EFFECTS OF TIO_2 NANOPARTICLES AND FUNCTIONALITY OF MONOMER ON THE ELECTRO- OPTICAL RESPONSE OF THE ACRYLIC MATRIX COMPOSITE MATERIAL PDLC

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Abstract— Composite materials type PDLC (Polymer Dispersed Liquid Crystal) are generally in the form of thin films consisting of a dispersion of micro or nano-droplets of liquid crystal in a polymer matrix, are prepared by phase separation induced by photopolymerization under ultra-violet (UV) in the presence of a photoinitiator.
Two types of polymer / liquid crystal composite materials were studied: PDLC and PDLC doped with TiO_2 nanoparticles. The systems studied are TPGDA/E7 and GPTA/E7. A comparative study of the opacity of these materials was carried out using an electro-optical bench by measuring the transmissions to the initial state "Toff". The effects of the monomer functionality on the morphology of polymer network, electro-optical of PDLC films were studied. The results obtained were correlated with those of optical microscopy with polarized light and infrared spectroscopy "FTIR". The doped PDLCs are elaborated by injection of TiO_2 nanoparticles in the initial mixture followed. An investigation of the morphology and the state of dispersion is made with the aim of highlighting the differences and improvements brought by this load on the optical and electro-optical properties of these materials.

Index Terms— E7, GPTA, PDLC, TiO_2, TPGDA.

I. INTRODUCTION

Polymer-dispersed liquid crystal films (PDLC) that consist of micrometer-sized liquid crystal droplets dispersed in a polymer matrix [1–3]. The important characteristic of these materials is the transition from an opaque state (OFF) to a transparent state (ON) by application of an external field (electrical, magnetic).
In the electric field-off state, the refractive index mismatch between the polymer matrix and the LC material gives rise to the light scattering of incident light. In the electric field-on state, the films become transparent because of the parallel alignment of the LC directors with the applied electric field if the refractive indices match between the LC droplets and polymer matrix [4]. The switching properties of the LC molecules within the domains depend on some variables, such as the size and shape of the domains, the molecular interactions between the LC material and the polymer matrix [5, 6].
The preparation of PDLC films is often based on the polymerization induced phase separation (PIPS) process by UV light. A proper control of the phase separation phenomena of the polymer/LC composite system is necessary to obtain different morphologies, depending essentially on the polymerization conditions [5].
Nanoparticles (NP) have attracted great interest in recent years because of unique mechanical, optical and magnetical properties [6]. Recently, the merging of nanomaterials and nanotechnology into electro-optical (EO) device technology such as LCDs may attract researchers who are interested in inaugurating a new kind of combination of different fields [7-9].
A comparative study on the functionality of the monomer will be made. This will help to clarify the correlation between the conditions of preparation and the properties of the films developed. We will study the opacity and the electro-optical responsive of the film prepared. A study on the effect of dilution by the liquid crystal on the reactivity of monomers (TPGDA, GPTA) will be made. This research is completed by physicochemical analyses by the use of powerful experimental techniques MOP: to establish the variation in mechanical properties due to the strengthening of networks by inorganic nanoparticles.

II. EXPERIMENTAL

The LC is an eutectic mixture of nematic LC, commercially known as E7, consisting four cyanoparaphenylene derivatives (5CB, 7CB, 8OCB, 5CT) [9]. It exhibits a single nematic isotropic transition temperature $T_{NI}(LC) = 61°C$.
For the monomer, we chose acrylates for their strong photopolymerizable character: a difunctional monomer; Tripropylene glycol diacrylate (TPGDA) and a tri-functional monomer; Propoxylene-glycerol triacrylate (GPTA). Lucirin TPO as photo initiator.
TiO_2 nanoparticles was obtained from Sigma-Aldrich. It exhibit sizes < 30nm.
The PDLC films are prepared from an initial mixture of monomer and liquid crystal and then irradiated

under a fluorescent UV lamp TL08 of wavelength 365 nm and intensity 1.5mW/cm^2 for 30 minutes.
The doping of the PDLC films was carried out by injection and dispersion of nanoparticles in the precursor mixture under ultrasound. The cells are prepared by depositing a drop of the sandwich precursor mixture between two conductive glass slides.

