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Description	

Incorporation of Low-Mass Compound
to Alter the Orientation Birefringence
in Cellulose Acetate Propionate

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ABSTRACT

A blend of cellulose acetate propionate (CAP) with bisphenoxyethanolfluorene (BPEF), a low-mass compound (LMC), was prepared using melt-mixing method. The effect of BPEF addition on the orientation birefringence of CAP films was analyzed and compared to the blend added with tricresyl phosphate (TCP), an LMC known to increase the orientation birefringence of cellulose esters. Contrary to TCP, BPEF addition is found to decrease the positive birefringence of CAP. Moreover, it is observed that stress-optical law is not applicable for the CAP/LMC blend. The different effect on the orientation birefringence shown by BPEF and TCP is due to the different polarizability anisotropy. The decrease in orientation birefringence indicates that the polarizability ellipsoid of BPEF molecules is aligned in a direction perpendicular to the stretching direction, as opposed to that of TCP molecules which is parallel to the stretching direction. This alignment is thought to be resulted from the so called nematic interaction, in which LMC molecules are forced to orient to the stretching direction by the alignment of polymer chains. Furthermore, it is found that the magnitude of orientation birefringence of BPEF is larger than that of TCP at the same stress value, i.e., the same degree of orientation of CAP molecules, despite having a smaller intrinsic birefringence. This suggests that the nematic interaction with CAP chains of BPEF is stronger than TCP.

Key words: Birefringence; Retardation film; Orientation; Cellulose; Rheology

1. Introduction

Cellulose esters are biomass-derived materials that have found their applications in various fields. In an optical film application, some cellulose esters such as cellulose triacetate (CTA) and cellulose diacetate (CDA) have been utilized as a photographic film base and a polarizer protection film for years [1-4]. The excellent inherent properties such as high transparency throughout the visible wavelength range and high heat resistance make cellulose esters suitable for optical film application. Furthermore, it has been found that the optical and mechanical properties of cellulose esters can be modified by blending with other polymers or plasticizers [4-7].

Conventionally, cellulose ester films with uniform thickness are prepared by solution casting. However, the method involves solvent evaporation into the environment, which is not favorable. From environmental and economic point of views, melt extrusion would be preferred over solution casting for the preparation of optical films. Fortunately, some cellulose esters can be prepared using melt extrusion method. Machell and Sand [8] successfully fabricated an oriented film of cellulose acetate propionate (CAP) by melt extrusion using CAP with a degree of substitution (DS) of acetyl ranging from 1.9 to 2.6, propionyl ranging from 0 to 0.9 and hydroxyl ranging from 0 to 0.5. The fabricated films were found to exhibit optical and mechanical properties comparable to the CTA film prepared by the solution casting method. Furthermore, with an equal degree of esterification and molecular weights, CAP shows a better moisture resistance property than CTA or CDA [9,10].

Orientation birefringence Δn in a stretched film can be expressed as

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

where $n_{\parallel}$ and $n_{\perp}$ are refractive indices for lights polarized in the directions parallel and perpendicular to the stretching direction, respectively. In other words, if the polarizability anisotropy parallels to the stretching direction is larger than that perpendiculars to the stretching direction, the value of orientation birefringence is positive, and vice versa. The value of orientation birefringence Δn is determined by the degree of orientation and the structural unit of polarizability anisotropy as expressed by the following equation

$$\Delta n = \Delta n^0 F \tag{2}$$

where Δn^0 is the intrinsic birefringence and F is the orientation function. The intrinsic birefringence is the maximum possible birefringence corresponding to all molecules aligned parallel to the stretching axis.

In optical device applications, films have to show a certain birefringence characteristic that fits their particular function. In order to achieve an extruded film with a controlled birefringence property, a modification of the polymeric material is necessary. Several methods such as polymer blending, doping of anisotropic crystal, and random copolymerization have been studied with an objective to produce a polymeric film with a controlled amount of birefringence. Hahn and Wendorff employed two miscible polymers with opposite sign of intrinsic birefringence, i.e., poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF), to produce a film without birefringence at a specific blend ratio [11]. Yamaguchi and Masuzawa showed that the blend with equal amount of CAP and poly(vinyl acetate) (PVAc) shows almost no birefringence [12].

Random copolymerization method, in which one monomer has the opposite polarizability anisotropy to the other, has been applied by other researchers to produce a polymer with no birefringence [13,14]. Furthermore, Ohkita et al. have successfully developed a zero birefringence polymer by using a crystal doping method on the copolymer of methyl methacrylate and benzyl methacrylate [15]. In the study, needlelike crystals (20 nm width x 200 nm length) of Strontium carbonate having polarizability anisotropy opposite to the host polymer were used to control the birefringence.

On the other hand, Uchiyama and Yatabe used the polymer blending technique to modify the wavelength dispersion of birefringence in poly(2,6-dimethyl-1,4-phenylene oxide) and atactic polystyrene blend [16]. Despite both polymers individually show ordinary wavelength dispersion, the blends at certain blend compositions were found to show extraordinary wavelength dispersion of orientation birefringence. They also studied the wavelength dispersion of birefringence for uniaxially oriented copolymer films containing positive and negative birefringent units [17]. The copolymers were synthesized using 2,2-bis(4-hydroxyphenyl)propane and 9,9-bis(4-hydroxy-3-methylphenyl)fluorine, of which show polarizability anisotropy perpendicular to each other. They found that the wavelength dispersion of birefringence in the copolymer is controlled by copolymerization ratio while the effect of the stretching condition is negligible.

In our previous studies [7,18], transparent films of cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) have been successfully prepared using melt mixing process, subsequently followed by compression molding. The films obtained by this method were found to show good uniformity in thickness, high transparency, and adequate mechanical properties. Both CAB and CAP films show positive orientation birefringence that increases with increasing wavelength. The wavelength dependence of orientation birefringence in cellulose esters was found to be dependent on the amount and type of the ester and hydroxyl groups as well as the drawing conditions.

Our previous study also found that enhancement of positive birefringence in cellulose esters can be achieved by tricresyl phosphate (TCP) addition, of which a certain amount (≤ 5 wt%) of TCP shows a good miscibility with CAP and CTA and resulted in highly transparent films [7,19]. Furthermore, the orientation birefringence of CTA changes from negative birefringence with ordinary dispersion into positive birefringence with extraordinary dispersion by the TCP addition. Upon hot drawing, TCP molecules are forced to orient into the stretching direction accompanying the alignment of the polymer chains, a mechanism described as nematic interaction [20,21]. The alignment of the TCP molecules contributes to the increase of polarizability anisotropy that is parallel to the stretching direction, which is manifested by the increase of positive birefringence in the system. This intermolecular interaction was originally used to explain the orientation relaxation of a short chain in a polymer melt with broad molecular weight distribution. Then it has been clarified that the nematic interaction takes place in a miscible system when a low-mass compound (LMC) has an appropriate size to move cooperatively with chain segments of a host polymer [22,23].

The orientation birefringence of CAP added with bisphenoxyethanolfluorene (BPEF) is discussed in this study. Our results show that the orientation birefringence of hot-drawn CAP films can be reduced by BPEF addition. Furthermore, the results are compared to that obtained from the CAP/TCP blend. All sample films were prepared using melt mixing method. The orientation birefringence of CAP containing the LMC is discussed by considering the effects of (i) degree of orientation and (ii) structural unit of polarizability anisotropy. Furthermore, the effects of drawing temperatures and draw ratio on the orientation birefringence of the LMC are studied to evaluate the nematic interaction.

