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STUDY OF CURING TEMPERATURE ON DYE DOPED POLYMER DISPERSED LIQUID CRYSTAL FILMS

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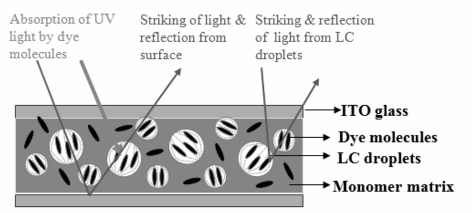
Dye doped polymer dispersed liquid crystal (D-PDLC) devices are alternative class of materials in smart windows that are renowned as polarizer-free colored devices. The present work has been performed on a dichroic dye S428 to investigate its electro-optical performance, LC droplets size variations while changing the various conditions such as the curing temperature (20-32°C), the LC contents (80wt%-75 wt%) and the dye contents (0.5wt%-1.5 wt%). It has been revealed that the electro-optical characteristics of both scattering colored state (OFF-state) and absorbing transparent (ON-state) depend on compositions and curing temperature independently. Moreover, the D-PDLC film fabricated at 32°C exhibited smaller LC droplets and turned ON at minimum threshold voltage (Vth) with higher contrast ratio (CR); regardless of the curing with higher percentage of dye (1 wt% - 1.5 wt%) and at low contents of LC (77wt%). Peculiarity in enhanced electro-optical properties of the film approved it, to employ such films in the large area display applications.



INTRODUCTION

Dye doped Polymer-dispersed liquid crystal (D-PDLCs) films are distinguished as colored devices in liquid crystal display. The following colored devices are famous in display applications such as flexible displays, projection displays, optical shutters, electrically switchable colored windows, in mobile device, electronic papers, decorative displays, electrically switchable curtains, and electrically controlled sun control films for automobiles and in homes or commercial buildings etc.[1-10] Consequently, these devices have higher reflectivity, wide viewing angle and low power consumption properties. The electro optical properties of such devices depend on several conditions for instance the composition, dichroic dye chemical behavior towards liquid crystals/ monomer mixture, curing temperature etc. Each of these methods yield D-PDLCs with diverse droplets morphologies and electro optical characteristics.[11-17] However, these the particular D-PDLCs have some limitations; essentially low contrast ratio (CR) at higher dye contents that associated with higher threshold voltage, high production cost due to higher consumption of LC and limited curing temperatures range. Following limitations are generally due to greater affinity of dye towards monomers and higher absorption of UV light by dichroic dye molecules.[18-21] Therefore, it is essential to seek a dichroic dye that can perform exceptionally at higher dye and lower LC contents.

In this attempt, the characteristics of barely investigated black dichroic black dye S428 doped in PDLCs with various compositions of dye, LC and monomers have been explored. Moreover, in this

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study, an effort has been made to examine the black dichroic dye S428 (supplied from Mitsui Chemical Co.) properties as D-PDLC at wider curing temperatures range. The aim was to find optimum temperature range to produce high contrast ratio, low threshold voltage (V_{th}, the minimum threshold voltage that requires to turn-ON the device from scattered OFF-state to transparent ON-state) with minimum LC and higher dye contents.

EXPERIMENTAL

In this work, D-PDLC devices are fabricated by sandwiching the mixtures of monomer PN393 (Merck, Seoul-Korea), liquid crystal TL203 (Merck, Seoul-Korea) and dichroic black dye S-428 (Mitsui) between the transparent indium tin oxide (ITO) coated glass plates with a 20µm cell gap thickness. PN393 is acrylate based commercially available monomer which consists of a cross-linker, a photo-initiator, and resin. The 2-Ethylhexyl acrylate has been used as the resin. The Darocur4265 (Ciba) has been used as a photo-initiator and trimethylolpropane triacrylate has been employed as the cross-linker in PN393. [20] Initially, the liquid crystal TL203 and dichroic black dye S-428 is mixed with various compositions. Next to this, PN393 is blended in the LC/dye composite with various combinations 20: 80, 23:77 and 25:75 by weight percentage, respectively. This compound is further filled inside ITO coated glass plates by capillary rise method. Further, D-PDLC device is fabricated with the polymer induced phase separation (PIPS) method. For the purpose, this composite is polymerized by flashing the UV light of 365 nm wavelengths with intensity of 1 mW/cm^2 for 20 minutes at various temperatures range between 20^{o}C - 32^{o}C.

