Reproducible Epoxy Networks with Tunable Physical Properties: Synthesis, Stress Relaxation and Recyclability

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Abstract In order to extend the application of epoxy vitrimer, 1,4-cyclohexanedicarboxylic acid (CHDA) was used as a co-curing agent and structure modifier for sebacic acid (SA) cured diglycidyl ether of bisphenol A (DGEBA) epoxy vitrimer to tailor the mechanical properties of epoxy vitrimers with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a transesterification catalyst. The glass transition temperature ($T_g$) of vitrimer increased gradually with the increase in CHDA content. Vitrimers behaved from elastomer to tough and hard plastics was successfully achieved by varying the feed ratio of CHDA to SA. Both the Young’s modulus and storage modulus increased apparently with the increase in CHDA content. Stress relaxation measurement indicated that more prominent stress relaxation occurred at elevated temperatures and the stress relaxation decreased with the increase of CHDA content due to the reduced mobility of the vitrimer backbone. The vitrimers showed excellent recyclability as evidenced by the unchanged gel fraction and mechanical properties after compression molded for several times. With tunable mechanical properties, the epoxy vitrimers may find extensive potential applications.

Keywords Epoxy vitrimer; Mechanical properties; Stress-relaxation; Recyclability

INTRODUCTION

The permanent network structures endow the thermoset polymers with superior dimensional stability, mechanical properties and environmental resistance, thus make them irreplaceable in numerous applications such as in aircraft industry, high performance composite and solar cell encapsulant[1]. However, thermoset polymers cannot be reshaped, processed or recycled due to the permanent crosslinking structures[2]. To construct the reversible thermoset polymer by dynamic covalent bonds provides an attractive way to impart processability, since the networks with reversible crosslinks are able to be rearranged under suitable conditions similar to thermoplastic[3–5].

Processable thermoset polymers, also known as covalent adaptable networks[6–7], can be fabricated by incorporation of various reversible covalent bonds, such as Diels-Alder (D-A) linkages[8–11], disulfide crosslinks[12–14], ionic crosslink[15] and dynamic exchangeable crosslinks[16–18]. These processable network polymers are simply classified into two groups according to the reversible mechanisms, namely, dissociative and associative[16, 18]. For the dissociative mechanism, the covalent bonds firstly break and then reform, while for the associative one, the former covalent bond is only broken when a new covalent bond has been formed. Polymer networks containing Diels-Alder (D-A) structures are a typical example of dissociative and exchangeable network with processibility[10]. The D-A linkage is a reversible covalent bond which breaks/reforms quickly upon heating, and the D-A linkage tends to dissociate due to the chemical equilibrium shifting relatively towards the endothermic side[7, 19]. Thus, the polymer with this type of networks undergoes fast topology rearrangement to show plasticity because of a decrease in connectivity and a sudden drop in viscosity. Transesterification between ester group and hydroxyl group in acid/anhydride cured epoxy represents a typical associative exchange mechanism[19]. The term “vitrimer” is introduced to describe such a processable epoxy resin as its viscosity behaves like a distinctive vitreous silica upon heating, namely, decreasing gradually[1].

Epoxy resin represents a kind of versatile network polymer with diverse industrial applications such as elastomer, coating, adhesive, electrical/electronic laminates and high performance composites[20, 21]. The global production of epoxy is projected to reach 3 million tons by this year, which may result in drastic thermoset waste accumulation after discarding, since they are neither thermally recyclable nor degradable due to their permanent network structure[21–23]. Therefore, the development of reprocessed epoxy resins is very attractive from the viewpoint of waste utilization and environmental protection.
Since Leibler and coworkers reported the zinc acetate catalyzed processable epoxy vitrimer in 2011[1], a number of epoxy vitrimers and their composites have been documented[24-32]. For example, Ji et al.[24, 25, 31] synthesized a series of elastic sebacic acid cured epoxy vitrimers and composites with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a transesterification catalyst. Legrand and Soulié-Ziakovic[29] reinforced the rubbery epoxy vitrimer by incorporation of modified nano-silica to form silica-vitrimer nanocomposites. Yang et al.[32] prepared thermally reconfigurable shape memory vitrimer composites by incorporation of graphene into TBD catalyzed sebacic acid cured diglycidyl ether of bisphenol A (DGEBA) vitrimer. It is noted that the vitrimers in these systems are usually elastic epoxy resins, which are cured with long-chained dicarboxylic acid. Thus, the obtained epoxy resins showed elastic mechanical behavior at room temperature due to their relatively low glass transition temperature[24, 25, 29, 31, 32]. The elastic epoxy vitrimers cannot meet the requirements for important applications, particularly for the electrical/electronic laminates and high performance composites. Therefore, to tailor the physical properties of epoxy vitrimers for expanding the practical applications of such reprocessing epoxy resins remains a challenging project.

