J Therm Anal Calorim (2010) 100:239–246
DOI 10.1007/s10973-009-0418-4

Synthesis and thermal properties of soybean oil-based waterborne polyurethane coatings

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Received: 29 June 2009 / Accepted: 12 August 2009 / Published online: 15 September 2009

Abstract Waterborne polyurethane coatings were prepared by a polyaddition reaction using toluene diisocyanate (TDI), 2,2-di(hydroxy-methyl) propionic acid, soy-based polyols with different hydroxyl values, plus 2-hydroxyethyl methacrylate (HEMA) as chain termination agent, triethylamine as neutralization agent, and DBTDL as catalyst. Six soybean oil-based polyols were used in this study with hydroxyl values of 100, 115, 128, 140, 155, and 164 mg KOH g^{-1}, respectively. The molar ratio of polyol hydroxyl to DMPA was varied from 1.6 to 2.6. The storage stability of the waterborne polyurethane coatings was greater than 6 months. The thermal properties of the coating films were investigated by TG and DCS. The results show that the soy-based polyurethane films decomposed in three stages. The glass transition temperatures, T_g, of the soy-based polyurethane films increased with the hydroxyl number of the soy-based polyol.

Keywords Waterborne polyurethane coating · Soy-based polyol · Synthesis · Thermal analysis

Introduction

Thermal analysis techniques have been used to characterize edible oils and fats by measurement of thermo-oxidative behavior and stability [1, 2]. The thermal stability of polyols derived from soybean oil depends upon their chemical structure, and improves with increasing content of hydroxyl groups. This property is of great practical importance in avoiding rupture of the glyceryl chains of these polyols, especially when the polyol reacts with 2, 4-toluene diisocyanate (TDI), 4, 4′-methylenebis(phenyl isocyanate) (MDI), 1, 6-hexamethylene diisocyanate (HDI) and other types of diisocyanate to produce polyurethane (PU) elastomers, foams, and resins, as these chemosynthesis reaction are drastic, exothermic, and foaming reactions [3].

There is a growing urgency to develop bio-based products and other innovative technologies that can reduce the widespread dependence on fossil fuels. Bio-based products from renewable resources can form the basis for a portfolio of sustainable and greener materials that can compete in, and capture, markets currently dominated by products derived exclusively from petroleum feedstocks. Among the advantages of bio-based products are ready availability and low cost. Nowadays, various renewable resources, for example, starch, proteins, fats, and oils, can be used to prepare polymers [4–8].

Waterborne polyurethane has been developed largely because of its excellent mechanical properties and its environmental friendliness, thereby making it an excellent replacement for the organic solvent type polyurethane materials currently used in the coating, printing, ink, and adhesive industries [9]. Waterborne polyurethane could be prepared by adding water into a segmented polyurethane ionomer containing a very small amount of solvent as diluent agent. During the addition of water, as the polyurethane ionomer disperses gradually into the water, phase reversal takes place, and the water-in-oil system becomes oil-in-water [10].

The preparation of polyurethane coatings from polyols has been the subject of many studies [11, 12], but limited attention has been paid to the relationship between the properties of the soybean oil-based polyol and the resulting

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polyurethane coating. In the present study, a series of soybean oil-based polyols with different hydroxyl values were generated by the epoxidation of soybean oil (SBO), followed by ring opening of the epoxidized soybean oil (ESO). These polyols were characterized prior to being used for the preparation of polyurethane coatings. The physical and thermal properties of the resultant polyurethane coatings were investigated.

Experimental

Materials

The refined soybean oil, iodine value 127.23 (g I/100 g oil), was kindly provided by Nanhai Oil Co. Ltd. Glacial acetic acid (99.5%), methanol (>99.5%), sodium carbonate, sodium hydroxide, hydrogen peroxide (30%), sulfuric acid (98%), ammonia (30% in water), tetrafluoboric acid (48% in water), 2, 4-Toluene diisocyanate (TDI), and triethylamine (TEA) were purchased as AR grade from Guangzhou Chemical Reagent Co. Ltd. Dibutyltin dilaurate (DBTDL) was supplied by Lingfeng Chemical Reagent Co. Ltd. 2-hydroxyethyl methacrylate (HEMA) was supplied by Zhenlin trade Limited Company.

