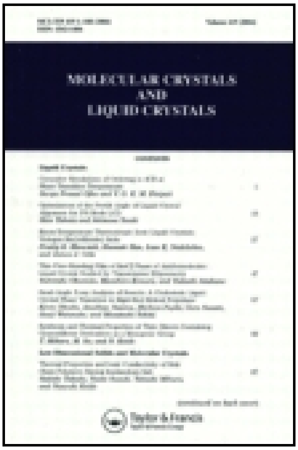

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Study of Epoxy-Based PDFLC Film Prepared Under Various Hardener Ratios

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Study of Epoxy-Based PDFLC Film Prepared Under Various Hardener Ratios

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The ferroelectric liquid crystal ZLI-4655-100 and the Epoxy-Based thermo-cured resin have been used to fabricate PDFLC film. The effect of hardener addition ratio and the surface morphology of PDFLC film are investigated. The result shows that the PDFLC film made by mixing FLC with almost cure hardener and epoxy-based thermo-cured resins possesses more rapid switching time, higher contrast ratio, and smaller droplets.

Keywords: FLC; liquid crystal; morphology; PDLC; response time

INTRODUCTION

The development of polymer-dispersed liquid crystals (PDLC) [1] is highly profitable. A PDLC film can be switched between a light scattering state and a transparent state by applying a voltage. PDLC cells have advantages over conventional displays, including such as nematic displays, in which the liquid crystal is sandwiched between two glass plates and placed between crossed polarizers. PDLC displays operate without polarizers, and they can be easily coated on large pieces of flexible plastic. They are simpler to fabricate at lower cost because they lack alignment layers or cell sealing procedures.

A new type of PDLC display device made of ferroelectric liquid crystals is known as the PDFLC composite film [2]. PDFLC devices

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respond more quickly than conventional nematic PDLC displays, and exhibit bistable switching, allowing information to be displayed in the field-off state. Pre-alignment of the PDFLC device provides some of the above advantages. The rubbing process orients both the ferroelectric liquid crystal and the polymer matrix. The optical axis of the ferroelectric liquid crystal is parallel to the rubbing direction in the rubbing process [3]. This approach yields a homogeneous planar molecular orientation of the PDFLC device.

The PDFLC composite film generated by the phase separation method [4] incorporates two phases: FLC phase (sphere phase) and a polymer matrix phase (continue phase) [5,6]. The electrical and optical characteristics of the PDFLC composite films are such that an AC electric field applied to the FLC molecule makes its helical structure bistable resulting in optical switching [7,8]. The degree of curing in the polymer matrix will affect the FLC molecule that is influenced by the applied field. Therefore, the factors that affect the effective electric field in the FLC phase must be understood.

In this study, the PDFLC films were made by adding a hardener at various curing degrees. The influence of adding hardener on the electric-optical characteristics of PDFLC at various curing degrees was investigated. Furthermore, the thermodynamic properties and, the optical switching properties are described in detail.

EXPERIMENTAL

The ferroelectric liquid crystal ZLI-4655-100 used in this experiment was purchased from E. Merck Ltd., as shown in Table 1. The epoxy resin was used as the polymer matrix to fabricate the PDFLC composite film. The epoxy resin is a two-component system that consists of an epoxy oligomer and a hardener. The epoxy oligomer is Epon 828,

TABLE 1 Physical Properties of Ferroelectric Liquid Crystal ZLI-4655-100

Properties	Value
Phase sequence	$k \xrightarrow{<10^\circ C} SmC^* \xrightarrow{61^\circ C} SmA^* \xrightarrow{72^\circ C} Ch \xrightarrow{76^\circ C} I$
Title angle (20°J)	25°
Spon. Polar. (20°J)	$+22.6\,\mathrm{nCcm^{-2}}$
$\Delta\varepsilon$ (7.5 kHz, 20°C)	−1.7
Δn ($\lambda = 589$ nm, 20°C)	0.13

k: Crystalline phase, SmC^*: Chiral smectic C phase, SmA^*: Chiral Smectic A phase, Ch: Cholesteric phase, I: Isotropic phase, Spon. Polar.: Spontaneous polarization value, $\Delta\varepsilon$: Dielectric anisotropic, Δn: Birefringence.

