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Thermally reversible light scattering films based on the melting/crystallization of organic crystals dispersed in an epoxy matrix

Ileana A. Zucchi, María J. Galante, Roberto J.J. Williams [*]

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET),
J. B. Justo 4302, 7600 Mar del Plata, Argentina

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Abstract

Films that can be reversibly switched from opaque to transparent states by varying temperature (TRLS films), have potential applications in thermal sensors, optical devices, recording media, etc. A dispersion of organic crystals in a thermoset may be used for these purposes provided that at temperatures higher than the melting point there is a matching of refractive indices of both phases. A model system consisting on a dispersion of diphenyl (DP) crystals in an epoxy matrix based on diglycidyl ether of bisphenol A and *m*-xylylenediamine, was analyzed as a possible TRLS film encapsulated between transparent covers to avoid sublimation of DP. To obtain a uniform dispersion of DP-rich domains in the epoxy matrix by polymerization-induced phase separation, it was necessary to add 5 wt% of polystyrene (PS) to the initial formulation. Phase separation induced by polymerization at 80 °C led to a dispersion of PS/DP domains in the epoxy matrix due to the low compatibility of PS with the epoxy and its high compatibility with DP. Crystallization and melting processes were confined to the interior of dispersed domains leading to an excellent reproducibility of the optical properties of TRLS films in the course of successive heating–cooling cycles.

Keywords: Thermally reversible opaque/transparent films; Polymer-dispersed organic crystals; Polymerization-induced phase separation

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1. Introduction

Thermally reversible light scattering films (TRLS) are materials that can be repeatedly switched from opaque to transparent states by varying temperature. They have potential applications in thermal sensors, optical devices, recording media, etc. [1–4]. A dispersion of organic crystals in a thermoset may be used for these purposes provided that at temperatures higher than the melting temperature (T_m) there is a matching of refractive indices of both phases. The film becomes transparent when heating above T_m and opaque when crystallization of the organic crystal takes place during the cooling cycle. An undercooling to a temperature (T_c) that depends on the cooling rate is necessary to produce crystalli-

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[*] Corresponding author. Tel.: +54 223 481 6600; fax: +54 223 481 0046.
E-mail address: williams@fi.mdp.edu.ar (R.J.J. Williams).

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zation. Therefore, in the temperature range comprised between T_c and T_m the film can be transparent or opaque depending on whether it is submitted to a cooling or a heating cycle, and this property might have practical applications (e.g.; to detect undesired exposures of temperature-sensitive products like foods to temperatures higher than a critical value).

In this paper, the feasibility of synthesizing TRLS films based on a dispersion of organic crystals in an epoxy matrix, is analyzed. Selected constituents were diphenyl (DP) and epoxy precursors based on diglycidyl ether of bisphenol A and *m*-xylylenediamine. Refractive indices of the cured epoxy and DP in the amorphous state are very close as required for the operation of the TRLS film. However, selection of these components fixes the temperature range where the opaque/transparent transition is produced as well as the glass transition temperature of the matrix (cured epoxy plasticized by DP). Therefore, the selected system must be regarded as a model system that enables to discuss the factors that control the morphologies generated by polymerization-induced phase separation. Obviously, TRLS films based on a low-molar-mass organic molecule as DP must be encapsulated between transparent covers (e.g. two glass covers), to avoid sublimation of the organic molecule.

2. Experimental

The epoxy monomer was based on diglycidyl ether of bisphenol A (DGEBA, Der 332 Dow), with an epoxy equivalent of 174.3 g mol^{-1}. The hardener was *m*-xylylenediamine (MXDA, Aldrich), used in a stoichiometric proportion. The other components used in formulations of TRLS films were 1,1′-biphenyl (diphenyl, DP, Aldrich) and polystyrene (PS, $M_n = 28{,}400$, $PI = 1.07$, Polymer Source). DP, PS and the cured epoxy have similar values of refractive indices ($n = 1.59$) [5–7]. Structures of the different materials are shown in Fig. 1.

Blends devoid of PS were prepared by dissolving DP in DGEBA at 75 °C, and adding MXDA after cooling to about 30 °C. For blends containing PS, this was first dissolved in DGEBA at 100 °C, the solution was cooled to 75 °C and DP was added, and finally MXDA was dissolved after cooling to about 30 °C. Binary blends of PS and DP were prepared using methylene chloride as a solvent, followed by its complete evaporation at room temperature as checked by the final weight. In the absence of a solvent it would have been necessary to heat to about 100 °C with the risk of DP sublimation.

