Polymer 53 (2012) 5864–5872

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Hyperbranched polyester as additives in filled and unfilled epoxy-novolac systems

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A R T I C L E I N F O

Article history:
Received 12 June 2012
Received in revised form
13 September 2012
Accepted 13 October 2012
Available online 22 October 2012

Keywords:
Hyperbranched polyester
Epoxy resin
Curing shrinkage

A B S T R A C T

The synthesis and characterization of a new type of hyperbranched polyester with a flexible ethoxylated Bisphenol-A structure and terminal hydroxyl groups is reported. The influence of the hyperbranched polyester on the curing and thermomechanical properties of both unfilled and silica filled epoxy-novolac systems was studied. The curing behavior was investigated by differential scanning calorimetry (DSC) and rheolometry. The addition of the hyperbranched polyester to the formulation reduced the contraction on curing of both unfilled and filled systems, while Tg of the cured samples dropped down with the increase of polyester content due to the flexible backbone structure of the modifier. SEM microscopy on the fractured surface of cured samples revealed a homogeneous morphology and a possible effect of polyester as a toughness enhancer.

1. Introduction

Epoxy resins are one of the oldest and most developed high temperature thermosets with applications in various industrial fields. With increasing focus on miniaturized designs and high performance of semiconductor electronic devices higher toughness and lower internal stress are required. Similar requirements are necessary for epoxy encapsulation materials for microelectronic packaging and epoxy composites for printed circuit boards (PCBs) [1,2]. The shrinkage during epoxy curing is one of the major sources of generation of internal stress or micro-cracks [3], which can result in a loss of mechanical properties, voids and wrapping, thus decreasing the protective capacity of the encapsulation materials [4–6].

Addition of inorganic fillers and modification with rubbers are the two major routes to reduce internal stresses [7–10] through diminishing either the cure shrinkage or flexural modulus. The chemical shrinkage decreases proportionally with the proportion of filler [7], while the flexural modulus is effectively lowered by the incorporation of a rubber in a “sea-island” two-phase structure [9].

Recently, as a new class of reactive rubbers, hyperbranched polymers (HBPs) have been applied as reliable modifiers for epoxy resins [11–19] to increase the toughness and processing ability. Foix et al. [20] synthesized epoxy-functionalized HBP and used it as toughening additive in DGEBA UV-curing formulations. The result showed an increase of the impact resistance by increasing the amount of HBP in the photocurable formulations. When the content of HBP reached 30 wt%, the impact strength increased nearly 100% compared to the neat resin. It has also been found in our previous works that the addition of HBPs could reduce the curing shrinkage when the HBPs become covalently incorporated into the epoxy network structure [21,22].

HBPs have lower prepolymer viscosity compared with their linear counterparts due to the branched structure preventing chain entanglements, while the high density of surface functional groups can provide strong adhesion to the epoxy matrix [23]. On these bases, HBPs have been applied as interfacial modifiers for nanoparticles due to their grafting capability and the simultaneous functionality of the particle surface [24,25]. Zou et al. [26] compared the properties of hyperbranched polyesters (Boltorn H20) with linear oligomers for preparing organic–inorganic hybrids, and the results showed that the hyperbranched polyester had much better compatibility with inorganic phase even at high inorganic component content due to its special spherical shape and of the high number of functional end groups. Rodlert et al. [27] obtained mainly exfoliated nanocomposites by simple physical blending of layered silica montmorillonite with hydroxyl terminated polyester type HBPs in water. Moreover, Ratna et al. [28] modified epoxy resin with the combination of HBP and layered silica montmorillonite, and the nanocomposites obtained showed improved toughness and retained modulus.

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0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2012.10.028

In the previous works related to HBPs modified epoxy systems, the epoxy precursors used are mainly DGEBA type, however, for microelectronic packaging *o*-Cresol novolac epoxy resin (ECN) is typically employed because of its well-balanced properties including low cure shrinkage, superior electrical properties, good adhesion to many substrates, excellent thermal and chemical resistance and low hydrophilicity. Nevertheless, this multifunctional epoxy resin still needs to be modified to improve mechanical properties, and to be filled with inorganic fillers to reduce thermal expansion coefficient, but till now, to our knowledge, no studies have been focused on HBPs modified ECN systems with fillers for microelectronic packaging.

In the present work, a novel hyperbranched polyester has been prepared by one pot polymerization of ethoxylated Bisphenol-A (A_2 type monomer) and trimesic acid (B_3 monomer) in the melt at 210 °C. This new HBP has a flexible ethoxylated Bisphenol-A structure and hydroxyl groups at the chain ends and has been used to modify filled and unfilled ECN systems cured with phenolic resin using imidazole as the accelerator (see Scheme 1). The curing process was monitored by DSC and rheometer, and the cured materials were characterized by thermal analysis, densitometry measurements and mechanical tests.

2. Experimental

2.1. Materials and sample preparation

o-Cresol novolac epoxy resin (ECN) DEN 438 was provided by Dow Chemical Co., with an epoxide equivalent of 176–181 g/eq. Phenol novolac resin (NOV) H-1 was provided by Sumitomo Co. (Japan) with a hydroxyl equivalent of 105–107 g/eq. The accelerator, 2-phenyl-4-methyl-5-hydroxymethylimidazole (2P4MHZ) was provided by Shikoku Chemicals Co. (Japan) and fused silica (Lianyungang Donghai Silica Powder Co, China) with a mean diameter of 23 μm was used as filler. Ethoxylated Bisphenol-A (Atlas G 1652, Uniqema, USA) with an average mole ratio of ethylene oxide to Bisphenol-A of 2.2, trimesic acid (Aladdin Reagent, China), and stannous octanoate (Aladdin Reagent, China) were used without further purification.