Experimental Measurements

To cure the D-PDLC at various temperatures a hot stage with digital temperature control is used. To get a regular temperature on D-PDLC device, initially it is placed on the hot stage at controlled temperature for 5 minutes. For the polymerization of D-PDLC mixture, this device is radiated under the UV light of 365 nm wavelengths with intensity of 1 mW/cm^2 for 20 minutes. The surface morphologies of the D-PDLC films are viewed by polarized optical microscope (Olympus Model BX-60, Japan) at 20x magnification fitted with a digital camera connected to a computer. The electro-optical properties of D-PDLC device for instance the threshold voltage (V_{th}) and contrast ratios (CR) are observed at a range of temperatures e.g (20^{o}C to 32^{o}C and by changing the LC/monomer/dye contents. Minolta UV–Vis spectrophotometer (model UV-3500d, Japan) is used to evaluate the following electro-optical properties. For the purpose an un-polarized HeNe laser light at wavelength range λ = 400-700 nm is passed through this spectrophotometer. In order to observe the transmitted light intensity to find the contrast ratio and threshold voltages the D-PDLC devices are oriented normal to the laser beam and the space between the devices with the detector is set at approximately 38 cm. At the same time, the collection angle of the transmitted light is fixed at 0^o angle to detect the forward scattering. This instrument is adjusted using appropriate calibration standards.

RESULTS AND DISCUSSION

In order to acquire the optimal electro-optical properties of D-PDLC, it is essential to find the appropriate temperature and concentration for S-428 D-PDLC. Initially, three different combinations of LCs are selected for fabrication of S-428 D-PDLC; such as 80:20, 77:23, 75:25 wt% with respect to LC/PN393 monomer. In the following D-PDLC compositions, 1wt% of dye is added. In the next step, this composite is filled inside the ITO glass for fabrication of D-PDLC film. For curing, temperature range from 20^{o}C to 32^{o}C is selected with interval of 2^{o}C (degree Celsius). After curing, the surface morphologies of following D-PDLC devices are observed from polarized optical microscope (POM) at 20x magnification while the voltage is turned off. The morphologies observed from POM are displayed in Figure 1. Figure 1 shows an obvious increasing trend in droplet morphologies with the increase in LC contents 75wt%-80wt%. This increase in droplet size can be clearly seen at all temperatures. All of this, little coalescence in LC droplets is visible at 80wt% of LC contents while cured in a temperature range from 20-26^{o}C (Figure 1). Earlier, development of coalescences is noticed with deteriorations in electro-optical properties. Existence of coalescence is generally considered due to inadequate polymerization of monomer, possibly due to absorption of UV light by the dye molecules.[21] However to get the noticeable scattering of light at voltage off state it is essential to have smaller droplets size as compare to wavelength of scattered light.[6, 22-24]

Figure 1 displays a decrease in droplet size while curing D-PDLC from 20^{o}C to 32^{o}C for all compositions. Earlier, formation of the smaller sized LC droplets at high temperature is considered due to rapid polymerization of monomer matrix. Hence, less time is available for the droplet to reach the larger size formation.[25] However, D-PDLC fabricated with 80 wt% of LC shows coalescence of droplets even curing at higher degree of temperature. Moreover, D-PDLC fabricated with 75 wt% of LC contents shows very small sized LC droplets. Earlier very small sized LC droplets are associated with increase in threshold voltage due to an increase in intermolecular anchoring forces. Despite of this, formation of adequate size of LC droplets with minor sign of coalescence is observed for 77 wt% of LC contents. Consequently, appropriate electro-optical properties are expected for S428 D-PDLC as cured with 77 wt% of LC. Hence, the device fabricated with 77 wt% of LC contents is considered for further studies.

