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ORIGINAL PAPER

Synthesis and characterization of polyurethane rigid foams from polyether polyols with isosorbide as the bio-based starting agent

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Abstract

In this study, with the isosorbide as bio-based starting agent, a series of bio-based polyether polyols with different hydroxyl values were synthesized and used to prepare polyurethane rigid foams (PURF). The structures of as-synthesized polyols were studied by FT-IR and ^{1}H NMR methods. The thermal properties, mechanical properties, microscopic morphology, thermal conductivity and dimensional stability of PURF have been characterized by several physico-chemical and ASTM methods. The initial decomposition temperature $T_{5\%}$ and the maximum decomposition temperature T_{max} for PURF from isosorbide-based polyols with 458 mg KOH/g hydroxyl value are about 312 °C and 354 °C, improved 61 °C and 75 °C comparing with the PURF from 1,2-propanediol-based polyols. The maximum compressive strength of PURF from isosorbide-based polyols is 141 kPa, comparing with 118 kPa of PURF from 1,2-propanediol-based polyols. Meanwhile, the dimensional stability of PURF from isosorbide-based polyols has been improved twofold, and the water absorption was obviously reduced by 50%. All these results suggest that polyols of isosorbide-based starting agent should be promising feedstock for PURF with high performance.

Keywords Polyurethane rigid foam · Isosorbide · Mechanical properties · Thermal stability · Dimensional stability

Introduction

In view of resource utilization efficiency, cellular structure is a fundamental principle of nature in the construction of highly efficient materials [1]. For example, bone and teeth are the typical examples with cellular structure, which demonstrates extreme mechanical performance with minimal matter [2]. Therefore, many polymers, ceramic and metal foams have found important applications in a plenty of fields [3, 4]. Among these foams materials, polyurethane rigid foams (PURF) materials are the most important category due to their unique combination of material and processing characteristics. Polyurethanes, the greatest materials breakthrough in twentieth century, are the only class of polymers that display thermoplastic, thermoset and elastomeric behavior depending on their chemical and morphological makeup, which has been wildly used in insulation, noise control, coatings, adhesives, and lightweight structures [5, 6]. Moreover, polyurethanes could serve the requirement of lightweight structures acting as matrix materials or adhesives for composite, which would contribute to energy and resource efficiency improvement [7]. In such applications, high compression strength, high thermal properties and super dimensional stability at low temperature are the properties of prime importance.

Chemically, PURF are foamed by reacting isocyanates with polyols. Both of these substances, especially the type of polyols, play important roles in foam properties. Normally, the most common polyols used in PURF are prepared by reacting petroleum-based starting agents containing hydroxyl groups (-OH) or primary amine groups (-NH_2) with ethylene oxide (EO) or propylene oxide (PO) by oxirane ring-opening reaction with alkali hydroxide as catalyst [8–10]. Driven by the requirement of improving the resource efficiency and realizing the sustainable

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development, many significant efforts over the decades have been devoted to develop bio-based polyurethane with naturally vegetable oils as raw materials for polyols. Recently, renewable and bio-based resources have been successfully developed and a range of bio-based polyols have been synthesized for polyurethane products, such as coconut oil, natural rubber, rubber seed oil, lignin and soybean oil [11–15]. However, there are few reports on making PURF from bio-based polyols with isosorbide as the bio-based starting agent.

Isosorbide could be produced through catalytic dehydration of sorbitol, which are the hydrogenated products of widespread bio-renewable glucose. In our previous reports, solid acid catalysts have been developed to transform greenly sorbitol to isosorbide [16]. As the typical bio-based chemical, isosorbide possesses many unique characteristics such as rigid structure of V-shaped diol molecule, high thermal stability, biodegradability, renewability, solubility in water and non-toxicity, which could contribute many features to the polymer materials with isosorbide as the monomer [17]. Recently, isosorbide has been used to prepare polyesters, polyethers, polyurethane, polycarbonates, polyphosphonates and so on [18–22]. In Zhang' report, isosorbide has been used as co-monomer to increase the glass transition temperature T_g and thermal stability of polyesters such as PET and PBS, which could broaden the high-temperature applications of polyesters such as molded parts or packaging materials [10]. In these researches, the thermal stability and mechanical properties of polymers based on isosorbide have been improved, which could be induced by the rigid structure of isosorbide. Chen et al. have reported that the synthesis of stereochemically pure diisocyanates from succinic anhydride and isosorbide or isomannide, which could be used to synthesize polyurethane with unique characteristics such as low polydispersity, high thermal stability, and stereochemistry-dependent morphology [23].

Today, plenty of researches have been devoted into the improvement of the thermal stability, dimensional stability and mechanical properties of polyurethane, because these deficient properties have shown a huge stumbling block for its further application extensions. Therefore, any solution of these problems will extend their industrial application. In this paper, isosorbide was used as the starting agent to initiate the ring-opening polymerization of propene epoxide. The reaction process parameters were optimized to obtain various polyether polyols with different hydroxyl values, whose structure have been characterized by FT-IR and ^{1}H NMR. These polyether polyols with isosorbide as the starting agent were used to prepare PURF, and the foam morphology, structure and physical performances were studied by several experimental protocols. The effect of isosorbide structure on foams structure and performances was discussed.

