Green Synthesis of a Bio-Based Epoxy Curing Agent from Isosorbide in Aqueous Condition and Shape Memory Properties Investigation of the Cured Resin (Postprint)

Authors: Li, C, Dai, JY, Liu, XQ, Jiang, YH, Ma, SQ, Zhu, J

Date: 2017-04-06T00:00:00+00:00

Abstract

The bio-based diamine and epoxy monomer derived from isosorbide are synthesized. Especially, the diamine is obtained using microwave assistant thiol-ene coupling reaction in the aqueous media and the influence of reaction parameters, such as initiator con

Full Text

Preamble

Green Synthesis of a Bio-Based Epoxy Curing Agent from Isosorbide in Aqueous Condition and Shape Memory Properties Investigation of the Cured Resin

A bio-based diamine and epoxy monomer derived from isosorbide were synthesized. In particular, the diamine was obtained using a microwave-assisted thiol-ene coupling reaction in aqueous media, and the influence of reaction parameters such as initiator content and reaction time was investigated. After curing the synthesized epoxy monomer with the diamine, the properties of the cured resin were studied by differential scanning calorimetry, dynamic mechanical analysis, and thermogravimetric analyzer. Results demonstrate that the cured resin has good shape fixity, good shape recovery, and satisfactory thermal stability despite the presence of heteroatoms. This bio-based epoxy resin shows great potential to be used as a candidate for shape memory material. Considering the bio-based feedstock and environmentally friendly synthetic process, a "green + green" strategy to prepare thermosetting resins with advanced properties is provided in this paper.

1. Introduction

Polymers derived from renewable resources have been gaining great interest partially due to increasing concern about the depletion of fossil reserves and greenhouse gas emissions. Up to now, a wide range of natural and bio-based polymers, such as starch, [?] cellulose, [?] lignin, [?] polylactic acid (PLA), [?] and polyhydroxyalkanoates (PHA) [?] as well as bio-based polyethylene [?] derived from sugar cane have been developed as alternatives to petroleum-based polymeric materials. Compared with the rapid and successful commercialization of some bio-based thermoplastics, research on bio-based thermosetting resins has just begun and very limited products have been reported.

In the last two decades, the most popular bio-based epoxy resins might be those derived from plant oils. However, the long aliphatic chain and low reactivity of epoxy groups usually lead to poorly crosslinked materials with unsatisfied mechanical or thermal properties, for instance low glass transition temperature (T_g). [?, ?] In order to develop bio-based thermosets with promising properties, a large quantity of bio-based chemicals possessing stiff ring structures or more reactive groups, such as rosin acid, [?] diphenolic acid, [?] tannin acid, [?, ?] itaconic acid, [?, ?] glucose, [?] eugenol, [?, ?] furan, [?] and isosorbide [?] have been employed as starting materials for bio-based thermoset synthesis. For example, Liu et al. developed a series of epoxy resins and epoxy curing agents from rosin acid, and their thermal or mechanical properties were better than or similar to their petroleum-based counterparts. [?, ?] Ma et al. synthesized epoxies from itaconic acid (IA), and the multiple functional groups ensured them good mechanical properties. [?, ?] Anthony et al. prepared epoxy monomers from diphenolic acid as bio-based alternatives to diglycidyl ether of bisphenol A (DGEBA) with controlled properties. Wang and co-workers reported a novel eugenol-based epoxy possessing good intrinsic flame retardancy, low smoke production, and excellent mechanical properties. [?] Apparently, more and more bio-based epoxies with satisfied mechanical and thermal properties have been reported. However, compared with traditional petroleum-based thermosetting resins, bio-based ones with unique functionalities such as shape memory, UV resistance, and flame retardancy have seldom been reported. [?]

