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Synthesis and properties of isosorbide based epoxy resin

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ABSTRACT

Isosorbide based epoxy resin (IS-EPO) of epoxy number: 0.44 mol/100 g was synthesised in the one step reaction from 1,4:3,6-dianhydro-D-glucitol (isosorbide) and epichlorohydrin in the presence of concentrated aqueous NaOH. The product obtained was characterised by means of NMR, FT-IR and ESI MS spectroscopy. Compositions with typical hardeners were prepared and cured. The thermal and mechanical properties of the resulting materials were evaluated. Comparison with commercially available epoxy resin Epidian 5 shows relatively good mechanical performance of IS-EPO which makes isosorbide a promising candidate to replace bisphenol A (BPA).

1. Introduction

The epoxy resins are used in many industrial applications including coatings, adhesives or composites [1]. Curing process turns them into a solid material known for its good thermal stability and superb chemical resistance, as well as excellent mechanical properties [2]. Bisphenol A (BPA) is one of the most widely used compounds in the synthesis of epoxy resins [3]. This bicyclic aromatic molecule is responsible for numerous favourable properties of final material. Unfortunately BPA has an adverse influence on human health especially on endocrine system what was investigated through decades and confirmed in many works [4–12]. The epoxy resin production and processing plants are recognised as places of highest human exposure to BPA. Due to a leaching from thin film of can-coating composition the presence of Bisphenol A was detected in canned food [13].

Cyclic aliphatic diol harmless to human health, such as isosorbide may be eventually considered as a candidate to replace BPA. This bioderived and biodegradable diol is qualified by Food and Drug Administration as a "generally recognised as safe" (GRAS) [14]. It is produced by the double dehydratation of sorbitol obtained in two step process from starch.

Isosorbide – a V-shaped bicyclic diol is composed of two fused tetrahydrofuran (THF) rings with 120° angle between them. It comprises two non-equivalent hydroxyl groups: OH-2 (which is exo oriented with respect to the fused rings system) that is more available and OH-5 (endo-oriented) that forms an intramolecular hydrogen bond with the oxygen atom from the nearby THF ring (Scheme 1) [15].

The fused rings structure of this cycloaliphatic diol provides high stiffness of its molecule and thermal stability up to 270 °C [16]. Many isosorbide derivatives have already found an application in pharmaceutical industry and in cosmetics. Its structure and properties make this "green" material an interesting candidate for synthesis of numerous polymers like polyethers, polyesters, polyurethanes and polycarbonates [17]. Literature review reveals several attempts to obtain isosorbide based epoxy resins [18–23]. East et al. show the possibility to cure isosorbide based epoxy resins but characteristics of both resin and hardened material are insufficient to judge whether it is possible to replace BPA based epoxy resins or not [21].

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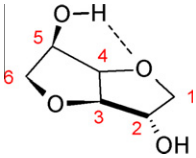


Scheme 1. Simplified structure of isosorbide showing the intramolecular hydrogen bond.

In this work a possibility to replace bisphenol A in the synthesis and application of epoxy resins with bioderived isosorbide was assessed. The resin obtained by etherification with epichlorhydrine in the presence of aqueous NaOH was characterised using complementary analytical methods (^{1}H and ^{13}C NMR, FT-IR, ESI-MS) and cured with use of typical hardeners. It was justifiable to make a comparison between obtained material and commercially available BPA based resin. In this work Epidian 5 as a reference resin was used. Subsequently mechanical properties and effects of exposition of cured samples to liquid media were investigated.

2. Experimental part

2.1. Materials

Following chemicals were used as received: isosorbide (IS, Aldrich, 98%); sodium hydroxide (NaOH, POCh); diglycidyl ether of bisphenol A (DEGBA) based low-molecular-weight epoxy resin Epidian 5 with epoxy number 0.51 mol/100 g, viscosity 25000 mPa s (in 25 °C) density: 1.18 g/cm^3 (Epi5, Organika-Sarzyna S.A.); triethylenetetraamine (hardner Z1, TETA, Organika-Sarzyna S.A.); isophoronediamine (IPHA, Acros); phthalic anhydride (PHA, PS PARK); tetrahydrophthalic anhydride (THPHA, Koch-Light Laboratories); acetone (POCh); ethyl acetate (Stanlab); hydrochloric acid 36% (Stanlab); ammonia solution 25% (POCh). Epichlorohydrin (Laborchemie Apolda) was purified before synthesis by distillation; fraction with b.p. 115 °C was collected.