Experimental

Material

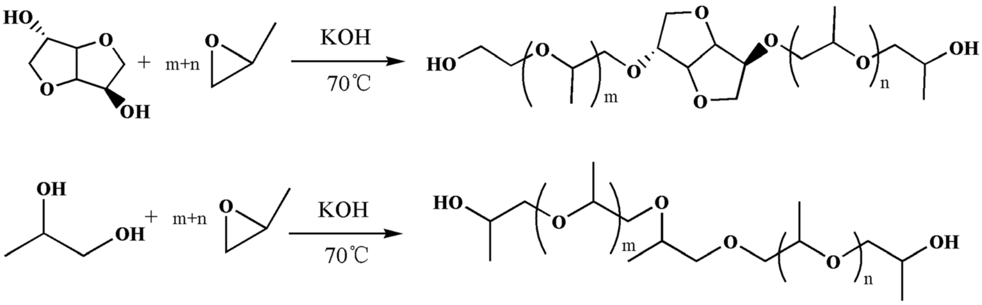
Isosorbide was obtained from Jinan Hongbaifeng industry and trade Co., Ltd. (Jinan, China). 1,2-epoxypropane (99%), 1,2-propanediol (99%), pyridine(98%), phthalic anhydride(99%) and hydrochloric acid (99%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). WANNATE, a polymeric diphenylmethane diisocyanate (MDI) with 30.5 wt% NCO, was obtained from Wanhua Chemical Group Co., Ltd. (Yantai, China). AK8818, a foam stabilizer, was obtained from Jiangsu Maysta Chemical Co., Ltd. (Nanjing, China). Stannous octoate (30%), potassium hydroxide (98%) and triethylenediamine hexahydrate (96%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). For all experiments, ultra-pure water with a resistivity of 18.2 mΩ·cm was used.

Methods

Synthesis of polyether polyols Polyether polyols were synthesized according to the modified methods reported by Frey [9]. In a typical process, isosorbide (29.2 g) and KOH (0.4 g) were weighted and transferred into a three-necked flask equipped with dropping funnel, thermometer and condenser pipe. The mixture was heated to melt isosorbide under stirring. At 70 °C, a certain amount of 1,2-epoxypropane was slowly introduced dropwise into the flask. The progress of the reaction was monitored by measuring hydroxyl value. When the desired hydroxyl value was obtained, stirring was stopped and the products were taken out and cooled to room temperature. The unreacted 1,2-epoxypropane was removed through rotary evaporation under vacuum. These polyols samples with different hydroxyl values were labeled as A, B, C, D and E, respectively. In order to comparing the effect of isosorbide, 1,2-propanediol with the same functionality was used to prepare polyether polyols and final PURF. The synthesis procedures were similar to the above process of polyols with isosorbide as the starting agent. The corresponding samples were labeled as a, b, c, d and e, respectively. The reaction diagram is depicted in Scheme 1.

Characterization of polyether polyols Fourier transforms infrared (FT-IR) spectra were collected on an infrared spectrometer (Nicolet, IS 5). The infrared spectra of solid samples were measured by the KBr tablet method, and that of the liquid samples were measured by painting method on KBr sheet. The infrared spectrum was recorded in the 4000 to 500 cm^{-1} range by accumulating 32 scans with the resolution of 4 cm^{-1}.

^{1}H NMR spectra were recorded on a Varian Inova spectrometer (400 MHz for ^{1}H NMR). Chemical shifts for ^{1}H spectra were referenced in ppm relative to tetramethylsilane



Scheme 1 Synthesis of polyether polyols with isosorbide and 1,2-propanediol as starting agents

with the solvent residual resonances as the internal standard ($CDCl_3$, δ 7.26 ppm).

The hydroxyl numbers of polyether polyols were determined by the titration method according to ASTM D4274–05. In a typical procedure, the polyether polyols were dissolved in phthalation reagent and were heated at 100 °C for 2 h. After cooling down to room temperature, the mixture was titrated by 0.5 mol/L NaOH solution with 1% phenolphthalein solution of pyridine as the indicator. The consumed volume of NaOH solution was used to calculate the hydroxyl value according to the corresponding formula.

The alkalinity correction of polyether polyols was determined by the titration protocol according to ASTM D4274–05. In a typical process, a certain amount of polyether polyols were mixed with redistilled pyridine and distilled water with 1% phenolphthalein solution of pyridine as the indicator. 0.1 mol /L HCl solution was used to titrate the above pink solution. The alkalinity correction was calculated according to the corresponding formula from the consumed volume of HCl solution.

The moisture content of polyether polyols was measured by the Karl Fischer method using a CBS-1A model moisture content meter. Each sample was measured three times and the reliable average moisture content was reported.

The viscosity of polyether polyols was measured at 25 °C with a viscometer (NDJ-8S). Each sample was measured five times and the reliable average viscosity was reported.

General procedure for synthesis of PURF The PURF from the as-synthesized polyether polyols were prepared according to the standard cup foam method (ASTM D7487–13). For all of PURF samples, the characteristic parameter R ([NCO]/[OH]) was 1.1. The other additives such as catalysts, foam stabilizer and foam agents were added according to the weight percentages listed in Table 1. The mixture was stirred with a propeller stirrer for 1 min at 1500 rpm to ensure a homogeneous mix, followed by addition of MDI to the mixture. It was mixed effectively for 10 s at 2000 rpm moving the cup slightly in the vertical plane to ensure adequate mixing. During the preparation, the foaming characteristics, such as the cream time, free rise time, string gel time and tack free time were determined using the stopwatch. The PURF samples were labeled as X-RF and x-RF, where X and x represents the letter similar to polyether polyols with different hydroxyl values.

Characterization of the prepared PURF The foam densities were calculated from the weight of foams with the specific volume. Six cubes pieces of 8 cm^3 were cut from three different foam batches and the reliable average density was reported.

The compressive strength was determined according to the method of ASTM D1621–10. The PURF samples were cut to meet the dimensional requirement of 30 mm × 30 mm × 50 mm. The rate of 2.5 mm/min was adopted. The compressive strength was expressed as the maximum applied force divided by the initial sample surface area.

