Thermal and Mechanical Properties of Cast Polyurethane Resin Based on Soybean Oil

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ABSTRACT: The soy polyols were prepared from epoxidation of soybean oil followed by ring opening of oxirane obtained by using methanol as the ring opener. Polyols of hydroxyl (OH) numbers ranging from 128 to 174 mg of KOH/g were obtained by the variation of epoxidation time of soybean oil. A novel cast polyurethane resin has been synthesized by these polyols and 2,4-toluene diisocyanate. Swelling of networks in toluene showed that the sol fraction varies from 1.13 to 72.06%. The thermal and mechanical properties of cast resins were characterized by differential scanning calorimetry and thermogravimetric analysis. The results showed that the glass transition temperature increases with the increase of OH number and that the thermal stability of the resins was slightly decreased with the increasing OH number. The tensile strength at break increases with the increase of OH number. Polyols with OH number of 174 mg of KOH/g gave glassy polymers, whereas those below this value gave rubbers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1122–1127, 2009

Key words: cast polyurethane resin; soybean oil; polyol; thermal stability

INTRODUCTION

Polyurethanes (PUs) are a class of polymers that have found many important applications such as thermoset and thermoplastic elastomers, adhesives, coatings, and both flexible as well as rigid foams. The general route to synthesize a thermoset network form of these polymers is by the reaction of a diisocyanate or one of the higher functionalities with a polyol that possesses an average functionality greater than 2. Polyols derived from soybean oil are interesting materials for polyisocyanate modification. These are raw materials from renewable resources, and with isocyanates they produce PUs that can compete in many aspects with those derived from petrochemicals.[1,2]

Soybean oil is one of the many vegetable oils that can be converted into a polyol by various methods, such as epoxidation,[3,4] hydroformylation,[5] and ozonolysis.[6] Because of the high functionality, these polyols can also be crosslinked with diisocyanates to give rigid PUs. The polymer properties are controlled by the crosslinking density as well as the structures of the polyols[4] and isocyanates.[7,8]

From the publications, most of the polyols employed have high functionality and are derived from epoxidized soybean oil (ESO) or soybean oil. In this article, a series of ESO with different epoxidation degrees were used to synthesize polyols. In the prepared polyols, there are still some double bonds in the molecules. The double bonds will give PUs with lower T_gs, and this kind of polymers may have different applications. So far, there are few reports focused on this research.

In this article, the polyols were prepared from epoxidation of soybean oil followed by ring opening of oxirane with methanol. These transformations have been outlined in Figure 1, where the structures of all the molecules have been idealized. All polyols were fully characterized by Fourier transform infrared (FTIR) spectrometry and by the measurement of the hydroxyl (OH) number and iodine value.

The objective of this work is the synthesis of cast PU resins by the reaction of polyols with 2,4-toluene diisocyanate (TDI). The swelling measurements in toluene were used to estimate the crosslinking density. The effect of OH number on the thermal and mechanical properties of resins has been studied using differential scanning calorimetry (DSC), thermogravimetric (TG) analysis, and mechanical tests.

EXPERIMENTAL

Materials

Refined soybean oil with an iodine value 127.23 (g I/100 g oil) was kindly provided by Nanhai Oil Co., Ltd. (Guangzhou, China). AR-grade glacial acetic
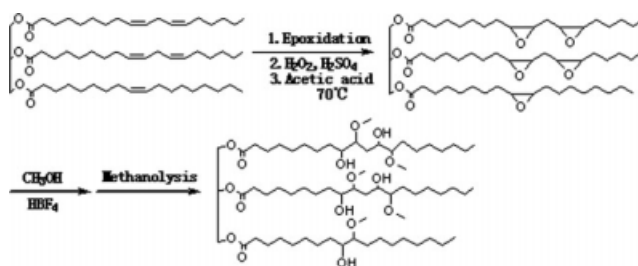
Figure 1 Idealized synthesis route of methoxylated polyol based on ESO.

acid (99.5%), sodium carbonate, sodium hydroxide, hydrogen peroxide (30%), sulfuric acid (98%), methanol, ammonia (30% in water), tetrafluboric acid (48% in water), and TDI were all purchased from Guangzhou Chemical Reagent (Guangzhou, China). They were used as supplied.

