

Memory effect of polymer dispersed liquid crystal by hybridization with nanoclay

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Abstract. The electro-optical performances of polymer dispersed liquid crystal (PDLC) were investigated in the presence of organically modified clays. With the addition and increasing amount of modified clay, driving voltage and memory effect, viz. transparent state of the film after the electricity is off simultaneously increased due most likely to the increased viscosity. Among the two types of modifier, 4-(4-aminophenyl) benzonitrile having greater chemical affinity with LC than hexylamine, gave finer dispersion of clay in liquid crystal, greater viscosity, larger driving voltage and response time, and greater memory effect.

Keywords: polymer composites, PDLC, polyurethane acrylates, clay, memory effect

1. Introduction

Polymer dispersed liquid crystals (PDLC) have been intensively studied as electro-optical display materials during the last few decades since they can be switched electrically from a light scattering state to a transparent state without polarizers and alignment layers [1, 2]. Improved electro-optical properties have been reported for new applications [3, 4]. Fan *et al.* [5] reported scattering-free PDLC for infrared light modulator. Nicoletta *et al.* [6] investigated application of PDLC for electro-chromic device by doping some electro-chromic materials. Regarding the electro-optic performance, low molar mass surfactant such as octanoic acid has also been used to reduce the operating voltage. Nowadays, nanocomposites employing spatially confined liquid crystals are of great interest due to the prospects of their application in opto-electric devices, photonic crystals, depolarizers, scattering displays, information storage and recording devices

and windows with adjustable transparency [7–10]. It has been shown that in such systems applied external electric field causes transparent state which under some conditions can be retained after the field is off, which is called memory effect [11]. The memory effect can be utilized for large area outdoor displays with high power consumption, which can significantly be reduced by utilizing the memory effect of PDLC with the field off. For spherical aerosol particles, it has been found that essential contribution to the memory effect is achieved due to formation of ordered branched network of the aerosol particles in the liquid crystal matrix [12].

The present work reports the memory effect of modified clay in PDLC, where modification was made with two different organic surfactants, viz. 4-(4-aminophenyl) benzonitrile (AB), and hexylamine (HA), and the effect has been studied by scanning electron microscopy (SEM) morphology,

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contact angle, transmittance, switching voltage, response time of the film.

2. Experimental

2.1. Materials and preparations of modified clay

The sodium montmorillonite (MMT) having cation exchange capacity of 92.6 meq/100 g of the clay was purchased from the Southern Clay (Gonzales, TX). MMT was added to water / ethanol (75/25 by vol%) solution at 70°C and stirred for 4 h. A 4-(4-aminophenyl) benzonitrile (AB), and hexylamine (HA) (Figure 1) were respectively added to hydrochloric acid and stirred for 24 h. The modified clay was filtered and washed repeatedly in the water/ethanol solution and dried for 12 h.

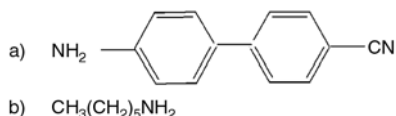


Figure 1. Chemical structures of clay modifiers: AB (a) and HA (b)

The LC-clay nanocomposite were prepared by dissolving a small amount (0.5, 1.0, 1.5 and 2.0 wt%) of clay in a commercially available cyano-based nematic LC mixture, E7 from Merck.

2.2. Polyurethane prepolymer synthesis

Bifunctional polypropylene glycol (PPG) having number average molecular weight of 750 was dried at 80°C, 0.1 mm Hg for several hr until no bubbling was observed. Extra pure grade of hexamethylene diisocyanate (HDI) was used without further purifi-

cations. Molar excess of HDI was reacted with PPG for over 1 h at 80°C to obtain NCO-terminated prepolymer. Then the reaction mixture was cooled down to 40°C and hydroxyl ethyl acrylate (HEA) was added to obtain HEA-capped polyurethane acrylate (PUA) oligomers [13, 14]. Basic formulation to prepare the PUA oligomer is given in Table 1.

