Phase-separated structure and light shutter characteristics for (polymer/liquid crystal) composite films

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The methods to control the size and uniformity of LC domains and electro-optical switching properties were investigated for the composite films in which LC molecules were embedded as a continuous phase in a three-dimensional polymer network. The phase-separated structure was controlled on the basis of the degree of interaction between matrix polymer and solvent. It was found that the time-resolved light scattering behavior during solvent evaporation and the resulting size and uniformity of LC domains were strongly dependent on the degree of solubility between solvent and polymer. The electro-optical properties of the composite films were directly dependent on the size and uniformity of LC domains in the polymer matrix. V_{∞} was remarkably decreased with increasing the size and uniformity of LC domains.

1. INTRODUCTION

The (polymer/liquid crystal:LC) composite films composed of polymer and LC, was developed by one of the authors for the first time in 1979[1]. The composite films have become high interest in recent years because of their potential applications in optical devices such as a large-area, flexible displays without polarizers, bright projections, light shutters, switchable windows and so on[2-4]. Various preparation methods of the composite films have been reported, that is, the emulsification method[2], the polymerization method[3], and the solvent cast method[1,4]. Also, the electro-optical properties depend on various factors such as the size of LC domains in the polymer matrix[5], the electric properties of polymer and LC[6], and also, the interfacial interaction between polymer and LC[7,8]. It has been reported that Pdi-iPF possessed many superior characteristics as the matrix of the composite film, such as little hysteresis and high repeating stability. But, a high voltage over 50 Vrms is necessary to drive the composite film about 8 μm in thickness[7]. This may arise from that the size of LC domains in the (Pdi-iPF/LC) composite films is small and not entirely uniform.
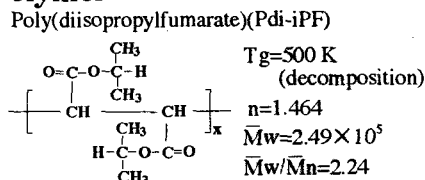
In this study, the methods to control the size and uniformity of LC domains were discussed for the composite films prepared by a solvent cast method from a homogeneous solution. Also, a change of light scattering properties of the composite films during solvent evaporation have been investigated to understand the control mechanism affecting the phase-separated structure. Furthermore, the phase-separated structure-electro-optical switching properties relationships of the composite films have been discussed.

2. EXPERIMENTAL

The chemical structure and the physico-chemical properties of polymer and LC are given in Figure 1. Poly(diisopropyl fumarate) (Pdi-iPF) supplied by Nippon Oil & Fats Co., Ltd. was used as the matrix for the (polymer/LC) composite system. The LC employed in this study was E8 (BDH). In the preparation of the composite films, Pdi-iPF and E8 were dissolved in good-solvent such as chloroform and the mixed solvent of chloroform and toluene. Also, the mixture solution including a small amount of methanol, which is a non-solvent for Pdi-iPF, was used to control the size and uniformity of LC domains for the composite film. The solutions were

Polymer

Poly(diisopropylfumarate)(Pdi-iPF)

$Tg = 500$ K (decomposition)

$n = 1.464$

$\overline{Mw} = 2.49 \times 10^5$

$\overline{Mw}/\overline{Mn} = 2.24$

Liquid crystal

E8(Nematic mixture)

$T_{KN} = 261$K, $T_{NI} = 345$K, $n_{\parallel} = 1.774$, $n_{\perp} = 1.527$,

$\Delta n = 0.247$, $\varepsilon_{\parallel} = 21.3$, $\varepsilon_{\perp} = 5.7$, $\Delta \varepsilon = 15.6$
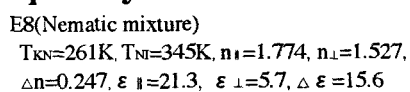
Figure 1. Chemical structure and physico-chemical properties of the constituent polymer and LC materials for the composite films.

bar-coated on an indium tin oxide(ITO)-coated poly (ethylene terephthalate)(PET) film with a doctor-blade. The thickness of the composite films was controlled about 8~10 μm. The phase-separated structure of the composite films was investigated by means of the scanning electron microscope (SEM, Hitachi S-2150).

