



New epoxy thermosets modified with amphiphilic multiarm star polymers as toughness enhancer



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ABSTRACT

The synthesis and characterization of two novel amphiphilic multiarm star polymers with linear polyethylene glycol (PEG) and poly(ϵ -caprolactone) (PCL) arms and their use as toughening modifiers of epoxy anhydride thermosets are reported. The new star polymers were obtained by partial pegylation of a hyperbranched polyester and subsequent growth of PCL arms. The curing process was studied by calorimetry and thermomechanical analysis, demonstrating the accelerating effect and the influence on gelation of the hydroxyl terminal groups. The curing kinetics was analyzed by model-free and model-fitting methods. The final properties of the resulting materials were determined by thermal and mechanical tests. The addition of the star-like modifiers led only to notable improvement on impact strength in the material containing a 10% of the star with PCL and PEG arms, without compromising glass transition temperature and thermal stability. The morphology of the resulting materials depended on the structure of the toughness modifier used, as demonstrated by electron microscopy, but all modified thermosets obtained showed phase-separated morphologies with nanosized particles.

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1. Introduction

Epoxy resins are widely used as coatings, electrical and electronic materials because of their high adhesion and other attractive properties such as thermal stability and electrical insulation [1–3]. However, in some applications their high crosslinking density leads to fragility, and sometimes damage of the substrate occurs because of the apparition of voids and cracks due to the generation of stresses that are originated by shrinkage during curing and processing. These drawbacks can be reduced by using dendritic polymers as reactive modifiers [4–11].

By adding a conveniently tailored dendritic polymer to the epoxy formulation, the impact resistance of the material can be enhanced many folds without compromising processability and thermomechanical characteristics and even the internal stresses can be reduced [8,12,13]. By this strategy, the best results are achieved when the modifier phase-separates during curing and there is good interfacial adhesion between phases. Enhancement of interfacial adhesion can be reached via chemical incorporation

of the modifier into the epoxy matrix or by establishment of effective physical interactions.

In a previous work, we reported the use of partially modified Boltorn H30 polyester with nonpolar 10-undecenoyl moieties in epoxy/anhydride thermosets. Concretely, when the degree of modification of hydroxyl groups with 10-undecenoyl moieties was 76%, a phase separated material was obtained and more than a 4-fold increase in impact strength was reached [8].

On the other hand, it is known that the use of block copolymers, with blocks of different miscibility, capable of self-assembling upon blending with uncured precursor, can lead to materials with phase-separated morphologies and a significant toughness enhancement. Mülhaupt et al. reported the modification of epoxy resin with a branched polysiloxane–polycaprolactone block copolymer [14]. It was found that in the modified thermosets, spherical particles of about 20 nm in diameter were uniformly dispersed in the continuous matrix. Meng et al. used star-shaped block copolymers and obtained phase separation in epoxy resin, and even increasing glass transition temperature of the resulting thermosets [7].

Amphiphilic dendrimers, whose surfaces have two distinct physical properties, prepared by coupling of tailored hydrophilic and hydrophobic segments, have shown the ability of self-assembling

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to form Janus particles [15]. Recently, Samuel and Ramakrishnan [16] have demonstrated that hyperbranched polyesters, bearing alkyl and polyethylene glycol segments randomly placed on their periphery, can reconfigure so as to self-segregate the hydrophobic and hydrophilic segments to form Janus-type structures. It has been found that the immiscibility of both segments, the strong tendency of the alkyl segments to crystallize and the conformational flexibility of the hyperbranched core, are the thermodynamic gradients responsible of the reconfiguration of the polymer backbone.

Miktoarm star polymers are a relatively new and versatile class of macromolecules due to their intriguing properties, which can be tailored by varying the nucleus and/or their arms. This kind of polymers, where any number of various types or polymer arms emanate from the core, shows as relevant property their self-assembly in solution and in the bulk [17]. The arms of this type of star can have different molecular weights and/or chemical natures. It is expected to obtain nano-structured thermosets, caused by a reaction-induced phase separation process or by self-assembly, when miktoarm polymers containing arms of different hydrophilicity/hydrophobicity are used as epoxy modifiers. The initial miscibility between the resin and the modifier, the viscosity of the mixture and the temperature of curing are the factors that control the morphologies obtained.