Based on earlier studies in D-PDLCs the higher dye contents that produced smaller droplets size with regular shape is considered responsible for enhanced light-scattering properties.[1,21,25,26] In order to achieve a high contrast D-PDLC various dye contents are utilize from 0.5 wt% to 1.5 wt% for fabrication of device with 77wt% of LC. The following devices later are cured under the UV light at various temperatures range. Figure 2 shows the POM images of following D-PDLC devices that are observed at 20x magnification. Figure 2 displays an increase in droplet size with increase in dye percentage. Moreover, Figure 2 demonstrate that D-PDLC with 0.5 wt% of dye curing at 22°C temperature exhibit smaller LC droplets size. However, a decrease in droplet size is observed as the curing temperature increases from 22°C to 30°C. Besides this, more uniform distribution in LC droplets size is noticed as the curing temperature reaches to 28°C for 0.5, 1.0 wt% of dye. Additionally, as the dye amount increases from 1.0 wt% the droplet size increased as well. However, with the increase in fabrication temperature from 22°C to 30°C the decrease in droplet size is seen. As described earlier, the smaller droplet size will lead to higher scattering in D-PDLC devices.[22] According to this a good electro-optical properties are expected from D-PDLC fabricated with 77 wt% of LC containing dye from 0.5wt% to 1.0 wt%.