whose epoxy equivalent is 182–194. The hardener is H3895 (A. C. R. Limited), and is one of the polyamine series with a low viscosity of 400 cps. Nylon 6/6 was coated on indium-tin-oxide (ITO) conductive glass as an alignment layer, with a thickness of about 300 Å, and rubbed in the same direction to generate the alignment effect. The mixing weight ratios of the FLC/epoxy oligomer/hardener were 3/7/2, 3/7/3, 3/7/4 and 3/7/5. The prepolymer was a mixture of epoxy oligomer, hardener and FLC. It was sandwiched between two ITO-coated glass pieces and then rubbed in opposite directions; an 8 μm spacer was used to control the cell gap. The curing temperature 80°C at which the PDFLC films were made exceed the temperature of the isotropic phase, and the curing time was 30 minutes.

The morphology of the PDFLC film was observed using a scanning electron microscope (Hitachi Model S-550 SEM). The samples were soaked in methanol to remove FLC, and the sample was stored in vacuum for several hours to remove methanol; channel spacing appeared. The electro-optical characteristics of the PDFLC films were measured using an He-Ne laser ($\lambda = 632.8$ nm, 10 mW) as a probe light and a photodiode (ET2000) as a detector. Figure 1(a) shows the equipment

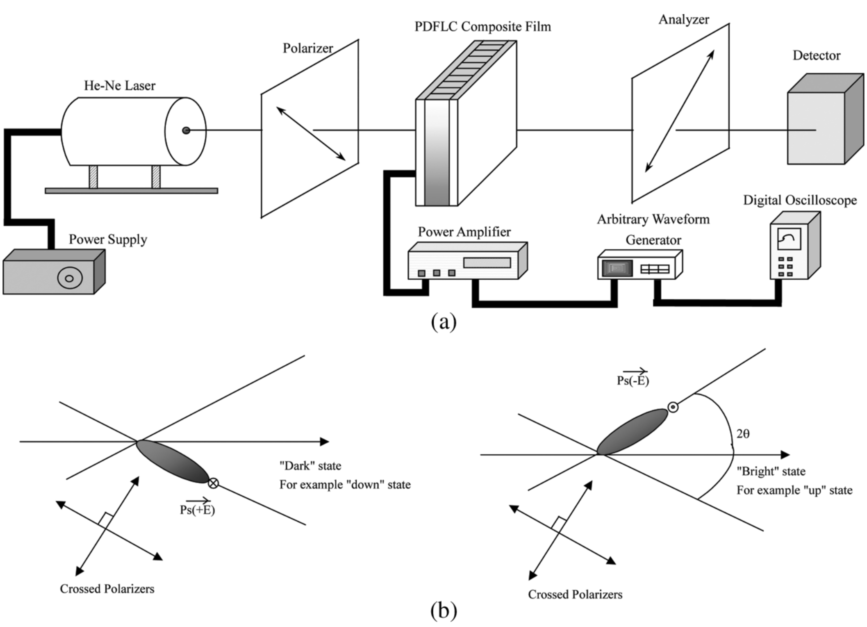

FIGURE 1 (a) The experimental set-up for the measurement of optical switching time. (b) Dark and bright state in a PDFLC composite film cell.

adopted in this electro-optical experiment. The response time was measured under cross polarizers, while positive and negative electric fields were applied to the cell to generate two transmission states, a bright state and a dark state. The response time was defined as the time needed to change the transmittance from 10% to 90%. The measurements were made at 30°C, 40°C, 50°C and 60°C. The cell temperature was controlled by the hotstage (Fp800 Thermo system). The thermodynamic characteristics were measured using a Modulated DSC 2910 (MDSC).

RESULTS AND DISCUSSION

Thermodynamic Properties

Liquid Crystals

The FLC ZLI-4655-100 was used to make the PDFLC composite film. MDSC was used to measure the phase transition temperature of the FLC ZLI-4655-100, as shown in Figure 2 to verify the phase transition temperature. The results reveal that the transition from the crystal phase to the chiral smectic C phase (K-SmC*) occurs at $T_{k\text{-}SmC^*} \approx -8.29$°C, and the enthalpy change $\Delta H_{K\text{-}SmC^*}$ is 14.44 J/g; the transition from the chiral smectic C phase to the smectic A phase