Methods

The OH values of the polyols were determined according to the ASTM E 1899-97 standard test method for OH groups using reaction with *p*-toluenesulfonyl isocyanate (TSI) and potentiometric titration with tetrabutylammonium hydroxide. The infrared spectra were recorded on a FTIR spectrometer (IR Prestige-21, Shimadzu, Japan). The samples were prepared as thin films on KBr salt plates.

Thermal properties were measured by DSC (DSC 200PC NETZSCH, Germany) with a heating rate of 20 K/min from −80 to 120°C. Nitrogen was used as purge gas at a 50 mL/min flow rate. Samples (10 mg) were used in aluminum pans for each analysis. The analysis of the thermogravimetric behavior of the samples were performed on a TG instrument, model STA 409PC (NETZSCH), with a heating rate of 10 K/min from 50 to 650°C. Air and nitrogen were used as the purge gas at a 100 mL/min flow rate. About 10 mg of each sample was used in each test. Swelling experiments were performed on square, 1- to 2-mm-thick samples weighing between 1 and 2 g. The samples were immersed in 50 mL of toluene for 2 weeks at 25°C. The weight of the sample was measured periodically, and the change with time was recorded. After reaching the maximum weight, the samples started losing weight because of the extraction of the sol fraction until constant values were obtained. The solvent was replaced three times after the maximum swelling was obtained. The samples were dried, and the weight of the gel fraction was recorded. The sol fraction was the difference between the initial weight and gel weight divided by the initial weight expressed as a percentage. The tensile properties were measured according to ASTM D 882-97 on a tensile tester model RGB-1

from Reger Instrument. (Shenzhen, China). The extension rate is 100 mm/min, and five specimens were used for each sample.

Synthesis of epoxidized soybean oil[9]

Epoxidation of SBO was carried out in a 1000-mL four-necked, round-bottomed flask equipped with a thermometer, a mechanical stirrer, a condenser, and an isobaric funnel. The whole apparatus was kept in a water bath to maintain the reaction temperatures at 70°C ± 1°C. SBO (150 g, 0.172 mol of double bonds) was placed in the round-bottomed flask. Peroxyacetic acid was prepared *in situ* by reacting various mixtures of 35 g (0.58 mol) of 99.5% glacial acetic acid and 165 g (1.46 mol) of 30% H_2O_2 in the presence of small quantities (0.1 mL) of concentrated sulfuric acid for about 12 h and added into the flask slowly through an isobaric funnel over 2 h. The stirring rate was controlled at 800 r/min so that the oil in the mixture was well dispersed. The reaction system was kept at 70°C for 30, 60, 90, and 120 min, respectively, and then the reaction was quenched by cooling to 5°C to stop the epoxidation reaction.

The samples were washed with 5% sodium carbonate solution until the pH was neutral, and then with distilled water. The solvent was removed by using a rotary evaporator under vacuum at 80°C for 1 h. The products (ESO) were used for the preparation of polyols.

Preparation of the polyol by ring opening of ESO with methanol[10]

Methanol and tetrafluboric acid were charged into a four-necked flask and heated to boiling, and then the prepared ESO was added to the system. The molar ratio of epoxy groups to methanol was 1 : 11. The concentration of the catalyst was 0.2% of the total weight of the reaction mixture. The reaction mixture was kept boiling for 1.5 h. After cooling to room temperature, ammonia (30% in water) was added to neutralize the catalyst. The solvent was removed on a rotary evaporator under low vacuum at 60°C for 0.5 h, followed by 95°C for 1 h,