The PUA oligomers are highly viscous and immiscible with LC. To this 2-ethyl hexyl acrylate (EHA) and trimethylol propane triacrylate (TMPTA) were added to form a miscible mixture with LC, leading to a composition of oligomer/EHA/TMPTA = 4/2/4 [15].

E7 (BL001, Merck), an eutectic mixture of three cyanobiphenyl and a cyanoterphenyl with $n_o = 1.5216$, $n_e = 1.7462$, and $TNI = 61^\circ\text{C}$ was used as LC. LC-modified clay mixture was added to the prepolymer mixture at a fixed composition of LC-modified clay/prepolymer = 4/6 by weight, together with a photo-initiator viz. Darocur 1173.

2.3. Cell fabrication

The reactive mixtures were mechanically mixed before they were filled into the indium-tin-oxide (ITO) coated cell by capillary action. Cell thickness was adjusted to 10 μm using glass bead spacers. Then, the mixtures were cured using a UV crosslinker (1.8 mW/cm², 365 nm) to give three dimensionally networked PUA matrix. The UV cured PDLC films sandwiched between two ITO coated cells were placed normal to the direction of collimated beam of He/Ne laser (wavelength of 632.8 nm) to measure the electro-optical properties of the cell.

Table 1. Formulations for the preparation of PDLC films

PU acrylate oligomer			Diluent	Virgin clay	Modifier	Content of clay [wt%]	LC	Remark				
Polyol	Diisocyanate	End-capping acrylate	EHA	Cloisite Na ⁺		0.0	E7	None				
						0.5		^a DC05				
						1.5		DC15				
					PPG	HDI		HEA	TMPTA	Hexylamine (HA)	0.5	HA05
											1.0	HA10
											1.5	HA15
4-(4-Aminophenyl) Benzonitrile (AB)	2.0	HA20										
	0.5	AB05										
	1.0	AB10										
						1.5		AB15				
						2.0		AB20				

^aDC – Dispersed virgin clay

PUA:TMPTA:EHA = 4:4:2 by weight

2.4. Measurements

A Jasco Fourier Transform Infrared (FT-IR) 430 Spectrophotometer was used to observe the chemical modification of the clay at a resolution of 2 cm^{-1} . Clay was grounded into KBr powder and pressed into discs prior to being placed in the FT-IR for scanning.

Transmitted light intensity was measured with a photodiode. The reference transmitted light intensity was obtained with blank cell of glass substrate. The output from a function generator was amplified and used to drive the shutter. The drive signal and the response of the photodiode were monitored with a digital storage oscilloscope (Hitachi VC-6023) at ambient temperature. Morphology of the films was studied using scanning electron microscopy (SEM, Hitachi S430). For this, UV cured cells were fractured in liquid nitrogen and LC was extracted in ethanol for 24 h [16]. Contact angle of the resin surface with a drop of LC has been measured using a contact angle meter (G-1, Erma). X-ray diffraction (XRD) patterns for LC-modified clay system were recorded with symmetric reflection mode by using Rigaku X-ray Diffractometer (30 kV, 25 Ma). A monochromatic $\text{CuK}\alpha$ radiation was used. For each scanning interval of $2^\circ/\text{min}$, diffracted X-ray intensity was automatically recorded.

3. Results and discussion

3.1. XRD profiles

Figure 2 shows XRD profiles of the virgin clay, hexylamine modified clay and 4-(4-aminophenyl) benzonitrile modified clay. The reflection peak at

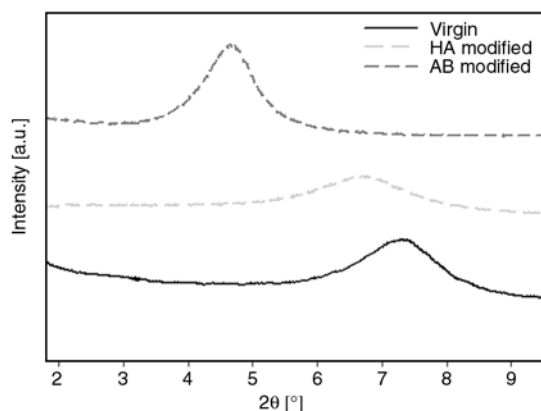


Figure 2. X-ray diffraction patterns of virgin clay, hexylamine (HA) modified and 4-(4-aminophenyl) benzonitrile (AB) modified clay

