Effect of nematic liquid crystals on optical properties of solvent induced phase separated PDLC composite films

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Abstract

In the present article the effect of two different types of nematic liquid crystals on electro-optical and thermo-optical properties of polymer dispersed liquid crystal films are discussed. Composite films composed of polymer poly(methyl methacrylate) and two different nematic liquid crystals E7 and E8 were prepared by solvent induced phase separation technique. Scanning electron microscopy and polarizing optical microscopic results showed that liquid crystal phase is continuously embedded in a sponge-like polymer matrix. The domains of E7 were found slightly larger and more elongated than E8 under the same conditions of preparation. Variation of optical transmission properties of the composite films under the conditions of an externally applied alternating electric field (0-300 Vp-p, 50-1000 Hz) over a wide temperature range was studied using He-Ne laser (wavelength 632.8 nm) as a light source. The experimental results showed that the E7-polymer film has better electro-optical as well as thermo-optical properties as compared to the E8-polymer system. The performances of both the composites improved significantly with increasing temperature. It was found that the physical properties such as viscosity, refractive index and transition temperature of liquid crystals play a major role on the properties and behavior of the polymer dispersed liquid crystal composite films.

Keywords: Optical materials, Electro-optical, Liquid crystal, PDLC, Hysteresis.

1. Introduction

Thin composite films composed of polymer and liquid crystal (LC) are potentially useful for a variety of applications ranging from switchable windows to modern display devices. Polymer dispersed liquid crystal (PDLC) films are relatively new composite materials currently revolutionizing liquid crystal display (LCD) technology due to their excellent electro-optical features (Wu et al., 1987; Drzaic 1988; Drzaic & Muller 1989; Doane, 1990; Bowley & Crawford, 2000; Lee et al., 2001; Senyuk et al., 2005; Han, 2006). In a PDLC film, a liquid crystalline material is embedded in an isotropic polymer matrix in the form of droplets of micron to sub-micron size. The film is then sandwiched between two Indium Tin Oxide (ITO) coated transparent glass slides. The resultant assembly forms an electro-sensitive material that can be switched from a light scattering (OFF-state) to a transparent state (ON-state) by applying an external electric field or thermal gradient (Ren et al., 2001; Petti et al., 2001; Kayacan et al., 2007). A slight change in the chemistry, molecular architecture or type of the constituent elements leads to novel sophisticated properties. These interesting properties are attractive for fundamental research and practical applications involving phase modulators, variable attenuators, polarizers, light switches, flexible displays, smart windows etc. (Vicari, 1997; Maschke, 2002; Baek et al., 2003; Ramanitra et al., 2003; Lin et al., 2004; Buyuktanir et al., 2005; Liu & Wu 2005; Ren et al., 2005). The operational principle of these PDLC films is based on the optical microstructure heterogeneties and/or homogeneties produced due to LC droplets. A beam of light incident on a PDLC film may undergo different processes such as scattering, absorption and transmission to a degree modulated by the composition and spectral selectivity of the film. In PDLCs, if one uses LCs with positive dielectric anisotropy, i.e. $\Delta \varepsilon > 0$, the resulting device is highly scattering (or opaque) when no electric field is applied (OFF-state) and becomes transparent in the presence of an electric field (ONstate). The surface anchoring causes a non-uniform director field within these droplets and the film scatters light due to the mismatch between ordinary refractive index (n₂) of LC and refractive index of polymer (n₂) (Yang et al., 1992; Jain et al., 1993; Whitehead et al., 1993). The inherent randomization of nematic directors in LC droplets and mismatch of refractive indices causes high scattering of incident light in these devices. Various methods such as solvent-induced phase separation (SIPS), polymerization-induced phase separation (PIPS), thermally induced phase separation (TIPS) and encapsulation can be used to prepare PDLC films (Drzaic, 1995). In the current study, we have used the SIPS method where the LC and the polymer are dissolved in a common solvent to create a single phase. As the solvent evaporates, the LC phase separates into droplets or domains surrounded by polymer walls. The electrically driven switching properties of PDLC films strongly depend on their aggregation structure, which can be controlled by solvent evaporation rate and LC content during film preparation process (Montgomery et al., 1991; Kajiyama et al., 1993; Drzaic, 1995). In

fact, by controlling these experimental conditions, a wide variety of morphologies can be obtained, ranging from spherical droplets to continuous channels. The electro-optic responses of LC molecules are greatly dependent on the anchoring conditions of the LC molecules on the surface of the polymer cavity surrounding an LC droplet. However, considerable research is still needed to understand and optimize the properties of PDLC films for effective use in newer technologies. In order to fabricate displays, it is important to understand the properties of the device based on the materials employed. In this context, we present our results devoted to the preparation and optical characterization of PDLC films based on polymer poly (methyl methacrylate) (PMMA) and two different types of nematic liquid crystals E7 and E8.

