

Preparation of Polyester Polyols from Unsaturated Fatty Acid

Xu Junming,^{1,2} Jiang Jianchun,^{1,2} Li Jing^{1,2}

¹Institute of Chemical Industry of Forestry Products, CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; National Engineering Lab. for Biomass Chemical Utilization; Key and Lab. on Forest Chemical Engineering, SFA, Nanjing 210042, China

²Institute of Forest New Technology, CAF, Beijing 100091, China

Received 20 February 2011; accepted 4 January 2012

DOI 10.1002/app.36740

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Oleic acid is a typical unsaturated fatty acid that is found widely in vegetable oils. The objective of this investigation was to produce a new type of oleic-based polyol from oleic acid. Possible advantages of this approach include the production of high-performance polyurethane materials from renewable resources and value-added research for oleic acid. Oleic-based polyols were synthesized by a three-step process consisting of epoxidation and ring-opening reaction, followed by esterification. The synthesized polyols appeared as a viscous

liquid at room temperature with hydroxyl numbers from 307 to 425 mg KOH/g. Preparation of polyurethane foams using oleic-based polyols and isocyanate was studied. An environmentally friendly blowing agent, HCFC-141b, together with a small amount of water, was used. The synthesized foams were characterized by FTIR, SEM, and TG/DSC. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polyester polyols; oleic acid; synthesis

INTRODUCTION

Polyester polyol is one of the predominant reactants in polyurethane synthesis. It is a low-molecular-weight polymer with hydroxyl end groups and is very useful for the production of polyurethane-based coatings and foams, as well as polyester applications. The basic reaction between a diisocyanate and a polyol produces a polyurethane polymer, with the liberation of heat.¹ In recent years, renewable and agriculture-based polyols are being used to replace petrochemical-based polyols to meet “green chemistry” and “sustainability” goals of urethane consumers.²

The use of renewable components as substitutes, either in whole or in part, for petrochemical-derived raw materials is an emerging trend in the chemical industry. At least one benefit includes the use of a renewable material that does not deplete fossil resources, and in some cases, a reduction in lifecycle global warming potential as a result of the fixation of CO₂ in plant biomass, from which the renewable materials are derived.³

In most of the studies reported in the literature regarding preparation of polyester polyols from glycerides, different kinds of plant oils, such as soybean, canola, palm, linseed, peanut, and safflower oil were used.^{4–8} However, there are challenges to the use of natural oils and their derivatives as raw materials for polyols to be used in isocyanate based foam products (e.g., polyurethanes and polyisocyanurates). The natural oils, with the exception of those oils having a hydroxyl functionality (e.g., castor oil or lesquerella oil), typically lack an isocyanate-reactive functionality, and must undergo chemical transformation, including transesterification with functionalized materials, epoxidation and ring opening,⁹ oxidation, ozonolysis,^{10,11} or hydroformylation to add a reactive functionality.

Generally, renewable polyol products could be obtained by reacting multihydroxy compounds such as diethanolamine (DEA) with natural glycerides. Some efforts had been made to modify these products for rigid polyurethane foam production.

Khoe et al. reported the use of hydroxymethylated oil in the synthesis of diethanolamide polyols to increase the number of hydroxyl groups and to improve their distribution.¹² The hydroxymethylated diethanolamides contained five primary hydroxyl groups per fatty acid. In another study, carboxylated oils and fatty acids from linseed and soybean oil were used to synthesize modified diethanolamides with increased distribution of primary hydroxyl groups in the polyols.¹³

Correspondence to: X. Junming (lang811023@163.com).

Contract grant sponsor: Commonweal research of CAF; contract grant number: 201104046.

Contract grant sponsor: National High Technology Research and Development Program (“863” Program) of China; contract grant number: 2010AA101602.

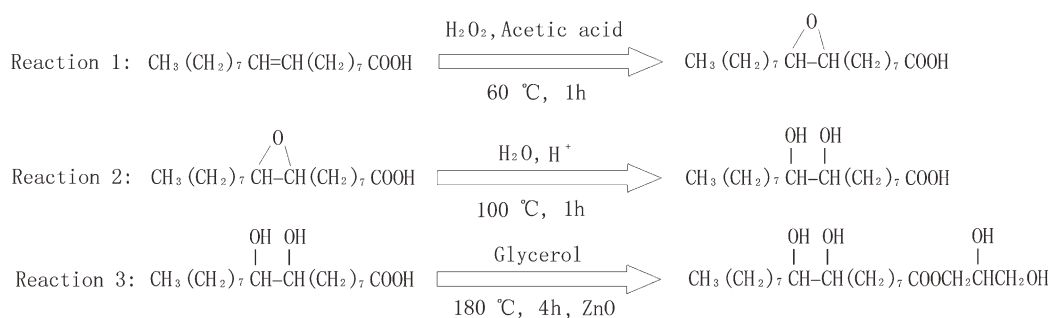


Figure 1 Synthesis of oleic-based polyol.