2.2. Synthesis of isosorbide based epoxy resin

The synthesis was carried out in the same manner as described by East et al. [21]. A three-neck 1 l flask equipped with thermometer, efficient magnetic stirrer, pressure-equalizing tap funnel and inverted Dean Stark trap with the Liebig condenser was charged with isosorbide (100.0 g, 0.685 mol) and freshly distilled epichlorohydrin (633.6 g, 6.849 mol). The mixture was stirred and brought to a gentle reflux. Next, 50% aqueous NaOH (54.8 g, 1.370 mol) was added dropwise (5 drops per minute) with continuous water separation. After the addition of alkali solution was completed, the reaction was run for next 30 min to ensure that all water was removed. The resulting slurry mixture was filtered through a sintered funnel and the filtrate collected. Remaining precipitate was then washed several times with acetone. Both filtrates were concentrated on a rotary evaporator and combined together. Any residual volatile components were removed under reduced pressure. The product was yellow viscous liquid (165 g).

2.3. Characterisation of isosorbide based epoxy resin

The resin obtained was characterised by means of NMR, IR, ESI-MS spectroscopy and GPC technique.

NMR spectra were recorded with UNITY/INOVA (Varian) spectrometer operating at 300 MHz (^{1}H NMR) and at 75 MHz (^{13}C NMR). $CDCl_3$ and tetramethylsilane (TMS) were used as a solvent and internal standard, respectively.

The IR spectra were recorded with BIORAD FTS 175L spectrophotometer at room temperature after applying a thin film of the sample on a KBr disk.

ESI-MS analysis was carried out on the Finnigan MAT 95, double-focusing high resolution mass spectrometer with BE-geometry. Samples were dissolved in solvents mixture: $CHCl_3 + CH_3OH$ (1:1).

GPC analysis was performed using apparatus working at 45 °C with DMF as the eluent at flow rate of 1 ml/min. It was equipped with refractive index detector Δn = 2010 RI (WGE Dr. Bures), MALLS detector DAWN HELEOS (Wyatt Technology) and set of columns: PL GEL GUARD, PL GEL MIXT-C x2, PSS GRAM 100 Å.

The density of the product was determined using the liquid pyknometer in 25 °C according to PN-EN ISO 1183-1:2006.

The viscosity of the resin was measured at 20 °C with the Brookfield FUNGILAB VISCO STAR Plus L viscometer (spindle L4) according to PN-ISO 2555:1999.

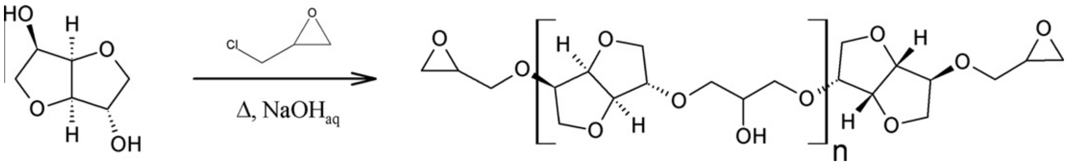
The epoxy value of the product was determined by titration of sample dissolved in HCl/dioxane solution, with ethanolic KOH solution according to PN87/C-89085/13. Phenolphthalein was used as an indicator.

2.4. Preparation and curing of epoxy resins compositions

Compositions of IS-EPO or Epidian 5 epoxy resins with selected curing agents were prepared. In case of aliphatic amine based hardeners both components of the composition were mixed at the room temperature while application of acid anhydrides needed resins to be preheated. Curing process was carried on in aluminium molds under conditions listed in Table 1. In case of amine hardeners samples were held in 80 °C for additional 24 h to ensure better curing. The life-time of the IS-EPO based composi-

Table 1
Curing conditions of the investigated resins.

Hardener	Amount of hardener [mol/ mol of epoxy gr.]	Curing temperature [°C]	Curing time [h]
Phthalic anhydride	0.85	150	12
Tetrahydrophthalic anhydride	0.85	150	12
Triethylenetetramine	0.17	25	24
Isophoronediamine	0.25	25	24



Scheme 2. Scheme of the synthesis of isosorbide based epoxy resin.

