

Thermal analysis characterization of isosorbide-containing thermosets

Isosorbide epoxy as BPA replacement for thermosets industry

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Abstract Sugar-based new monomers, polymers, and low molar mass additives have emerged as an exciting topic on green chemistry research, due to the worldwide focus on sustainable material. Isosorbide and its isomers, as “Generally Recognized as Safe” GRAS materials, possess unique stereochemistry and molecular geometry suitable for making cost-effective chemicals and polymers. With growing awareness of bisphenol A (BPA) as a xenoestrogen, isosorbide and its isomers holding the remarkable chemical properties and attractive price can be attached to glycidyl ether to make crosslinkable epoxy resin monomers with similar properties to BPA diglycidyl ether. By adding the hydrophobic functional group into the backbone of isosorbide epoxy or adjusting the amount and type of crosslinker, the mechanical properties and the water uptake ratios (from <1 to >50 wt%) of the isosorbide-derived epoxies could be optimized for different applications. The high water uptake epoxy with controllable biodegradation rate could be used as a drug delivery system or extracellular matrix for biomedical applications while the low water uptake epoxy with strong mechanical properties could be used for can coatings, bone cements, and other industrial additives and adhesives. The chemical structures and properties of the synthesized epoxy monomers and polymers were characterized by DSC, TG, and ^1H NMR.

Keywords BPA replacement · Isosorbide · Epoxy · Hydrophobic · Hydrophilic · Bio-based thermoset

Introduction

There is a growing importance to develop green materials from renewable resources that can relieve the widespread dependence on fossil fuels [1–5]. The urgency of replacing petroleum-based chemicals come from the fact that the depletion of petroleum reserves could happen in the next 50 years [6–8]. As a result, a dramatic increase in the price of the material based on the fossil fuels could lead to a series of materials from renewable resources that are considered expensive today to become attractive [9–12]. In the EU alone, annual consumption of bisphenol A (BPA) which is a petroleum-based compound was estimated at approximately 640,000 tones (640×10^6 kg) per year [13]. BPA is widely used in thermosets and thermoplastics. BPA-based epoxies are manufactured for plastic lining of cans used for food, polycarbonate baby bottles, and tableware; white dental fillings; and sealants [14]. The growing global production of BPA not only puts the burden on finite petroleum source but also causes detrimental effects in the environment [15, 16]. A low level of BPA has been found to possess “xenoestrogen” effects where BPA appears to mimic the female hormone estrogen to disrupt the chemical messenger system in the human and animal bodies [17–19]. The consumer attack, retail bans, and regulatory examination have sounded the alarm bells on BPA for its alleged health impacts. The growing environmental consciousness necessitates the bio-derived replacement of BPA in the near future. As one type of material derived from agricultural feedstock, isosorbide and its isomers—isoridide and isomannide hold the promising property to be used as “green” alternatives to BPA [20, 21]. Isosorbide and its isomers are dihydroxyethers made by dehydrating hexitols which are polyhydric alcohols derived from hexose sugars by reduction, chiefly glucose, mannose, and idose [22–24].

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Since isosorbide is classified by the Food and Drug Administration as a “General Recognized As Safe” GRAS material and can be made readily available, it is a safe and renewable building block for many applications including thermoplastics, thermosets, and specialty chemicals [25–30]. Its rigid structure and special molecular geometry provide its opportunity to replace BPA without the endocrine disrupting effect [31]. Multiple isosorbide-based epoxies have been developed to demonstrate its versatile functionalities in many different applications.

Experimental

Materials and methods

Isosorbide was obtained from the Iowa Corn Promotion Board; allyl bromide, *meta*-chloroperbenzoic acid, epichlorohydrin, sodium hydroxide, and all other organic chemicals including catalyst were all obtained from Sigma-Aldrich.

BRUKER ARX 300 MHz NMR was used for ^1H NMR characterization of all compounds.

The epoxy equivalent of the monomer was measured according to ASTM D1652-04.

The DSC curves were obtained in a TA Q100 instrument using aluminum crucibles with about 5 mg of samples, under nitrogen atmosphere (40 mL min^{-1}). An empty aluminum pan was used as reference for DSC characterization.

Synthesis of isosorbide diglycidyl ether

The isosorbide diglycidyl ether was prepared as shown in Fig. 1 [32]. Diallyl isosorbide ether was prepared by a Williamson ether reaction by heating the isosorbide with allyl bromide in sodium hydroxide solution. Freshly prepared unpurified diallyl isosorbide was treated with the *meta*-chloroperbenzoic acid in methylene chloride to generate isosorbide diglycidyl ether as shown in Fig. 1. The isosorbide diglycidyl ether with the epoxide equivalent mass of 129, which is defined as the total molecular mass divided by number of epoxy group, indicates that the two hydroxyl groups of isosorbide are linked with two glycidyl ethers.