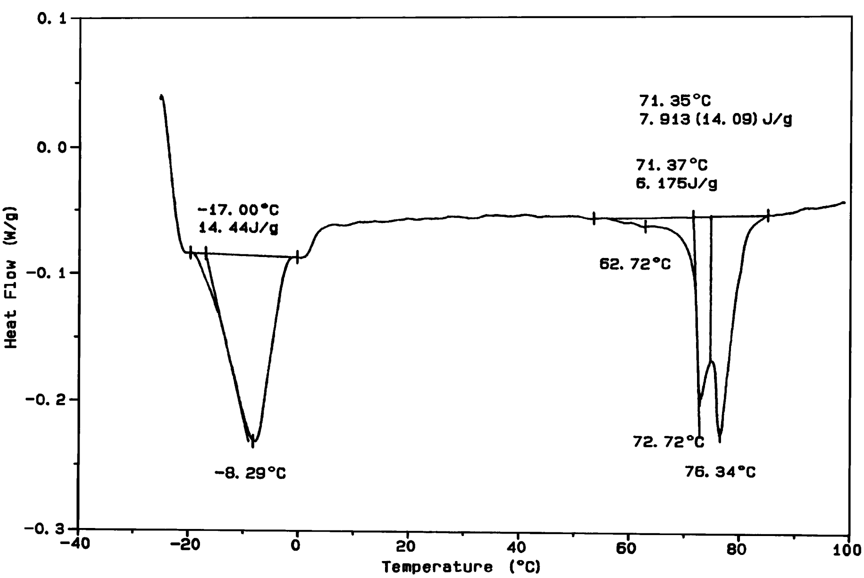

FIGURE 2 MDSC measurement for ZLI-4655-100.

(SmC*-SmA) occurs at $T_{SmC^*\text{-}SmA} \approx 62.72°C$; the transition from the smectic A phase to cholesteric phase (SmA-Ch) occurs at $T_{SmA\text{-}ch} \approx 72.72°C$, and the enthalpy change $\Delta H_{SmA\text{-}ch}$ is 6.175 J/g; the transition from the cholesteric phase to the isotropic phase (Ch-Iso) occurs at $T_{ch\text{-}iso} \approx 76.34°C$, and the enthalpy change $\Delta H_{ch\text{-}iso}$ is 7.913 J/g. The phase transition temperature of ZLI-4655–100 was measured to be K −8.29°C SmC* 62.72°C SmA 72.72°C Ch 76.34°C Iso. The data are in good agreement with the data from the catalogue.

Polymer Matrix

A PDFLC composite film was fabricated using epoxy resin as the polymer matrix. The epoxy resin is a two-component system, which comprises Epon 828 and hardener. Figures 3(a) and 3(b) plot the extent of the conversion of the polymer matrix versus time for various added hardener ratios. Figure 3(a) reveals that maintaining the curing temperature at 80°C for 30 min yields 69%, 72.5%, 76% and 80% conversion for the epoxy/hardener ratios of 7/2, 7/3, 7/4 and 7/5, respectively. Figure 3(b) reveals the conversion characteristics of varying hardener ratios at the curing temperature 80°C for 6000 min. The conversion percentages of epoxy/hardener 7/4 and 7/5 approach 100% within 3000 min and 2000 min, respectively. However, the conversion percentages of epoxy/hardener 7/2 and 7/3 approach only 95% and 97% within 3000 min, respectively. These results reveal that the epoxy/hardener weight ratios of 7/5 and 7/4 correspond to almost perfect curing hardener additives; the epoxy/hardener weight ratios of 7/3 and 7/2 do not enable curing.

Optical Switching Properties

Figure 4 plots the relationship between the response time and the applied frequency at an applied voltage of 10 Vp-p. A 10 Hz–100 Hz square-wave ac voltage was applied as the reference signal in the measurement system. Therefore, the response of the PDFLC film became more rapid as the applied frequency was increased. However, the PDFLC film, with the liquid crystal/epoxy oligomer/hardener weight ratio of 3/7/4, has a shorter response time, because the appropriate hardener ratio makes the FLC in PDFLC film rapidly transferred. Although the FLC molecules are well packed into the polymer matrix, the response time of the pure FLC varies by tens of μs; the response of PDFLC (3/7/4) is slower than that of pure FLC. Moreover, an improper hardener ratio causes the response time of PDFLC (3/7/3) to be longer than that of PDFLC (3/7/4); the response time of PDFLC (3/7/5), with an excess of hardener added, is more