2, 4-Tolulene-diisocyanate (TDI) was used without further purification. However, the HEMA and acetone were treated with 3 Å molecular sieves for three days, the polyols were dewatered under vacuum at 90 °C for 4 h, and the 2,2-di(hydroxy-methyl) propionic acid (DMPA), supplied by Carpoly Chemical Co., was dried at 80 °C for 4 h.

Methods

The epoxy oxygen content (EOC) of ESO was determined by the direct titration of epoxy groups with HBr according to the standard method for oils and fats [13]. The hydroxyl value determinations were carried out according to ASTM D 1957–86. This method used a solution of acetic anhydride in pyridine and was generally expected to quantitatively esterify all the hydroxyl (–OH) groups in the polyol.

The content of isocyanate was calculated according to the mass fraction of isocyanate (–NCO) measured by the di-n-butylamine method.

The IR spectra were recorded on a Fourier transformation infrared (FTIR) spectrometer (IR Prestige-20, Shimadzu, Japan). The samples were prepared as thin films on KBr salt plates.

A 200PC Netzsch, (Germany) differential scanning (DSC) calorimeter was employed to measure thermal properties over the temperature range -100 to 200 °C, applying a heating rate of 20 K min^{-1} plus a 30 mL min^{-1} nitrogen purge to the 8 mg samples, in sealed aluminum pans. The data of second running were recorded.

The thermal stability was tested by thermogravimetry (TG) and derivative thermogravimetry (DTG) using a Netzsch, STA 409 PC (Germany). Polyurethane samples, ranging from 8 to 10 mg, were placed in the sample pan and heated from 30 to 600 °C under N_2 at a heating rate of 10 K min^{-1}. During the heating period, the mass loss and temperature difference were recorded as a function of temperature.

Laser particle size analysis was performed on a Mastersizer 2000 (Malvern Instruments, Britain) with a 1.55 refractive index and a 10.5 ultrasonic displacement.

Synthesis of epoxidized soybean oil

The reaction was carried out in a 1,000 mL, four-necked, round-bottom flask equipped with a mechanical stirrer, a condenser, a thermometer sensor, and an isobaric funnel. SBO (180 g, 0.206 mole double bonds) was placed in the round-bottom flask, then peroxyacetic acid was added slowly through an isobaric funnel over 2 h (±5 min), maintaining the reaction temperature at 70 °C. This precaution was taken to prevent overheating of the system due to the exothermic nature of epoxidation reactions. The whole reaction system was kept in a water bath, which maintained the reaction temperature at 70 ± 1 °C. The peroxyacetic acid was prepared at 30–40 °C by mixing 42 g (0.696 mole) of 99.5% glacial acetic acid and 198 g (1.752 mole) of 30% H_2O_2 in the presence of small quantities (0.1 mL) of concentrated sulfuric acid and placed in a dark area for about 12 h. Uniform reactant dispersion during epoxidation was accomplished by maintaining a 600 rpm stirring rate. The reaction was quenched after a prescribed time by cooling the samples to room temperature. The samples were then poured into a separating funnel, the aqueous layer drawn off, and the oil layer washed successively with sodium carbonate solution until the pH was nearly neutral, and then with saturated sodium chloride solution and distilled water. The sample was further purified in a rotary evaporator at 80 °C, under low vacuum, for 1 h. The resultant ESOs had EOC values of 0.2411, 0.2769, 0.3089, 0.3393, 0.3750, and 0.3924 mole $(100\ \mathrm{g})^{-1}$.