Blends were cured at 80 °C to complete conversion of epoxy groups as assessed by near-infrared spectroscopy. Depending on the initial DP content the complete cure took from 4 to 10 h.

Near-infrared spectroscopy (NIR) was used to follow the conversion of epoxy groups at 80 °C for blends of different composition. An FTIR device (Genesis II, Mattson), provided with a heated transmission cell (HT-32 Spectra Tech) and a programmable temperature controller (Omega, Spectra Tech, $\Delta T = \pm 1$ °C), was employed. The initial formulation was placed between two glass covers separated by about 2 mm. The height of the epoxy absorption peak at 4530 cm^{-1}, assigned to the conjugated CH_2 deformation band with the aromatic CH fundamental stretch [8], was followed as a function of reaction time.

Differential scanning calorimetry (DSC) was performed using a Pyris 1 Perkin–Elmer device. Samples were first heated to 80 °C, cooled at 10 °C min^{-1} to a temperature below the transition to be determined and then heated at the same rate. From the thermograms obtained in heating scans the following parameters were determined: glass transition temperature (T_g) defined at the onset of the change in specific heat, melting temperature (T_m) defined at the end of the melting peak, and heat of fusion (area under the melting peaks).

Transmission optical microscopy (TOM) was performed employing a Leica DMLB microscope, with and without crossed polarizers, provided with a video camera (Leica DC 100) and a hot stage (Linkam THMS 600). TRLS films were obtained placing the initial formulation between two glass covers with a 0.2 mm-stainless steel spacer and performing the cure in the hot stage.

TOM was used to determine cloud-point times in the course of polymerizations at 80 °C. For blends of DP and PS in the epoxy precursors cloud-point times could be determined because of the slight mismatching of refractive indices at conversions where phase separation started [9]. For the cured TRLS films TOM was used to visualize the morphologies generated and to determine the intensity of transmitted light as a function of temperature. For this purpose a photodetector was incorporated to the optical path of the microscope.