Earlier studies on the effect of concentration of LC in polymer matrix indicated that a 70 wt% LC loading in polymer matrix was optimum (Deshmukh & Malik 2008a,b). Therefore, LC loading (70 wt%) has been kept constant in the present study. Here, the influence of physical properties such as refractive index, viscosity and phase transition temperature of LCs on the electro-optical properties of PDLC films are reported. These physical properties dictate aggregation structure and LC domain size in the PDLC matrix, which in turn influence the electro-optical properties such as threshold voltage, driving voltage and response time. The comparison of electro-optical and morphological data shows their correlation which enables us to find the morphology of samples most suitable for applications sought. Further, the optical and electro-optical responses of these films are studied as a function of temperature. The effects of temperature on electro-optical hysteresis have rarely been reported. Han (2003) studied the thermal hysteresis for PDLC film based on NOA61/E7 with low concentration of LC (E7) and the experimental results showed that PDLC films exhibited memory effects which could be erased by heating the film above the clearing temperature of LC. Consequently, this work is possibly a significant effort to investigate the thermal hysteresis effect in PDLC systems.

2. Experimental details

2.1 Materials

The nematic liquid crystals E7 (E. Merck, Japan) and E8 (E. Merck, Germany) used in this paper are a eutectic mixture of a number of cynophenyl derivatives with positive dielectric anisotropy. Poly (methyl methacrylate) (PMMA) ($T_g = 95 \text{ °C}$, $n_p = 1.4985$) was used as polymer matrix. Solvents used in this work are of HPLC grade purchased from Merck. The chemical structures of these materials are shown in Fig. 1 and the properties of the LCs used are listed in Table 1.

In the present study, these LCs have been selected for the following reasons:

- These systems of polymer-LC are suitable for the preparation technique employed.
- The ordinary refractive index of these LCs is close to the refractive index of the polymer chosen, and
- These LCs exhibit maximum miscibility with the polymer matrix to form a homogenous solution in the solvent.

	E7	E 8
n _o	1.5216	1.5270
n _e	1.7462	1.774
T _{NI}	61 °C	72 °C
Ell	19	22.1
ε _⊥	5.2	5.7
Viscosity [cSt]	40	54

 Table 1. Properties of LC mixtures

2.2 Preparation of PDLC films

In the present work, PDLC films have been prepared by solvent induced phase separation (SIPS) method (Deshmukh & Malik 2008a,b; Kajiyama *et al.* 1989; Kim & Ok, 1993). A 70 wt% of both E7 and E8 was dissolved with PMMA in chloroform (solvent) and the film was formed by spreading this solution over ITO-coated glass (with a surface resistance of 5.60 Ω) as a substrate at room temperature (25 °C). Both the composite films were prepared simultaneously to ensure identical preparing conditions. Another ITO-coated glass plate was used for sandwiching the PDLC films. An 18 μ m poly (ethylene terephthalate) (PET) spacer was used to control the film thickness. It was ensured that both the films were solvent-free before taking the measurements.

2.3 Morphology

Morphology of the PDLC composite films was observed using two different microscopy techniques. Dispersion of LC droplets in the polymer matrix and *in situ* observation in the presence of an applied electric field was viewed under crossed polarizers at a magnification of 40X through Olympus polarizing microscope, (model BX-53) fitted with charge coupling device (CCD) camera interfaced with computer. Further, for structural studies and continuity of LC channels, LCs were extracted from the films (at room temperature) using methanol, which is a non-solvent for PMMA and the films were then dried overnight before viewing under a scanning electron microscope (SEM) (Philips XL 30).

2.4 Electro-optical Measurements

The electro-optical properties of PDLC films were studied in terms of transmission changes using a driving AC field. The experimental system for these studies is reported elsewhere (Deshmukh and Malik 2008a,b). A collimated beam of He-Ne Laser (wavelength 632.8 nm with 10 mW power; Photochemical Inc. Canada Model 105P) was used as an incident light source. An AC

N

Fig.1. Chemical structures of the PDLC constituents (a) PMMA, (b) E7 and, (c) E8.





