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Sameet K. Shriyan[a]; Adam K. Fontecchio[a]
[a] Department of Electrical and Computer Engineering, Drexel University, Philadelphia, PA, USA

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Improved Electro-Optic Response of Polymer Dispersed Liquid Crystals Doped with Oxidized Multiwalled Carbon Nanotubes

SAMEET K. SHRIYAN AND ADAM K. FONTECCHIO

Department of Electrical and Computer Engineering, Drexel University, Philadelphia, PA, USA

This work focuses on improving the electro-optic response of thiolene and acrylate based Polymer Dispersed Liquid Crystals by doping them with oxidized multiwalled carbon nanotubes (MWNT). Results indicate a reduction in switching voltage which is attributed to the enhanced electric field experienced by the Liquid Crystal (LC) droplets trapped in the polymer matrix manifested by a decrease in resistivity and an increase in capacitance of the composite medium. Improved switching speeds is related to the reduction in size of the LC droplets since the MWNT act as physical barriers to the diffusing LC's preventing coalesce, confirmed with scanning electron microscopy imaging. PDLC's are doped with various concentrations of MWNT to determine an optimal doping level. An anomalous electro-optic behavior is noted at higher concentrations.

Keywords Carbon nanotubes; electro-optics; liquid crystals

I. Introduction

Polymer dispersed liquid crystals (PDLC) are electro-optic thin films which can be switched between a light scattering state and a transparent state by application of an electric field across the film. It comprises of sub-micron sized nematic liquid crystalline droplets with positive dielectric anisotropy trapped in a polymer matrix [1]. In the absence of an electric field across the film scattering arises due to index mismatch between the nematic droplets and polymer matrix. An electric field across the sample forces a reorientation torque across the LC droplets such that the ordinary refractive index (n_o) of the LC matches the refractive index of the polymer. This property along with its millisecond switching time has rendered it attractive for applications such as light modulators [2], displays [3] switchable windows [4] and numerous other applications. Enhancing the electro-optic properties of these devices has been a matter of research especially in terms reducing the switching voltage and improving switching speeds without significantly affecting the optical properties. The critical voltage required to reorient the LC droplet trapped in a polymer matrix is influenced by both

Address correspondence to Sameet K. Shriyan, Department of Electrical and Computer Engineering, Drexel University, Philadelphia, PA 19104, USA. Tel.: +1 (215) 895 0234; Fax: +1 (215) 895 1695; E-mail: sks48@drexel.edu

the conductivities of LC and polymer. Large LC conductivity when compared to the polymer results in a polarization field opposing the external applied field hence reducing its effective strength. However, large polymer conductivity enhances the electric field across the LC droplet hence reducing the critical field required to reorient the LC [1]. Chidichimo et al. have shown the dependence of switching voltage on the resistivity of the composite [5]. Cupelli et al. proved reduction in switching field and faster response in PDLC by addition of conductive polymers [6]. The LC droplet size and shape also effects the dielectric properties of the composite hence affecting the electro-optic performance of the device [7]. Sadovoy et al. observed an influence on LC droplet director orientation due to addition of CNT in PDLC and its response under crossed polarizers [8].

In this work we experimentally demonstrate the reduction in switching voltage and an improvement in switching speed of PDLC's by modifying the conductivity of the polymer matrix by addition of oxidized multiwalled carbon nanotubes and affecting the phase separation processes to form reduced droplet size. A comparison of electro-optic response is carried out at low, intermediate and high MWNT doping levels.

