

Shape memory hyperbranched polyurethanes via thiol-ene click chemistry



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ABSTRACT

Hyperbranched poly(amine-ester) (Hyper-OH) was synthesized from pentaerythritol tetraacrylate (PETTA) and diethanolamine (DEA) by Michael addition reactions. One-to-one stoichiometric reaction between diisocyanatodicyclohexylmethane (H_{12} MDI) and 2-hydroxyethyl acrylate (HEA) produced dimers carrying both NCO and vinyl groups at two chain termini, which were subsequently reacted with Hyper-OH to form hyperbranched polymers (HBP, Hyper-8). Replacing HEA by trimethylolpropane diallyl ether (TMPDE) produced Hyper-16. On the other hand, polyurethane prepolymers were synthesized from H_{12} MDI and polyol, end capped with 1,2-ethanedithiol, and UV cured to synthesize crosslinked polyurethanes via thiol-ene click chemistry. Hyperbranched polymers acted as multifunctional crosslinkers as well as reinforcing fillers and significantly enhanced mechanical, thermal and shape memory properties. Effects were more pronounced with thiol-ene click chemistry than ene-ene curing.

1. Introduction

Polyurethanes (PUs) are typically synthesized by polyaddition reactions of diisocyanates and polyols. Depending on the type, composition, sequence of the two, a broad property spectrum from elastomers to foams are easily implemented [1–3]. This leads to various products to include coatings, adhesives, sealants, fibers, cushions, and insulating materials with an annual production over 18 million tons 2015 [4,5]. During the last several decades, continuous efforts have been made for functionalization and performance enhancements by molecular design, hybridizations, and composite formations with other organic and inorganic materials [5,6].

Shape memory polymers are well-known rapidly moving intelligent materials that can be deformed into a desired temporary shape, and recovered original shape responding to external stimuli such as heat, light, and electricity while thermally induced shape memory polymers are most common [7–9]. Among the various types of polymer, polyurethane has most widely applied based on the ample freedom in performance design [10–12]. It could be amorphous or crystalline with a broad range of actuation temperature, –20–150 °C. Moreover, the performance can be much enhanced by forming chemical hybrids and composites with organic and inorganic reinforcing fillers [13,14].

The hybridization of shape memory polymers with fillers in the form of particles, platelets, tubes, fibers or fiber mats could achieve their mechanical reinforcement and functionalizations [15–18]. Notably chemical hybridizations with multifunctional fillers provided multiple crosslinks which increase rubber elasticity and elastic strain

recovery [13,14].

Hyperbranched polymers (HBPs) are synthetic tree-like macromolecules having densely branched globular structures and multiple functional groups at chain termini [19–21]. So, they have high chemical reactivity, low viscosity, and enhanced solubility, which open up ample potential applications as coatings, additives, patterning, biomaterials, and rheology modifier [22–24]. However, applications of HBP as multifunctional crosslinks to enhance rubber elasticity and hence shape memory effects are sparse in the literature.

Click chemistry is a term devoted to reactions that are high yielding, high rate, stereospecific, simple to perform, and conducted in easily removable solvents by Sharpless in 2001. Thiol-ene reaction is well accepted as a click chemistry reaction [25]. Further, the reaction is most frequently photoinitiated, particularly for photopolymerizations resulting in highly uniform polymer networks, and it has been used for surface and polymer modification [26].

The technology of UV-cure has a lot of interesting features like high efficiency, environmental friendliness and low energy consumption. It has been widely used as photo-resist, coating, printing inks, adhesives and so on [27–29]. However, UV curing has limitations as non-uniform crosslinking, high internal stress levels and wide mechanical transition ranges [30,31]. It is expected that thiol-ene click chemistry could significantly enhance the efficiency of UV-curing and their mechanical properties [32,33].

In this article, a series of crosslinked polyurethanes were synthesized by chemical hybridizations of HBPs with ene- or thiol-terminated polyurethane prepolymers by UV-curing. Two HBPs having eight

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(Hyper-8) and 16 (Hyper-16) functional groups were synthesized. Structures and molecular characteristics of the HBPs were determined by FT-IR, ^1H NMR and GPC measurements. Hybrid networks synthesized by thiol-ene click chemistry were favorably compared with ene-ene curing along with the effects of HBP functionality in terms of thermal, mechanical, surface properties and shape memory effects.

2. Experimental

2.1. Raw materials

Propylene oxide based polyol (PPG, 400Mn) (KPX, Korea) was degassed and dried at 70 °C in vacuum oven for 3 h. Diisocyanatodicyclohexylmethane (H_{12}MDI), 2-hydroxyethyl acrylate (HEA), 1,2-ethanedithiol, pentaerythritol tetraacrylate (PETTA), trimethylolpropane diallyl ether (TMPDE) and dibutyltindilaurate (DBTDL) (All from Sigma-Aldrich) and diethanolamine (DEA, ACROS) and *N,N*-dimethylformamide (DMF, Junsei Chemical) were used as received. 2,2-dimethoxy-2-phenylacetophenone (DMPA, Acros) and phenylglyoxylic acid methyl ester (Darocur MBF, BASF) were used as photoinitiator. Analytical grades of acetone, methanol and ethyl ether (Daejung Chemicals, Korea) were used as received.

