, suggesting that phase

separation occurs. This phenomenon is observed for the blends containing more than 3 wt% of PLA. Moreover, it should be mentioned that the peak position is almost unchanged by blending CAP, indicating that CAP molecules cannot incorporate into PLA chains.

Moreover, it is confirmed from the figure that the peak ascribed to T<sub>g</sub> of CAP is shifted to a lower temperature to some degree by blending with PLA. In Figure 4, the peak temperatures of  $E''$  are plotted against the PLA content. As shown in the figure, T<sub>g</sub> decreases rapidly with the PLA content when the amount is lower than 3 wt%. On the contrary, it is almost independent of the PLA content when it is beyond 3 wt%. This result suggests that a small amount of PLA, i.e., lower than 3 wt%, can dissolve into CAP. In the case of the blends containing more than 3 wt% of PLA, undissolved part will be excluded from CAP and segregated in another phase.

[Figure 4]

The optical transparency also provides the information on the miscibility, because light scattering occurs in polymer blends with phase separation. As shown in Figure 5, the transparency is evaluated by Haze values. The blends containing more than 3 wt% of PLA exhibit large values, demonstrating that the blends have phase-separated morphology. The results correspond with the dynamic mechanical properties.

[Figure 5]

### ***Optical Anisotropy of CAP and the Blends***

The wavelength dependence of orientation birefringence is shown in Figure 6 for CAP at various draw ratios. As shown in the figure, the orientation birefringence of CAP

is positive and increases with increasing the wavelength, i.e., extraordinary wavelength dispersion. The unique and important optical anisotropy is provided by the sum of the contributions from both acetyl and propionyl groups, in which the acetyl group gives negative birefringence with strong dependence of wavelength whereas the propionyl group gives positive one with weak wavelength dispersion. Furthermore, it is well known that the wavelength dependence of orientation birefringence cannot be modified by the draw condition. Based on the Kuhn and Grün model proposed for the stress-optical behavior of crosslinked rubbers,<sup>19,20</sup> the orientation birefringence  $\Delta n(\lambda)$  of an oriented polymer is expressed as follows;<sup>19-21</sup>

$$\Delta n(\lambda) = \frac{2\pi}{9} \frac{(n(\lambda)^2 + 2)^2}{n(\lambda)} N \Delta\alpha(\lambda) \left( \frac{3\langle \cos^2 \theta \rangle - 1}{2} \right) \quad (6)$$

where  $\lambda$ ,  $n(\lambda)$ ,  $N$ ,  $\Delta\alpha(\lambda)$ , and  $\theta$  are the wavelength of light, the average refractive index, the number of chains in a unit volume, the polarizability anisotropy, and the angle that a segment makes with the stretch axis, respectively. The last bracketed term  $(3\langle \cos^2 \theta \rangle - 1)/2$  is identically equal to the Hermans orientation function,<sup>22</sup> whereas the other part in the right term is called as intrinsic birefringence determined by chemical structure. Consequently, eq. (6) can be written by;

$$\Delta n(\lambda) = \Delta n^0(\lambda) F \quad (7)$$

where  $\Delta n^0(\lambda)$  is the intrinsic birefringence and  $F$  is the orientation function.

Wavelength dispersion of orientation birefringence is always expressed by the ratio of the orientation birefringence at various wavelengths  $\Delta n(\lambda)$  to that at the specific

wavelength  $\Delta n(\lambda_0)$ . Since the intrinsic birefringence is not changed by the draw ratio, the following relation is obtained;

$$\frac{\Delta n(\lambda)}{\Delta n(\lambda_0)} = \frac{\Delta n^0(\lambda)F}{\Delta n^0(\lambda_0)F} = \text{const.} \quad (8)$$

However, Figure 6 shows that the wavelength dispersion of the orientation birefringence becomes stronger with increasing draw ratio. Considering that the acetyl group shows strong wavelength dispersion in the wavelength of visible light, the contribution of the acetyl group to the total birefringence becomes large at high draw ratios.

[Figure 6]

Figure 7 shows the orientation birefringence at the draw ratio of 1.5 and 2.0 for CAP and the blends with PLA. The figures demonstrate that only 1 wt% of PLA enhances the orientation birefringence to a great extent, although the stress level at the drawing process for the blend with 1 wt% of PLA is almost the same as that for pure CAP (not presented here). This tendency becomes obvious for the samples with a draw ratio of 2.0. However, it should be noted that pure PLA does not exhibit the orientation birefringence at this stretching condition (not presented here). This is reasonable because the molecular orientation relax immediately at this temperature, leading to  $F=0$ .

[Figure 7]

As shown in eq. (6), the average refractive index has an impact on the orientation birefringence. However, in the present experiments, the effect of the refractive index can be ignored, because the refractive index of PLA, 1.459 at 589 nm, is smaller than that of

CAP, 1.474. Therefore, the enhancement of the birefringence is ascribed to the orientation of PLA chains in CAP.

Moreover, it is found that the difference in the orientation birefringence between pure CAP and the blend containing 1 wt% of PLA is approximately  $0.6 \times 10^{-4}$ , and almost independent of the wavelength. This result suggests that PLA shows weak wavelength dispersion. Considering that the intrinsic birefringence of PLA is 0.030-0.033,<sup>16</sup> the Herman's orientation function of PLA in the blend is approximately 0.002. The value of orientation birefringence is almost the same as that for PLA fiber spun at 75 °C, i.e., closed to  $T_g$ , although the drawing process at the present study is performed at considerably high temperature, 163 °C. This result can be explained by the nematic interaction discussed by Watanabe et al.<sup>23-25</sup> PLA chains having short relaxation time at this temperature can orient to a great extent along with the orientation of CAP molecules having long relaxation time. It is a similar situation of polydispersed polymer melt systems, in which long chains retard the orientation relaxation of short chains greatly as experimentally revealed by Kornfield et al. using a bidispersed entangled polymer melt.<sup>26</sup> Moreover, both theoretical and experimental approaches clarified that the orientation of short chains hardly contributes to the stress level, whereas it has a great impact on the optical property.<sup>23-25,27</sup> Consequently, the high level of polarizability anisotropy of PLA dissolved in CAP chains is responsible for the marked orientation birefringence.

