Effect of SiO_2 Nanoparticles on Phase Transitions of Composite Materials Polymers / Liquid Crystals

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ABSTRACT: *In this work, we are interested in the effect of the addition of inorganic SiO_2 nanoparticles with a size of 12 nm, in the composite materials PDLC, to optimize the thermo-physical properties of these materials in order to meet the needs of the new technology, intended for optical and electro-optical applications. These PDLC materials are generally in the form of thin films consisting of a micrometric droplet dispersion of CL in a solid polymer matrix. The photo polymerization under UV irradiation is envisaged in the preparation of these polymers "in-situ polymerization" with and without nanoparticles. We will examine the evolution of the morphology of films after addition of nanoparticles by polarizing optical microscopy (POM). A study on the influence of nanofillers on the different phase transitions (Tg and T_{NI}) of composite materials PDLC is carried out by DSC. It is important to understand and study the dispersion step of the silica nanoparticles in our polymer matrix.*

KEYWORDS – DSC, PDLC, Photo polymerization , SiO_2 nanoparticles, 5CB.

I. INTRODUCTION

Today, the field of display that goes from watches to high-definition television screens [1,2], holds an essential place in the transmission of information. The technology using liquid crystals with a high quality of visualization is the most used. The important anisotropic physical characteristics make the liquid crystal usable for display applications. These composite materials are in the form of a dispersion of micro liquid crystal droplets of low molecular weight, in a polymer matrix, are called "PDLC" (Polymer Dispersed Liquid Crystals). Their interest lies in their unique electro-optical properties, as evidenced by the growing number of publications devoted to them. The most important properties of these materials is the transition from an opaque state (OFF) to a transparent state (ON) by applying an external field (electric, magnetic) [3]. These materials can be developed by different methods, based on the phase separation between the liquid crystal and the polymer matrix. The most widely used technique is photo-polymerization induced phase separation under ultraviolet radiation (IPLP) [4, 5]. In recent years, new PDLC materials doped with inorganic nanoparticles have attracted great interest. The organic/inorganic mixture promotes the formation of nanocomposite materials having high thermo-physic, optical, electro-optical and mechanical properties. Recent research on the doping of PDLC films (TE + E7) by diamond nanoparticles has shown a change in the glass transition Tg and the nematic - isotropic transition [6]. Other published works [7] on the effect of gold (Au) NPs on the electro-optical properties of PDLCs have shown a change in this electro-optical response. Yu-Tse et al [7] propose a dimethyl methylphosphonate compound sensitive gas sensor (PDLC). The sensing element comprises a detection PDLC film doped with carbon nanotubes (CNT-PDLC).On the other hand, an important field of research opens on the doping of these composite materials PDLC with nanostructures (nanoparticles, nanowires ...) such as doping by silicon. Different research groups have shown that doping with Np-Si makes it possible to control the optical and electrical properties of the nano-composite materials obtained.

Our work aims to develop PDLC materials and to study the additive effect of SiO_2 nanoparticles on the thermo-physical properties of these composite materials PDLC.

II. Experimentals methods

Different types of materials are available to develop PDLC systems. The choice of materials has a pronounced effect on the optical and electro-optical properties of the composites formed. The chosen liquid crystal is a 4-cyano-4'-n-pentyl-biphenyl nematic liquid crystal called 5CB. It has a crystallization temperature T_{cry}=21°C and an isotropic nematic temperature T_{NI}=35.3°C. Between these two temperatures, the 5CB is in the nematic state. The extraordinary and ordinary refractive indices (n_e and n_o) are respectively 1.6812 and 1.5540 measured at a wavelength λ=546.1 nm [8]. The choice of the liquid crystal plays a very important role in the performance of the electro-optical cells. All the published works relate to the use of the liquid crystal with a positive dielectric anisotropy (Δε>0) and high values of the optical birefringence Δn=0.1272, these important parameters in the choice of the liquid crystal give a decrease of the fields of switching. The monomers used are acrylates. Ethylene glycol phenyl ether methacrylate EGPEM is a monofunctional monomer with a refractive index of 1.513.

A second di-functional monomer used as crosslinking agent is Hexane Diol Di Acrylate HDDA. The radical photo-polymerization is initiated by the photo-initiator Darocur 1173 wavelength of 345 nm.

Experimentally, the manipulation was carried out in a very low light room to limit the risk of degradation of the photo-initiator and acrylic monomers. 500 mg monomer / LC mixtures for a well-defined composition of 5CB and HDDA are left under mechanical stirring for 24 hours until the total homogeneity of the mixtures. The mass composition is given in Table 1:

Table 1: Constituents and mass composition of the PDLC mixtures.