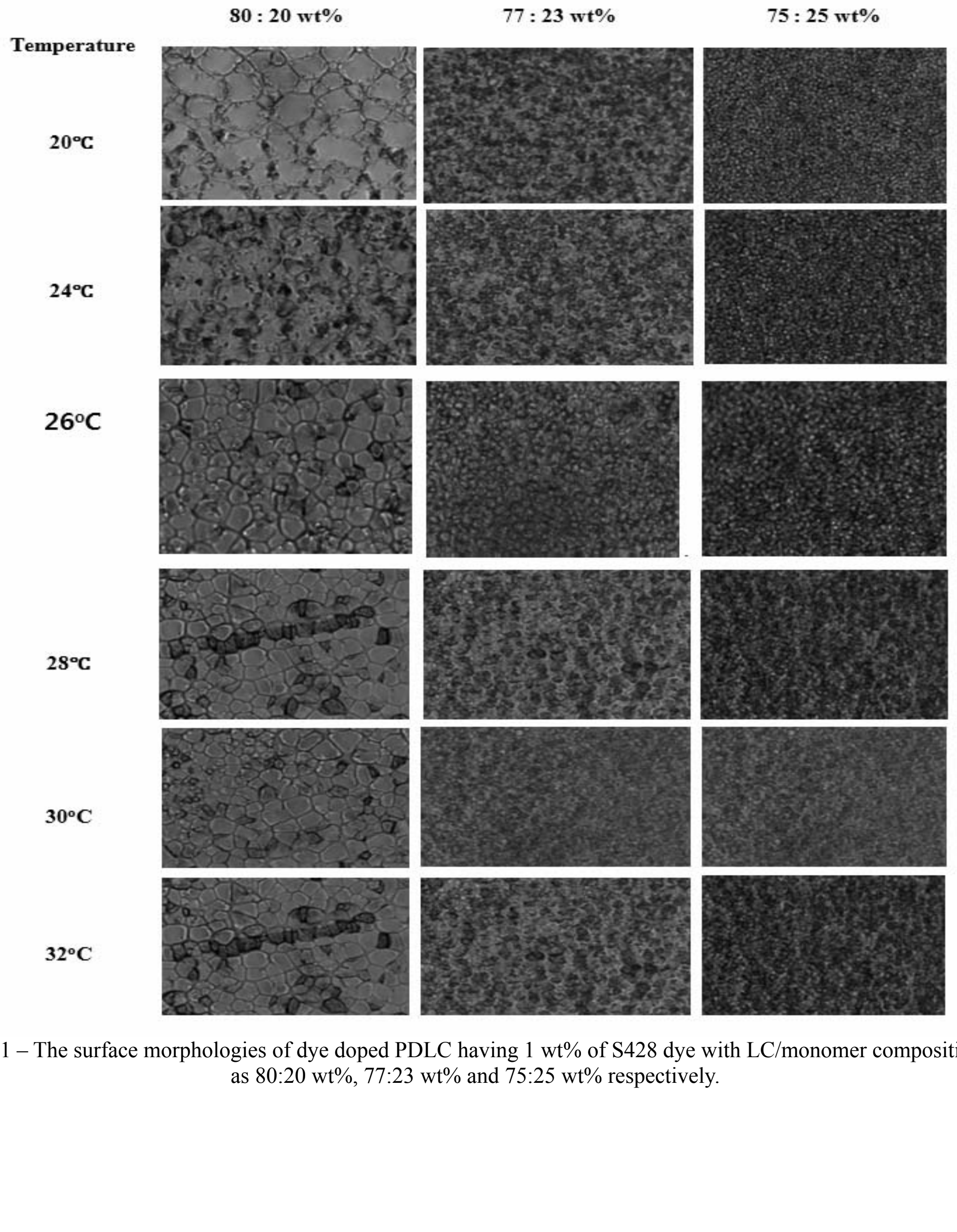

Fig. 1 – The surface morphologies of dye doped PDLC having 1 wt% of S428 dye with LC/monomer compositions as 80:20 wt%, 77:23 wt% and 75:25 wt% respectively.

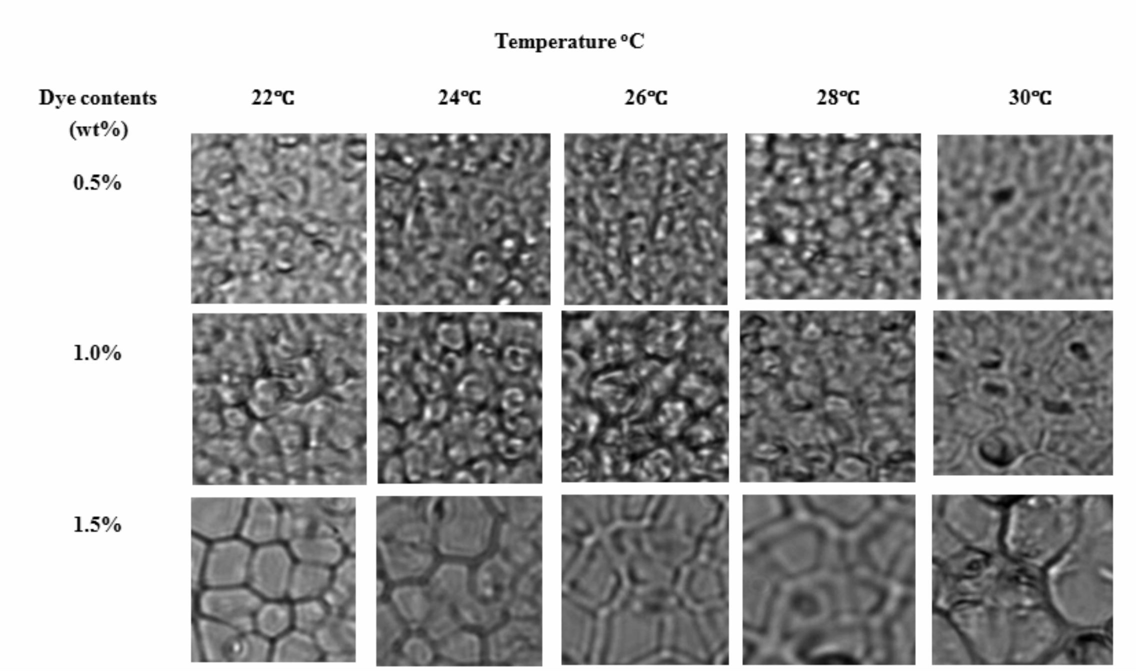

Fig. 2 – The POM images of dye doped PDLC fabricated with 77:23 wt% of LC/monomer while S428 compositions are remained as 0.5 wt%, 1 wt% and 1.5 wt% respectively.