On the contrary, the blends containing more than 3 wt% of PLA show similar level of orientation birefringence to the blend with 1 wt% of PLA. This is reasonable, because the PLA chains in PLA phase, which have no nematic interaction by CAP chains, will relax the orientation quickly as compared to CAP.

## CONCLUSION

Miscibility and orientation birefringence of biomass-based polymer blends composed of CAP with a small amount of PLA are studied. It is found that PLA is miscible with CAP when the amount of PLA is less than 3 wt%, whereas the blends containing more than 3 wt% of PLA show phase separation. Further, the dissolved PLA chains in CAP can orient to a great extent during hot-drawing process along with CAP chains although the relaxation time of pure PLA is significantly shorter than that of pure CAP at the stretching temperature. The orientation of PLA chains is attributed to nematic interaction. In the case of the immiscible blends, PLA molecules in PLA phase will orient to the stretching direction very slightly, because they relax the orientation immediately as compared with CAP.

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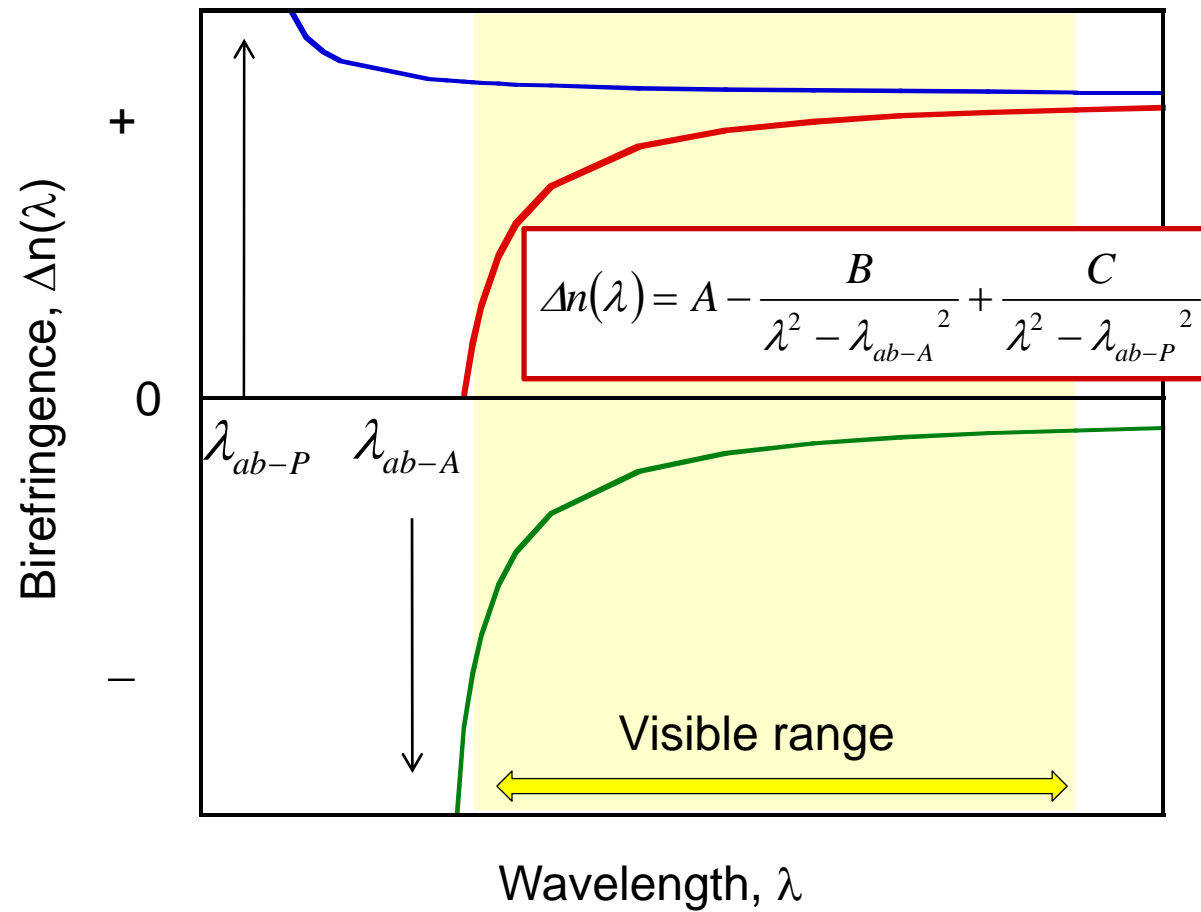
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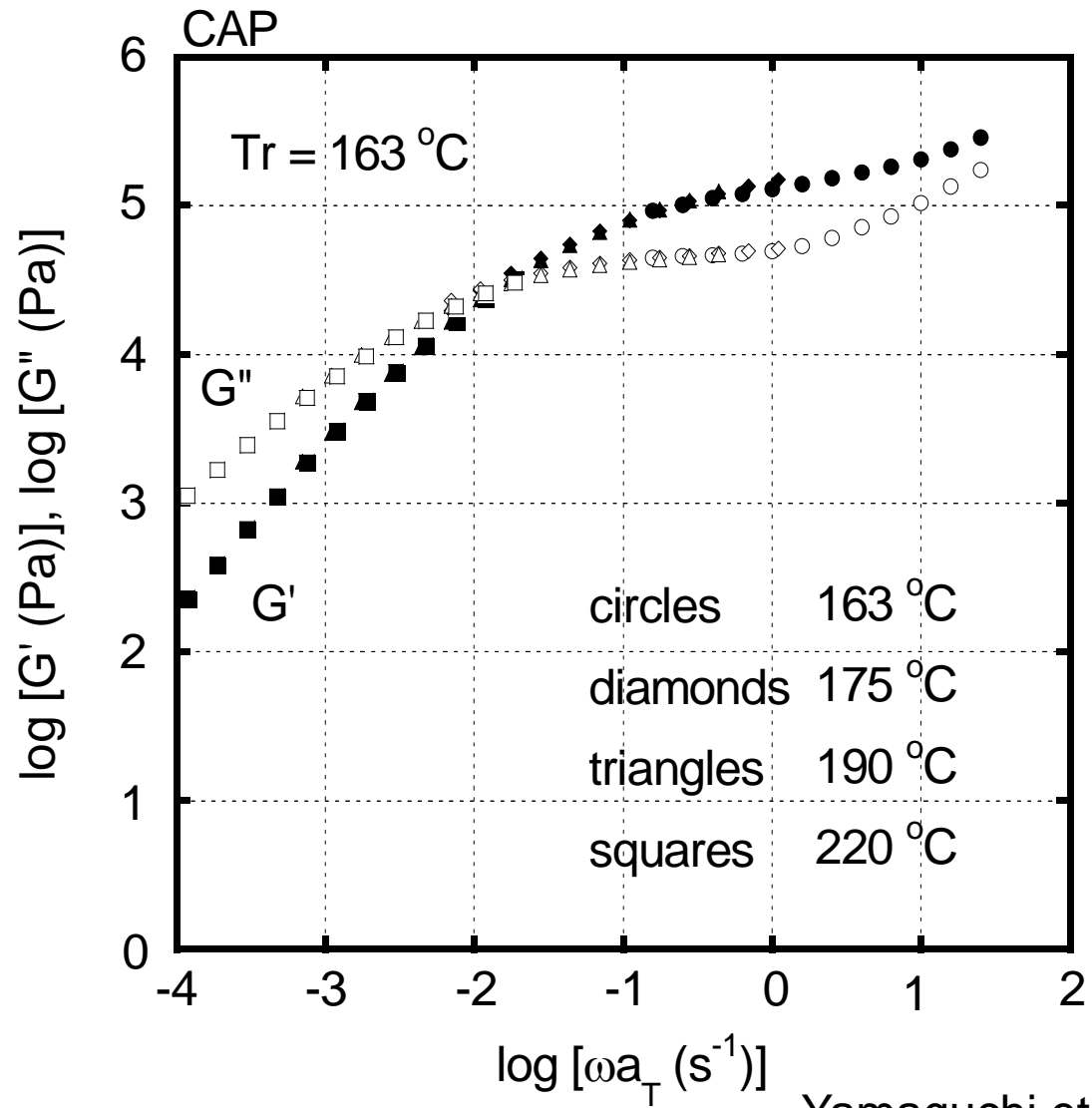


