**Morphology and Electro-optic Properties of SMA/Nematic Liquid Crystal Composite Films**

B. K. Kim, C. H. Choi, and Youngsook Ok

*Dept. of Polymer Science and Engineering, Pusan National University.*

Pusan 609-735, Korea

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**Abstract:** Morphology and electro-optic properties of composite films composed of poly(styrene-co-maleic anhydride) (SMA) and nematic liquid crystal have been studied for a wide range (30–70 wt% of liquid crystal) of film composition. Effects of temperature, frequency and voltage of applied AC electric field on the transmittance were measured for film containing 60 and 70 wt% LC, where the optical contrast was maximum, and the results were interpreted in terms of aggregation structure of the film, the geometry of LC domains, dielectric constant, conductivity, birefringence, and the solubility of LC in polymer.

**INTRODUCTION**

Thin polymer films containing polymer and low molecular weight liquid crystal (LC) are potentially useful for a variety of electro-optic applications ranging from switchable window to active matrix projection display.\(^1\)\(^-\)\(^5\) In most common form, they consist of LC droplets dispersed in polymer matrix known as PDLC (polymer dispersed liquid crystal). NCAP (nematic curvilinear aligned phase) is also used for a special type of PDLC, typically prepared by emulsification of LCs in aqueous polymer solution, before the film is coated and allowed to dry. Depending mainly on the composition of the film, LCs also can form continuous phase in sponge polymer matrix.

LCs are imbedded in polymer matrix, either as dispersed droplets or as continuous phase, and hence the films are self-supported in spite of the high fluidity of LCs.\(^6\) This makes the films suitable
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for the application of large area displays. The conventional LC devices have been small size due to the difficulty in fabrication in uniform thickness. In the composite films matrix polymer is plasticized by the dissolved LC molecules, which significantly reduces the glass transition temperature \(T_g\) of polymer, and provides the film with high flexibility. In addition, the absence of polarizers substantially reduces light loss and increases the brightness of both direct view and project displays.

In the absence of electric field (unpowered) LC molecules within each droplet or LC domain will adopt configuration which minimizes the free energy of the droplet under boundary conditions, which are determined by polymer-LC interfacial interactions. Most often in PDLC the configuration of minimum energy is a bipolar configuration where the axis for cylindrical symmetry is the axis for droplet. The nematic LC molecule is optically uniaxial, and thus it has an ordinary refractive index \(n_o\) and extraordinary refractive index \(n_p\). The orientation of optic axis and hence the nematic director varies randomly from droplet to droplet for the unpowered films; consequently light propagating normal to the film surface will probe a range of refractive index between \(n_o\) and \(n_p\). These indices do not generally match with the refractive index of polymer \(n_p\), and light will be scattered by the LC domains since they are comparable size with the wave length of light. For the typical droplets (0.1~10 \(\mu\)m), droplet concentration (~60 vol%), and the film thickness (~50 \(\mu\)m), light scatters many times while passing the film, and these multiple scattering causes the transluence of the unpowered film.

Upon applying an external electric field across the film (powered), the LC molecules will tend to align with long axis parallel to the field. The extent of director orientation depends on the electric field. If, then, \(n_o\) is close to \(n_p\), there will be very little scattering and the film will be highly transparent. For \(n_o \geq n_p\), maximum transparency is obtained with normal incidence due to the minimum path length of the light. However, for \(n_o < n_p\), maximum transmittance occurs at incident angle other than the normal where the space average refractive index \(n_{ave}\) of LC matches with \(n_p\).

This paper considers the morphologies and electro-optic properties of composite films composed of poly(styrene-co-maleic anhydride)(SMA) and nematic type liquid crystal. Films of broad composition (30~70wt % LC) were prepared, and intensive measurements were done for films containing 60 and 70wt % LC. The electro-optic performances of the films as a function of operating temperature, and voltage and frequency of the AC electric field were measured. Results were interpreted in terms of the aggregation state of the films and the solubility of LC in polymer.