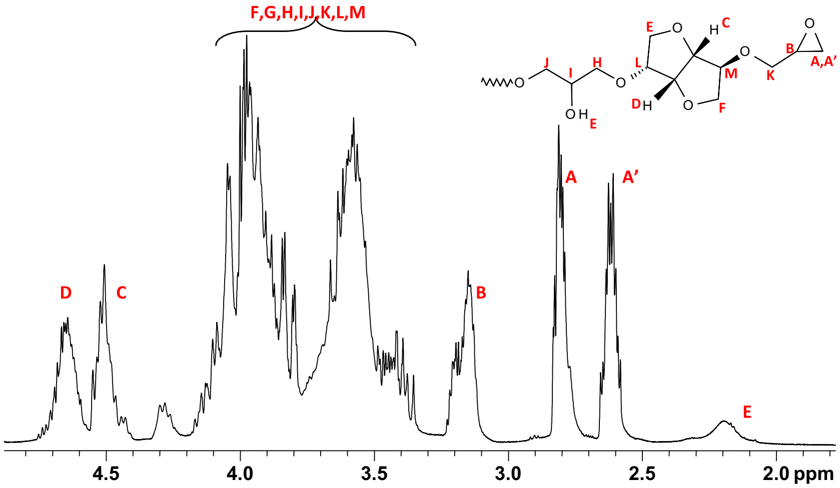


Fig. 1. 300 MHz ^{1}H NMR spectrum of IS-EPO (25 °C, CDCl$_3$).

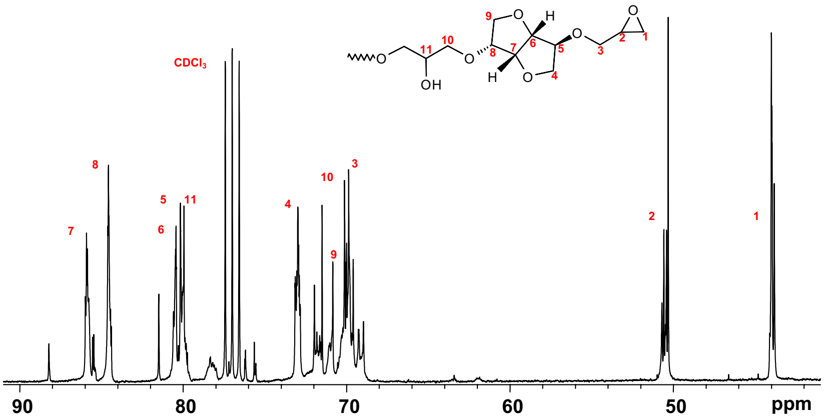


Fig. 2. 75 MHz ^{13}C NMR spectrum of IS-EPO (25 °C, CDCl$_3$).

tions was determined as the time passed until stirring of the reaction mixture became impossible.

2.5. Characterisation of cured epoxy resins

Mechanical properties of cured resins samples (beams and cylinders) were measured on Zwick 100N5A with extensometer in accordance with the following standards: PN-EN ISO 178:2006 (flexural properties) and PN-EN ISO 604:2006 (compressive properties).

Hardness was determined utilising the ball indentation method on Verstoffprüfmaschinen Leipzig 300/250 device following the PN-EN ISO 2039-1:2004 standard.

Impact strength was measured on the Dynstat Verstoffprüfmaschinen Leipzig 622/35 apparatus according to PN-EN ISO 79-2:2001.

