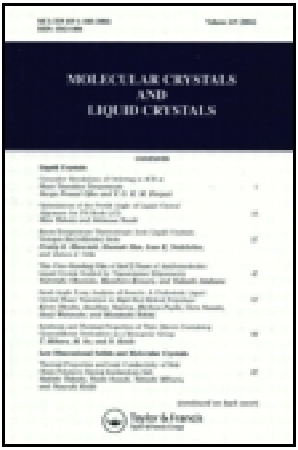

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Thermosetting PDLCs: Cure, Morphology and Thermo-Optical Response

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Thermosetting PDLCs: Cure, Morphology and Thermo-Optical Response

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Two thermosetting matrices based, respectively, on an unsaturated polyester resin and a bifunctional epoxy resin were employed to prepare Polymer Dispersed Liquid Crystal (PDLC) systems. A molecular, morphological and thermo-optical characterisation of these systems is presented. The unsaturated polyester based system was found to be phase-separated at all compositions. Image analysis demonstrated morphological features suitable to achieve interesting thermo-optical properties, particularly for the composition containing 40 wt % of LC. The epoxy based system was found to be miscible before curing at all compositions. A phase separation occurred upon curing for LC contents higher than 40 wt %. In this composition range also this system behaves as an efficient thermo-optical switch.

Keywords: Liquid Crystals; Thermosetting Resins; PDLC; FTIR Spectroscopy; Morphology; Thermo-optical Properties

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INTRODUCTION

One of the latest and more interesting organic materials for applications in the field of thermo and electro-optical devices is represented by the Polymer Dispersed Liquid Crystals (PDLCs)[1]. This class of materials is formed by phase separation of a low molecular weight liquid crystal (LC) from a solution with a prepolymer or polymer[2] in a two step process: 1) the LC component and a polymer precursor are initially mixed to form a homogeneous solution; 2) the prepolymer is hardened and during this process the LC phase separates from the matrix as microdroplets.

The dispersed mesophase results in a thermo-sensitive material, that can be switched from a light scattering state (OFF-state) to a transparent state (ON-state): when the LC is in the anisotropic phase its refractive index differs from that of the polymer matrix and the incident radiation is scattered by the LC domains; however, when the LC is in the isotropic phase its refractive index exactly matches that of the matrix and the system becomes transparent. These properties can be used to develop display devices, spatial light modulators, tunable filters, etc.[3-8]

In the present contribution we describe the molecular, morphological and thermo-optical characterisation of two types of PDLC systems, both obtained by a polymerisation-induced Phase Separation (PIPS) process.

The first system is based on a commercial unsaturated polyester resin and has been obtained by a photochemically induced polymerisation process. In the second system, the polymer matrix is a bifunctional epoxy resin, which has been thermally polymerised using nadic methyl anhydride as hardener.

EXPERIMENTAL

Materials

The unsaturated polyester prepolymer was kindly supplied by Lonza Italia S.p.A. and it was obtained by a condensation reaction between propylene glycol, maleic anhydride and isophtalic anhydride in the molar ratio 0.50/0.45/0.05. The polyester prepolymer had a number average molecular weight, $\overline{M}_n$, of 2.4 x 10^3, a weight average molecular weight, $\overline{M}_w$, of 8.0 x 10^3 and an average number of unsaturations per chain of 9.5. 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 epoxy prepolymer used in this study is the diglycidyl ether of bisphenol A (DGEBA) from Shell Italia S.p.A., commercially available under the trade name of Epikote 828. The methyl-5-norbornene-2,3-dicarboxylic anhydride (MNA) was used as hardener, and the 2,4,6-tris(dimethylaminomethyl)-phenol (DMP-30), was employed as initiator; both these products were Aldrich reagent grade, and were used without further purification. The weight ratio DGEBA/MNA/DMP-30 in the epoxy formulation was 0.53/0.46/0.01.