**EXPERIMENTAL**

SMA \((n_p = 1.564, T_g = 100^\circ\text{C})\) and a nematic mixture of phenyl cyclohexane and biphenyl cyclohexane derivatives (ZLI-3417-100, Merck) \((n_p = 1.62\), \(n_o = 1.4973, T_{K_N} (-40^\circ\text{C}) T_{N_I} = 93^\circ\text{C}\)) were used as polymer matrix and LC.

Composite films were prepared by SIPS (solvent induced phase separation) technique at room temperature. Approximately 10wt % of SMA and LC at desired film compositions, was dissolved in chloroform. Homogenized solutions were cast on a glass plate, using an applicator to control the thickness. The thickness of the dried films were ~30 \(\mu\)m.

For electro-optic measurements, the composite films were sandwiched between two indium/tin oxide (ITO) coated glass plates. When the effects of temperature were measured, the cell was placed in a heating stage to control temperature. The collimated beam of He/Ne laser (wave length of 632.8 nm) was passed through the film, normal to the film surface, and the transmitted light intensity without any polarizer was measured with a photodiode. The output from a function generator was amplified and used to drive the shutter. The drive signal and the response of the photodiode were
monitored with a digital storage oscilloscope (Hitachi VC-6023). The distance between the cell and photodiode was about 300mm.

Morphologies of the composite films were studied using a scanning electron microscopy (SEM). LCs were first extracted in methanol at 300K, and the films were dried overnight under vaccum. The weight loss upon extraction can be used to decide the continuity of LC domains in polymer matrix. When the LC domains are interconnected in three dimension, almost all of the LCs that was initially loaded extracted. The dried films were cryogenically (in liquid nitrogen) fractured, and sputtered with gold before viewing under SEM.

RESULTS AND DISCUSSION

Fig. 1 shows the typical SEM micrographs of the film cross sections. The dimension of LC domain, seen as circular cross section in the figure, increases with the content of LC weight fraction (ω). At ω = 0.3, it is 1–2μm, and at ω = 0.7, it become over 5μm in diameter. In these films, the off-state scattering is mainly controlled by the state of aggregation of LCs in the film. With domain size smaller than the wavelength of visible light, scattering is not expected to occur significantly. On the other hand, the transmittance of the powered film depends on the orientation of the nematic director along the external electric field direction. When the ordinary refractive index (n_o) of LC is equal to or higher than the n_p and when the electric field is strong enough, maximum transmittance is obtained at normal incidence of the beam since the closest indices matching is obtained between n_p and n_o. On the other hand, when the n_p is higher than n_o, index matching is obtained between n_p and space average value of LC, given by:

\[
n_{ave} = \frac{2n_o + n_p}{3}
\]  

Therefore maximum transmittance is obtained at angle away from the normal.

Fig. 2 shows the off-state (unpowered) and on-state (powered) (1kHz, 200 V_p-p) transmittance of the film for various compositions at 25°C. The off-state transmittance shows a drastic drop at ω = 0.4 and 0.5, and the on-state transmittance shows a rapid increase at ω = 0.6. Maximum optical con-

![Fig. 2. Optical contrast of SMA/LC films vs. LC content at 25°C (V_{on} corresponds to 1kHz, 200V_{p-p})](image)

![Fig. 1. SEM micrographs of SMA/LC films: a) 70/30, b) 50/50, c) 30/70 by weight.](image)
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Contrast, i.e., the maximum transmittance difference between off-state and on-state, is obtained at \( \omega = 0.6 \) and 0.7.

The drastic increase of off-state scattering at \( \omega = 0.4 \) and 0.5 should be related to the increase of LC domain size at these composition. At these and above concentration, the LC domains become comparable or significantly larger than the wave length of incident beam, leading to significant scattering.

At high LC loadings, the LC droplets are interconnected to form curved LC channels. In such films, the off-state scattering can also be caused by the spatial distortion of nematic directors among neighboring LC domains, separated by thin polymer walls, in addition to the mismatch of refractive indices. While considering the film for optical application, high contrast as well as high on-state transmittance is important. In this regard, films of \( \omega = 0.6 \) and 0.7 are most valuable, and the electro-optic responses with applied AC electric voltage and frequency, and temperature are measured with these two films.