Designation	Molecular formula	Structure	Composition (%)	Mass (mg)
EGPEM	$C_{12}H_{14}O_3$	Ethylene glycol phenyl ether methacrylate	34.5	189
HDDA	$C_{12}H_{18}O_4$	1.6-Hexane-Diol-Di- Acrylate	2	4
Darocur	$C_{10}H_{12}O_2$	2-hydroxy 1-Phenyl-Propane-1-one	2	4
5CB	$C_{18}H_{19}N$	4-cyano-4´-pentyl-1,1´-biphenyl	60	300

The same process for the preparation of PDLCs for the production of materials doped with SiO_2 nanoparticles is used. The dispersion of nanoparticles in the initial mixture is carried out by sonification for 1 h. The PDLCs are prepared by the PIPS process by exposing a drop of the reaction mixture placed between two conductive glass slides to a static UV irradiation source. The sample is kept immobile during the polymerization for a period of 30 minutes, the distance between the irradiation and the sample is constant. The temperature remains quasi-constant varies between 25 and 28°C independent of the duration of irradiation. The UV lamp is the TL08 of intensity 1.5 mW/cm^2; its spectral range corresponds to the absorption band of the Darocur photo-initiator 365 nm.

Table 2: Constituents and mass composition of the doped mixture.

Designation	Molecular formula	Structure	Composition (%)	Mass (mg)
EGPEM	$C_{12}H_{14}O_3$	Ethylene glycol phenyl ether methacrylate	34.5	189
HDDA	$C_{12}H_{18}O_4$	1.6-Hexane-Diol-Di- Acrylate	2	4
Darocur	$C_{10}H_{12}O_2$	2-hydroxy 1-Phenyl-Propane-1-one	2	4
5CB	$C_{18}H_{19}N$	4-cyano-4´-pentyl-1,1´- biphenyl	60	300
SiO_2	SiO_4^{2-}	Silicon dioxide	1.5	3

III. RESULTS AND DISCUSSION

3.1 Characterization by MOP

Optical microscope analysis allows us to learn about the morphology of materials. The size limit below which a structure is still observable is about one micron [9]. By operating in polarized light, the optical microscope, called MOP, makes it possible to distinguish the mesophase domains from the isotropic structures. This technique is very often used in the literature, to study the morphology and the phase transitions (example passage from the nematic state to the isotropic state) for the polymer/ liquid crystal composites. According to the morphology of the doped system (EGPEM/ HDDA/ 5CB/ SiO_2) with the mass composition 15/15/70/ 1.5 given by Fig 1(b), there is a dispersion and homogeneous distribution of SiO_2 nanoparticles in the formed network. The reduction in the size of the nematic domains fig 1(a) is due to the high crosslinking of the EGPEM/ HDDA/ 5CB system, we can say that the droplets of the 5CB segregated are hardly observable with a zoom 40x.

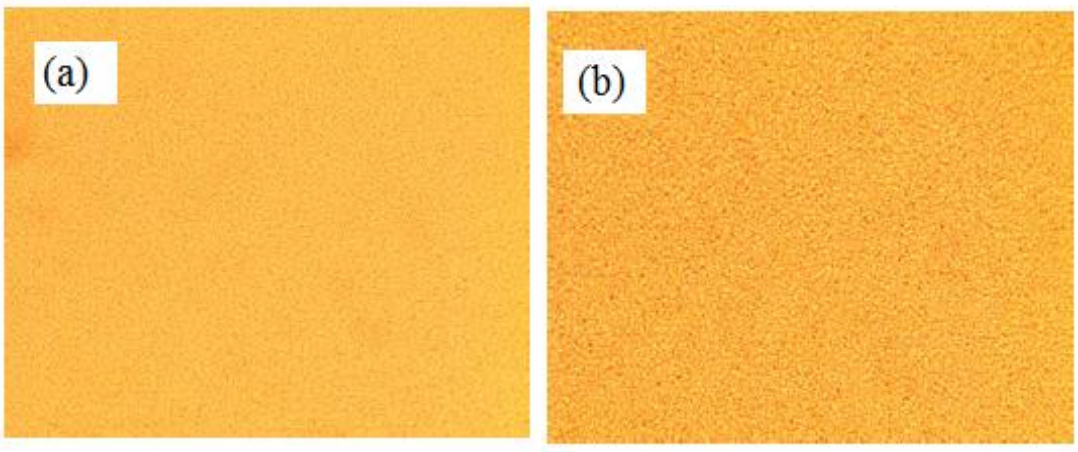

Fig 1: Morphologies of the EGPEM/HDDA/5CB system: (a) without and (b) with SiO_2 nanoparticles observed by MOP.