$2\theta = 7.31^\circ$ gives the interlayer spacing (d -spacing) of 12.07 \AA for the natural clay, which was calculated by Bragg's law (Equation (1)):

$$\lambda = 2d \cdot \sin \theta \quad (1)$$

where θ is the wavelength of X-rays, d is the spacing between the platelets of clay and θ is the diffraction angle. It is seen that the d -spacing is increased with the modified clay which is a direct indication of intercalation of LC molecules into the

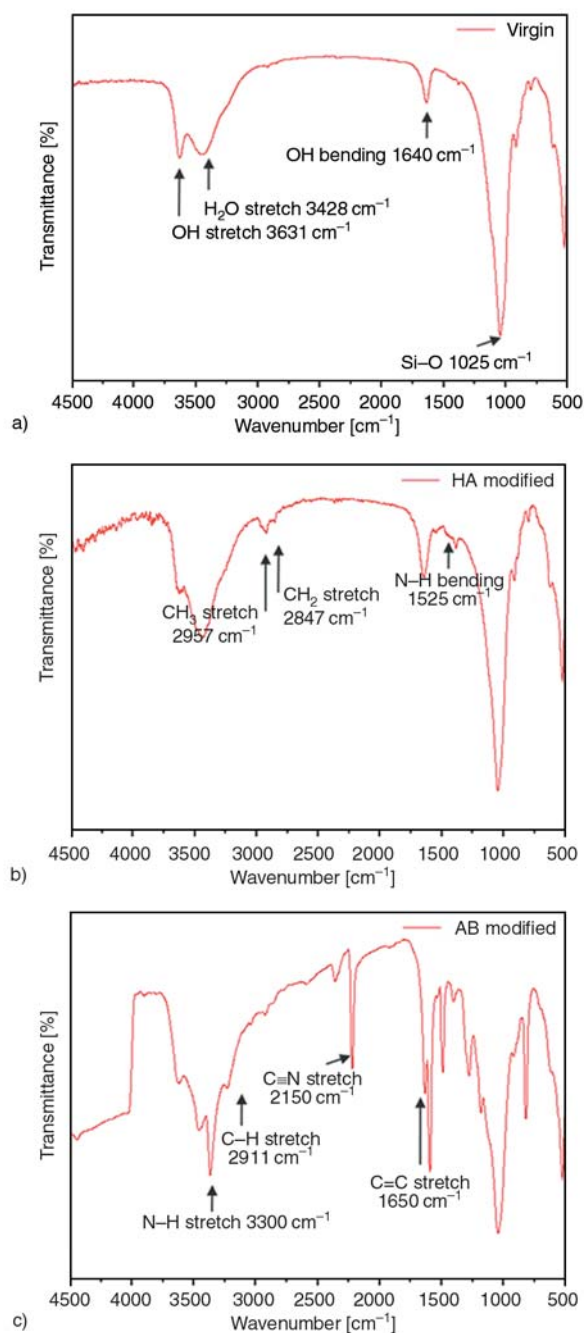


Figure 3. FT-IR spectra of virgin clay (a), hexylamine (b) and 4-(4-aminophenyl) benzonitrile modified clay (c)

layered structures of clay. It is also seen that the effect is more pronounced with AB than with HA due to the larger molecular size of the former.

3.2. FT-IR spectra

The FT-IR spectra of the virgin and modified clays are shown in Figure 3. For the virgin Na-MMT (Figure 3a), the broad absorption band centered at 1025 cm⁻¹ corresponds to different crystallographic sets of Si-Al-O layers. Also, the absorption bands of OH bending (1640 cm⁻¹) and stretching (3400–3700 cm⁻¹) vibrations are due to the hydroxyl groups of modified clay and absorbed water.