Synthesis of bisisosorbide triglycidyl ether

The bis-isosorbide triglycidyl ether was prepared by heating the isosorbide with 50 % sodium hydroxide solution and a large excess of epichlorohydrin, which was used to azeotrope away the water. Two equivalents of isosorbide react with three molecules of epichlorohydrin to form the epoxide dimer as Fig. 2 shows [33]. The bis-isosorbide triglycidyl ether with epoxide equivalent mass of 223

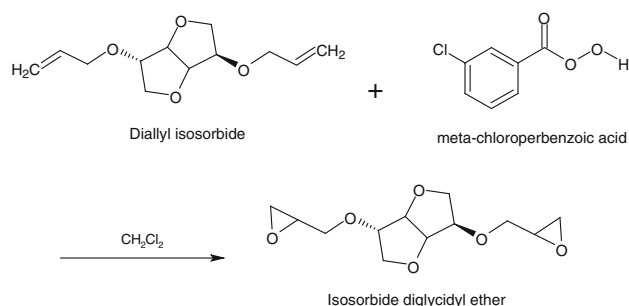


Fig. 1 Preparation of isosorbide diglycidyl ether

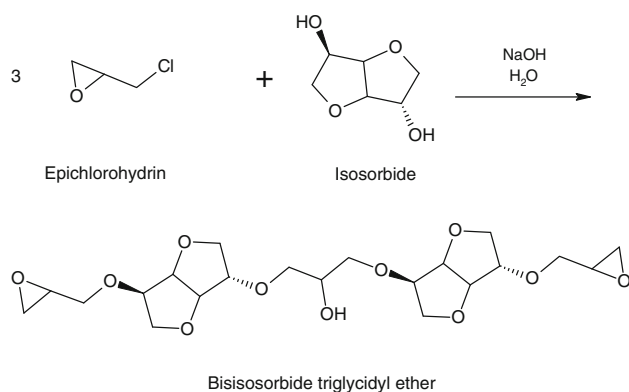


Fig. 2 Preparation of bis-isosorbide triglycidyl ether

corresponding to 446 of molecular mass of monomer, indicates a dimeric structure with two isosorbide units joined with a 2-hydroxy-1,3-propane diether link and capped with glycidyl ether units.

Synthesis of isosorbide bis(glycidyl benzoate) “IsoBGB”

Three variants of isosorbide bis(glycidyl benzoate)s including isosorbide bis(4-glycidyl benzoate), isosorbide bis(3-glycidyl benzoate), and isosorbide bis(2-glycidyl benzoate), also referred as IsoB4GB, IsoB3GB, and IsoB2GB, respectively, were prepared by reacting two equivalents of allyloxybenzoyl chloride with isosorbide followed by epoxidation with *meta*-chloroperbenzoic acid as shown in Fig. 3. Taking isosorbide bis(4-glycidyl benzoate) as an example, the esterification reaction was run in a 500 mL 3-neck round bottom flask with a magnetic stirrer. A 50 mL Kontes “Bantam–WareTM” pressure-equalizing (PE) tap funnel with a nitrogen inlet tube was fitted into its neck. A bubbler tube was connected to the 2nd neck to measure the nitrogen flow and a thermometer was set in the third neck to measure the temperature of the flask. In order to control the reaction temperature, the whole system was placed in an ice bath. After the flask was charged with 21.9 g of isosorbide and 200 mL dry pyridine, 58.95 g of

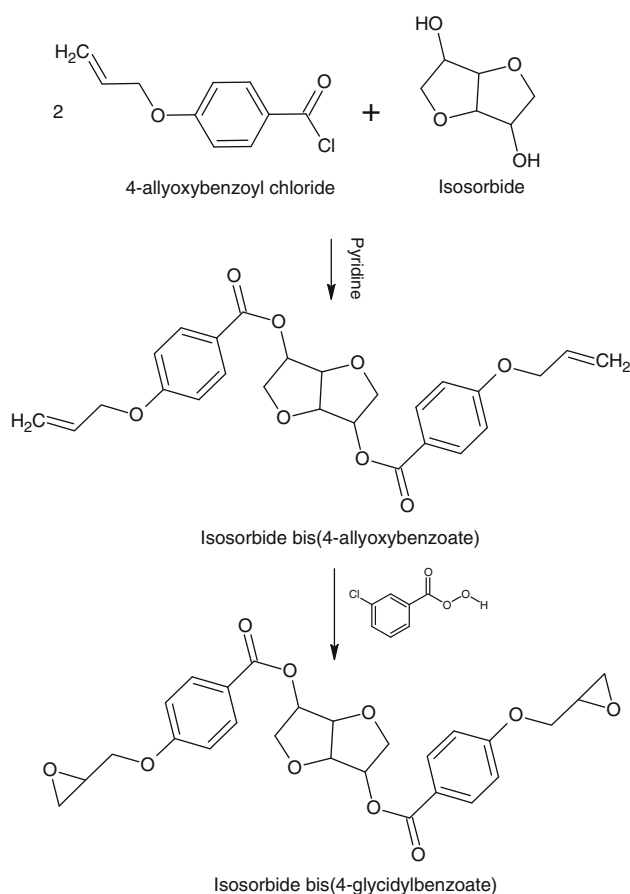


Fig. 3 Preparation of isosorbide bis(4-glycidyl benzoate)