Preparation of the polyols by ring opening of ESO

Methanol was charged into a four-necked, round-bottomed reaction flask, equipped with a reflux condenser, and was heated to 65 °C in a constant-temperature water bath. Tetrafluoboric acid was used as catalyst at a concentration of 0.2% of the total mass of methanol and ESO. ESO was then added to the reaction system through an isobaric funnel. The molar ratio of epoxy groups to methanol was 1:11. The reaction mixture was kept at 65 °C for 1.5 h, and then cooled to room temperature. A small amount of ammonia (30% in water) was added to neutralize the catalyst. The solvent was removed in a rotary evaporator under low vacuum at 60 °C for 0.5 h, followed by 90 °C for 2 h. The resultant hydroxyl values were 100, 115, 128, 140, 155, and 164 mg KOH g^{-1}.

Preparation of the polyurethane coatings

For each PU coating, 8 g of the polyol and a specified amount of DMPA were added into a four-necked flask equipped with a stirrer, a reflex condenser, an inlet for nitrogen, and an isobaric funnel. The molar ratio of the polyol hydroxyl groups to DMPA was in the range 1.0–2.6. The reactants were heated at 90 °C for 1 h to melt and mix the DMPA perfectly with the polyol, then 4–5 drops of DBTDL as catalyst and a specified amount TDI were added slowly into the reaction until the molar ratio of –NCO to –OH was 1.1:1. Stirring was continued for 3 h at 75 °C before HEAM was added into the reaction system until the theoretical content of –NCO was reached. Thereafter, acetone was charged into the flask to lower the viscosity of the formed, segmented polyurethane. TEA was then added, in an equivalent amount to the molar quantity of DMPA, in order to neutralize the reaction mixture, prior to adding deionized water into the flask at 40 °C for 10 min while stirring at 3,000 rpm. The product was then purified in a rotary evaporator under low vacuum at 50 °C for 10 min in order to remove the acetone. The solid content of the water dispersion was about 30%. The recipes for the soy-based polyurethane coatings are listed in Tables 1 and 2. The synthesis routes of soy-based polyols and polyurethanes are provided in Schemes 1 and 2.

The preparation of polyurethane-coated teflon fabrics

Preparation of the films was carried out by pouring the aqueous dispersion into a Teflon disk under ambient conditions [14]. The films (typically about 0.5 mm thick) were dried in a vacuum oven at 60 °C for 2 days prior to storing in a desiccator at room temperature.

Table 1 The recipes for polyurethane samples with different hydroxyl values*

Sample no.	m_{polyol}/g	m_{DMPA}/g	m_{HEMA}/g	m_{TDI}/g	V_{H2O}/mL
100-2.0	8.00	0.4777	0.4988	2.4826	27
115-2.0	8.00	0.5494	0.5737	2.8550	28
128-2.0	8.00	0.6115	0.6385	3.1777	29
140-2.0	8.00	0.6688	0.6984	3.4756	30
155-2.0	8.00	0.7405	0.7732	3.8480	31
164-2.0	8.00	0.7835	0.8181	4.0714	32

* The solid content of all samples was 30%

Table 2 The recipes for polyurethane samples with different molar ratios of polyol hydroxyl groups to DMPA*

Sample no.	m_{polyol}/g	m_{DMPA}/g	m_{HEMA}/g	m_{TDI}/g	V_{H2O}/mL
164-1.6	8.00	0.9793	0.8179	4.3515	33
164-1.8	8.00	0.8705	0.8179	4.1959	32
164-2.0	8.00	0.7835	0.8179	4.0714	32
164-2.2	8.00	0.7122	0.8179	3.9696	31
164-2.4	8.00	0.6529	0.8179	3.8847	31
164-2.6	8.00	0.6027	0.8179	3.8129	31

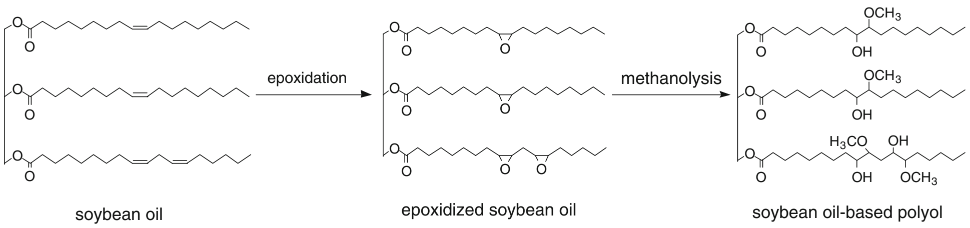
* The solid content of all samples was 30%