NC - - - C 5 H 11 45%

(c)

electric field was provided by amplifying the signal (50 Hz to 1 KHz square waves) from a function generator with a power amplifier and applying it to the conducting electrodes (ITO-coated glass plates). The voltage was increased in steps of 10 V from 0 V to 300 V during scan-up cycle to drive PDLC films and then decreased (scan-down cycle) in the same way to 0 V. Between all subsequent scan cycles the PDLC films were kept for 5 minutes in the OFF-state. The transmitted light intensity without any polarizer was measured in normal geometry through a photodiode (Jain-Laser Tech, India). A distance of 300 mm was maintained between PDLC cell and photodiode. The switching time response of the PDLC was measured using photodiode and its output was monitored with a digital storage oscilloscope (Tektronix TDS 430A, 400 MHz). The graphs were plotted using the average of three sets of readings and subsequently the variation is reported in terms of an error bar in the figures, wherever applicable.

3. Results and discussion

3.1 Morphology

The degree of light scattering in the absence of an applied field strongly depends on a number of factors such as the types of

materials used, their composition, casting solvent and on the details of film forming procedure (Doane, 1991; Vaz *et al.*, 1991). On the other hand, morphology of PDLC samples also influences the light transmittance properties in the presence of an applied field. In SIPS, shorter the evaporation time, lesser is coalescence, resulting in small LC dispersed domains. In the present case, films were prepared simultaneously under the same conditions to maintain identical rate of solvent evaporation.

The optical textures of the nematic LCs dispersed in rigid polymer matrix are shown in Figure. 2. A homogenous distribution of phase separated LC droplets can be clearly seen in both the composite films. We observed isolated spherical droplets, with few of them interconnected to form larger ones giving rise to a broad droplet-size distribution. It was seen that LC droplet sizes were relatively smaller ($\sim 4-6 \mu m$) in PMMA / E8 than those in the PMMA / E7 composite film ($\sim 6-8 \mu m$). However, the exact determination of domain size was difficult because of multiple overlaps across film thickness. Therefore, we employed scanning electron microscopy technique for better structural study of the composite films.

Fig.2. *Microscopic images in polarized light for* **(a)** *PMMA / E7 and* **(b)** *PMMA / E8 composite films.* **(c-d)** *represents the drop-let orientation under the influence of electric field (100 V, 200 Hz) at room temperature (25 °C) for PMMA / E7 and PMMA / E8 composites, respectively.* (a) (b)



Fig. 3 shows the SEM micrographs of PMMA / E7 and PMMA / E8 composite films (30/70 wt %) after removal of E7 and E8 with methanol for 24 hours. The extracting condition and continuity of LC domains in polymer matrix was proved sufficient as determined from a weight change upon extraction. The observation in the SEM micrographs is in good agreement with the POM images. It can be seen that for both the composites, PMMA forms a sponge-like structure in which E7 and E8 LC domains are continuously embedded. In fact with E7, which has less viscosity value, more LC domains are large and little elongated in comparison with E8 (more viscous compared to E7) where more spherical morphology can be seen. The difference is not very large though. This phase separation behaviour could be explained on the basis of the spinodal decomposition mechanism (Kajiyama *et al.*, 1993; Shen

& Kyu 1995). It should be noted that the LC domain size in the polymer/LC composite systems is affected by the solution viscosity of polymer and LC when the solvent evaporation rate is same during the formation process of each composite film, as in the present case.Now according to the spinodal decomposition mechanism, since the growth rate of each domain is higher in a less viscous medium, consequently the growth rate of E7 domains in PMMA during the formation process becomes higher as compared to PMMA/ E8 composite film. This larger size and elongation of droplets have a profound influence on the electro-optical properties as well as the final device performance.

Fig.3. Droplet morphologies of (a) PMMA / E7, (b) PMMA / E8 composite films.