In addition, the synthesis of diethanolamides using palm oil has also been reported. Badri et al. prepared diethanolamides by reacting Refined Bleached Deodorized Palm Kernel Olein (RBDPKOo) with DEA in the presence of potassium acetate as catalyst.¹⁴ Sieved empty fruit bunch fibers (EFB) from palm tree were added as an organic filler to improve the mechanical properties of the rigid polyurethane foam.

In China, a large amount of unsaturated fatty acids can be recovered every year from soapstock in oil refining plants. Most of these are used as feedstock for biodiesel production.^{15,16} As an important unsaturated fatty acid, oleic acid is an alternative potential precursor for the production of polyols by adding hydroxyl functionality to its double bonds and carboxylic group. Compared with biodiesel, polyester polyols are fine chemicals of high value that are used widely in polyurethane-based products. This article proposes a novel and facile method for preparation of polyester polyols using unsaturated fatty acid by a three-step reaction. The desired polyols are oleic-based oligomers with hydroxyl numbers suitable for use in polyurethane foam formulations. Optimum reaction conditions for synthesis of oleic-based polyols were evaluated regarding temperature, catalyst, and catalyst dosage. The main physical and chemical properties of synthesized polyester polyols were characterized. The synthesized foam was also characterized by FTIR, SEM, and thermogravimetric measurements/differential scanning calorimetry (TG/DSC).

MATERIALS AND METHODS

Materials

Glycerol, H₂O₂ (30%), acetic acid, cyclohexylamine, and methyl silicone were contributed by Sinopharm Chemical Reagent Co. and oleic acid (90%) was purchased from Lingfeng Chemical Reagent Co. Isocyanate (MDI) and blowing agent (HCFC-141b) were obtained from Nanjing KaiKai polyurethane Co.

The foaming systems used in this work consisted of two components: A and B. Component A is a

group of substances containing polyols, catalyst (cyclohexylamine), blowing agent (HCFC-141b and distilled water), and surfactant (methyl silicone). Component B is an isocyanate (MDI).

Synthesis of polyester polyols from oleic acid

A polyester polyol was created from oleic acid by epoxidation and a ring-opening reaction, followed by an esterification reaction. The synthetic sequences for the preparation of polyester polyol are shown in Figure 1.

In a typical reaction, 28 g of oleic acid was placed in a three-necked flask equipped with a thermometer, a drop funnel, and a magnetic stirrer. Twenty-four grams of H₂O₂ (30%) was added dropwise over 1 h to the mixture of acetic acid and oleic acid, while the temperature of the mixture was maintained at 60°C, and a solution of epoxidized oleic acid in acetic acid was obtained. Then, the mixture was stirred at 100°C for another 1 h to realize the ring-opening reaction. After completion of the ring-opening reaction, the reaction mixture was decanted into a separatory funnel. The upper phase (oil phase) was separated and reacted with glycerol (9 g) using ZnO (2%) as a catalyst at 180°C for another 4 h. After esterification was completed, the obtained product was dissolved in methanol, and filtered to recover the catalyst. Then, the solvent (methanol) was removed under vacuum, and a yellow oily liquid was obtained. The product was found to have a hydroxyl value of 425 mg KOH/g and an acid value of 1.7 mg KOH/g.

Preparation of foams

The foams were prepared in a single step from a two component (A–B) system with an isocyanate index (quantity of isocyanate for average hydroxyl number of polyols) equal to 1.1 for classical systems.¹⁷ Component A was obtained by accurate mixing of polyols, catalyst (cyclohexylamine, 2%), blowing agents [HCFC-141b (20%) and water (1.5%)], and surfactant (methyl silicone, 2%) in a beaker for 15 s using a mechanical stirrer (3000 rpm). Component B is an isocyanate (MDI). The two components were mixed together using a mechanical stirrer and poured onto an open tray.

