Electro-Optical Properties of Polymer/(Liquid Crystal) Composite Film Fabricated by Two-step Phase Separation Method

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A polymer/liquid crystal (LC) composite film was fabricated by a combination of a solvent-induced phase separation method and a photo-polymerization-induced one, using polymethylmethacrylate (PMMA), LC and photo-curable monomers. Electro-optical properties for the composite films had a low driving voltage of 18 V_{rms}, a rapid turn-on time of 0.8 *ms*, a rapid turn-off time of 10 *ms* and a small hysteresis of less than 1V_{rms}.

Recently we have reported a poly(vinyl alcohol)(PVA)/LC composite film adding with photo-curable monomers which had a low driving voltage and a rapid response time.[1-3] Improved electro-optical properties seemed to be obtained by an extremely thin photo-cured polymer layer which could reduce the interaction between the PVA matrix and the LC droplet. The LC droplet with photo-curable monomer could be formed in the emulsion of PVA solution because both LC and the monomer do not dissolve in PVA solution. In case of a solvent-induced phase separation (SIPS) method,[4-6] the LC droplet is formed after the evaporation of the solvent. Therefore the photo-curable monomers should not be in the polymer matrix when the composite film is fabricated before the UV irradiation. The purpose of this letter is to fabricate a thin photo-cured polymer layer between the PMMA and the LC droplet, and to improve the electro-optical properties of the PMMA/LC composite film using the SIPS method.

A polymer/LC composite film was prepared from a chloroform solution of PMMA (30 wt%), photo-curable monomers (9.5 wt% of BMA and perfluorooctylethyl-acrylate(FA) mixture), dimethoxyphenyl-acetophenone (DMPA, for a photo-initiator, 0.5 wt%) and the nematic LC (Merck-E7, 60 wt%). Weight ratio of the BMA and the FA was controlled at 100:0, 80:20, 65:35, 50:50, 20:80 and 0:100. The solution was spin-coated on an ITO coated glass substrate, resulting in a 16 - 19 *μm* thick phase separated film. Then the film was exposed for 60 min by using a UV lamp (11 -13 mW/cm^2 at 365 nm) followed by lamination with another ITO coated glass substrate. Conventional PMMA/LC composite film (P-film) was also fabricated by a SIPS method from a chloroform solution. Electro-optical measurements were performed in the same procedure as described previously.[1]

To form the thin photo-cured polymer layer between the PMMA and the LC, solubilities and compatibility of the materials should be important factors for the two-step phase separation method. The BMA showed a good solubility in PMMA and FA, and the film cast from a chloroform solution was transparent. On the other hand the cast films from PMMA/FA and PMMA/BMA/FA (60/32/8 - 60/0/40, wt%) were opaque, showing the incompatibility of FA in PMMA matrix. The LC was separated from the mixture of LC/BMA/FA mixture because the LC could dissolve in the BMA but not dissolve in FA. Figure 1 shows the morphology of the PMMA/BMA/LC composite film extracted with methanol before and after the UV irradiation. Both the LC and the BMA were extracted before the UV irradiation and only LC was extracted after the irradiation because both the BMA monomer and the LC could dissolve in methanol. The size of the hole after irradiation was 2 - 8 *μm* as shown in figure 1(b), while the extracted hole before the irradiation was larger than that of after the irradiation. This may be the consequence that the BMA dissolved in the LC droplet rather than PMMA matrix before UV irradiation and poly-BMA was separated from the LC after the irradiation. Since same results were obtained for the

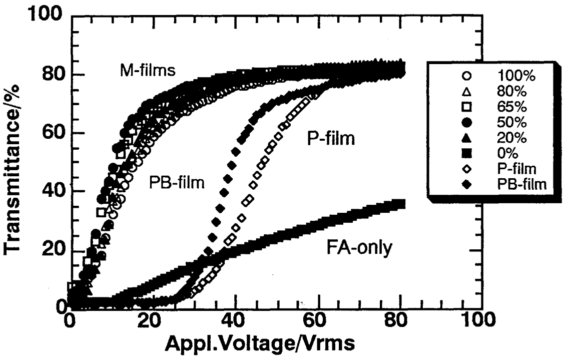

Figure 2. Influence of the BMA concentration and the polymer matrix on V-T properties. The weight ratios of BMA and FA were between 100:0 - 0:100.

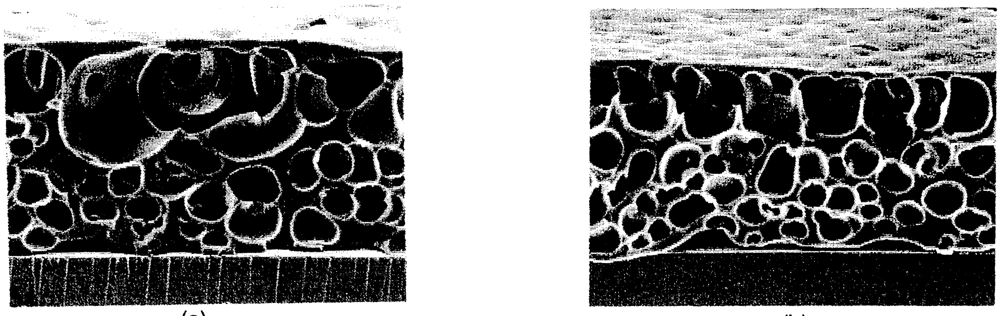
(a)
(b)

Figure 1. Scanning electron micrographs for PMMA/BMA/LC(30/10/60 wt/wt/wt) composite film. (a) before UV irradiation (b) after irradiation. Both films were extracted by methanol.

