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THERMALLY REVERSIBLE NANOSTRUCTURED THERMOSETTING BLENDS MODIFIED WITH POLY(ETHYLENE-b-ETHYLENE OXIDE) DIBLOCK COPOLYMER

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The main aim of this research was the generation of new intelligent materials, in this case thermoreversible material, based on epoxy matrix modified with semi-crystalline block copolymers. In this study, the epoxy system based on a diglycidyl ether of bisphenol-A (DGEBA), was cured with a stoichiometric amount of an aromatic amine hardener, 4,4'-methylene bis (3-chloro-2,6-diethylaniline) (MCDEA). A diblock copolymer of polyethylene-b-poly(ethylene oxide) (PEOE) was used as self-assembly agent.

Optical properties of the samples modified by addition of PEOE were studied by using transmission optical microscope (TOM) equipped with a hot stage. Additionally, morphology generated in the sample was studied by atomic force microscopy (AFM).

Keywords: *nanostructured thermoset, semi-crystalline block copolymers, thermally reversible materials, thermooptical properties*

Introduction

As it is well known, amphiphilic diblock copolymers are able to form well-defined ordered and disordered nanostructures in thermosetting epoxy resins [1–8]. Nanostructured thermoset epoxy resin blends can be self-organized by addition of block copolymers consisting of a thermoset-miscible block and thermoset-immiscible block. However, almost all the studied thermoset-immiscible blocks are noncrystallisable, amorphous polymers. Recently, Guo *et al.* [9] studied nanostructured thermoset blends of bisphenol A-type epoxy resin and a low molecular mass (Mn=1400) amphiphilic poly(ethylene-b-ethylene oxide) (PEOE) cured using 4,4'-methylenediamine (MDA). They concluded that up to 30 mass% PEOE in blends only PE crystals with the size on nanoscale can be formed, being them nanoscopically confirmed within the individual spherical micelles. For blends containing 40 and 50 mass% PEOE, spherical micelles appear highly aggregated. In other work, Sun *et al.* [10, 11] have shown that low molecular mass PEOE could have 'liquid crystals' behavior. Taken this into account, it seems to be interesting to check whether thermosetting blends modified with low molecular mass PEOE diblock copolymer with a ratio of the blocks, which allows that copolymers show 'liquid crystal' behavior for their use as thermally reversible materials. Additionally, also interesting seems to be check if self-assembly of these low molecular mass PEOE copolymers in thermosetting matrix stabilize the system for thermal reversibility by means of lower time of the switching between opaque and transparent state.

In this work, a thermosetting epoxy resin was modified by very low molecular mass (Mn=920) poly(ethylene-b-ethylene oxide) diblock copolymer. The main objective was to investigate the possibility of obtaining nanostructured thermoset materials, which can be thermally reversible. This was analyzed mainly by differential scanning calorimetry (DSC), transmission optical microscopy (TOM) and atomic force microscopy (AFM).

Experimental

Materials and sample preparation

A diglycidylether of bisphenol-A epoxy resin (DGEBA) (Dow DER 330 gifted by Dow Chemical) was used as reactive solvent. This epoxy resin was cured with a stoichiometric amount of an aromatic amine hardener, 4,4'-methylene bis (3-chloro-2,6-diethylaniline) (MCDEA), kindly supplied by Lonza. A diblock copolymer of poly(ethylene-b-ethylene oxide) (PEOE), supplied by Aldrich Chemical Co. Inc. was used as modifier, with number-average molecular mass of 920 g mol^{-1} and 50 mass% ethylene oxide content.

In order to prepare the samples, PEOE (30, 40 and 50 mass%) was dissolved in DGEBA with continuing stirring at 120°C. The curing agent MCDEA was then added to the mixture and homogeneous ternary mixtures were obtained. After that, the mixture was

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immediately degassed at 120°C in vacuum, and pre-cured for 12, 24 or 48 h at 120°C (in order to self-assembling of PEOE), followed by post-curing at 180°C for 12 h and 200°C for 8 h.