2. Experimental

2-1. Materials

The polymeric material used in this study was commercially available CAP (Eastman Chemical, CAP-482-20). The weight percentages of acetyl and propionyl groups are 2.5 and 46.0, while the nominal degrees of substitution (DS) are given as 0.19 and 2.58, respectively. The LMC used in this study are BPEF, produced by Aldrich Chemistry and TCP, produced by Daihachi Chemical Industry. The amount of LMC used in this study is 10 wt%. Figure 1 shows the chemical structure of the compounds.

[Fig.1]

Melt mixing of CAP with an LMC was performed using a 60 cc batch-type internal mixer (Toyoseiki, Labo-Plastomill) at 200 ^{o}C. The rotational speed of the blades was 30 rpm, and the mixing time was 5 min. The obtained mixture was compressed into flat sheets with thicknesses of 50 (for FT-IR measurements) and 200 μm by a compression-molding machine (Tester Sangyo, Table-type-test press SA-303-I-S) for 5 min at 200 ^{o}C under 10 MPa, and then cooled at 25 ^{o}C for 5 min.

The cooled sheet was cut into sample films of 10 mm in width and 20 mm in length. Subsequently, the films were hot-drawn using a uniaxial tensile machine with a temperature controller (UBM, DVE-3) to prepare uniaxial oriented films. Samples were drawn at various temperatures. All the samples can be drawn at least up to 2.0 of draw ratio without rupture at these experimental conditions. The initial distance between the clamps was 10 mm and the stretching rate used was 0.5 mm/s. The stress-strain data generated upon each stretching process were also recorded. The drawn samples were quenched by cold air blowing to avoid the relaxation of the molecular orientation. They were subsequently kept in a humidity chamber (Yamato, IG420) at 25 ^{o}C and 50 %RH at least for a day, before being measured for their orientation birefringence.

2-2. Measurements

The temperature dependence of oscillatory tensile moduli in the solid state was measured from -100 to 200 ^{o}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 ^{o}C/min, respectively.

The retardation of the drawn films was measured by an optical birefringence analyzer (Oji Scientific Instruments, KOBRA-WPR) at room temperature. The measurements were performed as a function of the wavelength between 450 and 800 nm by changing the color filters.

Infrared dichroic ratio was also measured by a Fourier transform infrared spectrometer (JASCO, FT-IR 6100) equipped with a polarizer. The absorbance of the band at 880 cm-1, assigned to the pyranose ring, was evaluated by a linearly polarized IR whose electric vector is parallel $A_{//}$ and perpendicular $A_{\perp}$ to the stretching direction.

3. Results and Discussion

Dynamic Mechanical Properties

The temperature dependence of tensile loss modulus E'' at 10 Hz is shown in Figure 2. Both BPEF and TCP are found to be miscible with CAP as indicated by a single peak ascribed to the glass-to-rubber transition in their respective E'' curves. In particular, the peak height of the CAP/BPEF blend is almost identical to that of the pure CAP, suggesting a good miscibility of the system. An abrupt drop of the storage modulus E' owing to the glass-to-rubber transition is observed for all samples (not shown here).

[Fig. 2]

Both BPEF and TCP additions reduce the glass transition temperature T_g. However, the shift of T_g is smaller in the CAP/BPEF blend, suggesting a weak plasticizing effect of BPEF. The T_g, defined as the peak temperature of the loss modulus E'' is around 146 ^{o}C for pure CAP, and reduced to 128 and 113 ^{o}C by the addition of 10 wt% of BPEF and TCP, respectively.

Orientation Birefringence

The wavelength dispersions of orientation birefringence of the stretched samples are shown in Figure 3. The samples were drawn at draw ratios of 2.0 and 1.5. The corresponding stretching temperatures, at which the tensile storage modulus E' is 10 MPa at 10 Hz, of pure CAP, CAP/BPEF and CAP/TCP blends were 163, 146 and 130 ^{o}C, respectively. Figure 4 shows the corresponding stress-strain curves.

[Fig. 3] [Fig. 4]

CAP shows a positive orientation birefringence with extraordinary wavelength dispersion, i.e. it increases with increasing wavelength, which is an anomalous characteristic since polymers show a decrease of birefringence with increasing wavelength in general, as described by the Sellmeier relation [24-26]. As reported in our preceding papers [4,18,27], the ester groups as well as the hydroxyl group play a dominant role in determining the orientation birefringence in cellulose esters rather than the orientation of the main chains. The anomalous characteristic of CAP can be explained as the result of the combination of a positive birefringence having weak wavelength dependence of the propionyl and hydroxyl groups, with a negative birefringence having strong wavelength dependence of the acetyl group.

As demonstrated in Figure 3, orientation birefringence increases with increasing draw ratio for all samples. The influence of draw ratio on the orientation birefringence corresponds to the stress-strain curves in Figure 4, in which the stress value at least increases by twofold, when the draw ratio is increased from 1.5 to 2.0. The tendency is in agreement with the stress-optical law for polymer melts and rubbers, which indicates an increase in birefringence with increasing stress as given by the following equation

$$\Delta n = C\sigma \tag{3}$$

where σ is the true stress and C is the stress-optical coefficient which is determined by chemical structure.

On the other hand, the species of the LMC also affects the orientation birefringence, but in a different manner. While addition of TCP increases the orientation birefringence of CAP, it is found that addition of BPEF decreases it, despite both CAP/BPEF and CAP/TCP blends show an increase in the stress value compared to the pure CAP as shown in Figure 5. The results are not in agreement with the stress-optical law.

The above phenomenon can be explained from the viewpoint of polarizability anisotropy of LMC. An increase in positive birefringence suggests an increase of polarizability anisotropy parallel to the stretching direction, while an increase in negative birefringence indicates an increase of polarizability anisotropy perpendicular to the stretching direction.

As the film is stretched, the neighbouring LMC molecules are forced to orient to the stretching direction accompanying the alignment of the CAP chains. The result indicates that the alignment of TCP molecules increases the polarizability anisotropy parallel to the stretching direction, demonstrated by the increase in positive birefringence. This phenomenon has been reported by our preceding papers with detailed characterization [4,5,7,19,27].

Contrarily, the alignment of BPEF molecules increases the polarizability anisotropy perpendicular to the stretching direction as evidenced by the decrease of the positive birefringence in CAP. The result should be noted because the reduction of orientation birefringence by the addition of an LMC has not been reported yet at the best of our knowledge.

[Fig. 5]

Wavelength dependence of orientation birefringence is often discussed by a normalized value, i.e., the ratio of the orientation birefringence at every measured wavelength $\Delta n(\lambda)$ to that of the reference wavelength $\Delta n(\lambda_0)$. The normalized orientation birefringence is usually determined by chemical structure and independent of the stretching condition and molecular characteristics for a conventional polymer.

