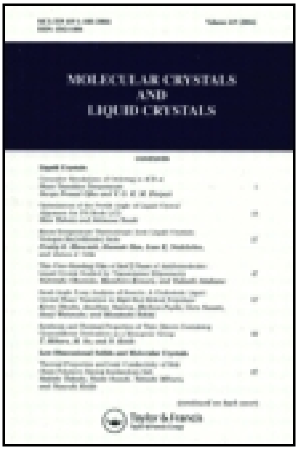

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Electro-Optical Studies on Polymer Dispersed Liquid Crystal Composite Films. II. Composite of PVB/E44 and PMMABA/E44

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ELECTRO-OPTICAL STUDIES ON POLYMER DISPERSED LIQUID CRYSTAL COMPOSITE FILMS. II. COMPOSITE OF PVB/E44 AND PMMABA/E44

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Aggregation states and electro-optical effects based on light scattering have been investigated for PVB/E44 and PMMABA/E44 composite films. The composite films were prepared by solvent-evaporation technique. Scanning electron microscopy observations showed that E44-phase is continuously embedded in a sponge-like PVB and PMMABA matrix polymers. Electro-optical responses of the composite films under the conditions of an externally applied AC electric field (0–240 Vp-p; 50, 100, 500 and 1 KHz) temperature (28°C) and film thickness ($10 \pm 2\,\mu m$) were determined using He-Ne (wavelength 632.8 nm) laser as a light source. The composite films (of both PVB/E44 and PMMABA/E44) with positive dielectric anisotropy exhibited characteristic reversible light scattering-light transmission switching, strongly dependent on the liquid crystal (LC) channel size and shape in the composite films. The electro-optical response of LC molecules in both of the composite systems is influenced by the miscibility of the LC molecules at LC-polymer interface. Thus the distribution of relaxation time for the interfacial polarization corresponds to the miscibility state at the interface between matrix polymer and LC. The miscibility between two phases at interface was investigated by employing Fourier-Transform Infrared Spectroscopy/Attenuated Total Reflectance (FT-IR/ATR) spectrophotometry and differential scanning calorimetry (DSC). The results obtained indicate that under the conditions imposed the output can be controlled and the response time is on the order of several milliseconds or less.

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A memory effect is observed in PVB/E44 composite films. The transmittance of the memory state is preserved for a longer time after an applied voltage is removed, which can be erased to the scattering OFF state by heating the film to the E44-clearing temperature. In the case of PMMABA/E44 composites, which exhibit electro-optical switching hysteresis, a possible mechanism that the applied electric field-induced phase-mixing of PMMABA and E44 would be a main cause of hysteresis is discussed.

Keywords: electro-optical response; PDLC; liquid crystal display device; light scattering; memory effect; hysteresis effect

INTRODUCTION

Nematic liquid crystal (LC) dispersed as submicron-size droplets in a polymer matrix (PDLC) exhibit, upon application of an electric field, an exclusive optical property due to their birefringent refractive nature as well as the mismatch of the refractive indices with the matrix polymer, [1–6]. In its normal OFF-mode operation (unpowered) a PDLC film strongly scatters light and appears opaque. On the other hand, a sufficiently strong electric field (powered state), reorients the LC molecules within the microdroplets and makes the film clear and transparent (ON-mode operation). The main advantages of PDLC films are that they draw very little current (on the order of few μA/cm^2) and consume low electric power. Moreover, such films are self-supported with flexibility and durability, and they are easy to fabricate without any restrictions on its geometry. Therefore, these optoelectronic devices are high potential candidates for exciting high control applications such as variable transmission windows and matrix projection displays [3–14]. For each application the electro-optical characteristics of the device are the basic information that determines its effectiveness.

The light scattering state of the PDLC film in AC electric field OFF state is highly dependent on the optical microstructural heterogeneties and/or homogeneties of the composite film [12]. These optical states correspond to modulated, external electric field-induced random unidirectional orientation of LC director, ultimately resulting in the mismatch of the refractive indices between phase-separated matrix polymer and dispersed LC phase. Kajiyama [12] proposed that the spatial distortion of nematic directors in the distorted LC, continuous channel s also contribute to optical heterogeneity. Therefore the high scattering and switching properties of PDLC films are highly influenced by the phase-separated structure of these films. The size of the LC droplets and LC channels can be controlled on the basis of the solvent evaporation rate during preparation of the films and depends upon a number of matrix material parameters, including viscosity and chemical potential. In fact, by controlling the solvent evaporation rate and composition of components a wide variety of morphology can be generated ranging from discreet, spherical domains to bicontinuous channels/network of polymer fibrils and LC domains. The larger domains (>1 nm) contribute to a large scattering cross-section and consequently serve to lower the switching voltages. Drzaic [15] has investigated the effect of domain size on a switching field and has shown that this field is inversely proportional to average droplet radius. Remarkably, the switching field is also inversely proportional to domain anisotropy. However the electro-optical responses of LC molecules are strongly dependent on the hydrodynamic properties, such as elastic constants and viscosity, of the LC molecules [12]. The decay response-time increases in a glass-transition temperature range of matrix polymer [16,17] and thus is strongly influenced by the interphase tension between LC molecules and matrix polymeric phase [16,17].

In continuation of our earlier work on electro-optical properties of PDLC composites [18], this paper describes microstructure light scattering relationships, electro-optical effects of the composite film, and the possible mechanism of light scattering-transmission switching of poly (vinyl butyral) PVB/E44 and poly (methyl methacrylate-co-butyl acrylate) PMMABA/E44 composites. The paper reports the memory effect in high transmission properties of PVB/E44 composite films, whereas PMMABA/E44 composite films show hysteresis of the electro-optical switching. The possible mechanism of appearance of both the phenomenan have been discussed.

EXPERIMENTAL

Materials

The chemical structures and physical properties of the constituent polymers and LC materials for the preparation of the PDLC composites are given in Figure 1. PVB supplied from Amrut Industries (Thane, India) and PMMABA supplied from Degussa Corporation (Germany) were used as the matrix polymers. The films of both the matrix polymers were optically isotropic and transparent with good dimensional stability, high temperature resistance and, high impact strength. A nematic mixture consisting of several of cyanobiphenyls derivatives E44 (purchased from E. Merck, UK) was used as a LC material.

Preparation of the Composite Films

PDLC composite films were prepared by solvent-induced phase separation SIPS technique [4,13,19]. The composite films of a different composition of

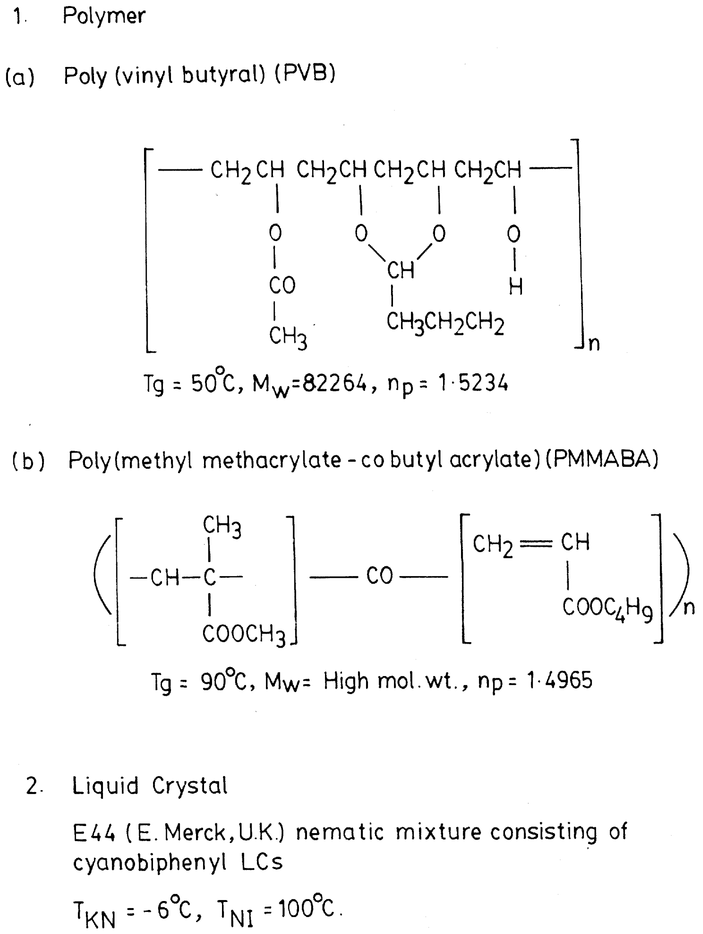


FIGURE 1 The chemical structures of the (1) matrix polymers and (2) liquid crystal material for the composite films.

