New aromatic–aliphatic hyperbranched polyesters with vinylic end groups of different length as modifiers of epoxy/anhydride thermosets

Adrian Tomuta [a], Francesc Ferrando [b], Àngels Serra [a], Xavier Ramis [c],*

[a] Department of Analytical and Organic Chemistry, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain
[b] Department of Mechanical Engineering, Universitat Rovira i Virgili, Països Catalans 26, 43007 Tarragona, Spain
[c] Laboratory of Thermodynamics, ETSEIB, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Spain

ABSTRACT

The synthesis and characterization of two new aromatic–aliphatic hyperbranched polyesters modified with long and short vinylic chains was reported. These hyperbranched polymers were used as toughening modifiers of epoxy/anhydride thermosets. The curing of mixtures of diglycidyl ether of bisphenol A and hexahydro-4-methylphtalic anhydride with different proportions of both hyperbranched polymers using *N,N*-benzyldimethylamine as catalyst was investigated by differential scanning calorimetry. The kinetic of curing process was established using an isoconversional integral procedure. The characterization of these materials was done by means of several thermal analysis techniques and their morphology was investigated by electron microscopy. The addition of highly branched structures led to homogeneous morphologies and a more toughening fracture of the thermosets in comparison to the neat epoxy/anhydride material. The modified thermosets presented slightly lower glass transition temperature than the unmodified one and the thermal stability barely changed by the addition of the modifiers.

1. Introduction

Epoxy thermosets present good overall properties, although they also present some drawbacks. In terms of structural applications, epoxy systems are in general rigid and brittle. While rigidity and strength are desired, brittleness reduces their applicability. As a result, considerable efforts have been made on improving the toughness of the materials during the past decades and many reviews in this area are available [1,2].

There are many approaches to improve toughness in epoxy resins. One of the most classical is based on increasing the flexibility of the final network by decreasing the crosslinking density or the rigidity of the epoxy backbone. This procedure leads to thermosets with low glass transition temperature, Youngs's modulus and thermal stability. However, the most successful route towards toughness improvement is the incorporation of a dispersed second phase that absorbs energy. Among the second phases used stand out rubbers, thermoplastics and hard inclusions such as silica, glass and beads [3–5].

In the last years hyperbranched polymers (HBPs) and more recently other dendritic highly branched polymeric structures with a large number of chain ends have demonstrated to be very interesting epoxy tougheners [6]. They have been found to give enhanced flexibilities and increased toughness to thermosets without affecting other properties, such as hardness, modulus and glass transition temperature [7]. Improved toughness is due to local inhomogeneities in the crosslinked network caused by the chemical or physical incorporation of HBP molecules into the matrix or to the formation of phase separated nanoparticles with good interfacial adhesion between the separated phases [8]. It has also been described that toughness improvement can be reached through an *in situ* homogeneous reinforcing and toughening mechanism. The compatibilization between the modifier and the matrix through different physical or chemical interactions may be the responsible of this mechanism [9].

In previous works, we studied the curing of different mixtures of epoxy matrices and HBP or star polymers [10,11]. The composition of the mixtures, the curing conditions, the curing agent used and the structure and chemical composition of the dendritic polymers (molecular weight, degree of branching, amount and type of terminal groups, length of the arms) are the parameters that control the structure of the network formed, the curing evolution and the final properties. In terms of improvement of toughness we achieved the best results when the modifier was initially miscible in the precursor and phase-separated during curing [12]. Phase-separated materials were obtained with unreactive modifier or when the modifier had only a small amount of residual reactive groups that enhanced the compatibility between the phases by the formation of an interphase [13]. Although to a lesser extent, we

* Corresponding author. Tel.: +34 934016592; fax: +34 934017389.
E-mail address: ramis@mmt.upc.edu (X. Ramis).

obtained improvements in toughness with systems that did not phase separate because of a high physical compatibility between the modifier and the matrix or because the modifier was chemically incorporated into the network structure [10,11,14,15].

The thermal stability and the glass transition temperature of the epoxy thermosets was not compromised by the addition of aliphatic–aromatic hyperbranched polyester hydroxyl terminated as reactive modifier, when Yb(OTf)$_3$ was selected as cationic initiator [16]. Although morphology was not studied in this work, it was expected that the materials were homogeneous without phase-separation due to the presence of hydroxyl chain-ends in the HBP that allows the modifier to be covalently linked to the epoxy matrix. In another study, commercial Boltorn H30 was esterified with long aliphatic chains having vinyl or epoxy terminal groups and used as toughness modifier of epoxy thermosets with the same curing system [13]. Whereas epoxy terminated HBP reached a completely miscible and homogeneous network, vinyl terminated HBP showed a limited solubility in the epoxy matrix and phase separated during curing. Taking into account these previous results, the aim of the present work is the synthesis of two new dendritic structures that combine the characteristics of the previously described HBPs. The novel HBPs are formed by an aliphatic–aromatic hyperbranched polyester core and a shell with aliphatic chains of different lengths (the longest, 10-undecenoyl moieties and the shortest, allyl groups). It should be noticed that the modification with allyl groups is quite easy because allyl bromide experiments nucleophylic attack by phenolate groups of the HBP, formed in a weak basic medium. The acylation with 10-undecenoyl chloride follows a typical acylation procedure, and also takes place with a high yield. The modification of the HBP with aliphatic chains of different length can influence the final morphology and mechanical characteristics of the HBP.

