PHOTOCHEMICALLY-INDUCED REFRACTIVE INDEX CHANGE ON FLUORINATED POLYIMIDE FILMS CONTAINING EPOXY RESIN

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Introduction

Polyimides have been widely used in microelectronics and optoelectronics applications because of their outstanding chemical and physical properties such as thermal stability, mechanical strength, resistance to organic solvents, and good processability. Moreover, several types of fluorinated and perfluorinated polyimides have been developed as the optical waveguide materials due to their small water sorption and high transparency in the visible and the near-IR regions. The single-step photo-patterning procedure is a fabricating method of polymer waveguides, which is directly forming channel waveguides without using photo-lithographic procedures (photore sist patterning and dry- or wet-etching). Compared with the traditional procedures, the single-step procedure has attracted much attention in recent years because of its high efficiency and low cost. And many kinds of materials applicable to such procedures, in which photo-chemical reactions induce refractive index changes between the exposed and the unexposed part, have been developed. For example, the polymer films doped with photochromic dyes can induce a large change in refractive index of ~0.01, but the removal of remained reactants is a serious problem for fabricating highly transparent films. The photosensitive cycloaliphatic-type epoxy compounds such as 3,4-epoxy cyclohexane carboxylate exhibit faster response to UV curing in the presence of photo-acid generator compared with epo- and bis-epoxy resins. Their good transparency and high heat-deformation temperatures enable the applications as electric-insulating varnishes and transparent sealants for optoelectronics (e.g., light-emitting diodes). However, cycloaliphatic epoxy monomers do not provide flexible films, which restricts their applications to optical thin films. In this study, a novel composite system that can induce refractive index changes by UV-initiated cationic polymerization is reported. The polymer used in this study is semi-aromatic fluorinated poly (amid acid) of 6FDA-DCHM containing photosensitive epoxy resin with photo-acid generator. The photochemically-induced variations in the refractive indices and birefringence are examined, and the mechanism of the generation of refractive index differences between the exposed and unexposed parts will be discussed.

Experimental

Materials. 4,4’-methylenebis-cyclohexylamine (DCHM) purchased from Tokyo Kasei Co., Ltd., was purified according to the literature. 4,4’-((1,1,3,3,6,6-Hexafluoro-2-propylidene) diphthalic anhydride (6FDA, kindly supplied by AZ materials Co. Ltd.) was dried overnight at 105°C under reduced pressure. Photo-acid generator (PAG) of hexafluoro-antimoniate salt was kindly supplied by Midori Kagaku Co. Ltd., 3,4-Epoxy-cyclohexylmethyl 3,4-epoxy cyclohexanecarboxylate (EEC) purchased from Daicel Chemical Industries, Ltd. was used without further purification. The solvent, N,N-Dimethylacetamide (DMAC, anhydrous grade), was purchased from Aldrich, Japan. The chemical structures of the materials are summarized in Scheme 1.

Synthesis of PAA. The 6FDA-DCHM poly (amid acid) (PAA), the precursor of polyimide, was prepared as follows: In nitrogen-purged glove box, DCHM (0.8764g, 7.66mol) was slowly added to 10 g of DMAC and then 6FDA (3.409g, 7.67mol) was slowly added, and the mixture was kept stirring for 2 days at room temperature, to give a concentration of 30wt% PAA solution.

Formulation of PAA/epoxy composite solutions. Several amounts of epoxy compound (0.6g, 0.9g, 1.35g, 2.25g) were added into PAA solution (3g) together with PAG (5% of epoxy in weight) and stirred for 1h at room temperature to give four kinds of homogeneous composite (mixture) solutions (PAA/epoxy) with the epoxy concentrations of 40, 50, 60 and 71 wt%, respectively.

Preparation of PAA/epoxy films. The composite solutions were spin-coated onto 3-inch fused silica substrates. The PAA/epoxy films were pre-baked at 70°C for 20 min, and then exposed to UV irradiation for 40 sec with the total exposure dose of 1 J/cm² by using a high-pressure mercury lamp. The PAA/epoxy films (ca.10 µm-thick) were cured by heating stepwise at 120°C for 20 min, 150°C for 1 h, and 200°C for 1 h under nitrogen flow.

Measurements. The in-plane (n∥) and out-of-plane (n⊥) refractive indices and the thicknesses of the PAA/epoxy films were measured with a prism-coupler (Metricon, PC-2000) at wavelength of 1320 nm. The experimental errors of the refractive indices and thickness are less than ±0.0003 and ±0.2 µm, respectively. The average refractive index (nav) and birefringence (Δn) were calculated as

\[ n_\| = \frac{2n^{2}\sin^2 \theta \sin^2 \phi}{n^{2} - 1} \]
\[ \Delta n = n_\| - n_\perp \]

where n∥ and n⊥ are the refractive indices in the in-plane and out-of-plane directions, respectively. The temperature to give four kinds of homogeneous composite (mixture) solutions (PAA/epoxy) with the epoxy concentrations of 40, 50, 60 and 71 wt%, respectively.