III. RESULTS AND DISCUSSION

1. Electro-optical characterization:
The electro-optical study is carried out by an "electro-optical bench" assembly. The sample to be characterized is placed on a support placed vertically. The light beam from a red monochromatic HeNe laser (l=632.8 nm) passes through the sample perpendicular to its surface. The light intensity transmitted at zero angle (collection angle of +/- 1°) is collected by a photodiode. A 1450Hz sine wavevoltage is applied to the sample terminals using software dedicated to this type of study (Keithley Viewdac 2.2). An investigation on the opacity of the films is carried out by determining the transmittances in the initial state, before application of the external electric field, designated by Toff. In figure 1, it is observed that for values in E7 of less than 10%, the TPGDA material has a certain transparency with respect to the GPTA. Between 10% and 60% in E7 the transmittance decreases up to 70% of the liquid crystal where the film is completely opaque. Unlike GPTA/E7, the Toff begins to decline around 30%. An opacity is observed at 80% of the LC. This difference in opacity can be explained by a distinct architecture of the formed network.

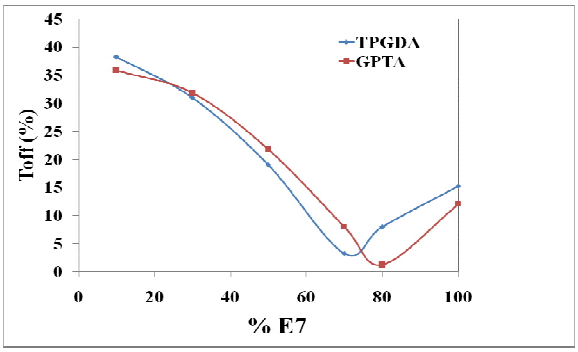


Fig.1: Transmittance of TPGDA/E7 and GPTA/E7 films as a function of the E7 content.

2. Infrared Spectroscopy
FTIR spectroscopy is a versatile method used to investigate the extent of curing using carbon-carbon double-bond consumption. The difunctional acrylate monomers lead to formation of cross-linked polymer networks. It is evident that high monomer conversions should be reached to minimize the undesired effects of unreacted monomer molecules.
Polymerization/cross-linking of monomer governs the architecture of the obtained polymer networks. At least two absorption bands are available to monitor polymerization /cross-linking processes and to evaluate the conversion of the acrylic double bonds of TPGDA and GPTA. One of the most characteristic absorption bands that is quite often used in FTIR analysis of acrylates is the one corresponding to the -CH=CH- vibration at 810cm^{-1}. Another peak that appears at 1637cm^{-1} is used for the analysis of the monomer.
The calculation of the monomer conversion is made by considering the peak heights of the absorption band at 1637cm^{-1}. The conversion ratio C is calculated using the following equation (1)

$$C(\%) = \frac{(A_{1637})_{(D=0)} - (A_{1637})_{(D)}}{(A_{1637})_{(D=0)}} \qquad [1]$$

Were $(A_{1637})_{(D=0)}$ is the height of the peak at 1637cm^{-1} (i.e. irradiation dose D is zero), and $(A_{1637})_{(D)}$ is the corresponding result for the system exposed to a dose D.
The interest of this study is to identify polymers TPGDA and GPTA and checked that the separation of phase took place. The acquisition of the spectra is done thanks to a spectrophotometer, models Perkin Elmer 2000, in the range of numbers of wave located between 4000 and 700cm^{-1}.
Measurements are made in the ATR by deposit of a drop of the monomer on a concave head. The evolution of the acrylic double-bond conversion as a function of UV light exposure time under UV-TL08 is represented in figure 2 witch shows a superimposed spectrum of monomers TPGDA and GPTA not irradiated.

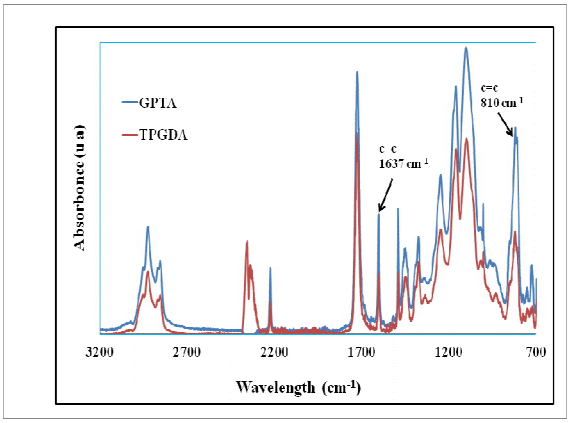
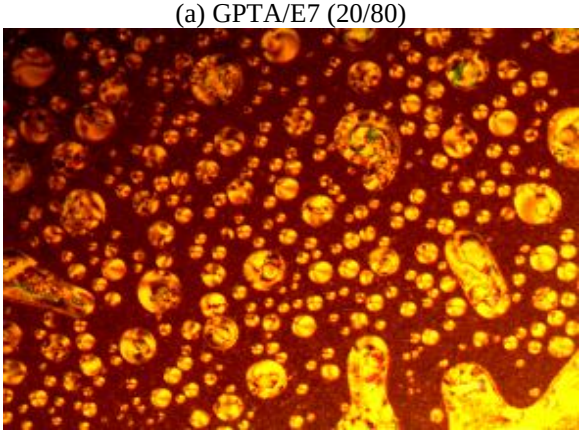