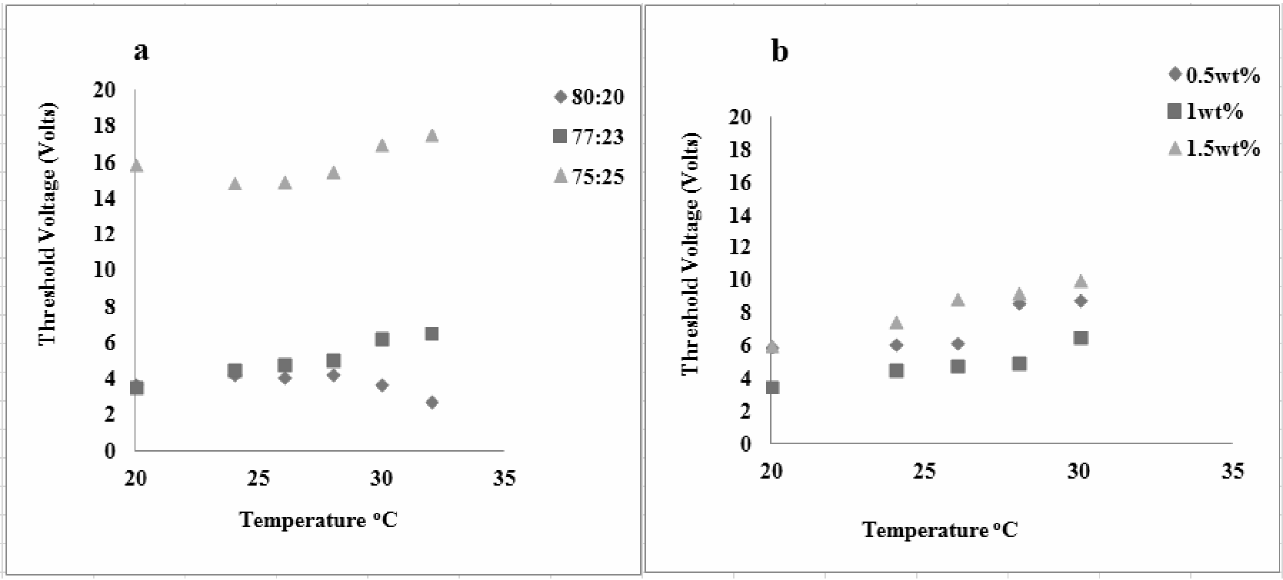

Fig. 3 – Electro-optical properties the threshold voltage of D-PDLC at various LC and dye compositions against varying the curing temperatures.

Electro-optical properties

To investigate the above stated D-PDLCs the different studies have been made which are described here. The electro-optical properties such as threshold voltage (V_{th}) and electro-optical contrast ratio (CR), of D-PDLC displays are significant to evaluate the work efficiency of such devices. Earlier, for bipolar LC droplets, an expression for V_{th} is explained as[12-13, 25] the minimum voltage that requires to turn On the device from scattered OFF-state to transparent ON-state.

$$V_{th} \propto \sqrt{\frac{k}{\Delta\varepsilon}} \qquad (1)$$

The threshold voltage (V_{th}) possibly depends on anchoring energies and intermolecular interactions forces as well as, on the elastic constant and dielectric anisotropy.[27] Whereas, the strength of anchoring energies and intermolecular interactions are mainly related with the droplet sizes. Generally, very small sized LC droplets observed strong anchoring with the surrounding surfaces of neighboring droplets as well as the walls of the polymer matrix.

The optical contrast ratio of a D-PDLC device is the ratio between the transmitted light at ON-state and OFF-state of voltages. It can be calculated as $CR=T_{ON}/T_{OFF}$. For large area display applications, a D-PDLC device with higher contrast ratio is required. To know the variations in V_{th}/CR with respect to ratios of materials and curing temperatures the threshold voltage and CR is determined and plotted in Figures 3 (a,b) and 4 (a,b).