Another purpose of this study is to show the effect of these novels HBPs on the curing of epoxy/anhydride systems, the kinetics of the curing process, the dynamomechanical properties, the impact behavior and the morphology of the resulting materials.
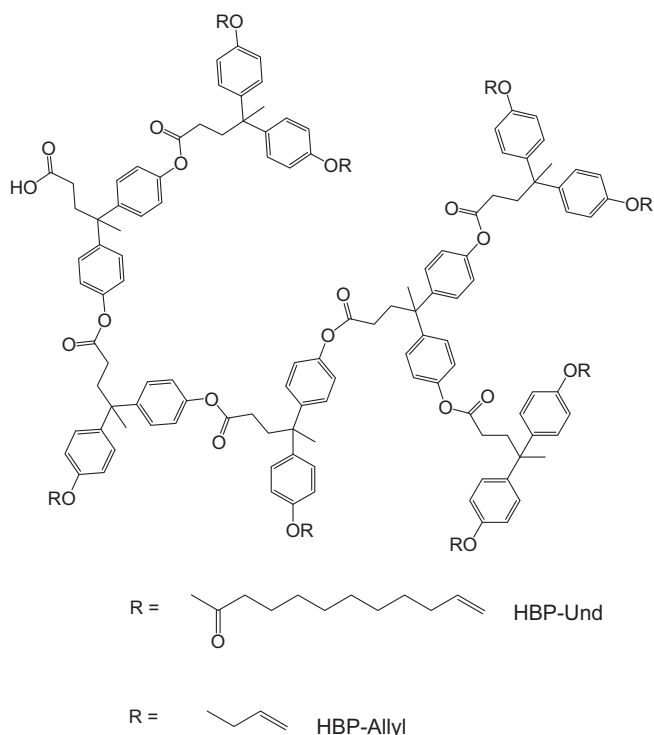
Scheme 1 depicts the structure of the HBPs used as modifiers (HBP-Allyl and HBP-Und, with allyl and undecenoyl chains respectively).

2. Experimental

2.1. Materials

4,4-bis(4-hydroxyphenyl) valeric acid, N,N′-dicyclohexylcarbodiimide (DCC), triethyl amine, allyl bromide, 10-undecenoyl chloride, hexahydro-4-methylphtalic anhydride (MHHPA) and N,N-dimethylbenzylamine (BDMA) were purchased from Aldrich and used without further purification. Diglycidyl ether of bisphenol A (DGEBA) Epikote Resin 828 was provided by Shell Chemicals with an epoxy equivalent of 184 g/eq and was dried in vacuum before use. Methanol, N,N-dimethylformamide (DMF) and tetrahydrofurane (THF) were purchased from Scharlab and purified by standard procedures. 4-(N,N-dimethylamino) pyridinium p-toluenesulfonate (DPTS) was prepared as described in the literature [17].

2.2. Hyperbranched polyester synthesis (HBP-OH)

The HBP-OH was synthesized according to a previously described procedure [18]. In a 500 ml two-necked round-bottomed flask, 50 g (1 eq) of 4,4-bis(4-hydroxyphenyl) valeric acid and 7.64 g (0.2 eq) of DPTS were dissolved in 200 mL of anhydrous DMF. Then, 43.24 g (1.2 eq) of DCC were added in portions and the mixture was kept under argon atmosphere for 24 h at room temperature. Then, the precipitate was filtered off and the solution was poured in methanol (1200 mL) to obtain a white powder after drying in a vacuum oven overnight at 60 °C. Yield 37 g (conversion: 80%).

The ^{1}H and ^{13}C NMR data are in accordance with those published [19].

Mn: 8700 g/mol, Mw: 12300 g/mol. Tg 121 °C (by DSC).

The amount of hydroxyl groups was determined according to ISO 2554-1997 standard.

An acetylating solution was prepared by dissolving 11.8 mL of acetic anhydride in 100 mL of pyridine. About 0.4–0.6 g of the polymer sample was dissolved in 5 mL of the acetylating solution. The mixture was stirred for 20 min at 130 °C.

Thereafter, at the same temperature, 8 mL of water was added in order to hydrolyze the excess acetic anhydride. Finally, the solution was titrated with 1 N ethanolic KOH solution to determine the equivalence point. An analogous "blank experiment" was performed without the polymer sample with exactly the same amount of the acetylating mixture. The hydroxyl number (HN) was calculated from the results of both titrations using the formula:

$$HN = \frac{(V_0 - V_1) \cdot C \cdot M_{KOH}}{m} + AN \qquad (1)$$

where V_0 and V_1 are the equivalence titration volume of KOH in mL from the blank experiment and from the sample titration, respectively, C is the concentration of KOH in eq/L, M_{KOH} is the molecular weight of KOH in g/mol, m is the mass of polymer sample in grams and AN is the acid number, which has not been taken into account in this case because it is very low. The number of hydroxyl groups per molecule found by titration was 36.

2.3. HBP-Undecenoyl synthesis (HBP-Und)

In a 500 mL three-necked round bottomed flask 10 g (0.04 mol of hydroxyl groups) of HBP-OH were placed and dissolved in 200 mL of THF and 15 mL (0.08 mol) of triethylamine were added. Under gentle magnetic stirring, 12 mL (0.06 mol) of 10-undecenoyl

R = [structure] HBP-Und

R = [structure] HBP-Allyl

Scheme 1. Chemical structure of HBP-Und and HBP-Allyl.