Methods

The miscibility between DGEBA and diblock copolymers was analyzed on a Mettler Toledo DSC 822 differential scanning calorimeter equipped with a Sample Robot TSO 801 RO. Nitrogen was used as a purge gas (10 mL min^{-1}). Temperature and enthalpy were calibrated by using an indium standard. Measurements were performed in sealed aluminum pans containing a sample mass of around 7 mg. All samples were initially heated to 150°C and maintained at that temperature for 10 min in order to erase the thermal history of each sample, then cooled down with controlled rate of 5°C min^{-1} and reheated to 150°C at a rate of 5°C min^{-1}.

A transmission optical microscope (Nikon Eclipse E600) equipped with a hot stage (Mettler FP 82HT) was used to study direct morphology changes during cooling/heating process. The objective lens magnification was 50×. Micrographs were captured with a Color View 12 camera by using the AnalySIS Auto 3.2 software (Soft Imaging System GmbH).

AFM topography images of the cryogenic fractured surfaces of cured mixtures were recorded in tapping mode at room temperature by using a scanning probe microscope (SPM) (Nanoscope IIIa, Multimode$^{\text{TM}}$ from Digital Instruments). Etched single beam cantilever (225 μm length) silicon nitride probes having a tip nominal radius of curvature of 5–10 nm were used. Scan rates ranged from 0.8 to 1.6 Hz s^{-1}. The sample line was 512 and the target amplitude was around 0.7 V. Height and phase images were recorded simultaneously during scanning. In order to obtain repeatable results of the blend morphology, different regions of the specimens were scanned. Similar images were obtained, thus demonstrating the reproducibility of the results. The flat surfaces of the PEOE-(DGEBA/MCDEA) systems used for examination were obtained by cutting with a diamond knife using a Leica Ultracut R microtome.

Results and discussion

The thermooptical curves in the isotropization region of poly(ethylene-b-ethylene oxide) block copolymer (PEOE) are shown in Fig. 1a. Additionally, the thermooptical curves in the isotropization region of PEOE/DGEBA and PEOE-(DGEBA/MCDDEA) systems both with 40 mass% PEOE content have been plotted in Fig. 1b and c, respectively. First of all, as shown in Fig. 1a, it should be pointed out that for PEOE block copolymer switching from opaque to transparent state and vice versa is thermally reversible, however, the range of this process during heating/cooling cycle is very large and clearly depends on melt-