Figure 6 shows the normalized orientation birefringence for pure and blended samples drawn at a draw ratio of 2.0. It is observed that the wavelength dispersion of orientation birefringence can be controlled by the LMC addition, which depends on the type of LMC. While TCP addition weakens the extraordinary wavelength dispersion of orientation birefringence, BPEF addition is found to be effective for enhancing it. Furthermore, the effect can be further amplified by increasing the draw ratio (not shown here). Considering the recent target in industry for a retardation film is to emphasize the extraordinary wavelength dispersion of the orientation birefringence, the technique is useful in the material design.

Molecular Orientation of LMC

Using the information regarding the drawing temperature and stress in Figure 4, the appropriate drawing temperatures for pure and blended samples are adjusted in order to obtain the same stress values of 2.15 MPa and 0.25 MPa at the strain of 1.0. In the following discussion, the drawing temperatures that yield the stress values of 2.15 MPa and 0.25 MPa are referred to as ‘low temperature’ and ‘high temperature’, respectively. The corresponding drawing temperatures for the pure CAP, CAP/BPEF and CAP/TCP blends are 154 ^{o}C (2.15 MPa) and 165 ^{o}C (0.25 MPa), 137 ^{o}C (2.15 MPa) and 150 ^{o}C (0.25 MPa), and 131 ^{o}C (2.15 MPa) and 147 ^{o}C (0.25 MPa), respectively.

[Fig. 6] [Fig. 7]

Furthermore, the degree of molecular orientation of CAP is directly evaluated by infrared dichroic ratio D ($\equiv A_{\perp} / A_{//}$) following the previous studies [18,28-30]. After stretching at the high temperature, the values of (D-1)/(D+2), which must be proportional to the Hermans orientation function, are found to be -0.08 for CAP and -0.10 for CAP/BPEF. The result indicates that the electric vector of the band is perpendicular to the main chain. Moreover, it is demonstrated that the orientation function of CAP is hardly affected by the addition of BPEF.

The wavelength dispersions of orientation birefringence for the pure and blended samples drawn at the high and low temperatures with a draw ratio of 2.0 are shown in Figure 6. The corresponding stress-strain curves are shown in Figure 7.

The intrinsic birefringence of a blend composed of polymer A and an LMC is given by the following equation) [21,31].

$$\Delta n_{blend}^{0} = \phi_A (\Delta n_A^0 + \phi_{LMC}\, \varepsilon\, \Delta n_{LMC}^{0}) \qquad (4)$$

where ϕ_i refers to the volume fraction of the i component, while ε ($0 \leq \varepsilon \leq 1$) refers to the nematic interaction coefficient between the LMC and the host polymer. The coefficient represents the strength of orientational coupling between the LMC molecule and the surrounding polymer chains. At $\varepsilon = 1$, the LMC molecules orient perfectly with the orientation of the host polymer. By using the relations given in eqs. 2 and 4, the orientation birefringence of the CAP blend is expressed as

$$\mathit{\Delta} n_{blend} = \phi_{CAP}\, \mathit{\Delta} n_{CAP}^{0}\, F_{CAP} + \phi_{CAP}(1-\phi_{CAP})\varepsilon\, \mathit{\Delta} n_{LMC}^{0}\, F_{CAP} \qquad (5)$$

Therefore, the orientation birefringence of this system is determined by the blend ratio, intrinsic birefringence of components, nematic interaction, and the orientation function of CAP.

Generally, samples drawn at low temperatures show a high value of orientation birefringence. This is attributed to the increase in the degree of chain orientation, which is proportional to the stress as well known by the classical rubber theory. Therefore, the effect of the LMC addition is also more obvious for the samples drawn at low temperatures due to the same reason, i.e., high degree of LMC orientation accompanying with CAP molecules, which further amplifies the effect of nematic interaction. The intrinsic birefringence of the LMC molecules has to be also considered.

The effect of the drawing temperature on the wavelength dispersion of orientation birefringence for the pure and blended samples is shown in Figure 8. The extraordinary wavelength dispersion characteristic is found to be enhanced for the pure CAP, by decreasing drawing temperature as shown by the increase in slope. However, in the case of the blended CAP, the drawing temperature does not significantly affect the wavelength dispersion of the orientation birefringence. In other words, the wavelength dispersion of birefringence of the pure CAP is more sensitive to the drawing temperature than the blended CAP.

[Fig. 8]

As clarified earlier, the change of orientation birefringence upon the LMC addition in CAP is attributed to the orientation of the LMC molecules via nematic interaction with the polymer chains. In order to examine the contribution of BPEF and TCP on the orientation birefringence at two different drawing temperatures, pure and blended samples are drawn at various draw ratios; 2.0, 1.7, 1.5 and 1.3, each at the two temperatures, i.e., low and high temperatures, as mentioned above, and the results are summarized in Figure 9. For the CAP/TCP blend, only the results from the draw ratios of 1.7 and 2.0 are shown.

The orientation birefringence of the LMC increases steadily with draw ratio but the increase is weakened at high draw ratios. This is reasonable since the orientation function is approaching its saturated value with the increase of draw ratio. At the high drawing temperature, the samples show a relatively small increase in stress with increasing draw ratio. However, at the high drawing temperature, a greater increase in the orientation birefringence of the LMC per stress value is observed as indicated by a steeper curve, than samples drawn at the low temperature. The result implies that a lower stress is enough to move the LMC molecules at high drawing temperatures.

As shown in Figure 9, the magnitude of orientation birefringence attributed to the BPEF orientation is found to be larger than that of TCP. According to eq. 5, the orientation birefringence of LMC is determined by these factors: (i) Orientation function, F of CAP (ii) Intrinsic birefringence, Δn^0 of LMC and (iii) Nematic interaction coefficient, ε. The degree of orientation is maintained to be equal for both blends in this study by having the same host polymer, i.e., CAP, and being drawn at the same stress. Therefore, they are assumed to show the same orientation function F.

The intrinsic birefringence Δn^0 is computed using Winmostar, a software program developed by Senda, for molecular modeling and calculation [29]. It is found that the intrinsic birefringence Δn^0 of TCP (0.257) is larger than BPEF (-0.117), which is contrary to the result observed in Figure 9. Therefore, this leads to a conclusion that the nematic interaction of BPEF is larger than that of TCP, indicating that BPEF shows a stronger orientational coupling with CAP chains than TCP.

[Fig.9]

4. Conclusions

Understanding the mechanism by which a low-mass compound (LMC) influences the orientation birefringence in cellulose esters is important in designing and producing an ideal film that fulfills its optical requirements. In this study, the effect of the LMC addition on the orientation birefringence as well as on its wavelength dispersion is evaluated. The orientation birefringence of CAP blended with different types of LMC, i.e., BPEF and TCP, is measured and then analyzed in comparison to that of pure CAP. Addition of the LMC affects the magnitude as well as the wavelength dependence of orientation birefringence. BPEF addition decreases the orientation birefringence, indicating the increase in polarizability anisotropy perpendiculars to the stretching direction. Furthermore, it is effective in enhancing the extraordinary wavelength dispersion behavior of the orientation birefringence. Lastly, it is found that BPEF shows a larger orientation birefringence than TCP, despite the values of their intrinsic birefringence are opposite. This indicates that the nematic interaction between BPEF molecules and CAP polymers is higher that that of TCP.

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Figure Captions

Figure 1 Chemical structure of bisphenoxyethanolfluorene (BPEF) and tricresyl phosphate (TCP).