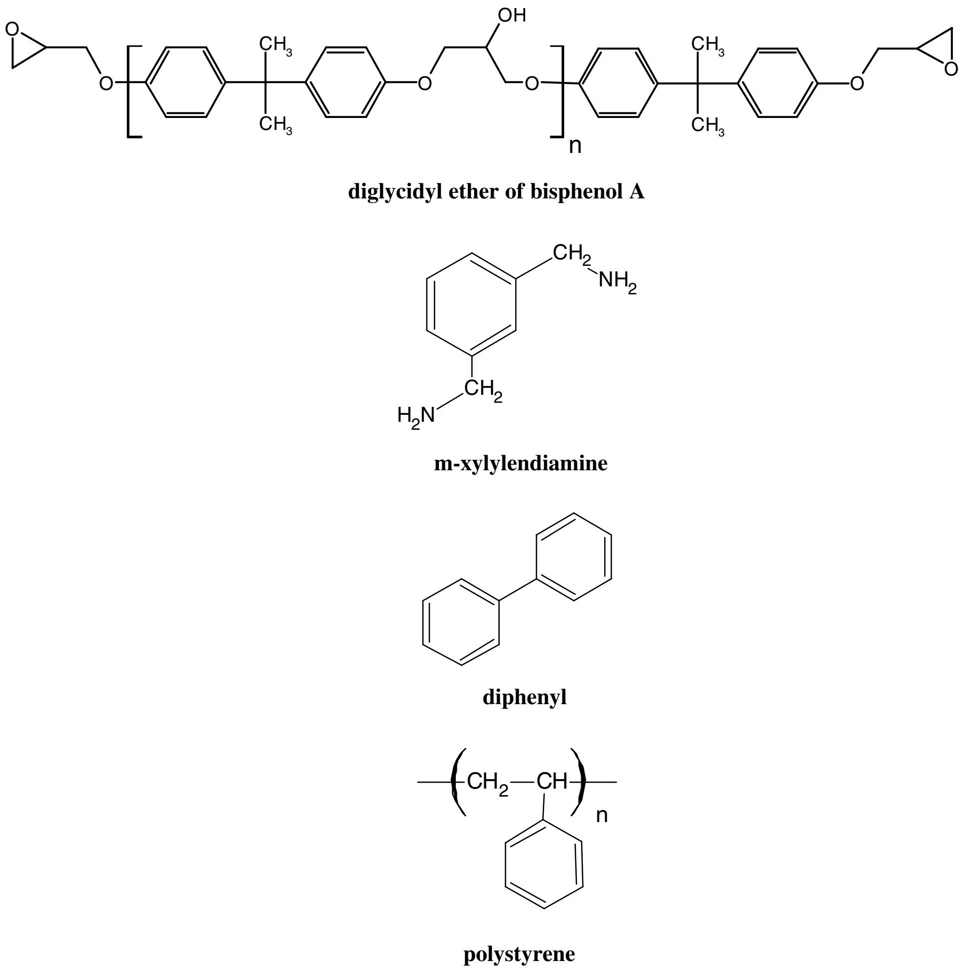

Fig. 1. Chemical structures of diglycidyl ether of bisphenol A (DGEBA), *m*-xylylenediamine (MXDA), diphenyl (DP) and polystyrene (PS).

3. Results and discussion

3.1. Phase diagram of DP in the cured epoxy

At the polymerization temperature (353 K) initial blends of DP in DGEBA–MXDA precursors were homogeneous in the whole composition range. Conversion vs. time curves at 80 °C obtained by NIR, enabled to determine the reaction time necessary to attain complete conversion (e.g., it was 4 h for a blend with 50 wt% DP and 10 h for a blend with 70 wt% DP). After curing to complete conversion and a storage period of several days at room temperature, DSC scans in the heating mode were used to obtain glass transitions, melting temperatures and melting heats. The resulting phase diagram for the DP/cured epoxy system is shown in Fig. 2.

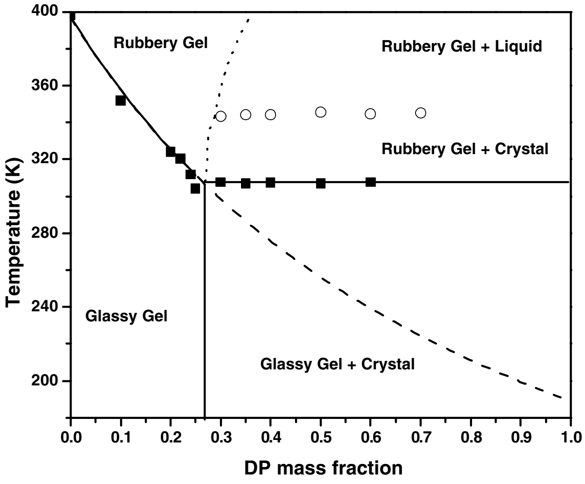

Fig. 2. Phase diagram of DP/cured epoxy blends.

Two homogeneous regions (rubbery gel and glassy gel) and three heterogeneous regions (rubbery gel + liquid; rubbery gel + crystal; glassy gel + crystal) are present in the phase diagram. The boundary between the rubbery gel and the liquid DP was arbitrarily drawn showing that the equilibrium concentration of DP in the swollen gel is expected to increase with temperature. This boundary could not be determined experimentally due to the matching of refractive indices of liquid DP and the swollen gel. The boundary between the rubbery gel and DP crystals was drawn joining the experimental point at 26 wt% DP in the constant T_g line with a point located at a composition close to 30 wt% DP in the constant T_m line.

For DP concentration up to about 26 wt% no phase separation was observed. When cooling these solutions the system evolved from a rubbery to a glassy homogeneous gel. The glass transition temperature of the neat cured epoxy was 397 K while the blend containing 26 wt% DP exhibited a T_g close to 307 K.

The total heat of fusion (total area under the melting peak) of blends that were stored for several days at 298 K showed a linear variation with the DP mass fraction (Fig. 3). Extrapolation of the straight line to a zero heat of fusion led to a composition of 26.8% DP, consistently with the limiting composition indicated in the phase diagram. This proves that all the DP exceeding the saturation concentration in the cured epoxy was phase-separated as crystals.