Taking all of this into account, in the present work, we propose the use of two new amphiphilic polymers with hyperbranched polyester core and poly(ethylene glycol) (SP-PEG) or poly(ethylene glycol)/poly(ϵ -caprolactone) arms (SP-PEGPCL), as toughness modifiers of an epoxy/anhydride formulation. Hyperbranched polyester and poly(ϵ -caprolactone) were separately selected as the hydrophobic core and shell and poly(ethylene glycol) as the hydrophilic shell. The selection of the core and arms aims to reach different phase-separated morphologies using star polymers with different flexibility and amphiphilicity. Moreover, the hydroxyl terminals groups of the hyperbranched polyester and the OH groups at the end of the poly(ϵ -caprolactone) arms can react with epoxy/anhydride thermoset precursors, allowing the chemical incorporation of the modifier into the network structure, enhancing the interfacial adhesion between phases, if they are present. The materials were characterized by means of thermogravimetry, thermomechanical analysis and the fracture surface explored by SEM microscopy. Impact resistance was evaluated by Izod impact tests.

2. Experimental section

2.1. Materials

Diglycidylether of bisphenol A (DGEBA) with an epoxy equivalent of 187 g/eq (Epikote 828, Hexion Speciality Chemicals B.V.) was dried in vacuum before use. N,N'-dicyclohexyl carbodiimide (DCC), tin (II) 2-ethyl hexanoate, monomethyl ether of poly(ethylene glycol) ($M_n = 550$ g/mol) ($\text{CH}_3\text{OPEG-OH}$), methyl hexahydrophthalic anhydride (MHHPA), benzyl dimethyl amine (BDMA), succinic anhydride and pyridine were purchased from Sigma-Aldrich and were used as received. ϵ -Caprolactone (ϵ -CL) (Sigma-Aldrich) was distilled under vacuum before use. 4-(N,N-dimethylamino) pyridinium p-toluenesulfonate (DPTS) was prepared as described in the literature [18]. The hyperbranched Boltorn H30 ($M_w = 3500$ g/mol, 32 OH) was donated by Perstorp and was used as received.

2.2. Synthesis of the acid terminated monomethyl ether of poly(ethylene glycol) ($\text{CH}_3\text{OPEG-COOH}$)

In a 100 mL two-necked round-bottom flask 10 g (0.018 mol) of monomethyl ether of poly(ethylene glycol) ($\text{CH}_3\text{OPEG-OH}$) were dissolved in 150 mL of chloroform (Scheme 1). Then, 9 mL of

pyridine were added and finally 9 g (0.090 mol) of succinic anhydride were added in portions. The mixture was heated up to 60 °C and allowed to react at this temperature for 72 h on stirring. After that, the solution was cooled down to room temperature and the solvent was eliminated under vacuum. The crude product was dissolved in 15 mL of 1 N HCl, washed with ether, to eliminate the excess of succinic anhydride, and then extracted with chloroform and dried. The solvent was removed under vacuum.

$^1\text{H NMR}$ (CDCl_3): δ (in ppm) 4.20 ($-\text{CH}_2\text{OOC}-$); 3.60–3.70 ($-\text{O}-\text{CH}_2\text{CH}_2\text{O}-$); 3.30 (OCH_3); 2.50–2.60 ($-\text{OOC}-\text{CH}_2\text{CH}_2-\text{COO}-$).

$^{13}\text{C NMR}$ (CDCl_3): δ (in ppm) 175.5 (COOH); 172.2 (COOCH_2); 71.9, 70.6, 69.0 (OCH_2CH_2); 63.9 (terminal PEG CH_2); 59.1 (OCH_3); 29.2, 28.8 (CH_2 succinic).

