Enhanced Electro-Optic Performances of the Optically Isotropic Liquid Crystal Displays Utilizing PEDOT: PSS

Srinivas Pagidi, Ramesh Manda, Junhyeok Lee, Hong Gwon Lee, Young Jin Lim, and Seung Hee Lee*

Applied Materials Institute for BIN Convergence, Department of BIN Convergence Technology and Department of Polymer-Nano Science and Technology, Jeonbuk National University, Jeonju, Jeonbuk 561-756, Republic of Korea

Abstract

Optically isotropic liquid crystal (OILC) composite film in which nano-sized LC droplets are embedded in a polymer matrix is highly useful for bendable displays and wearable photonics but a high operating voltage due to field shielding effect of the insulting matrix and low Kerr constant needs to be overcome. To address this challenge, a small amount of conductive materials PEDOT: PSS is doped into the OILCs. The LC cells with 2 and 3.5 wt% PEDOT: PSS doped OILCs exhibit improved driving voltages by 6.5% and 11.7% and on-state transmittance by 10.3% and 30.1%, respectively, compared to conventional one. In addition, faster switching response times are achieved while the dark level remains to be unaltered.

Author Keywords

Optically isotropic liquid crystal; conductive PEDOT: PSS polymer; operating voltage, high transmittance

1. Introduction

Optically isotropic liquid crystal (OILC) is an optically transparent film consisting of liquid crystal (LC) droplets embedded in a polymer matrix, in which the sizes of LC droplets vary below the wavelength of the visible light i.e. 300 nm. In contemporary LCD field, the OILC displays have gained great importance owing to its remarkable properties such as fast response time, wide and symmetric viewing angles without the use of complicated fabrication steps including alignment layer and rubbing process and high cost of optical compensation films [1,2]. In addition to this, the electro-optic properties such as transmittance, light leakages, and contrast ratio are remaining to be unchanged to the external stress conditions, unlike conventional displays with pure nematic LCs [2,3]. Applying OILCs to the flexible displays and photonic devices, it could offer unique properties including thinness, lightweight and free design structures with flexibility, bendability, and foldability [4,5]. To realize such properties in the flexible displays and photonic devices, the visible light scattering free OILC film is essential. In view of this, relatively higher monomer concentration i.e. > 50% was used, so that the desired OILC film can be achieved upon the UV polymerization [4-7]. However, despite optically transparent film, a thick polymer matrix between the nano-sized LC droplets, i.e., a high fill factor of the matrix is realized owing to the higher concentration of monomer. The low dielectric constant of the thick polymer matrix renders the Kerr constant (K) of the OILCs be 7.53×10^{-10} m/V^2 [8] so that it requires high driving voltages to induce maximum birefringence.

To overcome the drawback of OILCs, a few different approaches were reported in the literature to reduce the driving voltage of the OILCs. Among them, one is the utilization of flexible/weak anchored monomers with relative diluents [9], using a LC with high birefringence and dielectric anisotropy to get the high K (1 nm/V^2) [10], doping functionalized-carbon nanotubes (f-CNTs) [11], and using the acrylate monomers [12]. Even after these efforts, the high driving voltage is still an unsolved issue for practical applications. In previous report, the field screening effect in the polymer matrix was minimized up to some extent of the dopant concentration but a higher concentration of dopant causes agglomerations in the polymer matrix [11]. Considering these efforts, we also challenge to improve the conductivity of polymer matrix so that the applied field strength should pass without shielding by the polymer matrix.

In this report, we introduced commercially available high conductive poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) PEDOT: PSS polymer [13] into the host polymer matrix to reduce the driving voltage of the OILCs. The incorporated conductive polymer was successfully embedded in the host polymer matrix upon the polymerization induced phase separation method. By this approach, the field screening effect in the polymer matrix is significantly reduced, giving rise to maximum induced birefringence of the OILCs at low operating voltage. Consequently, the electro-optic performances are improved without affecting the other properties.