II. Experiment

MWNT's were suspended in dymethyl formamaide (DMF) to obtain a uniform suspension. The fabrication of oxidized MWNT is mentioned elsewhere [9,10]. Commercially available LC BL038 (Merck&Co. Inc) was doped with the following concentrations of MWNT suspended in DMF, measured per gram of LC BL038, 0.01 mg, 0.025 mg, 0.05 mg, 0.75 mg, 0.1 mg, 0.25 mg, 0.5 mg and 1 mg. DMF was subsequently evaporated form the LC. The thiolene formulation comprised of a homogenous mixture of NOA65 (Norland Optical Adheives, Inc.), LC BL038 with MWNT and a photoinitiator to sensitize the blend to visible wavelengths. The photoinitaitor comprises of Rhodamine 6G (Acros organics) and benzoyl peroxide (Aldrich). The percent weights of the components used are 68% NOA65, 25% BL038, 0.4% Rhodamine 6G, 3% benzoyl peroxide and 3.6% N-Vinyl Pyrrolidone. The acrylate formulation comprised of tri-functional and hexa-functional oligomers Ebecryl 4866 and Ebecryl 8301 (Cytec Industries Inc.), LC BL038 with MWNT, photo-initiator and surfactant Tween 80 (Aldrich Inc.); the photo-initiator for acrylates consists of 4% Rose Bengal, 10% of co-initiator N-Phenyl Glycine and 86% of N-Vinyl Pyrrolidone by weight. The percentage ratio weights of the components used are 22.5% (Ebecryl 4866): 22.5%, (Ebecryl 8301): 32.4%, (LC): 12.6%, (Photoinitiator): 10%, and Tween 80 (surfactant) 10%. The oxidized MWNT's had a maximum length of 10 μm and an outer diameter of 20 nm.

PDLC cells were prepared by sandwiching the prepolymer mixtures, doped with various concentrations of MWNT, between ITO glass slides spaced 20 μm apart using glass spacers. These cells were cured under a UV lamp to form PDLC's. Resistivity and capacitance of the fabricated samples were measured using a LCR meter, with a test voltage of 0.9 V at 1 kHz, to quantify the changes in the dielectric properties of the composite medium due to presence of various concentrations of MWNT. Optical microscopy with and without crossed polarizer's was performed on all the samples to determine the effect on LC droplet formation in presence of MWNT during photo induced phase separation.

Electro-optic performances of the samples were measured by illuminating the sample with an unpolarized halogen light and the transmittance was measured using

a spectrometer (Ocean optics) at various applied electric fields. Switching speed was measured by illuminating the sample with a 633 nm He-Ne laser inline with a photodiode connected to an oscilloscope and all samples were switched at the same voltage to determine the effect of various concentration of MWNT on the switching speeds.

The samples were frozen in liquid nitrogen and the cross section was obtained by fracturing the samples. The LC's were washed away using ethanol and Scanning electron microscopy (SEM, Zeiss supra) was performed on them to determine droplet formation in presence of MWNT. All samples were imaged at 4500x to determine changes in LC droplet distribution across the cross section and at 25000x to determine any changes in size and shape of the LC droplets.

III. Results and Discussion

Optical microscopy imaging indicates that the MWNT's were randomly distributed throughout the sample and tend to form aggregates especially at higher concentrations (1 mg of MWNT) as shown in Figures 1 and 2 for thiolene and acrylate based PDLC samples respectively. Under crossed polariszers the thiolene based PDLC's maintain a dark field at the lower and intermediate MWNT concentrations of 0 mg, 0.05 mg and 0.5 mg (Fig. 1a–c). However a total birefringent field is seen in the PDLC sample with 1 mg MWNT (Fig. 1d). This birefringent field indicates the presence of bulk LC's on the surface of the PDLC sample and failure of droplet formation. A similar observation is made for the thiolene based PDLC's where in a partial birfringent field is seen even at low MWNT concentrations (Fig. 2a–c) and this field turns to a total birefringent field at 1 mg MWNT (Fig. 2d) again showing presence of bulk LC's and prevention LC of droplet formation.