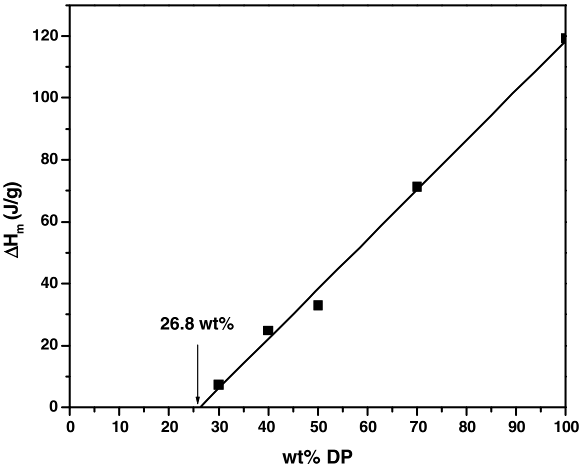

Fig. 3. Total heat of fusion of crystallized DP in samples stored several days at room temperature, as a function of the DP mass fraction.

3.2. Morphologies generated in DP/cured epoxy blends

The phase diagram indicated that formulations containing more than about 30 wt% DP should undergo a polymerization-induced phase separation at the cure temperature. However, for formulations containing up to 50 wt% DP phase separation was only observed during the cooling and storage stages, meaning that at the cure temperature the rubbery gel was in a metastable state swollen with an amount of DP higher than the equilibrium value. For the formulation with 60 wt% DP a partial phase separation took place at the cure temperature that was completed during the cooling and storage stages. But in every case a macroscopic phase separation was observed instead of the desired uniform dispersion of crystalline domains. Increasing the DP amount to 70 wt% led to phase inversion. For this composition the crystal-rich region percolated the whole sample. Dissolving the DP present in the blend with tetrahydrofuran (THF) led to a residual epoxy matrix that was also continuous throughout the sample (it did not disintegrate although it was extremely brittle). Possibly the crystal-rich phase and the epoxy matrix were present as two bicontinuous phases, a typical morphology when phase separation takes place in the critical composition region. Therefore, another strategy to produce a uniform dispersion of crystalline domains in the epoxy matrix was necessary.

To obtain the desired morphologies we explored the possibility of adding a small amount of polystyrene (PS) to the initial formulation, following the same idea that we have previously developed for polymer-dispersed liquid crystals (PDLC) films [10,11]. PS has the following characteristics: a similar refractive index than the one of DP and the cured epoxy, and a low compatibility with the epoxy (it phase-separates at very low conversions during polymerization). Therefore if DP is more soluble with PS than with the epoxy matrix, polymerization-induced phase separation of a PS/DP solution containing a large mass fraction of DP may be expected. Due to the low initial fraction of PS, the residual amount of DP in the epoxy matrix must be close to the saturation value. But the possibility of separating the DP excess in the course of polymerization may lead to a dispersion of PS/DP droplets in the epoxy matrix. Besides, the possibility of varying the initial amount of PS adds a degree of freedom for the control of the average size of dispersed domains.

3.3. DP/PS phase diagram

A phase diagram of the DP/PS binary blend was needed to analyze their mutual solubility and the DP crystallization from its solutions in PS. Thermal transitions were determined by DSC and the phase diagram shown in Fig. 4 was built-up. One-phase regions (liquid or glass) and two-phase regions (liquid + crystal and glass + crystal) are present in the phase diagram.

DP was completely soluble with PS up to a concentration close to 17 wt% DP. Crystallization was very slow for DP contents in the range comprised between 17 and 30 wt% but took place at a fast rate for DP concentrations higher than 50 wt%. After complete crystallization the T_g of the glassy phase is equal to 307.8 K.

According to the phase diagram, a PS/DP solution segregated from the epoxy matrix in the course of polymerization must be homogeneous at the cure temperature (353 K).

3.4. Phase separation of PS/DP domains in the course of polymerization

Phase separation in the course of polymerization was analyzed for blends containing 5 wt% PS and different amounts of DP (0, 30, 45 and 60 wt%). Fig. 5 shows conversion vs. time curves obtained by NIR for these PS/DP/(DGEBA–MXDA) blends. The dashed line joins cloud-point times determined independently by TOM. Increasing the DP amounts produced a decrease in the polymerization rate mainly by a dilution effect. The blend devoid of DP polymerized at a relatively fast rate but could not attain complete conversion due to vitrification (the glass transition temperature of the neat epoxy network is 397 K). Blends containing DP attained complete conversion due to the plasticization of the epoxy network produced by the dissolved DP. For the sample devoid of DP phase separation occurred at very low conversions ($x = 0.025$). Adding increasing DP amounts shifted cloud-point conversions to higher values ($x = 0.095$, 0.25 and 0.43, for wt% DP = 30, 45 and 60, respectively). This reveals that DP is a very good solvent of PS and, conversely, indicates that a significant fraction of DP should be separated together with PS giving PS/DP-rich domains.