Shape memory polymers (SMP) are stimuli-sensitive materials that can be deformed and fixed in a temporary shape and then recover their permanent shape when exposed to a suitable stimulus, such as temperature, light, electricity, pH, and so on. [?, ?] They have been used extensively as sensors, smart adhesives, actuators, and self-deployable medical devices. Due to their biocompatibility and expected biodegradability as well as public concern about sustainable development, a large quantity of bio-based plastics with good shape memory properties has been developed. [?, ?] However, there is hardly any literature information about bio-based thermosetting resins with good shape memory properties.

Isosorbide is a by-product of the starch industry obtained by the reduction of D-glucose. Due to its huge annual production capacity and specific chemical structure, isosorbide is a competitive feedstock for biopolymers. So far, some polymers and resins derived from isosorbide have been synthesized and their overall properties evaluated. [?, ?] As we know, molecular design plays a key role in manipulating the shape memory properties of materials. The stiffness of polymer chains and their crosslink density have a significant impact on T_g. [?, ?] Meanwhile, they also influence the shape fixity, shape recovery, and recovery speed of SMPs. Therefore, a suitable molecular structure is necessary for better shape memory properties. Considering the characteristic structure of isosorbide, it has an alicyclic dissymmetry structure composed of two cis-fused V-shaped tetrahydrofuran rings, which means that bond length and bond angle might be changed with temperature or external force field. [?] Therefore, it might be possible for us to design and synthesize an excellent SMP containing isosorbide blocks.

In this study, the epoxy monomer (ISE) and curing agent (ISA) derived from isosorbide were synthesized (Scheme 1). The microwave-assisted thiol-ene reaction was employed to synthesize the curing agent ISA. The effect of reaction parameters such as initiator concentration and reaction time on the yield of ISA was carefully investigated. After the ISE was cured with ISA, the almost fully bio-based epoxy resin was obtained and its thermal, mechanical, and shape memory behaviors such as dynamic mechanical properties, shape fixity, and shape recovery were investigated. The results in this study provide new insight into designing and developing bio-based epoxy with functionalization, especially shape memory properties.

2. Experimental Section

2.1 Materials

Isosorbide with food-grade purity was purchased from Rizhao Lishide Chemical Co., Ltd. Allyl bromide, cysteamine hydrochloride, and meta-chloroperbenzoic acid with 75% purity were all purchased from Aladdin Reagent, China. Methylene chloride (DCM), 1,4-dioxane, methanol, sodium hydroxide (NaOH), anhydrous sodium carbonate (Na_2CO_3), sodium bisulfite (Na_2SO_4), magnesium sulfate ($MgSO_4$), Tween-80, and ammonium persulfate ($(NH_4)_2S_2O_8$) were bought from Shanghai Hushi Limited Company.

2.2 Preparation of Diallyl Isosorbide

Into a 500 mL three-necked round-bottom flask equipped with a mechanical stirrer, 58.4 g (0.4 mol) of isosorbide together with 106.5 g (0.88 mol) of allyl bromide were added. The mixture was heated to 65 °C and maintained at this temperature for 10 min. Then 35.2 g (0.88 mol) of sodium hydroxide dissolved in 100 mL distilled water was added dropwise. After the reaction was conducted at 65 °C for another 5 h, the mixture was cooled to room temperature and 200 mL dichloromethane was added under vigorous stirring. Then it was kept stable for 10 min and the upper organic layer was separated. The residual water in the organic phase was removed by anhydrous $MgSO_4$, after which the dry organic solution was concentrated in a rotary evaporator. Finally, the target product diallyl isosorbide with a weight of 84 g was obtained and the total yield was calculated to be 94%.

Spectral Data: ^{1}H-NMR: 5.83 (m, 2H, CH_2CH), 5.20 (d, 2H, CH_2CH), 5.10 (d, 2H, CH_2CH), 4.6 (t, 1H, CH), 4.43 (d, 1H, CH), 4.1 (d, 1H, CHO), 4.0-3.8 (m, 8H, CH_2O, OCH_2), 3.5 (t, 1H, CHO). FT-IR (cm^{-1}): 3018 ($C{=}CH_2$), 2984 and 2945 (CH_2), 1649 (C=C), 1454, 1384, and 1349 (CH), 1290 (C-O), 1093 and 1008 (C-O-C), 991 ($C{=}CH_2$).