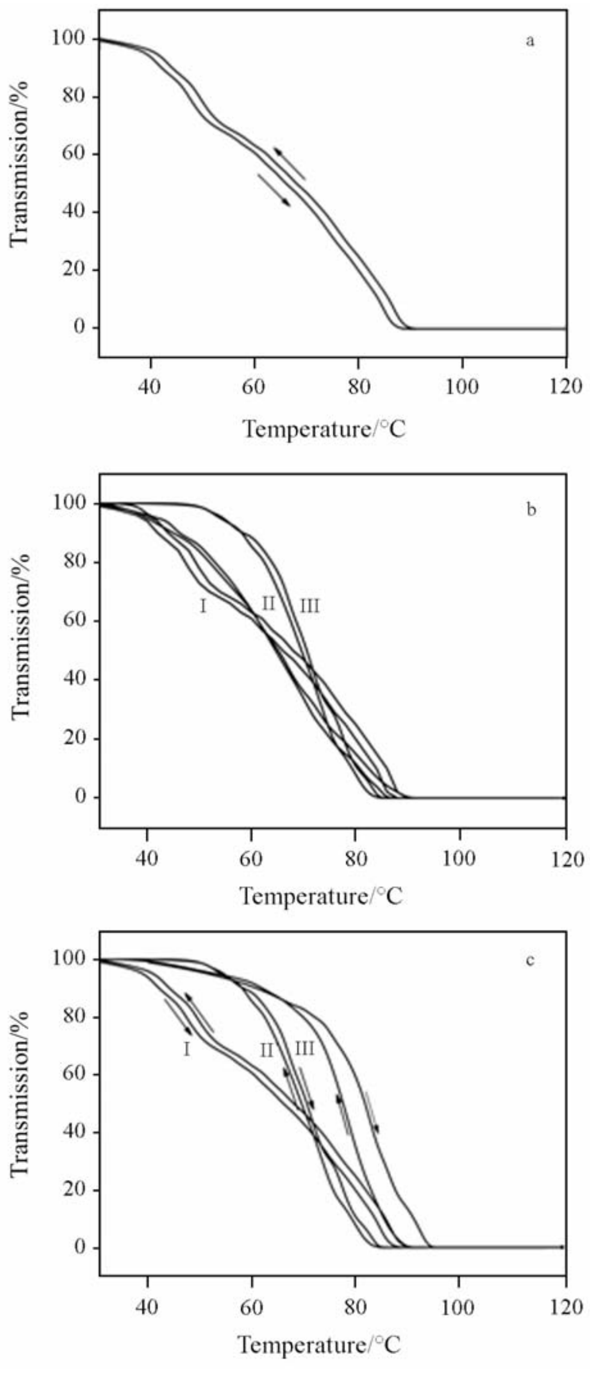

Fig. 1 Thermooptical curves in the isotropization region during cooling/heating regime from 30 to 120°C at 5°C min^{-1} for: a – PEOE; b – PEOE (I), 40 mass% PEOE/DGEBA after 12 h at 120°C (II) and 40 mass% PEOE/DGEBA after 24 h at 120°C (III); c – PEOE (I), 40 mass% PEOE-(DGEBA/MCDEA) pre-cured 12 h at 120°C (II) and 40 mass% PEOE-(DGEBA/MCDEA) pre-cured 24 h at 120°C (III)

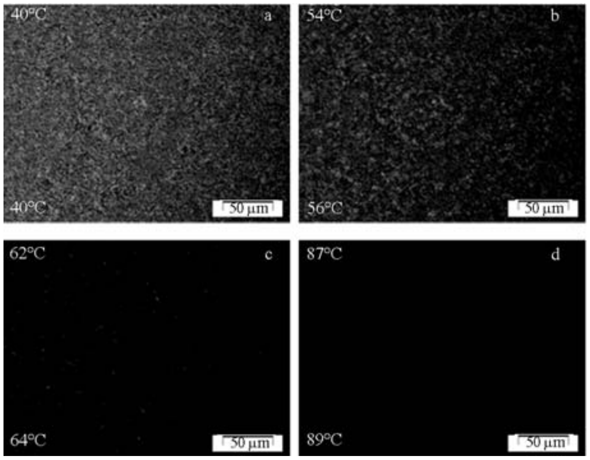

Fig. 2 TOM micrographs of PEOE taken in situ during cooling/heating regime from 30 to 120°C at 5°C min^{-1} between crossed polarizers

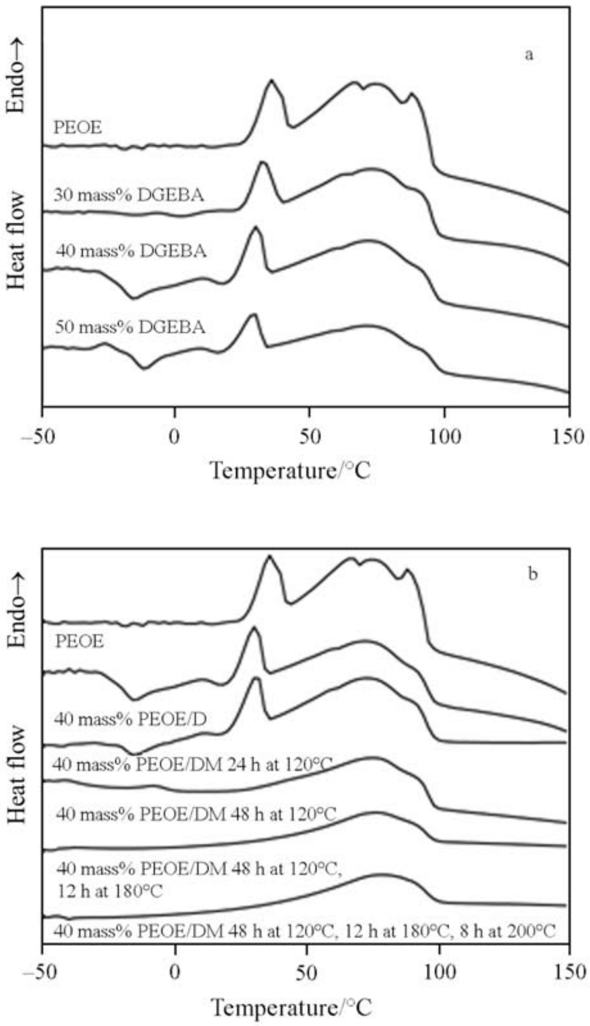

Fig. 3 DSC curves for a – uncured PEOE/DGEBA, b – fully cured PEOE-(DGEBA/MCDEA) systems followed the cooling scan at 5°C min^{-1}. D→DGEBA and DM→DGEBA/MCDEA