Figure 3 (a) displays V_{th} for the D-PDLC devices fabricated with varying LC/monomer proportions while dye is remained fixed as 1 wt%. Similarly the Figure 3b shows that the V_{th} of D-PDLC with varying dye contents (0.5-1.5 wt%) having 77 wt% ratio of LC. The morphologies of the following devices are shown as above in Figure 1 and 2 respectively. Figure 3a displays the three curves for V_{th} of 1 wt% of dye against the varying temperatures. It shows that D-PDLC at minimum LC contents (i.e. 75 wt%) produce higher V_{th} at all observing temperatures. Initially, at 20^{o}C it showed V_{th} at 15.8 volts that further decreased for two consecutive temperatures (24-26^{o}C). A second increase in V_{th} is observed once the curing temperature reaches to 26 ^{0}C. Further, it touches the highest V_{th} values that are 17-17.5 volts. However, the D-PDLC cured for 77 and 80 wt% of LC ratios consumed minimum threshold voltage. Figure 3(a) shows the minimum threshold voltage in a range as 3.5-6.5 volts as temperature is increased from 20-32^{o}C for 77 wt% of LC contents. However, the D-PDLC device cured at 80 wt% of LC contents showed a further decrease in V_{th} to minimum 2.7 volts with increase in temperatures. Earlier, it is established that LC drives more voltage to align vertically towards the electric field, once the LC droplets are smaller in size. Possibly this is the reason that 75 wt% of LC contents drain more V_{th} voltages at all curing temperatures.

The Figure 3b shows the values for threshold voltage (V_{th}) of D-PDLC at various dye concentrations against the curing temperatures while LC contents were fixed (77 wt%). The Figure 3b displays the V_{th} curves against the curing temperatures for 0.5 wt%, 1 wt%, and 1.5 wt% of dye. This illustrate a general increasing trend; such as the device fabricated with higher dye contents (1.5wt%) have maximum threshold voltage as compare to 0.5 wt% of dye. The reason for high threshold voltage for dye contents 1.5 wt% is established earlier due to higher absorption of UV light that enhanced once the dye contents are increased.[25] Moreover, it explains that threshold voltage increases when temperature elevated to 30^{o}C. Besides this Figure 3b demonstrates that, 1 wt% of dye exhibited minimum threshold voltages at all curing temperatures. Furthermore, Figure 3b displays the threshold voltages limit under the 10 volts for all curing temperatures and dye contents. This brings to a conclusion that a D-PDLC device fabricated with 77 wt% of LC exhibited optimum electro-optical property (V_{th}) even it cured at higher temperatures and having dye contents 0.5-1.5 wt%.

The Figure 4 (a, b) shows the graphs for the contrast ratio of D-PDLC at various LC and dye concentrations against the curing temperatures. While in Figure 4 a and b the dye and LC contents remained fixed as 1 wt% and 77 wt% respectively. Figure 4a shows an increase in contrast ratios (CR) for D-PDLC once cured at temperatures in range as 20-30^{o}C. In addition to this, it shows in Figure 4a that contrast ratio of D-PDLC with 75 wt% of LC contents has higher CR values as 12 at elevated temperature. A careful analysis of CR graph for 77 wt% of LC, it is revealed that it exhibited the optimal CR properties. Furthermore, this D-PDLC device attains CR at higher values (CR=10) as the temperatures increases. The device 77 wt% followed approximately the similar CR behavior as like the 75 wt% of LC contents perform at various temperatures. However, one can observe from Figure 4a that the device cured at 80 wt% of LC contents exhibited modest contrast ratio. The reason for this behavior is believed as being due to larger droplet size and coagulations of LC droplets. Generally, the device with higher LC contents showed more transmittance at ON state due to less anchoring forces of LC droplets. However, it shows less scattering at zero voltage as much light is transmitted from the wider edges of larger size droplets. Hence, following devices exhibited less CR values. This brings us to a conclusion that D-PDLC produced with 77:23 wt% have optimum electro-optical properties such as low V_{th} and high CR.