polymer and LC were prepared from a homogeneous solution of an appropriate amount of E44 and a polymer (PVB and PMMABA) in chloroform (AR grade) by spreading over indium-tin-oxide (ITO)-coated glass as a substrate at room temperature (28°C). The solvent evaporation rate during a film preparation process was controlled by regulating the pressure in the solvent evaporation chamber with a needle valve and a vacuum pump to get an identical aggregation structure. The composite films were sandwiched between two ITO—coated glass plates of dimensions 6 × 6 mm which were separated by a polyethylene terephthalate film spacer of various thickness in the wide range of 8.0 to 14.0 μm to control composite film thickness. The selected final thickness for various electro-optical experiments of both composite films was $10 \pm 2\,\mu m$. Here it is important to mention that the composite films with 70% w/w and above LC loading showed discomfort in handling the device. However, there was no problem in controlling the composition of LC in composite films, but, comparatively 30/70 composite films show poor adhesion to substrate and low electro-optical contrast [12].

Aggregation Structure

The aggregation structures of the composite films were investigated by using scanning electron microscope (SEM) (Cambridge Stereo scan 150 SEM). The LC phase in the composite film was extracted with n-hexane (for PVB) or methonal (for PMMABA) at 28°C and then the films were dried overnight under vacuum. The weight loss upon LC-extraction was used to decide the continuity of LC domains in polymer matrix. When the LC domains are three-dimensionally connected almost all the LC that was initially loaded was extracted. The dried films were fractured in liquid nitrogen and sputtered with gold before viewing under SEM. The crossed polarized microscopy (Carl Zeiss, Trinocular Research Microscope, AXIO-LAB-100) was used to record the director configuration behavior of the LC microdomains in composite films.

Electro-optical Measurements

Electro-optical switching properties of the composite films measured by means of the measuring system are shown schematically in Figure 2. A collimated beam of polarized He-Ne laser (5-mw power at 632.8 nm wavelength, Photo Chemical Inc., Canada, model 105P) was used as an incident light source. The transmitted light intensity without any polarizer was measured under the modulation of an AC electric field in normal transmission geometry employing a photodiode (Jain Lesser-Tech, India). An AC electric field was provided by amplifying the signal from a function generator (Wideband oscillator 1002, Systronic, India) with a power amplifier and applying it to the conducting electrodes to drive the shutter. We performed various experiments using 50, 100, and 500, IKHz square waves at 28°C. The response of the photodiode was monitored with a digital storage oscilloscope (Tektronix TDS 430 A, 400 MHz). For response time measurements the PDLC film was driven by a sinusoidal voltage with driving frequency 1 KHz of nearly 1 s pulse. The distance between the cell and photodiode was 300 mm. The same sample films were strictly used for both electro-optical measurements and SEM studies, as the developed

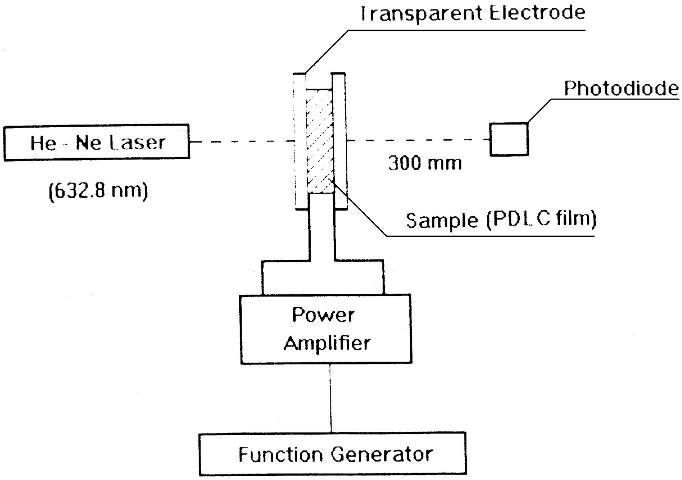


FIGURE 2 Schematic diagram of the measuring system of electro-optical properties of PDLC composite films.

morphology in PDLC composite films significantly influenced the measured electro-optical responses.

FT-IR Measurement

The relationship between the phase-mixing at the polymer-LC interface is studied by employing Fourier transform infrared (FT-IR) spectrometer (Perkin Elmer Paragon 500, USA) at a resolution of $4\,\mathrm{cm}^{-1}$. The internal reflection attachment was used for attenuated total reflectance (ATR) measurements. KRS-5 crystal for the incident angle of 45°C was used as an ATR subtract. In order to evaluate the amount of LC penetration into matrix polymer by ATR measurements the polymer films surface was contacted with the LC for 1 h and then the LC was rinsed with n-hexane (for PVB) or methanol (for PMMABA). To observe the effect of temperature on penetration of LC, the polymer matrix was contacted with the LC at room temperature (28°C) and above the clearing temperature of LC (100°C).

Thermal Analysis

The phase transition T_{NI} from nematic to isotropic state of LC (E44) and the glass transition temperatures T_g of the matrix polymers (PVB and

PMMABA) and polymer/LC composites were measured by employing differential scanning calorimeter, (DSC) (Perkin Elmer DSC-7). The scanning rate of DSC was 5°C/min, under a dry nitrogen atmosphere.

RESULTS AND DISCUSSION

Aggregation Structure of Polymer/LC Composite Films

The aggregation state of the composite films, such as the shape or size of LC domain depends on a number of factors such as the types of LC and polymer used, the composition, the casting solvent, in particular on the rate of solvent evaporation, etc. [20,21]. In SIPS, shorter the evaporation time allowed the less that aggregation occurs, resulting in the small-size LC droplets dispersed in the matrix.

Figure 3 shows the SEM micrographs of PVB/E44 composite films (80/20, 60/40 and 40/60% w/w) after extracting E44 with n-hexane which is a nonsolvent for PVB. In spite of the formation of surface skin layer, it is observed that almost all of the existing LC material in the composite films was extracted. The weight loss of the films after extracting E44 corresponds almost equally to the E44 weight fraction, indicating very limited miscibility of E44 in PVB matrix. It is observed that in PVB/E44 composite matrix polymer, PVB forms continuous phase with three-dimensional spongy, chink structures, whereas the LC (E44) domains are observed as the combination of more or less curved and stratified crack structure, embedded as a phase-separated continuous phase in the PVB matrix [18,22,23]. With increasing LC loading ($\geq$40% w/w) (Figures 3b and 3c), the number of these elongated domain structures formed out of coalescing process of small spherical droplets increases, which eventually leads to formation of continuous three-dimensional LC channels (15 ± 5 mμ) embedded in a spongy polymer matrix. These channels in 40/60% w/w composite are clearly interconnected through thick fibril morphology of PVB-matrix polymer (Figure 3c). Also, it seems reasonable from the phase-separated structures (as shown in SEM micrographs in Figure 3) that LC domains are uniformly well dispersed in the PVB matrix.