TABLE I
Chemical and Physical Properties of the Polyols

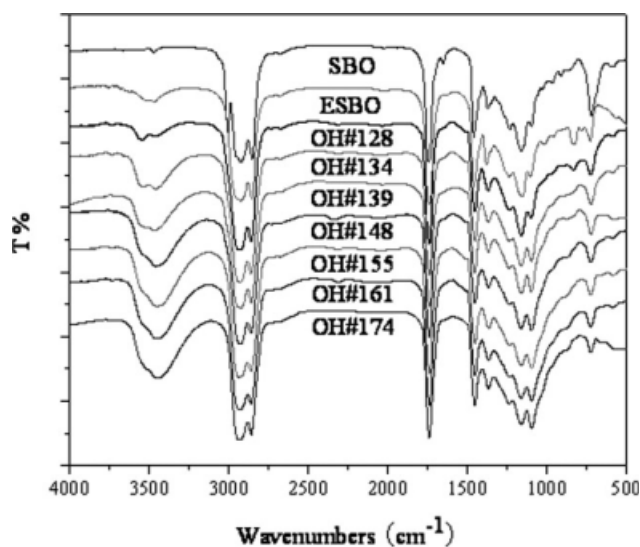| Epoxidation time (h)	OH number (mg of KOH/g)	Iodine value (g of I_2/100 g)
2.5	128	45.19
3	134	49.63
3.5	139	44.01
4	148	35.71
5.5	155	28.52
6	161	21.13
7	174	16.29

Figure 2 FTIR spectra of polyols based on soybean oil.

respectively. The OH values of the polyols were determined according to the ASTM E 1899-97 standard test method by reaction with TSI and potentiometric titration with tetrabutylammonium hydroxide.

Preparation of polyurethanes[11]

Seven PUs were prepared by mixing the soy polyol with TDI using an isocyanate index of 110. The polyol and the isocyanate components were stirred for 2 min, and then the mixture was poured into a mold and the unit was left under vacuum to evacuate bubbles (5 min at 60°C). The sample was put into an oven for 24 h at 110°C to complete the reaction. The sample was then cooled to room temperature and remolded.
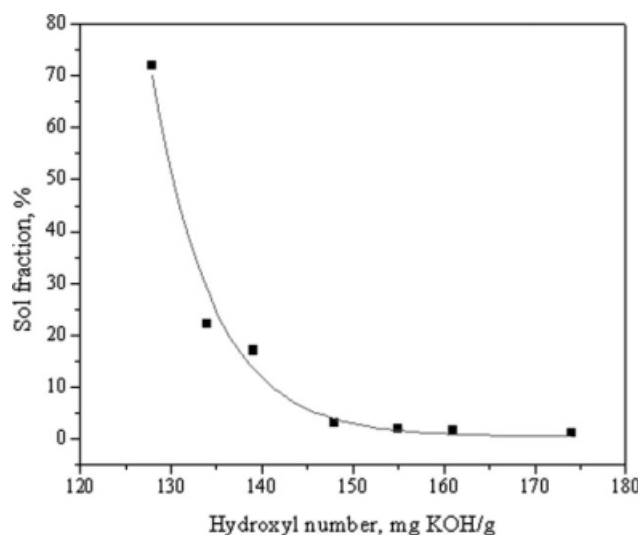

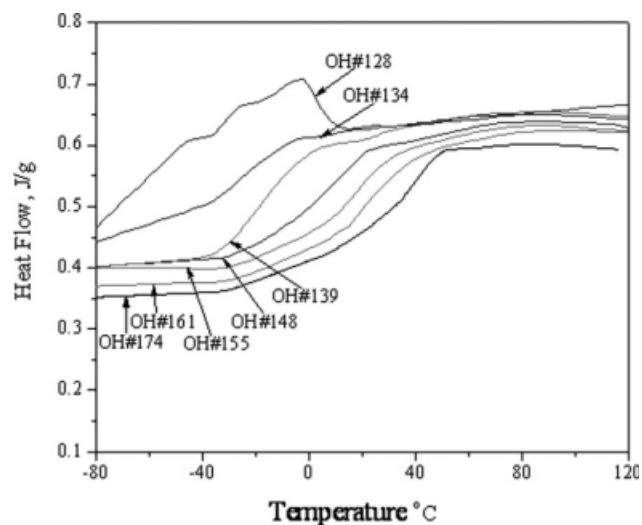**Figure 3** Effect of the OH number of polyols on the sol fraction of polyurethane.

Figure 4 DSC curves of cast polyurethane resins prepared from polyols and TDI.