2.2. Preparation of hyperbranched poly(amine-ester) (Hyper-OH)

Hyper-OH was synthesized by Michael addition reaction as shown in Scheme 1. PETTA (7.02 g, 0.02 mol) and DEA (8.41 g, 0.08 mol) with 40 ml methanol as solvent were added into a 150 ml three-necked flask, equipped with magnetic stirrer and nitrogen gas inlet [33]. Reactions proceeded for 40 h at 40 °C under nitrogen atmosphere, followed by

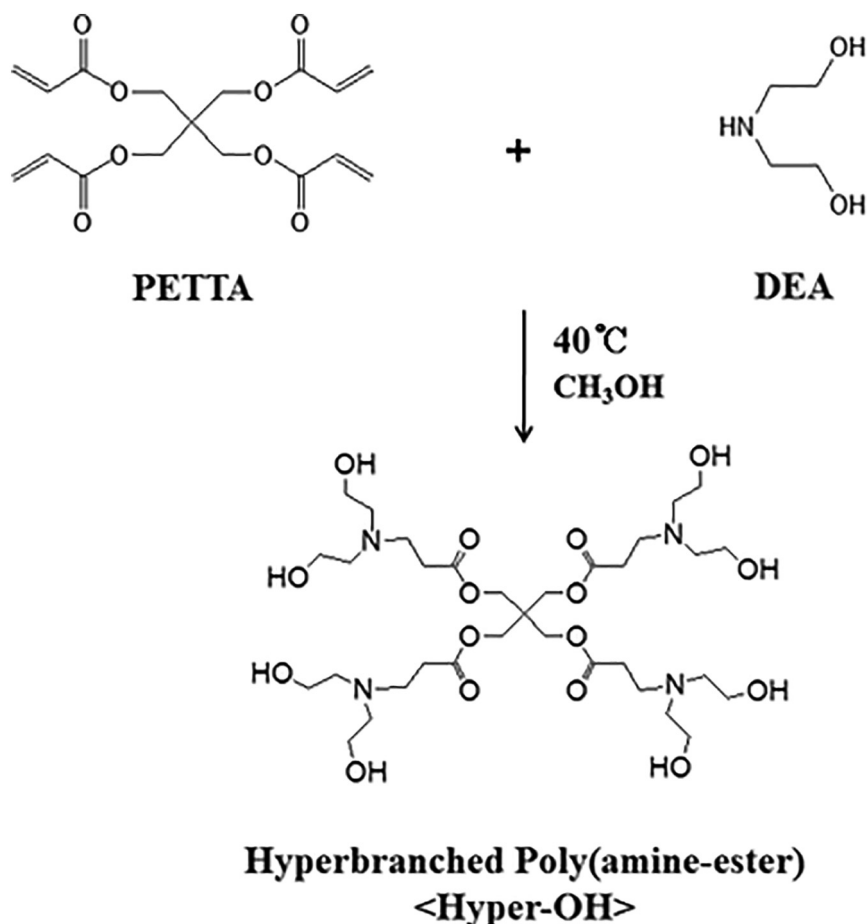
cooling down to 25 °C. The white precipitate was filtered, washed with acetone, and dried for 24 h in vacuum oven to obtain 1.62 g (84% yield) hyperbranched poly(amine-ester) (Hyper-OH).

2.3. Preparation of Hyper-8 and Hyper-16

The Hyper-8 and Hyper-16 were synthesized via two-step procedures as shown in Scheme 2. One-to-one stoichiometric reaction between H_{12}MDI and HEA produced dimmers carrying both NCO and vinyl groups at the two chain termini, which were reacted with Hyper-OH to form Hyper-8. Upon replacing HEA by TMPDE, Hyper-16 is obtained. Procedure is detailed below.

H_{12}MDI (5.25 g, 0.02 mol) and HEA (2.32 g, 0.02 mol) were mixed with 25 ml acetone at 25 °C for 2 h in a 150 ml three neck flask which was equipped with a magnetic stirrer and nitrogen gas inlet. Then the temperature was raised to 60 °C and mixture was reacted for about 12 h in the presence of DBTDL until the NCO group content reached the theoretical isocyanate value which was determined by standard di-*n*-butylamine back titration method (ASTM D 2572).

The product was reacted with Hyper-OH (1.93 g, 0.0025 mol) dissolved in 10 ml acetone. The reaction continued until NCO group disappeared from the Fourier transform infrared spectroscopy (FT-IR spectrometer, Mattson Instruments, USA) measurements. Then the mixture was precipitated in ethyl ether. The white solid was washed with acetone/ethyl ether (1:1) mixture and dried under vacuum for 24 h. By measuring the weight of solid, the yields of reactions were 81% for Hyper-8 and 55% for Hyper-16. The idealized structures of Hyper-8 and Hyper-16 are shown in Scheme 3.



Scheme 1. Reaction scheme to prepare hyperbranched poly(amine-ester) (Hyper-OH).

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