Results and discussion

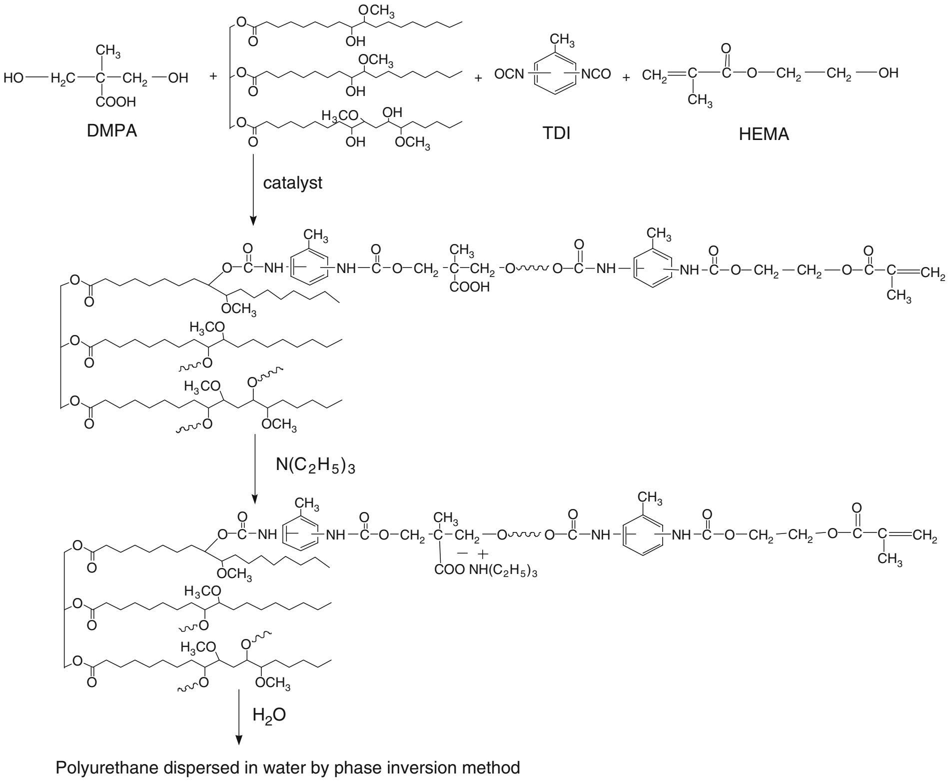
Soybean oil-based polyurethane coatings were prepared in two stages. In the first stage, soy-based polyols were obtained by the epoxidization of soybean oil followed by ring opening with methanol (Scheme 1). Polyols with different hydroxyl values were obtained by changing the epoxidization reaction time [15]. In the second stage, high solid content soy-based polyurethane pre-polymers were prepared from polyols, TDI, and other reactants (Scheme 2). The properties of the final polyurethane films were greatly influenced by the structure, chemical composition, segment length and concentration, the ratio of soft to hard segments, and various additional interaction parameters [16]. Whereas a change in any of the above parameters affects the quality of the polyurethane film, the ratio of soft to hard segments is the most important factor in determining the properties of the polyurethane prepolymer. The soft, flexible segments are in a viscous or rubbery state and provide the elastomeric characteristics of the polyurethane chains. The hard, rigid segments are in a glassy or semi-crystalline state and provide dimensional stability by acting as thermally reversible, multifunctional, pseudo or physical crosslinks, plus reinforcing fillers. Incorporation of chemical crosslinks and the presence of side products strongly influence the material properties [17]. In the present study, the molar ratio of polyol hydroxyl groups to DMPA was varied from 1.6 to 2.6, and several polyols with hydroxyl values between 100 and 164 were generated in the experiments. The “100-1.6” designation means that the hydroxyl value of the polyol is 100 mg KOH g^{-1} and the molar ratio of the polyol hydroxyl groups to DMPA is 1.6. The amounts of reactants used for the preparation of polyurethane samples are presented in Table 1.

