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Description	

Control of optical and mechanical properties of poly(methyl methacrylate) by introducing lithium salt

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ABSTRACT

We investigated the effect of lithium trifluoromethanesulfonate (LiCF_3SO_3) on the optical properties of poly(methyl methacrylate) (PMMA), known as a glassy transparent polymer. The absolute values of the stress-optical coefficients in both the glassy and rubbery states were found to be reduced by the addition of LiCF_3SO_3 . Furthermore, the linear coefficient of thermal expansion of the blend containing 10 wt.% of LiCF_3SO_3 was lower than that of pure PMMA, suggesting that the birefringence caused by thermal expansion in laminated display systems would be greatly reduced. These results indicate that PMMA/ LiCF_3SO_3 is an appropriate blend for optical films used for liquid crystal displays.

Keywords: poly(methyl methacrylate); stress-optical coefficient; thermal expansion coefficient; dynamic mechanical property; birefringence

1. INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a common plastic that is used for various optical applications, e.g., diffusing plates for liquid crystal displays (LCDs) [1-3], substrates for optical disks [4], and optical fibers [5, 6], owing to its high transparency. However, the heat resistance of PMMA is sometimes inadequate for such practical applications. Recently, we have succeeded in enhancing the glass transition temperature (T_g) of PMMA without losing transparency by adding lithium trifluoromethanesulfonate (LiCF_3SO_3) [7]. It has been reported that the T_g of PMMA can be enhanced by more than 40°C by the addition of 30 wt.% LiCF_3SO_3 , making it comparable with that of polycarbonate [8, 9], which is another transparent plastic with high heat resistance. We believe that this improvement would be valuable to industry because it would solve one of the serious defects of PMMA. The T_g enhancement can be attributed to a reduction of segmental motion due to ion–dipole interactions between the lithium cations and the carbonyl groups in PMMA. Furthermore, the reduced segmental motion also affects the β -relaxation of the dynamic mechanical properties, which results in a high modulus in the glassy region, even near T_g [7]. This also contributes to the improved heat resistance, such as heat-distortion temperature.

The addition of low-molecular-weight compounds is known to have a marked effect on various optical properties, such as refractive index, stress-optical coefficient in the glassy region, and orientation birefringence [10-12]. Therefore, it has become a conventional method of modifying the optical properties of transparent plastics.

The addition of the salt does not affect the transparency, but the impact on other optical properties should be determined based on the relationship with the structure of the blends, which is the purpose of this study. It is well known that PMMA has a relatively

low refractive index [13]. Furthermore, the birefringence detected under applied stress in the glassy region is small, which is important for use in LCDs [13-15]. Further reduction of the photoelastic birefringence in the glassy region improves the quality of LCDs. Moreover, PMMA also has low orientation birefringence because its intrinsic birefringence is low [13, 16]. Further reduction of the orientation birefringence makes it possible to prepare a polarizer protective film by a conventional melt-extrusion process. We also evaluated the thermal expansion behavior of the blend, because strain caused by thermal expansion often causes unfavorable birefringence. Moreover, thermal warpage, caused by thermal expansion due to the heat generated from fluorescent lamps in backlight units [2], is a serious problem for PMMA-based diffusing plates in LCDs. Therefore, the suppression of thermal expansion is particularly important for large LCDs.

2. MATERIAL AND METHODS

2.1. Materials

PMMA (Acrypet VH) was kindly supplied by Mitsubishi Chemical Corporation (Tokyo, Japan). The number- and weight-average molecular weights—evaluated using size-exclusion chromatography (HLC-8020; Tosoh Corp., Tokyo, Japan) with chloroform as a solvent and polystyrene as a calibration standard—were $M_n = 54,000$ and $M_w = 120,000$, respectively. The lithium trifluoromethanesulfonate ($\text{LiCF}_3\text{SO}_3 \geq 98.0\%$; Kanto Chemical Co., Inc., Tokyo, Japan) was used without further purification.

2.2. Methods

The PMMA and LiCF_3SO_3 were completely dissolved in a mixture of dichloromethane and methanol in a weight ratio of 9:1, and stirred for 1 h. The molar ratios of lithium ions to PMMA carbonyl groups were 0, 0.03, and 0.07, which

corresponded to 0, 5, and 10 wt.% of LiCF_3SO_3 . The mixtures were cast in polytetrafluoroethylene-coated aluminum bats, dried in an air stream to volatilize the solvents, and further dried at 160°C for 30 h in a vacuum. The samples were then compression molded at 30 MPa for 10 min. After quenching at 25°C in a compression molding machine, we obtained 300- μm -thick films.

3. EXPERIMENTAL

3.1. Measurements

The temperature dependence of the dynamic mechanical properties was measured between room temperature and 200°C using a dynamic mechanical analyzer (Rheogel-E4000; UBM Co., Ltd., Muko, Japan) at 10 Hz. The heating rate was 2°C/min.