Figure 4 shows the SEM micrographs of PMMABA/E44 composite (40/60 and 30/70% w/w) after extracting E44 with methanol, a nonsolvent for PMMABA. It is apparent from the SEM micrographs that the matrix polymer PMMABA forms a three-dimensional spongy network with LC (E44) domains uniformally dispersed and embedded as phase-separated continuous phase in the polymer matrix. Further, at low LC weight fraction (40/60% w/w). We observed spherical droplets, with few of them

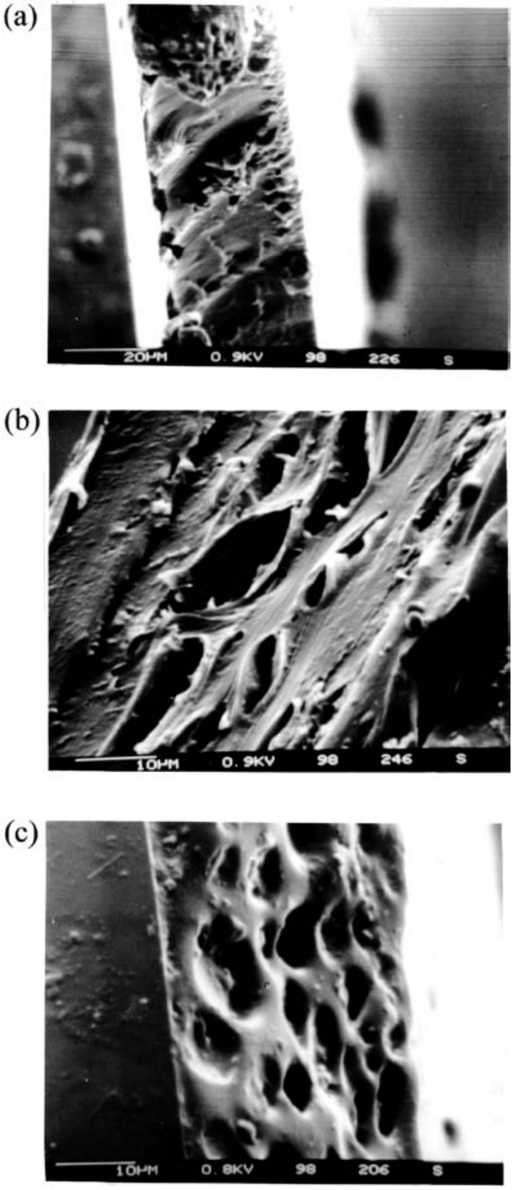


FIGURE 3 Scanning electron microscopic photographs for the PVB/E44 (a) 80/20, (b) 60/40, and (c) 40/60% w/w composite film after extraction of E44 with n-hexane at 28°C.

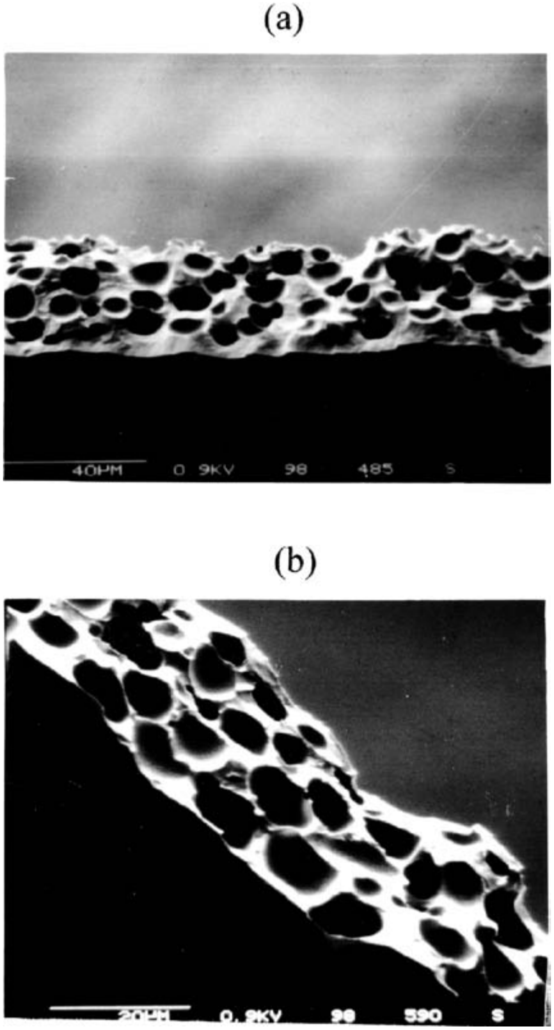


FIGURE 4 Scanning electron microscopic photographs for the PMMABA/E44 (a) 40/60 and (b) 30/70% w/w composite film after extraction of E44 with methanol at 28°C.

interconnected to form larger ones (Figure 4a). Thus, the droplet size ranges from submicrometer to several micrometers. As LC content increases (30/70% w/w) in the film, droplets become larger, irregular, elongated, and connected in three dimensions as a continuous phase separated by thin matrix polymer walls (Figure 4b).

The observed morphology indicates that both the composite systems PVB/E44 and PMMABA/E44 can be treated as binary dielectrics, and a polymer matrix and a LC as two components. Such a structural heterogeneity corresponds to a source of optical heterogeneity for the composites in the OFF-state external field.

Effect of Loading

Figures 5 and 6 show OFF and ON-state (1 kHz, 200 Vp-p) transmission of the PVB and PMMABA films of varying E44 content measured at 28°C, respectively. The purpose of these experiments is to obtain an optimized composite film composition which exhibits maximum optical contrast. It is observed that for the PVB/E44 composite films, the transmittance in the absence and presence of an applied voltage appears in E44 weight fraction in the range of 50–70% w/w, whereas in the case of PMMABA/E44 it is in the range of 60–70% w/w of E44. Similar experiments were performed to optimize the composite film thickness. Under the general conditions of experimental setup, particularly the intensity of light source and the magnitudes of the applied voltage and rise time (in both the cases), the composite films with thickness of about 10 ± 2 mμ give significant optical contrast, and thus further experiments were performed with films thickness of 10 ± 2 mμ.

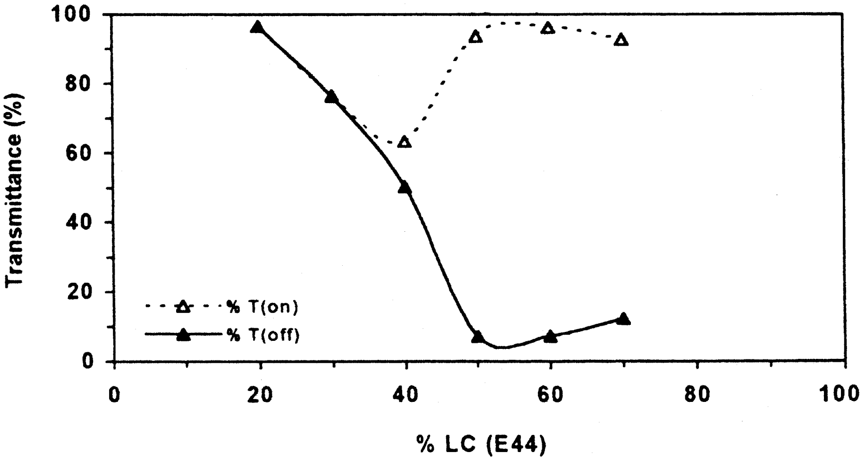


FIGURE 5 Variation of light transmittance through PVB/E44 composite film (10 ± 2 μm) with wt% of E44 without an applied field (▲-V_{OFF}) and with an applied field (△-V_{ON}) and under the conditions of 1 KHz AC field of 200 Vp-p at 28°C.