3.2 Electro-Optical Responses

In the present work, PDLC films prepared using SIPS technique were opaque when no electric field was applied. This opaque state is a result of incident light scattering due to LC droplets whose preferential alignment directions are randomly oriented in the polymer matrix resulting in the refractive index difference (a) between a LC droplet and polymer, (b) between two adjacent droplets, and (c) within a LC droplet. When an external electric field having strength greater than the anchoring energy of polymer-LC interface is applied, LC directors reorient and start aligning themselves parallel to the applied field direction. This makes the refractive index of LC phase sufficiently close to that of polymer matrix causing the optical boundaries to disappear and making the film transparent.

An important property concerns the reorientation of LC molecules undergoing a force balance between the electric torque forcing their alignment along the field and the elastic torque opposing any movement of these molecules. Assuming no other force acting on the molecules, one can estimate the field necessary to orient these LC molecules in the droplet as (Drzaic 1995)

$$E \approx \frac{1}{R} \sqrt{\frac{K}{\varepsilon_0 \Delta \varepsilon}} \tag{1}$$

where *R* is the mean droplet radius, *K* is the mean Frank elastic constant of the medium, \mathcal{E}_0 is the free-space permittivity and $\Delta \varepsilon$ is the dielectric anisotropy of LC. It is important to state that the above equation presumea a spherical droplet under strong anchoring conditions. Equation (1) clearly shows that stronger the anchoring forces, higher is electric field strength required to orient the LC directors. Also, if the dielectric anisotropy is enhanced, the LC molecules orient with relatively low fields.

However, for an ellipsoidal droplet, the field becomes

$$E = \frac{1}{aL} \sqrt{\frac{K(L^6 - 1)}{\varepsilon_0 \Delta \varepsilon}}$$
(2)

where L = a / b represents the ratio of the major to the minor axes (also known as droplet aspect ratio). The switching or the threshold voltage (V_{tb}) which is defined as the voltage required for raising transmission of a PDLC cell by 10 % of the original transmission is

expressed as (Drzaic & Muller 1989; Wu et al., 1989)

$$V_{th} = \frac{1}{c} \frac{d}{R} \left(\frac{K(L^2 - 1)}{\varepsilon_o \Delta \varepsilon} \right)^{\frac{1}{2}}$$
(3)

where d is the film thickness, 1 / c is related to the effectiveness of electric field across droplets due to dielectric mismatch between the polymer matrix and LC droplets. Here, c is given by $3\varepsilon_p / (\varepsilon_{1,C} + 2\varepsilon_p)$.

Fig.4. Applied voltage dependences of the light transmittances for (a) PMMA / E7 and (b) PMMA / E8 composite films at different frequencies.



Fig. 4 shows transmittance as a function of applied voltage for both the PDLC composites at 25 °C. The transmittance in PMMA / E7 is almost unchanged with voltage up to 20 V after which it increases drastically. On the other hand, in case of PMMA / E8, this threshold field is around 30 V. A comparatively high value of V_{th} in PMMA / E8 film can be accounted on the basis of LC droplet morphologies in Fig. 2 & 3. Owing to the viscosity of polymer/LC solution during phase separation, it is apparent that domains of E8 have smaller dimensions than that of E7 and simultaneously, the number of E8 droplets interacting with the polymer wall increases. This requires a stronger external field to overcome the interfacial interactions of more LC domains formed in PMMA / E8 composite, contributing to a high threshold field.

As the amplitude of the applied signal increased further, more alignment (parallel to the electric field direction) is induced on the LC molecular directors resulting in the reduction of mismatch between the refractive indices of polymer matrix and LC domains. A complete or maximum matching of refractive indices takes place at higher voltage [(Fig. 2c-d), where LC droplets exhibited a well defined maltese type crosses)], resulting in maximum value of light transmission. At this point, the scattering and/or transmission of incident light are dictated by the ordinary refractive index of LC droplets and refractive index of polymer. Since the ordinary refractive index of E7 ($n_o = 1.5216$) is nearer to the refractive index of polymer ($n_p = 1.4985$) as compared to E8 ($n_o = 1.5270$), PMMA/E7 shows better electro-optical properties. Thus, physical properties, viscosity and refractive index have substantial influence on the electro-optical characteristics of a PDLC film.

While performing the experiment with low frequencies (<50 Hz), a periodic flicker of light with twice the imposed frequency overlapping the asymptote was observed. However, in a high frequency range, the fluctuation of transmitted light was too small to be observed and the magnitude of transmittance was observed as a monotonous increasing curve. In this case, the time period of the applied field to change its polarity is shorter than that of the LC molecules to change from the homeotropic alignment to spontaneously random orientation (Kalkar *et al.*, 1999; Kalkar *et al.*, 2008; Deshmukh & Malik 2008a). For both the samples, applied field was driven by a square wave with frequency varying from 50 Hz to1 KHz and it was found that 200 Hz is the optimum frequency, above which the transmittance characteristics are more or less the same.