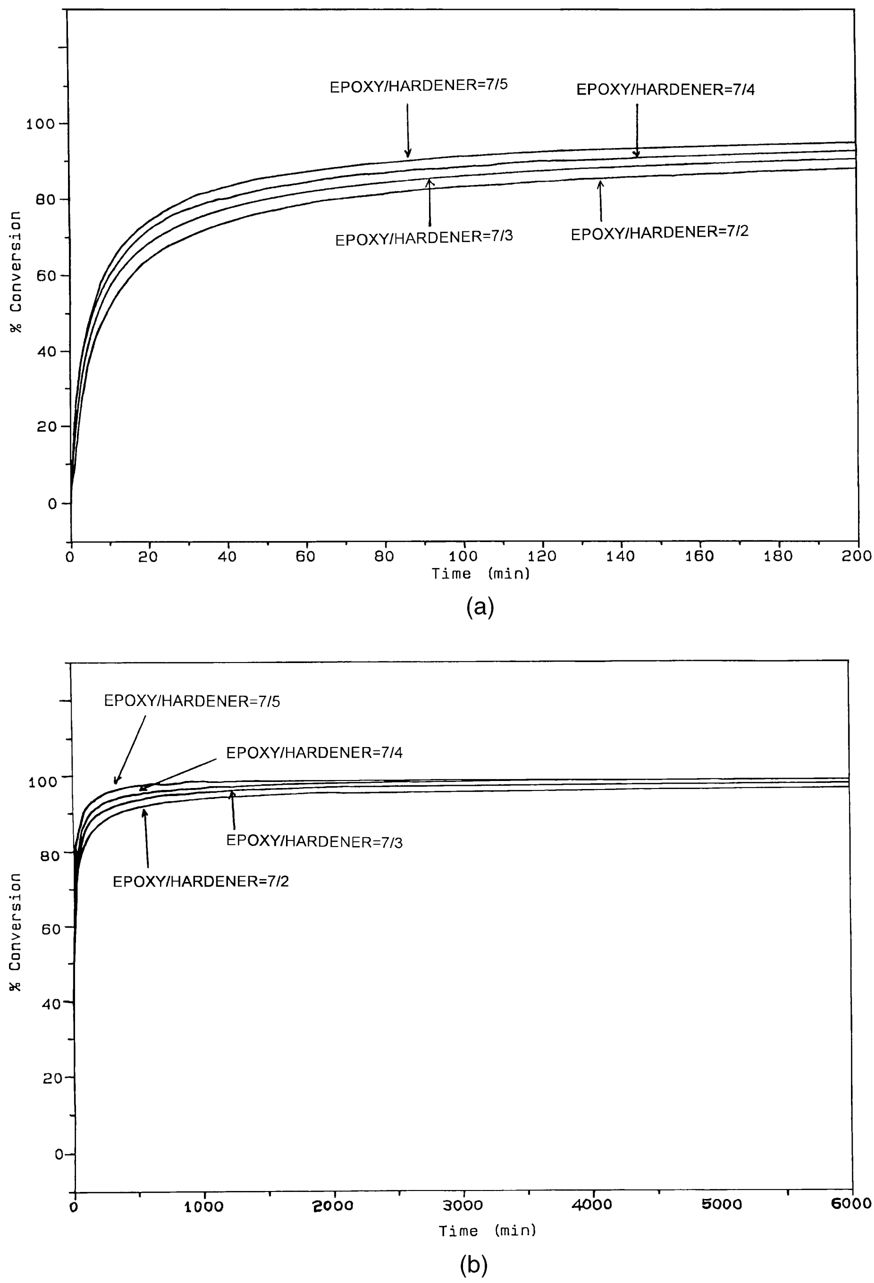

FIGURE 3 (a) Conversion of various weight ratios of epoxy/hardener as function of the reaction time at 80°C for 200 min. (b) Conversion of various weight ratios of epoxy/hardener as function of the reaction time at 80°C for 6000 min.