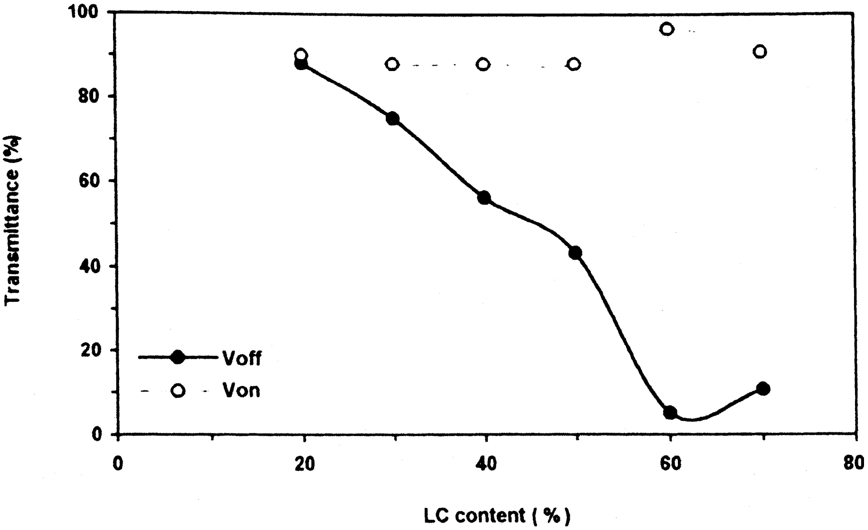


FIGURE 6 Variation of light transmittance through PMMABA/E44 composite film ($10 \pm 2\,\mu m$) with wt% of E44 without an applied field (●-V_{OFF}) and with an applied field (○-V_{ON}) and under the conditions, of 1 KHz AC field of 200 Vp-p at 28°C.

Voltage Dependence of Transmission

It has been shown that, for comparable droplet size bipolar configuration, which occurs in most of the cases, the threshold voltage for PDLC display is given by [7,23]

$$V_{th} = \frac{d}{3 \times a}\left(\frac{P_{\mathrm{P}}}{P_{\mathrm{LC}}} + 2\right) \times \left(\frac{\mathrm{K}(l^2 - 1)}{\Delta\varepsilon}\right)^{\frac{1}{2}}, \tag{1}$$

where d is the cell thickness, Pp and P_{LC} are the resistivites of polymer and liquid crystal, a and l are major axis and the aspect ratio (major dimension/minor dimension) of liquid crystal droplet (with the assumption that it is an ellipsoid), K is the elastic constant, and $\Delta\varepsilon$ is the dielectric anisotropy of the liquid crystal. It is also shown that the rise time T_R and the decay time T_d for an elongated droplet of an aspect ratio l should be given by [24]

$$T_R = \frac{1}{\gamma_1}\left[\Delta\varepsilon \times V^2 - \frac{K(l^2 - 1)}{a^2}\right], \tag{2}$$

$$T_d = \frac{\gamma_1 \times a^2}{K(l^2 - 1)}, \tag{3}$$

where γ_1 is the rotational viscosity of liquid crystal. The analysis of Equation [1] indicates that the threshold voltage (V_{th}) can be reduced by controlling various factors, such as film thickness and the resistivity ratio, increasing the size of the droplets. However dielectric studies of various PDLC composite materials have clearly indicated that the increasing $\Delta\varepsilon$, the dielectric anisotropy, by varying the frequency of applied signal, play a major role in lowering the operating threshold voltage [9,12,25–28].

Figures 7 and 8 show the typical response curves of transmittance for the PVB/E44 (50/50, 40/60, 30/70% w/w) and PMMABA/E44 (40/60% w/w) composite films respectively with the application of an AC electric field at various high frequencies. In the case of low frequency range ($\leq$50 Hz) a periodic flicker of transmitted light with twice of imposed frequency overlapping the asymptote was observed. However, as in high frequency range ($\geq$50 Hz), the molecular orientation cannot follow a superimposed electric polarity change, and the transmittances output vary in a fashion of simple monotonic asymptote [12,13].

From Figures 7 and 8, it is observed that for both the composite systems the transmission at the fixed applied voltage increases gradually with increasing frequency, reaching maximum frequency near one 1 Kz, with the experimental conditions of 200 Vp-p and 28°C. Such electro-optical response of the composite to electric frequency may be related with partition of external field (E_{ext}) to matrix polymer (E_{p}) and LC domains (E_{LC}) [9].

The ratio of E_{LC} to E_{p} in a composite film can be expressed by [9,28–30]

$$\frac{E_{\mathrm{LC}}}{E_{\mathrm{P}}} = \frac{|\ \varepsilon^{*}_{\mathrm{P}}\ |}{|\ E^{*}_{\mathrm{LC}}\ |} = \left[\frac{(\omega^2\varepsilon^2_{\mathrm{P}} + \sigma^2_{\mathrm{P}})}{(\omega^2\varepsilon^2_{\mathrm{LC}} + \sigma^2_{\mathrm{LC}})}\right]^{\frac{1}{2}}, \tag{4}$$

Where E, ε^* ε', ω, and σ are the amplitude of external electric field, complex and in phase components of dielectric constant, angular frequency, and conductivity, respectively. Equation (3) clearly indicates that at low frequency the ratio of the local electric field, ($E_{\mathrm{LC}}/E_{\mathrm{P}}$), is inversely proportional to the conductivity ratio ($\sigma_{\mathrm{P}}/\sigma_{\mathrm{LC}}$), whereas at the high frequencies it is inversely proportional to the dielectric constant ratio ($E'_{\mathrm{P}}/E'_{\mathrm{LC}}$). Since in general the magnitudes of these two ratios in composite are unbalanced in nature ($\sigma_{\mathrm{P}}/\sigma_{\mathrm{LC}} \neq \varepsilon'_{\mathrm{p}}/\varepsilon'_{\mathrm{LC}}$), an interfacial polarization is induced at low frequency [9]. As now, the conductivity ratio of polymer to LC becomes much smaller than the dielectric constant ratio ($\sigma_{\mathrm{P}}/\sigma_{\mathrm{LC}}$), the magnitude of effective electric field in the LC droplet rapidly decreases in a frequency range below the relaxation frequency range of the interfacial polarization. The frequency dependence of the transmittance as shown in Figures 7 and 8 for both the composite systems may be attributed to the effective electric field (E_{LC}) in the LC domain. Since the effective field buildup decreases with increasing frequency it is observed that the threshold voltage (V_{th}) decreases with increasing frequency. Also, the