**Figure Captions**

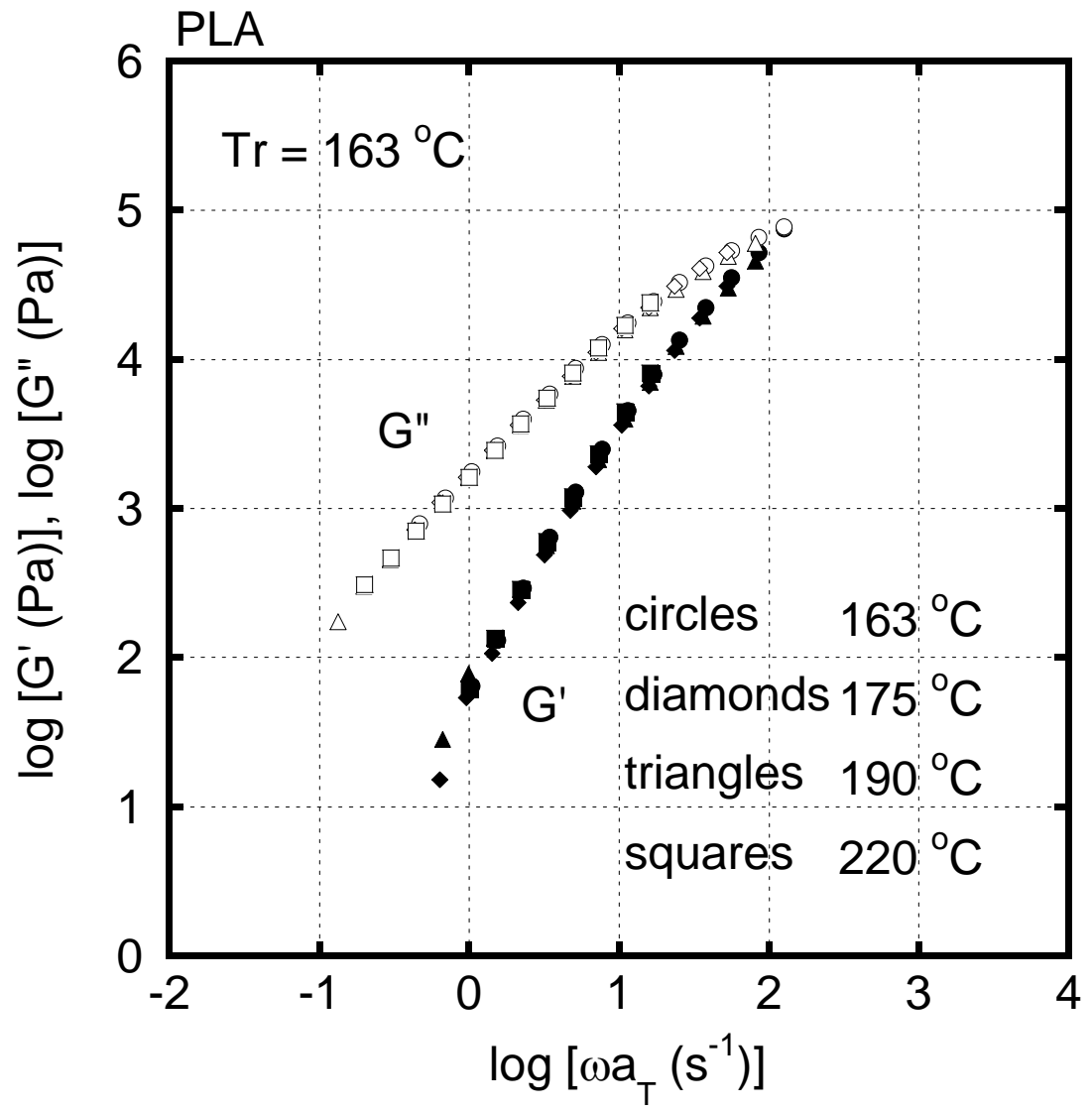
- Figure 1 Schematic illustration of extraordinary dispersion of orientation birefringence for CAP; the blue and red lines represent the wavelength dispersion of propionyl and acetyl groups, respectively. The red line denotes the sum of them.
- Figure 2 Master curves of frequency dependence of oscillatory shear moduli such as (open circles) storage modulus  $G'$  and (closed circles) loss modulus  $G''$  for CAP and PLA at 163 °C.
- Figure 3 Temperature dependence of (a) tensile storage modulus  $E'$  and (b) loss modulus  $E''$  at 10 Hz for (closed circles) CAP, (closed diamonds) PLA, and (open circles) CAP/PLA (90/10).
- Figure 4 Peak temperature of  $E''$  curves ascribed to Tg plotted against the PLA content.
- Figure 5 Haze values of the blends with 200  $\mu\text{m}$  thickness.
- Figure 6 Wavelength dependence of orientation birefringence  $\Delta n(\lambda)$  for stretched films of CAP at various draw ratios; (circles) 1.5, (diamonds) 2.0, and (triangles) 2.5.
- Figure 7 Wavelength dependence of orientation birefringence  $\Delta n(\lambda)$  for stretched films of CAP with various amounts of PLA at a draw ratio of (a) 1.5 and (b) 2.0; (circles) CAP, (diamonds) CAP/PLA (99/1), (triangles) CAP/PLA (97/3), and (squares) CAP/PLA (95/5).