DSC analysis of cured compositions was made using differential scanning calorimeter (METTLER-TOLEDO, DSC822e). Analyses were performed in temperature range from 0 to 250 °C, at a heating rate of 10 °C/min. Character-

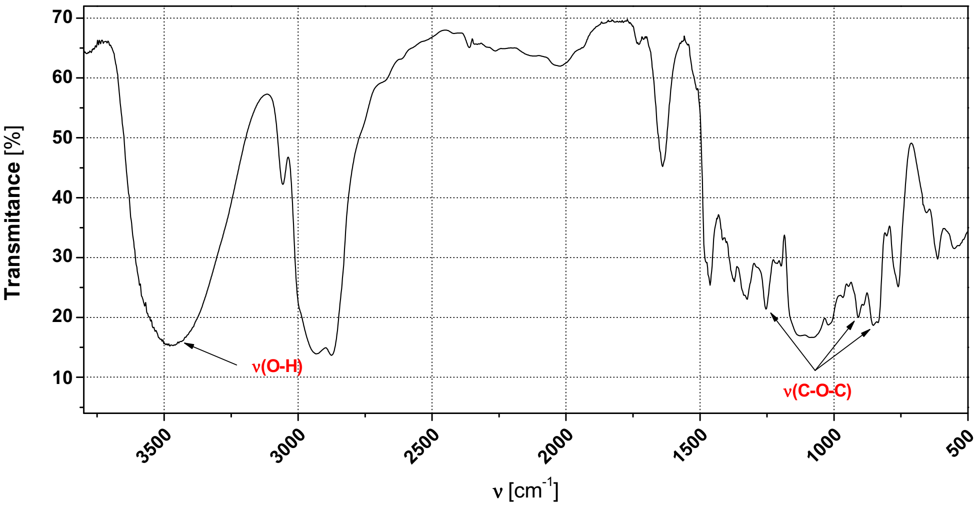


Fig. 3. FT-IR spectrum of IS-EPO.

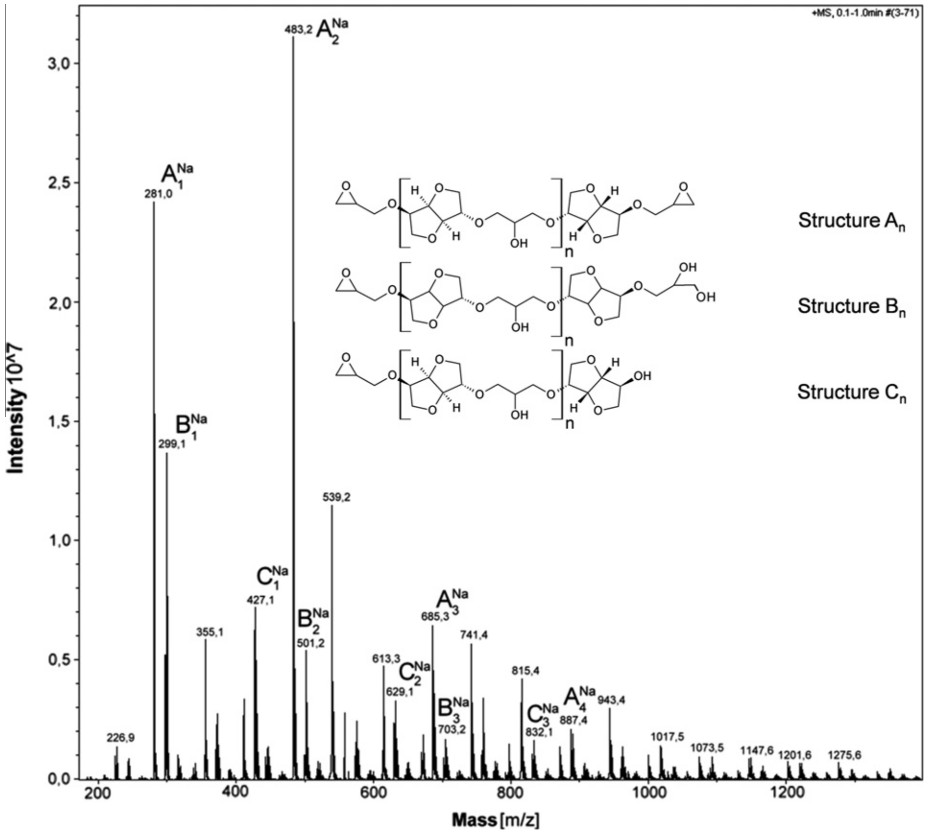


Fig. 4. ESI-MS spectrum of IS-EPO.

istic temperatures were determined from the first heating run.

The effects of immersion in liquid chemicals (i.e. HCl_{aq} 36%, NH_{3aq} 25%, acetone, ethyl acetate) and water sorption were determined by measuring changes in weight of disk-like samples immersed in selected liquids after 1 day and then, after 7 and 21 days. The investigations were made according to PN-EN ISO 175:2002.