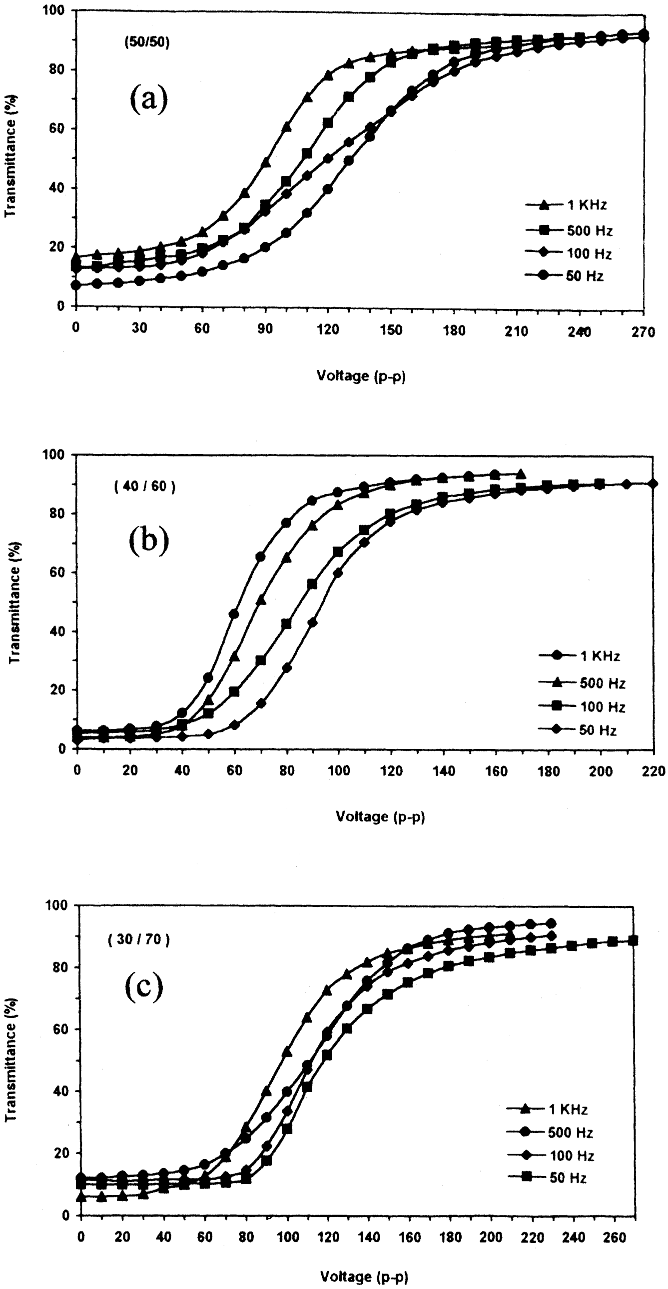


FIGURE 7 Applied voltage dependence of the light transmittance for the PVB/E44 (a) 50/50, (b) 40/60, and (c) 30/70% w/w composite films at different frequencies.

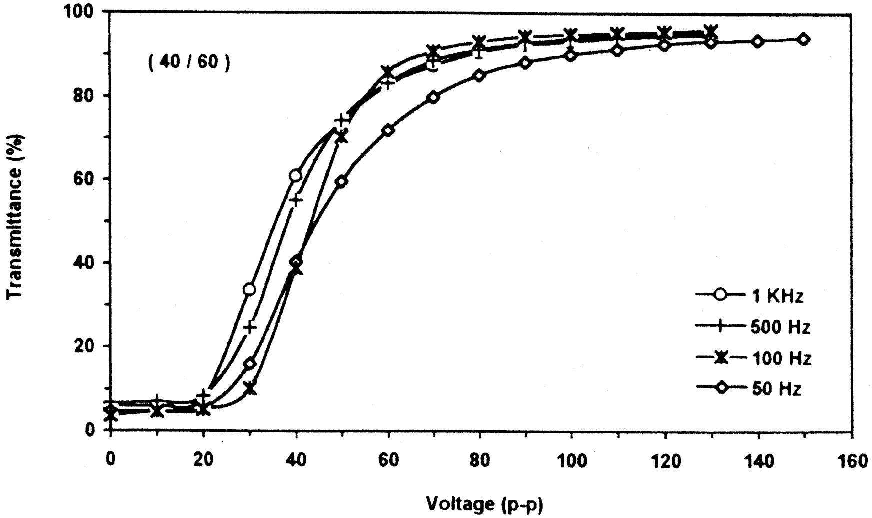


FIGURE 8 Applied voltage dependences of the light transmittance for the PMMABA/E44 40/60% w/w composite films at different frequencies.

V_{th}, defined as the voltage to raise the transmittance by 10%, is smaller for higher LC loading (say, from 60% to 70%), which is consistent with the polymer-LC series model [9,31] and composite with comparable droplet size bipolar configuration. Figure 9 shows polarized optical micrograph of both the composite systems viewed from the top of the film surface. The microscope-view was focused on a LC microdomain to ascertain the director configuration behavior. Both the systems show that the large domains are in bipolar configuration. In such cases with the large sections, the polymer-LC interfacial areas become smaller, leading to smaller total interfacial energy requirement for director alignment. These factors contribute physically to lower the V_{th} with increasing LC loading in composites. However, we observed that the PDLC films of PVB/E44 exhibit, in general, higher V_{th} compared to PMMABA/E44. It seems that with larger irregular elliptical LC droplets, the optical axis of LC droplets are distributed more randomly in PVB than in PMMABA, where the droplets are comparatively more regular in spherical shape (Figure 4). Thus the rotation of the bipolar axis and the reorientation of the LC molecules along the field occurs at higher V_{th} in PVB than in PMMABA. However, this may be one of the major contributing factors for such behavior. Taking into account the requirements of lower threshold voltage, one can select the 40/60% w/w composition as the most promising polymer/LC composition for PDLC preparation in both the systems.

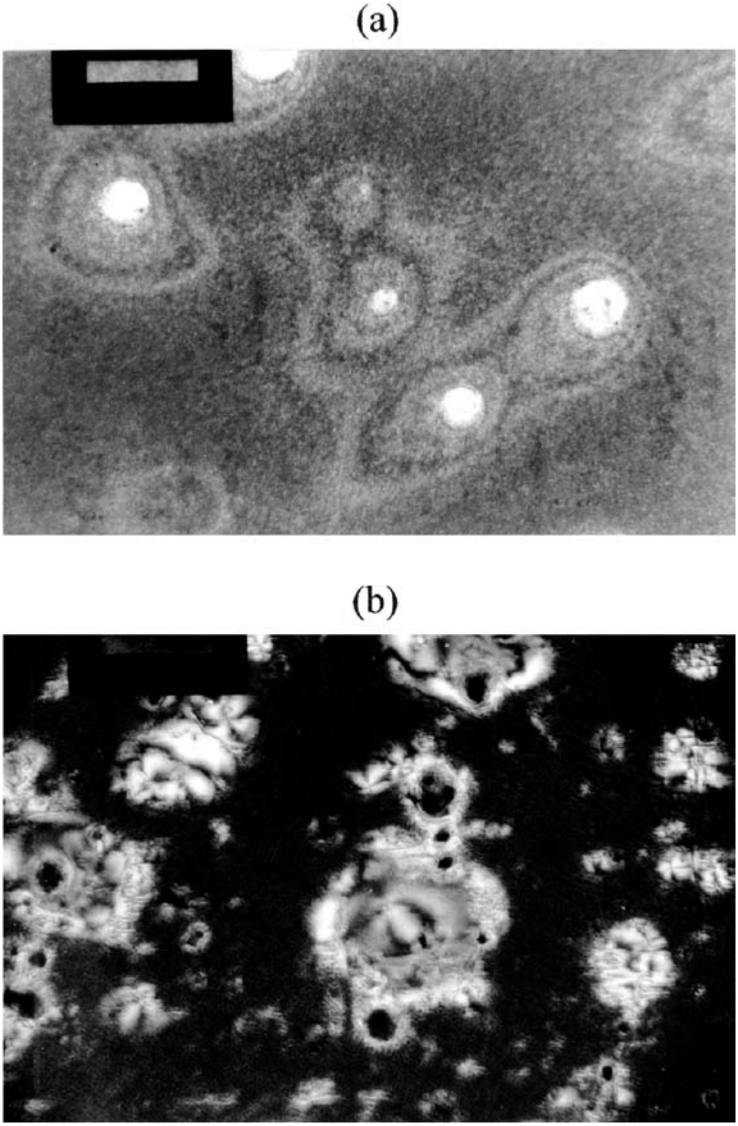


FIGURE 9 Director configuration of E44 droplets in the (a) PVB/E44 40/60 and (b) PMMABA/E44 40/60% w/w composite films observed under a microscope between crossed polarizers. (See Color Plate VI).

