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Effect of hydroxyl ended and end-capped multiarm star polymers on the curing process and mechanical characteristics of epoxy/anhydride thermosets

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ABSTRACT

Multiarm star polymers have been synthesized by cationic ring-opening polymerization of ε-caprolactone from a hyperbranched poly(ethyleneimine) core and end-capped with acetic anhydride. These star polymers have been used as modifiers in diglycidylether of bisphenol A/methyl tetrahydrophthalic anhydride/benzyl dimethylamine formulations. The curing process is studied by dynamic scanning calorimetry and rheometry and the resulting thermosets are characterized by dynamic mechanical thermal analysis and thermogravimetry.

Internal stresses generated during curing are measured and interpreted in terms of the thermal-mechanical properties of the cured materials. The influence of the modifier in the toughness improvement of the cured thermosets is determined by standardized impact tests and the microstructure of the material observed by scanning electron microscopy.

1. Introduction

Epoxy resins are commonly used as thermosetting materials due their good thermomechanical, adhesive and electrical properties and ease of processing. Due to their good characteristics, epoxy-based thermosets are widely used in technological applications such as surface coatings, adhesives and assemblies for electronic devices [1–3]. Although rigidity and strength are desired properties in engineering applications, toughness is one of the restrictions in the use of epoxy resins. The low toughness, coming from the high crosslinking density, in addition to the internal stresses appearing during processing, affects the durability of coatings and places strong constraints on design parameters [4].

The first attempts to improve toughness were based on the addition of liquid rubbers or thermoplastics, but usually these additives compromise the modulus and thermomechanical characteristics of the thermosets and the processability of the formulation [5]. Toughness implies energy absorption and it is achieved through various deformation mechanisms before failure occurs. One of the most effective methods to prevent free crack propagation after impact is the addition of a modifier that leads to the formation of particles that absorb the impact energy and deflect the crack. It has been recognized that a combination of cavitation around the rubber or thermoplastic particles with shear yielding in the matrix produces a cooperative effect in the energy dissipation [6]. It has been described that the formation of micro- or nanostructures in epoxy thermosets improves the overall properties without reducing crosslinking degree of the epoxy matrix [7]. Chemically induced phase separation (CIPS) is one of the methodologies in which the morphology develops during curing from an initial homogenous mixture composed of the resin, curing agent and modifiers [8–10] to form a blend of epoxy matrix filled with rubber or thermoplastic microspheres, with a final size of these particles controlled by the viscosity of the reacting mixture during curing.

To overcome the limitations before mentioned for rubbers or linear thermoplastics used as toughers, the use of dendritic structures was proposed by several authors [11–14]. Recently, star-like topologies are used to enhance some characteristics of epoxy thermosets because of their unusual physical and rheological properties which allow the enhancement of some characteristics of epoxy

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thermosets [15–17]. Depending on the chemistry of the curing and the structure of the stars, homogeneous or nanostructured materials were obtained.

In coating applications the formation of internal stresses during curing usually leads to the appearance of defects that finally leads to the reduction of the protection capability. The mismatch between the thermal expansion coefficients of the coating and the substrate, along with the glass transition temperature (T_g) of the coating, are relevant parameters with a strong influence on the generation of internal stresses. In previous studies we reported that dendritic structures not only lead to a reduction of the shrinkage during curing which produces the apparition of internal stresses, but also to a reduction of the thermal expansion coefficients (*CTEs*) [11].

The aim of the present work is the preparation and characterization of new epoxy thermosets to overcome the above mentioned drawbacks, namely, the enhancement of toughness or the reduction of the internal stresses on curing while maintaining the thermomechanical characteristics of the thermosets and the easy processability of the formulation.

In recent publications, we reported the use of multiarm stars with poly(ethyleneimine) core and poly(ε-caprolactone) or poly(lactide) arms as modifiers in the curing of DGEBA using 1-methylimidazole (1-MI) as anionic curing agent [18,19]. The T_gs of the final materials were not greatly affected while toughness was slightly improved in spite of the different flexibility and length of the poly(ε-caprolactone) and poly(lactide) arms.

We reported a significant increase in impact strength up to 400% with respect to the neat formulation without sacrificing thermal and thermomechanical properties by the addition of partially modified Boltorn type polyesters with 10-undecenoyl moieties in DGEBA thermosets cured with anhydrides [20]. Efficient toughening was obtained because of the formation of well dispersed hyperbranched microparticles covalently attached to the thermosetting matrix by the unmodified hydroxyl groups of the HBP.

Taking all of these precedents into account, in the present work we compared the properties of epoxy thermosets cured with anhydrides in the presence of a tertiary amine as a catalyst on adding multiarm stars with polyethylene imine core and poly(ε-caprolactone) arms in different proportions and arms lengths. These stars, which have hydroxyl end-groups, have been end-capped with acetyl moieties to investigate the influence of unreactive multiarm stars on the possible phase separation during curing and on the mechanical and thermal characteristics of the prepared material, with a focus on toughness and internal stresses formation.

