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Kinetics and Morphology of an Epoxy Resin Modified with PEO-PPO-PEO Block Copolymers

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Summary: Block copolymers are a special class of polymers having the ability to self-assemble into nanoscale ordered structures which depend on molecular composition of the blocks. With the aim of studying the influence of copolymer composition, the kinetics of a 4,4′-diaminodiphenylmethane-cured diglycidyl ether of bisphenol-A (DGEBA) epoxy system modified with a PEO-PPO-PEO block copolymers has been investigated by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR), taking into account the relation between blocks in the copolymer as well as different copolymer contents. DSC results show that the rate of cure reaction decreases when the copolymer is added, which can be attributed to the interaction between the hidroxyl groups of the growing epoxy thermoset and the ether groups of the block copolymer observed by FTIR. The experimental results obtained have been related to the morphologies observed by atomic force microscopy (AFM).

Keywords: block copolymers; epoxy; kinetics; nanostructures; self-assembly

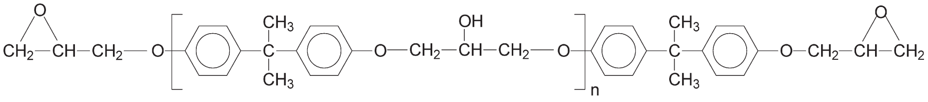
Introduction

Nanostructured polymers are finding an increasing number of applications, for example, functional coatings, membranes, barrier films and others more classical as structural systems to prepare polymer-based materials with high mechanical strength/weight ratio.

Block copolymers are materials known to self-assemble into nanoscale ordered structures [1–3]. Although these copolymers are not dispersible in epoxy resins, they are able to order epoxy networks at the nanometer scale in both cured and uncured states [4–6]. The nanostructure formed depends on the chemical composition of the blocks. Poly(ethylene oxide)-poly (propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers get an amphiphilic character with lipophilic (PPO) and hydrophilic (PEO) blocks, that leads to their self-assembling behaviour. In this work, the cure kinetics and the nanostructure formed have been studied when the composition of the copolymer is changed.

Experimental

The epoxy resin used was DER 332, a diglycidyl ether of bisphenol-A (DGEBA), kindly supplied by Dow Chemical.



The hardener used was HT 972, 4,4′-diamino diphenyl methane (DDM), supplied by Ciba.

Two different poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)

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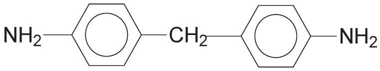
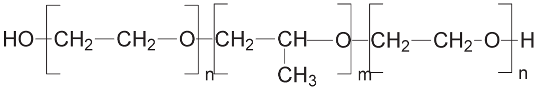


(PEO-PPO-PEO) triblock copolymers from Polysciences were used. The PEO/PPO molar ratios were 0.33 in the case of the commercially called EP1 copolymer, and 3.00 for EP3. Molecular weights of EP1 and EP3 copolymers are 3400 and 13300, respectively.



$$HO{-}\left[CH_2{-}CH_2{-}O\right]_n{-}\left[CH_2{-}\underset{CH_3}{\underset{|}{CH}}{-}O\right]_m{-}\left[CH_2{-}CH_2{-}O\right]_n{-}H$$

Epoxy/PEO-PPO-PEO samples were prepared by mixing the molten DGEBA with the block copolymer at 80 °C with continuous stirring. Afterwards, DDM was added to the mixture at amine/epoxy stoichiometric ratio and stirred at 80 °C until a homogeneous mixture was obtained. Then the samples were cured at 80 °C for 6 h and post-cured at 190 °C for 2 h.

Reaction kinetics were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7. All the reactions were conducted in hermetic aluminum sample pans. The weight of the samples ranged between 5 and 7 mg. Isothermal runs were carried out a 120 °C to determine the values of heat generated during the isothermal scans (ΔH_{iso}). Samples were then reheated from ambient temperature to 250 °C in the scanning mode at a heating rate of 10 °C/min to determine the residual heat (ΔH_{res}). Runs were also carried out in the scanning mode from ambient temperature to 250 °C at a heating rate of 10 °C/min to determine the maximum exothermic temperature.