ing/crystallization of both PE and PEO blocks. Changes in morphology during cooling/heating process, for PEOE block copolymer, are presented in Fig. 2. As can be seen, PEO block spherulites started melting at 54°C. At 62°C, only PE block spherulites can be still observed between crossed polarizers and finally at 87°C PEOE block copolymer becomes completely transparent. Similar behaviour is shown during cooling process of PEOE; up to 89°C system is completely transparent (Fig. 2d). First nuclei of PE block spherulites appear at 64°C and they grow up to 54°C, where PEO block spherulites start to be observed and finally the system becomes completely opaque.

For 40 mass% PEOE/DGEBA systems, the range of switching from opaque to transparent and vice versa during melting/cooling cycle became narrower if compared with the corresponding thermo-optical curves for PEOE (Fig. 1b), and it takes place only in range of melting/cooling regime of PE block, what indicates the PEO block is miscible with DGEBA. Additionally, the 40 mass% PEOE/DGEBA fully cured system (pre-cured 12 or 24 h at 120°C, post-cured at 180°C for 12 h and 200°C for 8 h) shows shorter range of switching from opaque to transparent state, which depends strongly on pre-curing time (Fig. 1c), thus longer annealing time leads to narrow range of switching between opaque to transparent state of PEOE-(DGEBA/MCDEA) blends.

The miscibility between DGEBA and diblock copolymers was studied by DSC. The results obtained for PEOE/DGEBA with 30, 40 and 50 mass% PEOE block copolymer content are shown in Fig. 3. As it has also been reported by other authors [6, 8, 11, 12], in this system the PEO block of PEOE diblock copolymer can be miscible with epoxy, thus hydrogen bonding interaction between PEO and epoxy can take place. The melting point of PEO block in the PEOE/DGEBA is shifted to lower temperature with increase of DGEBA content in the system (Fig. 3a). Moreover, the amount of crystalline phase of PEO block decreases with increasing of DGEBA in PEOE/DGEBA systems as it was also demonstrated by [6, 9, 12]. Additionally, as shown in Fig. 3b, the melting point of the PEO block in fully cured PEOE-(DGEBA/MCDEA) systems was not detected, what can indicate that PEO block is miscible with the cured resin. This behaviour can be seen if the curing of 40 mass% PEOE-(DGEBA/MCDEA) system is followed. In this system, after 12 h pre-curing at 120°C melting of PEO block is still detected but the melting point is shifted to lower temperature and the enthalpy is lower compared to the corresponding enthalpy of melting of PEO block in PEOE block copolymer. Additionally, after 48 h pre-curing at 120°C the melting point of PEO block in the DSC experiment conditions was not detected, what confirms miscibility of PEO block with epoxy matrix.