The refractive indices of the films with different salt contents were evaluated using an Abbe refractometer (DR-M2; Atago Co., Ltd., Tokyo, Japan) at 589 nm and room temperature. 1-Bromonaphthalene (purity 97%, refractive index 1.658; Sigma-Aldrich Co., Ltd., Dorset, UK) was used as a contact liquid.

The stress–strain curves were measured using a tensile machine equipped with a temperature controller (Rheogel-S1000; UBM Co., Ltd.). The initial length of the rectangular films was 10 mm, and the draw ratio was 2. One of the chucks moved at a constant speed of 0.5 mm/s; i.e., the initial strain rate was 0.05 s⁻¹. The tensile test was performed at the temperature at which the tensile storage modulus at 10 Hz was 100 MPa. After hot-stretching, the sample was immediately cooled in an air stream and taken out. The retardation (R_e) was then measured at room temperature using a birefringence-measuring instrument (KOBRA-WPR; Oji Scientific Instruments Co., Ltd., Amagasaki, Japan) at 450, 498, 550, 589, 629, and 751 nm.

The photoelastic birefringence in the glassy region was evaluated using the birefringence-measuring instrument under various loads at room temperature.

The linear coefficient of thermal expansion was measured using a thermal mechanical analyzer (TMA4000SA, Bruker AXS Co., Ltd., Karlsruhe, Germany) in the temperature range 30–80°C. The tension load and heating rate were 20 kPa and 5°C/min, respectively.

4. THEORY/CALCULATION

Birefringence is represented by the sum of three contributions corresponding to their origins [17, 18]:

$$\Delta n = \Delta n_O + \Delta n_G + \Delta n_F \quad (1)$$

where Δn_O , Δn_G , and Δn_F are the orientation birefringence, glassy photoelastic birefringence, and form birefringence, respectively. The first term derives from the orientation of the polymer chains caused by flow/deformation. The second component derives from the localized elastic deformation of the molecular chains in the glassy state. The third component derives from the anisotropic nano- and microstructures such as the array of nanostructured domains or lamellar structures. In the present report, the third term can be eliminated because the prepared samples were homogeneous. Therefore, we evaluated the effect of LiCF_3SO_3 on the orientation birefringence (Δn_O) and the photoelastic birefringence (Δn_G).

5. RESULTS AND DISCUSSION

5.1. Dynamic mechanical properties

The temperature dependence of the dynamic tensile properties of the samples with

various LiCF_3SO_3 concentrations is shown in Figure 1. The storage modulus E' decreased slightly in the glassy region and fell off sharply around at 120°C for pure PMMA, which is attributed to the glass-to-rubber transition, i.e., α -relaxation. Correspondingly, a distinct peak appeared in the $\tan \delta$ curve in the temperature range of $120\text{--}160^\circ\text{C}$. Furthermore, a broad ambiguous $\tan \delta$ peak, attributable to β -relaxation, was observed in the temperature range of $30\text{--}80^\circ\text{C}$ for pure PMMA, which was indicated by the arrow. Although the relaxation is significantly weak, the mechanism was well studied by several research groups [19-22]. According to them, this is owing to the local motion of the carbonyl side group having large dipole moment. It was also found from the figure that the LiCF_3SO_3 addition enhances E' . Moreover, its temperature dependence in the glassy region was reduced. The magnitude of $\tan \delta$ in the glassy region became low, suggesting that β -relaxation is suppressed by LiCF_3SO_3 . This is responsible for the high E' values in the glassy region.

[Fig. 1]

Moreover, the glass transition temperature (T_g), defined as the peak temperature of α -relaxation in this study, increased with increasing the LiCF_3SO_3 content, as reported in our previous paper [7]. The hot-stretching temperature was determined from this measurement.

5.2. Refractive indices

The refractive indices at 589 nm of the blends are shown in Figure 2.

[Fig. 2]

Because the refractive index of LiCF_3SO_3 is low owing to the large amount of fluorine, the blends had lower refractive indices. In the case of transparent glassy plastics, such as

PMMA, polycarbonate, and polystyrene, light transmittance as one of the most important properties for optical applications is mainly determined by the surface reflection. Therefore, the result in Figure 2 indicates that the surface reflection (r), given by the following equation [18], was reduced.

$$r = \frac{1 - n^2}{1 + n^2} \quad (2)$$

where n denotes the refractive index.

5.3. Orientation birefringence

The stress–strain curves obtained during film elongation are shown in Figure 3.

[Fig. 3]

As shown in the figure, the growth curves and the magnitude of the stress were almost the same for all the films, suggesting that the degree of molecular orientation, i.e., the orientation function, of the main chains was equal among these samples. The orientation birefringence (Δn_o) of each stretched film is shown in Figure 4.

[Fig. 4]

The orientation birefringence is provided by the following equation [17].

$$\Delta n_o = \Delta n^0 F \quad (3)$$

where F is the Hermans orientation function and Δn^0 is the intrinsic birefringence which is determined as follows;

$$\Delta n^0 = \frac{2\pi (\bar{n}^2 + 2)^2}{9 \bar{n}} N \Delta \alpha_p \quad (4)$$

where \bar{n} the average refractive index, N the number of molecules in unit volume, and $\Delta \alpha_p$ the polarizability anisotropy.