The LC component was an eutectic mixture of four liquid crystals, commercially available as E7 (Merck). The glass transition temperature of this mixture, as evaluated by Differential Scanning Calorimetry (DSC), is -65°C, while the nematic-isotropic transition occurs at 58°C.

The PDLC samples based on unsaturated polyester resin 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 a UV lamp producing ultraviolet radiation of either 254 or 366 nm. Intensity measurements at 366 nm indicated a power equal to 1.2 $mWcm^{-2}$ at a distance of 15 cm between the source and the sample, which is the distance actually used for the specimens preparation. The radiation time was equal to 5 minutes for all the samples.

The epoxy-based PDLCs were prepared by mixing the LC component with the uncured epoxy matrix, at room temperature under vigorous mechanical stirring up to the complete homogenisation of the mixture. It was then transferred in a stainless-steel mould and cured at 110°C for 2 h.

Techniques

Fourier Transform Infrared spectroscopy measurements were performed by a Perkin-Elmer System 2000 spectrometer, 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.

In the Near-infrared range (NIR, 8000 - 4000 cm^{-1}), transmission measurements were performed, using samples 0.5 mm thick.

Attenuated Total Reflectance (FTIR-ATR) spectra were collected in the Medium-infrared region (MIR, 4000 - 650 cm^{-1}) by using a horizontal ATR cell (Benchmark from Graseby Specac) having a ZnSe crystal. This unit was equipped with a temperature controlling system having an accuracy of ± 0.5 °C.

The calorimetric measurements were performed on a Mettler TA 3000 differential scanning calorimeter (DSC) in a dry nitrogen atmosphere. A heating rate of $10°Cmin^{-1}$ was used throughout.

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

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

The size and distribution of the LC domains within the UP matrix were determined from Scanning Electron Microscopy (SEM) micrographs of etched surfaces using computerised image analysis. The software package Image-Pro Plus Ver. 3.0 was employed.

Thermo-optical and optical bistability measurements were performed using experimental apparatus whose details are reported elsewhere[9].

RESULTS AND DISCUSSION

PDLC based on unsaturated polyester resin

In Fig. 1 are reported the transmission spectra in the NIR range (7800-4000 cm^{-1}) of a PDLC sample containing 30% by weight of the LC component before and after the photo-polymerisation process (curves A and B, respectively). For the assignment of the main peaks we have used a model compounds whose molecular structures mimic those of the different components of the system under investigation[13].

In Fig. 1A the peaks characteristic of the styrene unsaturations are clearly discernible at 6137 cm^{-1} and at 4490 cm^{-1}, and the fumaric double bonds along the polyester backbone give rise to a well resolved absorption centred at 4790 cm^{-1}.

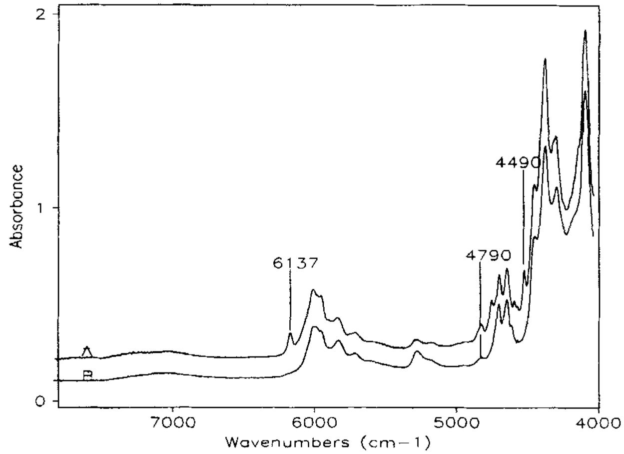

FIGURE 1. FT-NIR spectra in the range 7800-4000 cm^{-1} of the 70/30 PDLC formulation prior to curing (trace A) and after curing (trace B).

