Thermal study of photo-polymerization reaction in the preparation of composite materials based on polymers

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Abstract. Polymer Dispersed Liquid Crystals (PDLCs) were elaborated by polymerization induced phase separation under ultraviolet light (UV). A systems composed of Tripropyleneglycol diacrylate (TPGDA) monomer and a liquid crystal mixture (E7) were used as starting materials in the process of polymerization/cross-linking leading to a phase separation between polymer and liquid crystal. The time behaviour of the optical transmission of these films was experimentally studied during the period of exposure to UV-light in the absence of external applied fields. The transmission versus time curves of in-situ UV-cured TPGDA/E7 films reveal three regions: a first domain corresponding to a transparent film of the initial TPGDA/E7 mixture before exposure to UV light, a second time domain where the sample exhibits a fast relaxation process, just after the beginning of the UV irradiation of the monomer/LC blend, and an unusual third domain, characterised by an enhancement of the film transparency at longer relaxation times. This process depends on the sample preparation conditions and the film thickness. In this study, the temperature of the system (sample and two slats) was controlled before, during, and after the application of UV-light, with sample and without sample

Keywords: Monomer, liquid crystal, ultraviolet irradiation, phase separation, polymerization/cross-linking.

Résumé. Des cristaux liquides dispersés dans une matrice de polymère (PDLC) ont été élaborés par séparation de phase induite par polymérisation sous rayonnements ultraviolet (UV). Des systèmes composés de monomère tripropylèneglycol diacrylate (TPGDA) et d'un mélange de cristaux liquides (E7) ont été utilisés comme produits de départ dans le procédé de polymérisation / réticulation conduisant à une séparation de phase entre polymère et cristal liquide. Le comportement temporel de la transmittance optique de ces films a été expérimentalement étudié pendant la période d'exposition à la lumière UV en absence du champ appliqué. Les courbes de transmittance en fonction du temps des films TPGDA / E7 polymérisés par rayonnements UV révèlent trois régions: un premier domaine correspondant à un film transparent du mélange TPGDA / E7 initial avant exposition à la lumière UV, un second domaine temporel où l'échantillon présente un processus de relaxation rapide juste après le début de l'irradiation UV du mélange monomère / CL et un troisième domaine, inhabituel, caractérisé par une amélioration de la transparence du film à des temps de relaxation plus longs. Ce processus dépend des conditions de préparation de l'échantillon et de l'épaisseur du film. Dans cette étude, la température d'un échantillon a été contrôlée avant, pendant et après l'application de la lumière UV, avec un échantillon et sans échantillon.

Mots clés: Monomère, cristaux liquides, irradiation ultraviolets, séparation de phases, polymérisation / réticulation.

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1. Introduction

The mixtures of polymer and low-molecular-weight liquid crystal (LC) are of great interest scientifically and technologically due to their potential applications in the area of electrooptical devices and flat panel displays…[1, 2]. In their most common form, PDLC films are made of micron-sized liquid crystalline (LC) domains dispersed in a solid polymer matrix [3-9]. The orientation of the LC molecules inside the domains changes with the application of an electrical field, and under some conditions, the intensity of the transmitted light can vary between an opaque off-state to a transparent on-state [3]. These systems are generally prepared by a technique of polymerization/cross-linking induced phase separation (PIPS) of monomers under irradiation by UV light. The growth of polymer network and LC domains formed, leads to a drop in the optical transmission [4,5]. In this work, different processes, that take place during the preparation of PDLC films [5-9] by the phase separation method [7] under UV irradiation, were investigated. Model mixtures were considered to understand the kinetics of polymerization and phase separation which shows unusual relaxation phenomena [13,14]. During polymerization/cross-linking reactions the LC molecules become less miscible with the growing polymer. The length of polymer chains formed increases as polymerization proceeds; then the mixture will separate in two phases, one consisting of the isotropic chemically cross-linked polymeric network, and the other consisting of isolated LC domains [10,12]. In this study of phase separation kinetics, the transmitted light was measured as function of time without applying an electric field, before, during and after the period of UV-light exposure [13]. The transmission was measured until a constant value was reached indicating that the system is chemically and thermodynamically stable. The temperature of the sample was measured with a thermal probe before, during and after the irradiation by UV-light, in order to check the cause of this new increase in the light transmission.