3. Results and discussion

3.1. Characteristics of isosorbide based resin (IS-EPO)

The product of the reaction of isosorbide with an excess of epichlorohydrin in the presence of 50% aqueous NaOH (Scheme 2) was light yellow, viscous, water soluble liquid. Its density and kinematic viscosity at 20 °C were equal to

1.299 g/cm^3 and 60120 mPa s, respectively. Epoxy Number EN was equal to 0.44 mol/100 g, while for isosorbide diglycidyl ether it should be 0.77 mol/100 g. It means that reaction product contains also higher oligomers and/or compounds which are not terminated with two epoxy groups. ^{1}H and ^{13}C NMR spectra reveal the presence of expected diglycidyl ether of isosorbide.

In ^{1}H NMR spectra (Fig. 1) one can find three multiplet signals typical for glycidyl group protons: methylene protons A, A′ at $\delta \sim 2.62$ and 2.80 ppm and methine proton B at $\delta \sim 3.15$ ppm, as well as two broad signals at $\delta \sim 4.51$ ppm (C) and at $\delta \sim 4.64$ ppm (D) which can be assigned to methine protons in isosorbide. Broad signal at $\delta = 1.95–2.33$ ppm could be assigned to hydroxyl group of higher reaction products ($n \geqslant 1$ on the scheme 2) or products with hydroxyl group at the end of a molecule.

In ^{13}C NMR spectra (Fig. 2) three signals at $\delta = 44.01$ ppm, $\delta = 50.32$ ppm and at $\delta = 69.87$ ppm could be assigned to carbon atoms 1, 2 and 3 of the glycidyl group. The carbon atoms signals of isosorbide part of the reaction product(s) are at $\delta = 72.97$ ppm (4), 80.18 ppm (5), 80.44 ppm (6), 85.92 ppm (7), 84.58 ppm (8), 72.98 ppm (9). IR spectra (example see Fig. 3) of the reaction products confirm the presence of stretching vibration band of C–O–C in oxirane ring at $\nu = 1257$ cm^{-1}. Other vibration bands of C–O–C group at $\nu = 854$ and at 910 cm^{-1} can result from both isosorbide and glycidyl groups.

Table 2
Parameters of the curing process.

Curing agent	Curing temperature [°C]	Life-time [min]
Phtalic anhydride	120	14
Tetrahydrophtalic anhydride	115	37
Triethylenetetramine	25	38
Isophoronediamine	25	70

On ESI-MS spectra of IS-EPO (example shown at Fig. 4) three series of signals can be seen: one belonging to isosorbide diglycidyl ether and its homologues (series A$_n$), the second one belonging to isosorbide monoglycidyl ether terminated on one side with 2,3-dihydroxypropyl group and its homologues (B$_n$) and the third one belonging to isosorbide monoglycidyl ether and its homologues (C$_n$). From the intensity of particular signals one may conclude, that the main product of IS-EPO is a dimeric diepoxy resin A$_2$ composed of two isosorbide fragments ($n = 1$ at Scheme 2).

GPC analysis confirmed that in the resin IS-EPO there is more than one component (at least three low-molecular weight ones and some amount of higher-molecular weight product).

3.2. Curing of isosorbide epoxy resin and basic properties of cured ones

Practical application of epoxy resins needs their curing. In order to estimate the effect of replacing bisphenol A with isosorbide, epoxy resin based on isosorbide obtained in this work and commercial low-molecular weight,

Table 3
Selected mechanical properties of cured Epidian 5 and isosorbide based epoxy resin.

Composition	Flexural strength [MPa]	Flexural modulus [GPa]	Compression strenght [MPa]	Compression modulus [GPa]	Brinell hardness [MPa]	Izod impact strength [kJ/m^2]	Tg [°C]
Epidian 5/PHA	158.4	10.4	290.8	2.8	198.0	7.2	171
IS-EPO/PHA	225.5	17.4	254.1	2.1	202.4	30.9	108
Epidian 5/THPHA	27.9	9.8	122.2	2.5	209.4	4.1	172
IS-EPO/THPHA	100.5	15.1	88.8	2.2	214.3	2.9	95
Epidian 5/TETA	170.8	8.3	234.2	2.1	212.1	9.5	116
IS-EPO/TETA	228.3	5.5	311.6	2.1	193.8	20.8	49
Epidian 5/IPHA	175.4	10.4	193.9	2.3	231.2	13.5	141
IS-EPO/IPHA	158.5	14.6	318.1	2.0	205.7	33.8	73

Table 4
Chemical resistance and water absorption of cured Epidian 5 and isosorbide based epoxy resin.