The foam morphology was recorded by the low vacuum scanning electron microscopy (JEOL JSM-6510). Foams were cut into rectangular slices of 5 mm × 5 mm × 1 mm and the sample slices were sputter coated with gold.

The closed cell content was determined according to the method of ASTM D6226–05. The samples with dimensions of 25 mm × 25 mm × 25 mm were measured by the automatic true density analyzer (3H-2000TD, BeiShiDe Instrument).

The thermogravimetrical analyses (TGA) of the samples were measured according to the ASTM D3850–12 standard method. TGA was done using a thermal analyzer (Netzsch, STA409PC) by heating from room temperature to 800 °C at a heating rate of 10 °C/min under an air flux of 50 mL/min.

The apparent thermal conductivity was measured in accordance with ASTM Designation: C518–10 (2010). After

Table 1 Formula of additives for PURF

Additive	Percentage /% (Based on the mass of mixed polyols and MDI)
TEDA	0.2
SO	0.5
AK8818	1.5
H_2O	2

Table 2 Physico-Chemical characteristics of as-synthesized polyether polyols

Samples	Hydroxyl value (mg KOH/g)	Alkalinity correction (mg KOH/g)	Viscosity (Pa·s)	Moisture content (%)	Average molecular weight (g/mol)
A	457.75 ± 5.64	1.17 ± 0.08	13.79 ± 0.23	0.12 ± 0.02	247.63
B	397.06 ± 5.89	1.07 ± 0.06	13.54 ± 0.22	0.09 ± 0.01	286.45
C	358.18 ± 5.34	1.04 ± 0.05	12.82 ± 0.19	0.09 ± 0.01	317.09
D	256.03 ± 5.16	0.88 ± 0.03	11.77 ± 0.21	0.10 ± 0.01	441.47
E	160.83 ± 4.96	0.30 ± 0.01	10.71 ± 0.20	0.11 ± 0.02	698.93
a	464.96 ± 4.25	1.25 ± 0.10	3.26 ± 0.15	0.10 ± 0.02	243.01
b	393.92 ± 5.37	1.16 ± 0.07	3.05 ± 0.12	0.09 ± 0.01	285.89
c	350.55 ± 5.21	0.72 ± 0.06	2.87 ± 0.13	0.12 ± 0.02	321.28
d	258.77 ± 5.83	0.50 ± 0.06	2.09 ± 0.14	0.10 ± 0.01	421.37
e	162.72 ± 5.72	0.31 ± 0.01	1.67 ± 0.11	0.11 ± 0.02	699.02

curing at ambient temperature for 24–48 h, the sample (200 mm × 200 mm × 25 mm) was tested by a Fox 200 heat flow meter instrument (Laser Comp, Wakefield, Ma).

The dimensional stability tests were done according to the ASTM D2126–15. The samples with dimensions of 100 mm × 100 mm × 25 mm were firstly conditioned at 25 °C for 24 h, and then were transferred into the experimental chambers with the controlled temperature at 70 °C and − 25 °C for 24 h, respectively. The dimensional stability as volumetric swelling at 70 °C and volumetric shrinkage at −25 °C were measured, respectively (Table 2).

Water absorption was measured according to the ASTM D570–98. Foam samples with dimensions of 30 mm × 30 mm × 50 mm were immersed in a water bath at room temperature, the weight increase of the foams at different intervals was measured.

Results and discussion

Characterization of polyols

As shown in Scheme 1, polyether polyols based on isosorbide and 1,2-propanediol were synthesized through ring-opening polymerization of 1,2-epoxypropane with KOH as catalysts. The structure of as-synthesized polyether polyols has been characterized by FT-IR and ^{1}H NMR, and the corresponding results have been shown in Figs. 1 and 2. And their appearance was shown in Fig. 3.

As shown in Fig. 1, the strong absorption at 3460 cm^{-1} could be ascribed to the -O-H stretching vibration. The result demonstrates that hydroxyl groups exist in the as-synthesized polyether polyols. The strong absorption between 2887 and 2977 cm^{-1} could be attributed to the -C-H stretching vibration

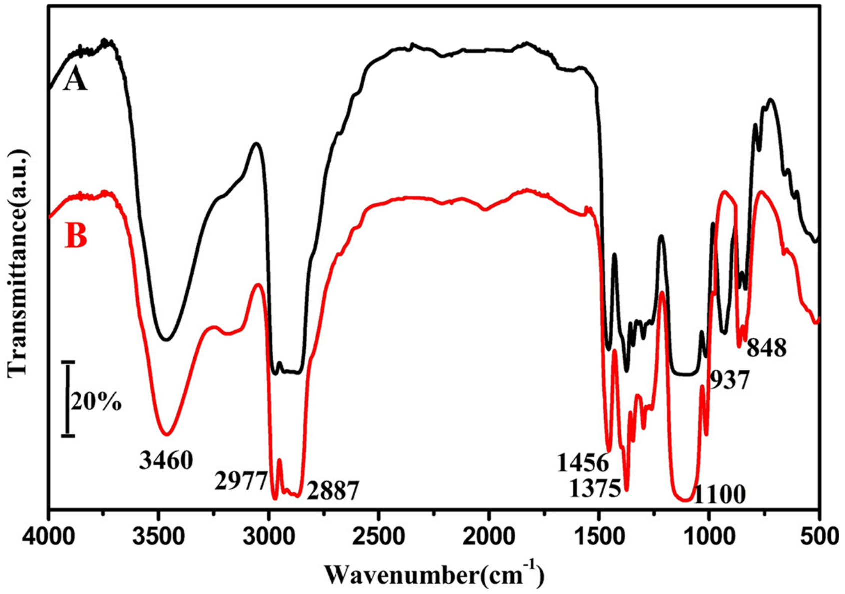


Fig. 1 FT-IR of as-synthesized polyether polyols. **a** polyols with isosorbide as the starting agent; **b** polyols with 1,2-propanediol as the starting agent