Figure 2 Temperature dependence of tensile loss modulus E'' for pure CAP (circles), CAP/BPEF (90/10) (diamonds) and CAP/TCP (90/10) (squares) at 10 Hz.

Figure 3 Wavelength dispersion of orientation birefringence Δn for pure CAP (circles), CAP/BPEF (90/10) (diamonds), and CAP/TCP (90/10) (squares) drawn at temperatures where the respective tensile storage modulus E' is 10 MPa. The samples were stretched at draw ratios of 2.0 (unfilled signs) and 1.5 (filled signs).

Figure 4 The stress-strain curves for pure CAP (circles), CAP/BPEF (90/10) (diamonds), and CAP/TCP (90/10) (squares) drawn at temperatures where the respective tensile storage modulus E' is 10 MPa.

Figure 5 Wavelength dispersion of orientation birefringence Δn for pure CAP (circles), CAP/BPEF (90/10) (diamonds) and CAP/TCP (90/10) (squares) drawn at a draw ratio of 2.0. Unfilled signs indicate a low drawing temperature that yields a stress value of 2.15 MPa, while filled signs indicate a high drawing temperature that yields a stress value of 0.25 MPa at a draw ratio of 2.0, respectively.

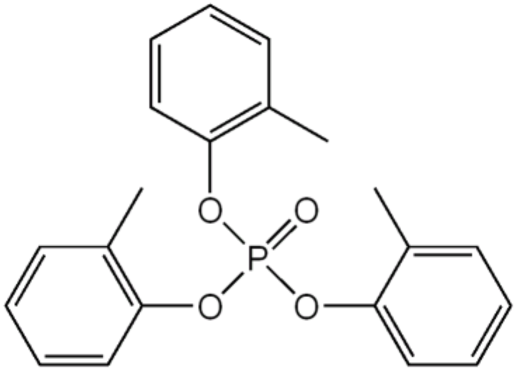
Figure 6 Normalized orientation birefringence $\Delta n(\lambda)/\Delta n(588)$ for pure CAP (circles), CAP/BPEF (90/10) (diamonds), and CAP/TCP (90/10) (squares) drawn at a draw ratio of 2.0. Drawings were performed at temperatures where the respective tensile storage modulus E' is 10 MPa.

Figure 7 The stress-strain curves for pure CAP (circles), CAP/BPEF (90/10) (diamonds) and CAP/TCP (90/10) (squares) drawn at a draw ratio of 2.0. Unfilled signs indicate a low drawing temperature that yields a stress value of 2.15 MPa, while filled signs indicate a high drawing temperature that yields a stress value of 0.25 MPa at a draw ratio of 2.0, respectively.

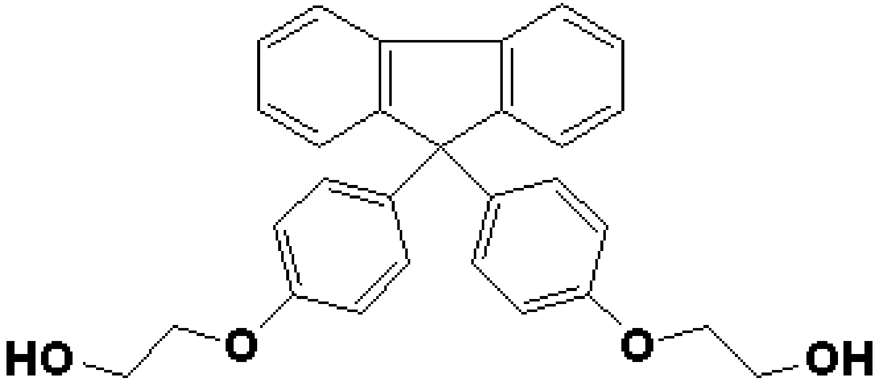
Figure 8 Normalized orientation birefringence $\Delta n(\lambda)/\Delta n(588)$ for pure CAP (circles), CAP/BPEF (90/10) (diamonds) and CAP/TCP (90/10) (squares) drawn at a draw ratio of 2.0. Unfilled signs indicate a low drawing temperature that yields a stress value of 2.15 MPa, while filled signs indicate a high drawing temperature that yields a stress value of 0.25 MPa at a draw ratio of 2.0, respectively.

Figure 9 Relation between the orientation birefringence contribution of BPEF (diamonds) and TCP (squares), with stress. Unfilled signs indicate a low drawing temperature that yields a stress value of 2.15 MPa, while filled signs indicate a high drawing temperature that yields a stress value of 0.25 MPa at a draw ratio of 2.0, respectively.

