PDLC based on unsaturated polyester resins: molecular, morphological and thermo-optical analysis*

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A thermosetting matrix based on an unsaturated polyester resin was employed to realise a Polymer Dispersed Liquid Crystal (PDLC) system by a UV induced curing process. A molecular, morphological and thermo-optical characterisation of this system is presented. The chemical and structural properties were investigated by transmission FT-IR spectra in the near infrared frequency range and by dynamic-mechanical analysis. The results indicated that, upon curing, the matrix retains its intrinsic properties even for compositions very rich in the LC component (40 wt %). The morphology, investigated by optical and electron microscopy, showed phase separation before and after the curing process. Image analysis demonstrated that the cured materials had morphological features suitable to achieve interesting thermo-optical properties. In particular, the composition containing 40 wt % of LC exhibited the typical behaviour of a thermo-optical switch. Interesting optical bistability effects were also demonstrated for this particular composition © 2000 Kluwer Academic Publishers

1. Introduction

The inclusion of a low molecular weight Liquid Crystal (LC) in a polymeric matrix represents one of the latest and more exciting applications of organic materials in the field of non linear optics [1]. This class of materials, generally referred to as Polymer Dispersed Liquid Crystals (PDLC), are formed by phase separation of the LC component from a homogeneous solution with a prepolymer or polymer [2]. The liquid crystal forms droplets whose size, shape and distribution depend on the technique used.

The dispersed mesophase results in an electro- and thermo-sensitive material that can be switched from a

light scattering state (off state) to a transparent state (on state). This effect occurs because, when the LC is in the nematic phase its refractive index, n_n , differs from that of the polymer matrix and the incident radiation is scattered by the LC domains, whose size is of the same order of magnitude as the wavelength of the light. However, when the LC phase become isotropic, its refractive index, n_i , exactly matches that of the matrix, the scattering vanishes and the system becomes transparent.

The polymer adds processability and mechanical performance to the whole system and molecular interactions between the components may induce very

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interesting non linear effects. The potential applications of PDLC films include display devices, spatial light modulators, tuneable filters etc [3–8].

Three general methods [2, 7, 8] have been developed for forming PDLC's:

a) Polymerisation-Induced Phase Separation (PIPS), where the LC is dissolved into the monomer, which is subsequently polymerised either thermally or photochemically.

b) Thermally-Induced Phase Separation (TIPS) in which the LC and a thermoplastic polymer form a homogeneous solution above the melting point of the polymer. The phase separation is obtained by rapid cooling of the melt.

c) Solvent-Induced Phase Separation (SIPS), in which the LC and the thermoplastic polymer are dissolved in a common solvent. Controlled evaporation of the solvent results in the phase separation of the LC component.

In the present contribution we report a novel PDLC system obtained by a PIPS method based on a photochemically initiated polymerisation process. The LC component is commercially available under the trade name of E7, while the polymer matrix is an unsaturated polyester resin. This PDLC system has been characterised with respect to its molecular structure by means of near infrared Fourier transform (FT-NIR) spectroscopy and by dynamic-mechanical analysis. Information on the morphology and on the phase structure has been obtained by optical and scanning electron microscopy.

The thermo optical characterisation of this material has been performed by analysing the light transmittance as a function of temperature for different concentrations of LC. Optical bistability effects were also investigated on such a PDLC system.

2. Experimental

2.1. Materials

The unsaturated polyester prepolymer was kindly supplied by Lonza Italia S.p.A. It was obtained by a condensation reaction between propylene glycol, maleic anhydride and isophthalic anhydride in the molar ratio 0.50/0.45/0.05. The polyester prepolymer had a number average molecular weight, \bar{M}_n , of 2.4×10^3 , a weight average molecular weight, \bar{M}_w , of 8.0×10^3 and an average number of double bonds per chain of 9.5. The chemical formula of the polyester prepolymer may be represented as follows:



The formulation used in the present contribution contained 35 wt % of styrene as co-reactive monomer; therefore the initial molar ratio between styrene and polyester unsaturations was 1.1. The molecular structure of the cured network is schematically represented below:



where n, the average cross-link length, depends on the stoichiometry of the reactive mixture and on the curing conditions.