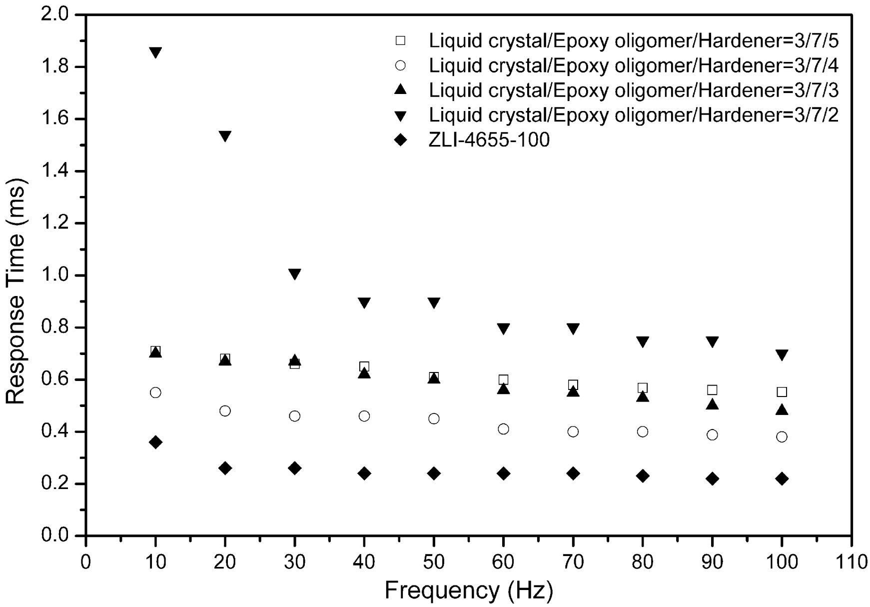

FIGURE 4 Response time vs. frequence for various PDFLC films and FLC ZLI-4655-100 (10 Vp-p, 30°C).

than that of the PDFLC (3/7/3). The excess hardener in PDFLC (3/7/5) is responsible for increasing the rotational viscosity of the liquid crystal, so the excess hardener slowed the response. Adding insufficient curing hardener to PDFLC (3/7/2) limited the action of FLC molecules in the polymer matrix because the epoxy resin did not harden. The polymer matrix prevented the FLC molecule from being transferred quickly back in the dark state and the bright state, slowing the response. Figure 5 plots the relationship between the response time and the applied voltage when 60 Hz square-wave ac voltage was applied. The response time of PDFLC film decreased upon increasing the applied field strength. Adding hardeners with various ratios supported this conclusion.

Figure 1(b) shows the transmission properties for the dark and the bright states in the PDFLC film. An applied field interacts with the FLC molecule and tends to orient it in the direction $\vec{P}_s$ (+E) (dark state). When the field is inverted, the FLC molecule is oriented in the direction $\vec{P}_s$ (−E) (bright state). A change in this direction corresponds to a change in the direction of the optical axis of the FLC material, by tilt angle 2θ [9,10].

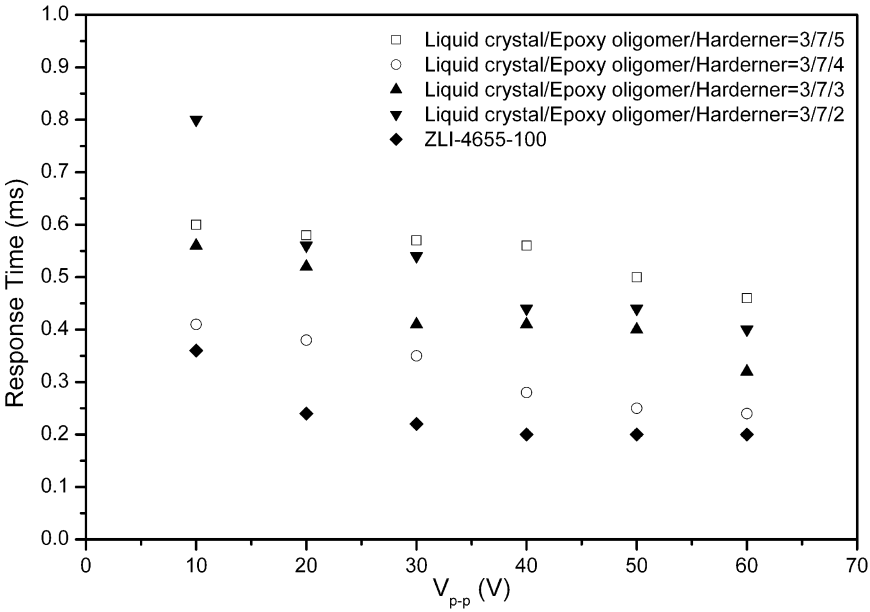

FIGURE 5 Response time vs. voltage for various PDFLC films and FLC ZLI-4655-100 (60 Hz, 30°C).