Fig.2: Infra-red spectrum of the monomers: TPGDA and GPTA

3. Study of morphology by MOP:
The morphology was studiedusing a polarizing optical microscope Olympus BX-41 connected to a digital camera and a computer that can record images with high resolution.
The results illustrated in fig.5a showed for the GPTA/E7 system, a phase separation at 50% in E7 and a heterogeneous distribution and dispersion of the

droplets. In contrast to the TPGDA/E7 system (fig.5b), and at 70% in E7, homogeneous distribution of the nematic domains with spherical forms of micron size was observed, which explains the high opacity of these films. At 80% in E7, the objects are larger, causing a reduction in opacity, whereas for the GPTA/E7 system the Toff is smaller, there is a large number of droplets, there are interconnected domains.

(a) GPTA/E7 (20/80)



(b) TPGDA/E7 (20/80)

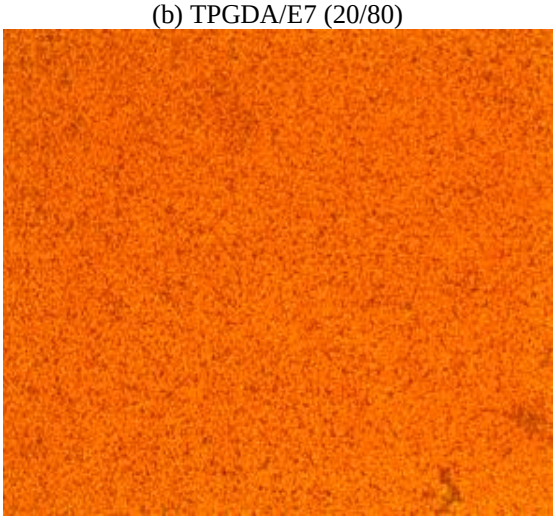
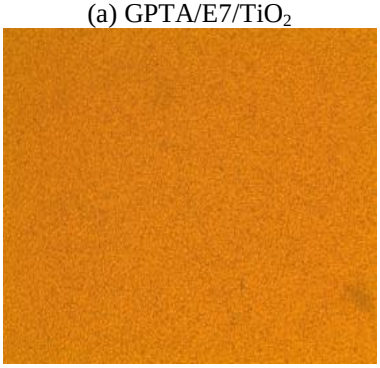


Fig.3: Morphology of a and b systems as a function of the concentration of the liquid crystal.

The doped systems have a different morphology compared with undoped as can be seen in figure 3b. The network is crosslinked, it can be said that the E7 droplets segregated with difficulty, this is due to the droplet size reduction after the addition of TiO_2. Also for the GPTA/E7/TiO_2 system, according to figure 3a.We can see that we have gone from morphology with very large droplet sizes with different shapes to a morphology showing droplets that are difficult to observe after the addition of the TiO_2 nanoparticles. This result is due to the functionality of the GPTA (f = 3), the network is highly crosslinked without the presence of TiO_2, which has caused the appearance of large domains.

(a) GPTA/E7/TiO_2



(b) TPGDA/E7/TiO_2

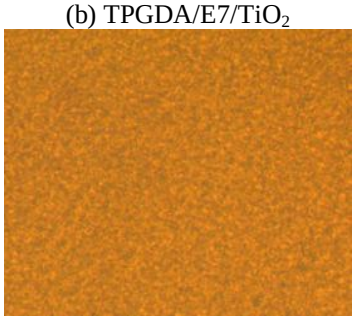
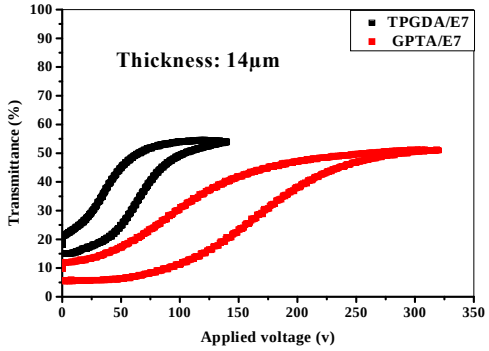


Fig.4: Morphology of a and b systems as a function of the concentration of the liquid crystal.

4. Comparison of the **electro-optical response** of systems TPGDA/E7 and GPTA/E7

Figure 5 shows an example of electro-optical response of the systems of weaker and stronger average functionality. It summarizes the various results obtained.