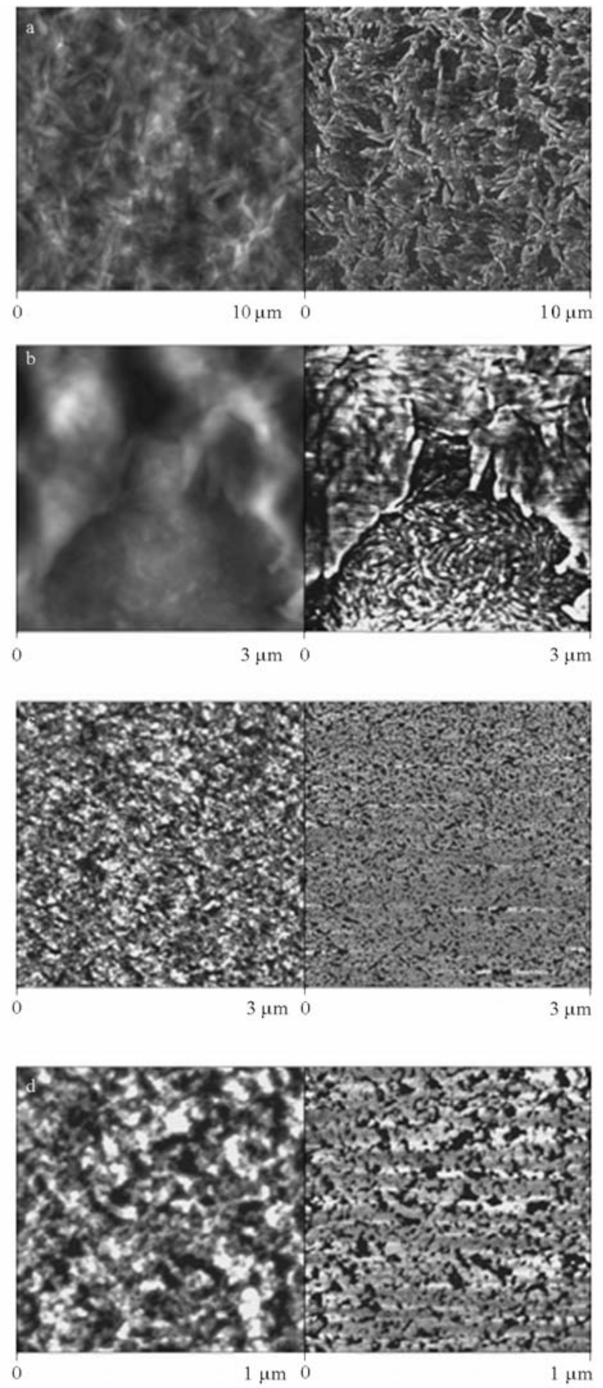

Fig. 4 AFM images of 40 mass% PEOE-(DGEBA/MCDEA) blends a – pre-cured 12 h at 120°C, b – detail of a), c – pre-cured 48 h at 120°C and d – detail of c)

Morphology of PEOE-(DGEBA/MCDEA) systems was studied by AFM. As shown in Fig. 4, the final morphology of the cured system strongly depends on both annealing and curing time, thus controlling these two parameters can allow obtaining nanostructured thermosetting epoxy resin blends. The 40 mass% PEOE-(DGEBA/MCDEA) system pre-cured 12 h at 120°C still shows spherulites of PE block but if observed in more detail (Fig. 4b) self-assembly of PE block can also be seen. In the contrary, this system pre-cured 48 h at 120°C results in spherical micelles nanostructure. PEOE block copolymer is initially miscible with DGEBA/MCDEA system, then PE block phase separates as the molecular mass of the epoxy matrix increases during curing, leading to self-assembly of the PE block into spherical micelles, what can be observed in Fig. 4c and in more detail in Fig. 4d. At this point, it should be recalled that, these results are in good agreement with DSC results, where was clearly seen that 40 mass% PEOE-(DGEBA/MCDEA) system pre-cured 12 h at 120°C still shows melting of PEO block. On the contrary, for the same system but pre-cured 48 h at 120°C melting of PEO block was not detected.

Nevertheless, it is worth to note that crystallization of the PE block in the PEOE-(DGEBA/MCDEA) system has strong influence on the final morphology as well as annealing and curing time.

Conclusions

Controlled annealing and curing time of epoxy resin modified with low molecular mass poly(ethylene-b-ethylene oxide) block copolymers containing 50 mass% PE blocks showed it is possible to obtain nanostructured thermosetting epoxy resin blends using 4,4'-methylene bis(3-chloro-2,6-diethylaniline) as curing agent. A more important result was that in this way nanostructured materials can be obtained, with thermo-reversible character. As it was shown, the PEO block of the PEOE diblock copolymer is miscible with epoxy resin. In the modified DGEBA/MCDEA, PE block is microphase separated from the epoxy formed micelles, what can have strong influence on the shape of thermooptical curves. The thermooptical curves of PEO blocks in the cooling/heating procedure do not show switching from opaque to transparent state and vice versa neither in the system PEOE/DGEBA annealed longer than 24 h nor in system PEOE-(DGEBA/MCDEA) fully cured, what confirms that PEO block in these systems are miscible with epoxy. It can be also shown that materials with longer annealing time have shorter range of transition from opaque to transparent state.

A work is in progress on demonstrating the effect of annealing and curing time on the thermo-reversible response of the materials.

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