The spectra 1B, which is relative to the cured PDLC sample, shows that the peaks characteristic of the styrene unsaturations are completely absent, while the absorption characteristic of the fumaric unsaturations is strongly reduced in intensity, but remains well detectable, with respect to the spectrum of the uncured sample. Thus, under the experimental conditions, the styrene monomer is fully reacted, while the polyester unsaturations are only partially reacted.

The final conversion percent of the reactive groups, α, has been evaluated from the spectroscopic data, as follows:

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

and, for the Beer-Lambert law:

$$\alpha = \left(1 - \frac{\bar{A}_f}{\bar{A}_0}\right) \cdot 100 \qquad (2)$$

In equation (1), C_0 and C_f denote the concentration of the reactive groups before and after the curing process, respectively. In equation (2), $\bar{A}_f$ represents the absorbance of the analytical peak after curing, which is 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 conversion per cent, is reported in Fig. 2 as a function of the mixture composition.

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. Thus, the spectroscopic analysis indicated that the cross-link density achieved with the present photo-polymerisation process remains acceptable even in the presence of very large amounts of the LC components (40 %).

The glass transition temperatures, T_g, evaluated by dynamic-mechanical analysis as the maxima of the tanδ spectrum, are reported in Fig. 3 as a function of the LC content.

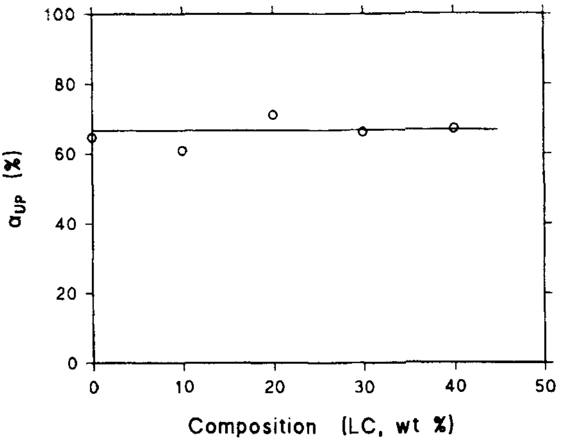

FIGURE 2. Conversion of the fumaric double bonds of the polyester after the photo-polymerisation process as a function of the LC content.

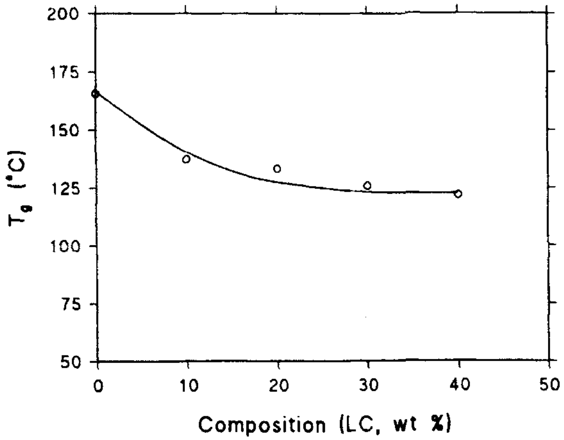

FIGURE 3. Glass transition temperatures as a function of the LC content in the cured PDLC systems.

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. The T_g of a two component, miscible system may be predicted by use of the Gordon and Taylor equation[14]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{3}$$

where the subscripts 1 and 2 refer, respectively, to the unsaturated polyester matrix (component 1) and the 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) it is 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 is phase separated after the curing process, while 6.5 % acts as plasticiser.

Optical microscopy shows evidence of a separate LC phase in the form of birefringent droplets at compositions higher than 10 wt %[13].

More detailed information on the morphology of the investigated samples was obtained by SEM analysis of the etched surfaces. For example, in Fig. 4A and 4B are shown the etched surfaces of an UP/E7 60/40 sample at low and high magnification, respectively.