Figure 1



TCP



BPEF

Figure 2

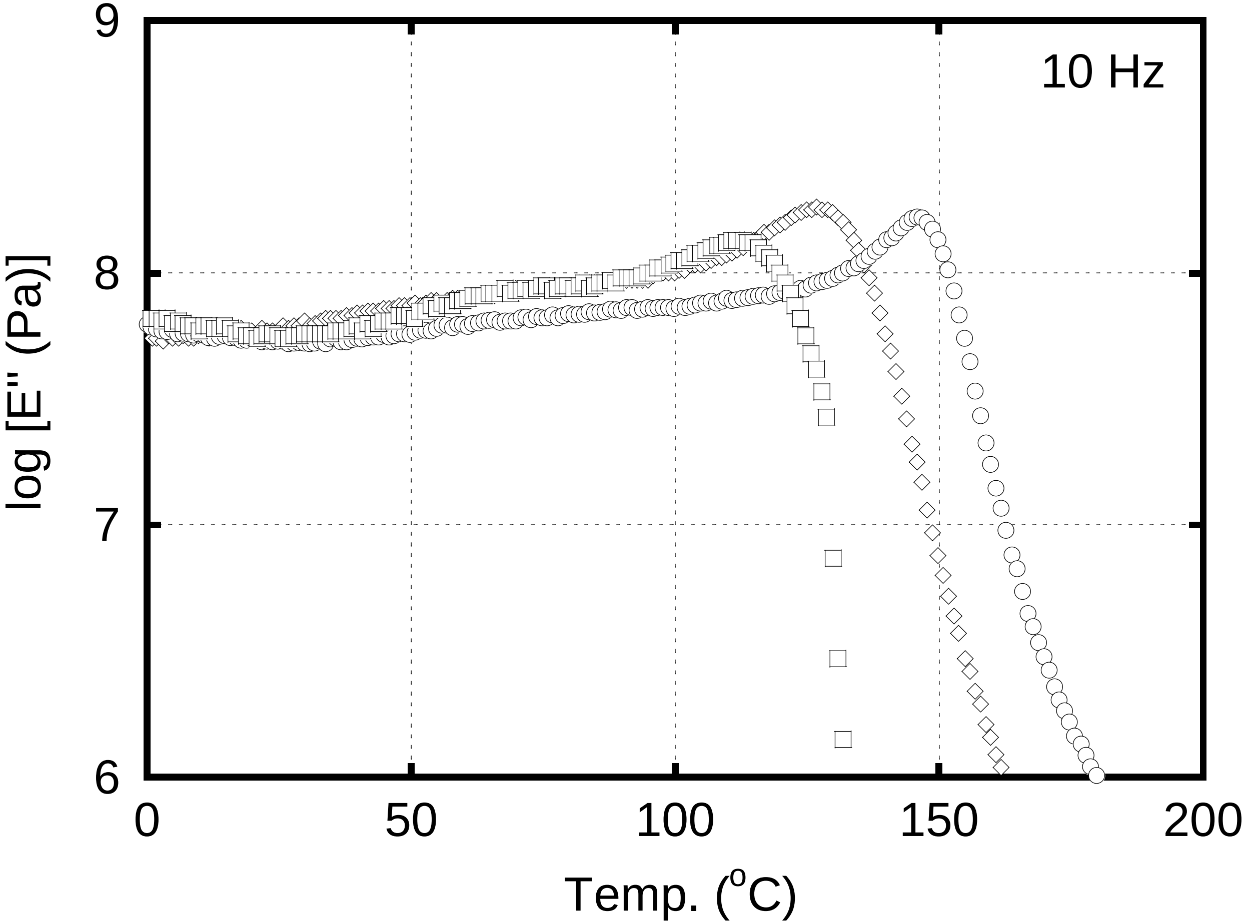


Figure 3

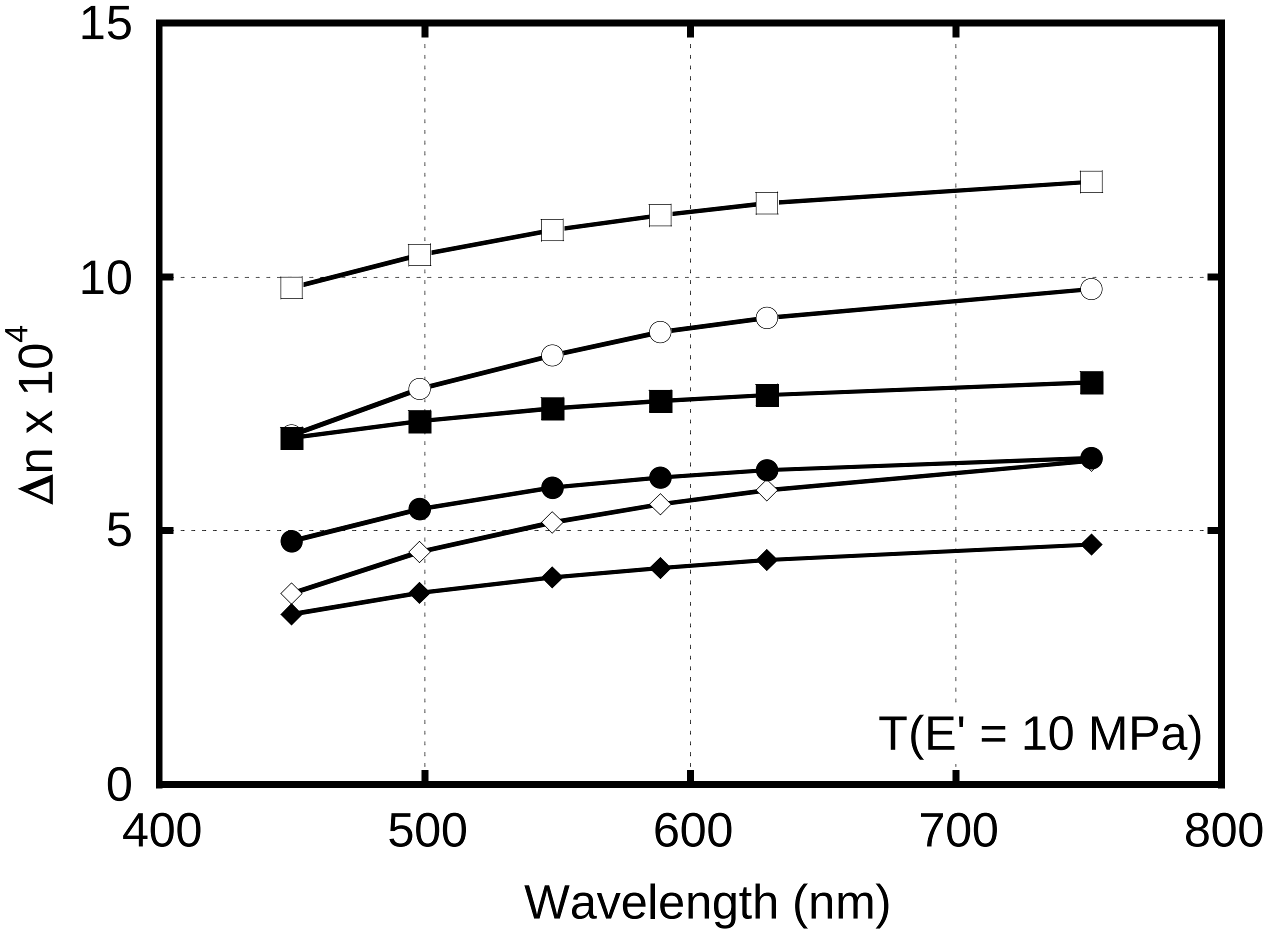


Figure 4

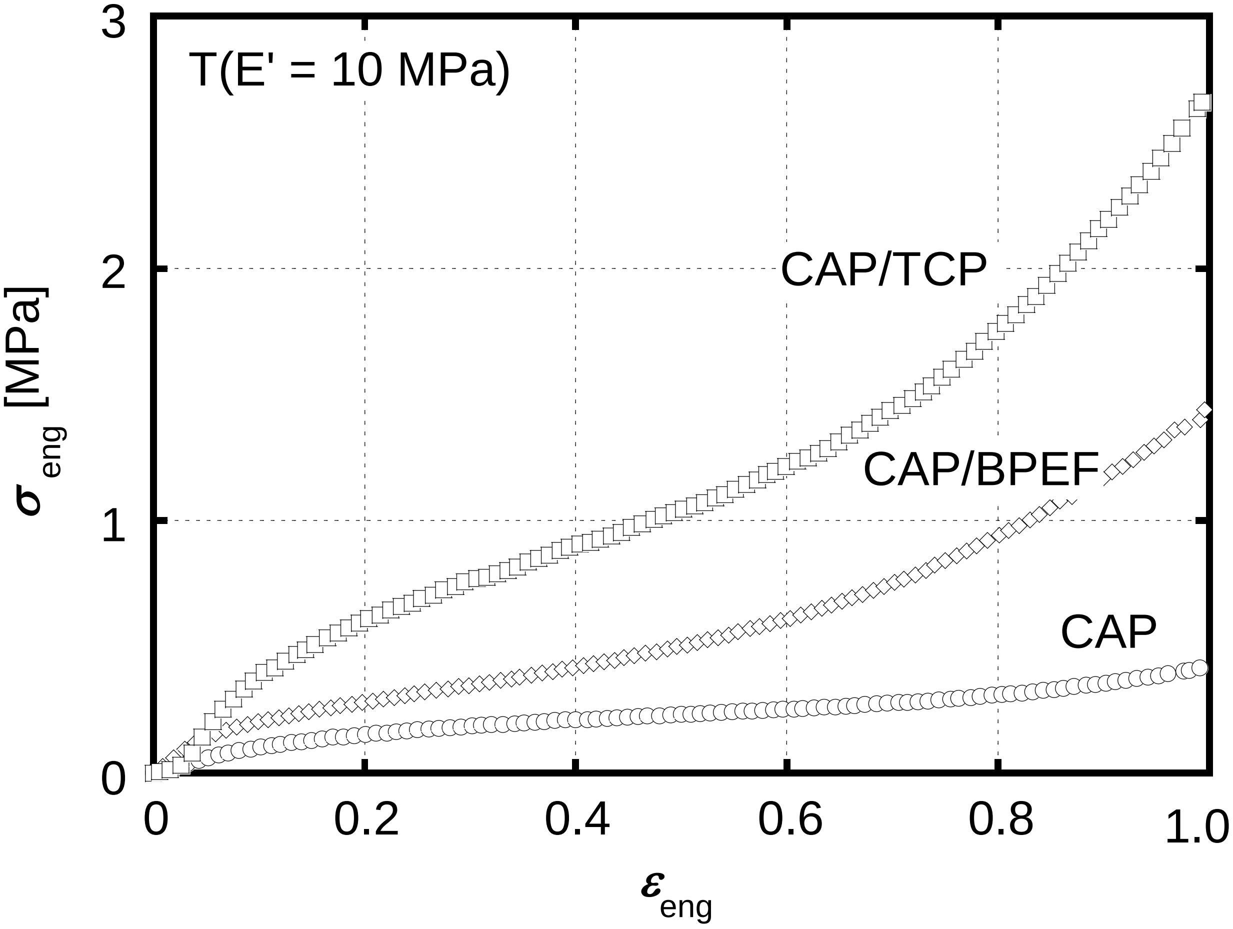