Figure 6 plots the relationship between the transmission properties and the applied voltage for the dark state and the bright state under the experimental condition as in Figure 1(b), for PDFLC films with the mixing weight ratios of 3/7/4. The contrast ratio is calculated using the transmission values of the dark and the bright states, as expressed by Eq. (1).

$$CR = \frac{T_{on}}{T_{off}} \tag{1}$$

CR: Contrast ration
T_{on}: Transmission of the bright state
T_{off}: Transmission of the dark state

Figure 7 plots the contrast for the various hardener addition ratios in PDFLC films, as a function of applied voltage. The contrast of each film increases with the voltage. The PDFLC (3/7/4) has the best contrast, followed by PDFLC (3/7/3) and then PDFLC (3/7/5) followed by PDFLC (3/7/2), which has the lowest contrast. When PDFLC (3/7/4)

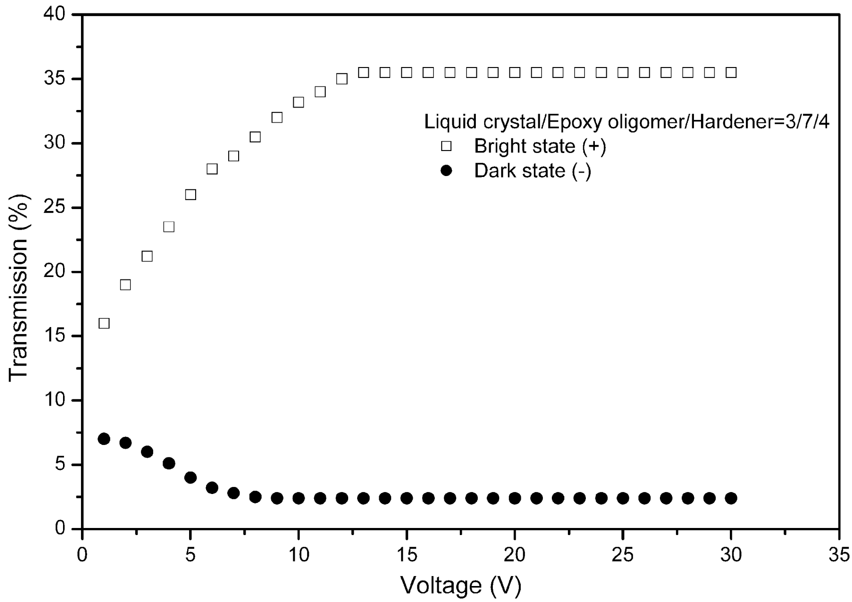

FIGURE 6 Transmission properties as a function of applied voltage for PDFLC film (3/7/4) in the dark state and bright state.

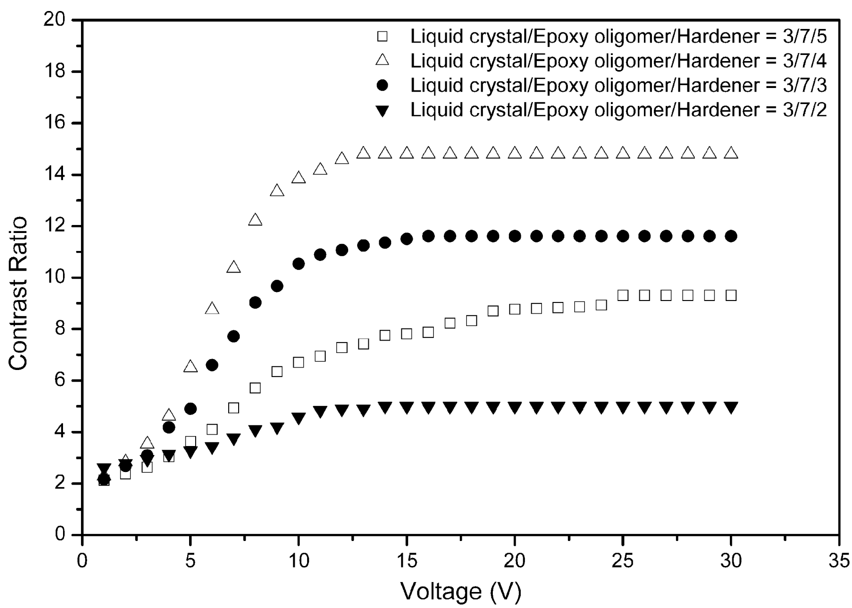

FIGURE 7 Contrast ratios as a function of applied voltage for various PDFLC films.