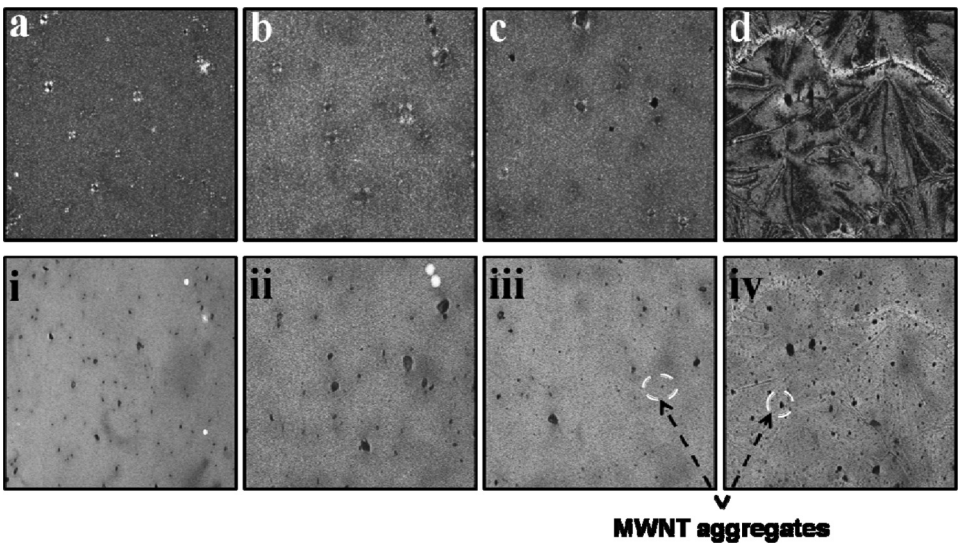

Figure 1. (a) through (d) shows Polarized optical images of thiolene PDLC doped with the following concentrations of MWNT 0 mg, 0.05 mg, 0.5 mg, and 1 mg respectively. (i) through (iv) shows the corresponding optical images without polarizers and MWNT aggregates at 0.5 mg and 1 mg.

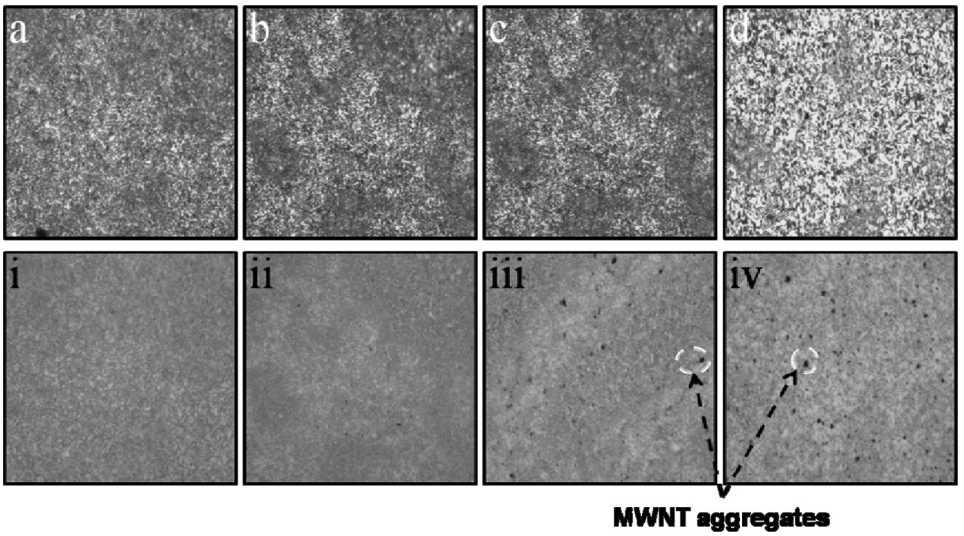

Figure 2. (a) through (d) shows Polarized optical images of acrylate PDLC doped with the following concentrations of MWNT 0 mg, 0.05 mg, 0.5 mg and 1 mg respectively. (i) through (iv) shows the corresponding optical images without polarizers and MWNT aggregates at concentrations of 0.5 mg and 1 mg.

The reorientational field in a PDLC cell depends largely on the size and shape of the LC droplet and the conductivities and dielectric constants of the medium. Addition of MWNT modifies both the conductivity and the dielectric properties of the medium as shown in Figures 3a and b for thiolene and acrylate based PDLC respectively. In both the systems, a drop in resistivity and an increase in capacitance is recorded for various doping levels of MWNT. A reduction in resistivity is an indication of an increase in conductivity of the medium especially the polymers used.