TABLE I
The Effect of Different Reaction Conditions on the Properties of Polyester Polyols

$n(\text{oleic acid}) :$ $n(\text{H}_2\text{O}_2) :$ $n(\text{acetic acid})$	Epoxidation reaction		Ring-opening reaction		Esterification reaction				Hydroxy number (mg KOH/g)	Acid value (mg KOH/g)
	R.T. (h)	R. Temp. (°C)	R.T. (h)	R. Temp. (°C)	Catalyst	Dosage (%)	R.T. (h)	R. Temp. (°C)		
Blank	Blank	Blank	Blank	Blank	PTS	2	1	180	237.4	5.4
1 : 1.5 : 0.5	4	60	1	100	H ₂ SO ₄	1	4	180	256	7.3
1 : 1.5 : 0.5	4	60	1	100	PTS	2	4	180	289	6.6
1 : 1.5 : 0.5	4	60	1	100	AlCl ₃	2	4	180	456	17.3
1 : 1.5 : 0.5	4	60	1	100	Phosphotungstic acid	2	4	180	418	17.7
1 : 1.5 : 0.5	4	60	1	100	NaHSO ₄	2	4	180	246	45
1 : 1.5 : 0.5	4	60	1	100	ZnO	2	4	180	425	1.7
1 : 1.5 : 0.5	4	60	1	100	ZnCl ₂	2	4	180	409	2.7
1 : 0.8 : 0.5	4	60	1	100	ZnO	2	4	180	307	1.9
1 : 1.2 : 0.5	4	60	1	100	ZnO	2	4	180	361	2.4
1 : 3 : 0.5	4	60	1	100	ZnO	2	4	180	406	1.9
1 : 3 : 1	4	60	1	100	ZnO	2	4	180	409	2.2
1 : 3 : 1.5	4	60	1	100	ZnO	2	4	180	413	2.1
1 : 1.5 : 0.5	4	60	2	100	ZnO	2	4	180	410.2	1.6
1 : 2 : 0.5	2	60	1	100	ZnO	2	4	180	366	2.8
1 : 2 : 0.5	4	60	1	100	ZnO	2	4	180	409.4	2.3
1 : 2 : 0.5	6	60	1	100	ZnO	2	4	180	417	2.2
1 : 1.5 : 0.5	4	60	1	100	ZnO	2	4	160	379	8.9
1 : 1.5 : 0.5	4	60	1	100	ZnO	2	4	200	393	2.1
1 : 1.5 : 0.5	4	60	1	100	ZnO	2	2	180	408	2.3
1 : 1.5 : 0.5	4	60	1	100	ZnO	2	6	180	417	1.8
1 : 1.5 : 0.5	4	60	1	100	ZnO	0.05	4	180	374	5.3
1 : 1.5 : 0.5	4	60	1	100	ZnO	1	4	180	409	3.7

R.T., reaction time; R. Temp., reaction temperature.

Analytical methods

Characterization of polyester polyols

Acid number was measured according to HG 2708-1995 (test method of acid value for polyester polyols). Water content was measured according to GB/T 606-2003 (chemical reagent-general method for the determination of water-Karl Fischer method). Viscosity was measured according to GB/T 15357-1994 (surface active agents and detergents-determination of viscosity of liquid products using a rotational viscometer). Gas chromatography-mass spectrometry (Agilent 6890N/5973N) was conducted to analyze the composition of liquefied product. The separation was realized on a column of HP-5, 30 m × 0.25 mm × 0.25 μm. Temperature program: 50°C (hold 2 min) → 280°C (10°C/min, hold 20 min).

¹H-NMR and ¹³C-NMR spectra were recorded using a Bruker DRX 500 NMR spectrometer operating at 500 MHz. The measurements were conducted in DMSO at 25°C and tetramethylsilane (TMS) was used as an internal standard.

Characterization of polyurethane foams

Density measurement. The test specimens (100 mm × 100 mm × 50 mm) were weighed to determine the

density in kilograms per cubic meter. Three specimens were tested and the average value was reported.

To identify the chemical structure of foams, the infrared transmission spectra (FTIR) of specimens were performed on a PerkinElmer Fourier transform infrared spectrophotometer in between the wave numbers of 4000 and 450 cm⁻¹.

SEM photographs were taken to explain the structural details of the foams by a Hitachi 3400N-I SEM instrument. A slice of foam about 1.0 mm in thickness was prepared for SEM analysis by coating with gold before scanning. The slice was done at an accelerating of 15 keV. The sample was observed in the free-rise direction.

Mechanical properties of rigid foams were measured on a CMT4303 testing machine at room temperature (load cell: 1 kN, error: 0.5%). The size of the specimen was 50 × 50 × 50 mm³. The speed of crosshead movement was 5 mm/min. Compressive strengths of five specimens per sample were measured and averaged.

Dimensional stability measurement. The samples were cut to dimensions of 100 mm × 100 mm × 25 mm. The length, width, and thickness of the samples were measured using a vernier caliper. The samples were conditioned at 25°C for 1 day before being

TABLE II
Reuse Performance of the Catalyst

Catalyst	Cycle	Conversion(%)					
		1	2	3	4	5	6
ZnO ^a	Acid value	2.3	2.7	2.1	1.9	2.2	4.2
	Hydroxy number	422	417	427	431	418	417

Reaction conditions: catalyst amount, 2%; reaction time, 4 h; reaction temperature, 180°C.