3.2 FTIR characterization:

It can be seen that the two monomers HDDA and EGPEM have the same characteristic bands of the acrylates (Fig 2). The liquid crystal 5CB has three important bands, that of the C=N nitrile function at 2227 cm^{-1}, a phenyl elongation band at 1607 'cm^{-1} and a mass around 800-1000 cm^{-1} corresponding to the deformation of the aromatic C-H bond (Fig 3). In general, in the case of carbon chain acrylates, two acrylic double bond absorption bands at 810 and 1637 cm^{-1} are often studied. For PDLC systems, the study of the polymerization kinetics is carried out by monitoring the decrease of the C=C acrylic band at 1637 cm^{-1}. The enlargement of the area between 1630 and 1645 cm^{-1}, shown in Fig 4, shows the decrease of the characteristic acrylate band at 1637 cm-1 for the doped PDLC and PDLC films. It is found that there is total consumption of these double bonds. The calculated conversion rate is close to 100 % for the EGPEM/ HDDA /5CB system after 30 minutes of irradiation. In the case of the systems doped with the SiO_2 nanoparticles, the analysis shows a difference in the intensity of the absorbance and no influence of the SiO_2 dopant is observed on the reduction of the characteristic band of the acrylic double bond, which shows that its presence does not influence the kinetics of photo-polymerization.

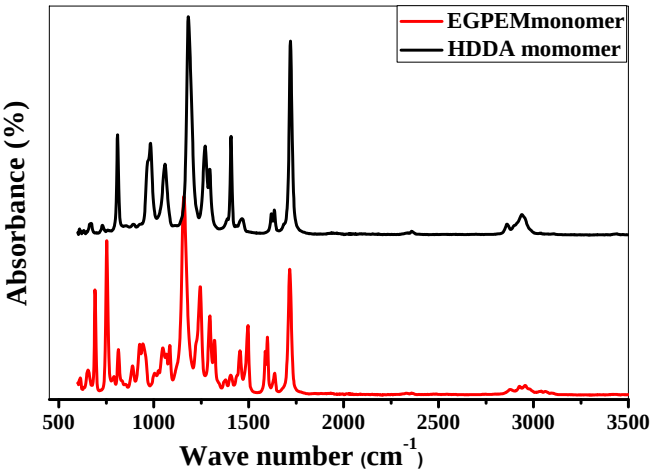

Fig 2: The FTIR spectrum of EGPEM and HDDA monomers.

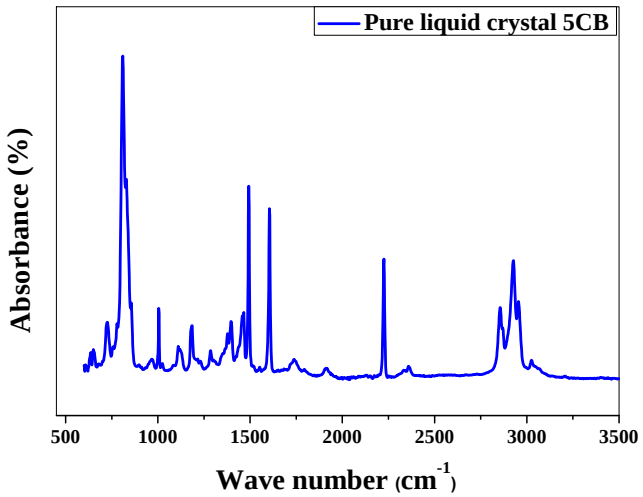

Fig3: The FTIR spectrum of pure liquid crystal 5CB.

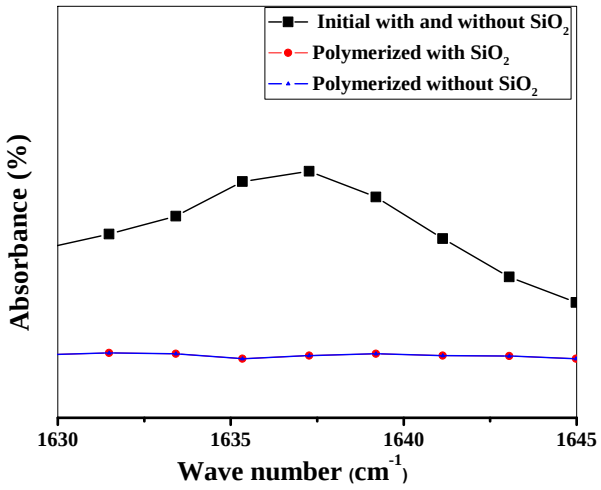

Fig 4: Effect of SiO_2 nanoparticles on monomer conversion.