2. Experimental

2.1. Materials

The hydroxyl terminated star polymers (PEI-PCLX) were synthesized as previously described [19]. To perform the end-capping process by acetylation, extra pure acetic anhydride was used and purchased from Scharlau. Triethyl amine (TEA) and *N*,*N*-dimethylaminopyridine (DMAP) were purchased from Fluka. Chloroform ($CHCl_3$) was dried under $CaCl_2$ and distilled before used. Solvents were purchased from Scharlab. Diglycidylether of bisphenol A (DGEBA; Araldite GY 240, Huntsman) (182 g/eq) and methyl tetrahydrophthalic anhydride (MTHPA; Aradur HY 918,

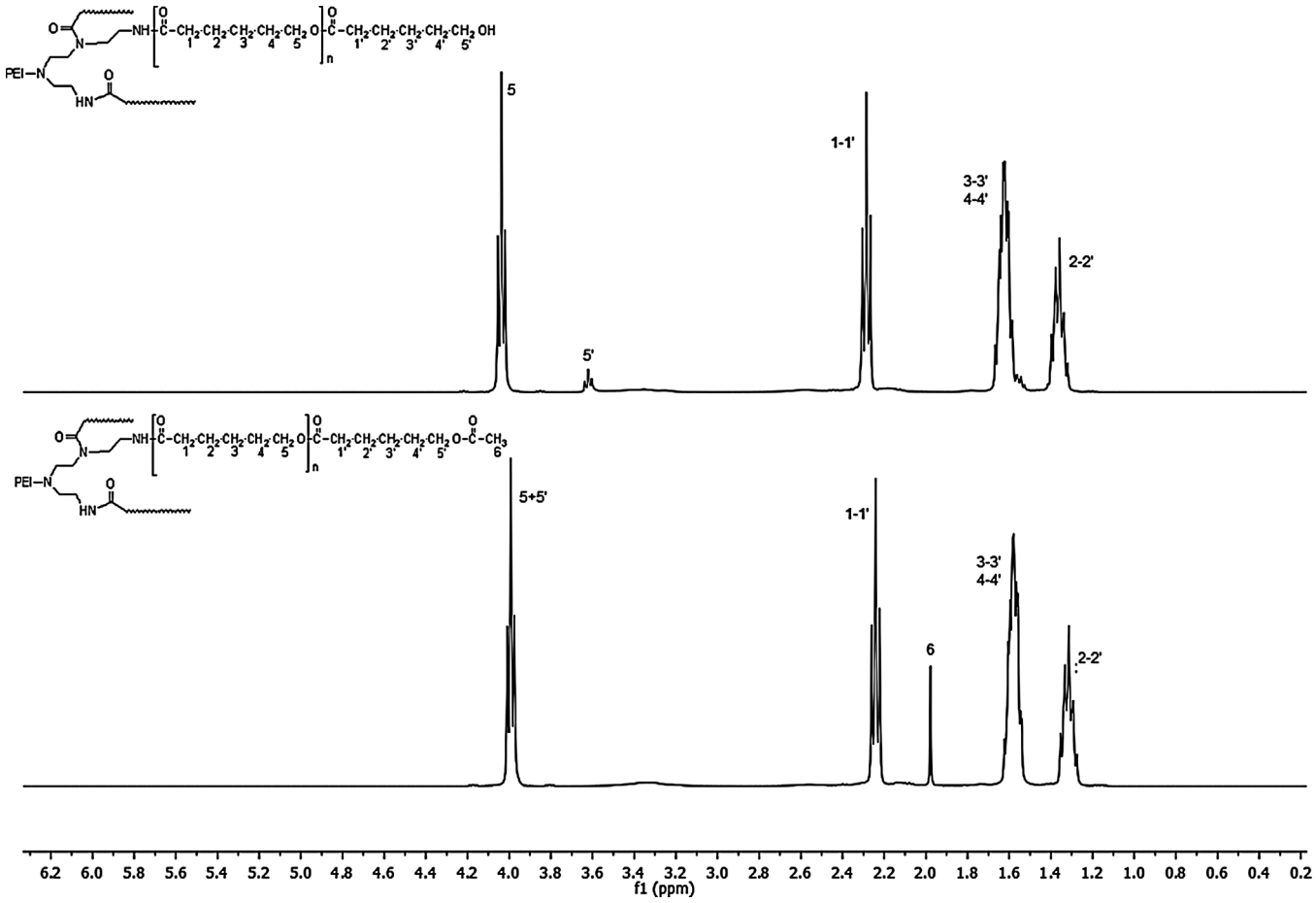

Fig. 1. ^{1}H NMR spectra of (A) PEI-PCL10 and (B) PEI-PCL10-B.