2. Experimental part

The liquid crystal used in this work is E7 which represents a mixture of four cyanobiphenylene derivatives. This mixture exhibits a nematic-isotropic transition temperature at $T_{NI}=60°C$ and presents a large nematic phase between -62°C and +60°C. Tripropyleneglycol diacrylate (TPGDA) was used as difunctional monomer. Initial mixtures containing 30 weight-percent (wt.%) of monomer, 70wt.% of E7, and 1wt.% (of the weight of the monomer) of a photoinitiator (Lucirin TPO, from BASF) were mixed together for several hours until the mixture became homogeneous. For optical investigations, the initial reactive mixtures were sandwiched between two standard glass-plates. The thickness of the polymer/LC films was measured by a micrometer calliper (Mitutoyo, uncertainty ±1µm). A thermal probe fixed between two standard glass-plates, fixed by silicone, is used for the measurements of sample temperature. The sample in the liquid phase is inserted between two glass-plates.

A phase separation induced by polymerization / crosslinking processes was carried out under UV radiation emitted by an irradiation source LC3 (from Hamamatsu) [14], equipped with a Xenon lamp covering the spectrum between 250 and 800 nm, and an optical fiber. The prepared samples were exposed to UV irradiation at distances of 3.5cm, 2cm, and 1cm from the end of the optical fiber. The light intensity was kept constant at its highest level, and the exposure time of the samples varied between 10s and 60s, by using an automatic shutter. The same experiment was repeated six times to check the reproducibility of the results. Temperature was also controlled during the irradiation processes by a thermal probe. Standard equipments, including a laser, a sample holder and a photodiode, together

with a computer-controlled data acquisition system, were used for the study of optical properties. The transmission of unpolarized He-Ne laser light (λ=632.8 nm) passing perpendicular through the monomer/LC film was measured as function of time, without applying an electrical field.

The distance between the photodiode and the sample was about 32 cm and the angle between the optical fiber and the axis Laser/sample/photodiode was 38°. Measurements of the light transmitted by the film was made in the homogeneous state during 20s, followed by data acquisition during 300s covering the exposure time to UV-light (10s and 60s) and the relaxation time after cutting UV irradiation [14]. Consecutive measurements of transmittance, in the absence of irradiation, were conducted during 300s every 5 min, up to a total evaluation period of 30min. The transmission data were corrected using appropriate calibration standards. The temperatures of sample were measured in this work before, during and after irradiation by UV-light, for continuous periods with a thermal probe. We also measured the temperature of a thermal probe without sample in order to compare the results. The dose of UV-light induced by LC3 source, and the one received by the sample, were measured as a function of time.

3. Results and discussion

Figure 1 shows the kinetics of phase separation of the TPGDA/E7 system, obtained by measuring the light transmission for samples which were exposed to UV light during 60s. Two different distances between the end of the optical fiber and the sample were considered, 3.5cm (Figures 1-a) and 1cm (Figures 1-b).
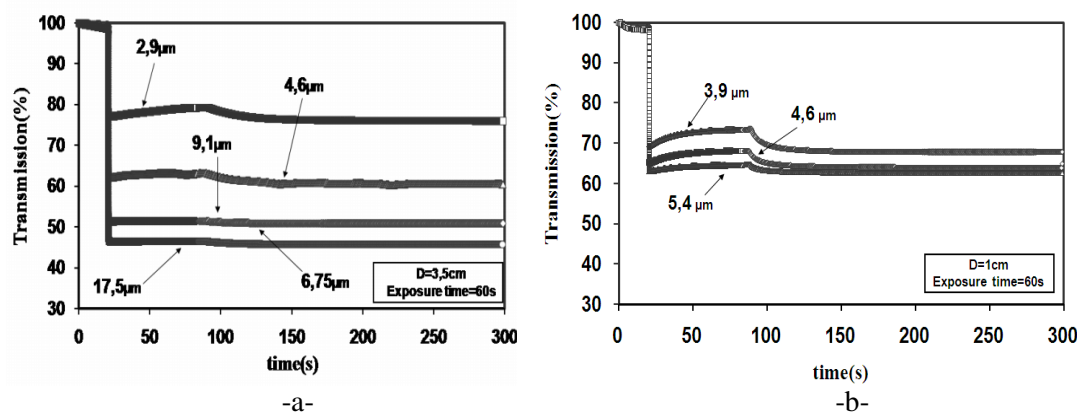

-a-   -b-

Fig. 1 :   Transmission of TPGDA/ E7 films exposed to UV-light for an exposure times of 60s.

The distance between the optical fiber and sample is: 3.5cm -a- and 1cm -b-.