Light scattering changes during a formation process of the composite film were studied by using a He-Ne gas laser(wavelength: 632.8 nm) as an incident light beam, and the periodic distance of concentration fluctuation during the formation process of the composite films was evaluated by observation of light scattering patterns.

In order to evaluate the electro-optical properties of the composite films, light scattering and light transmittance changes upon the application of an a.c. electric field were studied by an experimental setup [9]. A He-Ne laser was used as an incident light source.

3. RESULTS AND DISCUSSION

3.1 Solvent dependence of phase-separated structure in (polymer/LC) composite film

Figures 2(a), (b) and (c) show the SEM photographs of the matrix Pdi-iPFs after LC was extracted with methanol from the composite films which were prepared from a mixed solution of (Pdi-iPF/E8/chloroform), (Pdi-iPF/E8/chloroform/toluene) and (Pdi-iPF/E8/chloroform/methanol), respectively. All of the composite films exhibit the phase-separated structure that an entirely continuous E8 phase was embedded in a three-dimensional Pdi-iPF network. The morphology of the fibrillar network in the composite film(b) was similar to that in the composite film(a), though the size of E8

domains were different. On the other hand, the thickness of the matrix polymer fibrils in the composite film(c) was thicker than those of the the composite films(a) and (b). The domain size of E8 in the composite film(c) was remarkably larger and the distribution of E8 domain sizes was sharper compared with those of the composite films (a) and (b). These results indicate that when a non-solvent to the matrix polymer was added to the ternary solution of (Pdi-iPF/E8/chloroform), the size of LC domains and its distribution for the composite film could easily be controlled.

3.2 Effect of addition of non-solvent to polymer aggregation structure during formation process of (polymer/LC) composite film

It has been reported that the size of LC domains in the polymer matrix can be controlled by regulating the solvent evaporation rate during the film preparation[5,9]. That is, the larger LC domain size is generally formed in the case of the slower solvent evaporation rate. Also, it was confirmed that the phase-separated structure of the polymer and the LC components was formed via the spinodal decomposition[9,10]. Therefore, it is quite important to investigate that the LC domain sizes can be controlled by adding non-solvent to the solution, that is, the combination of non-solvent and good solvent as well as the rate of solvent evaporation or not. When a small amount of methanol or toluene was added to the (Pdi-iPF/E8/chloroform) solution, respectively, the solution was optically homogenous. The Pdi-iPF-rich phase and the E8-rich one in the solution were more apparently separated with an increase of the solution concentration, because the phase-separation state was more stable. A pure E8-rich phase was
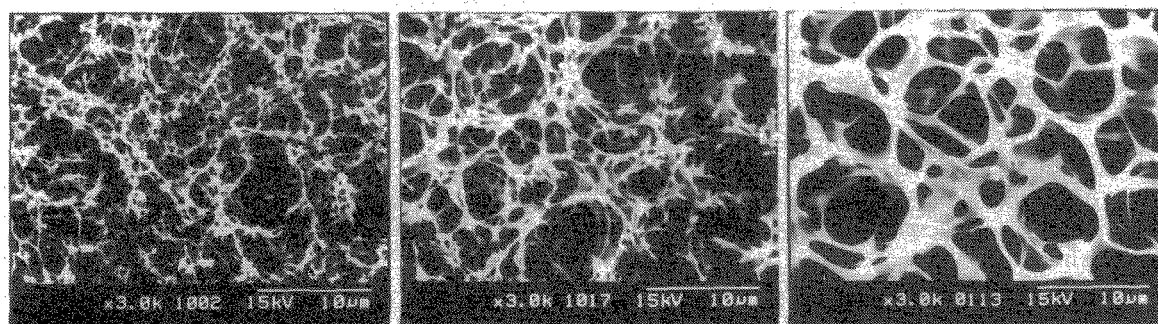
(a):Composite film(a)   (b):Composite film(b)   (c):Composite film(c)

