

New pegylated hyperbranched polyester as chemical modifier of epoxy resins in UV cationic photocuring

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ABSTRACT

A new hyperbranched polymer (HBPpeg) has been obtained via pegylation of an aromatic hyperbranched polyester. This polymer has been used as modifier of a commercially available cycloaliphatic epoxy resin in its cationic UV photocuring, using arylsulfonium salts as photoinitiator. The addition of the HBP slows down the curing as well as reduces the overall conversion achieved at room temperature, due to its interaction with the photoinitiator, but fully cured materials were achieved for formulations containing up to 10 phr of the HBP. The amphiphilic structure of the HBPpeg allows it to phase-separate in the epoxy matrix, which was confirmed by means of FESEM. The thermomechanical characteristics and the thermal stability have been also studied.

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1. Introduction

Epoxy resins are one of the most widely used thermosets in technological applications such as coatings, adhesives, structural applications or electronics due to their mechanical properties, relatively low shrinkage and high chemical and thermal resistance [1]. Moreover, they possess high versatility thanks to the many initiators and hardeners available for their curing. However, one of the main drawbacks that they present is the inherent brittleness. This is caused by the high crosslinking density achieved and it is even more pronounced in cationic systems because of the rigidity of the network and the short distance between crosslinks. There are many approaches in the literature to enhance the toughness of epoxy resins involving the modification of these systems with polymers such as thermoplastics, block-copolymers, liquid rubber or core-shell particles [2–6]. The initially miscible mixture of the epoxy/hardener system with the modifiers becomes immiscible as reaction proceeds due to a growing incompatibility between the developing network and the added polymer, which can phase-separate. This leads to a highly cross-linked and rigid matrix with dispersed polymer particles inside, which are responsible for the toughness enhancement [7].

Hyperbranched polymers (HBP) belong to a group of macromolecules called dendritic polymers, which have peculiar and often unique properties [8]. They possess a highly branched backbone,

which gives access to a large number of reactive groups; their structure gives them excellent flow and processing properties, and they are characterized by lower viscosity than those of linear polymers of comparable molecular weight. This type of polymers has been successfully used as toughening agents that phase-separate during curing [9–13].

The UV-polymerization of multifunctional monomers is one of the more efficient methods available to generate three-dimensional polymeric networks [14]. Among the advantages of this technology the high cure speed, the reduced energy consumption, and absence of VOC emissions are the most remarkable. It is well known that the UV curing can be performed either by a radical or a cationic mechanism. The cationic photoinduced process presents some advantages compared to the radical one [14], in particular lack of inhibition by oxygen, lower shrinkage, good mechanical properties of the UV cured materials, and good adhesion properties to various substrates.

Previously we reported the use of the unmodified polyester HBP in the thermal [15] and UV curing [16] of epoxy resins leading in both cases to homogeneous materials. In the present work, we have studied the effect of adding a hyperbranched polymer that we firstly synthesized, on the photocuring of a commercially available cycloaliphatic resin and on the characteristics of the corresponding thermosets. The new hyperbranched polymer that we synthesized contains a main structure of aromatic polyester with phenol chain ends, which were modified with a linear polyethylene glycol in order to get an amphiphilic structure that can undergo supramolecular assembly during curing, leading to phase-separated thermosets.

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2. Experimental part

2.1. Materials

4,4'-Bis(4-hydroxyphenyl)valeric acid, N,N'-dicyclohexylcarbodiimide (DCC), methanol, anhydrous N,N-dimethylformamide (DMF), monomethyl poly(ethylene glycol) (Mn = 550 g/mol), succinic anhydride and pyridine were purchased from Aldrich or Fluka and used without further purification. 4-(N,N-dimethylamino)pyridinium p-toluenesulfonate (DPTS) was prepared as described in the literature [17].

The bis-cycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexyl carboxylate (CE, Huntsman) and triphenylsulfonium hexafluoroantimonate (PI, Ph₃S⁺SbF₆⁻, Aldrich) (Scheme 1) were used as received.

2.2. Synthesis of the hyperbranched polyester (HBPE)

HBPE was synthesized according to a previously described procedure [18]. In a 500 ml two-necked round-bottom 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 anhydrous DMF (200 ml). 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: 80%).

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

Mn: 10,000 g/mol; Mw: 29,000 g/mol; PDI: 2.9.

DB_{frej} [20] = 0.50.

Tg = 105 °C.