The transmission versus time curves of several samples reveals three domains. The first, observed before the application of UV-light, is characterized by high transmission values attesting that the films are homogenous. In the second domain, which begins just after the application of UV light, the sample exhibits a fast relaxation process. Since the polymerization rate under UV-light is generally rather fast and the subsequent phase separation is also a rapid process, the initial growth of LC

domains induces a strong light scattering and hence a sharp decrease in the transmission. A third time domain was also observed, characterized by an unusual enhancement of the film transparency, at longer relaxation times.
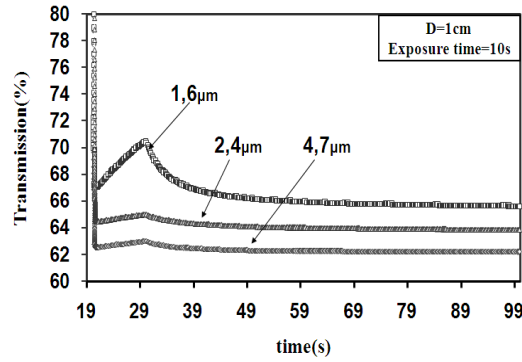
Fig. 2: Transmission of TPGDA/E7 films exposed to UV-light for an exposure times of 10s.
The distance between the optical fiber and sample is 1cm.

When the UV dose increases, the kinetics of phase separation become faster, and a certain decrease of the transmission values in the final OFF states was observed, depending on film thickness. The re-enhancement of the transmission values occurring after the sharp decrease of the relaxation curves, as shown in figures 1-b and 2, reveal that an unusual effect takes place. This increase in transmission is due probably to a heating of the films, which is more important with increasing UV dose. In this work, the temperature of the sample was controlled by a thermal probe before, during and after the application of UV-light. Figure 3 shows a temperature variation of a thermal probe without sample for three distances, between an optical fiber and a glass plate, 3.5cm, 2cm, and 1cm. These measurements, of the sample temperature, were performed for 300s.
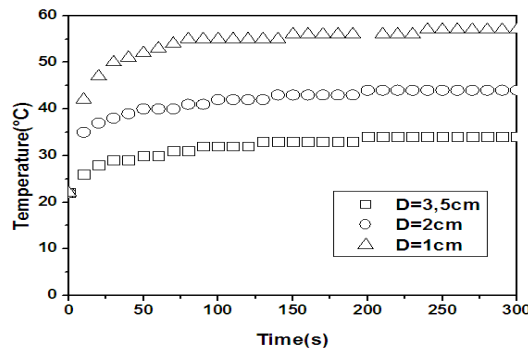

Fig. 3: Temperature of the thermal probe without sample for three distances between the optical fiber and the sample: D=3.5cm, 2cm and 1cm.

The processes of the variation in the temperature of the sample have a pace of associated exponential, where it is observed that the temperature without sample, under radiation UV, increases to reach a certain maximum value which depends on the distance between the optical fiber and the probe which is under a glass plate. Figure 3 shows that the temperature of a thermal probe reaches a

maximum value T_{max} depending on the distance between the fiber and the sample: $T_{max} \approx 60°C$ for;d=1cm, $T_{max} \approx 40°C$ for d=2cm and $T_{max} \approx 30°C$ for d=3.5cm. These three temperatures are lower than the isotropic nematic transition temperature T_{NI} of the liquid crystal E7 used for this study. The study of the temperature of sample TPGDA/E7 (30/70 wt. %) under UV-light irradiation, from the thermal probe, is shown in figure 4. The temperature of the sample presents a pick value in the ten

first seconds. The figure clearly shows that, for the short distances between the optical fiber and the sample, the maximal temperature T_{max} reaches a value of 72°C which is higher than T_{NI} of LC E7.

We also observed that the temperature of the sample decreases after this maximum value, to get to a stable state of a constant temperature from t=75s, although the lamp is always lit; this suggests that the new phenomenon observed in third time domain of transmission (see figure 1 and 2) is not due only to the IR part of the spectrum of UV-light emitted by LC3 source, but it is also due to a thermal effect which is an accumulation of two effects: the effect of the exothermic reaction of polymerization which takes place in the first millisecond when the UV irradiation is applied, and the effect of the thermal diffusivity of the mixture, between the molecules of LC and the monomers as well as between the molecules of LC and the polymeric network.
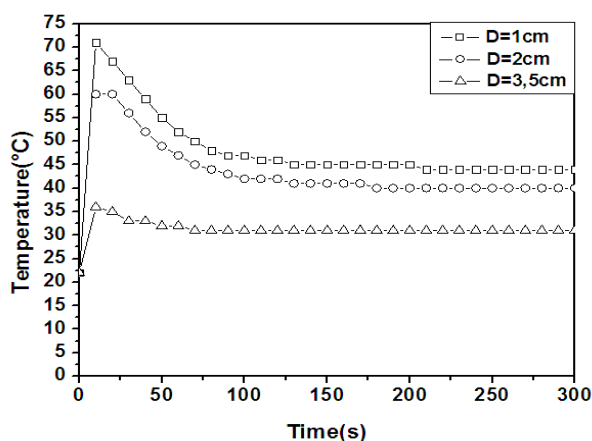

Fig.4: Temperature of the thermal probe with a TPGDA/E7 films for three distances between the optical fiber and the sample: D=3.5cm, 2cm and 1cm.