T(E' = 10 MPa)
CAP/TCP
CAP/BPEF
CAP
3
2
1
0
0
0.2
0.4
0.6
0.8
1.0
σ_{eng} [MPa]
ε_{eng}

Figure 5

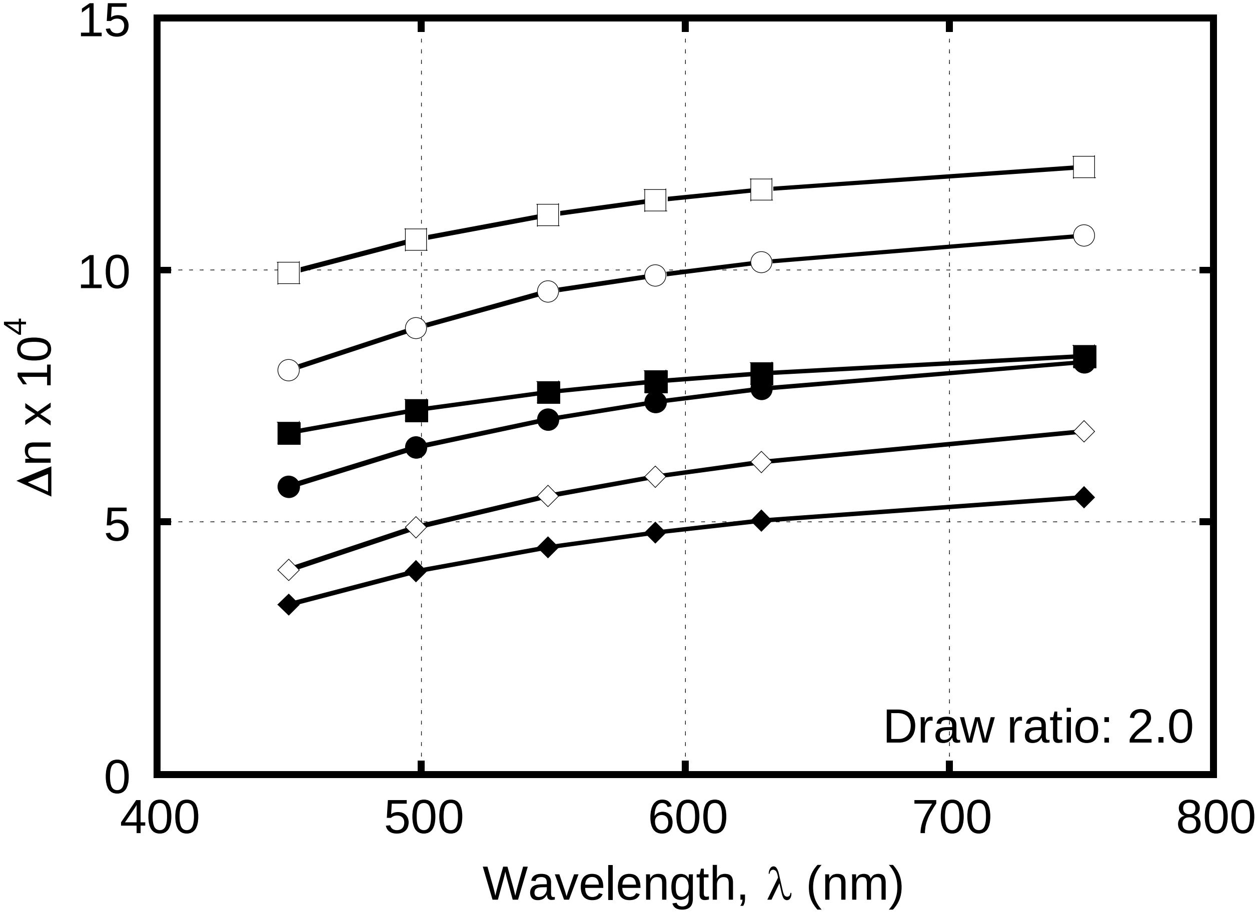
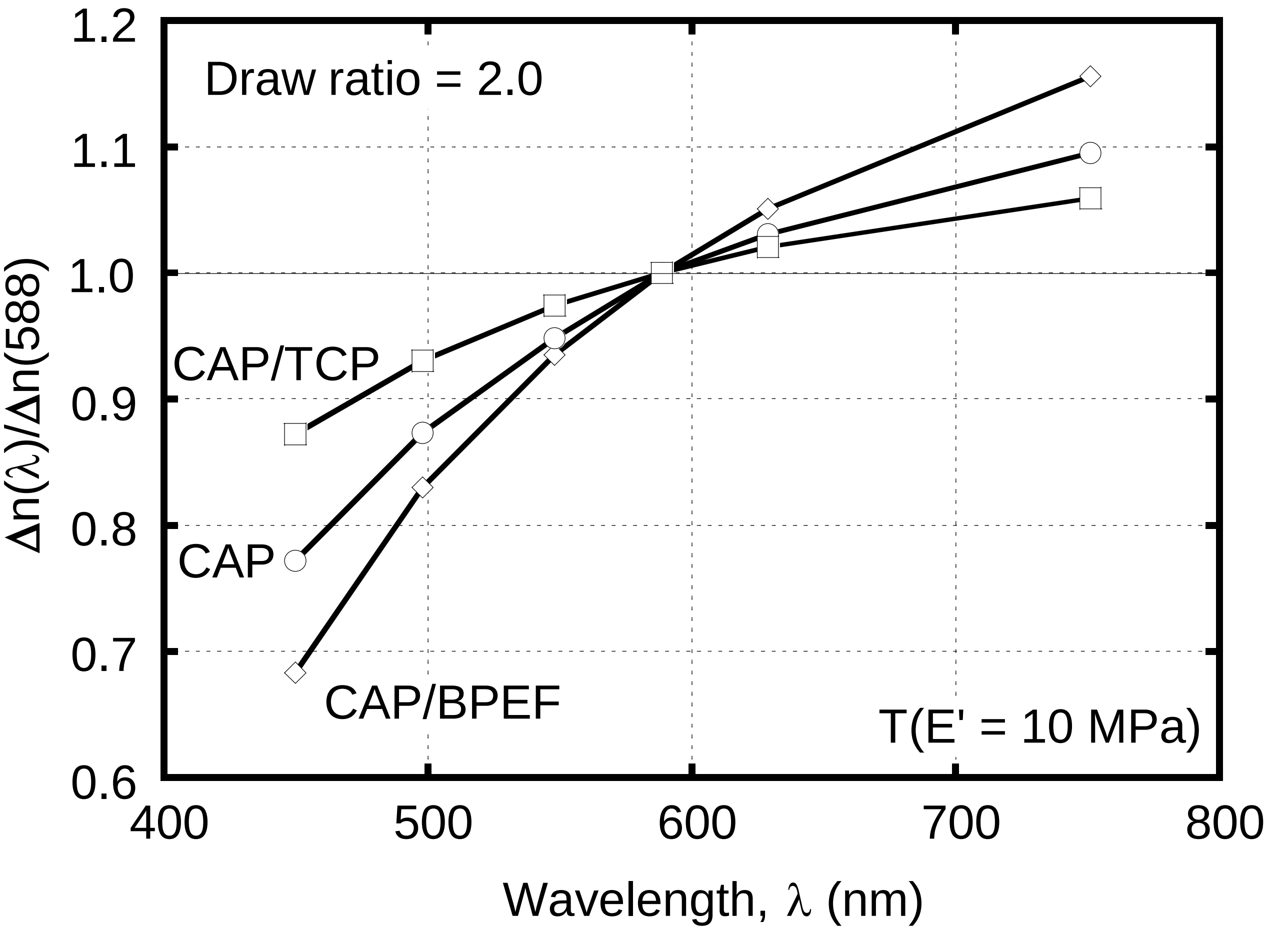