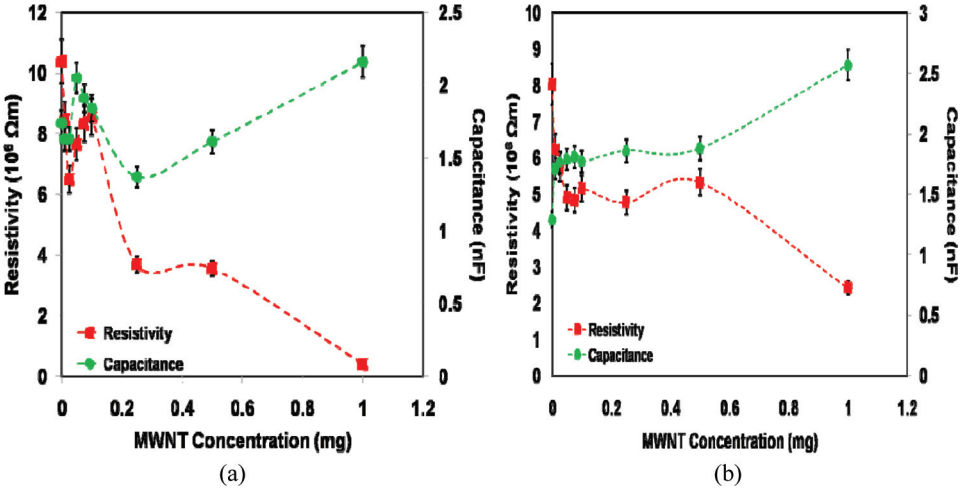

Figure 3. Change in resistivity and capacitance measurements of (a) thiolene and (b) acrylate based PDLC doped with various concentrations of MWNT.

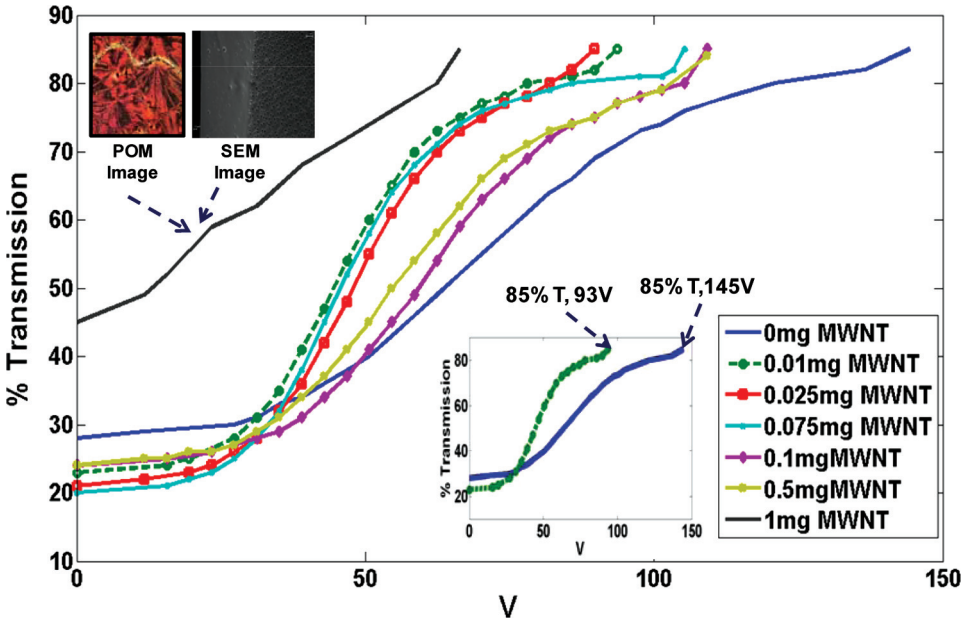

Figure 4. Transmission vs applied voltage curves for thiolene based PDLC dopes with various concentration of MWNT. The inset plot shows the reduction in switching voltage at 0.01 mg MWNT.