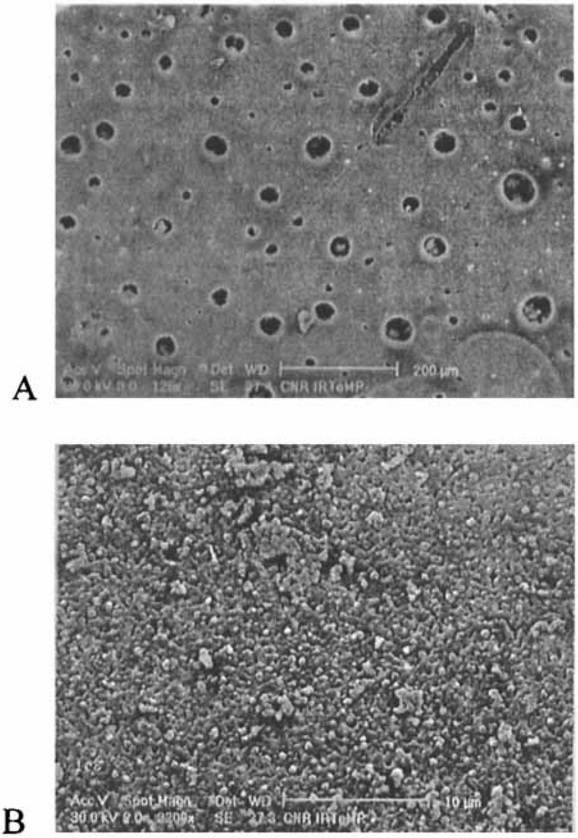

FIGURE 4. Low magnification (A) and high magnification (B) SEM micrographs of the etched surface of the 60/40 PDLC composition after curing.

The Fig. 4A clearly shows LC microdroplets whose diameter ranges between 3 and 12 µm. Conversely, Fig. 4B displays a microsphere morphology, which is indicative of a partial phase inversion. It may be concluded that the 60/40 is a limiting composition at which a phase inversion starts, but is incomplete[13]. The above described morphology was found suitable to achieve interesting thermo-optical properties.

In Fig. 5 the transmittivity versus temperature of a PDLC sample containing 40 wt % of LC[9] is reported. As can be see, the transmittivity remains constant at very low levels up to a critical temperature at which at abruptly increases by more than one order of magnitude. Such a transition occurs in a very narrow temperature range, about 5°C, which is the typical behaviour of an efficient thermo-optical switch. The onset transition temperature is located at 53°C and is clearly related to the nematic-isotropic transition of the LC phase.

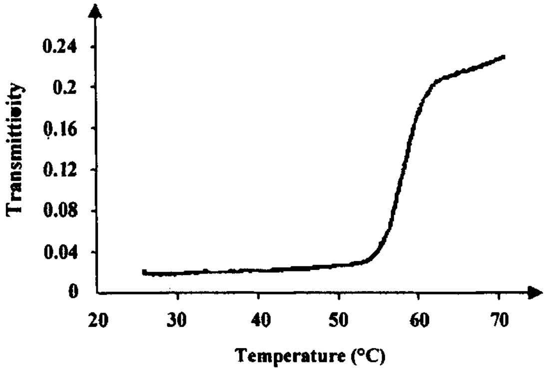

FIGURE 5. Transmittivity as a function of temperature curves in the range 20-80 °C for the 60/40 composition.

The above thermo-optical results suggests the possibility of optical bistability effects which may appear when we modulate the incident light intensity near the phase transition. This interesting effect is shown in Fig. 6, 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[9]. According to the literature[10-12] 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.

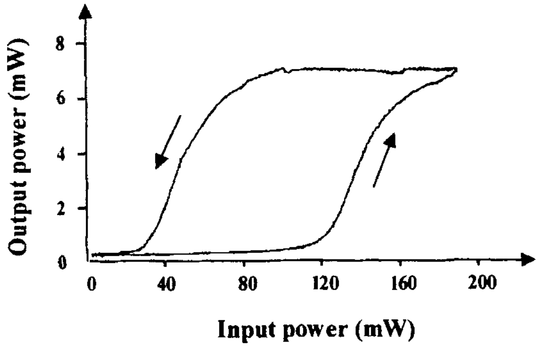

FIGURE 6. Output power as a function of the input power near the transition temperature for the vertical component of the light polarisation. Measurement taken on the 60/40 composition.