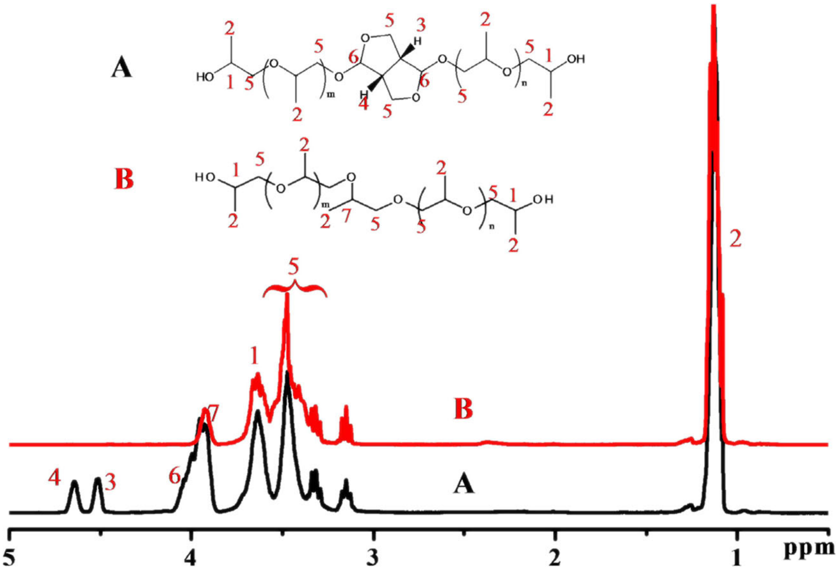


Fig. 2 ^{1}H NMR spectra of the as-synthesized polyether polyols. **a** polyols with isosorbide as the starting agent; **b** polyols with 1,2-propanediol as the starting agent

of saturated -CH_3, -CH_2 or -CH structural blocks. The absorption at 1456 cm^{-1} could be induced by the bending and twisting vibration of -CH_2 groups, and the absorption at 1375 cm^{-1} represents the bending vibration of -CH_3 and -CH groups. The absorption at 1100 cm^{-1} could be attributed to the bending vibration of -C-O-C-, while the absorption at 937 cm^{-1} could be ascribed to the bending vibration of cyclic ether bond in isosorbide, which is the typical absorption peak of isosorbide. These results indicate that the as-synthesized polyether polyols contain isosorbide blocks.

^{1}H NMR spectra shown in Fig. 2 demonstrate the structure of as-synthesized polyether polyols. The chemical shift at δ 1.12 could be ascribed to the protons of -CH_3 functional groups, while the chemical shift at δ 3.16–3.46 could be attributed to the protons 5 belonging to -O-CH_2- groups [24]. The chemical shift δ 3.63 could be ascribed to the proton 1 of methylene attached to hydroxyl -CH-OH [13], and the chemical shift δ 3.94, 3.91 could be attributed to the protons 6, 7 of -C-CH-O- groups in the as-synthesized polyether polyols. It is noteworthy that the polyether polyols with isosorbide as the starting agent show two signals at δ 4.51 and δ 4.64 ppm, which could be attributed to the protons 3 and 4 the isosorbide ring [25].

The hydroxyl value is the typical parameter for polyols, which could influence the mechanical and thermal performance of polyurethane. Therefore, the polyether polyols with different hydroxyl values have been synthesized through adjusting the ratio of 1,2-epoxypropane to isosorbide. Accordingly, the polyether polyols with the similar hydroxyl values have also been prepared with 1,2-propanediol as the

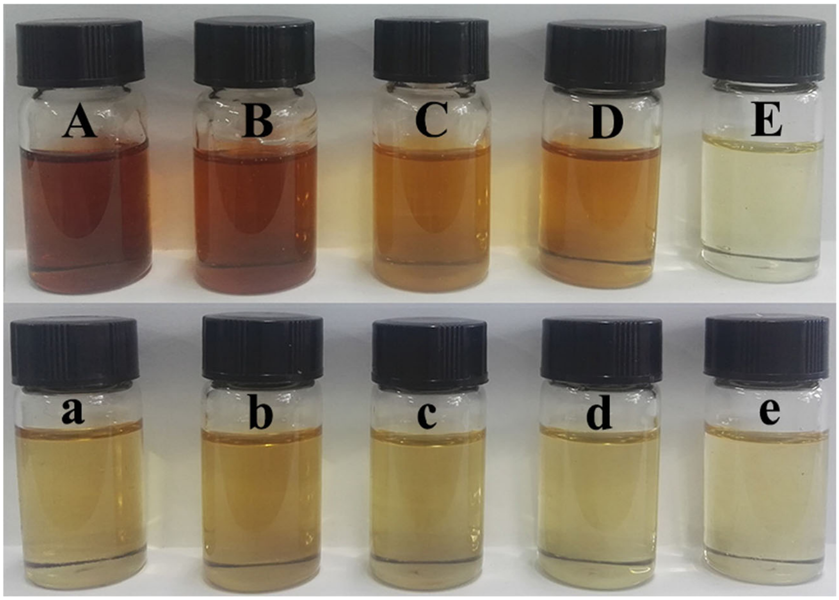


Fig. 3 The appearance of polyols samples. X represents polyether polyols with isosorbide as the starting agent; x represents polyether polyols with 1,2-propanediol as the starting agent