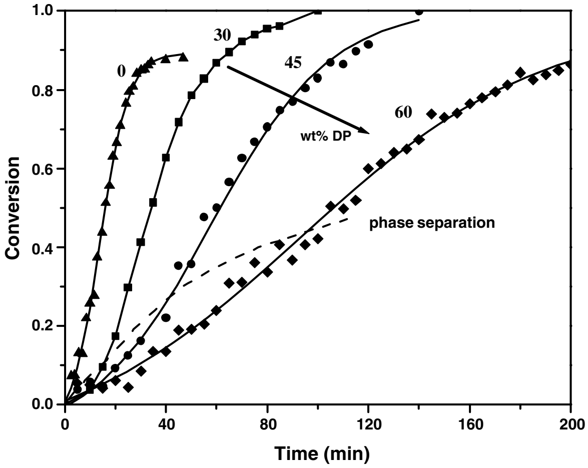

Fig. 5. Conversion vs. time curves obtained by NIR for PS/DP/(DGEBA–MXDA) blends containing 5 wt% PS and different amounts of DP: 0, 30, 45 and 60 wt%. The dashed line joins cloud-point times determined independently by TOM.

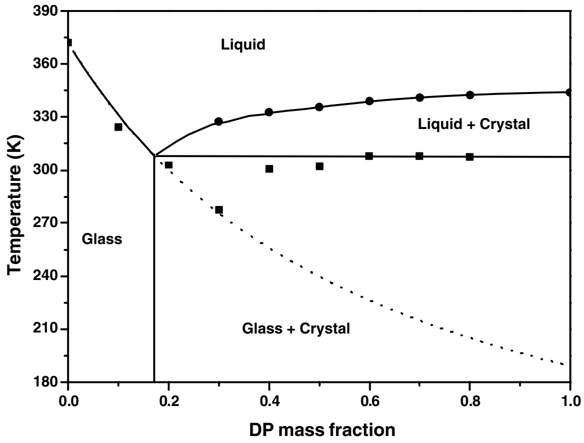

Fig. 4. Phase diagram of DP/PS blends.

When a polymerization is carried out in solution (in our case in a PS/DP solvent), at the time of phase separation there must be a sudden acceleration of the reaction rate due to the phase separation of part of the solvent and the resulting increase in the concentration of epoxy-amine species in the remaining solution [12–14]. Fig. 6 shows that this is indeed the case for blends containing 50 wt% solvent. The blend that includes 5 wt% PS began phase separation at the conversion indicated by the arrow (obtained by TOM); the other one did not phase-separate in the course of polymerization. The acceleration of the polymerization rate from the time where phase separation started is clearly noticed.

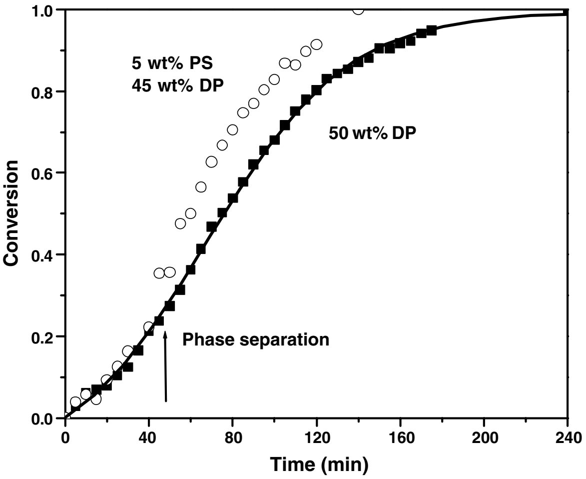

Fig. 6. Conversion vs. time curves obtained by NIR for a PS/DP/(DGEBA–MXDA) blend containing 5 wt% PS and 45 wt% DP, and for a DP/(DGEBA–MXDA) blend with 50 wt% DP. The arrow indicates the cloud-point time obtained by TOM for the blend containing PS.

