



New anhydride/epoxy thermosets based on diglycidyl ether of bisphenol A and 10-undecenoyl modified poly(ethyleneimine) with improved impact resistance

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ABSTRACT

New dendritic modifiers have been synthesized by amidation of hyperbranched poly(ethyleneimine) (PEIs) with 10-undecenoic acid to obtain hyperbranched polymers (HBPs) with different degree of modification. These HBPs have been used as toughness modifiers in a proportion of 10 and 20% in reference to the epoxy resin in diglycidyl ether of bisphenol A (DGEBA)/methyltetrahydrophthalic anhydride (MTHPA) formulations. The curing process has been studied by dynamic scanning calorimetry and by rheometry, which allow the kinetic constants and the gel and vitrification times to be evaluated. The materials obtained have been thermally characterized and their mechanical properties have been evaluated. An increase in impact resistance has been achieved and the T_g of all thermosets prepared was higher than 100 °C in spite of the flexible structure of the PEI modifiers.

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1. Introduction

Epoxy resins are ideal materials in the field of coatings, adhesives, molding compounds and polymer composites due to their excellent thermomechanical properties and chemical and environmental stability. They also present good processability before curing [1]. Their broad range of applications can be explained by the fact that they are probably one of the most versatile thermosets not only because the type of resin and the chemistry of the curing can be varied, but also a huge number of organic and inorganic modifiers and fillers can be added to improve their properties [2]. Although rigidity and strength are desired properties in engineering applications, toughness is one of the restrictions in the use of epoxy resins.

During the past decades considerable efforts have been made to improve the toughness of these materials. Toughness implies energy absorption and it is achieved through various deformation mechanisms before failure occurs. One of the most effective methods of preventing the crack from freely developing after impact

is the addition of a second phase that induces the formation of particles that absorb the impact energy and deflect the crack. A combination of cavitation around the rubber particles with shear yielding in the matrix produces a cooperative effect in the energy dissipation [3]. It has been reported that the formation of micro- or nanostructures in epoxy thermosets improves the overall properties without reducing crosslinking degree of the epoxy matrix and glass transition temperatures [4]. Chemically induced phase separation (CIPS) is one of the methodologies in which the morphology develops during curing. It starts from an initial homogenous mixture composed of the resin, curing agent and modifiers [5,6]. On curing, a blend of epoxy matrix filled with rubber or thermoplastic microspheres is formed, with a final size of these particles controlled by the viscosity of the reacting mixture during curing.

The first attempts to improve toughness were based on the addition of liquid rubbers or thermoplastics. However, these additives usually compromise the modulus and thermomechanical characteristics of the thermosets and the processability of the formulation [7]. Some years ago the use of hyperbranched polymers (HBPs) was proposed to overcome the limitations of traditional modifiers [8] and since then a significant number of research groups have adopted this strategy [9–12]. The dendritic structure of HBPs makes these modifiers very promising in terms of processability because

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of the low entanglement that leads to low viscosities in comparison to rubbers or linear polymers [13]. By partial or total modification of their reactive terminal groups, it is possible to tune their interaction or covalent linkage with the epoxy matrix. This can lead to phase separated or homogenous morphologies.

In previous papers we demonstrated that the addition of HBPs to a curing system improves mechanical properties [14–16]. In these cases, the chemical incorporation of hydroxyl ended HBPs to the epoxy matrix led to materials with homogenous appearances without any phase separation.

We reported the use of partially modified Boltorn type polyesters with 10-undecenoyl moieties in DGEBA thermosets cured with anhydrides, resulting in a significant increase in impact strength, up to 400% with respect to the neat formulation, without sacrificing thermal and mechanical properties [17]. Efficient toughening was obtained because of the CIPS process leading to well dispersed hyperbranched particles covalently attached to the thermosetting matrix by the unmodified hydroxyl groups of the HBP. Following the same approach, we synthesized end-capped multiarm star polymers as modifiers in the curing of DGEBA with anhydride and a significant increase in impact strength was also achieved, attributed to the nanophase separation observed [18].

In the present work, we propose the use of a series of partially modified poly(ethyleneimine) (PEI) with 10-undecenoyl chains as modifier of DGEBA thermosets cured with anhydride in the presence of a tertiary amine as a catalyst. Our interest is to investigate the influence of the degree of modification of the PEI structure with 10-undecenoyl groups and the proportion of this modifier in the formulation on the curing evolution and on the mechanical and thermal characteristics of the materials obtained, emphasizing toughness improvement.