2.3 Synthesis of Isosorbide-Based Epoxy Monomer (ISE)

Into a three-necked round-bottom flask, 184 g of meta-chloroperbenzoic acid was dissolved in 300 mL DCM via mechanical stirring. Then 84 g of the above diallyl isosorbide dissolved in 100 mL DCM was added slowly into the reaction over a period of one hour. After the reaction was conducted at room temperature for 12 h, the precipitate was removed via filtration. The filtrate was washed with 300 mL of 10% Na_2SO_4 solution followed by saturated Na_2CO_3 solution. After drying with anhydrous magnesium sulfate, the dichloromethane was removed by rotary evaporator. The obtained crude product was dissolved in 500 mL methanol before being cooled to -5 °C and kept at this temperature for 5 h. Finally, the solid precipitate was removed via filtration and the methanol in the filtrate was evaporated off to obtain the target product, isosorbide-based epoxy monomer, weighing 54.1 g (yield 56%).

Spectral Data: ^{1}H-NMR (ppm): 4.6 (t, 1H, CH-), 4.4 (d, 1H, CH), 4.1-3.7 (m, 6H, OCH_2), 3.3 (m, 2H, CHO), 3.1 (m, 2H, CH_2O), 2.7 (m, 2H, CH_2O), 2.5 (m, 2H, CH_2O). FT-IR (cm^{-1}): 2957 and 2893 (CH_2), 1251 and 918 (epoxy), 1100 (C-O).

2.4 Synthesis of Isosorbide-Based Diamine (ISA)

2.22 g of diallyl isosorbide, 2.27 g of cysteamine hydrochloride, 0.004 g of Tween-80 together with the predetermined amount of $(NH_4)_2S_2O_8$ were dissolved in 20 mL water in a three-necked round-bottom flask. The reaction was performed in a microwave-accelerated reaction system (Multiwave 3000, Anton Paar) with the temperature controlled by an infrared temperature sensor. Irradiation was carried out for times ranging from 1 to 24 h and the temperature was locked at 90 °C. After the reaction was finished, the mixture was extracted by DCM three times and the organic layers were collected before drying with anhydrous $MgSO_4$. Finally, the DCM was evaporated off and the target product was obtained.

Spectral Data: ^{1}H-NMR (ppm): 4.6 (t, 1H, CH), 4.4 (d, 1H, CH), 3.9-3.6 (m, 6H, OCH_2), 3.5 (t, 4H, CH_2NH_2), 2.8 (m, 4H, CH_2SCH_2), 2.5 (m, 8H, CH_2SCH_2), 1.8 (m, 4H, CH_2), 1.4 (s, 4H, NH_2). FT-IR (cm^{-1}): 3345 (N-H), 2931 and 2883 (CH_2), 1653 (NH_2), 1318 (C-N), 1098 (C-O), 1020 (C-S).

2.5 Curing of the Isosorbide Epoxy Network

ISE and ISA at a stoichiometric proportion were stirred together until a homogeneous mixture was formed before being degassed in a vacuum oven at room temperature for at least 30 min. Then the gas-free mixture was poured into a mold sprayed with mold-release agent and cured at 80 °C for 3 h and 120 °C for 2 h to obtain a completely cured resin. The cured resins were removed from the mold carefully and used for property investigation.

Characterization Methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Bruker AVANCE spectrometer (^{1}H at 300 MHz, ^{13}C at 75.47 MHz) with $CDCl_3$ as the solvent. Chemical shifts were referenced to the peak of residual $CHCl_3$ at 7.26 ppm for ^{1}H-NMR and 77 ppm for ^{13}C-NMR. The epoxy value of the product was determined by titration of sample dissolved in HCl/dioxane solution with KOH ethanol solution according to PN87/C-89085/13, using phenolphthalein as an indicator.