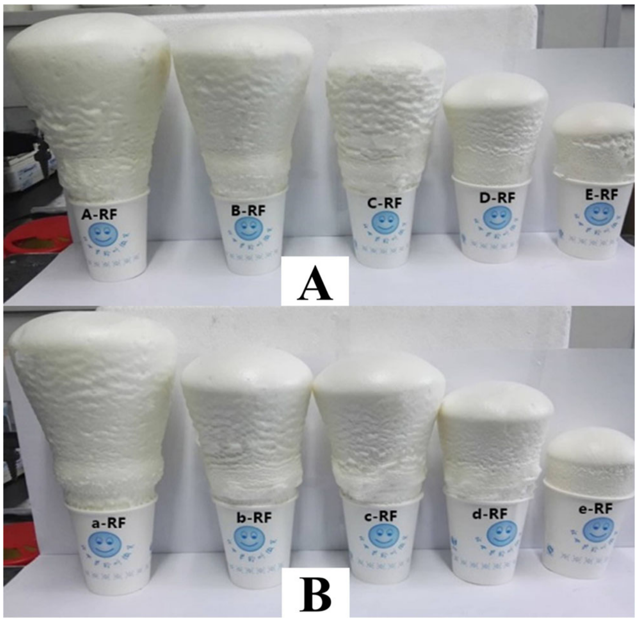


Fig. 4 Digital pictures of PURF samples from as-synthesized polyether polyols with different hydroxyl values. **a** polyols with isosorbide as the starting agent; **b** polyols with 1,2-propanediol as the starting agent

starting agent. The hydroxyl value, alkalinity correction, molecular weight and viscosity have been summarized in Table 1. Equation (1) shows the relation between the functionality (f), molecular weight (MW) and hydroxyl number [26]:

$$\frac{\mathrm{MW}}{f} = \frac{56100}{\#\mathrm{OH}} \tag{1}$$

The functionality of polyols $f = 2$, according to the measured hydroxyl number of different polyols, the average molecular weight of different polyols could be calculated. From Table 1, it could be observed that the viscosity of polyols with isosorbide as the starting agent is much larger than polyols with 1,2-propanediol as the starting agent. For example, the viscosity of isosorbide-based polyols with 358 mg KOH/g is 12.82 Pa•s, while the viscosity of 1,2-propanediol-based polyols with similar hydroxyl value is only 2.87 Pa•s. On the other hand, with the decrease of hydroxyl group, the average molecular weight of polyether polyols increased, and the corresponding viscosity decreased. As we know, viscosity reflects the inter-molecular interaction during the liquid flow process. Although these two kinds of polyether polyols are linear molecules, the rigidity of isosorbide ring structure could increase the rigidity of polyol molecular chain and inhibit the molecular rotation, which could contribute to the viscosity increase of polyols with isosorbide as the starting agent. Another possible reason is that the existence of ether bond of isosorbide could produce hydrogen bond effect with neighboring groups, thus inhibiting the molecular slipping, which could also increase the polyols viscosity.

Foaming behavior

The foaming behavior of PURF is significant in determining the foam formulation to ensure complete filling of the mold in practical applications. Łukaszczyk' results showed that polyols variations could influence the foam performance through changing molecular weight distribution and the ratio of primary to secondary hydroxyls [27]. Therefore, as-synthesized polyether polyols were used to prepare PURF as shown in Fig. 4, and the corresponding foaming parameters, including cream time, string time, end of rise time and tack free time, have been listed in Table 3. From Fig. 4, all of PURF showed perfect outlook, moreover, X-RF samples show slightly larger foam volume than x-RF samples. From Table 3, all of X-RF samples show slightly longer cream time and end rise time than x-RF samples, which could be induced by the high viscosity of isosorbide-based polyols. Meanwhile, the high viscosity of isosorbide-based polyols could also contribute to the longer string time of X-RF samples, which indicates the starting point of gelling process. On the other hand, the tack free time of X-RF samples was slightly shorter than the corresponding x-RF samples, ranging from 41 to 50 s. With the decrease of hydroxyl

Table 3 Foaming kinetics of PURF formulation

PURF	Cream time (s)	String time (s)	End of rise time (s)	Tack free time (s)
A-RF	16 ± 1	19 ± 2	42 ± 2	50 ± 2
B-RF	17 ± 2	19 ± 1	39 ± 2	48 ± 1
C-RF	16 ± 1	20 ± 2	38 ± 2	45 ± 1
D-RF	16 ± 1	19 ± 2	33 ± 1	43 ± 1
E-RF	18 ± 2	19 ± 1	30 ± 1	41 ± 1
a-RF	14 ± 1	15 ± 1	34 ± 2	62 ± 2
b-RF	14 ± 1	15 ± 1	30 ± 1	58 ± 2
c-RF	15 ± 1	15 ± 2	28 ± 1	57 ± 2
d-RF	15 ± 1	15 ± 1	25 ± 1	53 ± 1
e-RF	16 ± 1	16 ± 1	21 ± 1	48 ± 1

