

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.

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 or another polymer 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

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$M_w = 120,000$, 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 $2^\circ\text{C}/\text{min}$.

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 1.5. One of the chucks moved at a constant speed of 1 mm/s; i.e., the initial strain rate was 0.1 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_c) 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 $30\text{--}80^\circ\text{C}$. The tension load and heating rate were 20 kPa and $5^\circ\text{C}/\text{min}$, 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).

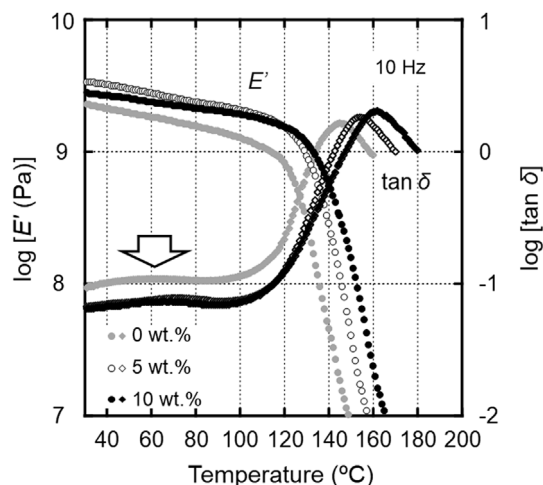


Fig. 1. Temperature dependence of storage modulus E' and $\tan \delta$ at 10 Hz for the blends with different LiCF_3SO_3 contents (0, 5, and 10 wt.%).

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 Fig. 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.

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 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 Fig. 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 Fig. 3.

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