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Synthesis, characterization and mechanical properties of polyester-based aliphatic polyurethane elastomers containing hyperbranched polyester segments ☆

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ABSTRACT

Aliphatic polyester-based polyurethane (PU) elastomers with hyperbranched polyester segments were synthesized from polyester diol, hydroxyl-terminated hyperbranched polyester (HB-20), isophorone diisocyanate (PDI) and 1,4-butanediol. The crosslinking density of the PU elastomer was calculated by using Flory–Rehner equation. The degree of hydrogen bonding, the microstructure and the morphologies of these PU materials were characterized by means of FT-IR, WAXD and DSC, respectively. The experimental results showed that the PU elastomers containing small amount of HB-20 exhibited the enhanced hydrogen bonding and mechanical properties. As compared with the comparable PU specimen, the tensile strength of the polyester-based aliphatic PU containing 6 wt% HB-20 increased by 71.2 times, up to 36.1 MPa, and the elongation at break was still as high as 333.1%, resulting from the dual effects of the hydrogen bonding and the crosslinking density in the PU system.

1. Introduction

Dendrimers with unique molecular architecture and performance have attracted considerable interests [1,2], but their synthesis processes are usually complicated. Hyperbranched polymers, however, have similar structure and performance as the dendrimers, and could be synthesized easily, so they have been paid more attention [3–5].

With non-yellowing performance, aliphatic polyurethane (PU) materials have been widely applied in preparing foams, elastomers and waterborne PUs etc. Compared with the aromatic PU with the same structure of soft segment and the same content of hard-segment, the aliphatic PU always exhibits poor mechanical properties, especially for that synthesized with isophorone diisocyanate [6]. The enhancement of the mechanical properties of the aliphatic PU can be realized through the increase of the hard-segment content, but the increase of the expensive aliphatic isocyanate should be expected, thus bringing a problem of high cost for such a kind of PU material.

Recently, the hyperbranched polymers have been used to synthesize the PU and other materials. Jena et al. [7] studied the effect of the generations and the symmetry of hyperbranched polyester on the morphologies and the thermal performance of the aliphatic poly(urethane urea) (PUU) cured with moisture. Sheth et al. [8] investigated the structure-property behavior of highly branched PUU (HBPUU) and its linear analog (LPUU) synthesized with *bis*(4-isocyanatocyclohexyl)methane and polyether polyol etc. They found that the tensile strength of the HBPUU was lower than that of the LPUU. Nasar et al. [9] synthesized an aromatic hyperbranched PU with amine-terminated hyperbranched polyamide and 4,4′-diphenylmethane diisocyanate (MDI)-based PU prepolymer,

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and found that its mechanical properties were enhanced slightly (tensile strength increased from 7.8 MPa to 10.9 MPa). Czech et al. [10–12] investigated the molecular dynamics of MDI-based PU network cross-linked with hyperbranched polyester, and observed the molecular relaxation and the crystallization behavior of such a PU network. Xu et al. [13] prepared a toughened polypropylene by using a modified hyperbranched polyester to enhance the compatibility between the polypropylene and PU. Han et al. [14] reported a urethane elastic fiber with hyperbranched polyester as a rheological modifier in spinning process. Up till now, however, the hyperbranched polymer has not been used in synthesizing the aliphatic PU materials.

In this article the polyester-based aliphatic PU elastomers with hyperbranched structure were synthesized with hyperbranched aliphatic polyester polyol (HB-20). Compared with the PU without containing HB-20, the mechanical properties of such polyester-based aliphatic PU were enhanced dramatically, which could be correlated to the microstructure and the morphologies of these PU materials.

2. Experimental

2.1. Materials

Hydroxyl-terminated hyperbranched aliphatic polyester (Boltorn™ H20, with 16 primary hydroxyl groups, $M_n = 1747\ g\ mol^{-1}$) was supplied from Perstorp AB, Sweden. Poly(neopentyl glycol adipate) diol(PNA-2000, $M_n = 2000\ g\ mol^{-1}$) was produced by Qingdao Yutian Chemicals Corp., China, and was dried in vacuum at 110 °C for 2 h. Isophorone diisocyanate (IPDI) was supplied from Bayer MaterialScience. 1,4-Butanediol(BDO) and *N*-methyl-2-pyrrolidone (NMP) were produced from Shanghai Feida Chemicals Corp. Prior to use, the BDO was dried and degassed in vacuum for 24 h at 60 °C and the NMP was treated with 4-Å molecular sieves for over one week. Other materials were standard laboratory reagents and were used as received.