^a Fresh catalyst was supplemented to replace the loss during recycling.

transferred into controlled temperature chambers at 70°C for 48 h. The measurements were conducted as described in JCT 998-2006.

TG/DSC analysis of the foams was conducted on a thermal analyzer, Netzsch409PC, to simultaneously obtain thermogravimetric data. About 4–5 mg of foam was used in the analysis of TG/DSC. Pyrolysis was started from 50°C and ended at 700°C with the heating rate of 10°C/min under a flow of 100 mL/min of nitrogen gas.

RESULTS AND DISCUSSION

Effect of different reaction conditions on the properties of polyester polyols

Production of oleic-based polyols was investigated by adding hydroxyl functionalities to the double bond and carboxylic group of oleic acid. The reaction conditions were examined, and the results obtained are given in Table I.

First, the activities of different catalysts were investigated. The performance of the catalysts was evaluated in terms of hydroxy number and acid value. From Table I, it was found that the products have relatively low hydroxyl number with high acid number by using conventional acid catalysts such as H₂SO₄ and PTS. Besides, these catalysts could not be separated from the products after reaction, which lead to corrosiveness of the products.

To solve above issues, we tried to use heterogeneous catalysts such as ZnO and ZnCl₂. We chose these Lewis acids as catalysts for their low price. Moreover, as a heterogeneous catalyst (undissolved in organic products), they could be recovered easily after esterification by filtration. It seems that ZnO showed high-catalytic performance because the product generated by this catalyst has high-hydroxyl number with low acid number.

From Table I, it can also be seen that oleic-based polyols having a hydroxy number from 307 to 406 mg KOH/g could be produced by using different amounts of hydrogen peroxide. This result suggested that polyols with different functionalities

could be produced to meet the requirements of the particular product. The optimum reaction conditions (product with hydroxyl number of 425) for esterification are as follows: catalyst amount, 2%; reaction time, 4 h; reaction temperature, 180°C.

The reuse performance of ZnO is shown in Table II. In our experiment, it was found that catalytic activity was easily recovered when additional fresh catalyst was supplemented for the loss during recycling. The catalyst (ZnO) could be used five times without an obvious decrease in catalytic activity.

To identify the structure of products a GC–MS analysis was carried out. Because of its nonvolatile

TABLE III
GC–MS Analysis of the Product After Ring-Opening Reaction

Retention time (min)	Component	Content (%)
9.018	Dodecanoic acid, methyl ester	0.521
9.561	Nonanedioic acid, dimethyl ester	2.152
11.698	Decanedioic acid, dimethyl ester	0.408
13.264	Methyl tetradecanoate	1.500
17.305	Hexadecanoic acid, methyl ester	9.121
21.003	Octadecanoic acid, methyl ester	3.404
23.632	Octadecanoic acid, 9,10-dihydroxy-methyle	1.790
23.820	Oxiraneoctanoic acid, 3-octyl-methyl ester, cis-	4.934
24.026	Octadecanoic acid, 10-oxo-methyl ester	5.461
24.426	Eicosanoic acid, methyl ester	0.432
25.243	Unknown	1.062
25.546	Unknown	0.567
25.672	Octadecanoic acid, 9-hydroxy-methyl ester	1.586
25.792	Octadecanoic acid, 9,10-dihydroxy-methyl ester	0.558
26.609	Octadecanoic acid, 9,10-dihydroxy-methyl ester	1.484
27.004	Octadecanoic acid, 9,10-dihydroxy-methyl ester	27.695
27.147	Octadecanoic acid, 9,10-dihydroxy-methyl ester	4.263
27.312	Octadecanoic acid, 9,10-dihydroxy-methyl ester	1.373
27.598	Octadecanoic acid, 9,10-dihydroxy-methyl ester	1.128
27.884	Octadecanoic acid, 9,10-dihydroxy-methyl ester	0.770
28.021	Octadecanoic acid, 9,10-dihydroxy-methyl ester	5.499
28.135	Octadecanoic acid, 9,10-dihydroxy-methyl ester	6.211
28.330	Octadecanoic acid, 9,10-dihydroxy-methyl ester	6.706
28.444	Methyl 6-acetoxytridecanoate	6.838
28.581	Octadecanoic acid, 9,10,16-dihydroxy-methyl ester	1.107
30.370	Hexadecanoic acid-(2-pentadecyl-1,3-dioxlan-4-yl)methyl ester	1.029
31.639	Unknown	1.482
34.748	Hexadecanoic acid-(2-pentadecyl-1,3-dioxolan-4-yl)methyl ester	0.919