Figure 5 shows the variations of the temperature of the thermal probe in the presence, and in the absence, of the TPGDA/E7 mixture. We clearly observe a fast decrease of transmission light or the enhancement effect, depending on the distance between the optical fiber and the sample. These curves show that without the mixture, the temperature increases slowly before reaching a stationary maximum value.

The behavior of the sample temperature with the initial mixture shows a peak corresponding to a relatively higher temperature, after a few milliseconds.
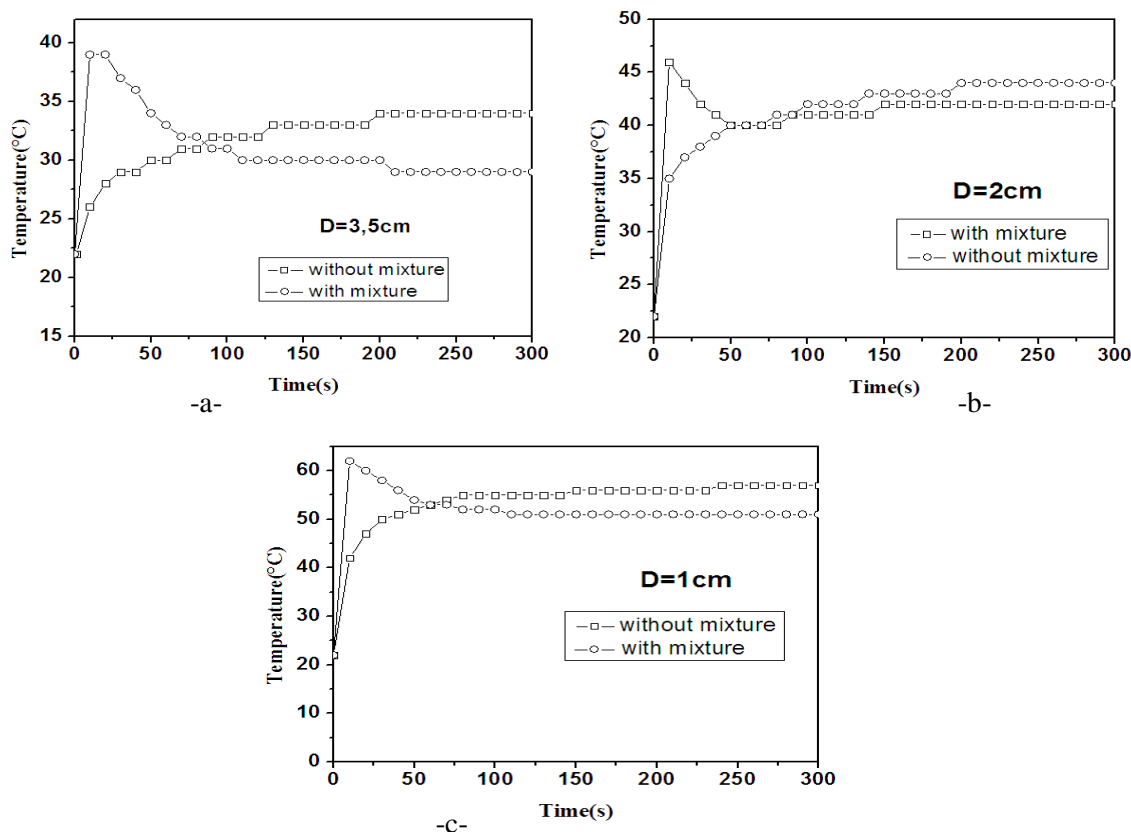
Fig. 5: Temperature of the thermal probe with and without the sample for three distances between the optical fiber and the sample: D=3.5cm for -a-, D=2cm -b-, and D=1cm -c-

The temperature, then, decreases for a period of about 40 seconds before reaching a stationary value which is slightly lower than that obtained without mixture. This rapid rise in temperature of the mixture is probably due to the exothermic nature of the polymerization reaction that occurs during the early stages of irradiation. The stationary value reached corresponds essentially to the infrared spectrum of the UV lamp which heats the system. This effect is more pronounced when the distance between the tip of the fiber and the sample is shorter.

4. Conclusion

A rapid decrease in transmission was observed when the films are exposed to UV irradiation. Moreover, the results show a marked increase in light transmission, which does not come simply from the thermal effect due to an increase in temperature of the sample by the infrared part of the spectrum of the UV source, but also from the exothermic reaction of polymerization leading to the formation of polymer network, and from a reaction between the diffusivity of monomer molecules and the liquid crystal molecules. This phenomenon depends strongly on the distance between the end of optical fiber and the sample, the initially chosen mixture, the film thickness and the architecture of the polymer chains.

5. References

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