



Morphological and mechanical study of nanostructured epoxy systems modified with amphiphilic poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide)triblock copolymer



Laida Cano^a, Daniel H. Builes^{a,b}, Agnieszka Tercjak^{a,*}

^a Group 'Materials + Technologies', Dpto. Ingeniería Química y del M. Ambiente, Escuela Politécnica/Eskola Politeknikoa, Universidad del País Vasco/Euskal Herriko Unibertsitatea (UPV/EHU), Pza. Europa 1, 20018 Donostia-San Sebastián, Spain

^b Research and Development Center 'DENOVO', Andercol S.A. Autopista Norte 95-84, Medellín, Colombia

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ABSTRACT

Thermosetting systems based on DGEBA epoxy resin and poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) (EPE) triblock copolymer were prepared and investigated. Different mixtures were obtained by using different contents of EPE block copolymer in order to study the influence of the modifier on the properties of the final materials. All thermosetting systems were prepared without using any solvent and were cured at ambient temperature, taking into account the lower critical solution temperature (LCST) behavior of the block copolymer. DSC results indicated that the addition of block copolymer affected to the curing reaction time and to the glass transition temperature of the mixtures and also the miscibility of EPE triblock copolymer in the epoxy resin was proved. The morphologies studied by AFM and TEM showed clear nanostructuring up to 25 wt % EPE content. The addition of 5 and 15 wt % of EPE block copolymer led to a considerable improvement in the toughness of the materials. When EPE block copolymer was added to the epoxy resin, the surface became more hydrophilic and the UV–vis transmittance decreased slightly maintaining a high level of transparency.

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1. Introduction

In the last years different materials such as rubbers, thermoplastic homopolymers and block copolymers have been used as additives for epoxy matrices. Among these materials, many studies have confirmed that block copolymers can provide new or improved properties to the epoxy resins [1–7]. The main contribution of the block copolymers is their capacity to self-assemble in ordered nanostructures leading to microphase separated morphologies and to generate nanostructured thermosetting systems when they are mixed with an epoxy resin. Beside the ability to get ordered nanostructures with different morphologies, the addition of block copolymers to thermosetting matrices can lead to an improvement in the mechanical properties of the matrix.

The most common way to obtain nanostructured epoxy systems is by using a block copolymer where only one of its blocks is miscible with the epoxy resin and consequently the non-miscible block can microseparate from the matrix [5,7] leading to a microphase separation. In the cases where the block copolymer does not

have any block miscible with the epoxy resin, it would be essential to modify chemically one of the blocks in order to make it miscible with the epoxy resin. Apart from the interaction between the blocks and the matrix, the nanostructuring is also controlled by other parameters like the volume fraction of each block, the interactions between blocks, etc. Nanostructured thermosetting systems can be mainly obtained by two different mechanisms. One of them is the called reaction-induced microphase separation (RIPS) mechanism [3], in which the microseparation of one block of the block copolymer occurs during the curing reaction. In the second case, the self-assembly of the block copolymer could occur before the curing [1] and consequently one block would microseparate before the curing process. In this case, the self-assembly of the block copolymer before the curing leads the microphase separation of nanostructured thermosetting systems.

Epoxy resins are one of the most widely used thermosetting polymers due to their good mechanical and thermal properties, high chemical and corrosion resistance and low shrinkage during curing. These properties lead to several applications in adhesives, surface coatings, moulds, and aerospace and electronics industries, among others [8]. However, one of their main drawbacks is their low toughness. There have been many studies in which rubbers and thermoplastics were employed in order to increase the toughness

* Corresponding author. Tel.: +34 943017169; fax: +34 943017130.
E-mail address: agnieszka.tercjaks@ehu.es (A. Tercjak).

of thermosets. Nevertheless, the modification of epoxy resins with block copolymers has resulted to be an adequate method to improve epoxy toughness at low contents of block copolymer as well as to create ordered microphase-separated structures [4,9–13].

The triblock copolymer poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) has already been used before to modify phenolic [14], unsaturated polyester [15–17] and epoxy resins [18–25]. Already published studies about the blend of DGEBA epoxy resin with poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) triblock copolymer revealed that different macroseparated or microseparated morphologies were obtained depending on the content of block copolymer in the matrix, molar ratio between blocks, molecular weight of the block copolymer and the curing cycle carried out. The miscibility of the blends and kinetics of the curing reaction were also investigated as a function of the block copolymer content. It was demonstrated that the presence of the block copolymer delayed the curing reaction of the epoxy system. The control of nanostructures by optimizing the curing conditions resulted to be essential to control the mechanical properties of the final materials.