Fig. 5 shows the scan-up and scan-down process dependence of transmission for the two PDLC composite films. It can be

clearly seen that both the composites exhibit hysteresis effect where the optical transmission during scan-down cycle is comparatively higher at all the voltages. These effects were seen even when the applied field was decreased very slowly. The hysteresis observed in PMMA / E7 composite film is almost negligible, whereas in PMMA / E8 it is more apparent.

Various sources are known to cause hysteresis (Drzaic, 1988; Reamey *et al.*, 1992; Kalkar & Kunte, 2002). It has been suggested that hysteresis might be due to possible defect movement in a droplet (Drzaic, 1988; Reamey *et al.*, 1992) which may ultimately depend on the polymer/LC compatibility induced interfacial polymerization influencing the relaxation time distribution in the droplets. Kalkar *et al.* (2002) have observed that interfacial structural changes induced by dielectric loss energy may be one of the main reasons for hysteresis where the original dielectric-structure always lags behind the applied field. It is well known that when a PDLC film is driven to ON-state, the actual field that appears across the LC droplet gets strongly masked by the space-charge buildup at the polymer-LC interface due to differences in their electrical conductivities (Jain *et al.*, 1993; Wu *et al.*, 1989). Now, on field removal, the LC molecules orient to their initial state in the presence of an additional electric field due to space charges and thus show higher transmission at each voltage level during scan-down cycle. The observed hysteresis in our samples might be due to the residual electric charge left which serves as a capacitor during the scan-down cycle.

Fig.5. Hysteresis curves for (a) PMMA / E7 and (b) PMMA / E8 films at 200 Hz.



Another decisive factor for the evaluation of film performance is its dynamic response to an applied field. It generally depends on the relative strength of the applied field and the elastic reorientation forces. We measured the response time (RT) of our samples as a function of the applied electric field. Rise time (T_R) is conventionally defined as the time required for transmittance to change from 10 to 90% when electric field is applied across a PDLC film, and decay time (T_D) as the reverse of T_R , is measured upon removal of applied field. T_R and T_D can be calculated by Eq. (4) and Eq. (5), respectively (Wu *et al.*, 1989)

$$\frac{1}{T_R} = \frac{1}{\gamma_1} \left[\Delta \varepsilon \times V^2 - \frac{K(L^2 - 1)}{a^2} \right]$$
(4)

$$T_d = \frac{\gamma_1 \times a^2}{K(L^2 - 1)} \tag{5}$$

where γ_1 is the rotational viscosity of liquid crystal, *a* is the major dimension of LC and V is the applied voltage and other symbols bear the same meaning defined earlier. Response time is the summation of T_R and T_D . The experimental results for rise time are displayed in Fig. 6. The measurements show that the responses were very good when V is higher than 50 V. This result is in good agreement with the transmittance–voltage curves shown in Fig. 4. Eq. (4) clearly indicates that T_R is dominated by applied field and it decreases as the voltage is increased. Also, it is observed that the composite with E7 shows smaller T_R as compared to the composite with E8. This is due to the low viscosity of E7 and larger E7 domains resulting in smaller interfacial area.

However, interestingly it was observed that up to an applied field of 70 V, the rise time for E7 is higher as compared to E8. This is because, up to 70 V, during rise time measurement, there is a considerable difference between the transmissions of both the composite films (Fig. 4). At a particular applied field value, the higher transmittance of composite with E7 requires much more

alignment of LC droplets which in turn takes more time compared to the composite with E8 LC droplets. With an applied field of 80 V or more, the transmission difference reduced greatly and the rise time now measured is for almost the same value of transmission achieved by both the composite films which completely depends on the LC domain size. The rise time values of our samples are only a few milliseconds indicating a fast switching of the nematic directors.

