ELECTRO-OPTIC PROPERTIES AND WAVELENGTH EFFECT IN POLYMER NETWORK LIQUID CRYSTAL

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Abstract—Polymer network liquid crystal (PNLC) films were prepared from poly(vinyl alcohol) (PVA) and E44 using an emulsion technique. Effect of the wavelength of incident light in addition to the input electric field has been studied. It was found that the morphology of the composite film mainly depends on the film composition. The transmittance of the powered film increased, rapidly at high and smoothly at low applied voltage, with increasing incident wavelength, however, it was slightly decreased for unpowered film. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Liquid crystal (LC) is used in a wide variety of electro-optic devices, including optical display, especially when relatively low power consumption and satisfactory response time are needed [1, 2]. However, it is quite difficult to maintain uniform thickness over entire LC surface areas due to the fluidity of LC and, hence, LC display devices have been of relatively small size [3–5].

During the last decade, encapsulated liquid crystals have been tested for LC display devices, called a nematic curvilinear aligned phase (NCAP) [6–8]. Methods to prepare the NCAP include simultaneous mixing of LC and a water-soluble polymer in water. Then the dispersed LC phase is encapsulated by a water-soluble polymer to form an emulsion. The emulsion is mounted on a transparent electrode, which is commonly indium–tin oxide (ITO) coated glass plate and dried until water evaporates completely. This method has been applied by Fergason [6] to obtain the polymer dispersed liquid crystal (PDLC).

When LC forms a continuous phase (rather than the isolated droplets as in PDLC) in a spongy-like polymer matrix, the polymer/LC composite film is called a polymer network liquid crystal (PNLC), where the LC molecules tend to align parallel to the polymeric wall [9–11]. This type of composite film has been reported to show better electro-optic properties to include enhanced optical transmittance, higher contrast and lower threshold voltage [3, 11, 12].

We consider poly(vinyl alcohol) (PVA)/LC(E44) composite film at 40/60 composition. Electro-optic properties as a function of applied voltage and frequency at a fixed wavelength of the incident light and the effect of the incident light wavelength have been studied throughout the UV–vis range.

EXPERIMENTAL

Materials and cell preparation [11, 12]

PVA (Fluka, degree of polymerization = 500, degree of hydrolysis = 97.5–99.5 mol-%, nD 1.51–1.52) is used as an encapsulating medium and E44 (Tg ≈ 0°C, Tm ≈ 100°C, nD 1.790, nD 1.528) as an LC. The LC was mixed with 8% aqueous solution of PVA. The mixture was cast on a PET film, with its thickness controlled by an applicator. The film was dried in an oven for 10 hr at 40°C to remove residual moisture. By adjusting the gap size of applicator, films having a thickness of 11 μm were prepared. The film was sandwiched between two ITO-coated glass plates (measuring cell) and sealed using an epoxy-type adhesive.

Morphology and electro-optic measurements

The morphology of the film was studied with scanning electron microscopy (SEM, Jeol JSM820). Micrographs were taken from the cast film surface and cryogenically fractured surface of the cast film, which were sputtered with gold before viewing.

For electro-optic measurements, a collimated beam of an He-Ne laser (wavelength = 632.8 nm) was passed normal to the film surface and the transmitted light intensity was measured with a photodiode. The transmittance through the cell was recorded in a digital storage oscilloscope (Hitachi VC-6023). The distance between the cell and the photodiode was 300 mm. An electric field was applied across the film. The effect of wavelength of the incident light was studied using an UV–vis spectrophotometer (Kontron, UVikon 860).

RESULTS AND DISCUSSION

Morphology

Since the polymer/LC composite film was prepared by the NCAP technique, droplet-in-matrix morphology was expected because LC droplets had been isolated individually before film formation [7]. Figure 1 shows SEM micrographs of PVA/LC(40/60) composite film, where LC has been removed by extraction with dichloromethane. The cast film surface shows that the LC phase is dispersed in the polymer matrix in nearly spherical form [Fig. 1(a)]. Similar SEM morphologies were reported by others.