4-allyloxybenzoyl chloride in 150 mL dichloromethane (DCM) was added slowly into the flask through the PE funnel. The solution immediately started to form a white solid. In order to keep the reaction proceeding steadily, the flask temperature was kept below 5 °C. After running overnight, some brown solid was formed in the flask. To neutralize unreacted pyridine, the reaction mixture was poured into a beaker containing 200 mL concentrated HCl and 250 mL de-ionized water. The mixture was separated in a 1,000 mL Squibb funnel. The aqueous phase was washed with 100 mL DCM three times to extract any traces of the organic-soluble products. The DCM layer was again shaken once with 200 mL sodium bicarbonate, 200 mL brine solution, and once with 200 mL de-ionized water. Anhydrous MgSO_4 was added to the DCM solution and the mixture was left to dry 3 h in the freezer. After that, the solution was filtered through a Buchner funnel with #4, 12 cm filter paper. The filtrate was taken down on a Büchi Rotovap™ to get rid of the DCM. The crude product was white solid weighing 68.4 g (97.8 % theoretical yield). Freshly prepared unpurified diallyl isosorbide was recrystallized from methanol and treated with the meta-chloroperoxybenzoic acid in DCM to generate IsoB4GB.

Crosslinked isosorbide-derived epoxide

The synthesized isosorbide epoxies were cured with different crosslinkers, namely (a) aliphatic amine–Jeffamine™ T403; (b) high molecular mass polyamine–Versamid® 140; (c) EPIKURE™ Curing Agent 3300 containing isophorone diamine; and (d) anhydride curing agent methyl-5-norbornene-2,3-dicarboxylic anhydride (NMA) with benzyl dimethyl amine (BDMA) as catalyst. The curing procedures were varied corresponding to the different curing agent as shown in Table 1.

Results and discussion

Characterization of glycidyl ether derivatives of isosorbide as high water uptake epoxy resins

Both glycidyl ether derivatives of isosorbide showed their strong affinity to water, in which isosorbide functions like a cyclized polyethylene glycol and it is chemically linked with different ratio of glycidyl ether. Since isosorbide is fairly hygroscopic and water soluble, one liter of water can dissolve 8 kg of isosorbide [34]. When isosorbide diglycidyl ether and bisisosorbide triglycidyl ether were cured with a water-soluble aliphatic polyether tri-amine, Jeffamine™ T403, the significant depression of T_g was observed for these epoxies down to 48 °C compared with BPA epoxies of 92 °C. After submerging these two cured epoxies in water for a few hours, due to the polymer hydrolysis and stress caused by the water expansion, both epoxies burst and fell apart into small pieces like burst drug release system. As isosorbide diglycidyl ether, bisisosorbide triglycidyl ether, and Jeffamine™ T403 are water soluble, different hydrogels derived from isosorbide can be formulated with variety of hydration levels as extracellular matrices for many biomedical applications. Isosorbide diglycidyl ether and bis-isosorbide triglycidyl ether themselves can also be used as “green” crosslinkers for different bio-composites.

When both epoxides were cured with a cycloaliphatic diamine, EPIKURE™ 3300, and soaked in water at RT for 6 day, the water uptake ratio of cured isosorbide diglycidyl ether was lower at 34.4 wt% compared with that of cured bis-isosorbide triglycidyl ether at 53.6 wt%. The lower moisture pickup property of isosorbide diglycidyl ether

Table 1 Curing schedule for different curing agents

Curing Agent	Curing Procedure
Jeffamine™ T403	80 °C for 6 h, 125 °C for 3 h
Versamid™ 140	80 °C for 6 h
EPIKURE™ 3300	80 °C for 6 h, 150 °C for 3 h
NMA + BDMA	80 °C for 6 h, 170 °C for 3 h

comes from the two facts: (1) Bis-isosorbide triglycidyl ether with a center hydroxide group showed higher affinity to water and (2) isosorbide diglycidyl ether offers almost twice the epoxy group content for curing compared with bis-isosorbide triglycidyl ether. The more epoxide content provides the higher crosslinking density therefore the higher T_g and the lower moisture pickup property.

When bis-isosorbide triglycidyl ether was cured with anhydride curing agent NMA with BDMA as catalyst, the material showed high T_g at 119 °C but strong affinity to water. The dried epoxies were treated with three media, air, distilled water, and phosphate buffer solution (PBS) for different period of time. The dramatic drop of T_g and tensile modulus of NMA-cured epoxies in water and PBS conditions demonstrate that water is the main effect for the degradation of the isosorbide glycidyl ethers as shown in Figs. 4 and 5.