The IR spectra presented in Fig. 1 clearly indicate characteristic peaks at: 3,472 cm^{-1} (–OH) for the polyols;

Scheme 1 The synthesis of a polyol from SBO



Scheme 2 The synthesis route of a soy-based polyurethane coating



3,371–3,209 cm^{-1} (–OH, –COOH) for DMPA; 3,444 cm^{-1} (–OH) for HEMA; 2,263 cm^{-1} (–NCO) for TDI; 3,329 cm^{-1} (–NH) and 1,740 cm^{-1} (ester group) for the polyurethanes. There was no absorption in the polyurethanes at 2,263 cm^{-1}, indicating that the isocyanate (–NCO) groups had fully reacted. There was no absorption in the polyurethanes at about 3,400 cm^{-1}, indicating that the –OH groups fully reacted with –NCO groups.

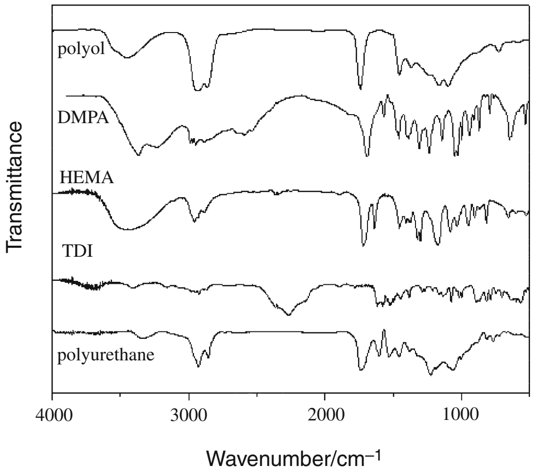


Fig. 1 The IR spectra of polyol, DMPA, HEMA, TDI, and polyurethane

The thermogravimetric technique is useful in the investigation of the thermal stability of vegetable oils and their derivatives [2]. The characteristic temperatures were obtained from thermo gravimetric (TG) and differential thermo gravimetric (DTG) curves. The values of T_i (the initial decomposition temperature for the first step of decomposition), T_{1MAX} (the temperature of maximum rate of mass loss for the first step), T_{2MAX} (the temperature of maximum rate of mass loss for the second step), T_{end} (the final decomposition temperature), $T_{10\%}$ and $T_{50\%}$ (the temperatures at which a mass loss of 10 and 50% occurred), and the char yield at 600 °C are listed in Table 3. The onset of degradation in a polyurethane film is governed by the weakest link in the chain, whereas, the predominant chain form and the relative arrangement of the various functional groups are the factors which determine the overall thermal stability. The backbone structure of the polyurethane coating affects its thermal behavior, as can be seen from Table 3.

The T_i and T_{end} values of the generated polyurethanes increase with the number of hydroxyl groups in the soy-based polyols, and indicate that 164-1.6 is the most stable, thermally (Table 4; Figs. 2, 3, and 4).

The 164-1.8 sample demonstrated the greatest thermal stability, with the highest values of T_i, $T_{20\%}$, $T_{50\%}$, and T_{end}, plus a char yield value of 8.64% at 600 °C, much lower than most of the other polymers generated. Thus, 1.8 was the optimal molar ratio of polyol hydroxyl groups to DMPA for a hydroxyl group value of 164 mg KOH g^{-1} (Tables 5 and 6).

Polyurethanes generally have relatively low thermal stability. Three mechanisms for the decomposition of urethane bonds have been proposed [18]:

1. Dissociation to an isocyanate and an alcohol

$$\mathrm{RHNCOOR'} \rightarrow \mathrm{RNCO} + \mathrm{HOR'}$$

2. Formation of a primary amine and an olefin:

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

3. Formation of a secondary amine:

$$\mathrm{RHNCOOR'} \rightarrow \mathrm{RHNR'} + \mathrm{CO_2}$$

All three reactions may proceed simultaneously. Polyurethanes from vegetable-oil-based polyols with secondary hydroxyl groups have been found to begin to degrade below 300 °C through the loss of carbon dioxide from the urethane bond. The polyurethanes generated during this research demonstrated superior thermal stability, which, as measured by the initial mass loss, increased with the polyol hydroxyl group number.