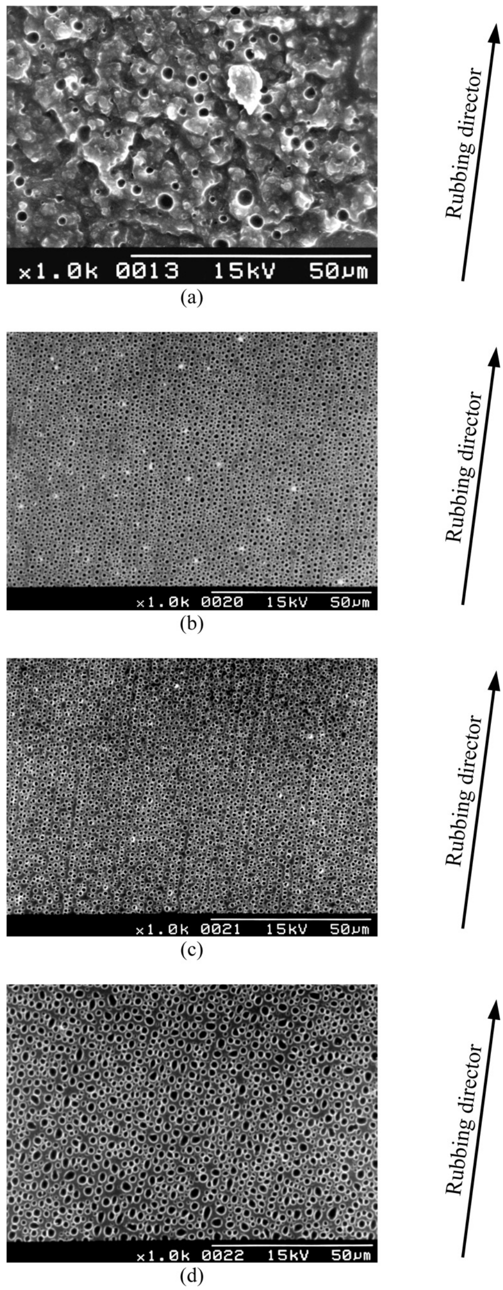

FIGURE 8 Scanning electron microscope photographs of various PDFLC films: (a) ZLI-4655-100/epoxy oligomer/hardener = 3/7/2, (b) ZLI-4655-100/epoxy oligomer/hardener = 3/7/3, (c) ZLI-4655-100/epoxy oligomer/hardener = 3/7/4, (d) ZLI-4655-100/epoxy oligomer/hardener = 3/7/5.

is placed under cross polarizers, with positive and negative field polarization, the helical structure of the FLC molecule easily exhibits Goldstone mode motion and achieves bistable status, and generates clear contrast between bright and dark states [11–15].

Figures 8(a), 8(b), 8(c), and 8(d) show the scanning electron microscope images of the PDFLC composite film with various hardener ratios. The polymer network is parallel to the rubbing direction, so the FLC in the composite film was aligned parallel to the direction of the polymer network. In Figure 8(c), the droplet in FLC is the smallest, and is parallel homogeneously to the rubbing direction, because the addition of an almost perfect curing hardener perfectly separates the FLC phase from the polymer matrix; causing the FLC droplet to be aligned parallel to the composite film, and to be the smallest microdroplet compared to other composite film droplets. Adding a little hardener to PDFLC (3/7/2) cured only a small proportion of epoxy resin and removing FLC using methanol removed only some of the epoxy resin, so the scanning electron microscope images reveal that the PDFLC (3/7/2) composite film is not very effective in curing.

CONCLUSION

In summary, PDFLC films whose matrices comprising epoxy resin with two components were investigated. The experiment on optical switching characteristics revealed that the PDFLC film has a short response time, because of the cone structure of FLC molecule is bistable and the optical switching is easy. When an appropriate hardener ratio was mixed in with the epoxy resin, a PDFLC composite film with better electro-optical characteristics was formed. However, the best alignment and fastest switching of the PDFLC film can be obtained by adding with the appropriate weight ratio.

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