In this study, we incorporate a rigid dicarboxylic acid, namely 1,4-cyclohexanediacarboxylic acid (CHDA) into sebacic acid cured epoxy resins in the presence of TBD as a transesterification catalyst. We find that the glass transition temperature and the mechanical properties are easily regulated by variation the weight ratio of CHDA and SA. The obtained epoxy vitrimers show the mechanical properties with the similarities of soft elastomer and tough or hard plastics. Although sporadic study has reported the shape memory performance regulation of epoxy vitrimer by combining mixed carboxylic acids as curing agents[33], the example referred to tailoring the mechanical properties and recyclability of epoxy vitrimers is rarely reported.

**EXPERIMENTAL**

**Materials**

Diglycidyl ether of bisphenol A (DGEBA, DER 332) with epoxy equivalent of 174 was procured from Dow Chemical Company. Sebacic acid (SA, 98.5%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 97%) and 1,4-cyclohexanedicarboxylic acid (CHDA, cis/trans isomer, AR grade) were obtained from Micxy Chemical Co., Ltd (Chengdu, China). Chloroform was purchased from Chuandong Chemical CO., LTD (Chongqing, China).

**Synthesis of Epoxy Vitrimer from DGEBA, CHDA and SA**

Epoxy vitrimer was synthesized via bulk curing of DGEBA with SA and CHDA by using TBD as the transesterification catalyst at 170 °C for 30 min. The molar ratio of −COOH/epoxy was kept at 1:1 for all the samples. Four different vitrimers containing CHDA and SA with weight ratio of 1/9, 2/8, 3/7 and 4/6 were synthesized. They were named as EVC₁₉, EVC₂₈, EVC₃₇ and EVC₄₆, respectively. The detailed synthetic procedures for the vitrimers were as follows: DGEBA, SA and CHDA with predetermined amounts were added into a 100 mL round-bottomed flask which was vacuumed and purged with N₂ for 3 times and then was put into a 170 °C silicon oil bath. Magnetic stirring bar was used to mix the reactants. TBD (2.5 mol% of −COOH group) was added into the flask when homogeneous mixtures were obtained and the reaction was terminated after 30 min. The products were taken out of the flask with a tweezer before cooling. The vitrimers consisting of DGEBA with CHDA or SA alone were prepared as the controls and abbreviated as EVC and EVS, respectively.

**Tensile Tests**

Dumbbell-shaped specimen with width of 4 mm for tensile test was cut from vitrimer sheet with thickness of 0.5 mm that was prepared by compression molding at 200 °C under 20 MPa for 10 min. The tensile test was performed on a MTS E44 universal testing machine at room temperature (~30 °C) with crosshead speed of 10 mm/min. The length between the two pneumatic grips was 25 mm. International standard ISO 527-3 was referenced during testing. Five measurements were carried out for each sample and the averaged result was reported.

**Fourier Transform Infrared (FTIR) Spectroscopy**

Fourier transform infrared (FTIR) spectra of the samples under reflective mode were recorded on a R-5301PC spectrophotometer (Shimadzu, Japan) in the wavenumber range from 4000 cm⁻¹ to 400 cm⁻¹ with the resolution and scanning time of 4 cm⁻¹ and 32 times, respectively.

**Gel Fraction Measurement**

The gel fraction of the sample was measured by solvent extraction. About 1 g (w₁) of sample was immersed in 25 mL of chloroform at room temperature for 3 days to dissolve the un-crosslinked part. The insoluble residue was isolated from the solution by filtration and weighed (w₂) after drying at 80 °C for 12 h. The gel fraction (Gf) was calculated by the Eq. (1):

\[ G_f(\%) = \frac{w_2}{w_1} \times 100 \]  

**Stress Relaxation**

Stress relaxation was performed on a TA DHR-1 rotational rheometer right after curing of the samples. After 10 min equilibration from the curing temperature to the selected temperature, a 1% strain step was employed and the plot of storage modulus versus time was recorded. Good contact between the sample and the plates was guaranteed by the in situ curing process.

**Differential Scanning Calorimetry (DSC)**

Differential scanning calorimetry analysis was performed on a NETZSCH instrument DSC-214. The samples with ~6 mg in aluminum pans were heated from −40 °C to 120 °C at a scanning rate of 10 K/min under N₂ atmosphere. The curves were recorded for glass transition temperature analysis.

**Dynamic Mechanical Analysis (DMA)**

Thermo-mechanical properties of the samples were measured on a TA DMA Q800 dynamic mechanical analyzer under a tensile resonant mode at a heating rate of 3 K/min from −60 °C to 120 °C and at a frequency of 2 Hz.