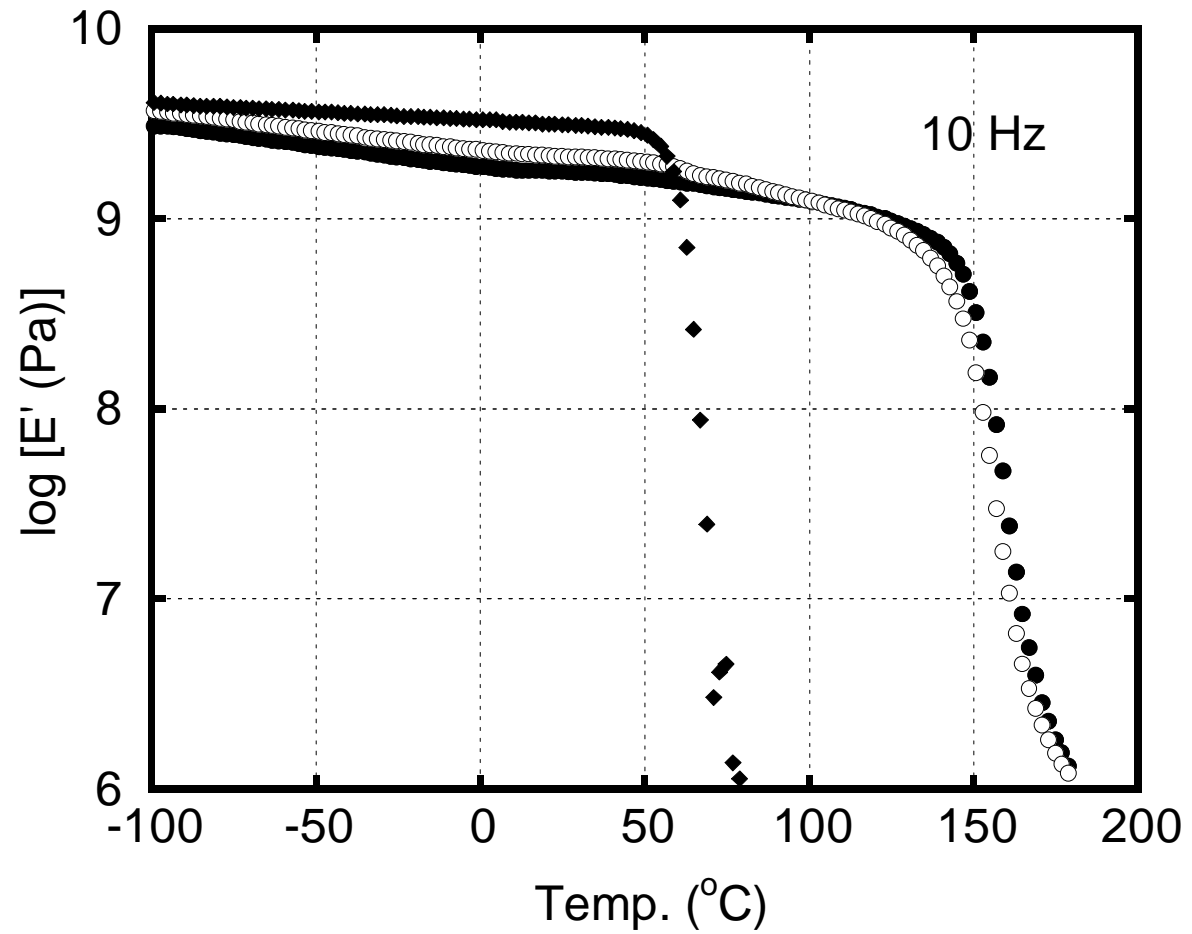
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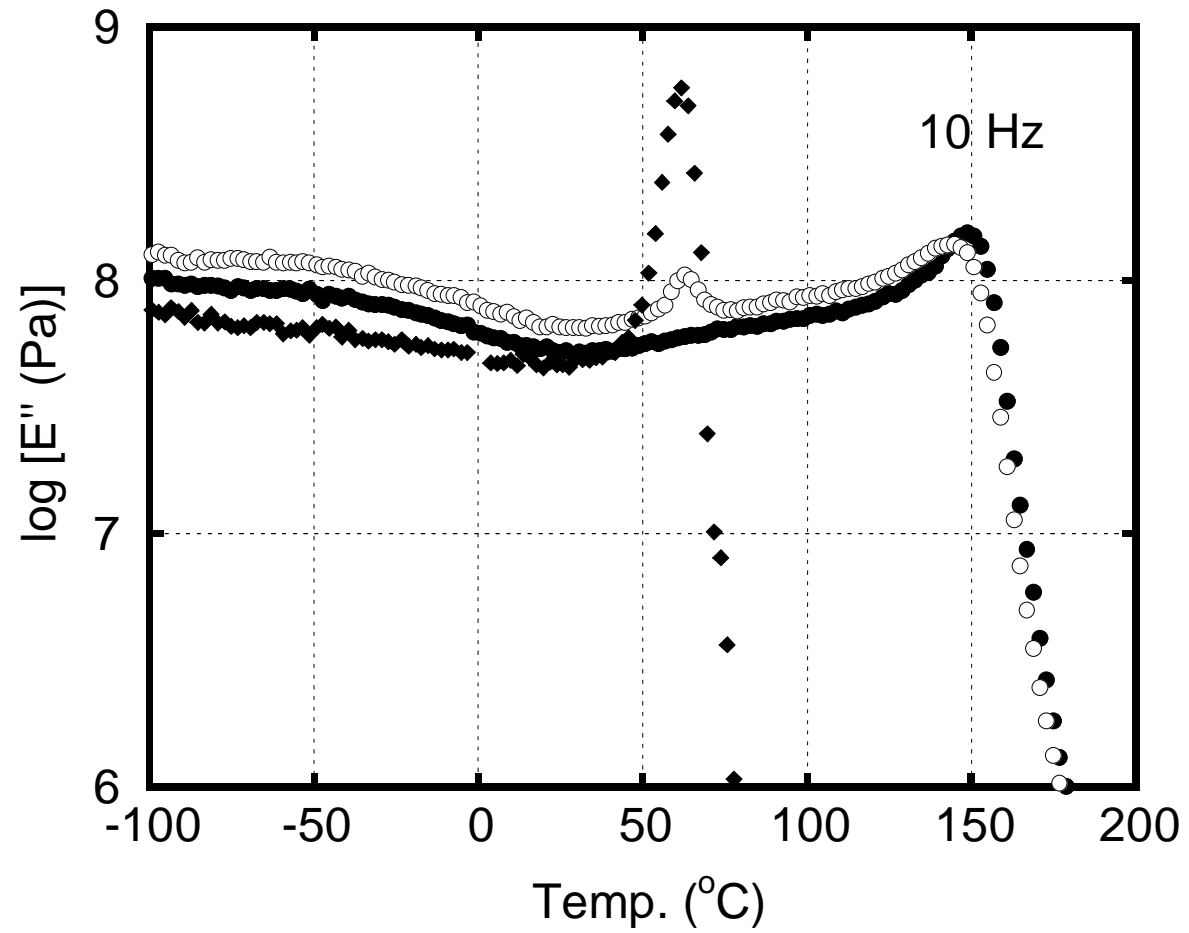