Meanwhile, since the T_g did not change much at first 2 weeks for all three conditions but change significantly at 6 weeks in water and PBS condition, it inferred that the degradation happened from the outer surface of the epoxy, then penetrated through the bulk of the specimen. The structural change on the sample surface can distinctly affect its mechanical property as shown in Fig. 5. Because degradation of isosorbide glycidyl ethers happened in both

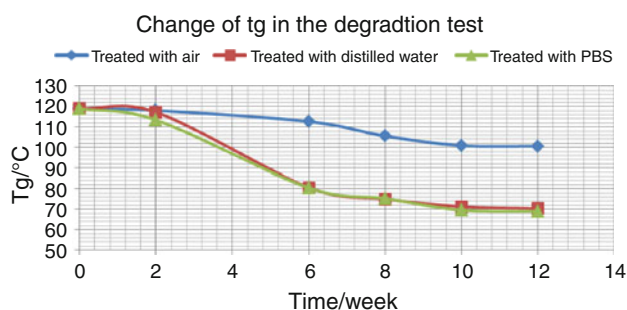


Fig. 4 Change of T_g in the degradation test (All the T_gs were measured after the specimens were dried entirely in the vacuum oven at 120 °C overnight)

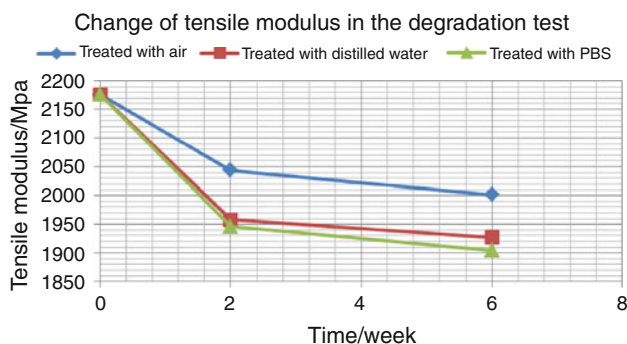


Fig. 5 Change of tensile modulus in the degradation test

chemical and physical way, where hydrolysis of polyesters and water swelling can both initiate formation of the small voids and cracks on the sample surface, the tensile modulus of water-treated epoxies dropped continuously when time lasted. With a slower degradation rate, NMA-cured Isosorbide glycidyl ethers can be used as continuous drug delivery system.

Characterization of isosorbide bis(glycidyl benzoate) (IsoBGB) as low water uptake epoxy resins

As discussed above, by direct glycidylation of isosorbide, useful epoxy monomers can be obtained for biodegradable products. However, they are not suitable as engineering thermoset, where higher T_g and lower water uptake are required. The isosorbide bis(glycidyl benzoate)s, also referred as IsoBGB, were designed to enhance the hydrophobicity of isosorbide-derived epoxies by aromatic modifying the backbones of the isosorbide epoxides and adding the steric hindrance between the hydroscopic isosorbide and glycidyl ethers. Three types of IsoBGB were developed with different steric profile: IsoB4GB, IsoB3GB, and IsoB2GB. The purity of the synthesized crystals was measured by DSC based on the Van't Hoff law of melting point depression of eutectic system. The purity of synthesized intermediate Isosorbide bis(2-allyloxybenzoate) was measured in DSC as an example shown in Fig. 6.

The final products, IsoB4GB, IsoB3GB, and IsoB2GB, as viscous liquids were characterized by NMR as shown in Fig. 7. The 1:1 integrated ratio of two protons around 5.4 ppm illustrates that the esterification reaction happened on both hydroxyl groups of isosorbide. The different chemical shift pattern of aromatic protons for three IsoBGBs was assigned between 7 and 8 ppm region to illustrate the different steric structure of three compounds. The disappearance of allylic protons at 6 ppm and appearance of epoxy protons at 2.5–4.5 ppm region were

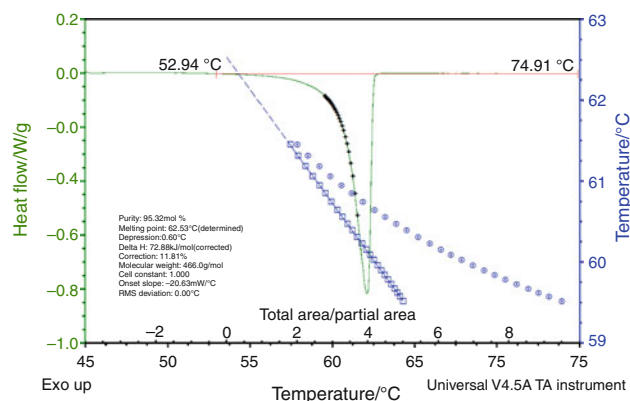


Fig. 6 Purity measurement of isosorbide bis(2-allyloxybenzoate) on DSC

used to follow the epoxidation reactions. Because the glycidyl ether group of IsoB2GB is on the *ortho*-position, its precursor isosorbide bis(2-allyloxy benzoate) was least approachable for epoxidation. More impurities were obtained in preparation of IsoB2GB. Its steric hindrance slowed down its epoxidation rate and epoxidation efficiency. In order to confirm the chemical structure of each IsoBGB, all protons were assigned on the NMR spectrum and the epoxy equivalent mass of IsoBGB was calculated at 249 g/epoxy based on its structure.