15
10
5
0
Δn x 10^4
400
500
600
700
800
Wavelength, λ (nm)
Draw ratio: 2.0

Figure 6



Draw ratio = 2.0
CAP/TCP
CAP
CAP/BPEF
T(E' = 10 MPa)
Δn(λ)/Δn(588)
1.2
1.1
1.0
0.9
0.8
0.7
0.6
400
500
600
700
800
Wavelength, λ (nm)

Figure 7

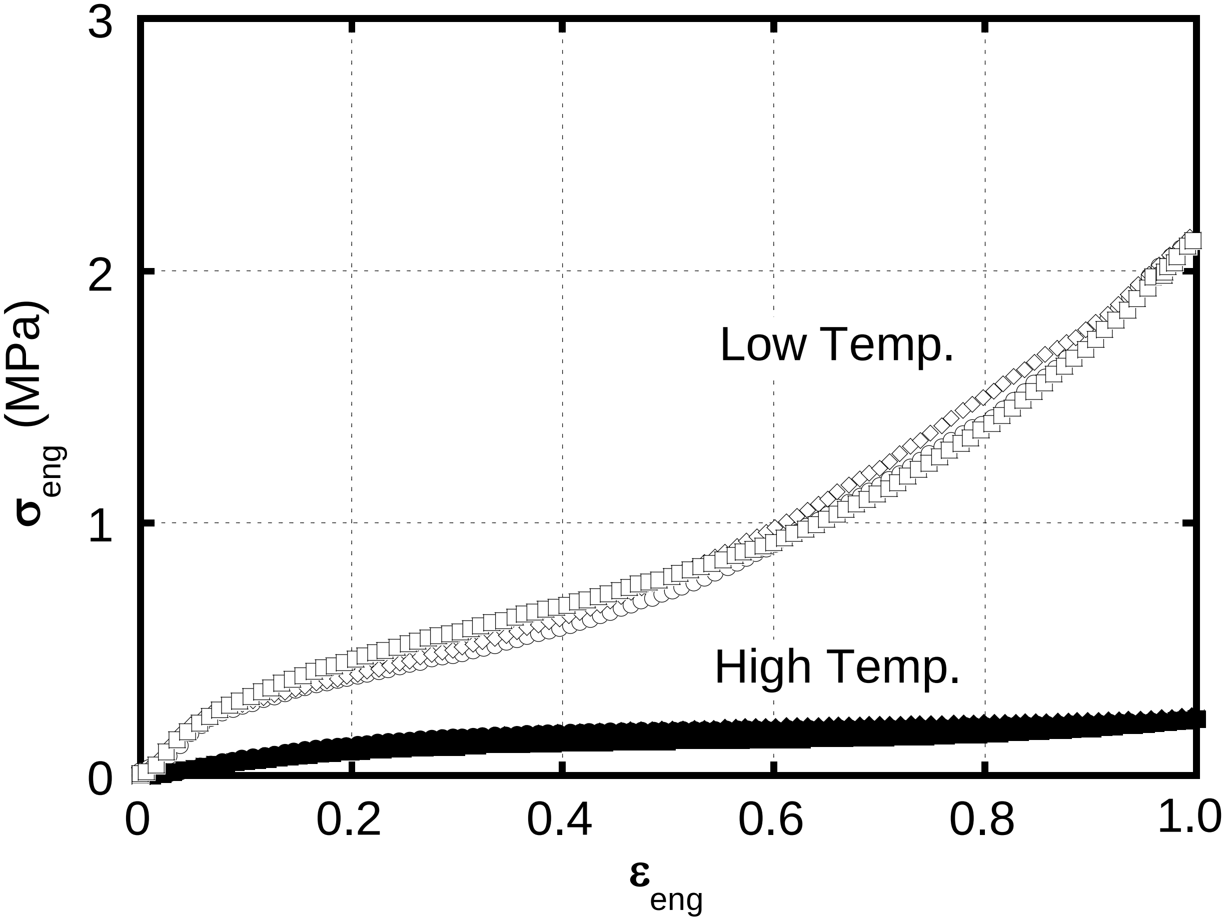
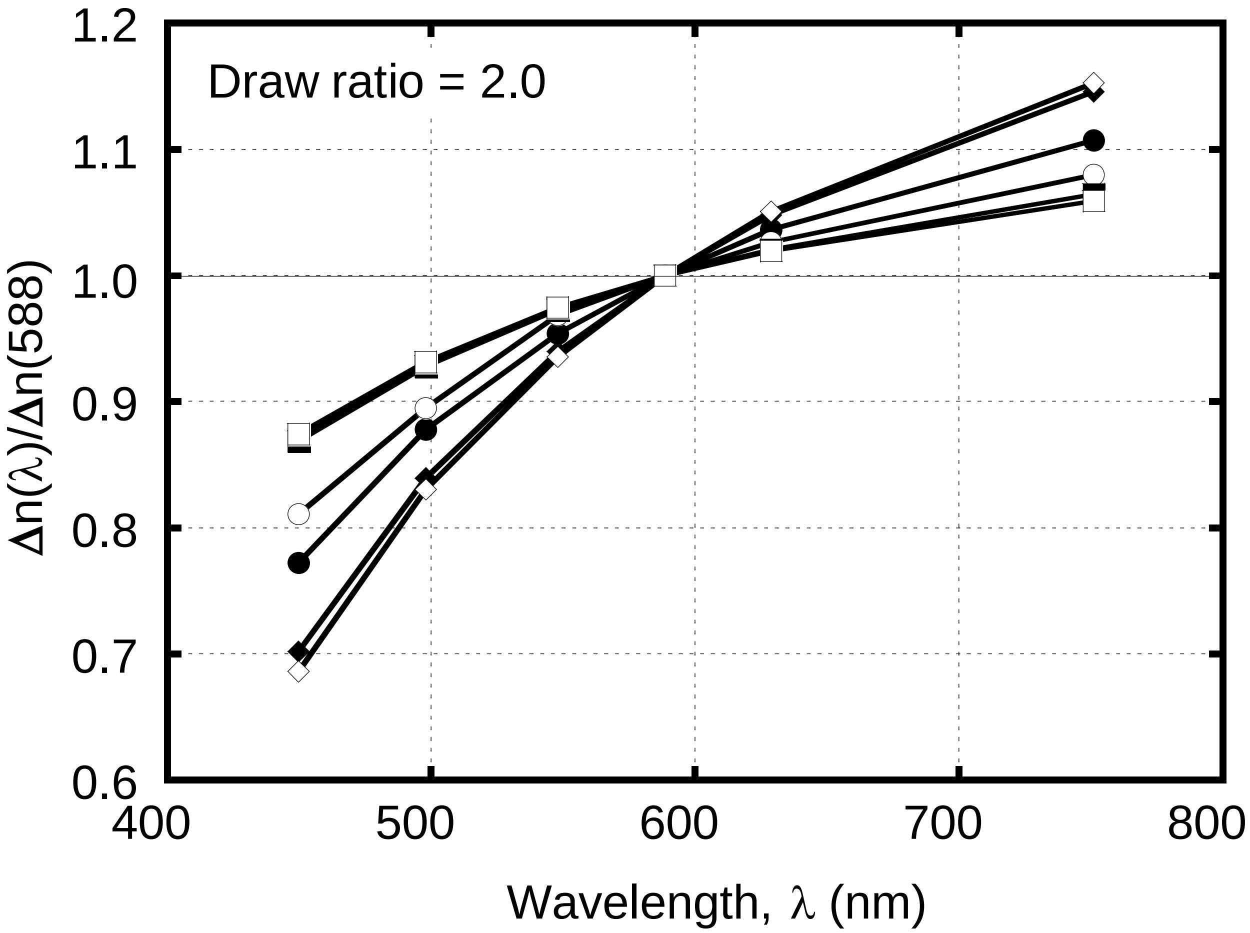
