Reactive & Functional Polymers 73 (2013) 1038–1045

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

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

Nucleation as a new concept for morphology adjustment of crystalline thermosetting epoxy polymers

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ARTICLE INFO

Article history:
Received 29 January 2013
Received in revised form 26 April 2013
Accepted 29 April 2013
Available online 7 May 2013

Keywords:
Thermosetting resin
Cationic polymerization
Crystallinity
Morphology
Phase separation

ABSTRACT

Partially crystalline thermosetting epoxy polymers of defined heterogeneous morphology are herein presented. Crystalline poly(ε-caprolactone) (PCL) domains are covalently integrated into the cationically polymerized epoxy network. Although crystallinity is common in thermoplastic polymers, these new materials are among the first examples of partially crystalline thermosetting polymers. Nucleation is crucial and leads to a defined heterogeneous morphology. Homogeneous and heterogeneous polymers with identical composition can be prepared by initiation below or above the melting point of the PCL, respectively. While the homogeneous polymer showed the expected decrease in crosslinking density of the epoxy network and low glass transition temperature (T_g), the epoxy phase is not substantially influenced in the case of the heterogeneous morphology, showing two separated modulus changes at the melting point of PCL and the T_g of the epoxy matrix polymer.

1. Introduction

The mechanical properties of materials are significantly influenced by their respective chemical structures and morphologies. In polymers, important changes in material properties can be achieved by the formation of molecular order, resulting in a heterogeneous morphology and, generally, crystalline phases. For thermoplastic polymers, the inclusion of annealing steps, processing to control molecular orientation, and the addition of nucleating agents for the controlled adjustment of crystallinity and morphology are common practices for property optimization [1]. Mechanical properties such as stress–strain behavior, flexibility and stiffness of the resulting polymers can be changed considerably. Partially crystalline thermoplastic polymers are heterogeneous and display defined morphologies, optimized for desired properties. Numerous slightly crosslinked elastomers are partially crystalline. While these processes are extensively studied and applied in the syntheses of thermoplastic polymers and elastomers, thermosetting polymers are commonly amorphous. Toughening by the creation of a defined heterogeneous morphology is widely practiced, but the formation of crystalline domains is rarely explored [2].

Thermosetting epoxy polymers are amorphous, with properties optimized by choices of chemical backbone, monomer reactivity and crosslinking density [3]. Due to the extraordinary properties of epoxy resins, their application and chemistry are under constant development. Such development includes work on ionic conductivity [4], syntheses of shape memory epoxy resins [5], formulation of dual curing systems by combination with acrylates [6], studies of systems containing liquid crystalline domains [7], and work toward the integration of hyperbranched structural units [8,9]. The primary drawback of epoxy polymers is their brittleness, so integration of elastomer phases and, more recently, inclusion of hard nanoparticles have been applied in hopes of providing material toughness [10]. In the present study, the degree of crystallinity is presented as a "key-factor" in the optimization of the mechanical properties of highly crosslinked thermosetting epoxy polymers. The objective of this work is to prepare thermosetting polymers consisting of partially crystalline polyol domains covalently bound to a highly crosslinked epoxy matrix. In this way, structure models determined from thermoplastic polymers will be applied to thermosets. Because macroscopic, uncontrolled crystallization of polymers usually negatively affect mechanical characteristics, precisely dispersed fine crystalline domains, as found in partially crystalline thermoplastic polymers, are desirable. Therefore, methods must be developed to prepare crystalline thermosetting polymers with fine control of crystallite size on microscopic scales.

In the present study, the concept of partially crystalline thermosetting polymers will be presented using the cycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate. If this monomer is cationically polymerized by decomposition of a latent superacid initiator in a living polymerization [11], a highly

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http://dx.doi.org/10.1016/j.reactfunctpolym.2013.04.014

crosslinked thermosetting polymer is formed. Due to the brittle nature of this material, modification by the addition of compounds such as liquid rubber or low molecular weight polyols, leading to a widened crosslinked network, is common. Furthermore, the addition of nanoparticles or hyperbranched polymers as preformed heterogeneous domains with low impact on matrix polymer properties and T_g provides toughness [12–16]. The mechanism of polymerization, described in literature as the activated monomer mechanism [11,17], allows for covalent binding of alcohol groups into the network. The type of polymeric alcohol applied to these ends not only strongly influences the properties of the final polymer but also augments the polymerization kinetics [18,19]. The presence of moisture was found to increase the reaction rate of cationic polymerization of this epoxy resin [20]. Previous work on the epoxy resin in combination with partially crystalline polyols [21,22] showed the syntheses of polymers with outstanding material properties. In particular, poly(ε-caprolactone) was chosen as a partially crystalline polymeric diol, able to produce phase separation via crystallite formation, as is frequently used for phase formation in heterogeneous thermoplastic epoxy polymers [23,24]. Fortunately, the cationic polymerization of epoxy resins initiated by latent onium salts may be initiated photochemically or thermally. This allows the preparation of samples with identical compositions but different morphologies. In other words, polymer samples can be prepared from the reactive epoxy resin/PCL mixture by polymerization below and above melting temperature of the PCL. These two options are ideally suited for studying the influence of morphology on the properties of thermosetting epoxy polymers. A similar strategy was applied to studying the cationic polymerization of liquid crystalline epoxy resins forming either mesostructured or amorphous thermosetting polymers with identical compositions [25–27]. For some time, interest in poly(ε-caprolactone) has increased, driven mainly by research into potential medical and biochemical applications [28]. In these studies, factors affecting crystallization such as cooling procedure [29], molecular weight of the PCL [30] and the post-catalyst polymerization procedure [31] were thoroughly examined. Self-nucleation [32] and anti-nucleation [33] were also examined for PCL-containing block copolymers. Polymer blends of epoxy resins and PCL were extensively examined by Groenickx, Guo and collaborators during recent years. Their work examined the crystallization kinetics [34,35], morphologies [36] and process induced phase separation [37] of these materials. Furthermore, the crystallization of PCL blends with crosslinked carboxylated polyester resin was examined by Madbouly [38]. In contrast to the previous work on PCL blended with crosslinked polymers, covalent integration of small PCL crystallites into a cationically-cured, crosslinked epoxy system will be herein presented. To prevent macroscopic segregation of PCL within the PCL/epoxy mixture, controlled crystallization of the polyol with the formation of small crystallites is desired. For this, nucleation is required as was shown in the syntheses of thermoplastic polyurethanes from partially crystalline polyol mixtures containing PCL and other crystalline polyesters [39].