For hexylamine modified clay (Figure 3b), absorption bands with peak positions at 2847, 2957 and 3300 cm⁻¹ are assigned to stretching of CH₂, CH₃ and NH groups, respectively. The IR absorption spectra of 4-(4-aminophenyl) benzonitrile modified clay (Figure 3c) contain the bands of C=C (1650 cm⁻¹), C–H (2911 cm⁻¹) stretching vibrations of benzene ring and CN (2150 cm⁻¹) stretching.

3.3. Contact angle

Contact angles of polymer matrix with an LC drop have been measured as a function of modified clay content and are given in Figure 4 which show that contact angle decreases with the addition and increasing amount of modified clay. It is also noted that the contact angle of AB modified clay is smaller than the HA modified one, implying that the biphenyl group commonly appearing in clay and LC molecules contribute to miscibility.

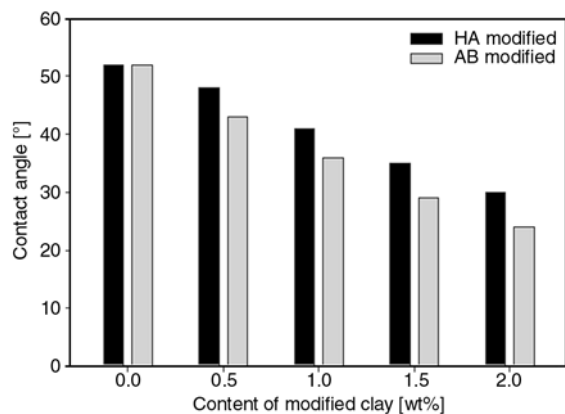


Figure 4. Contact angle of the film with LC drop

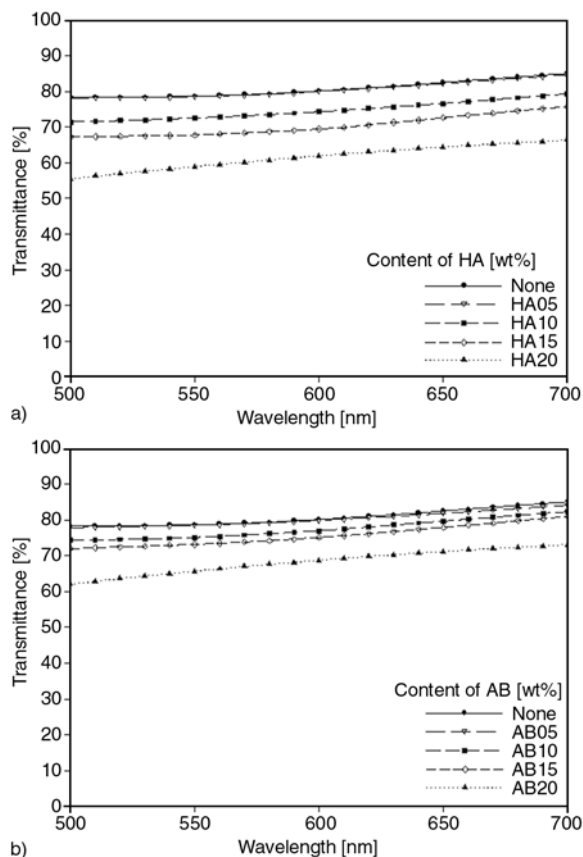


Figure 5. Visible spectra of various contents of HA (a) and AB (b)

3.4. Visible transmittance

Visible transmittance of the films with different resin compositions is shown in Figure 5 for various contents of modified clay. It is seen that the transmittance is slightly decreased with addition and increasing amount of modified clay. Also, the transmittance of AB is higher than HA due to the better dispersion of AB in LC.

3.5. Electro-optical properties

3.5.1. Driving voltage and memory effect

Typical switching characteristics of the film are shown in Figure 6 for various modifier contents, and parameters governing the effect are given in Table 2.