It is well known that PMMA has a small and negative intrinsic birefringence [13]. Therefore, we detected negative orientation birefringence. Furthermore, the wavelength dispersion was minimal because PMMA does not absorb strongly near the visible light region. As the LiCF_3SO_3 concentration increased, the absolute value of orientation birefringence decreased.

In a miscible blend comprising a polymer and a low-molecular-weight compound, orientation correlation—so-called nematic interaction—is expected during deformation/flow [23-28]. In other words, low-molecular-weight compounds orient to the deformation direction along with the polymer chains. Consequently, the optical anisotropy of the low-molecular-weight compound contributes to the total birefringence. Because the salt used in the present study, LiCF_3SO_3 , has a positive intrinsic birefringence, the orientation birefringence increased to the positive direction (the absolute value of orientation birefringence decreased). In general, it is thought that the strength of the nematic interaction is enhanced when the molecular size of the low-molecular-weight compound corresponds to the segment size of the host polymer [25-27]. In this system, however, the ion-dipole interaction with the carbonyl groups may induce the molecular orientation of LiCF_3SO . Moreover, another possibility should be considered: i.e., the ion-dipole interaction with the salt affects the polarizability anisotropy of PMMA. As shown in equation (4), when the ion-dipole interaction weakens the polarizability anisotropy of carbonyl groups, leading to a low intrinsic birefringence, the orientation birefringence decreases. Although the detailed mechanism is still unclear, the technique to reduce the orientation birefringence with the T_g enhancement will be attractive for PMMA to improve the quality of protective films.

5.4. Photoelastic birefringence

The stress-optical coefficient in the glassy region, which determines the photoelastic birefringence (Δn_G), is shown as a function of wavelength in Figure 5.

[Fig. 5]

The stress-optical coefficient of pure PMMA was approximately $-4.3 \times 10^{-12} \text{ Pa}^{-1}$, which corresponds with a previous report [29]. The result demonstrates that the photoelastic birefringence was reduced by LiCF_3SO_3 . The reduced local motion of carbonyl side groups with large polarizability anisotropy, which is caused by ion–dipole interactions as shown in the β -relaxation mode, is responsible for the phenomenon. Although a recent study indicated that filling free volume by adding an antiplasticizer reduces the stress-optical coefficient in the glassy state [30], the salt addition would be another good method of reducing the photoelastic birefringence without losing mechanical toughness or heat resistance [7].

5.5. Linear thermal expansion

The linear coefficient of thermal expansion (α) is described by the following equation:

$$\alpha = \frac{1}{l_0} \left(\frac{dl}{dT} \right) \quad (4)$$

where l is the length. The temperature dependence of the linear thermal expansion coefficient is shown in Figure 6. In this figure, the average values of the linear expansion coefficient are plotted per 10°C .

[Fig. 6]

It was demonstrated that the thermal expansion is reduced by LiCF_3SO_3 . Thermal

expansion often causes a problem in glassy polymers because the values are much larger than those of ceramics and metal [31]. In industry, inorganic fillers are added to reduce thermal expansion [32]. However, this technique is not applicable to optical films. Recently, an antiplasticized system with a low thermal expansion has been reported [25]. Although this seems to be an attractive method, the heat resistance and mechanical toughness were greatly reduced. Therefore, the present result should be noted, especially for optical applications such as laminated films with inorganic glass and polymer films with aluminum frames.

The coefficient of linear expansion of a metal is expressed by the anharmonic oscillatory behavior of lattice thermal vibration, generally described by the Lennard-Jones potential and so on. In the case of polymers, the coefficient of linear expansion depends on the skeletal vibrations of molecular chains. This can be explained using group interaction modeling (GIM) [33]. In other words, intermolecular vibration dominates the thermal expansion of a polymer. As the temperature rises, the anharmonicity caused by greater vibration increases the equilibrium intermolecular distance, resulting in positive thermal expansion. The addition of LiCF_3SO_3 restricts the molecular motion caused by ion-dipole interactions between carbonyl groups and lithium cations. The potential function consists of the sum of the attractive force and the repulsive force. Because the attractive force term is increased by introducing ion-dipole interactions, the minimum of the potential well of the intermolecular force deepens as a result of such strong intermolecular interactions. Therefore, the thermal expansion is reduced owing to the smaller equilibrium intermolecular distance caused by introducing ion-dipole interactions.

6. CONCLUSIONS

We evaluated the thermal and optical properties of PMMA/LiCF₃SO₃ blends. LiCF₃SO₃ decreased the orientation birefringence of films stretched at the same stress level. Because pure PMMA has a small intrinsic birefringence, the orientation birefringence of the blend was noticeably small. Furthermore, the photoelastic birefringence in the glassy state, i.e., the stress-optical coefficient, was reduced by the LiCF₃SO₃. We also found that the glassy region was extended into the high temperature range with reduced localized segmental motion, which may be attributed to the strong ion–dipole interactions between the lithium cations and the carbonyl groups of the PMMA. Such strong interactions are responsible for the small thermal expansion. The properties described above and the low refractive index of the PMMA blend make it an attractive choice for optical applications such as LCDs.