The LC component was an eutectic mixture of four liquid crystals, commercially available as E7 (Merck). The glass transition temperature, Tg, of this mixture, as evaluated by DSC, is -65° C, while the nematic-isotropic transition occurs at 58°C. The chemical formulas, the trade names and the relative amount of the four components are reported below:



The PDLC samples were prepared by mixing the appropriate amounts of E7 into the uncured resin at 70°C, obtaining a visually transparent, homogeneous solution. 1.0 wt % of the UV curing agent, 1,2 diphenyl-2,2-dimethoxyethan-1-one, (IRGACURE 651 from Ciba-Geigy) was added and the formulation was poured between two glass plates separated by teflon spacers of different thicknesses, according to the type of measurement to be performed on the specimen. The assembly was placed under an UV lamp and irradiated for 5 minutes. By this procedure PDLC samples containing 10, 20, 30 and 40 wt % of E7 were prepared.

2.2. Techniques

FTIR investigations were performed in the near infrared frequency range ($8000-4000 \text{ cm}^{-1}$) on samples 0.5 mm thick, as obtained after the curing process. A Perkin-Elmer Mod. System 2000 was employed, equipped with

a deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beam splitter. 30 to 300 spectra were signal averaged in the conventional manner to reduce the noise.

Dynamic-mechanical measurements were performed on 0.5 mm thick slabs by a Polymer Laboratories MKIII DMTA apparatus, operated at 1 Hz in the single cantilever bending mode.

Optical microscopy was employed to follow the mixing of the components and the phase separation before and after the curing process.

Morphological observations were carried out by scanning electron microscopy (SEM). Prior to SEM examination, the samples were treated with methanol for 12 h to selectively dissolve and remove the LC component. The size and distribution of the LC domains within the UP matrix were determined from SEM micrographs of methanol-treated surfaces using computerised image analysis. The software package Image-Pro Plus Ver. 3.0 was employed.

Thermo-optical analysis was performed using the experimental apparatus shown in Fig. 1. Samples 0.6 mm thick, were placed in a programmable thermostatic cell which allows temperature control to $\pm 0.1^{\circ}$ C and heating rates as low as 0.1° C/min. A heating rate of 2.0°C/min was used throughout. The light source was a cw Ar⁺ laser ($\lambda = 514$ nm) with a constant value of the incident power (15 mW).

Optical bistability effects were investigated using the experimental set-up shown in Fig. 2. A Pockels cell, driven by a sine voltage wave-form at a frequency of 0.01 Hz, was used to modulate the power of a cw Ar^+ laser beam in the range 0–250 mW. A beam splitter directs a fraction of the input power onto a photodiode. The transmitted power is measured by another photodiode. The signals from both photodetectors are plotted on an X-Y recorder, to obtain the input-output characteristics.



Figure 1 Experimental set-up for thermo-optical analysis. O: oven; S: sample; TC: temperature control; PD: photodiode.



Figure 2 Experimental arrangement for measuring output power vs input power. PC: pockels cell; CU: control unit; FG: function generator; P: polariser; BS: beam splitter; PD: photodiode; O: oven; S: sample; TC: thermocouple.

3. Results and discussion

3.1. Near infrared spectroscopy

Unsaturated Polyester resins and their blends have been extensively investigated by vibrational spectroscopy in the mid-ir range $(4000-400 \text{ cm}^{-1})$ to obtain information on the mechanism and kinetics of the curing process, as well as on the molecular structure developed thereupon [9–13]. No mention has been made in the literature to the use of the near-ir frequency range (10000- 4000 cm^{-1}) to get the same type of information. However nir spectroscopy shows a series of distinct advantages, among which the most relevant is due to the lower intensity of the overtone and combination bands occurring in this region, with respect to the fundamental vibrations observed in the mid-ir. Typically, the difference in molar absorptivity between an overtone and its fundamental vibration exceeds one order of magnitude. This allows the use of much thicker samples in nirspectroscopy, where films ranging from 0.1 to 3.0 mm can be easily analysed, while in the mid-ir range the film thickness seldom exceeds 50 μ m. In the present case the films used to perform the dynamic-mechanical and thermo-optical characterisation were unsuitable to be analysed in the mid-ir range because the signals were completely saturated, while they produced good quality spectra in the nir interval (see Fig. 5), with most of the peaks occurring in an absorbance range where, according to the Lambert-Beer law, linearity with concentration is usually observed (up to 1.2 A. U.)