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Fig. 1. SEM photographs of PVA/E44 (40/60, w/w) composite films after extraction of LC with dichloromethane: (a) cast film surface; (b) fractured surface.

[5, 9, 13]. However, the fractured surface shows that the dispersed LC droplets are interconnected with others [Fig. 1(b)] to form a continuous phase rather than a discrete one. The internal structure of the film is significantly different from the surface. Interconnected morphology has been generally observed when the films are prepared by solvent casting [11, 12, 14]. This indicates that the phase morphology of the polymer/LC composite film mainly depends on composition rather than the film preparation technique.

Effect of applied voltage

The mechanism of transition from light scattering to transmitting state originates from the anisotropic nature of LCs. Since the LC used in this study has a positive dielectric anisotropy ($\Delta \varepsilon = \varepsilon_1 - \varepsilon_2 > 0$), LC molecules will align with their long molecular axis parallel to the applied field to minimize their energy [1]. In order to measure the response characteristics of the film, a sinusoidal voltage at 1 kHz has been supplied for a period of 50 msec. The output signal was detected using a digital storage oscilloscope and the results were recorded by a laboratory computer. Figure 2 shows the time-dependent transmittance of PVA/E44 composite film at room temperature. At low applied voltages transmittance increases asymptotically with time. However, at high applied voltages, transmittance increases very rapidly to a much higher constant value.

Nematic director orientation within the LC domain is determined by the balance between elastic force, electric force and surface interaction [15, 16]. Therefore, there exists a threshold electric field ($E_{th} = V_{th}/d$), below which directors cannot rotate and orient along the field direction. Figure 3 shows transmittance as a function of applied voltage. Transmittance is almost unchanged with applied voltage up to 10–20 $V_{p-p}$, beyond which it increases abruptly with increasing voltage. Threshold electric field ($E_{th} = V_{th}/\text{film thickness}$) is observed at about 20 $V_{p-p}/\mu\text{m}$ or, 7 $V_{rms}/\mu\text{m}$. This is a significantly low value, which is due to the weak interfacial interactions between PVA and LC.

Figure 4 shows rise time ($\tau_R$) as a function of applied voltage. Rise time decreases rapidly above $E_{th}$ and is less than 1 msec at around 100 $V_{p-p}$. However, decay time ($\tau_D$, 4–5 msec, not shown) was almost constant due probably to the clean phase separation between PVA and LC. This is consistent with theoretical predictions given below: [5, 17]

$$\frac{1}{\tau_R} = \frac{1}{\eta} \frac{9e_0 \Delta \varepsilon V^2}{d^2 (\rho \tau / \rho_{LC} + 2)} + \frac{K (\rho - 1)}{\eta a^2}$$  \hspace{1cm} (1)

$$\frac{1}{\tau_D} = \frac{\eta a^2}{K (\rho - 1)}$$  \hspace{1cm} (2)

Fig. 2. Time-dependent transmittance for PVA/E44 composite film at 1 kHz, 25°C.

Fig. 3. Transmittance vs applied voltage for PVA/E44 composite film at 1 kHz, 25°C.
where, $\eta$, $\epsilon$, $\Delta \varepsilon$, $V$, $d$, $a$, $l$, $K$ and $l$ represent viscosity of LC, vacuum permittivity, dielectric anisotropy, applied voltage, film thickness, major dimension, resistivity, elastic constant, and aspect ratio (major dimension/Minor dimension) of LC domain, respectively, and subscripts P and LC denote polymer and liquid crystal. Equations (1) and (2) state that $t_R$ is inversely proportional to $\sim V^2$ and $t_D$ depends only on the inherent properties of LC and film geometry. Thus, $t_R$ decreases rapidly with $V$, whereas $t_D$ is independent of $V$. It should be noted that the response time ($t_R + t_D$) is less than 10 ms at $>80 \ V_{p-p}$ and this is much faster than that of a conventional twisted nematic-type display device [2].