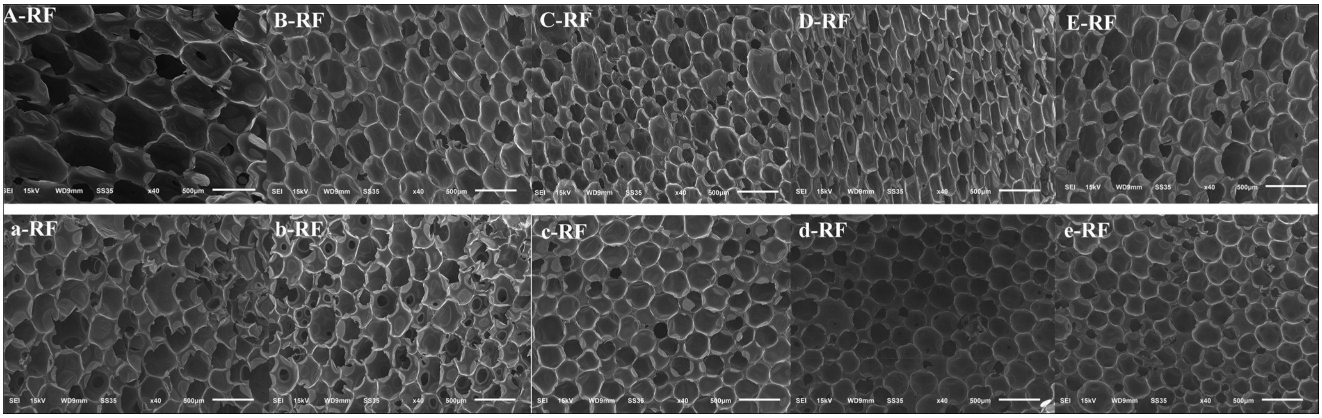


Fig. 5 Scanning election micrographs of the cut section of the PURF showing the cell morphology. X-RF represents rigid foam from polyether polyols with isosorbide as the starting agent; x-RF represents rigid foam from polyether polyols with 1,2-propanediol as the starting agent

value, the tack free time decreased, which could be induced by reduced foaming efficiency due to the decreased hydroxyl number per molecule [28]. Before gelling point, the reaction was mainly determined by the reactivity of hydroxyl groups of the polyols. During the process of gelling, the reaction was controlled by diffusion due to the rapid increase of viscosity and motion hindrance of the polymer chains. Therefore, the high viscosity of isosorbide-based polyols has obvious influence on the foaming kinetics and on the ultimate foam performance.

Foam morphology

Cell morphology of PURF samples were observed by SEM, and the representative photographs were shown in Fig. 5. All of samples showed the typical cellular polyhedron; no cell collapse or collision was observed. For series of isosorbide-based polyols, the cell size decreases with the decrease of hydroxyl values. For example, the cell size of A-RF sample is larger than 400 um, while the cell size of other samples is smaller than 300um. Moreover, X-RF showed the typical ellipsoidal cell shape, comparing with the sphere cell shape of x-RF. This kind of anisotropic cellular structure formation could originate from the special isosorbide structure. Meanwhile, as shown in Table 4, the closed cell content of X-RF was almost similar or increased slightly compared to x-RF. These results indicated that isosorbide-based polyols did not induce cell opening in PURF. In addition, some holes in the thin cell walls were observed, which could be induced by unbalanced foam growth or local internal stress. For samples of a-RF and b-RF, some wrinkles rather than cells were observed, which could be induced by microphase separation. The shorter chain length and the use of symmetric MDI in the preparation of PURF could contribute to the microphase separation [29].

Thermal conductivity and closed cell content

Low thermal conductivity is almost desirable for cellular insulation materials. Generally, thermal conductivity of PURF depends on many factors, such as cell size, cell orientation, the ratio of close cell, foam density and fillers [30]. The thermal conductivity of as-synthesized PURF samples was determined and the corresponding results have been listed in Table 4. As shown in Table 4, the thermal conductivity of X-RF is slightly smaller than that of x-RF, which is agreed with the high closed

Table 4 Properties of PURF prepared from two different polyols

PU Rigid foam	Closed cell content (%)	Thermal Conductivity (10^{-2} W/(m·K))	$T_{5\%}$ (°C)	T_{max} (°C)
A-RF	86.84 ± 2.84	2.77 ± 0.07	312	354
B-RF	88.34 ± 2.55	2.74 ± 0.03	301	342
C-RF	91.87 ± 2.38	2.67 ± 0.02	303	333
D-RF	91.35 ± 2.12	2.68 ± 0.05	286	317
E-RF	90.97 ± 2.92	2.70 ± 0.04	280	307
a-RF	83.4 ± 2.56	2.81 ± 0.06	251	279
b-RF	86.78 ± 2.63	2.76 ± 0.07	249	277
c-RF	91.41 ± 2.45	2.69 ± 0.05	279	314
d-RF	90.22 ± 2.53	2.70 ± 0.03	266	309
e-RF	89.55 ± 2.47	2.71 ± 0.05	263	319

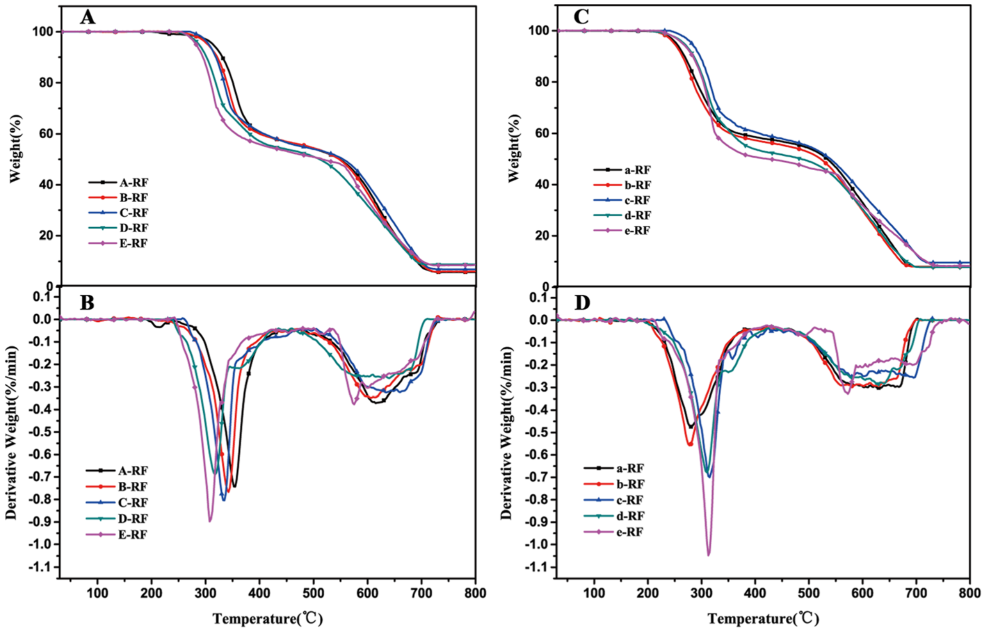


Fig. 6 The thermal analyses of PURF. X-RF represents rigid foam from polyether polyols with isosorbide as the starting agent, x-RF represents rigid foam from polyether polyols with 1,2-propanediol as the starting agent. **a** and **c** are the TG profiles; **b** and **d** are the corresponding DTG profiles

cell content. As reported in literatures the high closed cell content would contribute to low thermal conductivity [31, 32].