Transmittance, rise time (\( \tau_R \)) and decay time (\( \tau_D \)) of the films as a function of applied voltage are shown in Fig. 3 to 5. The electro-optic response of the composite films must to tailored for each application. For switchable window and large area signs, films with high on-state clarity and off-state scattering is required, while driving voltage and switching speed are relatively unimportant. However, the high resolution active matrix applications require low driving voltage, fast response time, and high resistivity.

The threshold voltage (\( V_{th} \)), defined as voltage to raise the transmittance by 10%, is smaller for \( \omega = 0.7 \) than for \( \omega = 0.6 \) (arrows in Fig. 3). The higher field requirement of film with low LC loadings is consistent with general trends and may due to the difference in dielectric constant of the polymers surrounding LC. The transmittance of powered film depends on average orientation of nematic directors, torque. The elastic torque consists of splay, twist, and band deformations, and depends on the director configuration. Consequently, \( V_{th} \) depends on the director configuration. For comparable droplet size bipolar configuration, which occurs in most cases, has substantially less \( V_{th} \) radial one, it is given by eq.(3).

\[
V_{th} = \frac{d}{3a} \left[ \frac{\rho_p}{\rho_{LC}} + 2 \right] \left[ \frac{K(l^2 - 1)}{\varepsilon_0 \Delta \varepsilon} \right]^{1/2}
\]

where \( d, a, \rho, K, \) and \( l \) represent film thickness, major dimension, resistivity, elastic constant, and aspect ratio (major dimension/minor dimension), respectively. The subscript P and LC designate polymer and LC phase, respectively. Orientation of the bipolar configuration parallel to the long axis of the cavity minimizes both the band and twist deformation energy. LC domains for \( \omega = 0.7 \) are

![Fig. 3. Transmittance vs. applied voltage for SMA/LC (40/60 and 30/70) films at 1kHz, 25°C.](image1)

![Fig. 4. Rise time vs. applied voltage for SMA/LC(40/60 and 30/70) films at 1kHz, 25°C.](image2)
larger and more eleogated along the thickness direction than for \(\omega = 0.6\). With larger cross section, the polymer-LC interface becomes smaller, which gives smaller surface anchoring energy that must be overcome by the electric force to be aligned along the electric field direction. This physically contribute to the lower \(V_{th}\) of \(\omega = 0.7\). On the other hand, a smaller value of \(V_{th}\) for \(\omega = 0.7\) may be predicted from eq.(3), by considering smaller value of \(K\) for \(\omega = 0.7\), and assuming that the order of magnitude of \((1/a)\) is the same with that of \((1^2 - 1)^{1/2}\).

\(\tau_R\) is conventionally defined as the time required for transmittance change from 10 to 90\% upon powering the film, and \(\tau_D\) as the reverse of \(\tau_R\), measured upon turning the electricity off. In these type of film, \(\tau_R\) is given by eq.4,\(^1\)

\[
\frac{1}{\tau_R} = \frac{1}{\eta} \frac{\eta \varepsilon_0 \Delta \varepsilon V^2}{d^2 (\rho_p/\rho_{LC} + 2)^2 + K(1^2 - 1) \eta a^2}
\]

where \(\eta\) is the viscosity, and other symbols bear the same meaning defined earlier. In general \(\tau_R\) is dominated by the first term, and the electro-optic response speed for these film is propotional to \(\Delta \varepsilon V^2\). However it is seen that film of \(\omega = 0.7\) shows smaller \(\tau_R\), when compared with \(\omega = 0.6\), due to the smaller interfacial area and elastic energy term. It should be noted that the rise time is only a few ms for \(V_{pp} \geq 150\) Volts.

The decay time(Fig. 5) can be predicted by eq. (4) by simply letting \(V = 0\).

\[
\tau_D = \frac{\eta a^2}{K(1^2 - 1)}
\] (5)

The larger \(\tau_D\) for \(\omega = 0.7\) over \(\omega = 0.6\) should come from the larger domain size \((a^2)\) and smaller elasticity \((1/K)\) at this composition.