7. FUNDING SOURCES

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9. FIGURE CAPTIONS

- Figure 1 Temperature dependence of storage modulus E' and $\tan \delta$ at 10 Hz for the blends with different LiCF_3SO_3 contents (0, 5, and 10 wt.%).
- Figure 2 Wavelength dispersion of refractive indices at 589 nm for PMMA/ LiCF_3SO_3 blends at 25 °C.
- Figure 3 Stress-strain curves at hot-stretching for the blends with different LiCF_3SO_3 contents (0, 5, and 10 wt.%).
- Figure 4 Wavelength dispersion of orientation birefringence for the blends with different LiCF_3SO_3 contents (0, 5, and 10 wt.%).
- Figure 5 Wavelength dispersion of stress-optical coefficient in the glassy region for the blends with different LiCF_3SO_3 contents (0, 5, and 10 wt.%).
- Figure 6 Temperature dependence of linear coefficient of thermal expansion α for PMMA and PMMA/ LiCF_3SO_3 (90/10).

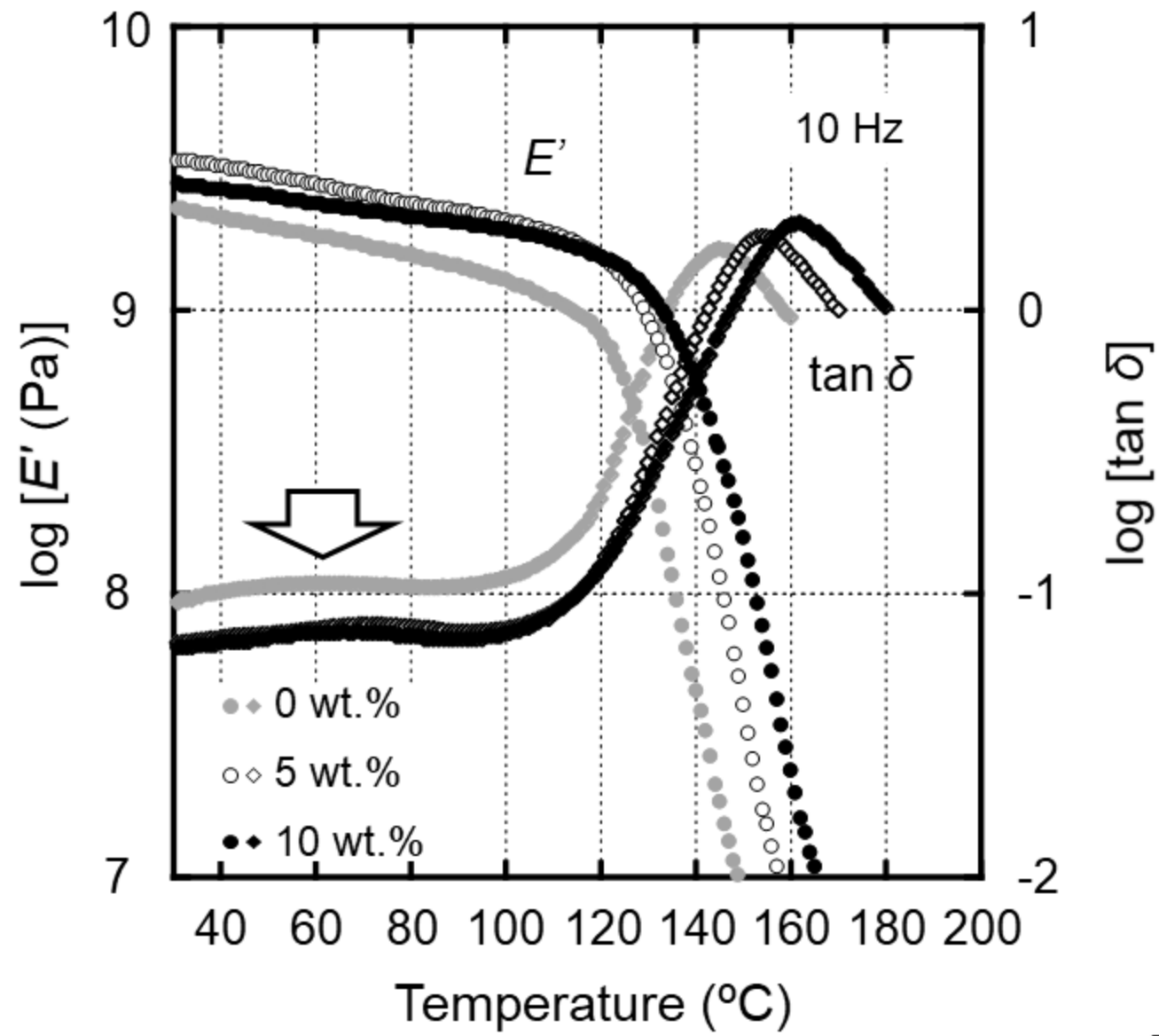


Figure 1

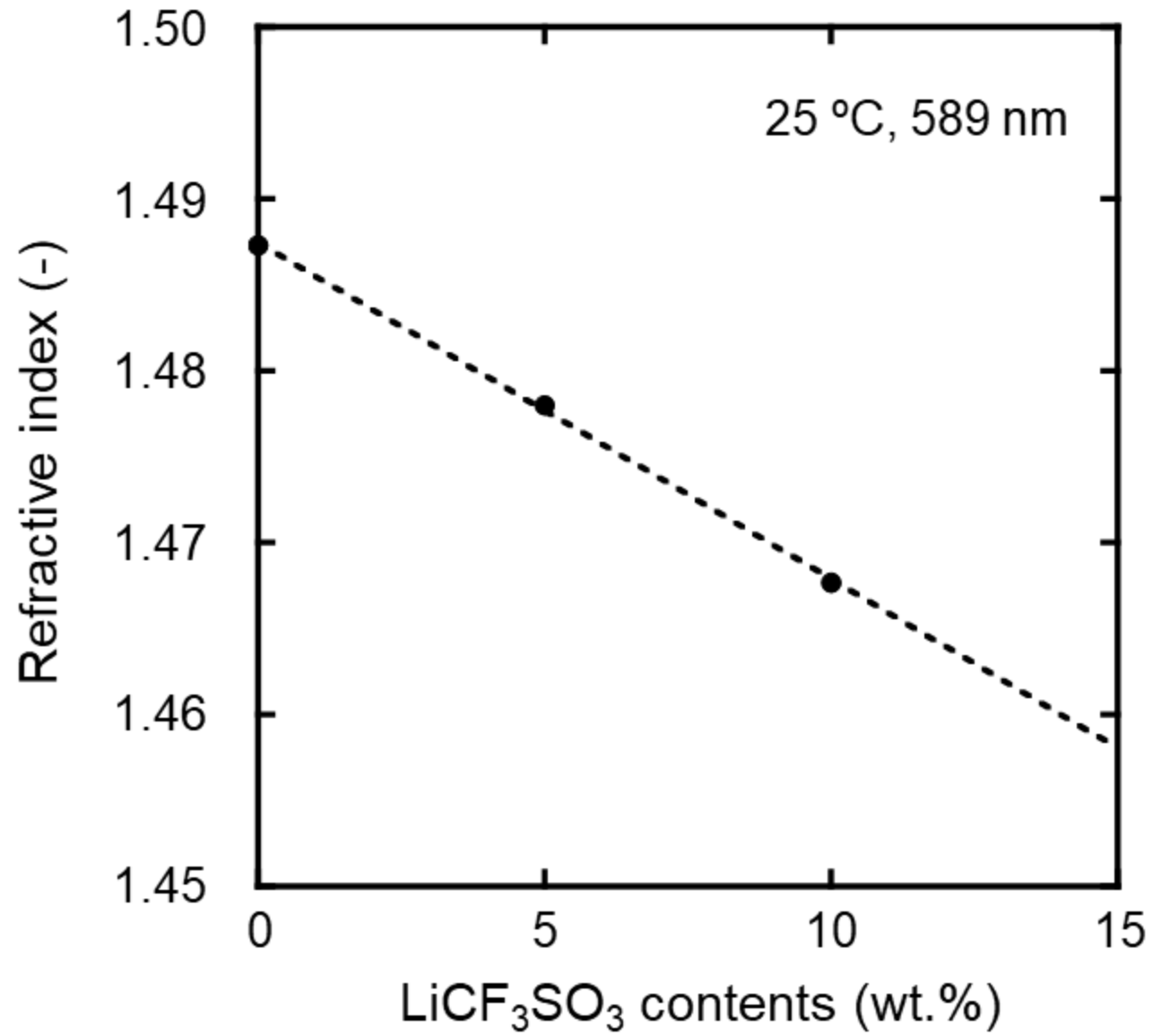