Figure 2. SEM photographs of the matrix Pdi-iPFs which were prepared from a mixed solution of (a) Pdi-iPF/E8/chloroform, (b) Pdi-iPF/E8/chloroform/toluene and (c) Pdi-iPF/E8/chloroform/methanol, respectively.
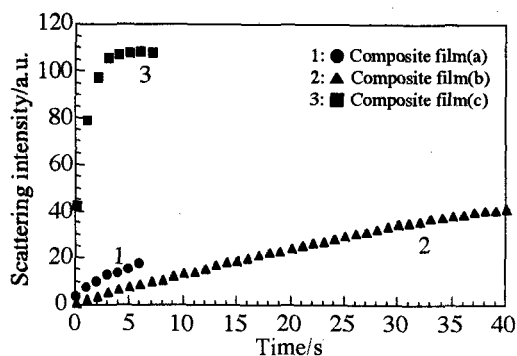
Figure 3. Time dependence of the light scattering intensity at an earyl period of B stage during the formation process of the composite films.

Figure 4. Time dependence of the periodic distance of concentration fluctuation during the formation process of the composite films.

found in the case of the extremely high E8 concentration. Also, a certain fraction of Pdi-iPF molecules might be contained in the E8-rich phase at the early stage of phase-separation. In the case of the composite film(c) prepared from the mixed solution including a non-solvent of the matrix polymer, it is reasonable to consider that few Pdi-iPF molecules might be contained in the E8-rich phase at the early stage of phase-separation, because methanol, non-solvent of Pdi-iPF, preferentially exist in the E8-rich phase. If the Pdi-iPF fractions in the E8-rich phase for the (Pdi-iPF/E8/good-solvent) system and the (Pdi-iPF/E8/good-solvent/non-solvent) system are different at an early stage of phase-separation, the growth rate for the amplitude of concentration fluctuation resulting from spinodal decomposition might be different. That is, the growth rate for the amplitude of concentration fluctuation during the formation process of the composite film(c) might be larger than those of the composite films(a) and (b), because of the presence of a poor-solvent of Pdi-iPF in the casting solution. The longer periodic distance of the concentration fluctuation at a late stage of spinodal decomposition should be finally generated in the formation process of the composite film(c). The composite film formation process could be roughly divided into the three stages A, B and C, based on the solvent evaporation time dependence of the transmittance changes[9]. Then, the magnitude of polymer fraction in the LC(E8)-rich phase and the periodic distance of concentration fluctuation in the stage B, corresponding to the early stage of phase-separation, were investigated on the basis of the time dependence of the light scattering properties. Figure 3 shows that the light scattering intensity of the composite film(c) rapidly increased in the initial several seconds of the phase-separation process.
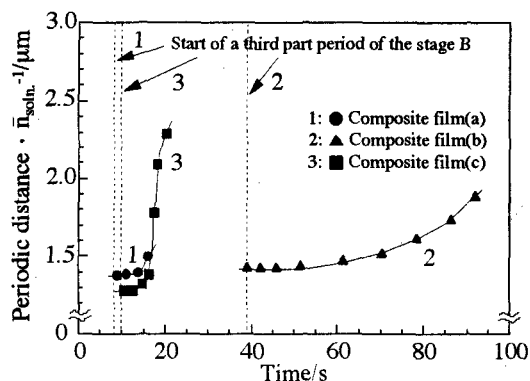
On the other hand, the light scattering intensities for the composite films (a) and (b) increased gradually during the phase-separation process. Since the light scattering intensity in the composite film(c) was much higher than those of the composite films(a) and (b), it can be reasonably concluded that the difference between refractive indices of the Pdi-iPF-rich phase and the E8-rich one in the solution might be much larger for the composite film(c) than those of the composite films(a) and (b). These results apparently indicate that the fraction of coexistence of E8 and Pdi-iPF in the film formation process of the composite film(c) was lower than those of the composite films(a) and (b).