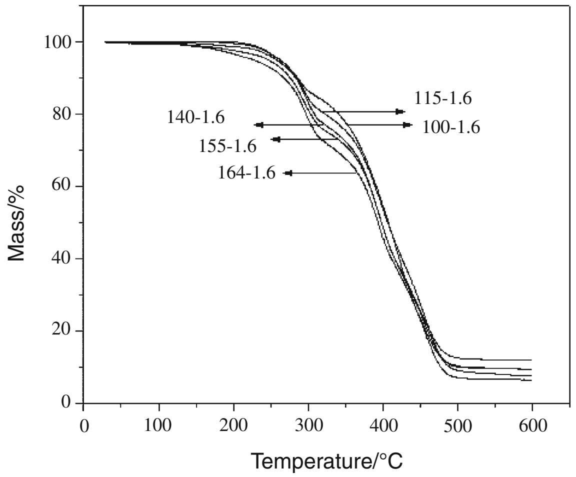


Fig. 2 The TG curves of polyurethanes prepared from toluene diisocyanate and polyols with different hydroxyl values

The glass transition temperature T_g of the polyurethane samples increased with the polyol OH value (Fig. 5), as higher hydroxyl values increase the density of crosslinking. The curves of the polyurethane samples with OH values of 100 and 115 mg KOH g^{-1} have a peak at about −10 °C, possibly due to the unreacted chains of ESO.

The minimum particle size was achieved with a 2.0 molar ratio of polyol hydroxyl groups to DMPA. In these

Table 3 The thermal properties of polyurethane samples with varying hydroxyl values

Sample	T_i/°C	$T_{10\%}$/°C	$T_{50\%}$/°C	T_{end}/°C	T_{1MAX}/°C	T_{2MAX}/°C	Char yield at 600 °C/%
100-1.6	250.0	294	416.6	474.8	288.9	423.1	6.98
115-1.6	257.7	284.7	406.1	477.0	292.7	396.7	7.43
140-1.6	259.9	283.3	398	480.2	296.1	394.2	8.42
155-1.6	261.2	276	397.6	483.6	293.8	393.3	10.6
164-1.6	264.6	267.4	393.1	486.1	295.5	392.5	9.39

Table 4 The effect of polyol hydroxyl group to DMPA molar ratio on the thermal properties of polyurethane

Sample	T_i/°C	$T_{20\%}$/°C	$T_{50\%}$/°C	T_{end}/°C	T_{1MAX}/°C	T_{2MAX}/°C	Char yield at 600 °C/%
164-1.6	259.6	295.5	392.5	476.1	297.2	393.1	9.39
164-1.8	260.9	303.1	397.0	485.8	298.0	389.6	8.64
164-2.0	259.8	295.8	394.4	473.1	300.8	393.1	8.78
164-2.2	253.9	291.8	391.5	471.5	299.3	392.3	11.38
164-2.4	255.7	290.5	391.5	471.4	299.6	391.5	10.31
164-2.6	258.2	297.1	392.7	470.4	304.7	394.3	9.15