2.3. Synthesis of the multiarm star with poly(ethylene glycol) arms (SP-PEG)

In a 250 mL round bottom two necked flask provided with magnetic stirrer and Ar inlet, 1 g of Boltorn H30 (9 meq OH), 0.54 g (1.5 mmol) of 4-(N,N-dimethylamino) pyridinium p-toluenesulfonate (DPTS) and 3 g (4.6 mmol) of $\text{CH}_3\text{OPEG-COOH}$ were dissolved in 30 mL of DMF (Scheme 1). Then 2.26 g (11 mmol) of dicyclohexyl carbodiimide (DCC) were added and the mixture allowed reacting at room temperature for 48 h. Then, the precipitate was filtered off and the volume of DMF was reduced to 10 mL. The crude product was dialyzed against the same solvent.

$^1\text{H NMR}$ (CDCl_3): δ (in ppm) 4.20 ($-\text{CH}_2\text{OOC}$ (A + c)); 3.60–3.70 ($-\text{CH}_2\text{CH}_2\text{OCH}_2-$ (B + d + e + f)); 3.30 (OCH_3 (g)); 2.50–2.60 ($-\text{OOC}-\text{CH}_2\text{CH}_2-\text{COO}-$ (a + b)); 1.15–1.20 ($-\text{CH}_3$ (C)) (Fig. 1).

$M_n = 11,300$ g/mol (by $^1\text{H NMR}$ analysis). 12 PEG arms/multiarm star molecule (from $^1\text{H NMR}$).

2.4. Synthesis of the miktoarm star with poly(ethylene glycol) and poly(ϵ -caprolactone) arms (SP-PEGPCL)

2 g of SP-PEG (0.18 mmol, 3.6 meq OH) and 4.11 g of ϵ -CL (36 mmol) were placed in a two necked flask at room temperature equipped with a magnetic stirrer and Ar inlet (Schemes 1 and 2). Then, four drops of $\text{Sn}(\text{oct})_2$ were added to the mixture and the reaction was carried out at 130 °C during 72 h in a thermostated oil bath. Then, the solid product was dissolved in chloroform and isolated by reprecipitation in 10-fold cold diethyl ether. Finally, the polymer was filtered and dried at 45 °C under vacuum for 2 days.

$^1\text{H NMR}$ (CDCl_3): δ (in ppm) 4.20 ($-\text{CH}_2\text{OOC}$ (A + c)); 4.0 ($-\text{CH}_2-\text{OOC}-$, 5); 3.60–3.70 ($-\text{CH}_2\text{CH}_2\text{OCH}_2-$ (B + d + e + f) and $-\text{CH}_2-\text{OH}$, 5'); 3.30 (OCH_3 (g)); 2.50–2.60 ($-\text{OOC}-\text{CH}_2\text{CH}_2-\text{COO}-$ (a + b)); 2.20 ($-\text{CH}_2-\text{COO}-$, 1 and 1'); 1.70–1.50 ($-\text{CH}_2-$, 3, 3' and 4, 4'); 1.40–1.30 ($-\text{CH}_2-$, 2 and 2'); 1.15–1.20 ($-\text{CH}_3$ (C)) (Fig. 2)

$M_n = 29,000$ g/mol (by $^1\text{H NMR}$ analysis). 12.2 PEG arms and 9 PCL arms by multiarm star molecule (from $^1\text{H NMR}$). Each PCL arm has a degree of polymerization of 17.

2.5. Samples preparation

Mixtures containing MHHPA and the selected proportion of the star polymer were heated mildly until the modifier was dissolved and the solution became clear. The mixture was then cooled down to room temperature and added to the corresponding amount of DGEBA and catalyst. Finally, samples were carefully stirred and degassed under vacuum (at 40 °C) during 15 min to prevent the appearance of bubbles during curing. The catalyst, BDMA, was used at a concentration of 1 phr (1 part of catalyst per hundred parts of DGEBA/MHHPA mixture). The modifier was added at concentrations of 5 and 10% with respect to DGEBA/MHHPA/BDMA mixture.

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