Thermal stability

In order to study the influence of the starting agent on the thermal properties of PURF, TGA were performed in dynamic mode from room temperature up to 800 °C. TGA and the corresponding DTG curves corresponding to X-RF and x-RF samples are depicted in Fig. 6. $T_{5\%}$, the weight loss value of 5%, was chosen as the criteria to evaluate the onset of thermal degradation of each sample, and the results have been listed in Table 4. The TG and DTG curves shown in Fig. 6 suggest that the decomposition of as-synthesized PURF show the two-stage characteristics. The weight loss happened from 250 °C to 500 °C, which could be ascribed to the breakage of the urethane bonds and the ether bonds of polyol to form volatile products [33]. The second weight loss took place from 500 °C to 750 °C, which could be induced by the oxidative decomposition of isocyanate and aromatic structures [34]. From Fig. 6 and the data in Table 4, $T_{5\%}$ and T_{max} for a-RF sample is about 251 °C and 279 °C under the classical temperature ramp β of 10 °C/min, respectively. However, $T_{5\%}$ and T_{max} for A-RF samples are about 312 °C and 354 °C, being improved about 70 °C, which indicated that isosorbide

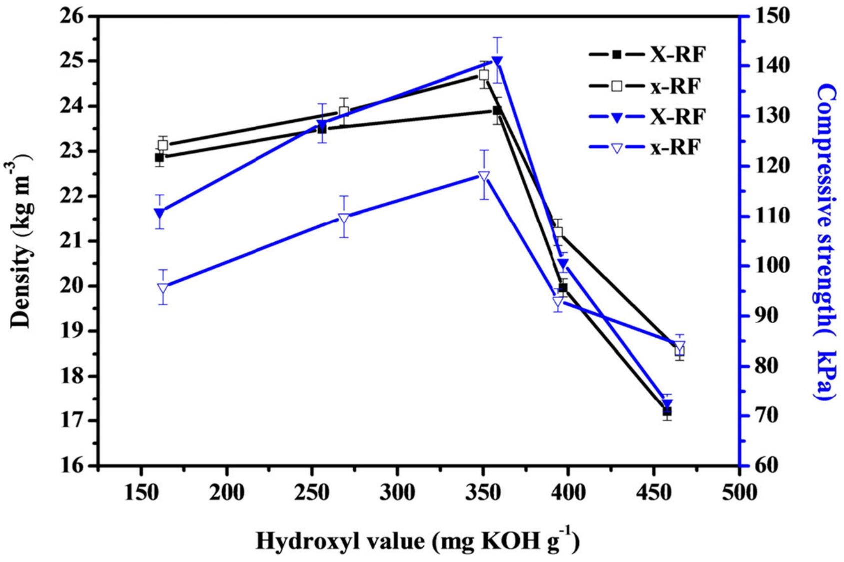


Fig. 7 The effect of hydroxyl values on the density and compressive strength of the PURF. X-RF represents rigid foam from polyether polyols with isosorbide as the starting agent, x-RF represents rigid foam from polyether polyols with 1,2-propanediol as the starting agent

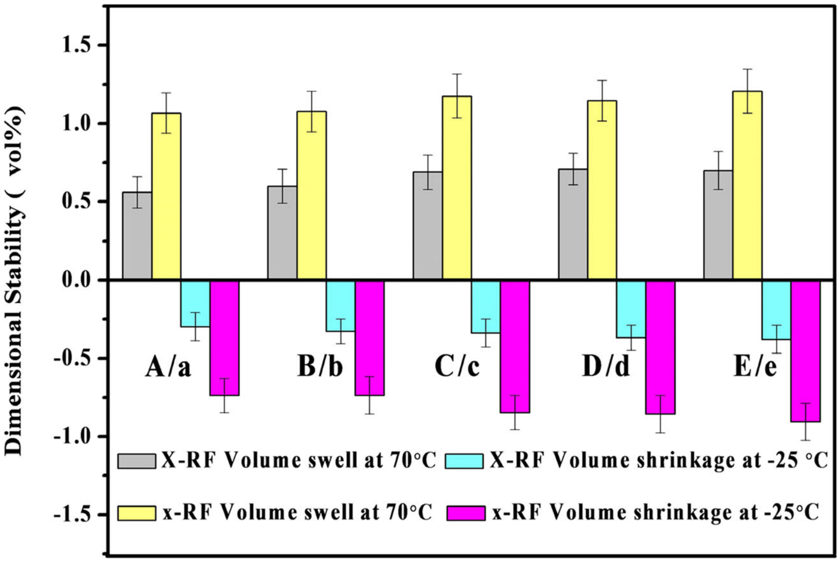


Fig. 8 Dimensional stability of prepared PURF. X-RF represents rigid foam from polyether polyols with isosorbide as the starting agent, x-RF represents rigid foam from polyether polyols with 1,2-propanediol as the starting agent

could improve obviously the thermal stability of PURF. With the decrease of hydroxyl values, $T_{5\%}$ and T_{max} for X-RF samples decreased, which could be induced by the reduced proportion of isosorbide among the total polyurethane [35]. These results demonstrate that the X-RF possess higher thermal stability, induced by the isosorbide with high thermal stability, which could serve to high temperature applications of PURF.