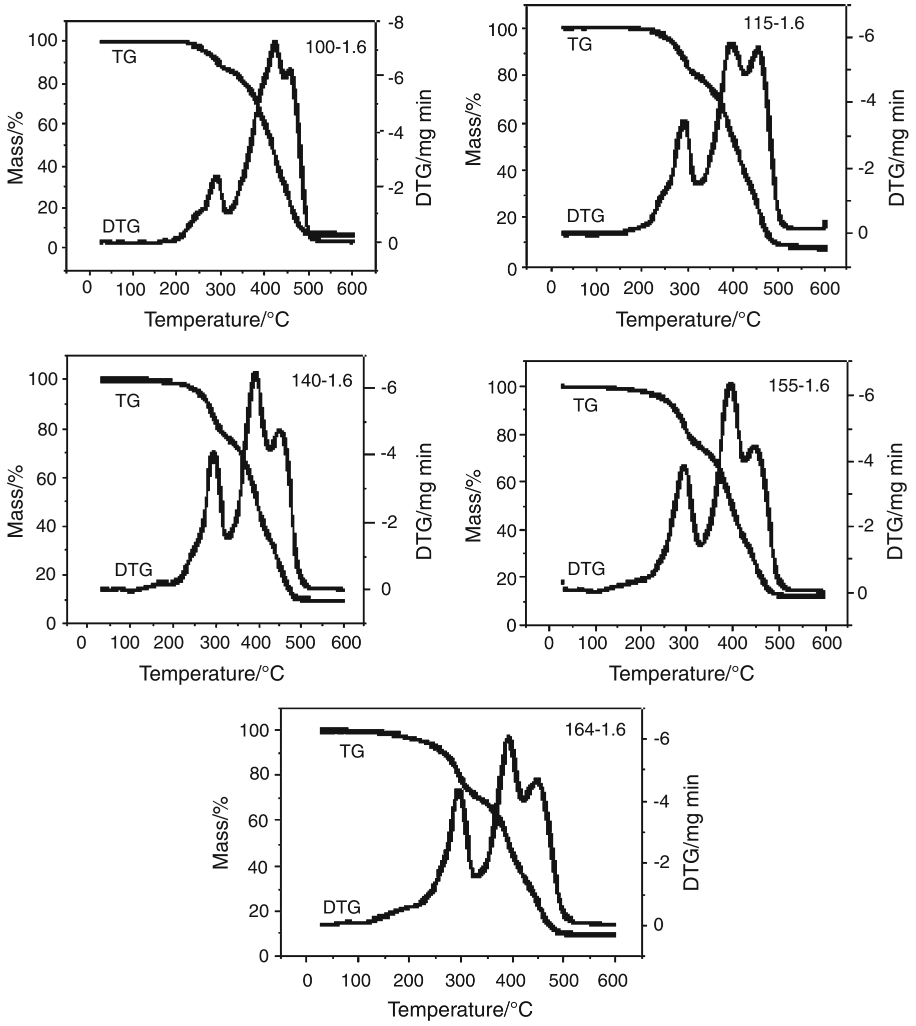


Fig. 3 The TG and DTG curves of polyurethane samples with a 1.6:1 molar ratio of polyol hydroxyl groups to DMPA

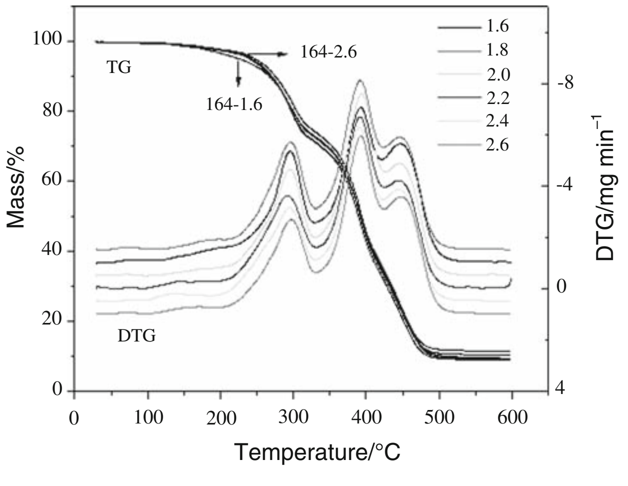


Fig. 4 The TG and DTG curves of polyurethane samples with different molar ratios of polyol hydroxyl groups to DMPA

experiments, DMPA acts as a hydrophilic agent, thus the size of the particle radius would be expected to increase as more DMPA was added. According to the Kelvin equation for the dissolution equilibrium of a solid in a liquid, small particles would aggregate with large particles causing instability of the dispersion. For this reason, the smallest particle size was attained at an optimal molar ratio of polyol hydroxyl groups to hydrophilic DMPA, and this molar ratio has a significant impact upon the quality of the dispersion of the PU particles in water (Fig. 6).