2.1.1. Synthesis of hyperbranched polyester (Scheme 2)

The synthesis of the hyperbranched polyester was done in the melt as follows: trimesic acid (4.2 g, 0.02 mol), ethoxylated Bisphenol-A (13.0 g, 0.04 mol) and a catalytic amount of stannous octanoate (0.02 g, 0.05 mmol) were introduced into a two-neck flask equipped with a thermometer, a gas inlet to fill the flask with nitrogen and magnetic stirring. The reaction mixture was gradually heated in an oil bath up to 210 °C and reacted for 8 h under nitrogen at this temperature. Then, to drive the reaction to higher conversion, vacuum was applied for a further 2 h maintaining a vigorous stirring. The product was dissolved in THF and precipitated from water, collected, and dried in vacuum. Yield: 78%. ^1H NMR ($CDCl_3$): δ in ppm. 8.87 (s, aromatic protons from trimesic acid ester), 7.1 and 6.82 (broad signals aromatic protons from Bisphenol-A), 4.57–4.78, 4.16–4.35, 3.98–4.14, 3.79–3.96, 3.69–3.78, 3.44–3.52 ($-OCH_2CH_2O-$), 2.06–3.02 (br, OH), 1.59 (s, $Ar-C(CH_3)_2-Ar-$). ^{13}C NMR ($CDCl_3$): δ in ppm 164.5 (C=O), 156 ($Ar(C)-O$), 143 ($Ar(C)-C(CH_3)_2$), 131, 134 (trimesic acid ester), 114, 128 (aromatic carbons of Bisphenol-A), 77, 69, 68, 66, 64, 61 (OCH_2CH_2-O), 41 ($-C(CH_3)_2$), 30.9 ($-C(CH_3)_2-$). FTIR-ATR: 3490 cm^{-1} (OH, broad), 1730 (C=O) cm^{-1}; Mw: 2.8×10^3 g mol^{-1}, Mn: 1.9×10^3 g mol^{-1} and a polydispersity of 1.5. Hydroxyl index: 110 mg KOH/g.

2.1.2. Preparation of mixtures of HBP modified epoxy resins

The samples used in this study were composed of constant stoichiometric ratio (1:1) of ECN epoxy resin and NOV hardener, 5–20 wt% (by weight) HBPs, 0–40 wt% of silica fillers, and 0.5 wt% accelerator 2P4MHZ. The blends without accelerator were heated at 140 °C with stirring until a well dispersed mixture was obtained, and then 2P4MHZ was added. The resulting mixture was stirred and cooled down to −10 °C to prevent polymerization. The composition of the formulations studied is detailed in Table 1. To make the formulations comparable between filled and unfilled systems, the weight ratios of HBP to epoxy resin were kept equal for filled and unfilled HBP modified systems. For example, 10% HBP–20% Si represents that the amount of HBP to the resin matrix is 10 wt% while the silica content in the filled material is 20 wt%.

2.2. Characterization techniques

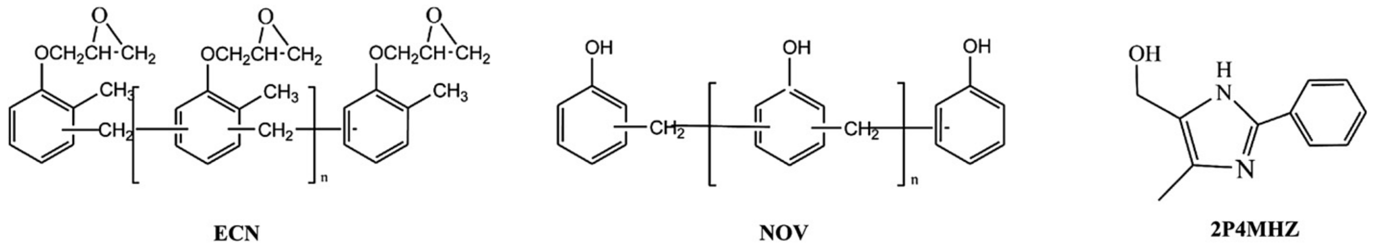
^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer with $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard.

The molecular weights and molecular weight dispersities of the samples were measured with a Perkin–Elmer S-250 gel permeation chromatograph (GPC) equipped with a Perkin–Elmer LC-235 UV detector set at 245 nm, an LC-30 RI refractive index detector, and using three Waters Styragel columns (HR 2, HR 4, and HR 5E), being the molecular weight detection range: 500–20,000, 5000–500,000 and 2000–4,000,000, respectively.

Infrared spectroscopy experiments were performed using a Thermo Nicolet Nexus 440 Spectrometer with a resolution of 4 cm^{-1}. The amount of hydroxyl groups was determined according to ISO 2554-1974.

The curing evolution was studied in a Perkin–Elmer Pyris 1 DSC instrument. The isothermal curing conversion was calculated from the residual heat of the exotherms observed in scans in the temperature range of 50–350 °C, with heating rates of 10 °C/min and normalized by the total heat of the exotherms corresponding to the complete curing obtained by dynamic experiments.

The melt viscosity variations of the blends during the curing reaction were recorded in an ARES-9A rheometer. About 1 g of the blend was sandwiched between two round plates with a diameter of 40 mm and softened at 80 °C for 2 min. The gap between plates was then adjusted to 1.0 mm and the temperature was raised



Scheme 1. Chemical structures of epoxy resin, hardener and accelerator.