Multiarm star with poly(ethyleneimine) core and poly(ε-caprolactone) arms as modifiers of diglycidylether of bisphenol A thermosets cured by 1-methylimidazole

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ABSTRACT

Well-defined multiarm star copolymers, with hyperbranched poly(ethyleneimine) (PEI) as the core and poly(ε-caprolactone) (PCL) arms with different degree of polymerization were synthesized by cationic ring-opening polymerization of ε-caprolactone from a hyperbranched poly(ethyleneimine) core and used to modify diglycidylether of bisphenol A formulations cured with 1-methylimidazole as anionic initiator. The curing process was studied by dynamic scanning calorimetry (DSC) and FTIR. By rheometry the complex viscosity of the multiarm stars synthesized and the influence of their addition to the reactive mixture was analyzed in detail. The resulting materials were characterized by thermal and mechanical tests. The addition of the multiarm star to the formulation led to homogeneous materials with a slightly toughened fracture in comparison to neat DGEBA thermosets without compromising thermal characteristics.

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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]. The objectives of our research on epoxy based materials are to face some of the limitations of this kind of materials for instance, the enhancement of toughness or the reduction of the internal stresses, maintaining their thermomechanical characteristics and easy processability.

In previous works it was proved the convenience of star-like topologies to enhance some characteristics of epoxy thermosets [4–11]. Star-like polymeric structures were also used in the improvement of other matrices, such as poly(vinyl ester urethane)s with a great success [12].

In general, the modification with dendritic structures like hyperbranched or star polymers leads to a significant improvement of mechanical properties of the thermosets without affecting thermomechanical characteristics [13–16]. Moreover, low shrinking thermosets have been prepared by the use of these structures [17,18] and chemically or thermally reworkable thermosets can be reached when the dendritic structure presents labile groups such as esters [13,19]. However, the most interesting item is that dendritic polymers offer a low formulation viscosity since the highly branched structure prevent chain entanglement, thus reducing the viscosity in comparison to linear polymeric modifier analogs [20].

In previous studies of our research team, we have synthesized multiarm stars with poly(glycidol) core and poly(ε-caprolactone) arms, which have been studied as modifiers in the curing of DGEBA using cationic and anionic initiators as curing agents [5,8]. In both studies the processability of the reactive mixtures was not worsened in reference to the neat formulation and even the viscosity was reduced when the multiarm star had arms with a degree of polymerization of 10. T_gs of the final materials were not much reduced and were even higher than those of the thermosets modified with linear poly(ε-caprolactone). In cationic cured materials the thermal stability was practically maintained whereas the use of anionic curing initiators allowed us to reach reworkable thermosets, because of the temperature of initial degradation was reduced more than 100 °C. Toughness characteristics were improved in both materials.

Following the "core-first" approach, which involves the living polymerization of a monomer from a multifunctional core [21–24], in the present study we have synthesized new multiarm stars with poly(ε-caprolactone) (PCL) arms of different lengths using as the multifunctional core a poly(ethyleneimine) (PEI) from a commercial source, with trade name Lupasol®. This is a promising strategy to reach star modifiers at low price by an easy procedure, which allows facing advantageous technological applications in the field of epoxy coatings.

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In a recent study, Lupasol® has been explored as a multifunctional crosslinker of epoxy resins, but its reactivity is too high and the short gelation time prevents technological applicability [25,26]. Thus, the modification of the amine terminal and linear active groups, capable of directly reacting with epoxides, with poly(ε-caprolactone) arms, changes dramatically its reactivity and applicability. This polymer, which is a hydrophobic semicrystalline polyester with a high chain flexibility, is miscible in most epoxy resins [27,28]. Its flexible structure is capable of promoting crazing and shear yielding and to absorb the energy locally. Therefore it can improve the toughness characteristics on incorporating it to the epoxy matrix [29].

The presence of tertiary amine groups in the core of the multiarm star prevents use of cationic initiators such as rare earth metal triflates. Thus, 1-methylimidazole has been selected in the present work as anionic initiator. Tertiary amines help to covalently link the multiarm stars ended with OH groups to the epoxy matrix, as has been demonstrated previously by us [5,30]. This is due to the fact that the initiation by the tertiary amine generates an alkoxide anion, responsible for the propagation by reaction with epoxides by a typical anionic ring-opening mechanism. Thus, a proton exchange can take place between this anion and the hydroxyl groups present in the reactive system, which allows the chemical incorporation of hydroxyl-terminated polymers into the network structure.

The goal of the present work is the improvement of DGEBA epoxy thermosets cured by 1MI by adding poly(ethyleneimine)-poly(ε-caprolactone) multiarm stars with different arm length in proportions of 5% and 10% w/w and the evaluation of the curing process.