Medium	Distilled water			36% HCl			25% NH$_3$			Ethyl acetate			Acetone		
	Weight increases [% w/w] after time [day]														
Composition	1	7	21	1	7	21	1	7	21	1	7	21	1	7	21
Epidian 5/PHA	0.4	0.8	0.9	0.1	0.0	0.0	6.9	15.9	20.2	1.5	9.1	16.2	0.1	0.3	0.4
IS-EPO/PHA	1.5	3.0	4.7	8.0	–	–	9.8	–	–	0.0	0.0	0.2	0.0	0.4	0.8
Epidian 5/THPHA	0.3	0.7	0.9	0.4	0.2	0.3	65.4	132.0	177.6	44.4	64.3	49.9	68.0	50.2	48.0
IS-EPO/THPHA	12.6	24.2	24.4	–	–	–	–	–	–	1.1	2.5	4.6	12.9	26.7	21.2
Epidian 5/TETA	0.3	0.8	1.1	1.2	2.3	5.3	0.4	0.8	1.1	0.2	0.3	0.2	0.2	0.6	1.7
IS-EPO/TETA	–	–	–	5.6	–	–	19.6	39.3	44.0	0.0	−0.1	0.1	0.1	0.2	0.2
Epidian 5/IPHA	0.2	0.5	0.7	1.0	2.5	3.2	0.2	0.8	0.8	1.6	11.2	21.2	0.0	0.8	0.9
IS-EPO/IPHA	25.1	41.7	42.1	–	–	–	10.2	27.4	31.1	0.0	0.0	0.3	0.2	1.0	2.3

bisphenol A based liquid epoxy resin Epidian 5 were cured with selected low and high temperature hardener and their basic properties have been measured and compared. Curing conditions (duration and temperature) as well as hardener active groups to epoxy ones molar ratios were the same for both resins.

Selected mechanical properties of cured resins, i.e. of IS-EPO and Epidian 5 shown in Table 3 appeared to be rather similar, for the former are sometimes even better.

The presence of two condensed furane rings in IS-EPO provides similar rigidity to the cured resin as the presence of phenylene rings in cured Epidian 5 resin. Impact strength of cured IS-EPO resins is usually better than that of cured Epidian 5 one. For IS-EPO–hardener compositions also life-time was determined. Results collected in Table 2 show that life-time is long enough for most of the practical applications.

Chemical resistance of cured resins was estimated by soaking the samples in selected liquids up to 21 days and controlling their appearance as well as weight increase. Exposition in distilled water reveals much higher hydrophilicity of IS-EPO in comparison with Epidian 5. Water sorption of the samples of the former was much higher than that of the latter and for the samples of IS-EPO cured with TETA even their disintegration was observed (Table 4).

4. Conclusions

The isosorbide based low molecular, liquid epoxy resin synthesised in this work according to known procedure is composed mainly of diglycidyl isosorbide ether and its dimeric analogue and contains some monoglycidyl ethers with free hydroxyl groups. They are partially responsible for relatively high hydrophilicity of this resin as well as for its cured compositions. High hydrophilicity is the reason of insufficient resistance to acidic and basic aqueous media. In the special case such as water-borne paints the solubility of the resin in water could be however an advantage. Hydrophilicity of cured compositions could be reduced by use of acid anhydride hardeners and their resistance to polar solvents is comparable or even better than that of cured bisphenol A based commercial resin. Results of measurements of basic mechanical properties of isosorbide based cured resin are comparable to those obtained for commercial bisphenol A based resin. It may be stated that at least for some applications non-toxic, bioderived isosorbide is real alternative to health uncertain, petroderived bisphenol A in synthesis of low-molecular, liquid epoxy resins.

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