Infrared analyses were performed on a Perkin-Elmer 16PC spectrometer. Samples were prepared mixing the solid mixture with KBr. The spectra were taken with a 2 cm^{-1} resolution in a wave number range from 4000 to 400 cm^{-1}.

The morphology of the specimens was studied by Atomic Force Microscopy (AFM). A scanning probe microscope (Nanoscope IIIa, Multimode^{TM} from Digital Instruments) operating in tapping mode was used. The images were obtained under ambient conditions with the scan speed of 1 line/s, using scan heads with a maximum range of 16×16 μm or 100×100 μm.

Dynamic mechanical tests were carried out with a Metravib viscoanalyser and a three-point bending device with a span length of 44 mm. Specimens were machined to $60 \times 12 \times 5$ mm from plaques prepared as described above. Tests at 10 Hz were made at a heating rate of 3 °C/min over the temperature range 20–250 °C.

Results and Discussion

The cure behaviour of the epoxy resin modified with a block copolymer depends on the composition of the copolymer as well as the content of the copolymer employed. In this sense, DGEBA/DDM blends containing 10, 20 and 30 wt% PEO-PPO-PEO block copolymer were analyzed.

Figure 1 shows the dynamic curves obtained by DSC for the systems modified with PEO-PPO-PEO block copolymers with different PEO/PPO ratios and different copolymer contents. It can be seen that the temperature at which the exothermic peak occurred is higher when the content of the copolymer added is also higher. This indicates that the copolymer causes the retardation of the cure reaction.

This retardation, higher for the system modified with EP3 copolymer, can also been observed when the evolution of conversion vs. time is analysed, as it can be seen in Figure 2. The conversion (X) was calculated from $X = (\Delta H_{iso})_t/(\Delta H_{iso} + \Delta H_{res})$, where $(\Delta H_{iso})_t$ is the heat generated in time t, which is obtained by integrating the isothermal curve area at each curing time.

As it is shown in Figures 1 and 2, the retardation of cure reaction is higher in the case of the copolymer with a higher PEO/PPO ratio, which can be due to the miscibility of the PEO block, which can

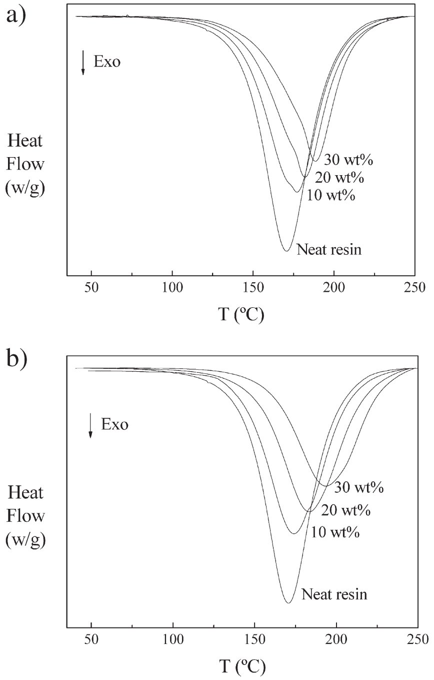


Figure 1.
DSC scans for DGEBA/DDM/PEO-PPO-PEO systems with different PEO/PPO ratios a) 0.33 and b) 3.00.

interact with the resin. The interactions between the hydroxyl groups of the growing epoxy thermoset and the ether groups of the block copolymer were followed by FTIR. Infrared spectra of DGEBA/DDM/PEO-PPO-PEO with different copolymer contents and for systems with different PEO/PPO ratios are shown in Figure 3. The band assigned to the vibration of free hydroxyl groups appears at 3559 cm^{-1}, while the one at 3427 cm^{-1} corresponds to the hydroxyl groups associated by hydrogen bonds.