Measurements of decay time (T_D) as a function of applied field are displayed in Fig. 7. In both the composites, decay time increases with applied voltage probably due to the more perfect alignment of nematic directors along the field direction at higher voltages. This requires greater restoration energy for the nematic director upon field removal resulting in overall slow relaxation process at higher voltages. Similar trend was also reported earlier (Petti *et al.*, 2001; Kim & Ok, 1993; Kalkar *et al.*, 2008; Pan *et al.* 1997; Choi *et al.* 1993). However, the reason given by these researchers is mainly dependent on the Eq. (4), which does not have voltage term at all. We believe that more emphasis should be given to find the contribution of voltage in this phenomenon as the space charges are induced due to the residual electric fields at the interfaces. Notably, T_D for E8 is smaller than E7 and this is more likely due to the smaller dimension of E8 domain morphology in PMMA (Fig. 2 and 3) resulting in stronger polymer/LC interactions facilitating faster randomization of nematic directors. Moreover, it is clear from Eq. (5) that T_D depends on LC domain shape and size. Since the aspect ratio (L) is not far from unity, T_D should be much more sensitive to a^2 than to $1 / (L^2 - 1)$ and hence composites with larger LC domains should have comparatively high value of decay time.





Fig.7. Decay time vs. applied voltage for (a) PMMA / E7 and (b) PMMA / E8 composite films.



3.3 Temperature Dependence of electro-optical responses

Apart from the concentration of LCs in polymer matrix, LC domain shape and size, another dominant factor affecting the optical transmittance properties of PDLC composite films is the temperature. Fig. 8 shows the effect of temperature on the OFF-state transmittance of the films. It is observed that transmittance of both the PMMA / E7 and PMMA / E8 films increases with temperature to a level corresponding to the nematic-isotropic (NI) transition temperature (T_{NI}) of their respective LC components. This increase in OFF-state transmittance with temperature is caused by the decrease in birefringence (Δn) of LC (Doane 1990; Vaz and Montgomery 1987) and an increase in solubility of LC in polymer phase. The extraordinary refractive index (n_e) decreases, and ordinary refractive index (n_e) increases with increasing temperature resulting in an overall decrease in birefringence ($\Delta n = n_e - n_o$) as (Pohl & Merck, 1990; Coates *et al.*, 1990)

$$\Delta n \propto \left(1 - \frac{0.98T}{T_{NI}}\right)^{0.22} \tag{6}$$

where T is the absolute temperature and T_{NI} is the nematic to isotropic transition temperature of LC. As temperature increases, the solubility of the LC in polymer also increases.

It is interesting to see that for both the composites, transmittance is almost constant up to a certain temperature, known as the critical temperature (T_c), after which it increases abruptly. It was also seen that for PMMA / E7 and PMMA / E8 composite films (with 70 wt% of both E7 and E8), the value of T_c is in close proximity to the nematic-isotropic temperature of the LCs used. Transmittance was constant above T_{NI} since refractive indices of isotropic LC and polymer are almost independent of temperature.

Fig.8. Effect of temperature on OFF-state transmittance for (a) PMMA / E7 and (b) PMMA / E8 composite films



Fig.9. Optical Transmittance vs. applied voltage at various ambient temperatures for (a) PMMA / E7 and (b) PMMA / E8 composite films.



Fig. 9 shows the temperature dependence of electro-optical transmission properties for the composite films. The observed decrease in V_{th} with increasing temperature for the films can be qualitatively explained in terms of Eq. (3). It is known that the effective elastic constant K and dielectric anisotropy $\Delta\epsilon$ of a nematic liquid crystal are strongly dependent on the temperature. According to mean-field theory proposed by Maier and Saupe (Maier and Saupe 1960), K is proportional to the square of order parameter S and $\Delta\epsilon$ is proportional to S. If only temperature-dependent terms are considered in Eq. (3), then V_{th} is directly proportional to (K / $\Delta\epsilon$)^{1/2}. Now, with increasing temperature, the order parameter S of liquid crystals decreases strongly reducing V_{th} , and hence, the transmission becomes a characteristic of lower voltages.

Fig.10. Hysteresis curves at various temperatures for (a) PMMA / E7 and (b) PMMA / E8 composite films.



One of the interesting properties of PDLC films is hysteresis. This effect has been studied and well understood where applied electric field is increased and decreased systematically. However, thermal hysteresis has rarely been reported in literature and needs more systematic study. Therefore, it was thought necessary to study the thermal hysteresis at various temperatures. The thermal hysteresis effects of composites are shown in Fig. 10. Here we see that the hysteresis for these curves extends to zero field.