To proceed to a tentative assignment of the main peaks, we turned the attention to a number of model compounds whose molecular structures mimic those of the different components of the system under investigation. In Fig. 3 are reported the FT-NIR spectra of styrene (trace B), which is the co-reactive monomer present in the formulation, and of polystyrene (trace A) which resembles the intermolecular bridges between polyester chains formed upon curing. The main peaks characteristic of the carbon-carbon double bond can be identified as those completely absent in the polystyrene spectrum. They occur at 6135 cm^{-1} (tentatively assigned to the first overtone of the out-of phase H-C= stretching fundamental occurring at 3080 cm^{-1}); at 4720 cm⁻¹ (a combination of the $v_{H-C=C}$ and the C=C stretching fundamental at 1630 cm^{-1}); at 4488 cm^{-1} (likely associated with a combination of the $v_{H-C=C}$ and the in-plane deformation of the =CH₂ group located at 1420 cm^{-1} ; and at 4378 cm⁻¹. In Fig. 5A, where is reported the spectrum of the reaction mixture containing 30 wt % of LC prior to curing, the peaks at 6135 cm⁻¹ 4720 cm^{-1} and 4480 cm^{-1} are clearly identified. They are well resolved and posses sufficient intensity to be employed for the quantitative evaluation of the conversion of styrene unsaturations after curing.

With respect to the fumaric double bonds present along the polyester chains, a peak characteristic of this functional group has been identified by comparing the spectra of diethyl fumarate, the same molecular segment present in the polyester, with its saturated counterpart, diethyl succinate (see Fig. 4B and A, respectively). The absorption occurring at 4790 cm⁻¹ can be tentatively assigned to a combination of the $v_{H-C=C}$ vibration



Figure 3 FT-NIR spectra of polystyrene (trace A) and styrene (trace B) in the frequency range $6500-4000 \text{ cm}^{-1}$.



Figure 4 FT-NIR spectra of dibutylsuccinate (trace A) and dibutylfumarate (trace B) in the frequency range 6500–4500 cm⁻¹.

of the polyester at 3080 cm^{-1} with the C=C stretching fundamental at 1645 cm^{-1} . Also this peak is readily detectable in the uncured formulation (see Fig. 5A) and is well suited for quantitative evaluation.

The spectra reported in Fig. 5B and C, relative to the cured PDLC samples containing, respectively, 30 and 40% by wt of LC, show that the peaks characteristic of styrene unsaturations (at 6135, 4720 and 4480 cm⁻¹) are completely absent, while that of the fumaric double bonds (at 4790 cm⁻¹) is strongly reduced in intensity

with respect to the spectrum of the uncured sample, but remains well detectable. Thus, under the experimental conditions employed, the styrene monomer is fully reacted at all compositions, while the final conversion of the polyester unsaturations is incomplete.

The percent final conversion, α , has been evaluated as follows:

$$\alpha = \left(\frac{C_0 - C_f}{C_0}\right) \cdot 100 = \left(1 - \frac{C_f}{C_0}\right) \cdot 100$$



Figure 5 FT-NIR spectra in the 7000–4000 cm⁻¹ of the 70/30 PDLC formulation prior to curing (trace A); the same sample after curing; the 60/40 formulation after curing.

and, for the Beer-Lambert law:

$$\alpha = \left(1 - \frac{A_{\rm f}}{A_0}\right) \cdot 100$$

In the above equations C_0 and C_f denote, respectively, the concentration of the reactive groups before and after the curing process. \bar{A}_f represents the absorbance of the analytical peak after curing, normalised for sample thickness, while \bar{A}_0 is the same parameter evaluated on the specimen prior to the curing process.

The amount of residual polyester unsaturations, in terms of per cent conversion, are reported in Fig. 6 as a function of the mixture composition.



Figure 6 Conversion of the fumaric double bonds of the polyester after the photo-polymerisation process as a function of the LC content in the PDLC system.