Figure 2

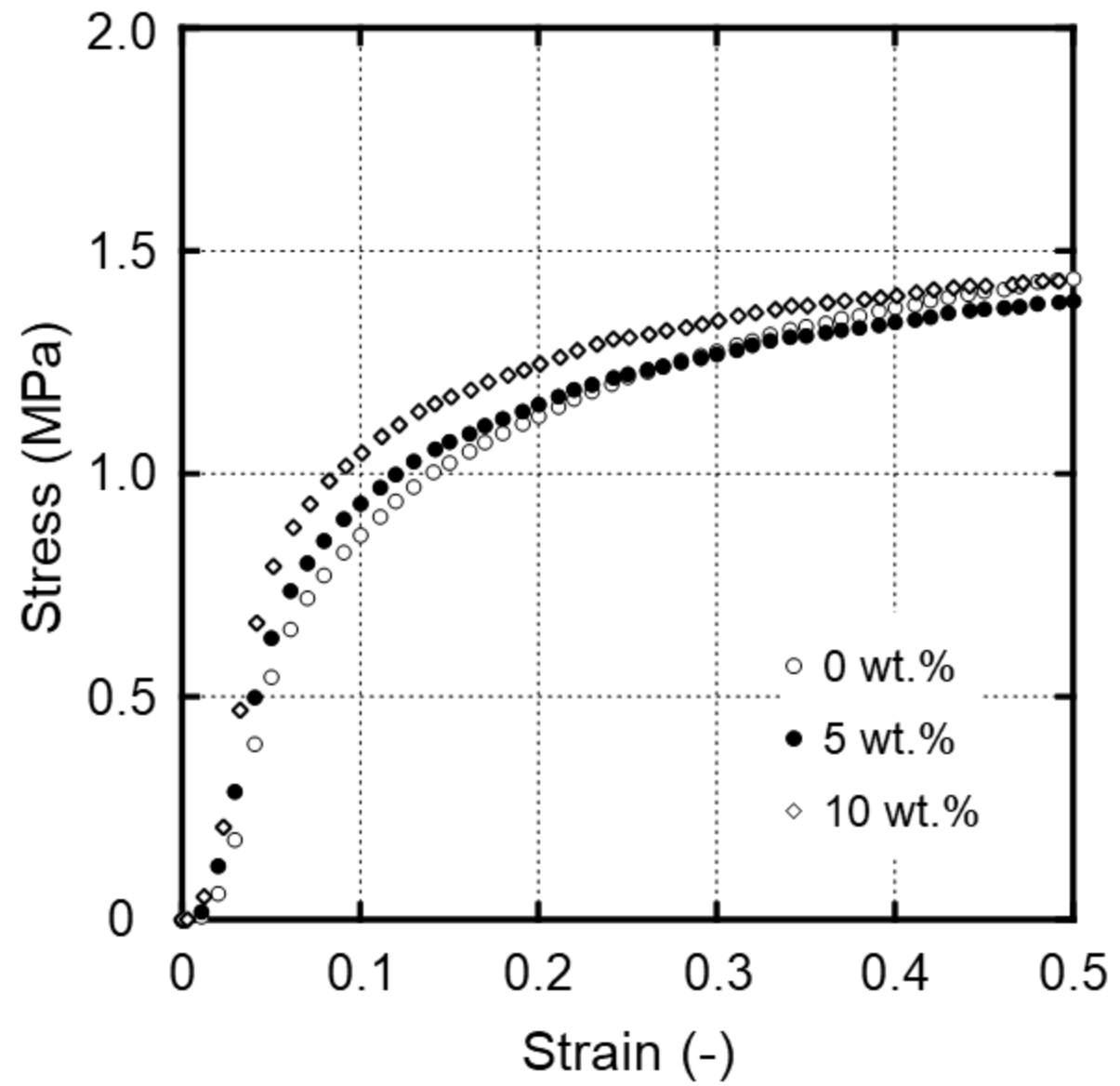


Figure 3

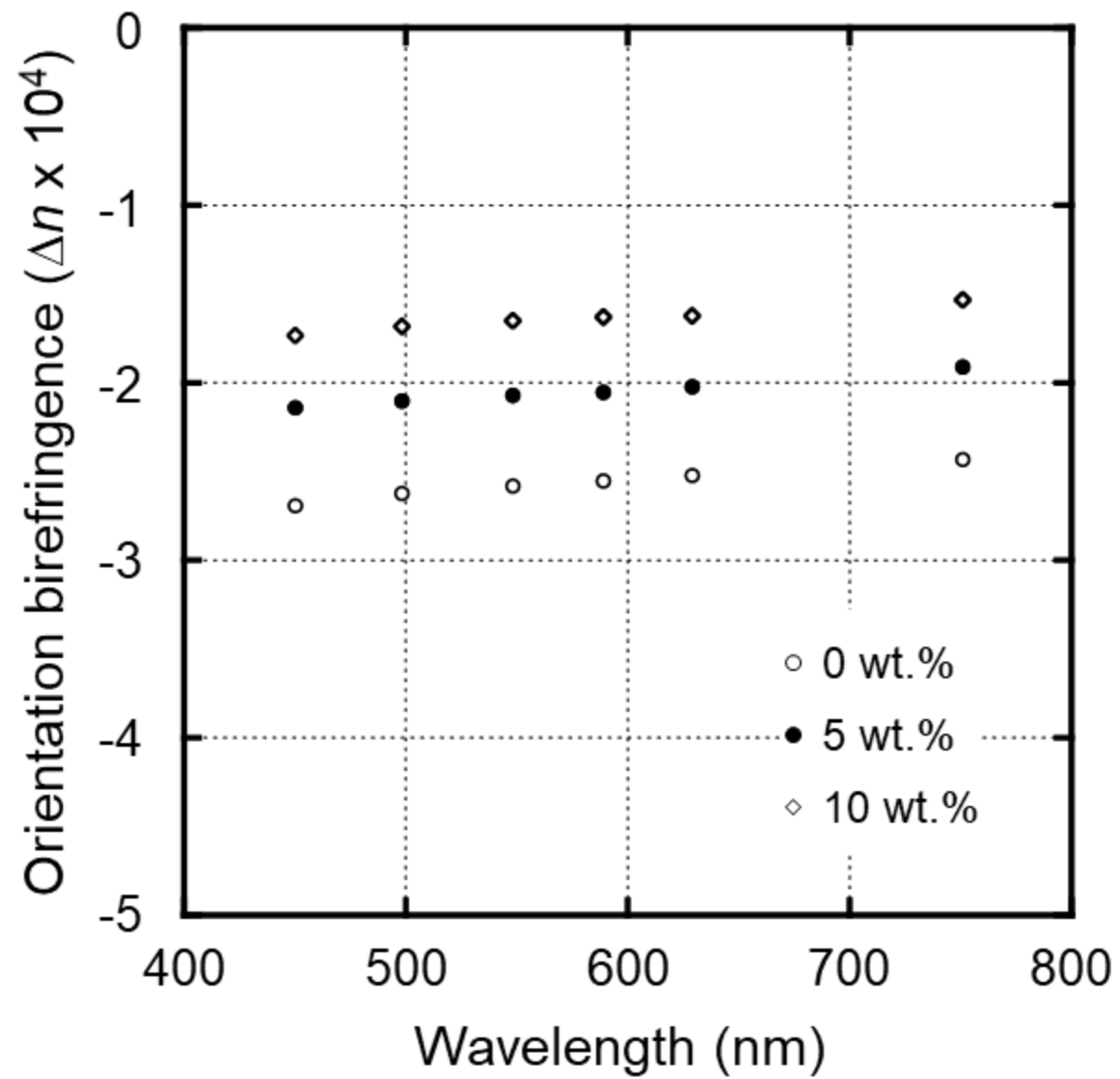


Figure 4

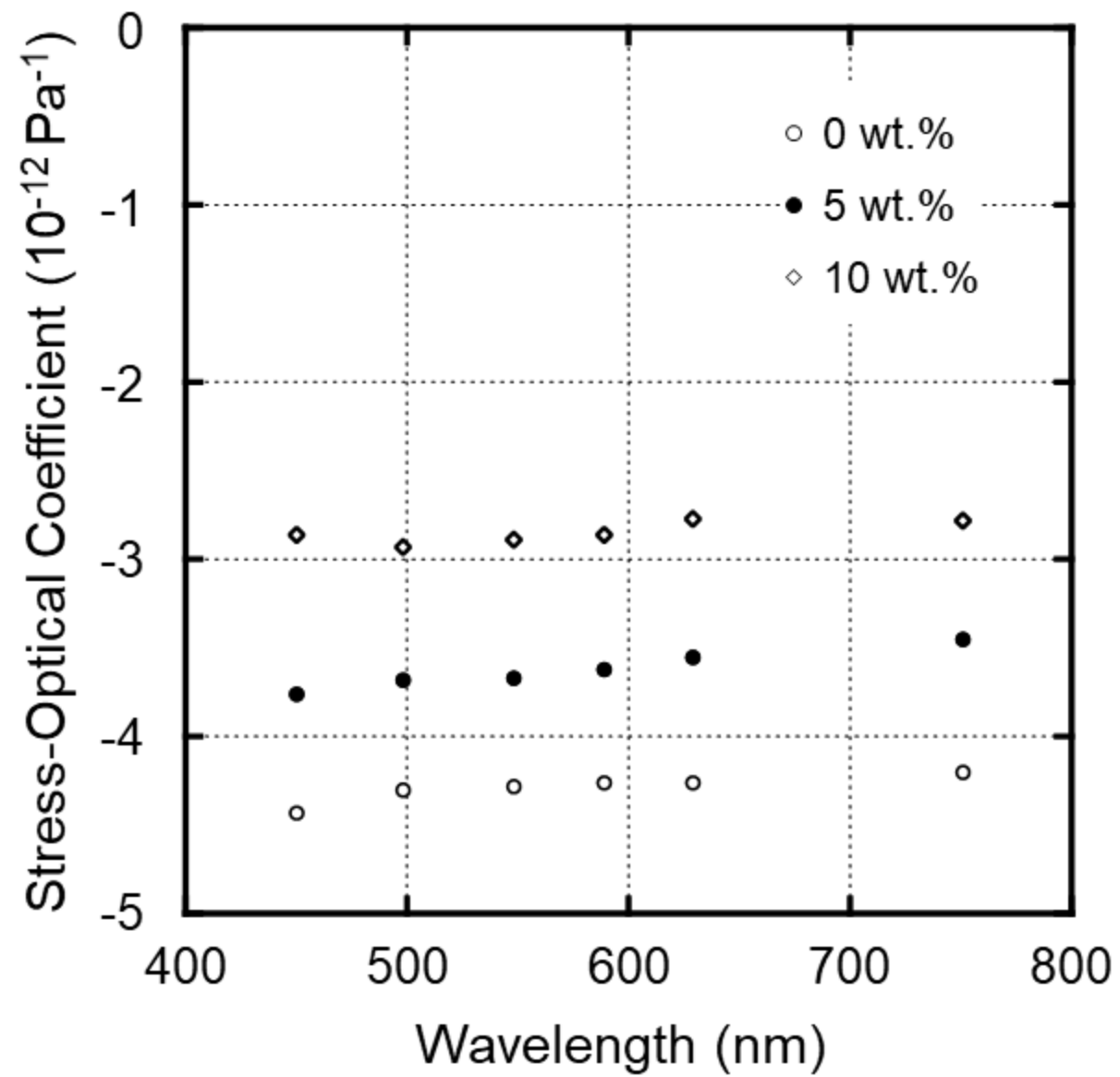


Figure 5

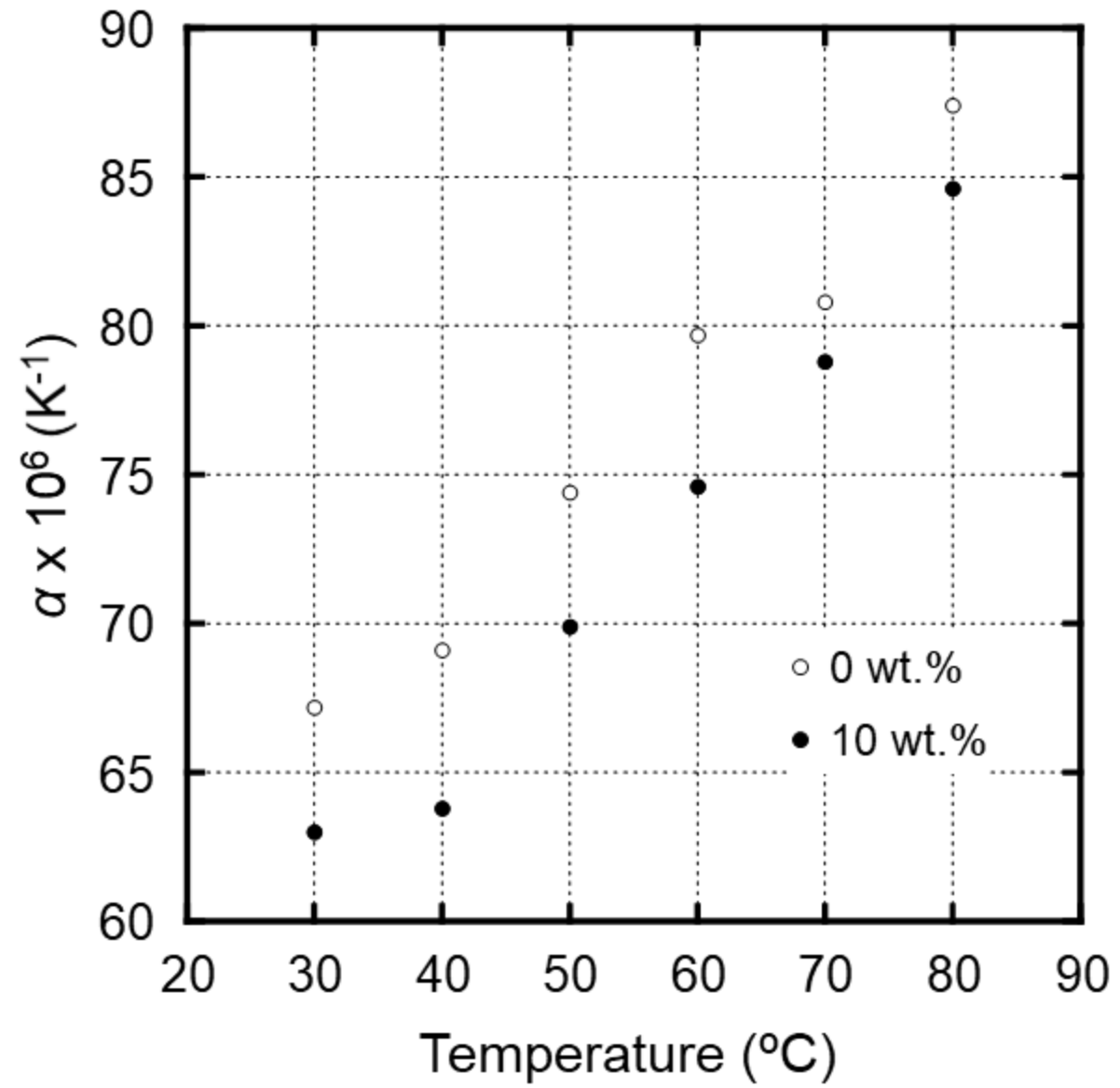


Figure 6