In the Table 2 memory parameter was defined by Equation (2):

$$M = \frac{T_m - T_0}{T_s - T_0} \quad (2)$$

where T_0 , T_s and T_m are the initial transmittance of the sample, the transmittance of saturation in an

electric field and the residual transmittance after removing the field, respectively [17]. So, higher M gives greater memory effect. It is seen that the memory effect increases with the addition and increasing amount of modifier, and the effect is more pronounced with AB.

It is seen that the driving voltage increases with the addition and increasing amount of modified clay due to the decreased droplet size to follow, which on the other hand is caused by the increased viscosity [18]. And the effect is more pronounced with AB than HA modifier.

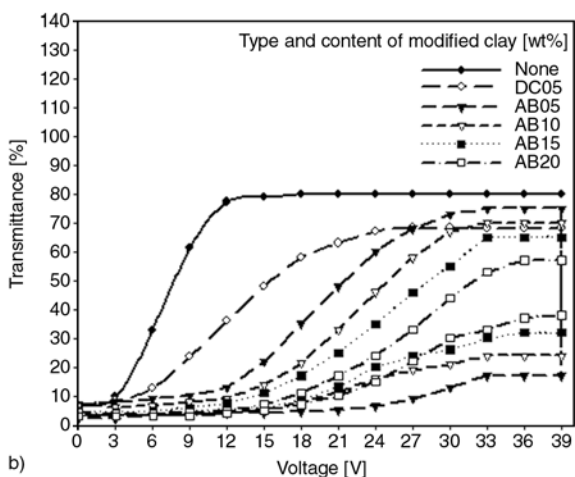
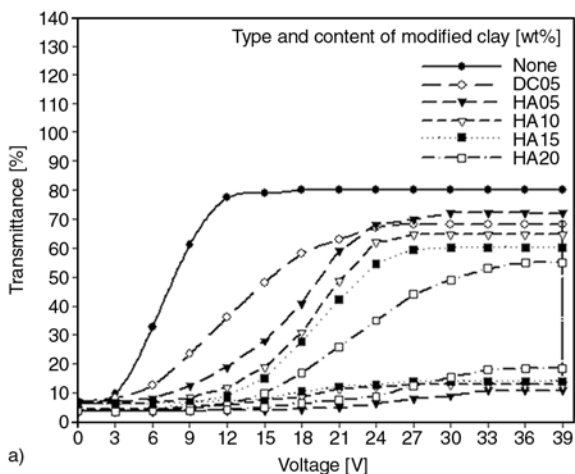


Figure 6. Transmittance vs. applied voltage at various contents of HA (a) and AB (b) (The upper and lower lines of the same caption respectively designate on state and off state transmittance. It is seen that films without clay and with virgin clay show no memory effect.)

Table 2. Memory effects of the film vs. type and content of clay

Type and content of modifier	Memory parameter (M)
None	0.00
DC05	0.00
HA05	0.11
HA10	0.14
HA15	0.15
HA20	0.29
AB05	0.22
AB10	0.33
AB15	0.48
AB20	0.66

3.5.2. Response times

The rise time is defined as the time required for the transmittance to increase from 10 to 90% points of the wave form upon turn on and the decay time is defined as the time required for the transmittance to fall from 90 to 10% upon turn off [19]. It is known that the reorientation field scales inversely with droplet size because the small liquid crystal domains produce high free energy of elastic deformations within the liquid crystal [20].

Typical response times of the films are shown in Figure 7, Table 3 and Table 4 for different types of clay and clay contents. Rise time and decay time increases with the addition and increasing amount of modified clay. These are due both to the decreased droplet size of LC (increased interfacial