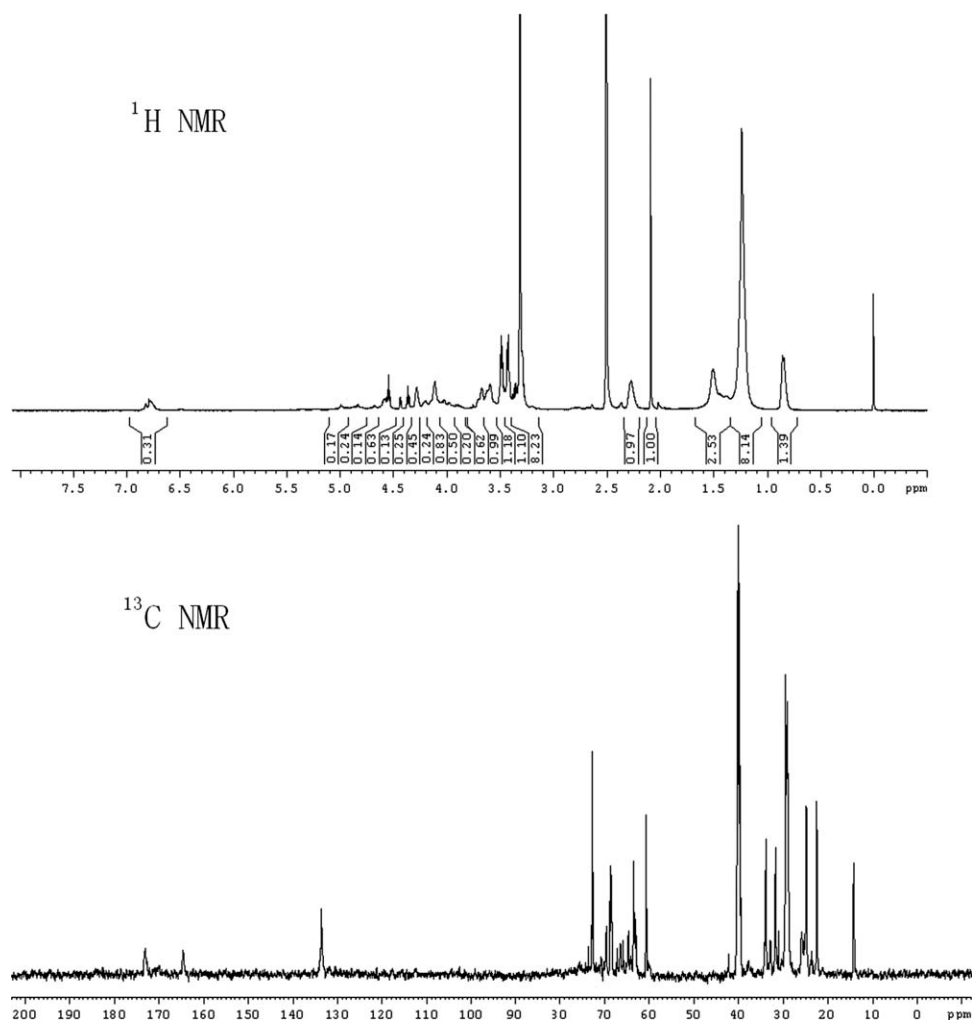


Figure 2 NMR analysis for oleic-based polyol (hydroxy number: 425).

properties, the final product (Fig. 1, reaction 3) can not be detected by GC-MS. Therefore, we tried to analyze the structure of product after ring-opening reaction (Fig. 1, reaction 2). Methyl ammonium hydroxide is used as methylation reagent for GC-MS analysis. Table III shows compositions for the product after ring-opening reaction. Among the classes of compounds formed, polyhydroxylated compounds such as 9,10-dihydroxy-octadecanoic acid and 9,10,16-dihydroxy-octadecanoic acid were identified. It was calculated that the percentage of dihydroxy compounds is $\sim 60\%$. This result suggests that the double bond in oleic acid was changed into hydroxyl functionalities successfully.

^{13}C -NMR and ^1H -NMR were used to analyze the structure of synthesized polyols (Fig. 2). From ^1H -NMR spectrum, presence of multiplet between 3.0 and 5.0 ppm indicates the presence of $-\text{OH}$ or aliphatic H adjacent to oxygen. Those low intensity peaks at 6–8 ppm which is indicative of olefins presence (a small amount of unreacted double bounds in product). The peaks between 1.0 and 2.5 ppm

indicate the presence of aliphatic groups. Percentage of different kinds of protons in polyol structure were summarized as follows: aliphatic H (46.4%), protons in hydroxyl groups or aliphatic H adjacent to oxygen (52.6%), and H in olefins (1.0%).