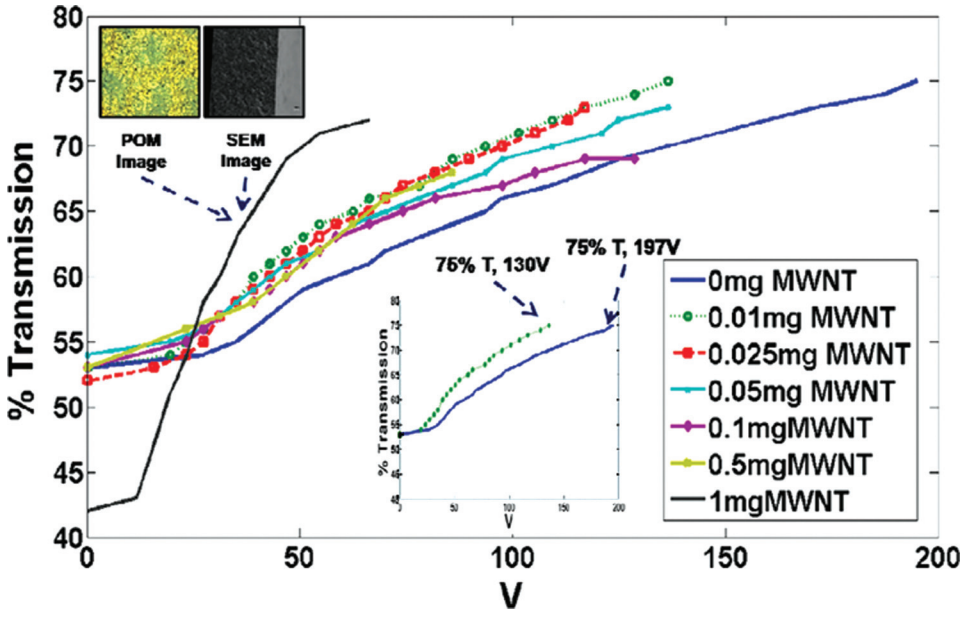

Figure 5. Transmission vs applied voltage curves for acrylate based PDLC dopes with various concentration of MWNT. The inset plot shows the reduction in switching voltage at 0.01 mg MWNT.

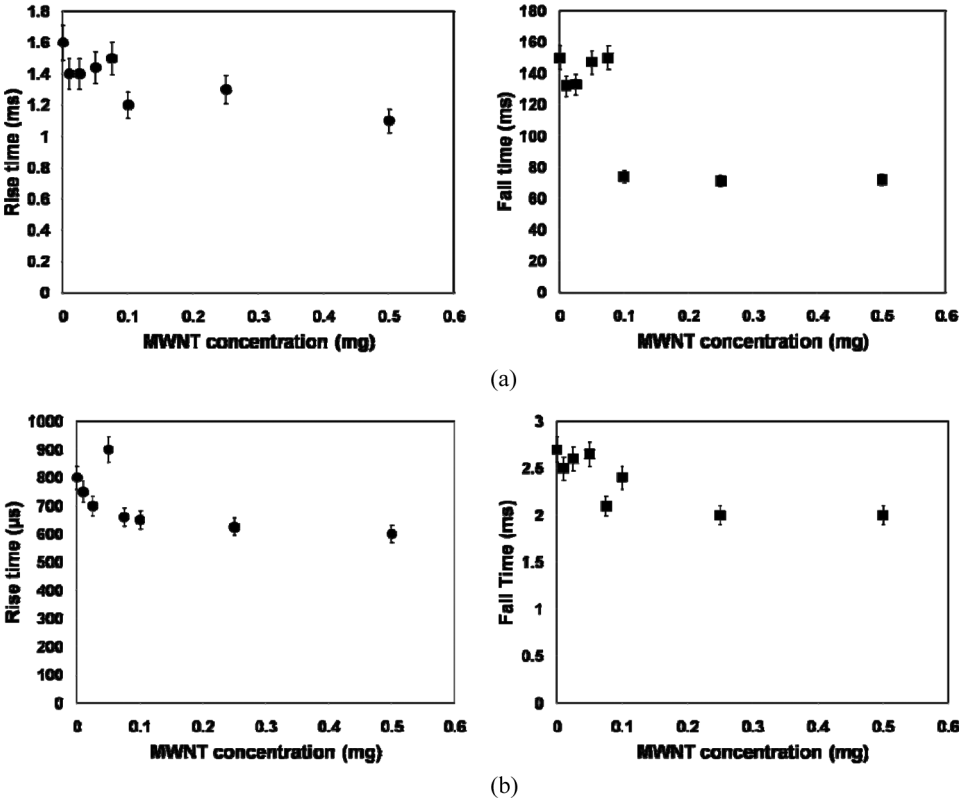

Figure 6. Rise and fall time measurements for (a) thiolene and (b) acrylate based PDLC doped with various concentrations of MWNT.

The MWNT does not diffuse along with the LC during the phase separation due to its size compared to the participating monomers and LC molecules and hence remains trapped in the polymer matrix adding to its conductivity. This enhances the electric field across the LC droplets. The enhanced electric field is now given by:

$$E_{LC} = E_{appl}\left(\frac{3\sigma_{p+mwnt}}{2\sigma_{p+mwnt} + \sigma_{LC}}\right) \tag{1}$$

where σ_{p+mwnt} is now the composite conductivity of the polymer matrix doped with MWNT.