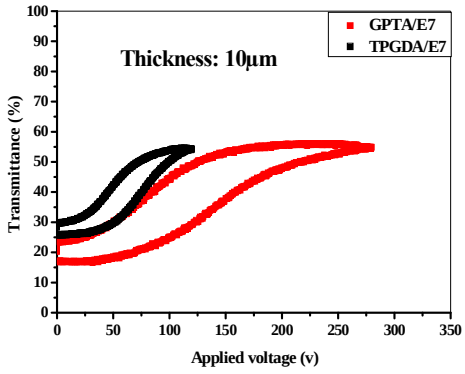


Fig.5 : Comparison of the electro-optical response of samples comparable thickness (10 and 14 µm) prepared starting from the TPGDA/E7 and GPTA/E7 systems.

One can note two principal characteristics concerning these results.

On the one hand, concerning Toff, one can distinguish two cases. The system TPGDA/E7 whose Toff is higher than 15-20%, and the systems GPTA/E7 whose Toff remains lower than 15%. That indicates a better separation of phases in the second case, which contributes to a better opacity of the samples in the state off. This more important opacity can in particular be caused by a size of the smaller and more diffusing objects.

On the other hand, for a given thickness, the values of tension threshold, saturation, hysteresis are in the order ascending according to: system TPGDA/E7 and GPTA /E7. We saw that one has systems whose conversion increases with the average functionality of the precursory starting mixture. Moreover, one can suppose that the formed network will be increasingly réticulé with the higher average functionality of the starting mixtures. That can lead as that already was observed in the literature with a size of diffusing fields smaller and would thus explain the higher values of tension threshold, of saturation with the average functionality of the samples.
The increase in hysteresis seems more difficult to bind to the size of the diffusing fields. It depends mainly on the interface fields liquid crystal/polymer and the distribution of the size of the fields. Moreover, for a given thickness, there is an increase in difference V90-V10 with the average functionality of the starting mixtures. That can represent a broader distribution of the size of the diffusing fields. And thus a heterogeneity of larger morphology. Two factors which are not inevitably dependant appear to play a crucial role in the properties obtained. Not only density of reticulation of the formed network but also homogeneity of the formed network.

CONCLUSION

PDLC composites based on TPGDA and GPTA carrying matrix and E7 LC have been obtained by TIPS methods.
The functionality of the monomer has a significant influence on the electro-optical properties thermally cured PDLC films. When it increases, the crosslinking density and polymerization rate become higher, resulting in a decrease in the LC domain size of PDLC films, which decreases Toff and increases Ton, Vth and Vsat.
In the presence of TiO_2 the network becomes less cross-linked, hence the reduction of the droplet size of the LC and the increase in the number of nematic objects. All these results remain to be confirmed with electro-optical analysis to see the effect of TiO_2 on the orientation of the droplets of E7 under application of the electric field.

REFERENCES

[1] Cheng, Z., Wang, T., Li, X., Zhang, Y. NIR-VIS-UV actuator films of PDLC /graphene oxide nanocomposites. ACS Appl. Mater. Interfaces **2015**, 7, 27494–27501.
[2] Yu, L., Cheng, Z., Dong, Z., Zhang, Y., Yu, H.F. Photomechanical response of PDLC/graphene oxide nanocomposites. J. Mater. Chem. C **2014**, 2, 8501–8506.
[3] Doane, J.W., West, J.L., Whitehead, B.G. PDLC for display application. MCLC. **1988**, 165, 511–532.
[4] Malik, P., Raina, K.K. Droplet orientation of PDLC composite films. Opt. Mater. **2004**, 27, 613–617.
[5] Kovalchuk, A.V., Kurik, M.V., Lavr, O.D., Sergan, V.V. Structural transformations in nematic drops located in an external electric-field. SPJ **1988**, 67, 1065–1073.
[6] Kovalchuk, A.V., Lavr, O.D., Sergan, V.V. Kenetic of electrooptical effects in drops of nematic with different structure. Sov. Tech. Phys. Lett. **1989**, 15, 529–533.
[7] Liu, Y.J., Ding, X., Lin, S.C., Shi, J., Chiang, I., Huang, T. Surface acoustic wave driven light shutters using PDLCs. AM. **2011**, 23, 1656–1659.
[8] Lee, J.W., Kim, J.K., Ahmad, F., Jamil, M. Properties of thiol–vinyl PDLC films without additional photoinitiator. Liq Cryst. **2014**, 41, 1109–1115.
[9] Su, Y.C., Chang, W. Characterization of optically switchable PDLC trans gratings. OM. **2011**, 34, 251–255.

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