RESULTS AND DISCUSSION

Characterization of polyols

The reaction for the preparation of polyols by epoxidation of soybean oil followed by ring opening is shown in Figure 1. The OH number and iodine value of polyols are presented in Table I. The OH number of polyols increases with the epoxidation time of soybean oil while the iodine value decreases. Figure 2 shows the FTIR spectra of the polyols, which exhibit an increasing OH peak at 3450 cm^{-1} as the reaction time increases. The peak at 1100 cm^{-1}, attributed to the vibration C—O—C, increases with the reaction time showing the ring opening of oxirane by the methanol reaction. In OH#128 curve, the characteristic absorption peaks at
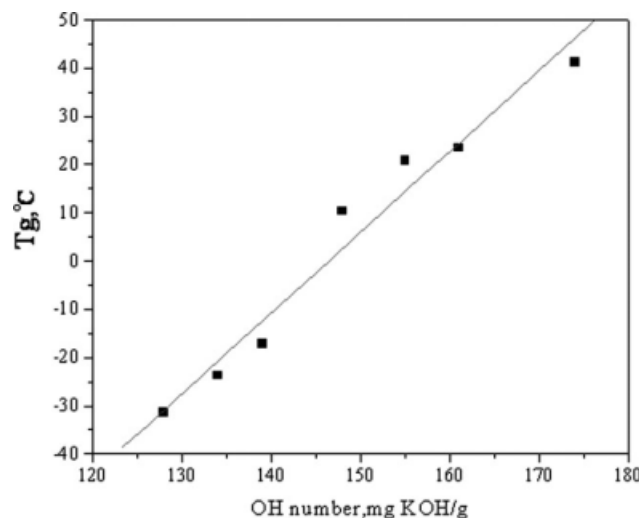

Figure 5 Effect of the OH number of polyols on the glass transition temperature of polyurethanes determined by DSC.

TABLE II
Glass Transition Temperatures and Mechanical Properties of Polyurethanes from Different OH Number Polyols

Polyol OH number (mg of KOH/g)	128	134	139	148	155	161	174
T_g by DSC (°C)	−31.4	−23.7	−17.2	10.4	20.9	23.5	41.2
Tensile strength (MPa)	–	–	0.4	6.37	10.36	14.02	20.24
Elongation at break (%)	–	–	38	184	122	49	31

822 and 845 cm^{-1} are attributed to the residual epoxyl groups. Therefore, the iodine value is smaller.

As can be seen in Table I, the iodine value shows that there are still double bonds in the polyol molecules, which may give rubbery properties to the PUs.

Swelling of polyurethane networks in toluene

The results of swelling experiments are shown in Figure 3. As can be seen in Figure 3, none of the samples are completely soluble. The crosslinking density of the PUs correlates directly with the OH number of the polyols.

Thermal and mechanical properties of polyurethanes

The properties of PUs are related to the crosslinking density of the networks, i.e., directly with the OH number of the polyols. Thus, the properties are discussed as a function of the OH number of polyols.

DSC curves of PUs, as shown in Figure 4, show clear glass transitions for samples prepared with polyols and TDI. The glass transition of the samples with OH number of 128 mg of KOH/g was not clearly defined because of the high heterogeneity of the samples, the variable degree of the crosslinking density of the network, and the high sol fraction. An endothermic peak between 0 and 20°C of OH#128 sample may be due to the melting peak of the sol.
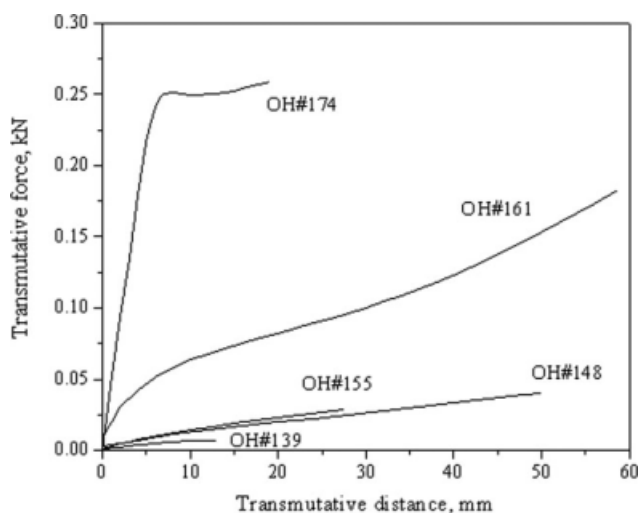
Figure 5 displays the linear relationship between the OH number and T_g, as expected from the Fox-Losheak equation[12] relating the crosslinking density and T_g as follows:

$$T_g = T_{g\infty} + \frac{K}{M_c} = T_{g\infty} + kv$$

As presented in Table II, the mechanical properties of PUs were also reported, and the stress–strain curves are given in Figure 6. The mechanical analysis confirmed the DSC results. When the OH number is lower than 139 mg of KOH/g, the mechanical tests cannot be performed because of the lower mechanical properties indicating that they are fairly imperfect networks because of the low average functionality of the polyols and the absence of oligomers. For the other samples, the tensile strength of PUs increases with the crosslinking density and glass transition temperature, whereas the elongation at break decreases with the crosslinking density and glass transition temperature apart from the OH number of 139 mg of KOH/g, as displayed in Figure 7. All samples had a low tensile strength except the glassy sample with an OH number of 174 mg of KOH/g, which showed a moderate value of the tensile strength equal to 20 MPa. The elongation at break of PUs increases with the decreasing OH
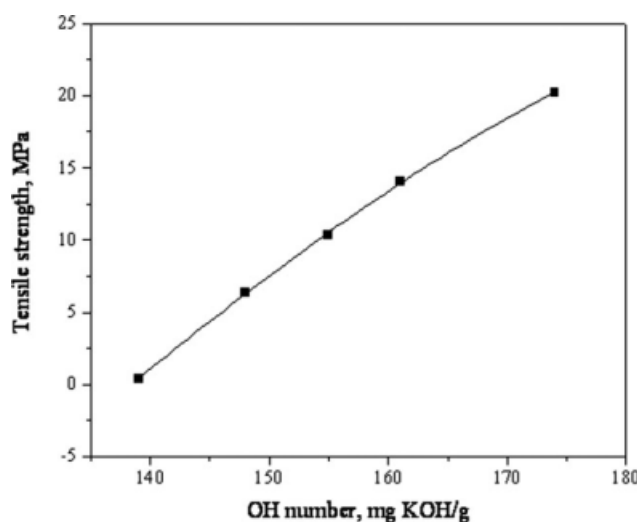

Figure 6 Stress–strain curves of polyurethanes.

Figure 7 Effect of the OH number of polyols on the tensile strength of polyurethanes.

Figure 8 TG curves in air of cast polyurethane resins with different OH numbers.

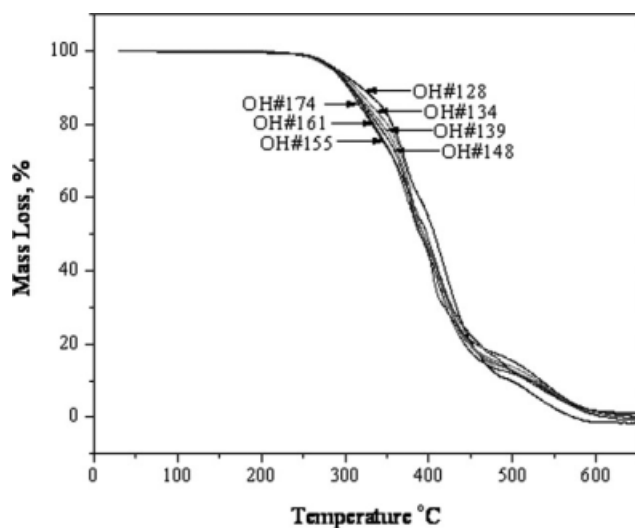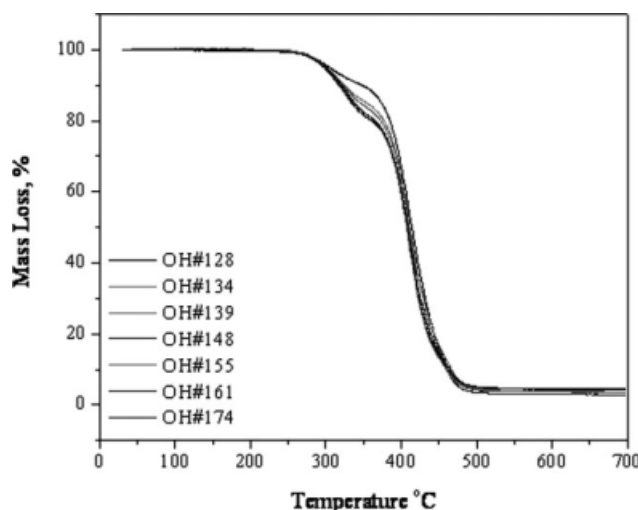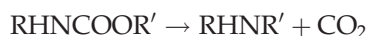**Figure 10** DTG curves in N_2 of cast polyurethane resins with different OH numbers.