The frequency response of the films are shown in Figs. 6 to 8. In most dielectric composite composed of polymer and LC, the applied external electric field is not entirely imposed on LC phase. The distribution of external field to polymer and LC phase strongly depends on the magnitude of dielectric constants and conductivities.\(^2\) For series connected dielectric composite which finds close analogy to the films of present concern, the partition of external electric field is given by eq.(6).

\[
\frac{E_{LC}}{E_p} = \frac{|\varepsilon^*|_{vLC}}{|\varepsilon^*|} = \left[\frac{\omega_p \varepsilon_p^2 + \sigma_p^2}{\omega_{LC} \varepsilon_{LC}^2 + \sigma_{LC}^2}\right]^{1/2}
\] (6)

where \(E, \varepsilon^*, \sigma\) and \(\omega\) represent electric field, complex and dielectric constants, conductivity and angular frequency, respectively. This equation states that at very low and very high enough frequencies the electric field of each phase is inversely propotional to the conductivity. and dielectric constant, respectively. However, in general,

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**Fig. 5. Decay time vs. applied voltage for SMA/LC(40/60) and SMA/LC(30/70) films at 1kHz, 25°C.**

**Fig. 6. Transmittance vs. electric frequency for SMA/LC(40/60) and SMA/LC(30/70) films at 200Vp-p, 25°C.**
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Fig. 7. Rise time vs. electric frequency for SMA/LC (40/60 and 30/70) films at 200V_{pp}, 25°C.

Fig. 8. Decay time vs. electric frequency for SMA/LC (40/60 and 30/70) films at 200V_{pp}, 25°C.

![Graph](image1)

![Graph](image2)

\[ \frac{E_p^{'}}{E_{LC}} \approx \frac{\sigma_p}{\sigma_{LC}} \tag{7} \]

and an interfacial polarization is induced. Therefore the distribution of external electric field to polymer and LC phases strongly depends on the electric frequency.\(^6\) Since the conductivity of LC domain is generally larger than the polymer, the magnitude of \(E_{LC}/E_p\) drops dramatically in a frequency range near and below the relaxation frequency of the interfacial polarization. With a sharp drop of the local electric field in LC domains at low frequencies, transmittance decreases drastically (Fig. 6), rise time increase rapidly (Fig. 7) with the decrease of frequency. Decay time (Fig. 8) also shows identical trend with \(\tau_g\).

Fig. 9. Effect of temperature on transmittance of SMA/LC(40/60 and 30/70) films.

Fig. 9 shows the effect of temperature on the off-state transmittance of the films. Transmittance gradually increases as the temperature is raised above room temperature. However as the film is warmed above room temperature, an abrupt increase in slope, more with \(\omega=0.7\) and less with \(\omega=0.6\), occurs, due to the abrupt change of surface anchoring energy of LC at this temperature.\(^16\) The abrupt change in slope corresponds to the glass transition temperature (\(T_g\)) of polymer. \(T_g\) of the polymer is significantly decreased in these composite films due to the plasticizing effect of LC, and the effect is more pronounced with higher LC content, as our results indicate. Abrupt change of electro-optic response at \(T_g\) has also been reported for PVFM/E7(1 : 1 by weight), and PVFM/E8(1 : 2) films.

The increase of off-state transmittance with temperature is caused by the decrease in birefringence of LC,\(^18\) and increase of the solubility of LC in polymer phase. The extraordinary refractive index decreases, and ordinary refractive index increase with the increases of temperature, and the birefringence (\(\Delta n=n_e-n_o\)) decreases with temperature as,\(^19,20\)

\[ \Delta n \approx \left[ 1 - \frac{0.98}{T_{NI}} \right]^{0.22} \tag{8} \]

where \(T\) is the absolute temperature, and \(T_{NI}\) is the nematic to isotropic transition temperature. As
temperature increases, the solubility of LC in polymer increases. The refractive index of LC dissolved in polymer is its isotropic value ($n_i$) which is lower than $n_c$, and higher than $n_o$. Therefore, mismatching of refractive index is significantly decreased with the increase of temperature giving rise to the increased transmittance.

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