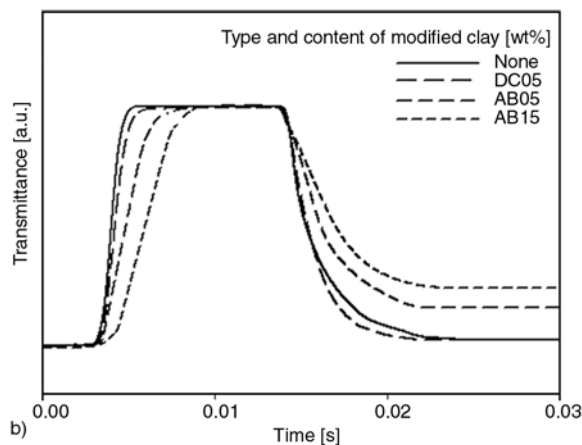
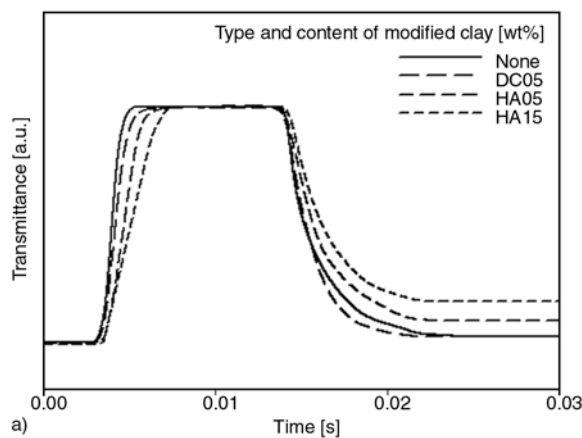


Figure 7. Response time vs. content of HA (a) and AB (b)

area) and increased anchoring strength. The response time of AB is longer than HA due mainly

Table 3. Response time of the film vs. HA content (30 V)

Type and content of modify agent	Rise time [ms]	Decay time [ms]
None	2.04	8.26
HA05	2.77	10.04
HA15	3.42	10.48
DC15	2.17	8.02

Table 4. Response time of the film vs. AB content (30 V)

Type and content of modify agent	Rise time [ms]	Decay time [ms]
None	2.04	8.26
AB05	3.02	10.51
AB15	3.91	10.82
DC15	2.17	8.02

to the higher viscosity of AB. Virgin clay (DC) increases rise time over the None (AB00 and HA00) due to the increased viscosity, while the decay time decreased due mainly to the decreased droplet size of LC.

Surprisingly, the transparent state was maintained upon removal of the electric field, thus exhibiting memory effect. Upon field on, chain segments of modification are likely to orient along the field direction with LC molecules. Even after the field is off, the transmittance of the film remains high with modified clays and the effect is more pronounced with AB than HA modification. This implies that the modified clay maintains their orientation due to their bulkiness. Among the two types of modification, the pendant cyano-biphenyl group is expected