3.5. Morphologies, thermal and optical properties of TRLS films

Morphologies generated after complete conversion are illustrated in Fig. 7 for blends containing 5 wt% PS and 40, 45 and 60 wt% DP. PS/DP domains were effectively dispersed in the epoxy matrix. The average size of these domains increased with the DP amount in the formulation, giving evidence of the significant DP concentration present in the dispersed phase (a 5 wt% PS could not have given such a significant volume fraction of dispersed phase). Dispersed domains appear black in the micrographs due to the light scattering produced by DP crystals. The epoxy matrix remains homogeneous and appears transparent. Heating above the DP melting point produced a transparent material due to the matching of refractive indices of the three components. The morphologies remained invariant in the course of successive heating–cooling cycles and crystallization and melting processes were confined to the interior of dispersed domains.

Thermal transitions of PS/DP/cured epoxy blends are illustrated by the DSC thermogram shown in Fig. 8, for the blend containing 5 wt% PS and 45 wt% DP. A single glass transition temperature was observed at 309.3 K. This value is close but slightly higher than the T_g of the epoxy network plasticized by DP (307 K) and the T_g of PS plasticized by DP (307.8 K). This means that the amount

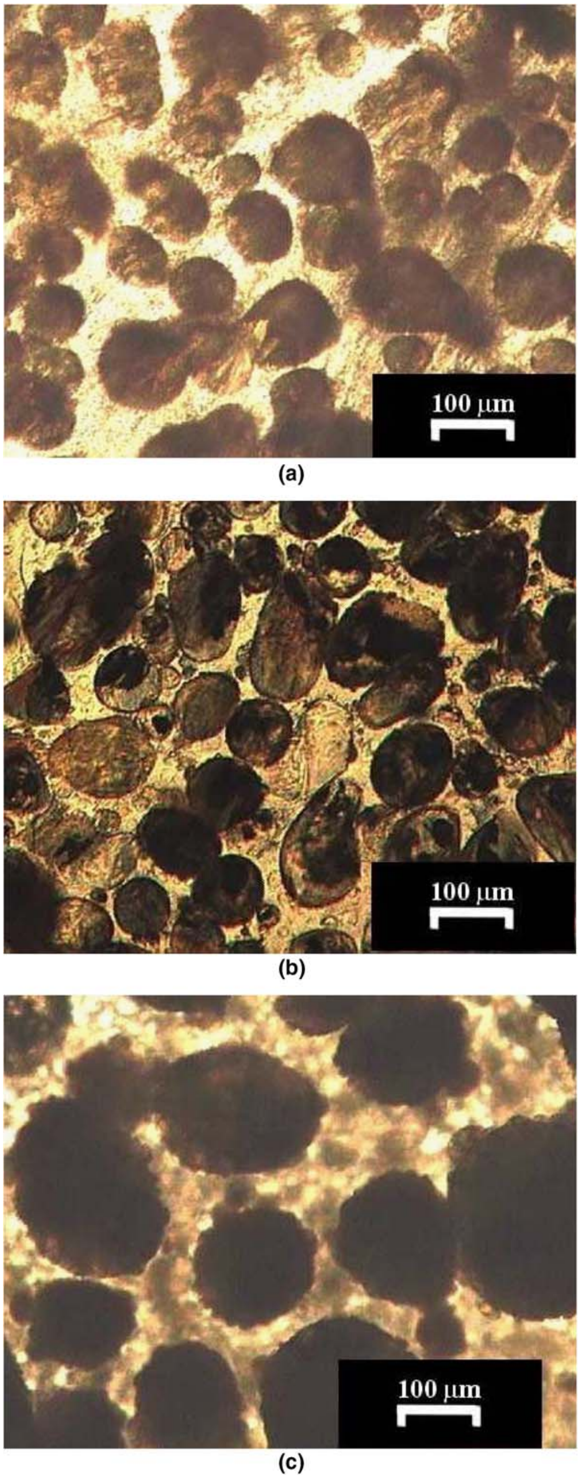

Fig. 7. TOM micrographs obtained at room temperature showing morphologies generated in PS/DP/cured epoxy blends containing 5 wt% PS and 40 wt% DP (a), 45 wt% DP (b) and 60 wt% DP (c).