2. Switching mechanism
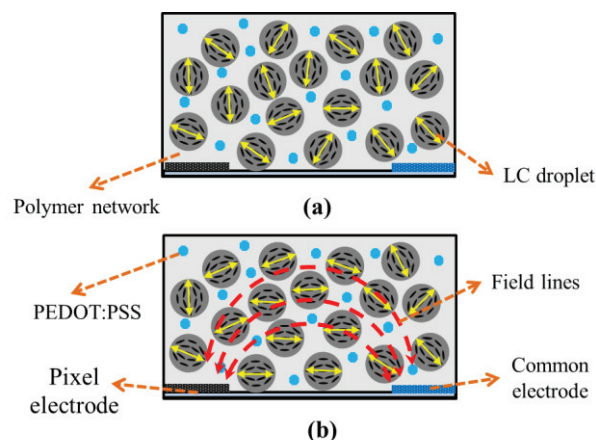
Figure 1. Schematic switching mechanism of LCDs with OILC in which the conductive material is embedded in a host polymer matrix and size of LC droplet is less than 300 nm (a) Field-off and (b) Field-on state.

Feeble light scattering-free OILC film is essential for achieving a high contrast ratio of the devices. However, utilization of a higher concentration of monomer causes thicker polymer matrix

between nano-sized LC droplets which results in reducing the K of the OILCs [8]. Therefore, the relative applied field strength to nano-sized LC droplets is decreased due to field shielding effect by the polymer matrix. Also, the field screening increases with increasing thickness of the polymer matrix. In view of this, the conductive PEDOT: PSS is doped into OILCs and its switching mechanism of the same is schematically shown in Figure 1. Herein, we anticipate the doped PEDOT: PSS is homogeneously dispersed in the host monomer and the dopant is embedded inside the host polymer matrix upon the UV light polymerization. The embedded conductive polymer acts as a conductive pathway between the nano-sized LC droplets, so the field screening in the polymer matrix could be reduced, giving rise to reduced driving voltages of the OILCs.

The threshold voltage (V_{th}) of the PEDOT: PSS doped OILC change with the concentration of dopant in the composite medium. So, the modified V_{th} of the PEDOT: PSS doped OILC is written as [11,14],

$$V_{th} = \frac{1}{c} \frac{\pi l}{R} \sqrt{\frac{k_{eff}}{\varepsilon_o \Delta \varepsilon}}, \qquad [1]$$

where R is the droplet size, l is the electrode gap, k_{eff} is the effective elastic constant and c is the prefactor expressed as,

$$c = \frac{3\varepsilon_M}{\varepsilon_{LC} + 2\varepsilon_M}, \qquad [2]$$

where ε_M is the effective dielectric constant of the polymer matrix and ε_{LC} is the dielectric constant of the host LC. The decay (τ_{off}) time of the device is expressed as [15],

$$\tau_{off} = \frac{\gamma_1 R^2}{k_{eff} \pi^2} \times \frac{1}{W_s}, \qquad [3]$$

where γ_1 is the rotational viscosity of the LC, W_s is the surface anchoring energy.

3. Experimental procedure

The prepared OILC and its composites consist of a high dielectric anisotropy nematic LC mixture, photo-curable monomers, and a conductive polymer. We utilized the MLC-2053 ($\Delta\varepsilon$ = 42.6 at 1 kHz, T_{NI}= 86 °C, from Merck Advanced Technology, Korea) as Nematic LC, PN393 (n_p = 1.473 at 589 nm), (trimethylolpropane triacrylate) TMPTA (n_p = 1.474 at 589 nm) as host monomers and commercially available PEDOT: PSS (Sigma Aldrich) is used as a dopant. In the first step, the OILC mixtures were prepared with concentrations of 42% of LC, 48% of PN393 and 10% of TMPTA. The conductivity of pristine PEDOT: PSS is improved by adding an IPA solution in the ration of 1:1 [16]. Two different concentrations of PEDOT: PSS polymer (2 and 3.5 wt% to OILC mixture) is added to the naïve composite mixture of LC and monomer. The reaction mixture was heated to elevated temperatures and subjected to ultrasonication for 2 hrs to improve the degree of dispersion of the dopant into the composite mixture. Then the IPA content present in the resultant composite mixture was evaporated while stirring it at 70 ºC in the air atmosphere. Finally, the obtained mixture was injected into the in-plane switching (IPS) (w x l = 4 x 4 µm) cell by capillary action at 90 ºC, followed by UV light irradiation 110 mW/cm² for 6 mins. The