Theoretically, the reorientational filed required to reorient the LC droplet is given by [11]:

$$V_c = \frac{d_0}{3a}\left(\frac{\sigma_{LC}}{\sigma_p} + 2\right)\left(\frac{K(l^2+1)}{\varepsilon_0 \Delta\varepsilon}\right)^{1/2} \tag{2}$$

a, σ_{LC} and σ_{p} are the radius of the LC droplet, conductivity of the LC and conductivity of the polymer. K and $\Delta\varepsilon$ are the LC constants and dielectric anisotropy

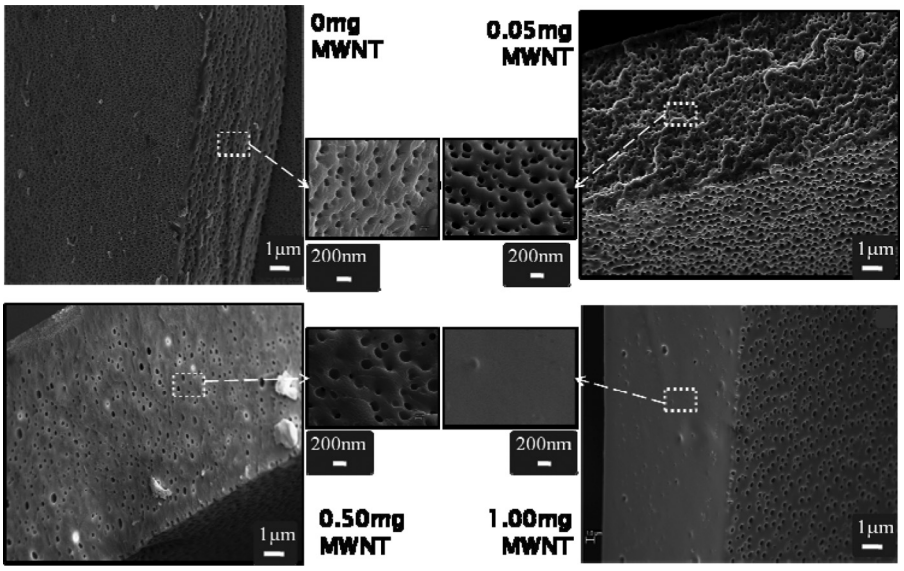

Figure 7. SEM images of thiolene based PDLC doped with MWNT at various concentrations.

respectively. Since the conductivity of the polymer increases with addition of MWNT, a reduction in the switching voltage is observed as shown in Figures 4 and 5 for thiolene and acrylate based PDLC-MWNT composites. Experimental observation shows that an optimal concentration range (lying between 0.01 mg to 0.075 mg) of MWNT doping exists beyond which the electro-optic response deteriorates.

As shown in Figure 4, the switching voltage reduces for MWNT doping levels of 0.01 mg, 0.025 mg and 0.075 mg when compared to a PDLC with no MWNT. However an increase in switching voltage is observed at 0.1 mg and 0.5 mg MWNT, this is primarily due to the fact that the MWNT's form a short between the ITO coated electrodes and was seen as sparks during the switching. An anomalous behavior is seen at 1 mg MWNT where the PDLC sample had increased transparency even at zero electric field. This behavior is due to the fact that the LC's did not form droplets and were found on the surface of the samples as seen in Figure 1d. A very similar response is seen in acrylate based PDLC's as seen in Figure 5 where a reduction in switching voltage is seen at MWNT concentrations of 0.01 mg and 0.025 mg. An increase in switching voltage is seen at concentrations of 0.05 mg, 0.1 and 0.5 mg and an anomalous response is recorded at 1 mg MWNT. A lower electro-optic response is seen in acrylate based PDLC's when compared to thiolene based PDLC doped with MWNT, which is due to the fact that surfactant was used in the acrylates and surfactants are known to reduce the electrical properties of MWNT due to adsorption on its surface [12].