**Effect of applied frequency**

Figure 5 shows the wave forms of transmittance at different frequencies. At low frequency, the periodic flicker of transmittance [Fig. 5(a)] is exactly twice the input a.c. electric pulse because LC can follow the driving voltage. However, with increasing frequency, amplitude decreases and eventually the oscillation damps out at 1 kHz. This indicates that at higher external frequency, the response of LC is no longer quick enough to follow the electric polarity change [3, 11, 18].

Figure 6 shows transmittance as a function of frequency. Transmittance increases with frequency, showing an S-shaped curve. When the transmittance oscillates following the external field, an average between the minimum and maximum was taken to report. In most dielectric composites 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 phases strongly

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**Fig. 4.** Rise time vs applied voltage for PVA/E44 composite film at 1 kHz, 25°C.

**Fig. 5.** Response curve for PVA/E44 composite film at 100 $V_{p-p}$, 25°C: (a) 10; (b) 30; (c) 100 Hz; (d) 1 kHz.
depends on the magnitude of dielectric constant and conductivity. For a series-connected dielectric composite model, which finds close analogy to the films of present concern; the partition of external electric field is given as [10, 12]:

\[
\frac{E_{LC}}{E_p} = \frac{|\varepsilon|}{|\varepsilon_L|} = \left( \frac{\omega |\varepsilon| + \sigma_0}{\omega |\varepsilon_L| + \sigma_L} \right)^{1/2},
\]

(3)

where \( E \), \( \varepsilon \), \( \varepsilon' \), \( \sigma \) 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 proportional to the conductivity ratio (\( \sigma_0/\sigma_L \)) and dielectric constant ratio (\( \varepsilon/\varepsilon_L \)), respectively. Since \( \varepsilon/\varepsilon_L \) is generally larger than \( \sigma_0/\sigma_L \), the magnitude of \( E_{LC}/E_p \) decreases in a frequency range near and below the relaxation frequency of the interfacial polarization [10, 11, 19]. This agreed well with our results.

Figure 7 shows the rise time as a function of frequency. According to equation (3), \( \tau_R \) decreases with applied frequency since \( E_{LC} \) is larger at high frequency, \( \tau_0 \) (~4 msec, not shown) was also constant in most of the frequency range measured. It seems that when interfacial interaction or anchoring strength is small, neither voltage nor frequency can affect \( \tau_0 \) significantly.

**Effect of wavelength**

Figure 8 shows transmittance as a function of wavelength (\( \lambda \)) at various voltages. For unpowered film, transmittance decreases slightly with increasing wavelength. However, for powered film transmittance increases with increasing wavelength, slowly at low applied voltage and rapidly at high applied voltage. Following Montgomery [20], when a beam incidents to a sample cell, internal reflection also occurs as well as backward and forward scattering. The magnitude of internal reflection also depends on droplet size and concentration. Drzaic et al. [21] reported the multiple scattering effect is unimportant on powered films, whereas it is very important in unpowered film. The decreased transmittance with decreasing wavelength in powered film is most likely due to back scattering effect, that is, some lights scatter back into the original direction resulting in the decrease of transmittance.

Light scatterings in PDLC film are basically caused by the mismatches in the refractive indices of polymer and LC. For a single droplet Zummer and Doane [22] using Rayleigh–Gans approximation showed that scattering in PDLC follows Rayleigh \( 1/4 \) dependence when \( kR \ll 2 \) (\( k = 2\pi/\lambda, R = \) droplet radius), whereas the anomalous diffraction approach is useful when the droplet size is similar to \( \lambda \). However, the LC domains in PDLC films (Fig. 1) are heterogeneously dispersed in the polymer matrix, forming channels as well as droplets, and theoretical approximation seems not possible [23–26]. The decrease of transmittance with lower wavenumber is at least due in part to the increased scatterings of smaller droplets.

**REFERENCES**

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