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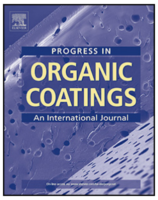

Non-reactive and reactive block copolymers for toughening of UV-cured epoxy coating

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ABSTRACT

Reactive and non-reactive diblock copolymers based on polyethylene oxide (PEO) and a poly(glycidyl methacrylate) (PGMA, reactive) or polystyrene (non-reactive) block, respectively, are prepared via ATRP and those are incorporated into a cycloaliphatic epoxy matrix. Crosslinking of the matrix is then performed by cationic UV curing, producing modified thermosets. ^{1}H NMR and SEC measurements are carried out and used to analyze the composition, the molar mass and dispersity of the prepared block copolymers. The viscoelastic properties and morphology of the modified epoxy are determined using DMTA and FESEM, respectively. The addition of 4 and 8 wt% of the reactive PEO-b-PGMA block copolymer into epoxy resin has only minor effects on the glass transition temperature, T_g. The reactive homopolymer PGMA significantly increases and the non-reactive block copolymer PEO-b-PS slightly decreases the glass transition temperature of the epoxy matrix. The non-reactive block copolymer PEO-b-PS causes a little decrease in T_g values. The measurement of the critical stress factor, K_{IC}, shows that the fracture toughness of the composite materials is enhanced by inclusion of the non-reactive block copolymer. In contrary, the reactive block copolymer has negative effect on the fracture toughness especially in case of short PEO block. FESEM micrographs studies on the fracture surfaces sustain the microphase separation and the increase in surface roughness in the toughened samples, indicating more energy was dissipated.

1. Introduction

Epoxy resins have been widely used for many industrial applications such as adhesives, coatings, and electronic encapsulation. Despite high thermal and chemical resistance their high crosslink density achieved after curing leads in most cases to a low impact strength material which shows poor resistance to crack propagation. Consequently, brittleness of epoxy resins is the major drawback. Therefore, toughness modification of epoxy thermosets has attracted widespread attention over the last decades and still remains a major topic in the developments of these materials [1–6].

Improved toughness still remains a desired feature and needs to be addressed scientifically. An important criterion for toughness modification is introduction of microphase separation into the epoxy system [7]. The use of binary blends to enhance phase separation in ternary blends of epoxies has been demonstrated [8]. Besides polymer blends, the use of block copolymers (BCPs) is widely acknowledged as toughening strategy [9] and widely reported, also for generating of nanophase-separated surfaces [10].

Block copolymers are characterized by phase separation on the nanoscale level which is caused by demixing of two or more thermodynamically immiscible blocks [11–13]. By mixing BCP into epoxies before curing, the state of phase separation in the system after hardening can be controlled by several parameters such as molar mass, dispersity, molar ratio of the blocks and surface tension between the blocks. In fact, the surface tension between the two blocks is directly related to the Flory–Huggins interaction parameter [14].

Pospiech et al. [15,16] reported methacrylate-based BCP with blocks of different surface free energy for the creation of nanostructured materials in which the wettability with external liquids can be tuned by the BCP composition. Poly(pentylmethacrylate)-b-poly(methylmethacrylate) (PPMA/PMMA) diblock copolymers with varied molar masses of the blocks were synthesized by

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sequential anionic polymerization by Werner et al. [17]. The phase separation behavior of the block copolymers in bulk and in thin films was investigated using a combination of appropriate methods as SAXS, AFM and TEM and it was demonstrated that a strong and reproducible state of phase separation could be achieved without order–disorder transition until 300 °C.

Amphiphilic block copolymers are also known for their ability to form micelles in a selective solvent [13,18]. For an A–B diblock copolymers, in a selective solvent which is good for A but not for B, the block copolymer molecules tend to associate into B-core/A-shell spherical micelles [19]. If the BCP is used as phase-separating additive in epoxies, the non-cured epoxy works as solvent which can either be selective or non-selective and miscible or immiscible with one or two of the blocks. [20,21].

In this way, the BCP with one block miscible in the thermoset precursor is not only dispersible in the reactive system, but also able to self-assemble in micelles both in the non-reacted and in the reacted state of the matrix [22,23]. Significant influences of such distributed BCP on the matrix properties can be expected from this behavior, and some previous work has been reported to show a profound impact on the thermomechanical properties of the thermosetting polymer [24,25], e.g., epoxy can be greatly toughened by the formation of nanostructures in the materials. It is critical to understand the formation of nanostructures to establish the correlation of the morphology with the properties of nanostructured reinforced epoxy [26].

The formation of nanostructures in thermosets with BCP includes two different mechanisms: (i) self-assembly of BCP as known from literature [11] and (ii) reaction-induced microphase separation. Both processes are combined and influence each other. These nanostructures can be further fixed via subsequent suitable curing processes [27]. The reaction-induced microphase separation mechanism is well known from literature [7]. In this approach, it is not required that the amphiphilic BCP is self-organized in microphases before curing reaction, i.e., all segments of the BCP may be miscible with the epoxy precursors and segments only partially microphase-separate upon curing [28].

So far, thermal curing was applied in this concept which causes major problems since the crucial miscibility/non-miscibility balance of the block copolymer as well as the miscibility balance between BCP and epoxy matrix strongly depends on the temperature (note the strong temperature-dependence of the χ interaction parameter [29]). In this context, fast UV-induced curing reactions can be a useful technique to induce network formation at ambient temperature. The fast UV-induced network formation will assure to freeze in the self-assembled micelles avoiding further reorganization.