Compressive strength

Compressive properties are the important parameters for practical engineering design of PURF insulation materials. The deficiency of compressive properties could deteriorate the total insulation systems. Therefore, the compressive properties of as-synthesized PURF with different polyols were determined and the results have been shown in Fig. 7. Meanwhile, the effect of hydroxyl value on PURF was also shown in Fig. 7. For E-RF sample from polyols with isosorbide as the starting agent of 160 mg KOH/g hydroxyl value, the compressive strength is 110 kPa, while the compressive strength of e-RF sample is 96 kPa. With the increase of hydroxyl value, the compressive strength of PURF samples increases to the maximum values when the hydroxyl value of polyether polyols is 350 mg KOH/g. The compressive strength of C-RF sample is 141 kPa, and that of c-RF sample is only 118 kPa. Meanwhile, the density of X-RF samples is lower than that of x-RF samples, which could be induced by the larger viscosity of isosorbide-based polyols than that of 1,2-propanediol-based polyols. Therefore, these results

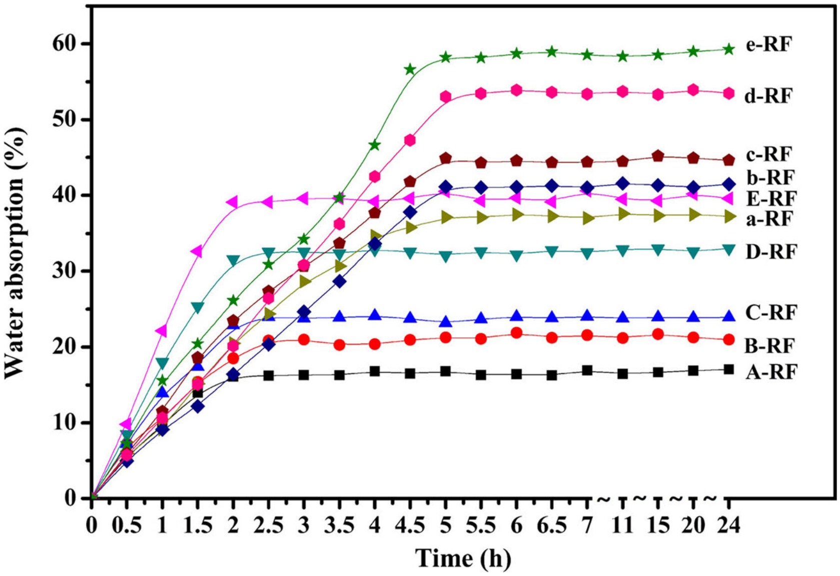


Fig. 9 The effect of as-synthesized polyether polyols structure on water absorption of the prepared PURF. X-RF represents rigid foam from polyether polyols with isosorbide as the starting agent; x-RF represents rigid foam from polyether polyols with 1,2-propanediol as the starting agent

demonstrate that PURF from isosorbide show the superior compressive properties, which could originate in the rigid structure of isosorbide.

Dimensional stability

Dimensional stability of PURF is very important for many applications such as insulation materials of choice for many commercial and residential construction applications.[6] Therefore, the dimensional stability of X-RF and x-RF was determined and the corresponding results have been shown in Fig. 8. From Fig. 8 the shrink ratio of all X-RF at −25 °C is lower than 0.4%, while the shrink ratio of x-RF at −25 °C is higher 0.75%. Moreover, with the decrease of hydroxyl values, the shrink ratio of X-RF increases less than that x-RF. On the other hand, the swelling ratio of X-RF at 70 °C is lower than 0.75%, while the swelling ratio of x-RF at 70 °C is higher 1.0%. Meanwhile, the swelling ratio of PURF samples with two kinds of polyols increased slightly with similar degree. These results indicate that the X-RF possess higher dimensional stability than x-RF.

Water absorption

Comparing with other polymer foams, PURF possesses lower water absorption. However, under low temperature, the familiar improvement of water absorption would deteriorate the insulating performance of PURF. The water absorption properties of PURF from different polyols have been determined and the results have been shown in Fig. 9. From Fig. 9, the maximum water absorption is about 16% for A-RF samples from isosorbide-based polyols when the hydroxyl value is about 457 mg KOH/g. With the decrease of hydroxyl values, the maximum water absorption increased to 20%, 23%, 32 and 39%. In comparison, the maximum water absorption is about 35% for a-RF samples from 1,2-propanediol-based polyols when the hydroxyl value is 465 mg KOH/g. With the decrease of hydroxyl values, the maximum water absorption increased to 40%, 42%, 53 and 58%. Moreover, the kinetic of water absorption of X-RF is faster than that of x-RF. Totally, X-RF possess lower water absorption, which could be benefit to practical applications.

Conclusions

In summary, a novel polyether polyol with isosorbide as the starting agent was prepared through ring-opening polymerization of propylene epoxide. The as-synthesized polyols with isosorbide as the starting agent with different hydroxyl values were used to prepare PURF. Comparing with polyols with 1,2-propanediol as the starting agent, polyether polyol with isosorbide as the starting agent with similar hydroxyl values showed the obviously higher viscosity, which has shown significant influence on foam kinetics, such as cream time, string time, end of rise time and tack free time. On the other hand, the rigid ring structure of isosorbide has contributed to the superior performance of PURF such as improved thermal stability, increased compressive strength, improved dimensional stability and reduced water absorption. Overall, the results of this study show that isosorbide-based polyols could improve the comprehensive performance of PURF, which could result in a variety of application extension for PURF materials.

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