For a constant 1.6 molar ratio of polyol hydroxyl groups to DMPA, particle size increases (and specific area decreases) with hydroxyl value (and hence crosslink density). It becomes more difficult to disperse the particles in water as the molecular mass increases.

Table 5 Variation of the dispersion sample physical data with the molar ratio of polyol hydroxyl groups to DMPA

Sample	Particle size/m	Specific area/$m^2\ g^{-1}$	Consistency	External appearance	Storage stability/months
164-1.6	20.974	0.688	1.21	Yellowish white	6 < but < 12
164-1.8	5.946	1.23	1.22	Slightly yellow	>12
164-2.0	4.702	5.54	1.05	Yellowish white	>12
164-2.2	16.001	1.1	1.52	Yellowish white	>12
164-2.4	26.828	0.81	1.77	White	6 < but < 12
164-2.6	30.072	0.376	0.726	White	6 < but < 9

Table 6 Variation of dispersion sample physical data with polyol hydroxyl values

Sample	Particle size/m	Specific area/$m^2\ g^{-1}$	Consistency	External appearance	Storage stability/months
100-1.6	2.283	3.76	0.669	yellow	>12
115-1.6	4.052	2.824	1.475	yellow	>12
128-1.6	6.279	2.55	1.17	yellow	>12
140-1.6	8.131	1.35	6.38	slightly yellow	>12
155-1.6	10.298	1.49	1.55	slightly yellow	9 < but < 12
164-1.6	20.974	0.688	1.21	yellowish white	6 < but < 12

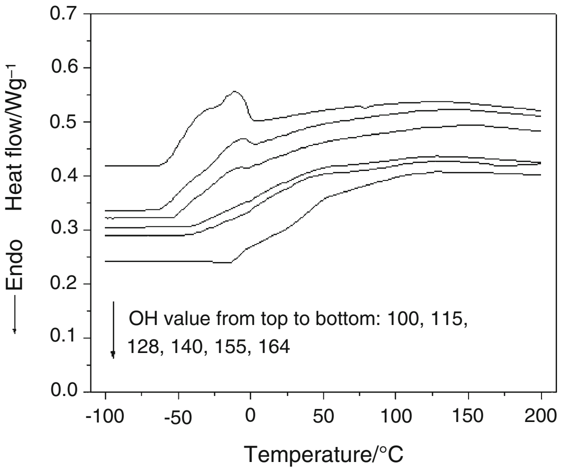


Fig. 5 DSC thermograms of polyurethanes with different hydroxyl group values

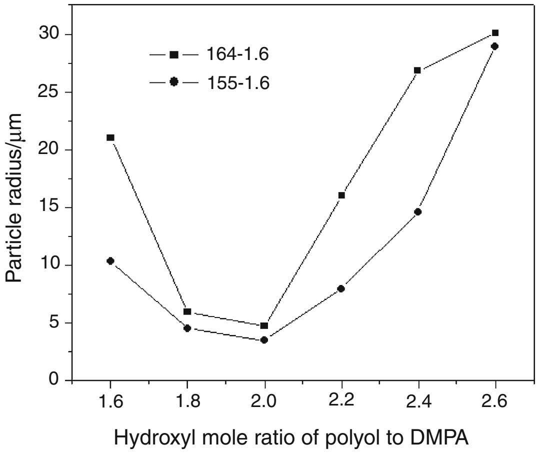


Fig. 6 Variation of PU latex particle size with the molar ratio of polyol hydroxyl group to DMPA

Conclusions

Soy-based polyurethane coatings were successfully synthesized from soy-based polyols and TDI. The physical properties and storage stability of these waterborne polyurethane coatings appear to meet the requirements for industrial applications. The initial decomposition temperatures were above 250 °C, and the temperatures at which a mass loss of 50% occurred were greater than 390 °C. The glass transition temperatures of the polyurethane films were in the range from –10.2 to 48.6 °C, and increased with increasing polyol hydroxyl value. The advantages of these polyurethanes are their low cost, availability from a renewable, natural resource, and potential biodegradability.

Acknowledgements This study was supported by a grant (No. 06025028) from the Natural Science Foundation of Guangdong Province.

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