In this work, the poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) triblock copolymer (EPE) was employed as modifier of a DGEBA based epoxy matrix with the aim of obtaining nanostructured thermoset systems with improved mechanical properties. It was demonstrated that EPE triblock copolymer resulted to be an effective modifier to lead to a remarkable improvement effect on the toughness value of an epoxy resin, which was the main interest of this paper. Different contents of a triblock copolymer up to 50 wt % were added to the matrix in order to study the influence of the content of block copolymer on the morphology, mechanical properties and curing reaction time of the epoxy system. The curing process was the same for all mixtures and it was chosen taking into account the lower critical solution temperature (LCST) behavior of EPE [21,26]. Consequently, all investigated thermosetting systems curings were carried out at 25 °C, what in our opinion is a big advantage from an industrial point of view since the low temperature allows to reach nanostructuring of the DGEBA/MXDA system with a very high EPE content and improve drastically the toughness of investigated thermosetting systems. The morphology of the blends and the size of the microseparated phase were investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The optical transparency was investigated by UV–vis spectroscopy. The mechanical properties measurements were carried out by the universal testing machine (MTS). The glass transition temperatures as well as the curing behavior were determined by differential scanning calorimeter (DSC). Contact angle measurement was employed to characterize the surface properties of the samples.

2. Experimental

2.1. Materials and sample preparation

The triblock copolymer poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) (referred to as EPE from this point forward), purchased from Sigma–Aldrich, had a number average molecular weight (M_n) of 5800 g/mol and 30 wt % of polyethylene oxide content. The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA) (DER 330) provided by The Dow Chemical Company with an epoxy equivalent weight between 176 and 185 g/eq. The curing agent used to cure this epoxy resin was *m*-Xylylenediamine (MXDA) supplied by Sigma–Aldrich. The employment of this curing agent allows to reach a low curing temperature for the fabrication of the investigated thermosetting systems.

The neat epoxy system was prepared by mixing DGEBA resin with MXDA in stoichiometric proportions using a magnetic stirrer. After stirring it for around 10 min, when the mixture was homogeneous, it was degassed in a vacuum bell at ambient temperature. Then, the mixture was poured into a glass mold to be cured. To prepare the block copolymer/epoxy systems, firstly a certain amount of EPE block copolymer was dissolved in DGEBA resin. This mixture was heated at around 60 °C in order to melt the block copolymer and favor its solution and then continuously stirred until a complete homogenization was achieved. A stoichiometric amount of MXDA was added and the same procedure as for the neat epoxy system was followed. All the blends were first cured at 25 °C for 12 h, followed by 9 h at 35 °C, 2 h at 50 °C and finally 1 h at 150 °C. This procedure was chosen to avoid long time curing in high temperature. Apart from the neat epoxy system, four blends were prepared, with 5, 15, 25 and 50 wt % of EPE block copolymer.

2.2. Techniques

Differential scanning calorimetry (DSC) measurements of the neat epoxy system as well as EPE/epoxy systems were performed using a Mettler Toledo DSC 822^e differential scanning calorimeter. The miscibility of EPE triblock copolymer with uncured DGEBA resin was investigated by dynamic scans performed from –50 °C to 150 °C at 5 °C/min. The thermal history of the samples was deleted by a first heating from –50 °C to 150 °C at 5 °C/min followed by a cooling from 150 °C to –50 °C at 1 °C/min. All blends were analyzed during curing by an isothermal scan performed at 25 °C (followed by a dynamic scan from 25 °C to 200 °C at 5 °C/min). Thermal transition temperatures of cured blends were determined by dynamic scans performed from –25 °C to 220 °C with a heating rate of 5 °C/min. Prior to this scan, a heating from –25 °C to 220 °C followed by a cooling from 220 °C to –25 °C was carried out in order to delete the thermal history of the material. All experiments were conducted under a nitrogen flow of 10 mL/min using 10–15 mg samples in aluminum pans.

The morphologies of the cured epoxy and EPE/epoxy systems were studied by atomic force microscopy (AFM) under ambient conditions. AFM images were obtained using a scanning probe microscope (Nanoscope IIIa Multimode™, Digital Instruments). Tapping mode (TM) was employed in air using an integrated tip/cantilever (125 μm in length with ca. 300 kHz resonant frequency). Typical scan rates during recording were 0.7–1 line/s using a scan head with a maximum range of 16 × 16 μm. Samples were cut using an ultramicrotome Leica Ultracut R with a diamond blade.

For TEM measurements, samples were prepared by using an ultramicrotome Leica EMFCS instrument equipped with a diamond knife at room temperature. A Tecnai G2 20 Twin transmission electron microscope operated at 200 kV with resolution of 2.5 Å was used. Moreover, TEM samples were stained in RuO₄ vapor for 4 min in order to enhance the contrast between micro-separated PPO rich phase and epoxy rich phase.

UV–vis transmittance spectra of the cured neat epoxy and EPE/epoxy systems sheets (thickness of 1 mm) were obtained using a spectrophotometer (Shimadzu UV-3600) in the range between 200 and 800 nm.

Regarding mechanical properties of the neat epoxy and EPE/epoxy systems, flexural tests were carried out following the ASTM D790-10 standard test method and using universal testing machine (MTS, model Insight 10) provided with a 250 N load cell. Three-point bending tests without notch were performed at a rate of crosshead of 5.6 mm/min using specimen dimensions of 36 × 9 × 1.5 mm³ (rectangular shape). Flexural modulus was determined from the slope of the load-displacement curve in the zone of linear elasticity. Fracture toughness tests were performed

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