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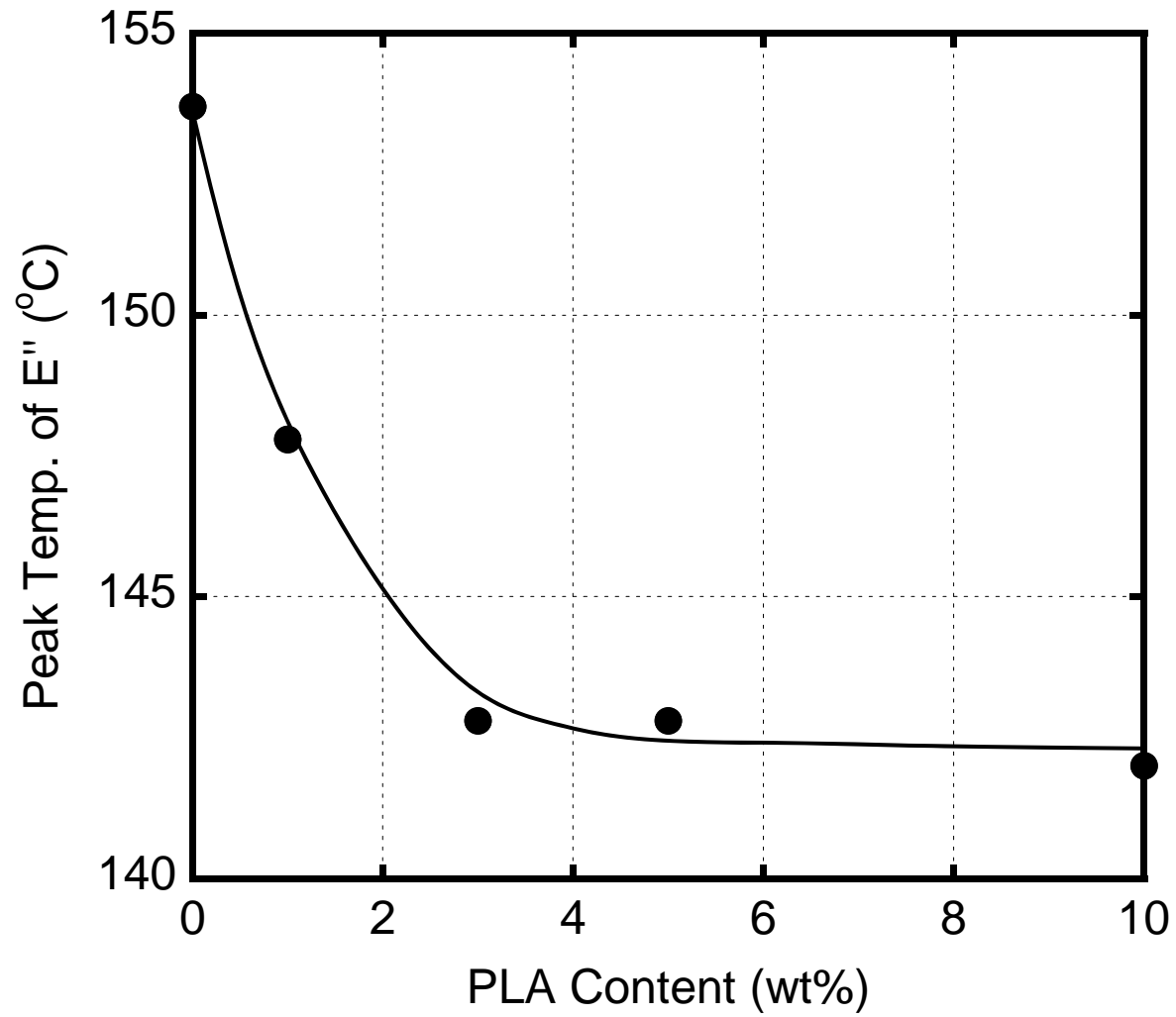
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