From ^{13}C -NMR, presence of multiplet at 10–40 ppm indicates alkyl groups and another multiplet at 60–75 ppm indicates the presence of C atom adjacent to oxygen. Olefins presence is indicated by multiplet between 120 and 140 ppm. Those peaks between 160 and 180 ppm indicate the presence of $\text{C}=\text{O}$ (ester

TABLE IV
Physical and Chemical Properties of Polyester Polyols

Properties	Polyester polyols		
Hydroxyl value (mg KOH/g)	425	361	307
Density (g/cm^3)	1.03	1.05	1.06
Acid number (mg KOH/g)	1.7	1.6	1.8
Moisture (%)	0.12	0.58	0.44
Viscosity (mPa s, 25°C)	4613	5147	6192

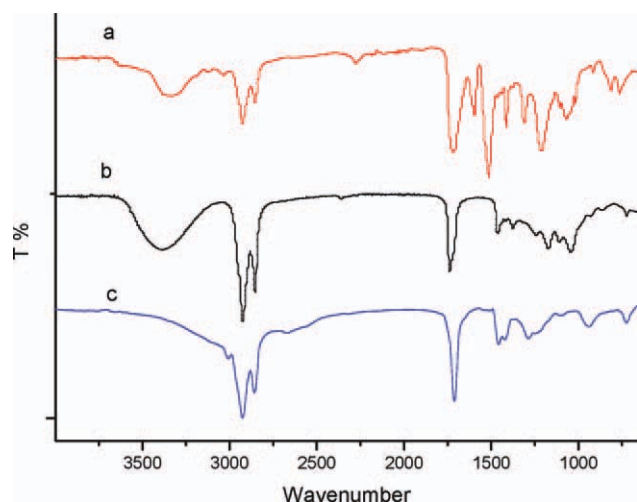


Figure 3 IR spectra of synthesized foam (a), polyester polyol (hydroxy number: 425) (b), and oleic acid (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

group in polyol structure). These results are in good agreement with the analysis in $^1\text{H-NMR}$.

Table IV shows the physical and chemical properties of the synthesized polyols. The products appeared as a viscous liquid at room temperature, with a viscosity of 4613–6192 mPa s at 25°C, and 0.12–0.58% of water content. The hydroxyl and the acid value of the polyols were determined as 425–307 mg KOH/g and 1.6–1.8 mg KOH/g, respectively. The physical and chemical properties suggested that the synthesized polyols have great potential for further reaction with isocyanate to produce rigid foam applications.

Characterization of manufactured polyurethane foams

FTIR spectra evaluations

FTIR spectra of oleic oil, the polyester polyol and synthesized foam are presented in Figure 3. The sample underwent significant changes between oleic-based polyol and polyurethane foam (PU

foam), as revealed by the appearance of the peak of C=C stretch for the aromatic ring at around 1600 cm^{-1} . This change indicated the formation of the polyurethane groups. The spectrum of synthesized foam presents all the distinctive bands of the polyurethane polymer. The band of OH stretching vibration at 3400–3600 cm^{-1} is associated with the free H_2O , –OH groups of nonbonded polyol, or OH groups within the polymer structure. The intensities of transmission bands at 2972–2953 cm^{-1} are related to CH_2 and CH chain formation. Peaks related to C=C and C=O at 1600 and 1710 cm^{-1} were observed in the spectrum of the synthesized foam (Fig. 2). The intensities of transmission bands at 1500–1230 cm^{-1} are related to C–N and C–N–H chain formation. It was noted that the IR spectrum of this foam matched the IR spectra of many other MDI based foams that were formulated using different polyols.¹⁸

SEM photographs of foam structures

SEM photographs of a polyurethane foam sample are shown in Figure 4. The particles have a honeycomb structure, with a size distribution of 200–400 μm in diameter, and a uniform and smooth surface texture. The cell size of the rigid foam has an important effect on thermal conductivity and mechanical properties.¹⁹ The excellent honeycomb structure obtained during foam formation made it possible for a considerable amount of still air to be trapped, thus, leading to an increased passive insulation. It is well known that the cell size of rigid foam is closely related to the density. We tried to use three specimens (100 mm \times 100 mm \times 50 mm) to determine the density in kilograms per cubic meter. It was found that the density of the foam sample (0.0313 g/cm^3) is well within the standards for rigid foam in China (JC/T 998-2006).