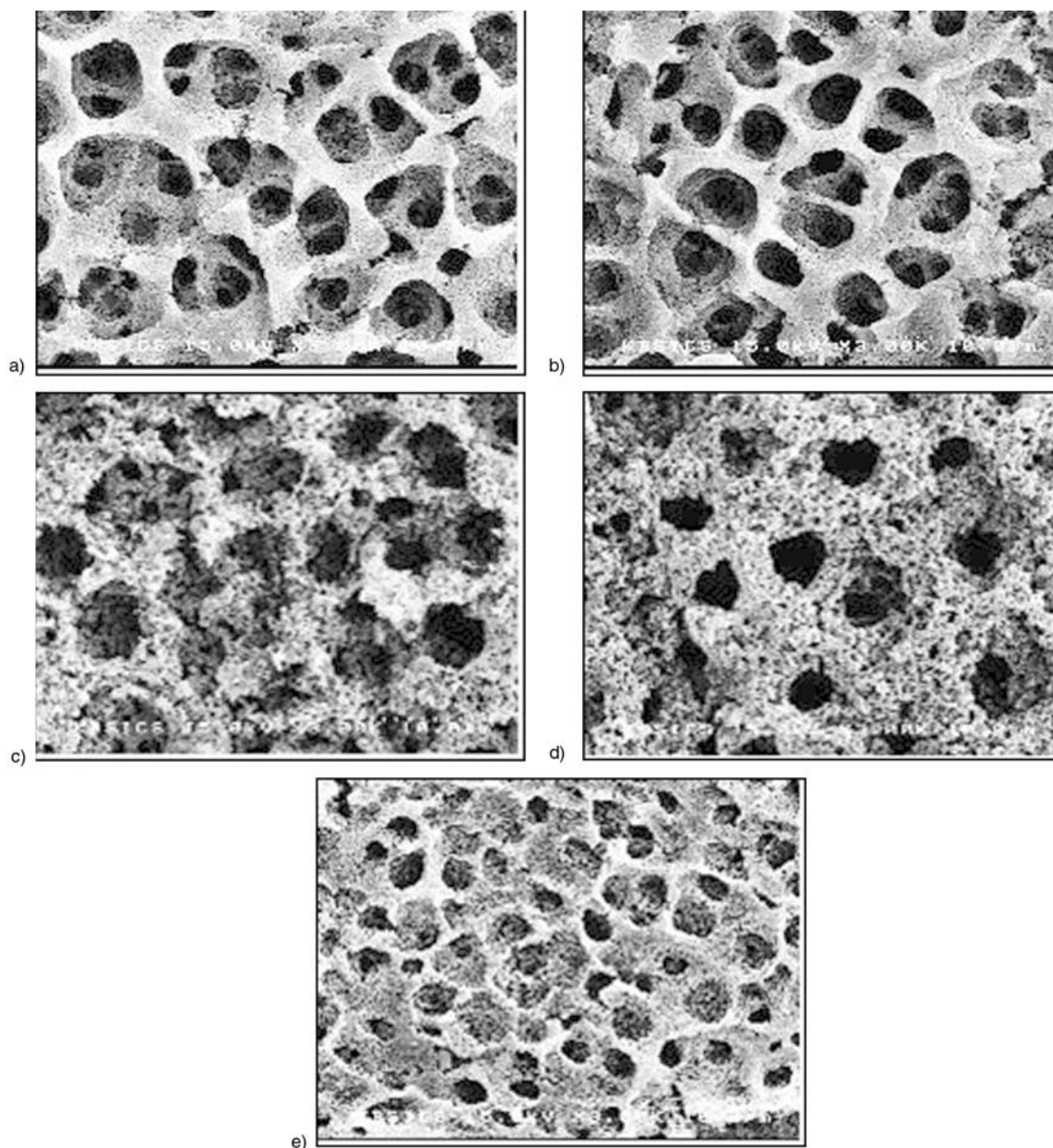


Figure 8. SEM image of the PDLC films vs. content of HA: 0 wt% (a), 0.5 wt% (b), 1.0 wt% (c), 1.5 wt% (d) and 2.0 wt% (e)

to show greater effect than the straight alkyl chain (HA) in terms of bulkiness and viscosity. The driving voltage of AB is higher than HA due to its smaller droplet size by high viscosity.

3.6. Morphology

Figure 8 and Figure 9 show SEM morphology with 3.00 K magnification of the PDLC films as a function of the type and content of the modified clay. With the addition and increasing amount of modified clay, droplet size of LC monotonically decreases due to their high viscosity. The AB shows smaller droplet size of LC than HA. This implies that miscibility of AB with LC molecules is

greater than HA. At the same content of dispersed phase smaller droplet gives larger viscosity due to the larger effective volume of the droplet.

4. Conclusions

The addition of clay to the conventional polymer dispersed liquid crystals (PDLC) introduced significant effects in terms of morphology and electro-optical properties of the films. The memory effect exhibited by the modified clay is rather unusual since most of conventional nematic liquid crystals do not exhibit such effect.