It is observed that the final conversion of fumaric double bonds remains constant at values around 65%, irrespective of the amount of LC present in the formulation. It is worth noting that the plain UP formulation, cured isothermally at 70°C for 10 h, exhibits α_{UP} values close to 75% [12]. Therefore, it can be anticipated that the cross-linking density obtained with the photopolymerisation process is lower than that achieved by thermal curing and so will affect the $T_{\rm g}$. This expectation will be confirmed by the dynamic-mechanical measurements to be discussed later, which gave $T_{\rm g}$ values of 165°C and 175°C, respectively, in the two cases. However, such a slight decrease in T_g is more than compensated for by the velocity of the curing process (5 min versus 10 h) which is essential for obtaining a suitable morphology in this particular PDLC system.

With respect to the details of the molecular structure developed upon curing both in the plain resin and in the PDLC samples (see the structure of the polymer network reported in Section 2.1), taking into consideration the system's stoichiometry and the final conversion of the reactants, it is found that 1.70 styrene vinyl groups are consumed for every polyester vinylene reacted. This value represents the average crosslink length, n, of styrene chains bridging together the vinylene groups located on two adjacent polyester molecules (intermolecular cross-links) or on the same polyester backbone (intramolecular cross-links). For comparison, the same formulation, cured isothermally at 70°C has an average crosslink length equal to 1.17 [12].

In summary, the spectroscopic analysis indicated that the curing protocol employed is suitable for the investigated system and that the cross-link density achieved remains acceptable even in the presence of very large amounts of the LC components (40%).



Figure 7 Optical micrograph taken at ambient temperature under polarised light of the 60/40 PDLC composition before curing.

3.2. Morphological analysis

All the PDLC compositions investigated were examined by optical microscopy under polarised and unpolarised light. Evidence of a separate LC phase in the form of birefringent droplets started to appear at compositions higher than 10 wt %. Since, as reported in the literature [6, 14–18] most PDLC applications require substantial amounts of LC (i.e. more than 35%), a deeper morphological analysis was carried out on the 60/40 composition.

In Fig. 7 is shown the optical micrograph, taken at ambient temperature under polarised light, of a PDLC system containing 40 wt % of LC before the photopolymerisation process. It is observed that, prior to curing, the system is clearly phase separated. The LC component forms spherical-like droplets uniformly distributed within the polyester matrix, whose dimensions range from 3 to 65 μ m. However, rising the temperature above the nematic/isotropic transition of the LC $(58^{\circ}C)$, the characteristic birefringence of the droplets disappears, and the system becomes featureless. This has been interpreted by several authors as evidence of dissolution at the molecular level of the LC component in the polyester matrix, taking place above the transition temperature. Thus, it has been proposed that mixtures of this type behave as upper critical solution systems.

In this particular case, however, under unpolarised light, the LC particles are clearly discernible (see Fig. 8). This observation demonstrates that the system under investigation is phase-separated irrespective of temperature, and that the transparency observed visually at temperatures above the nematic/isotropic transition of the LC, is due to the matching of the refractive indices of the two components and not to the disappearance of the LC phase, as a consequence of its molecular dissolution within the matrix.

After the photo-polymerisation process carried out at 70°C, the system's morphology is considerably affected. In particular, as shown in Fig. 9, the number of large particles having diameters ranging from 10 to 40 μ m strongly decreases with respect to what is observed in the uncured specimen. At the same time, a diffuse birefringence is found across the whole area,



Figure 8 Optical micrograph taken at 70° C under unpolarised light of the 60/40 PDLC composition before curing.



Figure 9 Optical micrograph taken at ambient temperature under polarised light of the 60/40 PDLC composition after curing.



Figure 10 Low magnification SEM micrograph of the etched surface of the 60/40 PDLC composition after curing.

likely due to the presence of a large number of particles whose size is lower by one order of magnitude or more.

These morphological features have been investigated in deeper detail by scanning electron microscopy (SEM), after an etching treatment with methanol, which selectively removes from the specimen's surface the LC phase. In Fig. 10 is shown the low magnification SEM



Figure 11 Distribution of particle sizes evaluated by computerised image analysis from several micrographs as Fig. 10.