The OFF-state transmittance after scan down cycle does not return to its original scattering state and both the films retain some portion of the saturating transmission even after removal of applied field. This phenomenon is known as persistence (Drzaic 1995; Deshmukh & Malik, 2008). Unlike memory effect, where a film is in a particular transmission state indefinitely or unless heated above $T_{\rm NP}$ the film in persistence requires some time to relax to the original OFF-state. In the present study, both the PDLC samples showed relaxation time of 1 to 2 minutes for applied electric field above room temperature. It can also be observed that, as the temperature increases, the persistence gap (i.e. the difference in the intercept of scan up and scan down cycles on Y axis for a given temperature as shown in Fig. 10) also increases. This effect is more predominant in case of E7 system. This may be due to the presence of polarization fields at higher temperatures which align the liquid crystal molecules even after field removal. We can, therefore, argue that these experimental changes can be due to a synergetic action of both applied field and temperature. Nevertheless, the understanding of persistence in PDLCs needs careful study as the relation between electric field and temperature alone cannot justify the phenomenon.



Fig.11. Rise time vs. applied voltage at various temperatures for (a) PMMA / E7 and (b) PMMA / E8 composite films.

The rise time T_R of the PMMA / E7 and PMMA / E8 composites as a function of both applied field and temperature is shown in Fig. 11. It follows that at any given voltage, T_R decreases with temperature. This decrease in rise time is due to the decrease in rotational viscosity of LC, affecting its interfacial interaction with the matrix polymer. According to Wu's model (Wu *et al.* 1989) for large voltages, T_R is approximately proportional to $\gamma_1 / \Delta \varepsilon$ and the dependence of rise time on temperature can be given as $T_R V^2 T^{1.5}$ = constant.

The results given in Fig. 11 show this correlation to some extent. For PDLC composite films, besides the strength of anchoring, T_R is also affected by the dimension of LC domains. In the present case, at any given value of applied field at various temperatures, T_R is always smaller for E7 compared to E8 predominantly due to larger LC domain formation in the former one (Fig. 2).

The temperature dependence of decay time for the composite films is shown in Fig. 12. An increase in T_D with increasing temperature for both the films supports the fact that T_D strongly depends on temperature. On the other hand, Eq. (5) indicates that decay time T_D is approximately proportional to γ_1 / K. However, the increase of T_D is not properly related to the decrease in K of LC as γ_1 also decreases with increasing temperature. In fact, T_D depends on a time constant by simply letting V=0 in Eq. (4) and according to Wu's model (Wu *et al.* 1989), its dependence on temperature can be given as $T_D T^{0.8}$ = constant. Therefore, the observed increase in T_D with increase in temperature may be understood in terms of enhanced thermal agitation dominating over the intermolecular interactions which produces randomization of nematic directors causing a delay in the orientation of LC directors from aligned state to their original random state (Parab *et al.*, 2012). It can also be seen that E7 domains take a longer time to decay and return to their original scattering state as compared to E8 LC domains. This observation again supports the LC domain shape and size dependence of T_D as in Eq. (5) where smaller dimension morphology in polymer matrix results in greater restoration energy of nematic directors to their random original state. This is also in good agreement with Fig. 10 where we have observed more persistence for E7 having low viscosity as compared to E8.





4. Conclusions

In the present study the electro-optical properties were investigated for PDLC films composed of E7 and E8 nematic liquid crystals dispersed in PMMA matrix polymer using SIPS technique. With 70 % weight fraction of both E7 and E8, prepared films showed good light scattering in the OFF-state. Microscopic views of the phase-separation process revealed that the LC domains in PMMA at this composition formed continuous channels where domains of E7 were larger and slightly more elongated than E8. The PMMA / E7 composite film showed smaller threshold and driving voltages, high transmittance, lesser rise time and a higher decay time over a wide range of temperatures. Physical properties such as viscosity, refractive index and phase transition temperatures, of liquid crystals play a key role in the electro-optical properties of PDLC films. The behaviour of both the composites with applied electric field and temperature depends upon the physical properties of LCs as well as their domain shape, size and distribution in the polymer matrix. These results suggest that the interaction forces between the polymer surface and the liquid crystal molecules existing in large elongated domains should be smaller where a less electric field is required for the orientation of random nematic directors to their homeotropic alignment. Hence, by properly selecting the liquid crystal and polymer, one can manipulate the optical properties of the PDLC devices.

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