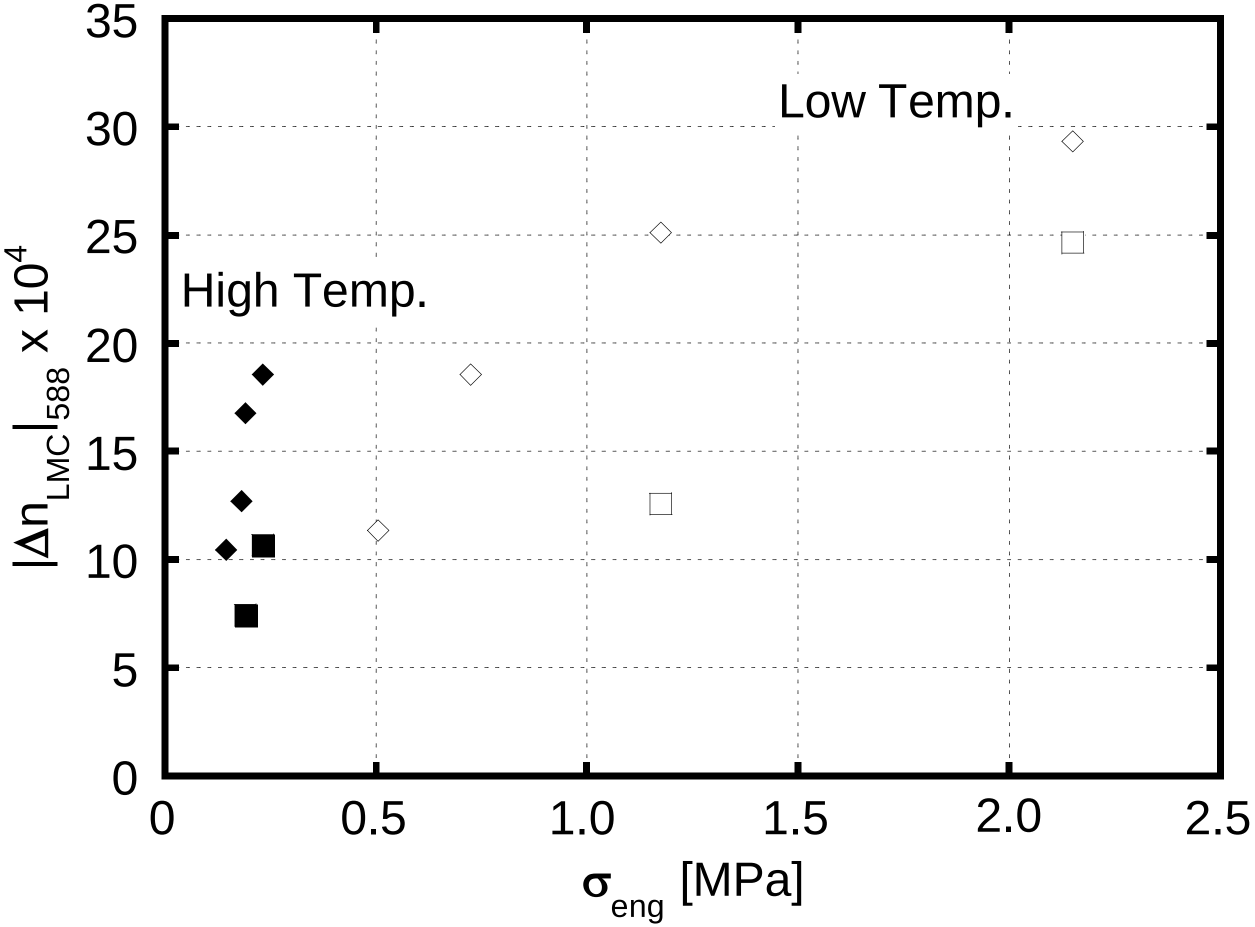

3
2
1
0
σ_{eng} (MPa)
Low Temp.
High Temp.
0
0.2
0.4
0.6
0.8
1.0
ε_{eng}

Figure 8



Draw ratio = 2.0
1.2
1.1
1.0
0.9
0.8
0.7
0.6
400
500
600
700
800
Δn(λ)/Δn(588)
Wavelength, λ (nm)

Figure 9



35
30
25
20
15
10
5
0
0
0.5
1.0
1.5
2.0
2.5
Low Temp.
High Temp.
$|\Delta n_{LMC}|_{588} \times 10^4$
σ_{eng} [MPa]