Figure 12 High magnification SEM micrograph of the etched surface of the 60/40 PDLC composition after curing.

micrograph of the etched surface of the sample containing 40% of LC. Image analysis performed on a series of these micrographs, allows to obtain the distribution of particle sizes, which is shows, in the form of histogram, in Fig. 11. The distribution appears very broad, ranging from 3 to 50 μ m; however more than 50% of the particles detected at this magnification have average diameters comprised between 3 and 12 μ m. The areas between the larger domains, which appear featureless in Fig. 10, when examined at higher magnification, show an interconnected texture characteristic of a two phase system, in which irregularly shaped holes left behind by removal of the LC phase are evident (see Fig. 12). This type of texture is completely absent in the neat UP resin cured in the same conditions and etched accordingly. Image analysis has been performed also on this type of micrographs, and the results are reported in the histogram of Fig. 13. In this case the particle size distribution is considerably narrower, with most of the domains ranging between 0.1 and 0.6 μ m; The peak of the distribution (exceeding 30%) is located between 0.2 and 0.3 μ m.

As reported in the literature, the size of the LC droplets plays a fundamental role in determining the



Figure 13 Distribution of particle sizes evaluated by computerised image analysis from several micrographs as Fig. 12.



Figure 14 Dynamic-mechanical spectra in terms of tan δ in the temperature range -50 to 300° C. a) Plain UP resin; b) 80/20 composition; c) 70/30 composition; 60/40 composition.

thermo- and electro-optical response of a PDLC system. In particular it has been reported that optimum results have been obtained with submicron particle dimensions; therefore, in this respect the morphology of the system under investigation is at least partially satisfying. In the next sections it will be shown that very interesting results are indeed obtained in terms of thermooptical behaviour.

3.3. Dynamic-mechanical behaviour

The tan δ versus temperature curves relative to the plain UP resin and three different compositions of the PDLC system, are reported in Fig. 14.

The UP resin shows a main relaxation peak, associated with the glass transition temperature, T_g , at 166°C, and an unresolved shoulder centred around 75°C. This secondary transition has been attributed to the styrene units bridging the polyester chains [19] and/or to the relaxation of short chain segments in the proximity of residual fumaric unsaturations (network defects) [20]. A decrease of the temperature at which the main relaxation occurs is found in the investigated PDLC's. The



Figure 15 Glass transition, T_g , as a function of the LC content in the PDLC system.



Figure 16 Transmittivity versus temperature curves in the range $20-80^{\circ}$ C for a) plain UP resin; b) 90/10 composition; c) 80/20 composition; d) 70/30 composition.

 T_g values as a function of composition are plotted in Fig. 15. A considerable drop is observed at 10% composition with respect to the plain resin (30°C); afterwards the T_g vs composition curve seems to reach a plateau region. The T_g reduction is to be ascribed to a plasticization effect of a fraction of the LC which remains dispersed at the molecular level into the polymeric matrix, in so far the spectroscopic analysis has shown that no significant reduction of the average cross-link density is brought about in the presence of the LC phase. By use of the Gordon and Taylor expression [21]:

$$\frac{1}{T_{\rm g}} = \frac{W_1}{T_{\rm g1}} + \frac{W_2}{T_{\rm g2}}$$

where the subscripts 1 and 2 refer, respectively, to the unsaturated polyester matrix (component 1) and E7 (component 2), and W represents the weight fraction. By using a T_{g1} value of 166°C and a T_{g2} value of -65° C (from DSC measurements), we found that a drop of 30°C is accounted for by 6.5 wt % of LC. Thus, for instance, in the 90/10 composition, 3.5% of LC remains phase separated after the curing process, while 6.5% acts as plasticiser. This conclusion is further confirmed by the morphological observations described in the previous paragraph. The 90/10 composition does not show birefringence effects when examined under polarised light before and after the curing process. It is likely that 6.5 wt %, represents the maximum amount of LC which can be dissolved in the polyester matrix. Afterwards the resin becomes saturated and the remaining amount of LC separates out in the form of discrete domains. This is the underlying reason why the $T_{\rm g}$ decrease at compositions higher than 10% is very limited, and the $T_{\rm g}$ vs composition curve has a plateau type of behaviour.