2. Experimental section

2.1. Materials

Polyethyleneimine (PEI) Lupasol®FG (800 g/mol) was purchased from BASF and used without further purification. From the molecular weight of the polymer and of the repeating unit an average degree of polymerization of 18.6 was calculated. According to the data sheet, the relationship (NH_2/NH/N) was (1/0.82/0.53) and thus by calculations the equivalent number of primary, secondary and tertiary amines is 0.010, 8.37×10^{-3}, and 5.3×10^{-3} eq/g. ε-Caprolactone (ε-CL, 97%) was distilled under vacuum. Tin (II) 2-ethylhexanoate ($Sn(oct)_2$, 98%) and 1-methylimidazole (1MI, 99%) were used without further purification. All these chemicals were purchased from Sigma–Aldrich. Solvents were purchased from Scharlab. Diglycidylether of bisphenol A (DGEBA) Araldite GY 240 was provided by Huntsman (EEW = 182 g/eq).

2.2. Synthesis of poly(ethyleneimine)-b-poly(ε-caprolactone) multiarm stars (PEI-PCLX)

In the acronym PEI-PCLX, X accounts for the degree of polymerization of the ε-caprolactone arms in the star and can take the values 10, 30 and 50.

The synthesis is exemplified for PEI-PCL10. PEI (0.5 g, 0.625 mmol) and 10.28 g of ε-CL (90.06 mmol) were placed at room temperature in a two-necked flask equipped with a magnetic stirrer and a gas inlet to fill the flask with argon. Then, 0.12 g of $Sn(oct)_2$ (0.3 mmol) was added to the solution mixture and the flask was immersed in an oil bath thermostatized at 130 °C during 48 h. After that, the crude product was dissolved in chloroform and the polymer was isolated by precipitation in methanol and then filtered and dried at 45 °C under vacuum for two days.

^{1}H NMR (400 MHz, CDCl$_3$, δ in ppm): 4.08 (–**CH$_2$**–OCO–, **5**), 3.66 (–**CH$_2$**–OH, **5′**), 2.32 (–NHCO–**CH$_2$**–, –**CH$_2$**–COO, **1** and **1′**), 1.70–1.40 (–**CH$_2$**–, **2–4** and **2′–4′**) and 3.5–1.5 (PEI core) (see Fig. 1).

Average molecular weights and thermal data of all the multiarm stars obtained are given in Table 1.

2.3. Preparation of epoxy thermosets

The mixtures were prepared by adding the required amount of PEI-PCLX to the epoxy resin and gently heating until it was dissolved and the solution became clear. Then, 5 phr of 1MI (part of initiator per hundred parts of mixture) were added and the resulting solution was stirred and cooled down to −10 °C to prevent polymerization. Mixtures containing 5–10 wt.% (by weight) of PEI-PCLX were prepared. The compositions of the formulations studied are detailed in Table 2.

2.4. Characterization

2.4.1. NMR spectroscopy
^{1}H NMR measurements were carried out at 400 MHz and in a Varian Gemini 400 spectrometer. CDCl$_3$ was used as the solvent. For internal calibration, the middle solvent signal corresponding to CDCl$_3$ was taken as $\delta(^1$H) = 7.26 ppm.

2.4.2. Size exclusion chromatography
Molecular weight and molecular weight distribution was determined by means of an Agilent 1200 series SEC-system with a combination of PL-GEL 3, PL-GEL 5 and PL-GEL 20 μm mixed A columns in series, equipped with an Agilent 1100 series Refractive Index detector. Calibration curves were based in polystyrene standards having low molecular weight dispersity using a flow rate of 1 mL/min and THF as eluent, the sample concentrations were between 5 and 10 mg/mL and injection volumes of 100 μL were used.

2.4.3. Differential Scanning Calorimetry
Calorimetric analyses were carried out on a Mettler DSC-822e thermal analyzer. Samples of approximately 10 mg were placed in aluminum pans under nitrogen atmosphere. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium-lead-zinc standard (temperature calibration).

Multiarm star polymers (PEI-PCLX) were heated from 25 to 120 °C with a heating rate of 20 °C/min, cooled down to −120 °C with a cooling rate of −10 °C/min and then heated again to 120 °C with a heating rate of 20 °C/min. Melting temperature (T_m), the heat of fusion (Δh_m) and the glass transition temperature (T_g) were obtained from the second heating curves. The degree of crystallinity (χ) was calculated as the quotient between the experimental heat of fusion and the theoretical heat of fusion of a perfect crystal of infinite size, obtained from additive group contributions [31] for poly(ε-caprolactone). Thermal data are collected in Table 1.

Non-isothermal curing of DGEBA/PEI-PCLX/1MI mixtures was performed from 30 to 300 °C at heating rate of 10 °C/min to determine the reaction heat associated with the complete conversion of all reactive groups.

The glass transition temperatures ($T_{g\infty}$s) of the completed cured materials were determined, by means of a second heating scan at 10 °C/min after dynamic curing at 20 °C/min, as the temperature of the half-way point of the jump in the heat capacity when the material changed from glassy to the rubbery state under N$_2$ atmosphere and the error is estimated to be approximately ±1 °C.

2.4.4. Thermogravimetry
Thermogravimetric analyses were carried out in a Mettler TG50 thermobalance. Samples with an approximate mass of 8 mg were