PDLC based on bifunctional epoxy resin

A preliminary investigation on the epoxy-based PDLC system, over the composition range 0 - 60 wt % of LC, was performed by differential scanning calorimetry. The thermograms of all the investigated mixtures, prior to the curing process display a single T_g, intermediate among those of the two components, which decreases by increasing the LC content.

This behaviour indicates that, in the composition range investigated, the LC is miscible in the uncured epoxy resin. This conclusion is further confirmed by the absence, in the thermograms of the uncured blends, of the nematic-isotropic transition of the LC at about 60°C.

The thermograms of the cured blends, strongly depends on the composition: up to 30 wt % of LC a single glass transition is observed and no nematic/isotropic endotherm. In this composition range, the experimental T_g vs composition curve is well described by the Gordon-Taylor equation[14] describing the behaviour of a miscible polymer/solvent system (see diagram of Figure 7). Therefore, up to 30 wt % of LC the mixture is as a single phase, homogeneous system even after curing; the LC component remains molecularly dispersed into the epoxy matrix and acts as a plasticizer. At 40 wt % of LC and above, new features are observed in the thermograms: a T_g at very low temperatures, coincident with that of the neat E7 and the isotropization endotherm of the LC at about 60°C (see Figure 7).

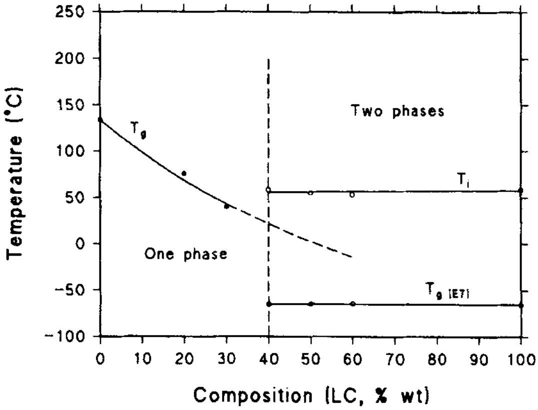

FIGURE 7. Transition temperatures as a function of composition for the cured PDLC systems.

Thus, in this composition range, a phase separation process takes place upon curing: the fact that the temperature relative to nematic/isotropic transition, T_i, and the T_g of the LC remain invariant with composition at values close to that of the pure E7, indicates that the phase separated LC droplets are not contaminated by epoxy impurities. It is to be noted that, in the phase-separated mixtures, the T_g of the epoxy matrix is not detectable calorimetrically. This is partly due to the reduced amount of resin in this composition range, and partly to the fact that such a transition is likely to occur in the same temperature range of the LC endotherm. Preliminary dynamic-mechanical data indicate a T_g of the polymer matrix consistent with that of a plasticised epoxy network. The transition temperatures detected calorimetrically are collectively reported, as a function of composition, in Fig. 7; such a diagram evidences the phase boundary of the system.

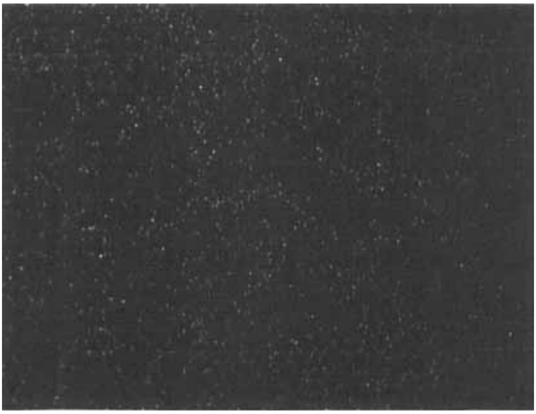

FIGURE 8. Optical micrograph taken at ambient temperature under polarised light of the cured 60/40 PDLC composition based on the bifunctional epoxy resin. Magnification 160X.