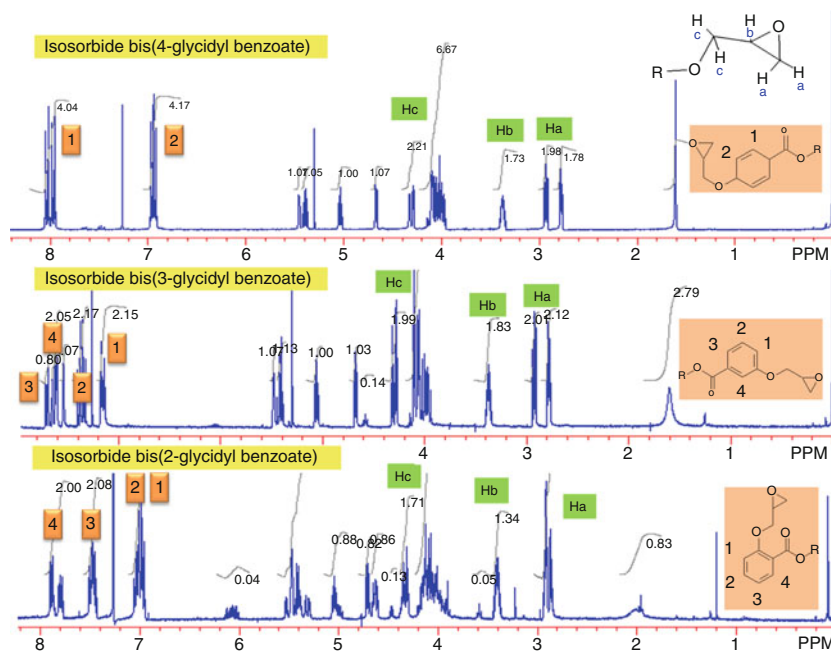
The prepared IsoBGBs were cured with 4 different commercial hardeners at various crosslinking conditions

(a) When IsoBGBs were cured with Jeffamine™ T403 (depicted in Fig. 8), one epoxy group can react with one amine hydrogen of hardener. Based on the ratio between the epoxide equivalent mass and amine-hydrogen equivalent mass of Jeffamine™ T403 (82.5 g/eq.), the theoretical stoichiometric ratio between the epoxy and hardener can be calculated as indicative information. Since both the epoxy and the hardener are not pure chemicals, the actual stoichiometric ratio needs to be found experimentally. Different mixing ratio of the epoxy and the hardener was tested to obtain the maximum crosslinking density and hence maximum Tg in the curing system. As shown in Fig. 9, with different amounts of incorporated curing agent, the Tg of Jeffamine™ T403-cured IsoBGBs can vary from 78 to 106 °C. Any excess hardeners with extra aliphatic amines and free epoxy monomer in the curing system can act as

plasticizers to depress the Tg of the epoxy resin. When the amount of epoxide group matched to the amine hydrogen of hardener, the maximum Tg was reached at 106.77 °C for IsoB4GB and 94.87 °C for IsoB3GB. Since IsoB2GB contains more impurity thus lower crosslinking density due to the steric hindrance of epoxidation, its Tg is much lower than IsoB4GB and IsoB3GB. IsoB4GB and IsoB3GB showed comparable and even higher Tgs when compared with Jeffamine™ T403-cured BPA epoxide (EPON828 with Tg at 92 °C). Adding the benzoyl group between isosorbide and glycidyl ether is efficient in modifying the backbone structure of isosorbide glycidyl ethers.

After soaking the cured IsoBGBs in water for a few days until saturation, the mass gain of the epoxy was measured and converted to water uptake ratio. Compared with bis-isosorbide triglycidyl ether with water uptake ratio of 35 wt% after a few hours of water storage, IsoBGBs showed significant improvement in hydrophobicity. IsoB3GB with maximum Tg showed the lowest water absorption ratio down to 0.55 wt%. It is already close to the water uptake ratio of Jeffamine™ T403-cured EPON 828 at 0.25–0.5 wt%. The increased water resistance emanates from the addition of hydrophobic aromatic moiety in the polymer chain and reduced intramolecular hydrogen bonding by putting the steric hindrance between hygroscopic isosorbide and glycidyl ether. Since both Tg and moisture pickup show similar dependence on the hardener concentration which highly relates to the