2.3. Synthesis of the acid terminated monomethyl poly(ethylene glycol)

In a 100 ml two-necked round-bottom flask 10 g (1 eq) of monomethyl poly(ethylene glycol) (CH₃OPEG—OH) were dissolved in 150 ml of chloroform. Then, 9 ml of pyridine were added and

finally, 9 g (5 eq) 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. After that, the solution was cooled down to room temperature and the solvent eliminated under vacuum. The crude product was dissolved in 15 ml of 1 N HCl, washed with ether and then extracted with chloroform. The solvent was removed under vacuum (Yield: 99%).

¹H NMR (CDCl₃): δ (in ppm) 4.20 (terminal PEG CH₂); 3.60–3.70 (OCH₂CH₂); 3.30 (OCH₃); 2.50–2.60 (CH₂ succinic).

¹³C NMR (CDCl₃): δ (in ppm) 175.5 (COOH); 172.2 (COOCH₂); 71.9, 70.6, 69.0 (OCH₂CH₂); 63.9 (terminal PEG CH₂); 59.1 (OCH₃); 29.2, 28.8 (CH₂ succinic).

2.4. Synthesis of the hyperbranched polyester with terminal poly(ethylene glycol) chains (HBPpeg) (Scheme 1)

In a 250 ml round bottom two necked flask provided with a magnetic bar and Ar inlet 3 g (1 eq) of HBP, 0.72 g (0.2 eq) of dimethylaminopyridinium p-toluenesulfonate (DPTS) and 6.9 g (1 eq) of CH₃OPEG—COOH were dissolved in 100 ml of DMF. Then 2.82 g (1.2 eq) of dicyclohexylcarbodiimide (DCC) were added and the mixture allowed to react at room temperature for 48 h. Then the precipitated was filtered off, the volume of DMF reduced to 20 ml and the crude product dialyzed against the same solvent (Yield 80%).

¹H NMR (CDCl₃): δ (in ppm) 1.50–1.65 (CH₃); 2.33 (CH₂); 2.50–2.60 (CH₂COO); 3.30 (OCH₃); 3.60–3.70 (OCH₂CH₂); 4.20 (terminal PEG CH₂); 6.90–7.15 (aromatics).

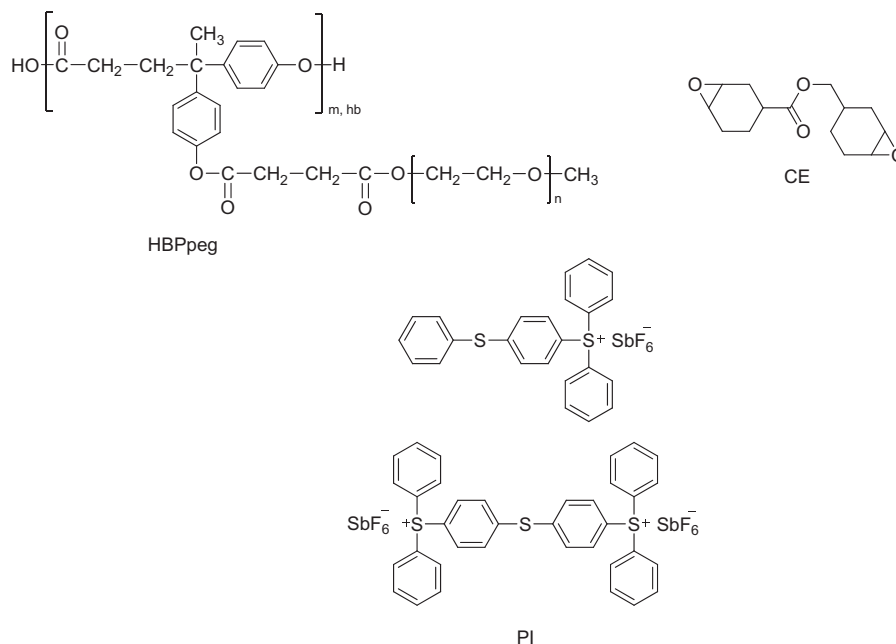
¹³C NMR (CDCl₃): δ (in ppm) 172.5, 172.0, 171.0 (COO—CH₂); 148.7, 128.4, 121.2 (aromatics); 71.9, 70.5, 69.0 (OCH₂CH₂); 63.9 (terminal PEG CH₂); 59.0 (OCH₃); 45.2 (C); 36.2 (CH₂); 30.3 (CH₂); 29.2, 29.1 (CH₂ succinic); 27.8 (CH₃).

Mn: 24,000 g/mol; Mw: 47,000 g/mol; PDI: 2.0.

Tg = -38 °C and 95 °C.

2.5. Film preparation

To photocurable formulations containing the appropriate amount of HBPpeg (0, 5, 10 and 15 per hundred resin, phr) in the



Scheme 1. Components of the curing mixture.

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