Figure 1 shows the measured changes in n∥ for the PAA/epoxy films, which are plotted against the initial weight concentration of epoxy. By comparing the values of n∥ for the films with and without UV-irradiation, it is evident that the PI film with 40wt% epoxy shows the largest refractive index change of ca. 0.010. The typical refractive index difference between the core and cladding for a single-mode waveguide with core-diameter of 8 µm is 0.005, corresponding to a 0.3% difference in refractive index. Hence, the photochemically-induced refractive index change observed in this study demonstrates that it can be used for fabricating optical waveguides. Moreover, the values of n∥ are smaller than 0.002, and the composite films showed high thermal decomposition temperatures (5% weight-loss) above 230°C.

The FT-IR spectra of the PAA/epoxy films with different epoxy concentrations are shown in Figure 2. The spectral shapes for the films with UV-irradiation at 1770, 1650, 1530, and 1370 cm⁻¹ differ from those without UV-irradiation. The signal assignments of such characteristic peaks are indicated in Figure 2. The peaks at 1650 cm⁻¹ (stretching at amide linkage [amide-I band] and 1530 cm⁻¹ (vibration at amide linkage [amide-II band]) were observed in the irradiated films, which clearly indicates that the imidization of the irradiated area was not completed. In contrast, the peaks appearing at 1770 cm⁻¹ and 1370 cm⁻¹ for the film without UV-irradiation indicate the formation of imide rings. The reaction mechanisms with and without UV irradiation can be inferred as follows. In the UV-irradiated films, PAG molecules absorbing UV light promptly liberate strong acid (H⁺), which promotes the coupling reactions between the epoxy ring and the amide groups of PAA. The carbonyl ester linkages thus formed effectively inhibit the PAA from thermal cyclizations (imide-ring formation) at 200°C. In contrast, for the films without UV-irradiation, the thermal imidization of PAA was completed after curing because the amide groups in PAA were not protected. The reactions occurring during curing for the films with and without UV-irradiation are shown in Scheme 2. The formation of imide rings gives higher refractive indices for the films with UV-irradiation than those without UV-irradiation. The refractive index change observed for the 40wt%-epoxy film is mainly attributed to the different degrees of imidization caused by UV-irradiation.

Moreover, different behaviors were observed in the photochemically-induced changes in refractive indices and the IR spectra of the...
films with different epoxy concentrations. For the film containing more than 50 wt% of epoxy (corresponding to 68 mol% epoxy), no difference is observed between the exposed and unexposed films in the range of 1200–1800 cm⁻¹ of the IR spectra, which indicates that the imidization was not completed even in the un-irradiated films. Since the molar fractions of epoxy are much larger than those of PAA, the PAA chains seem to be dispersed as droplets (islands) in the sea of epoxy. The phase-separated structure may lead to the incomplete reaction of curing among epoxy molecules formed in the UV-irradiated film. Therefore, the increased molecular packing density of the film without UV-irradiation is thinner than that with UV-irradiation. It has been considered that the increased molecular packing density of the film without UV-irradiation and the cross-linking networks among epoxy molecules formed in the UV-irradiated film should be the origins of the refractive index change observed in the PAA/epoxy composite films with 60wt% of epoxy.

**Figure 1.** Refractive indices of PI/epoxy composite films containing different concentrations of epoxy. The films were prepared with (▲) and without (■) UV-irradiation prior to curing at 200°C.

**Figure 2.** FT-IR spectra of PI/epoxy films with different concentrations of epoxy prepared with (dotted line) and without (solid line) UV-irradiation. IR band A: imide stretching (imide I); B: amide stretching (amide I); C: vibration of amide linkage (amide II); D: vibration of imide linkage (imide II); E: stretching of ether linkage.

**Scheme 2.** Reaction schemes during curing of PAA/epoxy films containing lower epoxy contents with and without UV-irradiation. The UV irradiation promotes the coupling reactions between PAA and epoxy, generating ester linkages. The resultant structures are not fully imidized by curing at 200°C.

**Conclusions**

Novel polyimide(PI)/epoxy composite films were prepared by the blending of semi-aromatic fluorinated poly(amic acid) (PAA), epoxy resin, and photo-acid generator. Relatively large changes in refractive index (~0.01) were observed between the films prepared with and without UV-irradiation. The refractive index changes observed for the films with lower epoxy contents are generated by cationic reactions between PAA and epoxy molecules which was initiated by irradiation, and successive thermal imidization. However, the changes in refractive index are significantly affected by the epoxy concentrations, and different mechanisms were confirmed by FT-IR analysis for the films with higher epoxy contents. The PI/epoxy composite films thus obtained exhibit small birefringence and high thermal stability above 230°C, which are desirable to waveguides for optical inter-connects. Based on the above merits, this new composite system is promising for facile fabrication of thermally stable optical waveguides by single-step photo-patterning procedure.