Differential scanning calorimetry (DSC) analyses were carried out using a Mettler Toledo Star 1 apparatus. Cured resin weighing about 6 mg was heated to 100 °C and held there for 5 min to eliminate any thermal history. Then it was cooled to -60 °C at a cooling rate of 100 °C min^{-1} followed by heating again to 100 °C at a rate of 10 °C min^{-1}. The glass transition temperature was obtained from the peak temperature of the differential curve of the second heating curve for the cured epoxy resins.

Dynamic mechanical analysis (DMA) was performed using a Q800 DMA from TA Instruments equipped with a tension fixture. Controlled heating and cooling were achieved using a GCA cooling system with liquid nitrogen. The experiment was performed at a frequency of 1 Hz and a heating rate of 3 °C min^{-1} from -30 to 150 °C.

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/DSC1 Thermogravimetric Analyzer (METTLER TOLEDO, Switzerland). The sample was heated from 50 to 800 °C with a heating rate of 10 °C min^{-1}.

Thermomechanical cycle experiments were also performed on a TA DMA Q800 machine to investigate the shape memory properties of the cured resin. Prior to deformation, the sample with dimensions of 10.0 mm × 4.0 mm × 0.7 mm was heated to 60 °C and equilibrated at this temperature for 10 min. In step 1, the sample was stretched to a predetermined tensile strain value of 5% at a rate of 0.1 N min^{-1} (deformation). In step 2, the sample was cooled to 0 °C with a cooling rate of 3 °C min^{-1} and maintained at this temperature for 5 min (cooling). In step 3, the force applied to the sample was unloaded to the preloaded value (0.005 N) at a rate of 0.1 N min^{-1}, followed by an additional 5 min isothermal step to ensure shape fixing at 0 °C (unloading and shape fixing). In step 4, the sample was reheated at a rate of 3 °C min^{-1} to 60 °C and then held there for 10 min to recover any residual strain (recovery). This four-step thermomechanical cycle was repeated three times for each sample.

In the deformation process, the strain of the sample increased from ε_0 to ε_m. Upon unloading, part of the strain $(\varepsilon_m(N) - \varepsilon_u(N))$ was recovered, leaving an unloading strain $(\varepsilon_u(N))$. The recovery process left a permanent strain $(\varepsilon_p(N))$. Shape fixity (R_f) and shape recovery (R_r) are defined as follows:

3. Results and Discussion

3.1 Synthesis of Isosorbide-Based Epoxy Monomer (ISE)

According to literature information, isosorbide can be converted into epoxy resins via two strategies. [?] However, when isosorbide was reacted with epichlorohydrin, the product was a mixture of different oligomers with varied epoxy values, not an epoxy monomer with a specific structure, and it was almost impossible to conduct separation. Additionally, neither mechanical property nor thermal stability of the cured mixed oligomers was satisfied. [?] In contrast, isosorbide diglycidyl ether prepared via epoxidation of diallyl isosorbide is a highly pure monomer. After curing with amine or anhydride, a highly crosslinked network could be obtained. In this study, the epoxidation route was employed and the isosorbide-based epoxy monomer (ISE) with a specific chemical structure was obtained via epoxidation of diallyl isosorbide by meta-chloroperbenzoic acid.

Figure 1 [Figure 1: see original paper] shows the ^{1}H-NMR spectrum of the resulting ISE, and the characteristic peaks were clearly identified. The signals ranging from 3.3 to 4.6 ppm corresponded to protons attached to the isosorbide ring. The signals centered at 3.1 ppm were assigned to the Hc and Hc of the glycidyl group, and the peaks at 2.7 and 2.5 ppm were related to Ha, Ha , Hb, and Hb , respectively. At the same time, its epoxy value was determined to be 0.75 by titration, which is in accordance with the theoretical value of 0.79. These results indicate that the pure monomer of ISE was synthesized successfully.