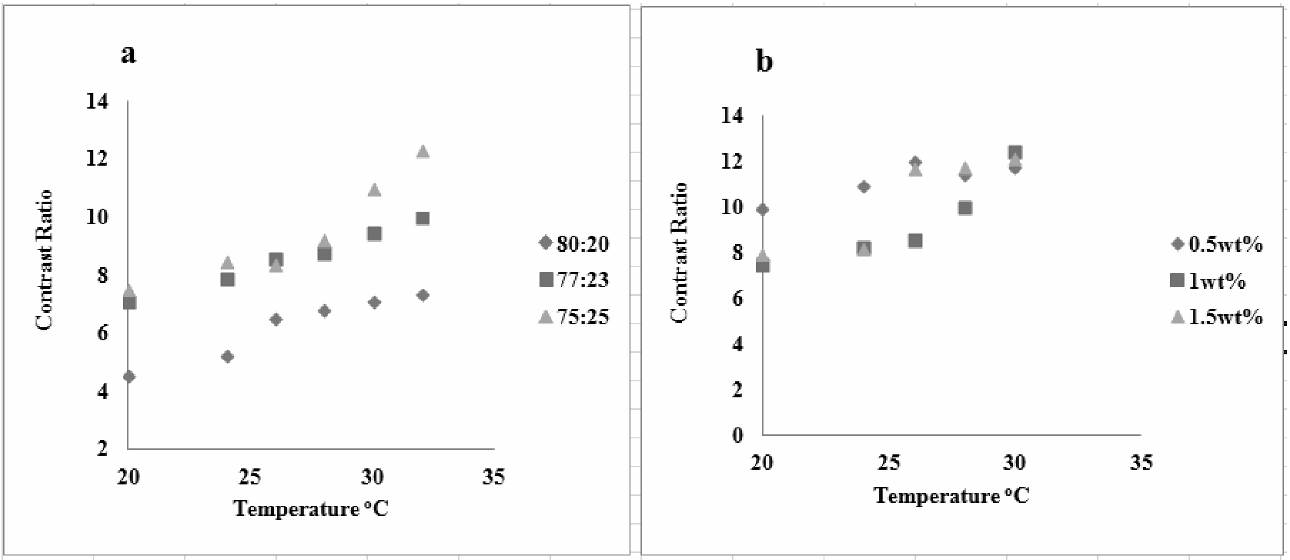

Fig. 4 – Electro-optical contrast of D-PDLC at various LC and dye concentrations against the varying temperatures.

Figure 4b showed the contrast ratios of following D-PDLCs as plotted against the curing temperature and having various dye contents. This graph present that initially CR values for least curing temperature the 0.5 wt% of dye has CR values at higher end (CR=10). However, once temperature crossed 28°C during that CR for every dye contents showed almost the same level. Since, the dichoric black dye S428 is generally established as a noble candidate in D-PDLC with higher CR values and less V_{th} values (10 volts). Our findings revealed this dye showed optimum electro-optical properties while cured at higher temperatures such as 30°C. Based on the following facts this dye can participate as good candidate for large area display industries.

CONCLUSIONS

In this work, a dichroic black dye S428 is used to fabricate D-PDLC with LC (TL203) and monomer (PN393) (75-80 wt%) at wide temperatures range (20-32°C). This is performed to find the optimum electro-optical properties such as minimum voltage required to turn ON and the best ratios to get the high contrast ratio D-PDLCs. Our findings revealed that the following dye showed smaller V_{th} and higher CR values at wide curing temperature range (20-32°C). Moreover, it is observed that for higher weight ratios of dye 1.5 wt% the CR raised to higher values (CR=12) while cured at 30°C. In addition to this, the optimum electro-optical properties achieved at less consumptions of LC (77 wt%). This is an achievement in dye PDLC devices for large area display applications. Hence, the use of following dye to fabricate a D-PDLC can be a better choice because of low cost production, higher contrast ratio at wide curing temperatures and less threshold voltage. Moreover, this dye in display technology can further open a new opportunity for trim-able electronic papers, decorative displays, electrically switchable curtains, and electrically switchable sun control films for the automobiles, homes or commercial buildings.

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