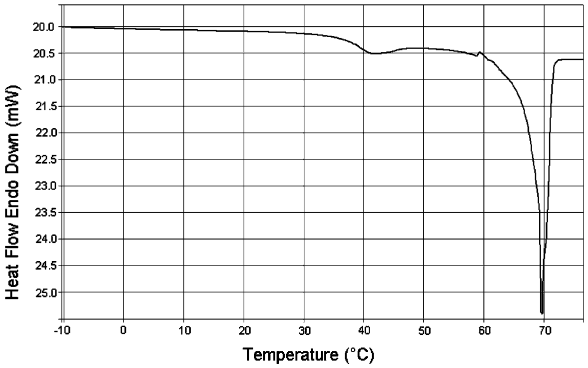

Fig. 8. DSC thermogram for a PS/DP/cured epoxy blend containing 5 wt% PS and 45 wt% DP.

of DP dissolved in the epoxy matrix was practically the same (in fact slightly less) than in blends devoid of PS. Melting of DP crystals began at about 60 °C and ended at 71 °C, indicating that there was a distribution of compositions in dispersed domains.

The behaviour of PS/DP/cured epoxy blends as TRLS films is illustrated in Fig. 9 for a 0.2 mm-film of a blend with 5 wt% PS and 45 wt% DP. The film started in the opaque state (18% transmittance), after the storage at room temperature. When heating at 5 °C min^{-1} the intensity of transmitted light showed a sharp increase at temperatures close to 70 °C, and the TRLS film attained a transmittance higher than 95%. In the cooling cycle the intensity of transmitted light decreased sharply at temperatures close to 50 °C where the DP crystallization began to take place in dispersed domains. The transmittance level rapidly attained a value of about 30% and then it exhibited a slow continuous decrease due to the continuation of DP crystallization in dispersed domains (when the TRLS film was stored at room temperature the transmittance attained the starting value of 18%). An excellent reproducibility was observed among successive cycles giving evidence of the invariance of morphology. The selected blend exhibited a very good behaviour as a TRLS film. The contrast ratio between both states might still be improved by varying the initial amounts of PS and DP.

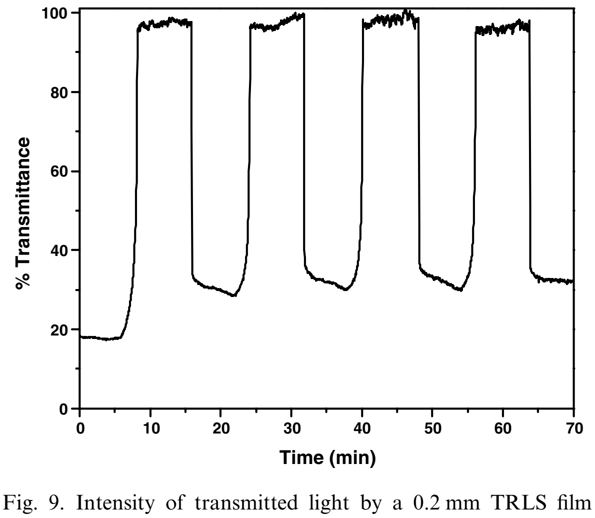

Fig. 9. Intensity of transmitted light by a 0.2 mm TRLS film composed of a PS/DP/cured epoxy blend with 5 wt% PS and 45 wt% DP. The film was submitted to successive heating and cooling cycles at a rate of 5 °C min^{-1}.

4. Conclusions

TRLS films based on dispersions of low-molar-mass organic crystals in a thermoset are difficult to obtain by a polymerization-induced phase separation of the binary solutions. Phase separation was observed to take place partially or totally during cooling or storage stages leading to the generation of macroscopic domains. This problem could be avoided by adding a third component with the following characteristics: (a) it phase separates at low conversions from binary solutions in the thermosetting polymer, (b) it is much more compatible with the low-molar-mass organic molecule than with the thermoset precursors, (c) it has the same refractive index than the thermoset and the low-molar-mass organic component in the amorphous state. A small addition of this third component enabled to disperse the crystallizable organic component in the thermoset matrix. In this way, TRLS films of excellent optical properties could be obtained. The concept was illustrated for a model system based on diphenyl (DP) and DGEBA–MXDA epoxy precursors, using PS as the third component. Melting and crystallization of DP was confined to the interior of dispersed domains a fact that led to a reproducible optical behaviour in the course of successive heating–cooling cycles.

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