3.3 Characterization by UV-visible spectroscopy

Among the characterization techniques that achieve a deep knowledge of functional materials, and consider their optimization for applications, the UV-visible technique is a proven method, simple and fast, provides information on the nature chemical properties, physico-structural properties, and optical characteristics of materials. It also allows the analysis of thin films for applications in optics or microelectronics (diffusion or absorption). The purpose of the UV-visible analysis was to determine the absorbance of these nanoparticles in the spectral range of the irradiation lamp. As well as the characterization of the PDLC and PDLC/SiO_2 films. Measurements of the transmissions are carried out by placing the lamellae on the sample holder in front of the beam of light. The transmission UV spectra were recorded separately, for the glass lamella alone and the polymerised mixtures. The UV-visible spectrum of the EGPEM/HDDA/5CB system represented by Fig 5, it gives us in the region between 260 and 320 nm, a characteristic band of the PDLC composite is doped or undoped. On the other hand, no characteristic band is observed in the region of interest for the polymerization under ultraviolet radiation (at 365 nm), which shows that the presence of the dopant SiO_2 does not affect the kinetics of polymerization. These results confirm those obtained by FTIR.

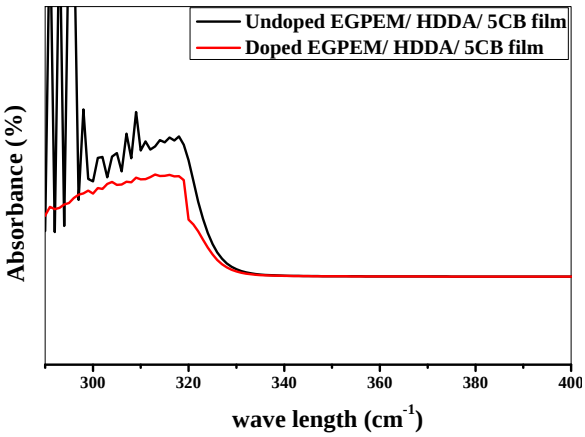

Fig 5: UV-Visible Curves of PDLC/SiO_2 and PDLC Films.

3.4 DSC analysis

In general, differential enthalpic analysis provides information on phase transitions [10, 11]. It offers, in addition, quantitative data that the MOP can not do. This method can be used to estimate the percentage of crystallinity in a semi-crystalline polymer and is particularly used in polymer / liquid crystal composites to quantify the mass fraction of the segregated liquid crystal between the polymer and the liquid crystal [12, 13]. Our study carried out on the system EGPEM/ HDDA/ 5CB (15/ 15/ 70) doped with 1.5% of SiO_2 in comparison with the same undoped system, shows that there is a decrease of the TNI of the liquid crystal such as that it varies from 32.62 °C to 29.55 °C, as Fig 6 indicates:

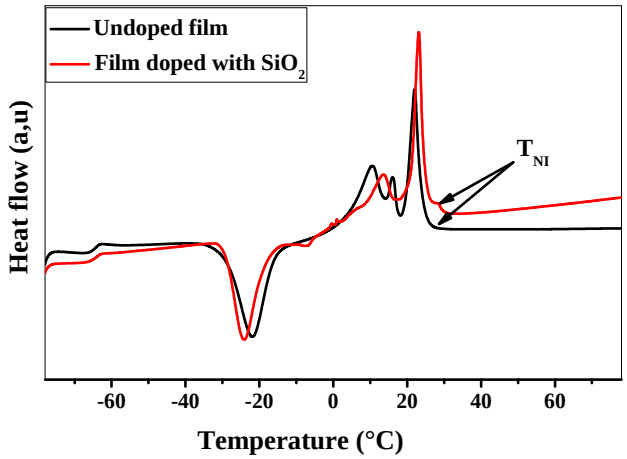

Fig 6: Thermograms of the undoped and doped PDLC.

IV. CONCLUSION

In this study, FTIR and UV-visible analysis shows that the presence of SiO_2 nanoparticles in our elaborate PDLC systems has no influence on the kinetics of polymerization, but on the other hand, the study by polarized

light microscope revealed well-defined structures of the PDLC and PDLC/ SiO_2 systems. Thermo-physical characterization by DSC and the MOP studies have shown that the presence of the dopant influences the transition temperatures (Tg and T_{NI}) and morphology.

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