It is interesting to note that in the case of PMMABA/E44 composite, where the matrix polymer PMMABA is a copolymer of PMMA, the V_{th} is substantially reduced when compared to PMMA/E44 composite reported by Kajiyama et al. [9,29,30]. This may be basically understood in terms of the spatial distortion of the nematic director induced by the anchoring forces exerted from the nonparallel or curved matrix polymer walls. The electo-optical response of PDLC material originates in the orientational order of the LC molecules generally defined by the order parameters, S_s [31]. The sample order parameter S_s averaged overall droplets in the PDLC cell, which gives a measure of the alignment of the droplet directors with the assumption that the orientation distribution of the similar axes of droplets is uniform is expressed by

$$S_S = \frac{1}{4} + \frac{3(e^2+1)}{16\ e^2} + \frac{3(3\ e^2+1)(e^2-1)}{32\ e^3} \ln\left|\frac{e+1}{e-1}\right|, \tag{5}$$

where e is a dimensionless electric field given by

$$e = \frac{E\ g(S_S)R_{\mathrm{eff}}}{\varepsilon}\sqrt{\Delta\varepsilon/k}, \tag{6}$$

and $g(S_S)$ is a dimensionless factor which describes the order to which the optical field is shielded by depolarization charge at the droplet-polymer interface and is given by

$$g(Ss) = \frac{3\varepsilon_p}{\varepsilon_{\mathrm{LC}} + 2\varepsilon_{\mathrm{P}} - V_{\mathrm{LC}}(\varepsilon_{\mathrm{LC}} - \varepsilon_{\mathrm{P}})}. \tag{7}$$

Using Equation (7) we find g(0) = 0.60 and g(1) = 0.46 for PMMABA/E44 (40/60% w/w) composite, whereas it is g(0) = 0.68 and g(1) = 0.54 for PMMA/E44 (40/60% w/w). These results indicate that during the droplet orientation the applied field in PMMABA/E44 composite is comparatively less shielded by depolarization charge buildup at the droplet-polymer interface than in PMMA/E44 and thus has the important implication of lowering of V_{th} in PMMABA/E44 composite.

Response Time and Voltage

Figures 10 and 11 show the applied voltage dependence of the rise time (T_{R}) and decay time (T_{d}) at room temperature (28°C) only for the PVB/E44 (40/60% w/w) and PMMABA/E44 (40/60% w/w) composite films of 12 μm thickness, respectively. Under the experimental conditions of 1 KHz, AC electric field and 28°C room temperature, the T_{R} and T_{d} are only on an order of a few milliseconds for both the composite system. Here the T_{R} is defined as the time for transmittance change from 10% to 90% upon on

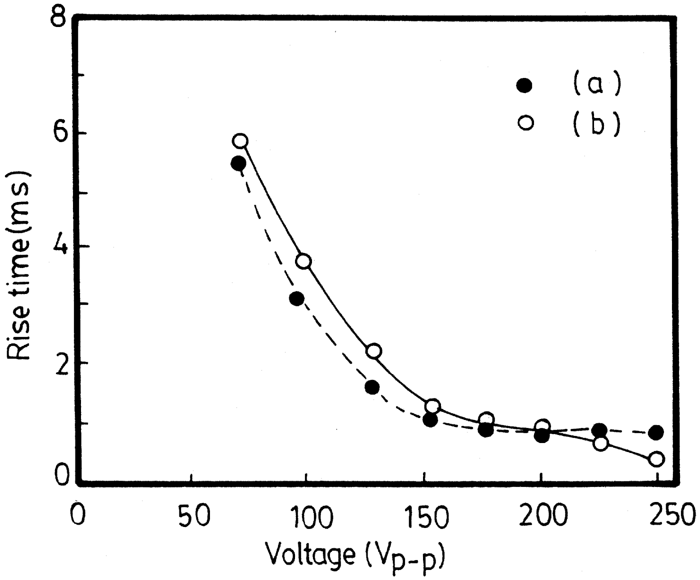


FIGURE 10 The measured rise time (T_R) vs. applied voltage of (a) PVB/E44 40/60 film and (b) PMMABA/E44 40/60% w/w composite films (thickness 12 µm) as a function of the applied voltage under the conditions of 1 kHz and 28°C.

electric field-ON. It is an important to note that T_R can be continuously controlled with voltage variation. A rapid response of about 4 to 5 ms and 2 to 3 ms for light transmission in composite films PMMABA/E44 (40/60% w/w) and PVB/E44 (40/60% w/w), respectively, is observed under the above-mentioned experimental conditions. The T_d, which is defined as a time period to decay to 10% of light transmission, is about 50 ms for PVB/E44 and 40 ms for PMMABA/E44 composite (at 28°C).

Rise time and decay time responses with voltage depend on the size, shape, and distribution of LC domains. The larger rise time (T_R) for PMMABA/E44 than PVB/E44 composite may be attributed to its smaller LC domain size, where more LC molecules are tangentially anchoring on the matrix polymer wall. As expected, the smaller decay time (T_R) obtained for PMMABA/E44 supported the LC domain size dependences of decay time. Additionally, from the shape of the decay curve (Figure 11) it seems that the rotation of the bipolar axes and the complete reorientation of the LC molecules along the field occur at higher driving voltage (>100). For example, Figure 12 shows the reversible turbid and transparent changes of PVB/E44 (40/60% w/w) composite film (thickness 12 µm) prepared by bar-coating method corresponding to OFF-(a) and ON-(b) 1 kHz AC electric

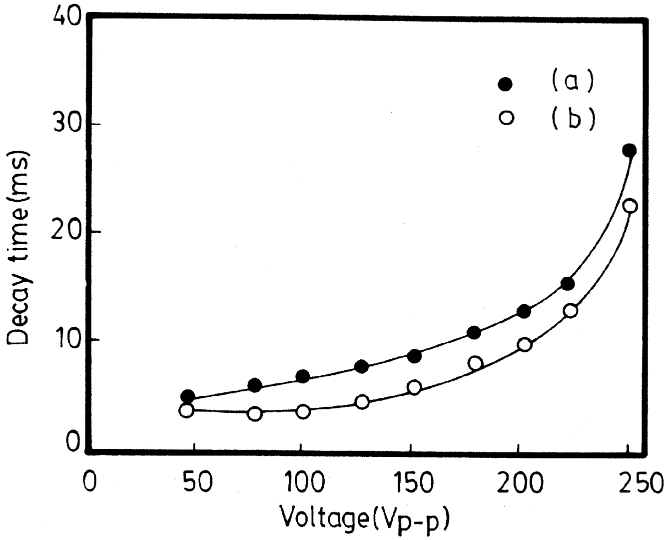
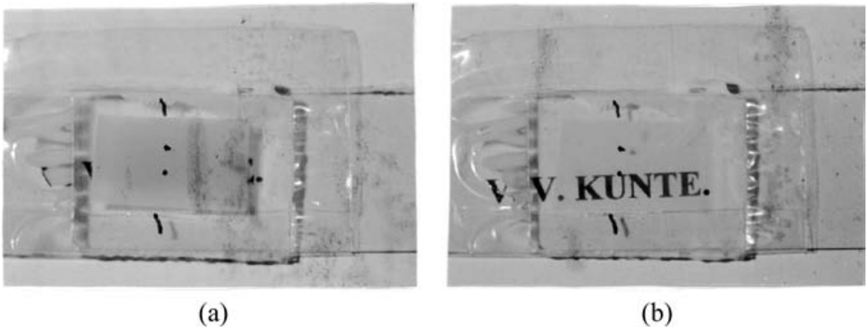


FIGURE 11 The measured decay time (T_d) of (a) PVB/E44 40/60 and (b) PMMABA/E44 40/60% w/w composite films (thickness 12 μm) as a function of applied voltage under the conditions of 1 KHz and 28°C.

field with 200 Vp-p, respectively. As remarkable light intensity control of the PVB/E44 composite film was observed, the film can be used as a display device. A similar display device was made for PMMABA/E44 composite film.