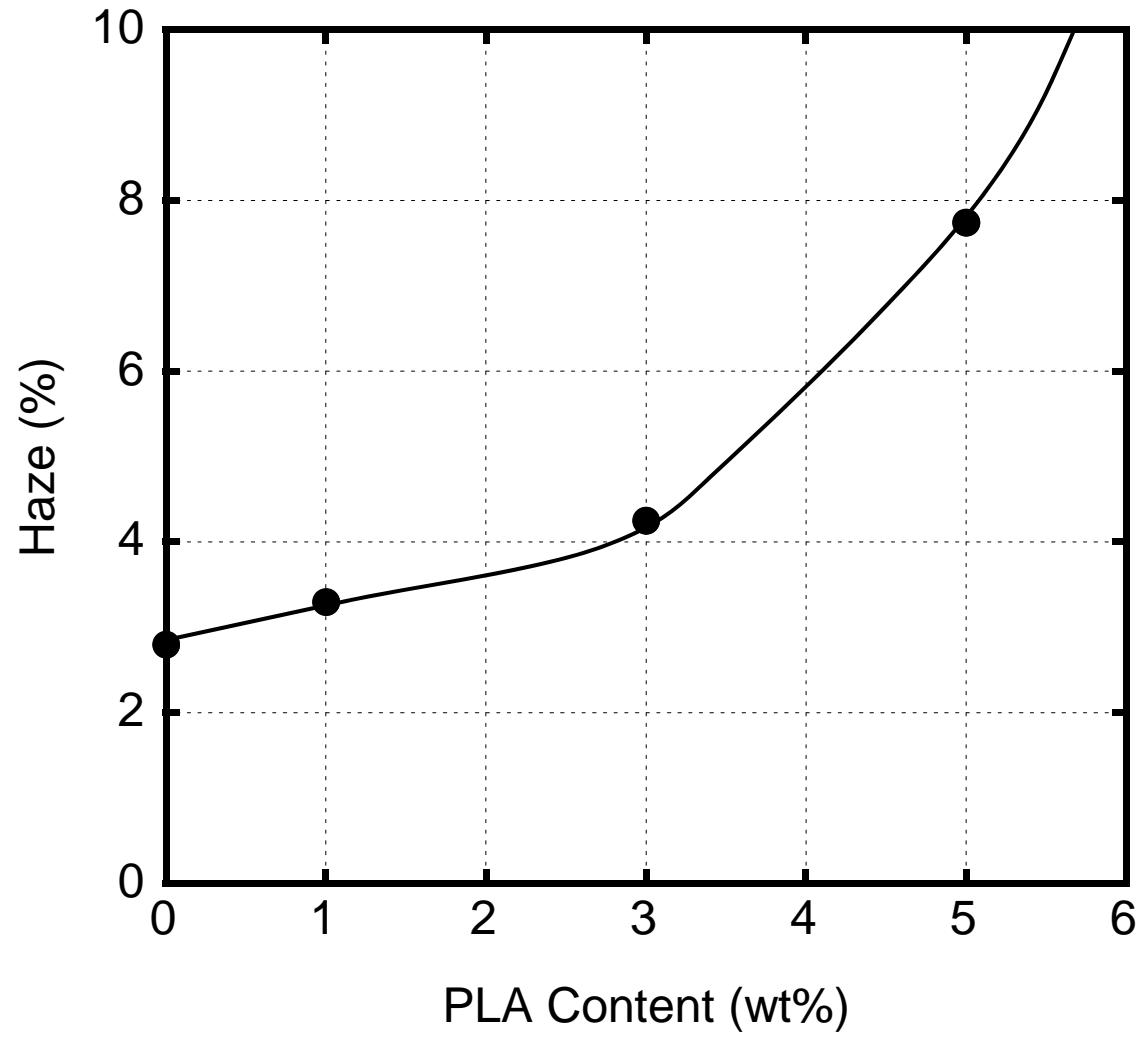
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Yamaguchi et al., Figure 3(b)