Fig. 7 NMR spectrum of IsoBGBs



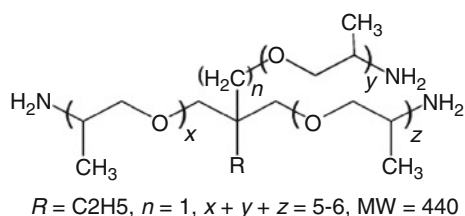


Fig. 8 Chemical structure of Jeffamine™ T403

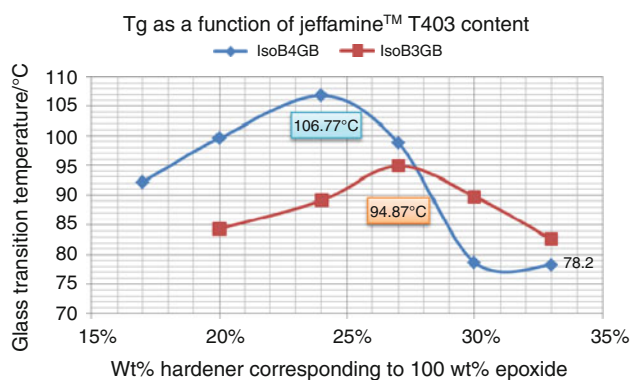


Fig. 9 Tg of Jeffamine™ T403-cured IsoBGBs as a function of hardener content

crosslinking density of epoxy, the higher crosslinking density of epoxy can lead to higher Tg thus lower water absorption property of isosorbide epoxy resins as shown in Fig. 10.

- (b) When IsoBGBs were cured with a polyfunctional aliphatic amine, Versamid® 140 (depicted in Fig. 11), the ratio of polyamide to epoxy becomes less critical as the average H-equivalent could be significantly different due to the polymer development (molecular mass distribution) and the purity of commercial amine.

With variation of hardener concentration, Tg of Versamid® 140-cured IsoBGBs remains around 95 °C for IsoB4GB and 85 °C for IsoB3GB as shown in Fig. 12.

The 10 °C difference of Tg between IsoB4GB and IsoB3GB is likely related with their different steric profile of epoxide group on the benzene ring. The stronger steric hindrance for epoxidation leading to the lower efficiency of crosslinking can result in the lower crosslinking density of epoxy resin. With lower crosslinking density thus lower Tg, IsoB3GB showed slightly higher water uptake up to 5 wt%, and slower saturation as shown in Fig. 13.

- (c) When IsoBGBs were cured with EPIKURE™ 3300, a very low viscosity, light-colored cycloaliphatic amine curing agent containing isophorone diamine

Tg and water uptake ratio as function of jeffamine™ T403/IsoBGB ratio

	1	2	3	
IsoB4GB	33	30	27	Ratio/wt%
	78.2	78.8	98.83	Tg /°C
IsoB4GB	33	30	27	Ratio /wt%
	82.6	89.75	94.87	Tg /°C
IsoB2GB	35	33	30	Ratio /wt%
	60.28	62.86	69.77	Tg /°C

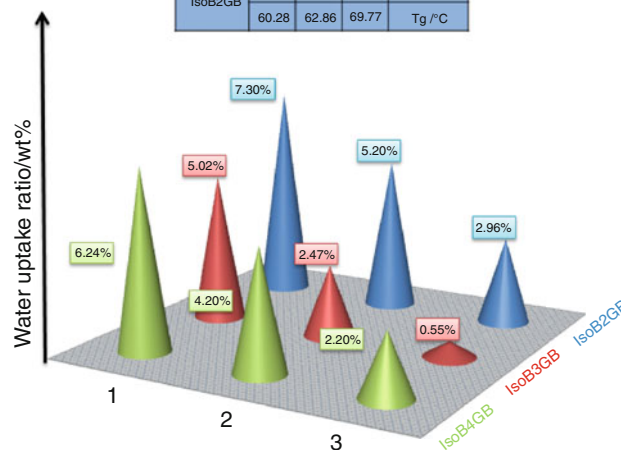


Fig. 10 Tg and water uptake property of Jeffamine™ T403-cured IsoBGBs as function of hardener content

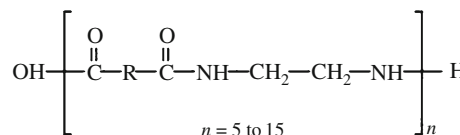


Fig. 11 Chemical structure of Versamid® 140

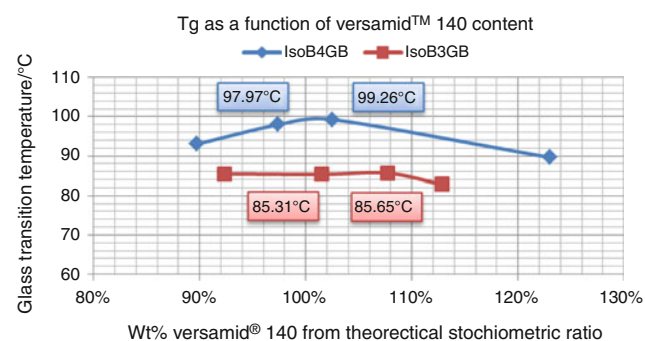


Fig. 12 Tg of Versamid® 140-cured IsoBGBs as a function of hardener content

(depicted in Fig. 14), the rigid structure of isophorone diamine stiffens the polymer chain thus raising Tg and increasing the solvent resistance of crosslinked epoxide.