The morphological analysis is consistent with the results discussed above. Prior to curing all the investigated compositions appear to be featureless under cross-polarised light (completely dark field). After curing, no changes are observed up to the 30 wt % composition. However, starting from the 40 wt % mixture, a homogeneous distribution of birefringent LC droplets is clearly identifiable (see Figure 8). Preliminary image analysis of the above micrograph has shown than the distribution of droplet sizes is very narrow and ranges between 1 and 3 μm.

Several PDLC samples have been investigated by FTIR-ATR spectroscopy in the mid-ir range to obtain information at molecular level about the orientation of the LC phase during the transition from the nematic to the isotropic state.

The basic principle of the measurement rely on the fact that the main molecular axis of the LC molecules in the nematic phase, tend to align spontaneously in a direction normal to the surface of the crystal on which they have been lied down. These aligned molecules would not absorb IR radiation in the case of a molecular vibration whose transition moment lies parallel to the main molecular axis. In the isotropic state this partial alignment is lost, causing a sudden increase of the absorption intensity of the above vibrational transition[15].

In practice, intensity *vs* temperature diagrams of this type allow to detect very clearly nematic/isotropic transitions of the LC phase even when the amount of the LC component is very low and close to the detectability limits of the DSC technique. In Fig. 9 we report the FTIR-ATR spectrum collected at room temperature in the wavenumber range 4000 - 650 cm^{-1} of the 60/40 PDLC formulation. The analysis has been performed using the 2226 cm^{-1} peak due to the -C≡N stretching vibration because of the appropriate geometry of the transition moment and for the absence of interfering peaks of the polymeric matrix.

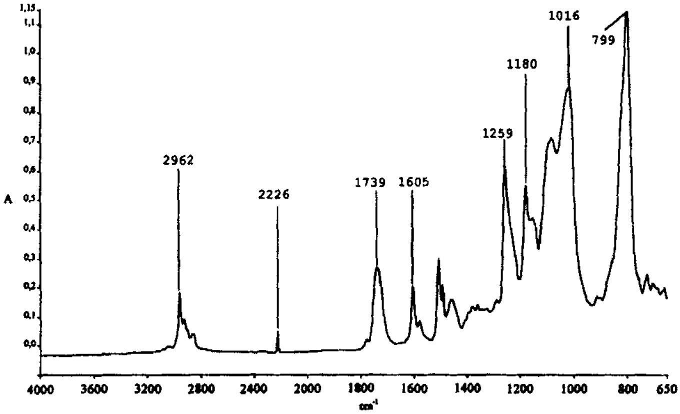

FIGURE 9. FTIR-ATR spectra in the range 4000-650 cm^{-1} of the 60/40 PDLC formulation prior to curing.

In Fig. 10 we compare the absorbance vs temperature curves relative to the uncured PDLC sample containing 40 wt % of LC (curve B), to the same sample after curing (curve A) and to the cured PDLC with 30 wt % of LC (curve C). The nematic/isotropic transition starting at 58°C is evident in curve A. No transition is observed in the same sample prior to curing, which confirms the single phase nature of the uncured system. The transition is also absent in the cured 70/30 mixture, indicating that no phase separation of the LC occurs upon curing at this composition.

The above results are in agreement with the calorimetric and morphological results.