(a) (b)

FIGURE 12 Reversible turbid and transparent changes of the PVB/E44 (40/60% w/w composite film (thickness 12 μm) upon (a) OFF- and (b) -ON under the conditions of 1 KHz AC electric field with 200 Vp-p. (See Color Plate VII).

During the study of the response times of various PDLC films as a function of the applied voltage, it is observed that the PMMABA/E44 films in general exhibit hysteresis effect where the PDLC composite films from PVB/E44 show memory effect. Figure 13 shows the hysteresis effect, observed in PMMABA/E44 (40/60% w/w) composite at various frequencies of an increasing and a decreasing applied voltage. These effects were seen even when the voltage was varied very slowly. The basic reason of hysteresis in nematic droplet dispersed polymer films has been the topic of several discussions [32–34]. It has been suggested that the hysteresis might be due to possible defect movement in a droplet [32–34]. However, during their video-microscopy observations Reamey et al. [32] have observed that the hysteresis may be related to the mechanism of orientation of the droplet director [31] which ultimately may depend on the LC/polymer compatibility induced interfacial polymerization [15]. However, out of many studies reported in the literature, it has been observed that apart from the type of polymer and liquid crystal used, the shape, size and density of the droplet cavities, and the film thickness, a number of other factors influence

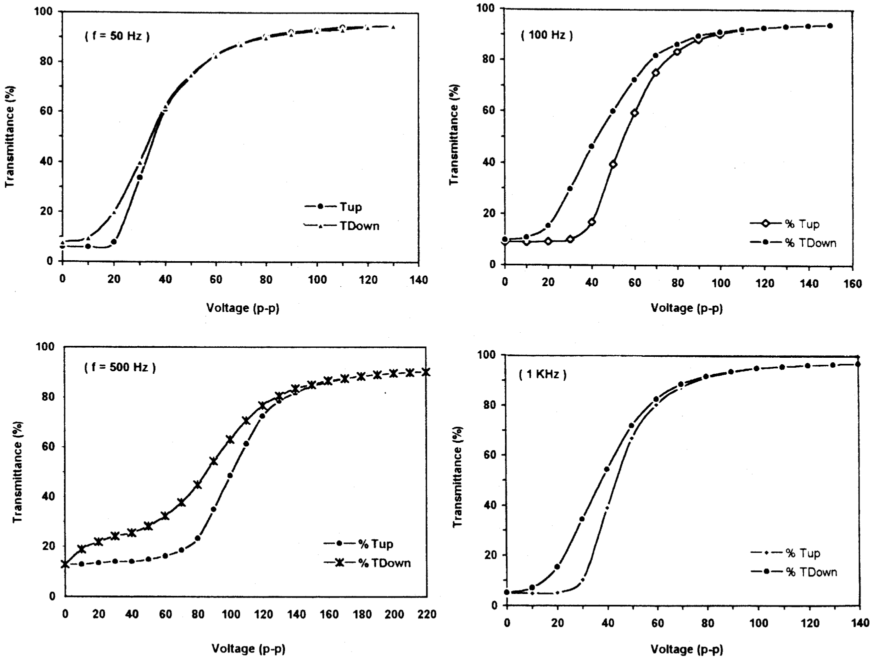


FIGURE 13 The applied voltage dependence of the light transmittance with hysteresis for the PMMABA/E44 40/60% w/w composite film (thickness 12 μm) at different frequencies.

the electro-optical response of the PDLC, including the resistances and dielectric properties of the polymer and nematic liquid crystal and anchoring properties of the LC at the polymer interface [7,35–39]. To measure experimentally the effects of each of these parameters on the electro-optic response of PDLC, it is very difficult to change independently any one parameter. In the present case we discuss here the relationship between the phase mixing at the polymer-LC interphase and observed switching hysteresis and memory effect in PMMABA/E44 and PVB/E44 films, respectively.

In the PMMABA/E44 composite, the degree of the hysteresis becomes more apparent with increasing electro-optical switching frequency (50 Hz) or short-range of reciprocating period. $(\mathrm{T}_S = \frac{1}{f}H_Z)$ (0.05 S) as shown in Figure 13, may be understood in terms of the retardation of the LC molecular reorientation [27]. However, in the higher frequency range (in present case >50 Hz), the electro-optical response of LC molecules is strongly governed by the degree of the LC-polymer two-phase miscibility, which influences the distribution of relaxation time for an interfacial polarization process. In the present case the limited miscibility between two phases (PMMABA and E44) has been confirmed from a lowering of the glass transition temperature (T_g) of PMMABA in PMMABA/E44 composite (Figure 14). Additionally, the phase-mixing behavior at the interface of the composite has been experimentally evaluated using FT-IR–ATR spectra. An absorption peak at 2226 cm^{-1} corresponding to $\mathrm{C{\equiv}N}$ stretching was observed (Figure 15) even after E44 was removed with methanol from the PMMABA surface. This indicates PMMABA/E44 phase mixing at the inferface. Also, the intensity of the absorption peak at 2226 cm^{-1} increases with increasing E44-contacting temperature, suggesting that E44 penetrates into the contacting PMMABA film and the magnitude of penetration increases with increasing temperature. In such a situation of endothermic structural changes in composite, the interfacial mixing induced by dielectric loss energy lowers the optical heterogeneity [27], resulting in an increase in the light transmission upon an AC electric field ON-state. However, now during lowering of an AC electric field the recovery process of the original dielectric-structure lags behind to the applied electric field, resulting in a decrease in the intensity of the light transmittances, as shown in Figure 13. Thus it seems that interfacial structural changes induced by dielectric loss energy is one of the main origins for a hysteresis in an electro-optical switching of PMMABA/E44 composite.

Figure 16 shows transmission profile through PVB/E44 cell at 1 KHz frequency as a function of applied voltage. It is observed that, after reaching saturation voltage across the films, the composite films continue

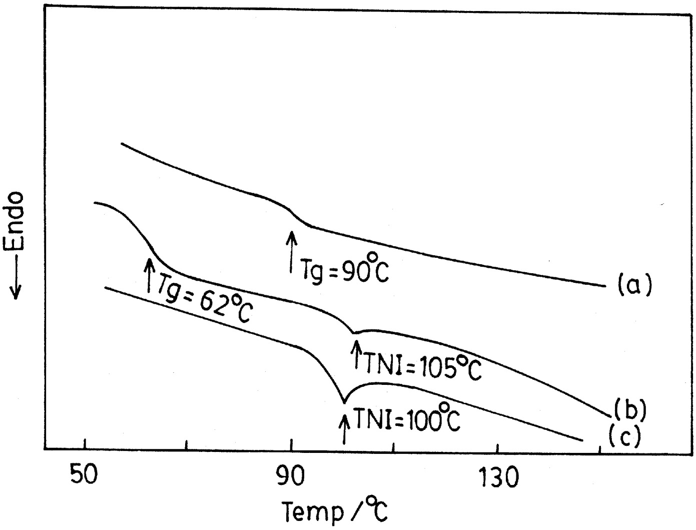


FIGURE 14 DSC thermograms of the (a) pure PMMABA polymer, (b) PMMABA/E44 50/50% w/w blend, and (c) pure E44 liquid crystal.