2. Experimental

2.1. Materials

Poly(ethyleneimine) (PEI) (Lupasol®FG, 800 g/mol, BASF) was used after drying under vacuum. 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 (NH₂/NH/N) was (1/0.82/0.53) and thus by calculations the equivalent number of primary, secondary and tertiary amines resulted to be 0.010, 0.00837, and 0.0053 equiv./g. 10-Undecenoic acid was purchased from Fluka and 1,1-carbonyldiimidazole (CDI) was purchased from Sigma–Aldrich. Chloroform (CHCl₃) was dried under CaCl₂ and distilled before used. Diglycidyl ether of bisphenol A (DGEBA, Araldite GY 240, Huntsman, 182 g/equiv.) and methyl tetrahydrophthalic anhydride (MTHPA, Aradur HY 918, Huntsman) (166 g/mol) were used as received. Benzyl dimethylamine (BDMA, DY 062, Huntsman) was used as catalyst.

2.2. Amidation of hyperbranched polyethylenimines

The amidation of PEIs was performed according to a reported procedure [19,20]. The modified PEIs were achieved by reaction of the PEI with different ratio of 10-undecenoic acid and the degree of modification was calculated by means of ¹H NMR spectroscopy. The synthesis of amidated PEIs was exemplified for the polymer PEI₉₁: 8.49 g (52 mmol) of CDI were slowly added to a solution of 9.66 g (52 mmol) of 10-undecenoic acid in 40 mL of chloroform. The solution was stirred at room temperature for 1 h, and then 3 g (3.75 mmol) of PEI in 10 mL of chloroform were added. The mixture was stirred at room temperature for 4 h, and then at 50 °C overnight. After cooling down, the mixture was washed several times with NaCl aqueous solution. The organic phase was dried by anhydrous

Table 1

Characteristics of the modified HBPs synthesized.

Notation	DA (%) ^a	M _n ^b (g/mol)	T _g ^c (°C)	T _{5%} ^d (°C)
PEI ₉₁	91	2925	–56	204
PEI ₇₈	78	2626	–49	196

^a Degree of amidation calculated by ¹H NMR.

^b Determined by ¹H NMR spectroscopy.

^c Determined by DSC.

^d Temperature of 5% of weight loss determined by TGA under N₂ atmosphere.

MgSO₄ and after filtration and removal of the volatiles, the residue was kept at 40 °C in vacuum oven overnight and a honey-like polymer was obtained. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 1.20–1.36 (–CH₂–, **4–8**), 1.59 (–CH₂–CH₂–CO–, **3**), 2.04 (–CH₂–CH=CH₂, **9**), 2.15 (–CH₂–CO–NH–, **2**), 4.77 (–NH–, **1**), 4.95 (CH₂=CH–, **11**), 5.80 (CH₂=CH–, **10**) and 3.46–2.55 (PEI core) (Fig. 1).

Average molecular weights and thermal data of all the modified HBPs obtained are collected in Table 1.

2.3. Preparation of mixtures

Neat formulations were prepared by mixing the DGEBA with the stoichiometric amount of MTHPA. Then, the selected proportion of BDMA was added and the mixture was homogenized by mechanical stirring. The formulations containing 10–20 wt% of PEIs (by weight of DGEBA) were prepared by first adding the required amount of PEIs to the epoxy resin and gently heating until they were dissolved and subsequently mixing with MTHPA and BDMA by mechanical stirring. For all the formulations, the quantity of MTHPA was calculated taking into account that 1 mol of anhydride reacts with 1 mol of epoxide group and the amount of BDMA was always 1 phr (1 part per hundred) with respect to the anhydride. The samples were kept at –20 °C before use to prevent polymerization. Table 2 collects the composition of the formulations studied.

2.4. Characterization

2.4.1. NMR characterization

¹H NMR measurements were carried out at 400 MHz and in a Varian Gemini 400 spectrometer. CDCl₃ was used as the solvent. For internal calibration, the middle solvent signal corresponding to CDCl₃ was taken as δ (¹H) = 7.26 ppm.

2.4.2. Differential scanning calorimetry (DSC)

Calorimetric analyses were carried out on Mettler DSC 822e and Mettler DSC 821e calorimeter with a TSO01RO robotic arm. The kinetic studies were performed at heating rates of 2, 5, 7.5, 10 °C/min to determine the kinetic parameters and the reaction heat. The glass transition temperatures (T_g) of the HBPs were determined from a dynamic scan from –100 °C to 200 °C at 10 °C/min. The glass transition temperatures of the completely cured materials (T_g[∞]) were determined by means of a heating scan at 10 °C/min, after isothermal curing process performed during 3 h at 100 °C and 1 h at 150 °C.

Table 2

Composition of DGEBA/MTHPA/BDMA formulations with different percentages of modifiers.

Formulation	Modifiers, wt (g)	DGEBA, wt (g)	MTHPA, wt (g)	BDMA, wt (g)
Neat	–	1	0.912	0.00912
10% PEI ₉₁	0.1	1	0.912	0.00912
20% PEI ₉₁	0.2	1	0.912	0.00912
10% PEI ₇₈	0.1	1	0.912	0.00912
20% PEI ₇₈	0.2	1	0.912	0.00912

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