Since the crosslinking reaction with EPIKURE™ 3300 is sensitive to the hardeners concentration, different mixing ratios between epoxide and

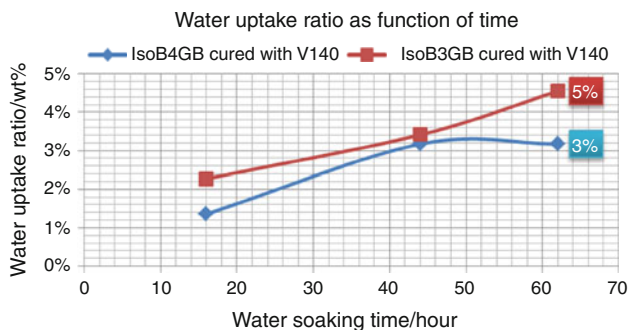


Fig. 13 Water uptake property of Versamid® 140-cured IsoBGBs as function of time

Fig. 14 Chemical structure of isophorone diamine

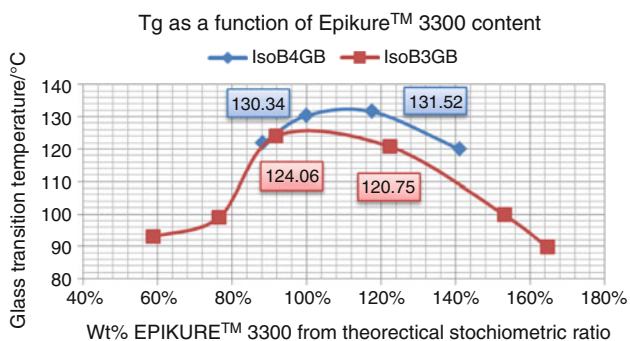
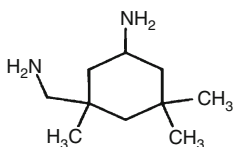


Fig. 15 Tg of EPIKURE™ 3300-cured IsoBGBs as a function of hardener content

crosslinker were tested using theoretical H-equivalent of EPIKURE™ 3300 at 42.6 as indicative information. Tg of EPIKURE™ 3300-cured IsoBGBs was raised to 131 °C for IsoB4GB and 124 °C for IsoB3GB as shown in Fig. 15.

With less steric hindrance, IsoB4GB showed higher maximum Tg and lower water absorption (2.11 wt%) when compared with IsoB3GB (5.76 wt%) with the same Tg as shown in Fig. 16.

- (d) When IsoBGBs were cured with more hydrophobic anhydride curing agent NMA with catalyst BDMA (depicted in Fig. 17), Tg of the cured IsoBGBs were raised to 136 °C for IsoB4GB, 116 °C for IsoB3GB, and 100 °C for IsoB2GB. The maximum crosslinking density was reached when 100 % stoichiometric ratio of hardener was used, as calculated based on the ratio

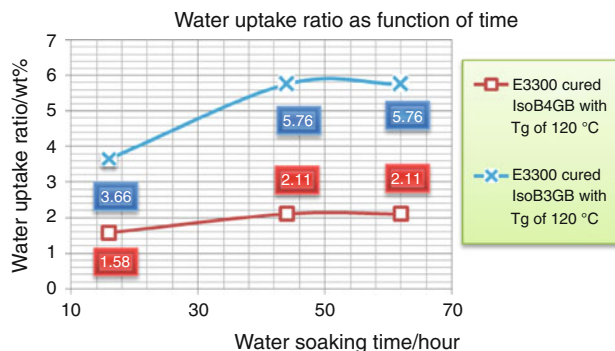


Fig. 16 Water uptake property of EPIKURE™ 3300-cured IsoBGBs as function of time

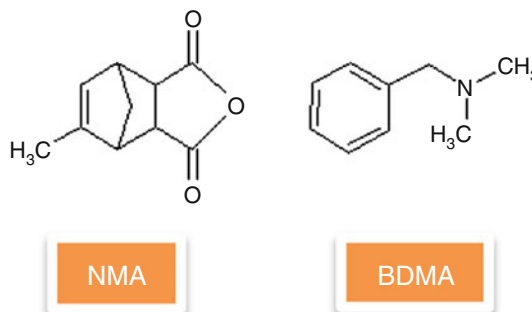


Fig. 17 Chemical structure of NMA and BDMA

of epoxy equivalent mass of IsoBGBs at 249 g/epoxy and amine-hydrogen equivalent mass of NMA at 178. By changing the position of glycidyl ether group from *para*-substitution to *meta*- to *ortho*-substitution on the benzene ring, both epoxidation rate and crosslinking efficiency of epoxide follows the order:

$$\text{IsoB4GB} > \text{IsoB3GB} > \text{IsoB2GB}$$

in which IsoB2GB possessed the most amount of unreacted allyoxy benzoate ester as impurity therefore it had the lowest Tg, while IsoB4GB and IsoB3GB presented the higher Tg as shown in Fig. 18. With lower crosslinking density, IsoB2GB also showed the higher water uptake ratio at 4.36 wt% compared to IsoB3GB with water uptake ratio of 1.96 wt% and IsoB4GB with water uptake ratio of 1.28 wt% as shown in Fig. 19.