The thermal properties of polyurethane foams

Figure 5 shows the curves of TG and DSC. The bimodal weight loss in the DTG curve with maxima

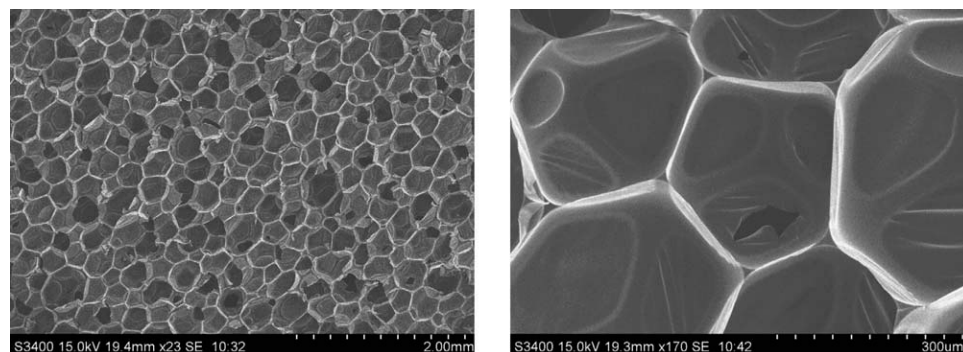


Figure 4 SEM photographs of a foam sample produced by oleic-based polyol.

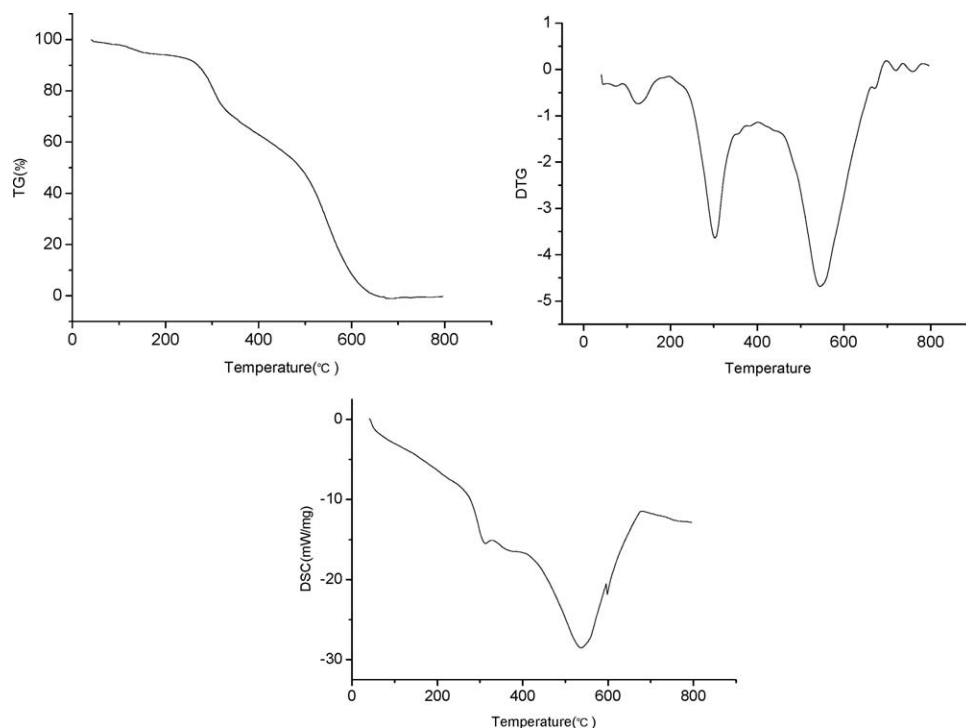


Figure 5 Thermal analysis of a foam sample produced from oleic-based polyol.

at 300 and 550°C is similar to curves from other urethane foams reported in the literature.²⁰ No apparent weight loss for the foam sample was found below 200°C. When the temperature was increased to 300–350°C, the decomposition of the foam gave an endothermic peak at around 300°C in the DSC data. Finally, the decomposition temperature was recorded from 450 to 600°C. The decomposition could be related to the depolymerization of the isocyanurate rings.²⁰ The DSC curve exhibited

exothermic peaks at 300 and 550°C. This is in good agreement with the observations from the DTG analysis.

The physical properties of polyurethane foams

The physical properties of the rigid PU foam made from the oleic-based polyol were measured and are shown in Table V. The experimental data reveal that the thermal conductivity of the foam made from

TABLE V
Physical Properties of Polyurethane Foams

Properties	Foam 1 ^a	Foam 2 ^a	Foam 3 ^a	China specification ^b
Thermal conductivity W/(m K)	0.028	0.037	0.076	0.024
Density (kg/m ³)	31.3	40.6	58.1	30–50
Compressive strength (vertical to foam rise direction, kPa)	150	210	230	150–300
Modulus of compression (MPa)	3.44	4.58	5.66	–
Bending strength (MPa)	0.28	0.34	0.41	–
Dimensional stability (70°C) ^c				
<i>L</i>	0.12%	0.55%	2.54%	1%
<i>W</i>	0.05%	0.76%	1.13%	1%
<i>T</i>	0.06%	0.37%	2.11%	1%

^a Foam 1 was synthesized using polyols with hydroxy number of 425 (Table IV). Foam 2 was synthesized using polyols with hydroxy number of 361 (Table IV). Foam 3 was synthesized using polyols with hydroxy number of 307 (Table IV).