An improvement in the rise and fall time is seen for both thiolene and acrylate based PDLC with MWNT. The rise and fall time for PDLC devices is proportional to the size of the LC droplets trapped in the polymer matrix and are is given by [11]

$$\tau_{off} = \frac{\gamma_1 a^2}{K(l^2-1)} \quad \text{and} \quad \tau_{on}^{-1} = \frac{1}{\gamma_1}\left(\Delta\varepsilon E^2 + \frac{K(l^2-1)}{a^2}\right) \tag{3}$$

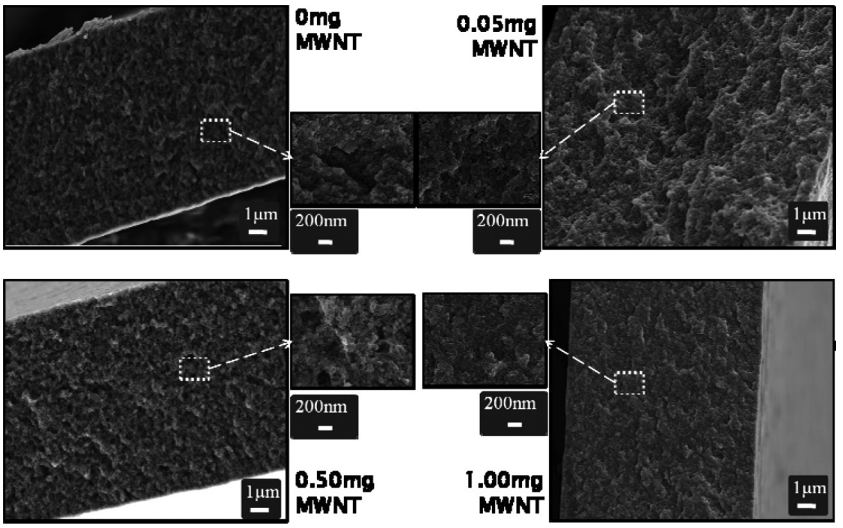

Figure 8. SEM images of acrylate based PDLC doped with various concentrations of MWNT.

where γ_1 is the viscosity coefficient of the LC. Figures 6a and b shows the reduction in rise and fall times for thiolene and acrylate based PDLC dopes with various concentrations of MWNT. The rise and fall time improve in samples with increasing the concentration of MWNT. This is an indication of reduction in the formed LC droplet size in the PDLC samples. In thiolene PDLC's, the rise time improved form 1.6 ms (at 0 mg MWNT) to 1.4 ms (at 0.01 mg MWNT) and the fall time from 150 ms (at 0 mg MWNT) to 130 ms (at 0.01 mg MWNT). In the acrylate PDLC's, the rise time improved from 810 μs (at 0 mg MWNT) to 750 μs (at 0.01 mg MWNT) and the fall time from 2.75 ms (at 0 mg MWNT) to 2.5 ms (at 0.01 mg MWNT).

Scanning electron microscopy imaging of the MWNT doped PDLC samples reveals the effect on LC droplet formation. As shown in Figure 7 for a thiolene based PDLC doped with MWNT, the effect of the presence of MWNT on the droplet formation is clearly seen. At 0 mg MWNT a good distribution of LC droplets is seen across the cross section of the sample. A slight reduction in average size of the droplets is observed at 0.05 mg MWNT. However, at 0.5 mg MWNT a reduction in the number of LC droplets is seen across the cross section and at 1 mg MWNT no droplet formation is seen across the cross section. This result is consistent with the polarized optical images in Figure 1d where most of the bulk LC's were found on the surface. Hence, at higher MWNT concentrations hinder the phase separation process and hence LC droplet formation. A very similar observation is made for the acrylate based PDLC samples doped with MWNT as seen in Figure 8.

IV. Conclusions

In summary, we have experimentally quantified the electro-optic and morphology effects of doping oxidized multiwalled carbon nanotubes in thiolene and acrylate based PDLC. A reduction in the switching voltage is observed for both the thioene and acrylate based samples. In thiolene PDLC doped with MWNT, the switching voltage reduced from 145 V to 90 V at 0.01 mg MWNT concentration. In acrylate

based PDLC doped with MWNT, the switching voltage reduced form 197 V to 130 V at 0.01 mg MWNT. This is attributed to the increase in conductivity of the polymer medium hence enhancing the electric field across the LC droplets at lower applied voltages. An improvement in the rise and fall times is also recorded for both the thiolene and acrylate based PDLC samples with MWNT which is attributed to the reduction in overall average droplet sizes. SEM imaging confirms that optimal levels of MWNT doping prevents coalesce of LC droplets however higher concentrations of MWNT prevent the LC droplet formation and hinders the phase separation process since the MWNT's do not participate in the phase separation process and act as physical barriers o the counter diffusing LC's.

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