2. Experimental

2.1. Materials

Butanediol-initiated, partially crystalline poly(ε-caprolactone) with molecular weight of 4000 g/mol, melting point of 55 °C, and a melting enthalpy of 87 J/g (DSC, 10 K/min) was obtained from Perstorp Polyols (Capa2402, Perstorp, Sweden). The cycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate was obtained from IGM resins (Omnilane OC1005, Krefeld, Germany). For the syntheses, all chemicals were purchased from Sigma–Aldrich and were used without further purification.

2.2. Preparation

Poly(decanediol adipate) (DDO-PA) was synthesized by esterification of appropriate amounts of adipic acid and 1,10-decanediol required for a the formation of a decanediol terminated DDO-PA with a molecular weight of 2000 g/mol (1:1.146 mol:mol). In a reaction flask with dean–stark trap and reflux condenser, 60 mL of toluene and 50 mg of tin (II) chloride were added to 15 g of adipic acid and 20.496 g of 1,10-decanediol. After purging with nitrogen the mixture was preheated to 70 °C for 30 min under stirring. The resulting clear solution was refluxed for 22 h. After removal of the reaction water and toluene using the dean–stark trap, the mixture was heated to 180 °C for another 2 h to complete the reaction. The resulting white solid was used without further purification. DSC (10 K/min): T_m = 68 °C; 132 J/g. No T_g was observed. The molecular weight was calculated from the integral ratio of the ^{1}H-NMR signals of CH_2 groups adjacent to either the esterified OH (δ = 4.04 ppm) or the terminal OH (δ = 3.63 ppm). This ratio was found to be 4:28, corresponding to a molecular weight M_n of 2164 g/mol.

Cationic epoxy polymerization was initiated by the latent thermoinitiator benzyl tetrahydrothiophenium hexafluoroantimonate, prepared according to literature methods [40]. The initiator (1 wt.%) was pre-dissolved in the epoxy resin with stirring at 20 °C for 3 h. A mixture of 90 wt.% PCL and 10 wt.% DDO-PA was added to the epoxy resin (9.1, 16.7, and 23.1 wt.%), and homogenized under stirring at 75 °C. The preheated epoxy/PCL/DDO-PA mixtures were coated, with a doctor knife, as 150 μm thin films on both aluminum foil and microscopy slides, and were subsequently cured in two different ways.

For thermal polymerization, specimens were heated for 30 min at 75 °C. Then, three consecutive heating steps were applied: 1 h at 110 °C, 1 h at 125 °C and 30 min at 145 °C. For UV-polymerization the specimens were stored for 18 h at 20 °C. The films were cured with a UV-portable lamp from Köhler Technische Produkte of 2×6 W and 254 and 366 nm wavelength (500 and 850 μW/cm^2 in 15 cm distance, respectively), irradiated at a distance of 3.5 cm. To prevent structuring of the polymer surface due to thermal heating, irradiation steps of 4×5 s and 4×10 s and 3×20 min were applied with a 10 min wait-time after each irradiation. After complete curing, the aluminum foil was dissolved in 10% HCl and the polymer films were washed with water and dried in a desiccator.

For dynamic mechanical analysis (DMA) the polymer films were cut to $10 \times 35 \times 0.15$ mm^3.

For light scattering experiments, the epoxy/PCL/DDO-PA (9.1, 16.7 and 23.1 wt.% PCL/DDO-PA) and epoxy/PCL (13, 23, and 31 wt.% PCL) were homogenized without initiator at 75 °C and filled into preheated UV-cuvettes. The hot samples were directly placed in the spectrometer (see below), equilibrated at 20 °C.

For X-ray diffraction (XRD), samples of phase-separated epoxy/PCL/DDO-PA mixtures as well as the pure epoxy were coated and UV-polymerized (as described above) on aluminum discs. The pure PCL was preheated and added to an aluminum sample holder in the shape of a 1.7 cm disk of 2 mm thickness.

2.3. Measurements

For differential scanning calorimetry (DSC) a TA Instruments DSC 2920 was used with a heating and cooling rate of 10 K/min in temperature ranges between −150 °C and 220 °C. The DDO-PA was measured between −150 °C and +120 °C. Cyclic DSC was performed by heating from 20 °C to 120 °C, holding for 5 min, cooling to 0 °C, holding again for 10 min and heating a second time to 120 °C.