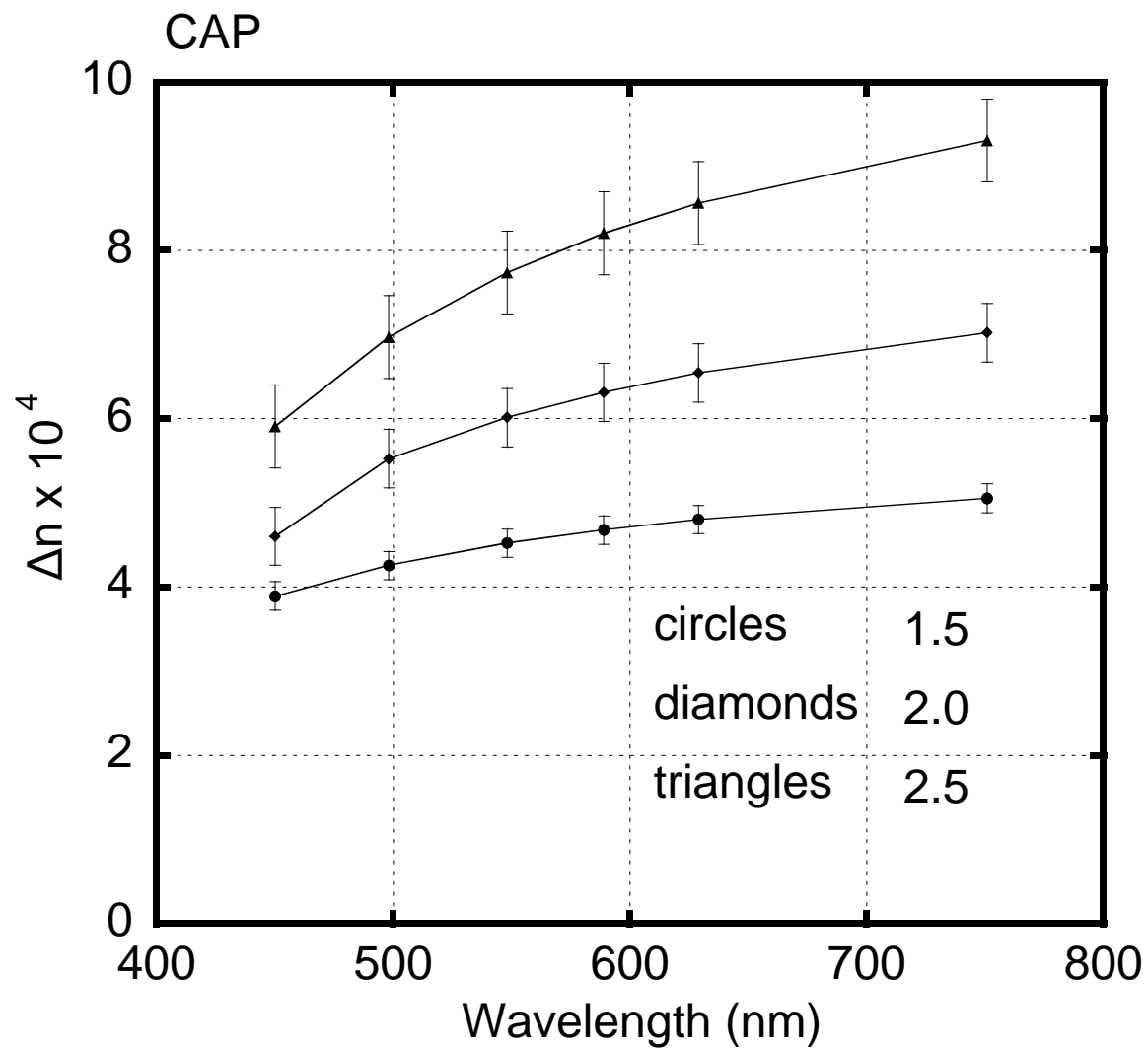


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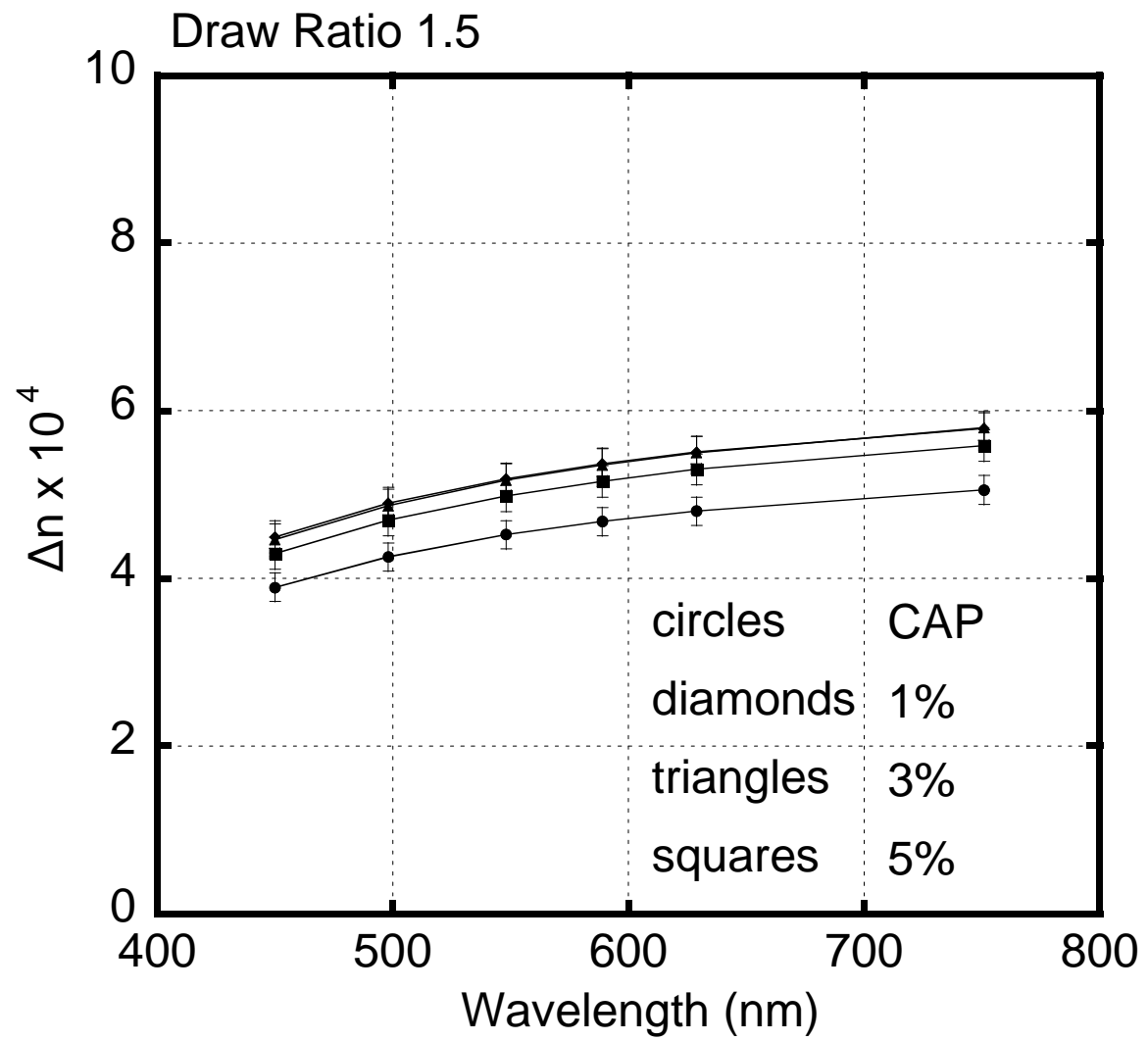