Here, we present synthesis, characterization and application in UV-curable epoxy resins of diblock copolymers with poly(ethylene oxide) (PEO) connected either to a poly(styrene) (PS) block or to a poly(glycidyl methacrylate) (PGMA) block. Atom transfer radical polymerization (ATRP) was employed for synthesis to achieve control over molar mass and dispersity and to avoid side reactions of the glycidyl groups of GMA which would result in cross-linking. PEO acts as soft block enabling toughness modification, while PS acts as hydrophobic hard block which should form micelles with outer PS shell and soft PEO core. PGMA contains reactive glycidyl groups able to co-react in the curing process of the epoxy matrix, thus yielding chemical linkage between BCP and matrix. These linkages should influence the toughness of the material. To demonstrate this, the BCP prepared were mixed into a UV-curable epoxy matrix and the mechanical properties of the cured composites were examined by dynamic mechanical analysis and fracture toughness measurements (K_{1c}).

2. Experimental

2.1. Materials

Bis-cycloaliphatic diepoxy resin 3,4-epoxy-cyclohexylmethyl-3,4-epoxycyclohexyl carboxylate (CE), and the cationic photoinitiator triphenylsulfonium hexafluoroantimonate, $Ph_3S\ SbF_6$ (as a 50% solution in propylene carbonate) were obtained from Aldrich. Diphenyl ether (>99%, Sigma–Aldrich) was used as solvent for polymerization as received and tetrahydrofuran (THF, inhibitor-free, >99. 9%, Sigma–Aldrich) as solvent for macroinitiator preparation. THF for size exclusion chromatography was stabilized with 0.025 wt.% BHT.

The monomers glycidyl methacrylate (GMA, >97.0%, Aldrich) and styrene (S, >99%, Aldrich) were destabilized by treatment with basic alumina (Aldrich) prior to use. Either copper(I) bromide (CuBr, p.a., >98%, Aldrich) or copper(I) chloride (CuCl, p.a., >99%, Aldrich) were employed as salts in ATRP and were complexed by using *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich). Ethyl 2-bromoisobutyrate (EBrIB, 98+%, Alfa Aesar) was used as initiator and 2-bromoisobutyryl bromide (98%, Sigma–Aldrich) to synthesize the macroinitiators from poly(ethylene glycol) methyl ether (PEO) with different number of repeating units DP (45, 113), samples obtained from Sigma–Aldrich. Triethylamine (>99.5%, Sigma–Aldrich) was dried with KOH and distilled prior to use.

2.2. Block copolymer synthesis

2.2.1. Homopolymerization of GMA as control experiment

GMA polymerization was carried out by ATRP [30] under the conditions used for diblock copolymer synthesis. In a modified procedure, the destabilized and degassed monomer (6 mmol), PMDETA ligand (0.15 mmol), diphenyl ether (12 mmol) were added to a dry Schlenk flask with CuBr (0.15 mmol). The flask was degassed through three freeze-pump-thaw cycles. Then, the initiator (EBrIB, 0.15 mmol) was introduced into the flask by means of a degassed syringe. The flask was immediately placed into an oil bath at 30 °C. After 60 min, the reaction was stopped by adding an excess of methylene chloride and passed through neutral alumina to remove the catalyst. The solution was minimized in a rotary-evaporator to reduce the solvent. The residual solution was precipitated into a large excess of hexane. The polymer was filtered off, and dried under reduced pressure.

^{1}H NMR (500 MHz, $CDCl_3$), δ: 4.29 (2H, $C\underline{H}_2$—OCO—), 4.09 (2H, —$C\underline{H}_2$—OCO—, terminal group), 3.83 (2H, $C\underline{H}_2$—OCO—), 3.23 (1H, $C\underline{H}$, epoxy group), 2.84 (2H, $C\underline{H}_2$, epoxy group), 2.63 (2H, $C\underline{H}_2$, epoxy group), 1.91 (2H, —$C\underline{H}_2$, main chain), 1.25, 1.10, 0.95 (3H, CH_3—, terminal group), ppm.

Molar mass: calculated from $[M_0]/[I] = 40$: 5680 g/mol; found (NMR, using the —CH_2 group of the terminal group as reference): 5800 g/mol; found (SEC): M_n: 7000 g/mol, M_w: 8400 g/mol, Đ: 1.2 g/mol.

2.2.2. Synthesis of poly(ethylene glycol) macroinitiators (PEO-Br)

The PEO-Br macroinitiators were synthesized according to Armes et al. [31], and Yassin et al. [32]. The procedure is given here in general for all PEO with different molar masses. Thus, PEO-OH (5 mmol) was dried in a Schlenk flask under reduced pressure at 60 °C for 60 min followed by adding anhydrous THF (80 mL). The reaction flask was cooled to room temperature followed by adding triethylamine (10 mmol) and flushing with nitrogen. 2-Bromoisobutyryl bromide (10 mmol) diluted in anhydrous THF (10 mL) was added dropwise to the reaction solution over 20 min. After 48 h of stirring at ambient temperature, the mixture was filtered to remove the precipitated triethylammonium bromide salt