cell gap is fixed to 11.8 µm. Hereafter, the pure OILC sample is named as S1 and the composite samples are named as S2 for 2 wt% and S3 for 3.5 wt%, respectively. The polarizing optical microscope (POM) (Nikon, ECLIPSE E600, Japan) attached with CCD camera (Nikon, DXM 1200), was used to observe phase separation and switching of the LC cell under the crossed polarizers. The transmittance and response time were measured as a function of the applied filed by using a lab-made set-up consisted of the photodetector, a function generator (Agilent 33521A) and oscilloscope (Tektronix DPO 2024B). To measure the conductivity prepared samples, the capacitance measurements have been performed by Agilent 4284A precision LCR meter (20 Hz to 1000 kHz).

4. Results and Discussion

Firstly, to measure the capacitance of the test samples the resultant mixture was polymerized between the top and bottom ITO electrodes. The conductivity of the samples was estimated by measuring the real and imaginary dielectric constants as a function of frequency depicted in Figure 2. The real dielectric constant is measured using the relation, $\varepsilon' = C_p/C_0$, where Cp is the capacitance of the filled cell and C_0 is the capacitance of the empty cell, $C_0 = \varepsilon_0 A/d$, where ε_o is the permittivity of the free space, A and d is the effective area and thickness of the capacitor and the dissipation factor, $\mathrm{Tan}\,\delta = \varepsilon''/\varepsilon'$, where ε'' is the imaginary dielectric constant. The ac conductivity is calculated using the formula $\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon''$, where f is the applied frequency. The estimated σ_{ac} is 5.67×10^{-8}, 6.38×10^{-8} and 7.10×10^{-8} S/m, respectively, for the samples S1, S2, and S3 at the frequency of 1 kHz. It is found to be noticed that the σ_{ac} is increased by 12.52% and 25.22% for sample S2 and S3 when compared to sample S1.
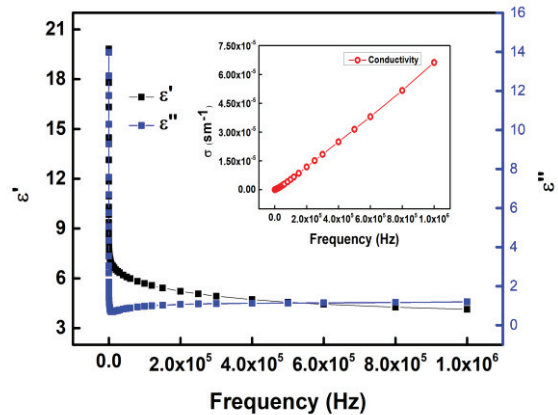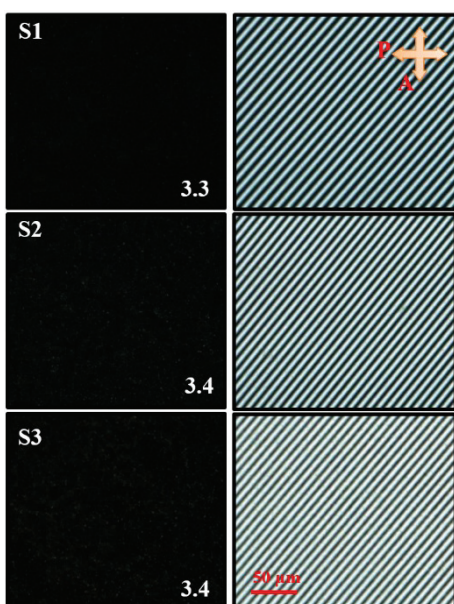

Figure 2. Real (ε') and imaginary (ε'') dielectric constant as a function of frequency measured for the sample S3.
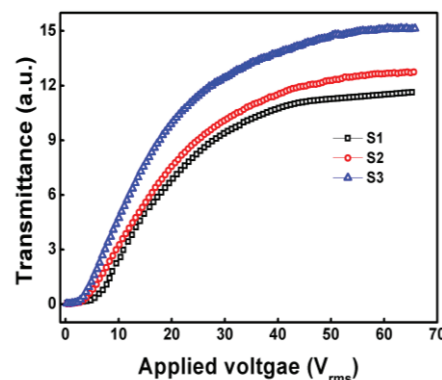
To understand the influence of PEDOT: PSS polymer on OILC, the POM characterization was used to identify phase separation of the composite medium. Figure 3 illustrates the POM images captured under crossed polarizers while keeping the backlight intensity unchanged for all samples. The dark state of the POM image depicts the efficiency of the isotropic phase, which remains to be unchanged for all samples while the sample stage rotated under crossed polarizers. The relative light leakages showed on