With the addition and increasing amount of modified clay driving voltage and memory effect simul-

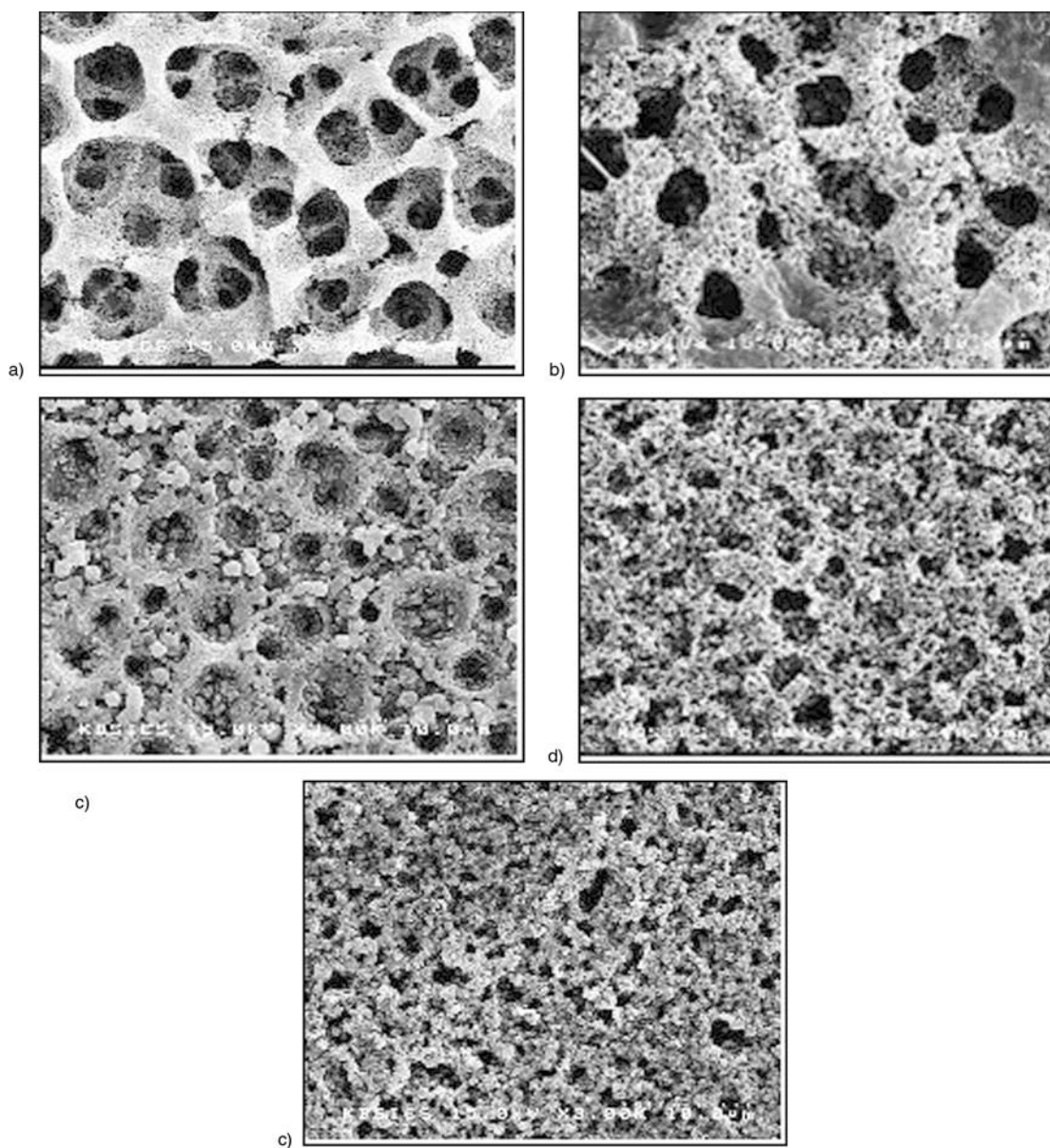


Figure 9. SEM image of the PDLC films vs. content of AB: 0 wt% (a), 0.5 wt% (b), 1.0 wt% (c), 1.5 wt% (d) and 2.0 wt% (e)

taneously increased due to the increased viscosity. Among the two types of modifier, AB gave finer dispersion of clay in LC due to the greater miscibility of AB in LC than HA. The greater miscibility is based on the similar chemical structure. So, AB gave greater viscosity, larger driving voltage and response time, and greater memory effect.

Acknowledgements

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