The dynamic-mechanical results also demonstrate, in agreement with the spectroscopic data, that materials with excellent properties in terms of rigidity, T_g , and therefore service temperatures, can be obtained even when a very large amount of the low molecular weight component is present in the formulation.

3.4. Thermo-optical analysis

When an intense light beam propagates in a PDLC system, it undergoes a scattering process due to the difference between the refractive indices of the two phases. The self-transparency phenomenon, i.e. the suppression of scattering, may occur when the difference between the refractive indices of the two components reduces to zero ($\Delta n = 0$). This mechanism operates when the temperature is increased to a threshold value corresponding to the nematic/isotropic phase transition of the LC phase.

In Fig. 16 are reported the transmittivity versus temperature curves for PDLC samples containing, respectively, 10, 20 and 30 wt % of LC. For comparison, in the same figure is reported the behaviour of the plain UP resin.

Two effects are apparent:

- At room temperature a considerable decrease in transmittivity is observed with enhancing the amount of LC in the specimen.
- Up to 20 wt % of LC the transmittivity is nearly constant with temperature. At 30% the transmittivity increases gradually in a broad temperature range encompassing more than 35°C, and eventually reaches a plateau value of 0.6.

The curve relative to the 40% composition is reported in Fig. 17. In this case the behaviour is strikingly different: the transmittivity remains constant at very low levels up to a critical temperature at which abruptly increases by more than one order of magnitude. Such a transition occurs in a very narrow temperature range (about 5°C compared to the 35°C of the 30% composition): this is the typical behaviour of a thermo-optical switch. The above results indicate that only the 40% composition is able to perform as an optical switch. The transition temperature of the 60/40 PDLC is located at 53°C and is clearly related to the nematic/isotropic transition of the LC phase.



Figure 17 Transmittivity versus temperature curves in the range $20^{\circ}C-80^{\circ}C$ for the 60/40 composition.



Figure 18 Output power as a function of the input power near the transition temperature for the vertical component of the light polarisation. Measurement taken on the 60/40 composition.

The existence of a transition temperature suggests the possibility of optical bistability effects which may appear when we modulate the incident light intensity near the phase transition. This interesting effect, investigated using the set-up reported in the experimental section, is shown in Fig. 18, relative to the 60/40 composition.

As the incident power increases, there is a threshold value for the switching-on of the output power occurring at $I_1 = 120$ mW. Thereafter, by decreasing the input power, the switching-off of the output power occurs at a lower power value ($I_2 = 80$ mW). This effect is less pronounced at lower concentration of LC.

According to the literature [22–24] a bistable behaviour is produced by the combination of a feedback process and an optical nonlinearity. In our case the feedback mechanism, which is purely optical, is due to the light modulation around the phase transition that determines an even better matching of the refractive indices of the two phases. The non-linear optical properties of the LC inside the polymeric matrix represent the second condition for the appearance of optical bistability effect.

4. Conclusion

An unsaturated polyester resin was used as matrix for the preparation of a PDLC system, using a Polymerisation Induced Phase Separation (PIPS) method. Curing of the thermosetting matrix was carried out by a fast photopolymerization process.

A study of the molecular structure, morphology and thermo-optical properties of the PDLC samples realised has been reported. The main results can be summarised as follows:

1. Suitable processing conditions have been developed to obtain PDLC's in which the polymeric matrix retains its intrinsic properties in terms of rigidity and dimensional stability, even for compositions very rich in the LC component (40%).

2. Before curing all the investigated compositions are immiscible, and remain phase separated at 70° C, which was the curing temperature. Upon curing the morphology of the system changed towards a reduction of the average size of the LC domains and an improved homogenisation. Such a morphology was suitable to achieve very interesting thermo-optical properties.

3. Thermo-optical analysis showed that the composition containing 40 wt % of LC behaves as an efficient thermo-optical switch. The same sample exhibited a thermally induced, optical bistability effect. These results suggest the possibility of employing this PDLC system as temperature sensor and/or optically bistable devices which can be integrated in guiding systems for logic operation.

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