Figure 4 shows the time dependence of the periodic distance of concentration fluctuation during the formation process of the composite films(a), (b) and (c), respectively. The periodic distance of concentration fluctuation during the formation process of the composite film(c) was longer than those of the composite films(a) and (b). This clearly indicates that the size of LC domains for the composite film is strongly depended on the LC fraction in the LC-rich phase at an early stage of phase-separation.

3.3 Electro-optical switching of (polymer/LC) composite film

Figure 5 shows the applied voltage dependence of the transmittance for the composite films(a), (b) and (c) upon application of a 1 kHz rectangular-wave field at 298 K. The magnitude of V_{90} is defined the applied voltages at the 90 % transmittance of T_s-T_{min}, where T_s and T_{min} are the saturated transmittance upon application of an electric field and the transmittance in an electric field-off state, respectively. In the case of the

composite film(c), V_{90} decreased remarkably, and the saturated transmittance was 89 %. The electro-optical properties of the composite film(c) clearly indicate that the magnitude of V_{90} is strongly dependent on the size and uniformity of LC domains in the polymer matrix. The anchoring effect resists the LC molecular reorientation along the direction of an applied electric field. It is well known that when an equal magnitude of an electric field is applied to the composite film, the value of coherence length affected by anchoring effect from the polymer wall or networks was strongly dependent on the original properties of the polymer and the LC[11]. Namely, the value of coherence length is essentially dependent on the magnitude of an electric field in the case of using the same type of polymer and LC. It seems reasonable to consider that when the size of polymer network was much greater than the magnitude of coherence length, the fraction of oriented LC molecules upon application of an electric field was increased, because the LC molecules existing enough far apart from the polymer wall could reorient along the direction of an applied electric field. In other word, the fraction of LC molecules strongly anchored by the polymer wall decreased with an increase of the size and uniformity of LC domains. LC molecular reorientation behavior also could be detected optically as a light transmittance change upon application of a low driving voltage. Therefore, it is reasonable to conclude from Figures 2 and 5 that the fraction of oriented LC molecules along the direction of an applied electric field in the composite film(c) is much larger than that of the composite films(a) and (b) upon application of a low
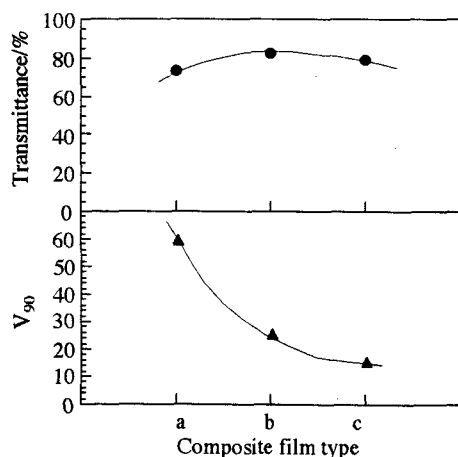

Figure 5. Composite film type dependence of the electro-optical properties.

driving voltage, resulting in a remarkable decrease of V_{90} for the composite film(c).

4. CONCLUSIONS

The phase-separated structure for the composite film could be controlled on the basis of interaction between the matrix polymer and the solvent. In case of the composite film formed from a mixed solution including a small amount of non-solvent for the matrix polymer, it was found from morphological observation that the domain sizes of LC were remarkably increased and the distribution of LC domain sizes was decreased. From the time-resolved light scattering study during the solvent evaporation process, the control mechanism of the phase-separation for the composite film could be explained. With increasing the size and uniformity of LC domains, V_{90} remarkably decreased.

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