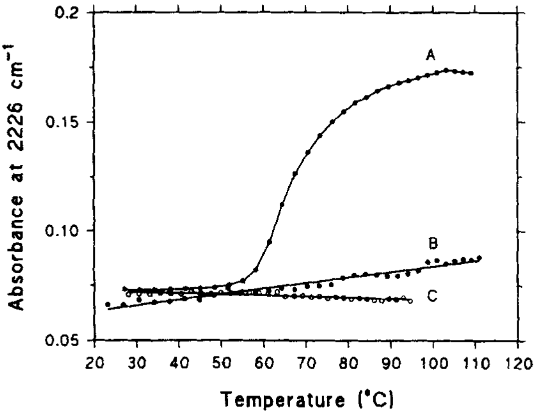

FIGURE 10. Absorbance at 2226 cm^{-1} vs temperature for the 60/40 PDLC sample prior to curing (curve B), after curing (curve A) and for the 70/30 formulation after curing (curve C).

In Fig. 11 are reported the experimental results for the thermo-optical analysis of epoxy based PDLC samples containing, respectively, 30, 40 and 50 % b.w. of LC. For comparison, in the same figure is reported the behaviour of the plain epoxy resin.

The typical behaviour of a thermo-optical switch, analogous to that observed for the polyester based PDLC, is found for the 60/40 and the 50/50 compositions. Conversely, the 70/30 composition shows a constant transmittivity close to that of the neat epoxy matrix, over the whole temperature range investigated. This behaviour is clearly related to the fact that no nematic phase exists at this composition, as already observed with the characterisation techniques described above.

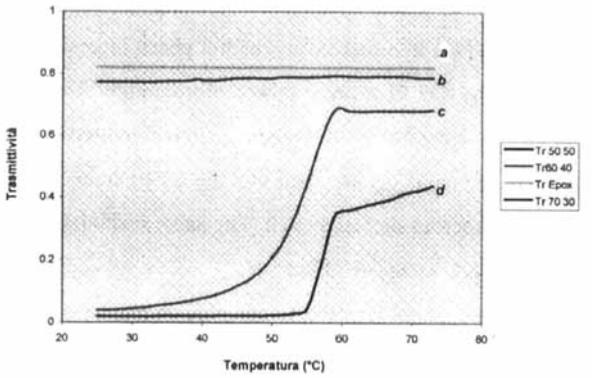

FIGURE 11. Transmittivity as a function of the temperature curves in the range from 20°C to 80°C for a) plain epoxy resin; b) 70/30 composition; c) 60/40 composition; d) 50/50 composition.

CONCLUSIONS

In the present contribution, two PDLC systems have been investigated, based, respectively, on unsaturated polyester resin and on a bifunctional epoxy resin.

With respect to the first system, the following conclusion can be drawn:

- The photo-polymerisation process employed for the PDLC preparation ensures suitable properties of the polymeric matrix in terms of rigidity and dimensional stability, even for compositions very reach in the LC component.
- The system morphology is complex and depends on composition. In particular, the 60/40 mixture, which has been analysed in details, shows

the coexistence of discrete LC domains ranging from 3 to 12 μm, uniformly dispersed in a matrix in which a phase inversion process has occurred, giving rise to a microsphere morphology. This features are well suited to achieved interesting thermo-optical properties.

- Thermo-optical results demonstrate that the 60/40 composition behaves as an efficient thermo-optical switch. The same formulation exhibits an interesting optical bistability effect.

The epoxy-based PDLC system is miscible in the whole composition range investigated, prior to the curing process. After curing, no phase separation occurs up to an LC content of 30 wt %. A polymerisation induced phase-separation process takes place for the 40 wt % composition and above, which generates a very homogeneous dispersion of LC microdroplets within the polymer matrix. The size of the nematic domains ranges between 1 and 3 μm. Calorimetric and spectroscopic data demonstrated the occurrence of the nematic-isotropic transition of the LC phase in the 60/40 composition.

No such transition was observed at lower LC content, which further confirmed that, in this composition range, the LC component remains molecularly dispersed within the polymer matrix, after the curing process. Preliminary thermo-optical results indicated that the 60/40 and the 50/50 composition could be employed as efficient thermo-optical switches.

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