3.2 Synthesis of Isosorbide-Based Diamine (ISA)

With the rapid progress in click-chemistry, a large quantity of quantitative and regioselective reactions have been developed. Due to its tolerance of water and oxygen as well as the simple and efficient process, click-chemistry has been considered to have great potential in the chemical industry. As we know, thermal initiation is the traditional method to conduct a free radical reaction, and chain transfer reactions or other by-products are usually inevitable. In recent literature, cysteamine was often used to functionalize biomass via radical thiol-ene addition reaction, and side reactions could be controlled or restrained. [?] However, in order to ensure higher yield, the thiol-ene addition reaction has to be conducted in organic solution because of the solubility problem of organic reagents such as mercaptan and olefin. [?] In this study, the thiol-ene reaction in aqueous condition was developed for the synthesis of ISA. Unlike other mercaptans, cysteamine hydrochloride is easily soluble in water and its chemical structure is similar to a surfactant, which can conveniently promote the water solubility of organic reagents. Hence, the thiol-ene coupling of cysteamine and diallyl isosorbide could be finished in aqueous condition. As described in the Experimental Section (Section 2.4), microwave irradiation was also employed here to accelerate this reaction, [**?**] and a small amount of Tween-80 was added to enhance the solubility of diallyl isosorbide. [**?**] In addition, the water-soluble initiator $(NH_4)_2S_2O_8$, as an alternative to AIBN, was used in our experiment.

In order to optimize the reaction conditions, the effect of initiator concentration and reaction time on the conversion of thiol-ene coupling was studied. The reaction process was monitored via periodic sample detection. Figure 2 [Figure 2: see original paper] shows the ^{1}H-NMR spectra of the reaction mixture at different reaction times. It was easy to notice that at the beginning of the reaction, the signals at 5.1-5.2 and 5.8 ppm related to protons attached to the double bond of diallyl isosorbide were very strong. With the reaction proceeding, these signals became smaller and completely disappeared when the reaction was conducted for 6 h. Additionally, newly appeared characteristic peaks at 1.7 and 3.4 ppm representing the thiol-ene coupling reaction were detected, and they became stronger with increasing reaction time.

Table 1 shows the conversion of thiol-ene reaction under varied initiator concentration and different reaction time. Apparently, higher initiator concentration and longer reaction time resulted in higher conversion. However, when the initiator concentration was increased to 3.5%, the increase in conversion slowed down. In our experiment, 3.5% initiator together with a reaction time of 6 h was selected as the optimal condition for ISA synthesis.

Figure 3 [Figure 3: see original paper] shows the NMR spectrum of the synthesized ISA. In Figure 3a, the multiple peaks in the range of 3.7-4.6 ppm corresponded to protons attached to the isosorbide ring. The signals at 3.5 and 1.7 ppm were related to He, He , Hd, and Hd , and the peaks centered at 2.5 ppm were assigned to Hb, Hb , Hc, and Hc , which are close to the sulfur atom. Figure 3b shows the ^{13}C-NMR spectra of ISA, and all characteristic peaks were also assigned accordingly. These results demonstrated that the target compound ISA was synthesized successfully via thiol-ene coupling reaction in aqueous condition.

3.3 Thermal Properties of the Cured Epoxy

As far as shape memory epoxy resin is concerned, when the temperature is below T_g, it will be fixed into a temporary shape. When heated above T_g without stress, the covalently crosslinked networks will lead the polymer chains to their equilibrium conformation. Therefore, the shape transition temperature of epoxy resin has a close tie with its T_g. [**?**, **?**] After curing the synthesized ISE with ISA, its T_g was determined to be 34.4 °C using DSC. According to the

DMA result (Figure 4 [Figure 4: see original paper]), the T_g value should be 37 °C. This was reasonable and means that the cured resin has a relatively lower shape transition temperature.