^b China specification (JC/T 998-2006): Spray polyurethane foam for thermal insulation.

^c *W*, *L*, and *T* indicate the width, length, and thickness of the foam, respectively.

oleic-based polyol is lower than that of the reference foam. However, this value is comparable with that obtained with renewable PU foam reported in the literature.²⁰ The other physical properties of the foam made from the oleic-based polyol are similar to the China specifications (JC/T 998-2006) for rigid foam. Thus, the oleic-based polyol could be used to make rigid polyurethane foam, if the formulation is adjusted carefully.

CONCLUSIONS

Oleic-based polyols are proposed as a new type of natural oil-derived polyol. The oleic-based polyols could be produced with a hydroxy number of from 307 to 425 mg KOH/g using different amount of H₂O₂ to meet the requirements of specific products. The components and structure of oleic-based polyols were characterized by GC-MS, FTIR, and NMR. The results showed that double bonds and carboxylic acid group were changed into hydroxy functionalities successfully. The newly synthesized oleic-based polyols, consisting of four reactive hydroxyl groups, are proposed to have plenty of reactive functionalities during polyurethane foam production. We believe that the highly crosslinked structure of the rigid polyurethane foam will show good mechanical properties. Based on comprehensive FTIR, SEM, and TG-DSC analyses and dimensional stability tests, we have shown that physical and chemical characteristics of polyurethane foams from oleic-based polyols could be possess acceptable values according to the specification of rigid foam in China. Further studies are needed on the production of rigid polyurethane

foams, including those utilizing unsaturated fatty acids from vegetable oil and preparation of fire-safe foams, and are currently under investigation in our research group.

References

1. Sarier, N.; Onder, E. *Thermochim Acta* 2007, 454, 90.
2. Kiatsimkul, P.; Suppes, G. J.; Sutterlin, W. R. *Ind Crops Prod* 2007, 25, 202.
3. Lambert, T. L.; Hickey, L. F. W.O. 2009,045,926 (2007).
4. Narine, S. S.; Kong, X.; Bouzidi, L.; Sporns, P. *J Am Oil Chem Soc* 2007, 84, 65.
5. Badri, K. H.; Ahmad, S. H.; Zakaria, S. *J Appl Polym Sci* 2001, 82, 827.
6. Chian, K. S.; Gan, L. H. *J Appl Polym Sci* 1998, 68, 509.
7. Guo, A.; Zhang, W.; Petrovic, Z. S. *J Mater Sci* 2006, 41, 4914.
8. Lee, C. S.; Ooi, T. L.; Chuah, C. H.; Ahmad, S. *J Am Oil Chem Soc* 2007, 84, 945.
9. Petrovic, Z.; Guo, A. U.S. 61,074,33A (1998).
10. Sebedio, J. L.; Ratnayake, W. M. N.; Ackman, R. G. *Chem Phys Lipids* 1984, 35, 21.
11. Benecke, H. P.; Garbark, D. B. W.O. 2010,078,498 (2008).
12. Khoe, T. H.; Otey, F.; Frankel, E. N.; Cowan, J. C. *J Am Oil Chem Soc* 1973, 50, 331.
13. Khoe, T. H.; Frankel, E. N. *J Am Oil Chem Soc* 1976, 53, 17.
14. Badri, K. H.; Othman, Z.; Ahmad, S. H. *J Mater Sci* 2004, 39, 5541.
15. Chen, Y. M.; Chang, J.; Fu, Y.; Lu, J. D.; Xiao, B. *J Fuel Chem Technol* 2008, 36, 236.
16. Guo, F.; Wu, R.; Liang, Z.; Liu, Z.; Wang, T.; Yang, T.; Xiu, Z. *China Oils Fats* 2009, 34, 35.
17. Wojciech, Z.; Zbigniew, K. B.; Andrzej, K. *Polym Degrad Stab* 2008, 93, 2071.
18. Mumford, N. A.; Chatfield, D. A.; Einhorn, I. N. *Fire Res* 1977/78, 1, 107.
19. Li, X. B.; Cao, H. B.; Zhang, Y. *J Wuhan Univ Technol: Mater Sci* 2008, 23, 125.
20. Lee, C. S.; Ooi, T. L.; Chuah, C. H.; Ahmad, S. *J Am Oil Chem Soc* 2007, 84, 1161.