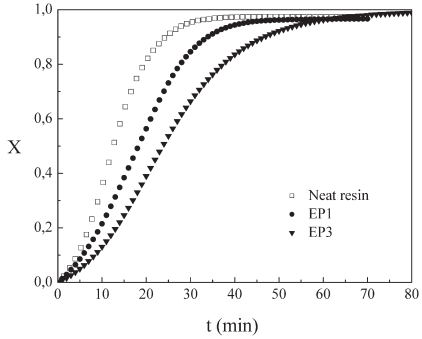


Figure 2.
Conversion vs. time for DGEBA/DDM/PEO-PPO-PEO systems cured at 120 °C, and modified with 20 wt% EP1 or EP3.

The formation of hydrogen bonds between the hydroxyl groups generated during cure reaction and the ether group of the copolymer can be followed by the band at 3427 cm^{-1}, which appears at a lower wave number when the copolymer is added for the two systems studied. This effect is more pronounced when the PEO content is higher, as it can be seen in Figure 3 b), due to the increase of the strength of the interactions.

The morphologies obtained by AFM for the system modified with the block copolymer that has a lower PEO/PPO ratio are shown in Figure 4. These blends were opaque which indicates that phase

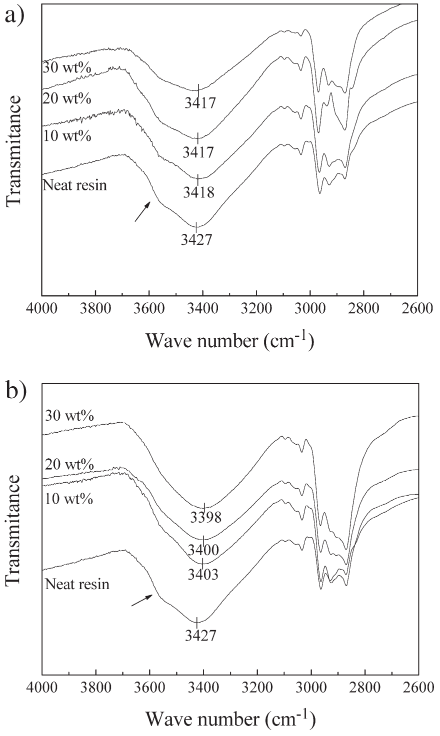


Figure 3.
Comparison of FTIR spectra for DGEBA/DDM/PEO-PPO-PEO systems with different PEO/PPO ratios a) 0.33 and b) 3.00.

separation takes place. Morphology is particulate and the size and number of these particles increase with copolymer content.

The morphologies for the system modified with the block copolymer that has a higher PEO/PPO ratio shown in Figure 5, present a completely different structure. In this case, the cured blends were transparent and images show nanoscopic phase-separated morphology. This difference is due to the fact that PEO content is higher in this case so that the affinity with the resin is also higher. As it has been reported in previous works [7,8], the block copolymer used is initially miscible with DGEBA/DDM sys-