the inset of the dark image imply that the dopant does not show any considerable effect on the efficiency of the dark state. On the other hand, when the field is subjected to IPS cells, the maximum birefringence is induced giving rise to a bright state. Interestingly, the transmittance between electrodes is amplified as increasing the concentration of dopant for sample S2 and S3 and it is also noticed that the increased transmittance is higher for the same cells as the comparison to sample S1 when the same fields are applied to all samples. Improved transmittance clearly emphasizes that the field shielding effect in the polymer matrix is realized to be minimized with the concentration of dopant.
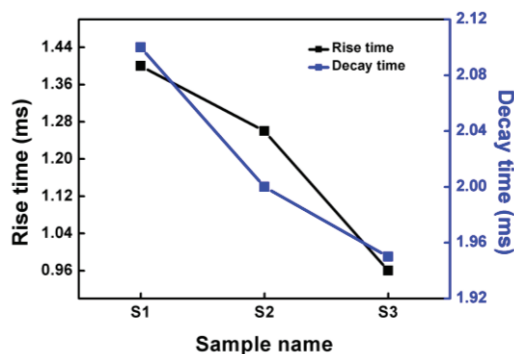

Figure 4. Voltage-dependent transmittance curves of the PEDOT: PSS doped OILC.

Furthermore, the transmittance as a function of time measured with a square wave voltage of 80 V_{rms} was applied with a frequency of 1 kHz. The rise (τ_{on}) and decay (τ_{off}) times are defined as the transmittance increased from (10% to 90%) and decreased from (90% to 10%), respectively. The measured τ_{on} times are 1.4, 1.26 and 0.96 ms and τ_{off} times are 2.1, 2 and 1.95 ms for the sample S1, S2, and S3, respectively, as indicated in Figure 5. Improvement of electro-optical performances includes V_{th}, V_{op}, relative change in transmittance and response time of OILC is an indication of minimized shielding effect between nano-sized LC droplets and that may be due to the presences of conductive PEDOT: PSS polymer in the host polymer matrix. Similar kind performances are reported in polymer-dispersed liquid crystals with f-CNTs [11,17].

Figure 3. POM images of the dark (0 V_{rms}) and bright (60 V_{rms}) states captured under crossed polarizers without changing the intensity of incident light. The numbers in dark states represent relative light leakages. P and A indicate polarizer and analyzer, respectively.

Figure 4 depicts the voltage as a function of transmittance (V-T) curves measured under crossed polarizers. To perform the V-T measurement, we used He-Ne laser with the wavelength of λ = 633 nm and the transmittance of light intensity was measured under the crossed polarizer. The V-T curve implies the light leakage measured under crossed polarizer is the same for all samples, in the field-off state. Whereas the field is subjected to IPS cell, the transmittance increases with increasing the field and it saturates at higher fields giving rise to maximum induced birefringence. Here, the V_{th} and V_{op} are defined as the 10% and 90% transmittance change from a dark state, respectively. The measured V_{th} are 9.8, 8.1 and 6.9 and V_{op} are 42.9, 40.1 and 37.9 respectively for the sample S1, S2, and S3. The improved V_{th} is 17% and 30% and V_{op} is 6.5% and 11.7%, respectively, for the sample S2 and S3 compared to the conventional one. Besides, the relative change in transmittance is found to increase by 10.3% and 30.1% for the samples of S2 and S3.

Figure 5. Electro-optic switching response time of the PEDOT: PSS doped OILC samples.

5. Impact

To achieve enhanced field-induced birefringence of the OILC, we doped a small amount of the PEDOT: PSS into the OILCs. Consequently, the electro-optic performances include V_{th}, V_{op}, and response times are effectively improved owing to improved conductivity of the polymer matrix. Interestingly, on-state transmittance is also found to be increased between electrodes with increasing the concentration of dopants. The proposed mechanism has a high potential in improving the electro-optic properties of the OILC, so the device could be applicable for developing flexible display and photonic devices.

6. Acknowledgments

7. References

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