Since water sensitivity of isosorbide-based epoxy is a function of the local chemical environment, the aromatic-modified isosorbide epoxy with increased hydrophobic moiety and decreased intermolecular hydrogen bonding showed significant reduction of water absorption in all four curing systems. Through modifying the backbone of isosorbide epoxy with hydrophobic functional group and adding the steric hindrance between the hydroscopic

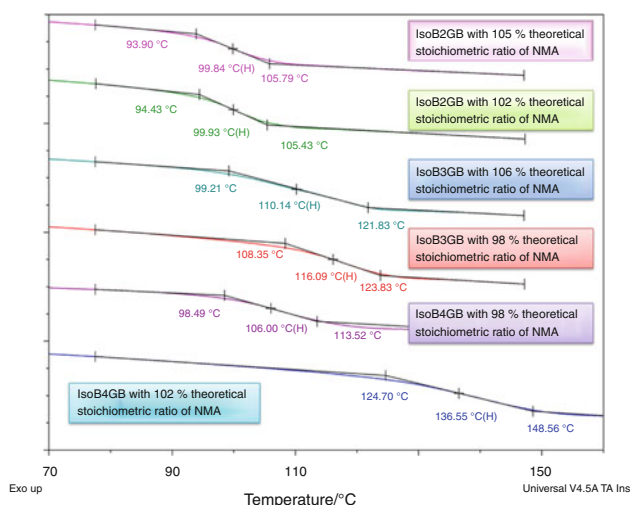


Fig. 18 T_g of NMA-cured IsoBGBs

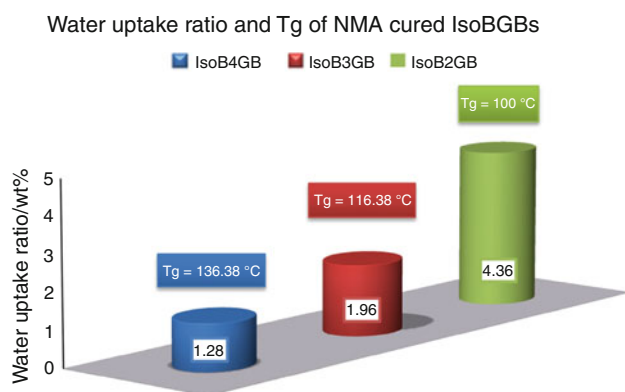


Fig. 19 Water uptake property of NMA-cured IsoBGBs

isorbide and glycidyl ethers, aromatic or aliphatic spacers can be used as useful backbone modifiers to manipulate the property of isorborne-derived epoxies. IsoBGB in this work, as a good example, represents a promising potential as hydrophobic building block to replace “xenoestrogen” BPA in many different end-uses, notably in the food packaging and surface coating markets.

Meanwhile, because crosslinking density also plays an important role in determination of epoxy performance, different types and amounts of hardeners need to be matched to each epoxy system to improve the thermal and solvent resistance of epoxies. In the case of IsoBGBs, since both the type and concentration of hardeners and steric environment of epoxides showed their ability to influence the crosslinking density, understanding the composition–structure–property–performance relationship in IsoBGB-based thermosets becomes more important in designing new sugar-based epoxides. Especially in case of isorborne and its

isomers, isorborne and isorbornide, possessing the unique built-in molecular geometry, chirality, and stereochemistry, a ubiquitous research platform is being created for sugar-based chemistry. As fundamental knowledge improves, more sugar-based thermosets can be developed with designable performance and strong potential for commercial success. As a renewable, eco-sustainable sugar compound, isorborne with controllable chemistry provides a price-competitive starting material for high volume production of bio-composites in the next generation thermoset industries.

Conclusions

Isorborne-based epoxies have been developed as “safe and renewable” alternatives to petroleum-based BPA epoxies. By changing the curing agent and the curing conditions, the water uptake ratio of isorborne-based epoxy could range from below 1% to above 50%. The controlling factors include crosslinking density, the chemistry of cross-linking agent, and the amount of free hydroxyl groups on the backbone of the epoxy. By adding the hydrophobic functional group into the backbone of isorborne epoxy or adjusting the amount and type of crosslinker, the mechanical properties and water uptake ratio of the isorborne-derived epoxy could be optimized for different applications. The high water uptake epoxy with controllable biodegradation rate could be used as a drug delivery system or extracellular matrix for biomedical applications while the low water uptake epoxy with strong mechanical properties could be used for can coatings, bone cements, and other industrial additives and adhesives.

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