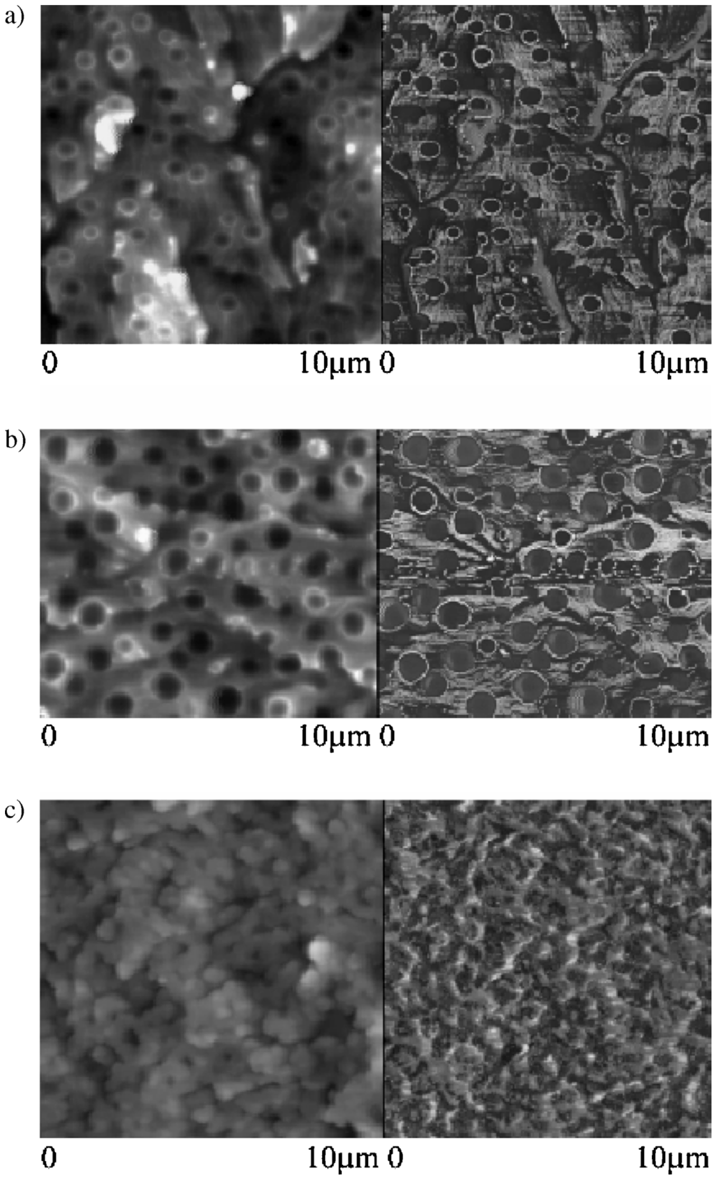


Figure 4.
TM-AFM images for DGEBA/DDM blends containing a) 10, b) 20, c) and 30 wt% PEO-PPO-PEO copolymer (PEO/PPO ratio = 0.33). Topographical (left) and phase (right) images.