PMMA/BMA/FA/LC composite film (M-film), photo-curable monomers (BMA and FA) might be dispersed around the LC droplet not in the PMMA matrix before the UV irradiation.

The relation of applied voltage and transmittance is shown in figure 2. The maximum transmittance (T_{max}) was the same value of 82 % as the P-film in all cases of the M-films. The M-films were lower in the driving voltage(V_{90} : a voltage at which the transmittance reached 90 % of T_{max}) than the P-film and the value was between 18 and 24 V_{rms}. The minimum V_{90} was achieved when the ratio of BMA/FA was 50 : 50. These values were about 1/3 of that of the P-film and the similar range as the composite film composed of the copolymer of poly-benzylmethacrylate(BMA)-co-perfluorooctylethylmethacrylate (BF -polymer) with the same LC. [7] Improved V_{90} could be explained by the change of the boundary condition at the interface between the LC droplet and PMMA due to the addition of the photo-cured polymers same as described in the composite film fabricated from the PVA. [1] The extremely thin layer of the photo-cured polymer should be formed at the interface between the PMMA and the LC. In addition, V_{90} of a composite film using a mixture of the PMMA and the BF-polymer (3/1, wt/wt) as a polymer matrix (PB-film) was slightly smaller than that of the P-film as shown in figure 2, but the hysteresis and response time were not improved. In this case, the BF-polymer was dispersed in the PMMA matrix and could not form a thin layer around the LC droplet. In contrast the T_{max} of the PMMA/FA/LC composite film was less than 40 %. Because the FA monomer was insoluble both in the PMMA and the LC, the photo-cured FA might form its own droplet in the PMMA matrix and could not form a thin layer at the interface between the PMMA and the LC, resulting in a light scattering due to the refractive index mismatching between the PMMA and the poly-FA.

The M-film was lower in the hysteresis and faster in the response time than the P- and PB-films as listed in Table 1. The lowest hysteresis was less than 1 V_{rms} and it was achieved when the ratio of the BMA and the FA was 50/50 and 65/35 wt/wt%. This value is smaller than that of the a poly(vinyl alcohol)(PVA)/LC composite film adding with same photo-curable monomers. [1] The fluorine containing polymer matrix is known to reduce the hysteresis of the composite film. [8] Rise time (T_{on} : the time for a transmittance change from T_{min} (minimum transmittance) to 90 % of the T_{max} upon turning the electricity on) of the M-film was less than 1 *ms*, while T_{off} (the time for a transmittance change from T_{max} to 10 % of the T_{max} upon turning the electricity off) became faster with increasing the FA content within the range of 10 - 22 *ms*. For example,

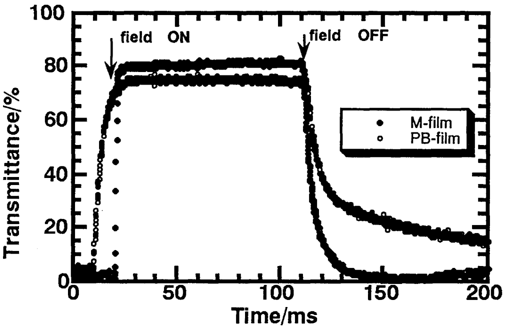

Figure 3. Electric switching charasteristic of M- and PB-films. M-film consists of 60% of LC, 30% of PMMA, 14.47% of BMA, 14.75% of FA and 0.5% of DMPA. PB-film consists of 60% of LC, 30% of PMMA and 10% of BF-polymer. All films were measured by using 80Vrms output with 1kHz square wave.

switching behaviors of the M- and PB-films are shown in figure 3. The M-film had a faster response than the PB-film which had fast and slow decay because of the local molecular motion as described previously. [7] It is known that T_{on} becomes faster and T_{off} slower with increasing the LC droplet size. [4] In the case of the composite films in this study, the size of the droplet was almost the same as long as the SEM observation. The improvements of the electro-optical properties of the M-films can be explained by the photo-cured copolymer at the interface between the PMMA and the LC. If the copolymer of the BMA-co-FA was formed at the interface between the PMMA and the LC, the M-film might be lower in an anchoring force than the P-film, reducing inherent bistability in the droplets.[1] Because T_{off} depends on the molecular weight of the polymer matrix [7], the fast response might be the consequence of the suppressed local molecular motion of the matrix polymer due to the thin layer of photo-cured copolymer at the interface between the PMMA and the LC for the M-films.

In conclusion, improved electro-optical properties for the polymer/LC composite film fabricated from two-step phase separation method using PMMA as the polymer matrix was obtained by the addition of small amount of the photo-curable monomers. These results were the consequence of the change of the boundary condition at the interface between the LC and the PMMA. Thin layer of the poly-BMA-co-FA might be formed between the PMMA and the LC and it could reduce the interaction between them.

Table 1. Electro-optical properties of the composite film

BMA content (wt%)	Hysteresis[a] (V_{rms})	*Ton* (ms)	*Toff* (ms)
100	3	0.9	21.6
80	3	0.8	19.7
65	<1	0.8	11.7
50	<1	0.9	10.4
20	1	0.4	10.0
P-film[b]	24	9	>100
PB-film	20	10	>100

[a] Defined as the voltage difference between up- and down-processes reached to half of T_{max}-T_{min}.
[b] Reference 7.

References and Notes

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