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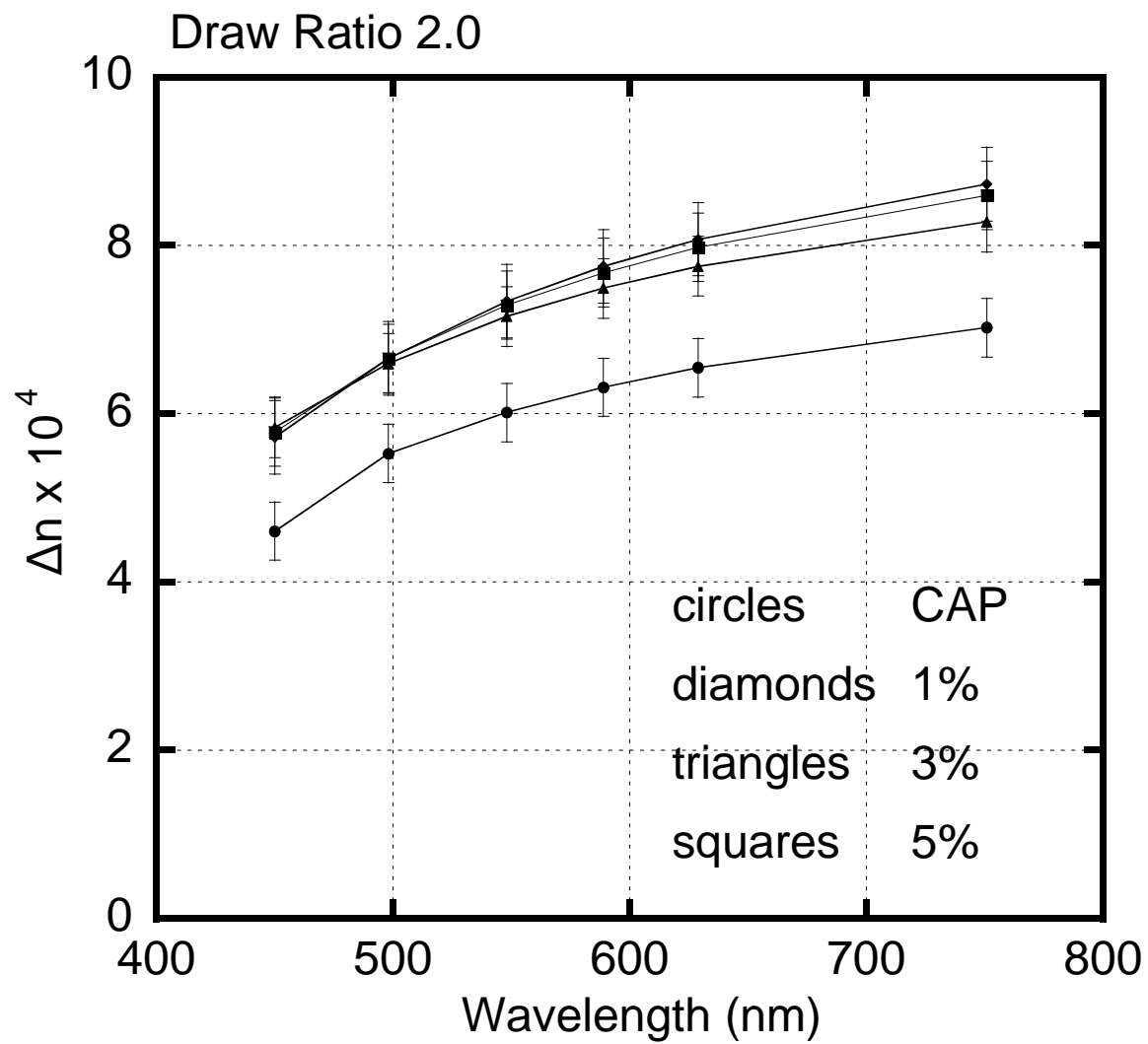




Yamaguchi et al., Figure 6



Yamaguchi et al., Figure 7(a)



Yamaguchi et al., Figure 7(b)