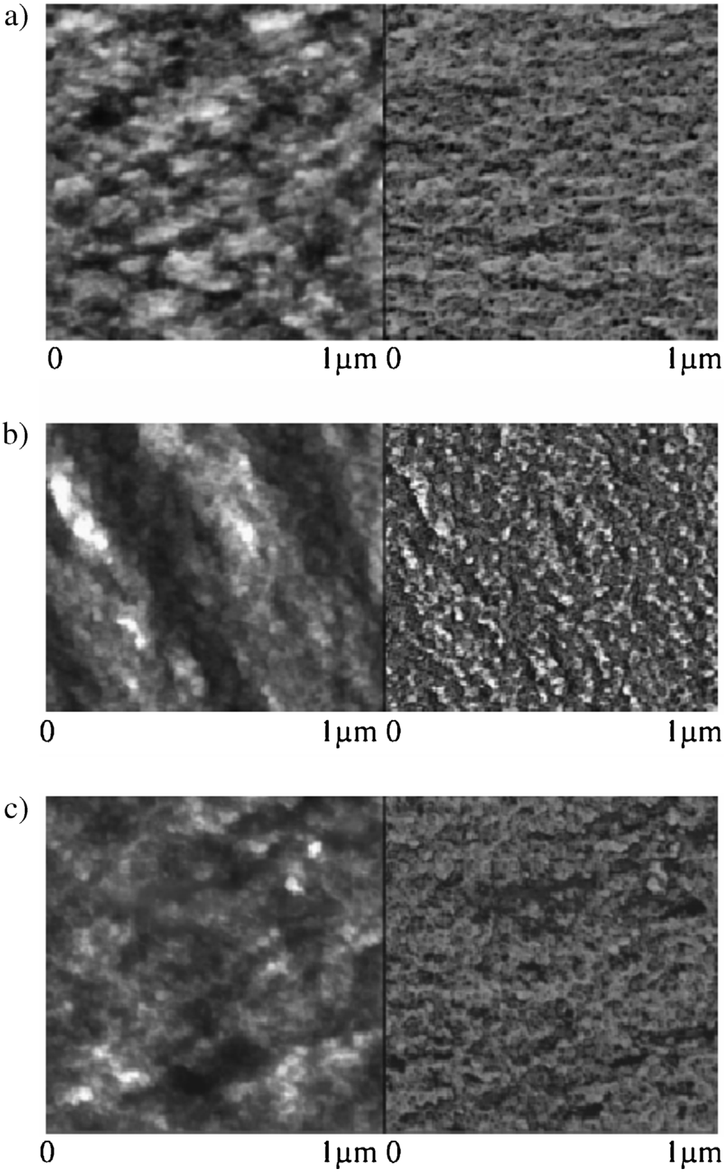


Figure 5.
TM-AFM images for DGEBA/DDM blends containing a) 10, b) 20, c) and 30 wt% PEO-PPO-PEO copolymer (PEO/PPO ratio = 3.00). Topographical (left) and phase (right) images.

tem but PPO block phase segregates as the molecular weight of the epoxy system increases during curing, leading to self-assembly of PPO into spherical micelles.

To explain the results obtained, dynamic mechanical analysis have been carried out. Figure 6 shows the dynamic mechanical behaviour for systems modified with the two different copolymers, EP1 and EP3, as well as the ones modified with the homopolymers PEO and PPO. When the system is modified with a copolymer that remains miscible after curing[9], the maximum of the tan δ, the glass transition temperature, diminishes considerably comparing with the neat resin and the peak is broader.

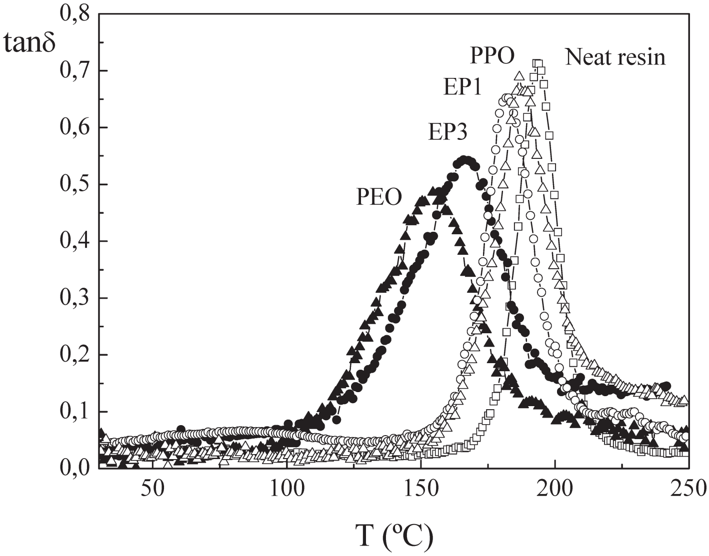


Figure 6.
Dynamic mechanical loss tangent for the neat resin (□) and for mixtures modified with 10 wt% EP1 (○), EP3 (●), PPO (△), and PEO (▲).

This is the case of the system modified with EP3, which presented nanoestructured morphology. However, when the system is not miscible, the peak is narrower and the glass transition similar to the unmodified system, which corresponds to the phase separation at a macroscale observed in AFM micrographs.

Conclusions

In this work, different aspects of the self-assembling behaviour of block copolymers into epoxy systems have been analyzed. PEO-PPO-PEO block copolymers of different molar ratio between blocks have been used to study the influence of composition on the kinetic and morphological behaviour of DGEBA/DDM systems.

FTIR analysis confirms the interaction between hydroxyl groups of the resin and the ether groups of the copolymer, which can explain the decrease in the reaction rate observed by DSC analysis.

The structures observed depend on the composition of the block copolymer employed. Higher PEO block contents increase the miscibility between DGEBA/DDM epoxy system and the block copolymer, thus allowing the possibility to generate nanostructured thermosetting materials.

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