number, and the highest value is 184% with the OH number of 148 mg of KOH/g.

PUs generally have a relatively low thermal stability. Three mechanisms of decomposition of urethane bonds have been proposed[13]:

1. Dissociation to isocyanate and alcohol:

$$RHNCOOR' \rightarrow RNCO + HOR'$$

2. Formation of a primary amine and olefin:

$$RHNCOOCH_2CH_2R' \rightarrow RNH_2 + CO_2 + R'CH = CH_2$$

3. Formation of a secondary amine:

$$RHNCOOR' \rightarrow RHNR' + CO_2$$

All three reactions may proceed simultaneously. PUs from vegetable oil-based polyols with secondary OHs have been found[13] to start degradation below 300°C because of the loss of carbon dioxide from the urethane bond, and this process is faster in PUs from secondary OHs as in our PUs. The thermal stability of PUs as measured by the initial weight loss (Fig. 8) showed a good correlation with the OH number of polyols, increasing with the decreasing OH numbers, but increasing with double bonds in the polyols. TG and DTG curves of PUs under nitrogen are shown in Figures 9 and 10. Figures 9 and 10 also suggested that the thermal stability of PUs increases with the decreasing OH number, but the decomposition processes have only two steps whereas those in air have four steps (Fig. 11).
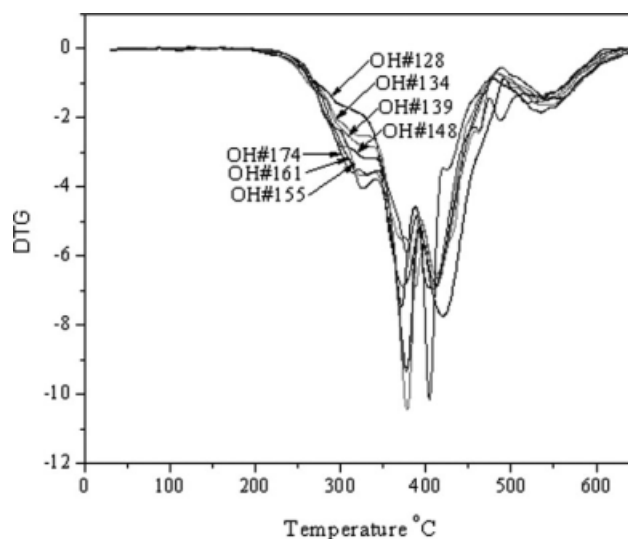

Figure 9 TG curves in N_2 of cast polyurethane resins with different OH numbers.

Figure 11 DTG curves in air of cast polyurethane resins with different OH numbers.

CONCLUSIONS

In this work, the PUs based on soybean oil were synthesized, and the effect of OH number on the crosslinking density, thermal, and mechanical properties of PUs was studied. As a result, the tensile strength of PUs increases with the increasing OH number. However, the thermal stability of PUs decreased with the increasing OH number. This could be caused by the the low crosslinking density of hydroxyl network because ofthe low reactivity of OH of the resins.

PUs prepared from these polyols and TDI were glassy when the polyol OH number was 174 mg of KOH/g and rubbery below that value. Glassy PUs displayed decent mechanical strengths, whereas rubbery samples showed relatively poor elastic properties characterized by lower strengths. This cast PU resin appeared as a rigid plastic having a glass transition temperature of 41°C. The cast resin may be molded into electroinsulating components.

The advantages of these PUs are their low cost, availability from a renewable natural resource, and their possible biodegradability.

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