Generally speaking, when the storage modulus of resin demonstrates two orders of magnitude difference before and after passing the glass transition temperature, it has the potential to be used as shape memory material. [**?**] Based on Figure 4, it was obvious that when the temperature was below 20 °C, the storage modulus of the isosorbide-based epoxy was over 3000 MPa. This would provide the resin enough strength to hold its temporary shape—in other words, it might have good shape fixity. When the cured resin turned from glass state to rubber state with increasing temperature, its storage modulus decreased quickly to about 10 MPa, which could ensure the resin experienced no permanent deformation after unloading at higher temperature. In addition, the crosslink density (ν_e) of the cured systems could be calculated by the following equation derived from the theory of rubber elasticity:

$$\nu_e = \frac{E'}{3RT}$$

where E' is the storage modulus after T_g in the rubbery plateau region (E' at the temperature of T_g + 40 K at which all crosslinked networks were in a rubbery state was chosen in this study), R is the gas constant, and T is the absolute temperature. The crosslink density (ν_e) was calculated to be 1.2×10^3 mol m^{-3}, which was high enough to ensure satisfied mechanical strength. After all, according to the DMA results, the isosorbide-based epoxy demonstrated its potential to be used as a shape memory material.

3.4 Shape Memory Cycle Test

In order to investigate the shape memory properties of the cured resins in detail, cyclic thermomechanical experiments were performed on a DMA machine, and the four-step procedure was schematized in Figure 5 [Figure 5: see original paper]. The calculated shape fixity ratio (R_f) and shape recovery ratio (R_r) in different cycles are listed in Table 2 . It was notable that the cured resin showed a constant R_f of about 97% during the three cycles. As for R_r, the value was only 81% in the first cycle, but it increased to near 100% in the second and third cycles. The reason might be that there was internal stress remaining in the specimen after the curing reaction. When a heating-stretching-cooling cycle was applied, the molecular chain segments could be equilibrated adequately and the internal stress was released completely. Only after that could the inherent R_r of about 100% be demonstrated. This indicated good shape memory performance. In addition, we should note that all curves representing the three thermomechanical cycles were almost overlapped in Figure 5 [Figure 5: see original paper], which meant that the shape memory behaviors remained quite constant and repeatable after several cycles. [**?**, **?**, **?**]

As shown in Figure 6 [Figure 6: see original paper], the spiral shape at 60 °C was stretched into a temporary linear shape and then quenched to 0 °C. When the stretched specimen was immersed in a water bath at 60 °C again, it changed into the original spiral shape in less than 4 s, which indicated fast shape recovery speed.

3.5 Thermal Degradation Behavior

Bio-based materials always contain heteroatoms such as oxygen, nitrogen, and sulfur, and thus they usually show relatively lower thermal degradation temperature. [**?**] Figure 7 [Figure 7: see original paper] shows the TGA curves of the cured isosorbide-based epoxy resin. As can be seen, there was no obvious thermal decomposition observed below 300 °C, and 5% weight loss occurred at 306 °C. The isosorbide ring structure contains two oxygen atoms, and additionally the sulfur atom was introduced into the cured system via thiol-ene reaction. However, the oxygen atoms were confined in the closed five-member rings, and together with the high crosslink density of the cured resin, this might be the reason for the acceptable thermal stability.

4. Conclusions

Isosorbide-based diamine (ISA) was synthesized via microwave-assisted thiol-ene coupling reaction in aqueous media. The effect of initiator content and reaction time on ISA yield was investigated, and the optimal reaction condition was determined to be 3.5% $(NH_4)_2S_2O_8$ initiator together with a reaction time of 6 h. In addition, the isosorbide-based epoxy monomer (ISE) was also prepared via the epoxidation strategy. The cured resin demonstrated good shape memory properties in terms of near 100% shape recovery ratio, 97% shape fixity ratio, constant thermomechanical cyclic behaviors, and fast shape recovery speed. It is possible for us to design and synthesize bio-based epoxy resin with good shape memory properties from renewable resources.

Acknowledgements: J.D. contributed equally to this work. The authors are grateful for the financial support from the National Natural Science Foundation of China (NSFC Nos. 51473180 and 51373194), Youth Innovation Promotion Association of the Chinese Academy of Sciences (2012229), and Natural Sciences Foundation of Ningbo City (No. 2014A610110).

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.