2.2. Synthesis of PU elastomer with hyperbranched polyester segment

A stoichiometric amount of PNA, IPDI, dibutyltin dilaurate (DBTDL, 0.1 wt% based on the total mass of raw materials) were charged into a 250 mL, four-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a condenser, and a thermometer. A light yellow and viscous NCO-terminated aliphatic PU prepolymer was obtained by keeping the reaction at 90 °C for 5 h until the NCO content reached the theoretical value determined by using a standard dibutylamine back-titration method.

For fixing the content of hard-segment (HS) in the PU elastomer to 40 wt%, a stoichiometric amount of BDO was mixed with HB-20/NMP solution (HB-20/NMP = 1/1, w/w) first. Then, it was rapidly mixed with the prepolymer synthesized, and was degassed in vacuum. Finally, this mixture was cast into a glass mold (20 cm × 15 cm × 2 mm), and then was cured at 70 °C for 1 h, 90 °C for 2 h as well as was post-cured at 110 °C for 6 h in a vacuum oven to remove the residual NMP. Thus, the polyester-based PUs with hyperbranched structure were synthesized, as shown in Scheme 1. For simplicity, they are called ES-X, where X indicates the weight content of HB-20 in the systems. The PU elastomers were placed in a dryer for 7 days at ambient temperature before testing their performances. The comparable polyester-based PU without containing hyperbranched structure (ES-0) was also synthesized.

2.3. Synthesis of NCO-terminated hyperbranched model-compound (HBI)

A stoichiometric amount of HB-20 dissolved in NMP (HB-20/NMP = 1/1, w/w), IPDI([NCO]/[OH] = 4:1, molar ratio), DBTDL (0.1 wt% based on the total mass of raw materials) were charged into a 250 mL, four-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a condenser and a thermometer. HBI was obtained by keeping the reaction at ambient temperature around 6 h. until the NCO content reached the theoretical value determined by the standard dibutylamine back-titration method. Cyclohexane was added into the system and well mixed with the reaction product. Then, it was transferred into a separatory funnel to remove the residual IPDI by extracting repeatly with cyclohexane, until the extractant was not opaque, while it was checked with ethylenediamine. The extracted product was finally dried at 60 °C for 5 h under vacuum to a constant weight. HBI was a white powder at ambient temperature and its synthesis process is shown in Scheme 2.

2.4. Characterization

Fourier transform infrared (FT-IR) spectra of the PU specimens were recorded with a Nicolet 5700 FT-IR spectrometer at 25 °C. The PU elastomers with hyperbranched structure were directly formed on KBr disc and the NCO-terminated prepolymer was coated on KBr disc for testing. Thus, the HB-20 and HBI were dissolved in NMP and acetone first, and then were coated on KBr disc, respectively. The nuclear magnetic resonance (^1H NMR) measurement was performed with a Bruker 500 NMR spectrometer at 25 °C, DMSO and TMS were used as solvent and internal standard substance, respectively. Wide angle X-ray diffraction (WAXD) was analyzed with a RINT2000 analyzer at 25 °C. Differential scanning calorimetry (DSC) was measured with a TA DSC 2010 analyzer at a heating rate of 20 °C/min under a nitrogen atmosphere. The mechanical properties for all the specimens were conducted on a Shimadzu AG-2000A testing machine under a 50 mm/min cross-head rate at 25 °C, and the specimens were made in accordance with GB1040-79. For each tensile test, five specimens were made and an average value was calculated. The crosslinking density of PU elastomer was measured with an equilibrium swelling method. Thus, the percentage of the weight increase for PU specimen was tested in dimethylformamide for 7 days at 25 °C and the crosslinking density V (mol/cm^3) of the PU network was calculated using Flory–Rehner equation [15]: