

Nanostructured epoxy based thermosetting systems modified with poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) triblock copolymer to enhance fracture toughness

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Abstract

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 their several applications in adhesives, surface coatings, moulds, and aerospace and electronics industries, among others [1]. 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 of thermosets. In this field, one of the most effective methods to improve epoxy toughness is their modification with block copolymers, which also create thermosetting materials with ordered microphase-separated structures [2-4].

The triblock copolymer poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (EPE) has already been used before to modify phenolic, unsaturated polyester and epoxy resins. 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 macro- 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 [5-9]. In our work, the EPE triblock copolymer was employed as modifier of a DGEBA based epoxy matrix with the aim to obtain nanostructured thermoset systems with improved mechanical properties. 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 and surface properties of the epoxy system.

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) performing flexural and fracture toughness tests. The glass transition temperatures as well as the curing behavior were determined by differential scanning calorimeter (DSC).

Epoxy based nanostructured thermosetting systems modified with different contents of poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) triblock copolymer were successfully synthesized. The curing process was carried out at 25 °C owing to the lower critical solution temperature (LCST) behavior of the EPE block copolymer. The addition of the triblock copolymer to the epoxy resin caused a delay on the time of the curing reaction as well as a decrease in the T_g of the systems compared to the neat epoxy resin T_g , due to the plasticization effect provoked by the addition of the block copolymer. This indicated the partial miscibility between EPE block copolymer and DGEBA epoxy resin and in particular between PEO block and DGEBA resin.

As was confirmed by AFM (Figure 1) and TEM, the cured samples showed well nanostructured morphologies up to 25 wt % EPE content. As a result of the interactions between PEO block and epoxy resin, this block is miscible with epoxy resin and consequently PPO appeared as a microseparated phase. The morphology obtained resulted to be dependent on the EPE block copolymer content as it changed from spherical structure to worm-like structure with the content of block copolymer. In the case of 50 wt % EPE content, a macroseparated morphology could be observed.

Regarding the mechanical properties (Figure 2), both flexural modulus and fracture toughness (in terms of critical stress intensity factor, K_{IC}) were analyzed. The flexural modulus decreased whereas the toughness improved considerably with 5 and 15 wt % EPE block copolymer content and it almost remained the same with 25 wt % content if compared with neat epoxy system. UV-vis measurements mainly indicated a decrease in the transmittance with the increase of EPE block copolymer content. This decrease of transmittance was also reflected in the visual appearance of the samples, although all samples except for 50 wt % EPE sample remained transparent.

References

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Figures

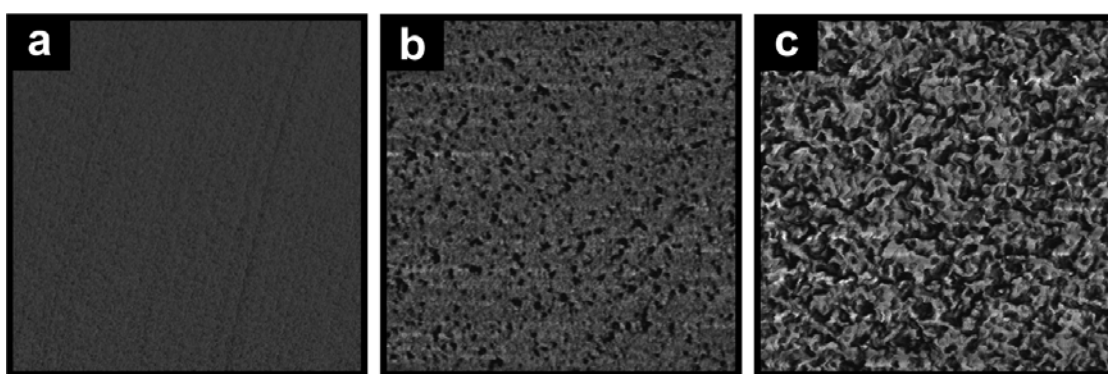


Figure 1. AFM phase images (1 μm x 1 μm) of a) neat epoxy, b) 5 wt % EPE/epoxy and c) 25 wt % EPE/epoxy systems.

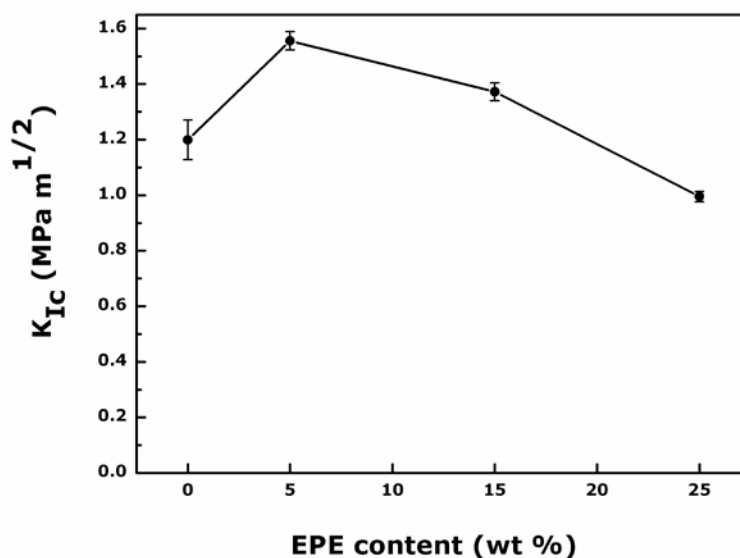


Figure 2. Critical stress intensity factor (K_{IC}) of the cured neat epoxy system and all EPE/epoxy systems.