to show higher transmittance after the voltage application (memory State) than those in their initial OFF-state. In the memory state the transmittance of 50/50, 40/60, and 30/70% w/w PVB/E44 composition films is 60%, 40%, and 10% respectively. The memory states observed here are stable for long period of several moths at room temperature and can be erased by heating the cell to the clearing temperature of the E44 (100°C). These memory states may be attributed to the partial alignment of the LC molecules along the direction of the electric field even in the OFF-state [22]. In the present case, similar to PVB/E7 composites [18], the E44 loading lowers the T_g of PVB, sufficiently below the clearing temperature of E44. (for 40/60 PVB/E44 <28°C (R. T.)) Also, similar to PMMABA/E44 composites, the phase-mixing behavior was observed during the measurements of the FT-IR—ATR performed at the PVB/E44 interface. Thus, in the ON-state dielectric loss energy in composite would result in an endothermic structural change hindering recovery process to the original structure in OFF-state. These changes induce greater disorder of the bipolar orientation, which takes a longer time to create memory states. In such a situation, the increased PVB flexibility resulting out of the plasticizing effect in the composite, may allow the droplets on the chink structure to relax from irregular to a more regular domain shape [20,40—43]. This relaxation could result from the relief of stored up strain in the PVB.

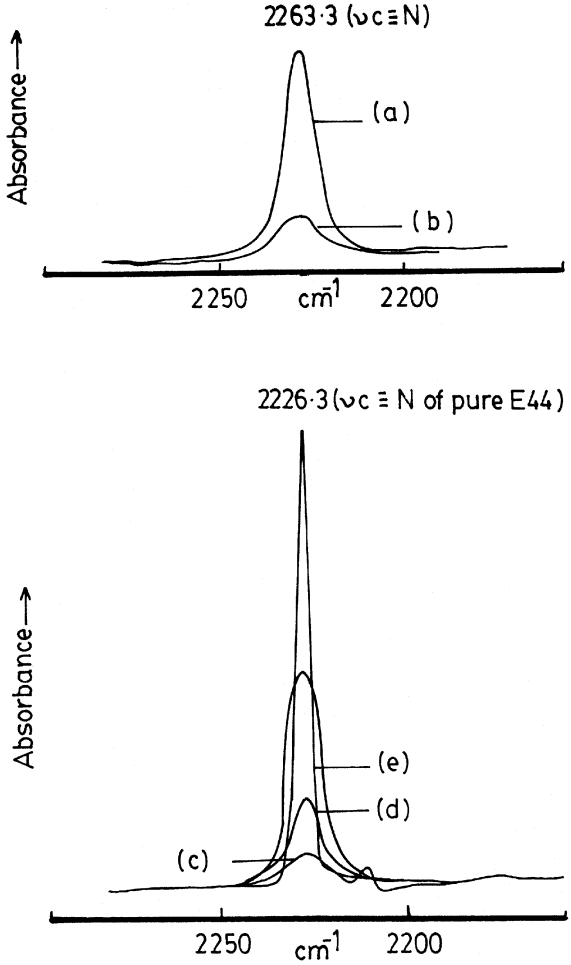


FIGURE 15 The FT-IR–ATR spectra of the C≡N stretching vibration taken for the PMMABA film surface (a) after surface contacting with E44 at room temperature (28°C) and (b) after removing E44 from the film surface by methanol washing. The spectra of PMMABA film surface after contacting the film with E44 at different contacting temperatures (c) 28°C, (d) 105°C, and (e) 115°C.

CONCLUSION

Aggregation structure, electro-optical properties, and the mechanism of light switching of PMMABA/E44 and PVB/E44 composite films have been discussed in this paper. The LC domains in these composite films are predominantly in the bipolar configuration. In PVB/E44 most of the

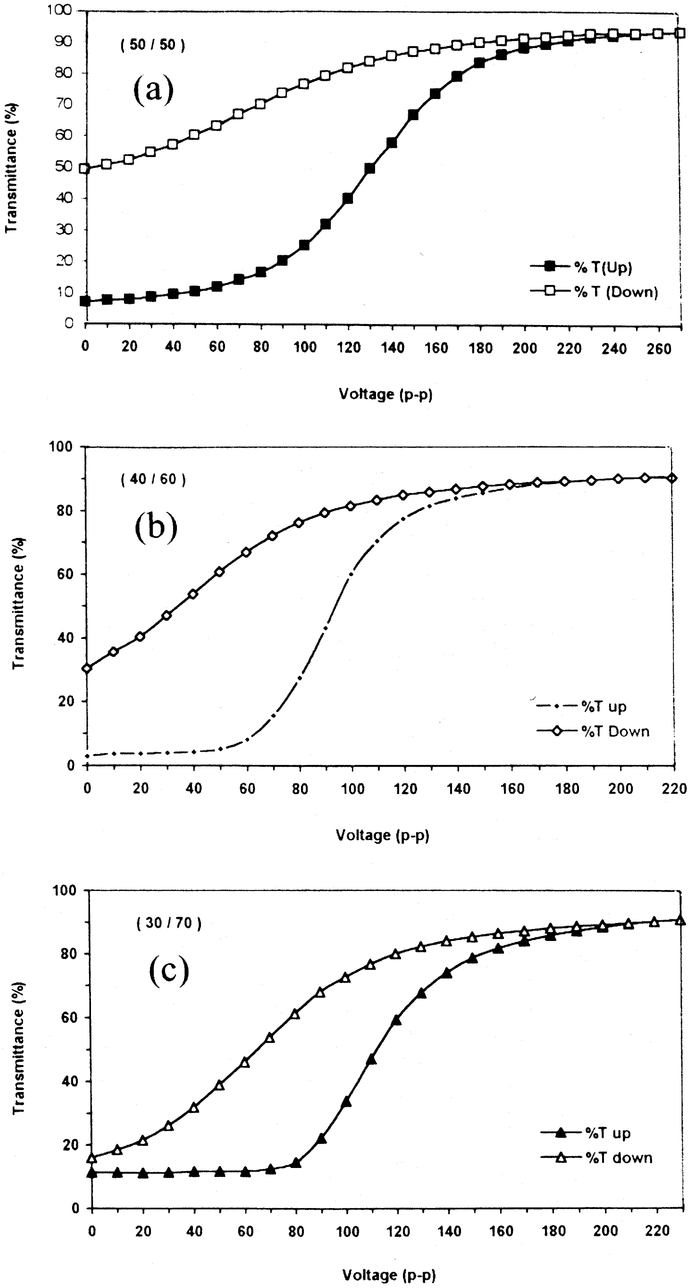


FIGURE 16 The applied voltage dependence of the light transmittance with memory for the PVB/E44 (a) 50/50, (b) 40/60, and (c) 30/70% w/w composite films (thickness 12 μm) at 1 kHz frequency.

chinklike structures are interconnected to form curved continuous channels where PMMABA/E44 composites exhibit interconnected, longer, irregular elongated droplet morphology. As droplet morphology contains more of tangentially oriented LC molecules on the wall in bipolar configuration, the PMMABA/E44 composite (40/60) exhibit higher and lower values of T_{R} and T_{d}, respectively. The electro-optical switching hysteresis and memory states observed in PMMABA/E44 and PVB/E44 composites, respectively, in the increasing and decreasing processes of an applied electric voltage depend on the applied electric field-induced interfacial mixing between matrix polymer and LC. The memory effects showing composites (PVB/E44) are promising candidates for optical storage, i.e., read and write devices, whereas hysteresis effects showing composites (PMMABA/E44) are useful for display applications where fast rise and decay of electro-optic response is required.

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