

Liquefaction of Wheat Straw and Preparation of Rigid Polyurethane Foam from the Liquefaction Products

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ABSTRACT: Wheat straw was liquefied in the mixture of polyethylene glycol (PEG 400) and glycerin in the presence of acid at the temperature 130–160°C. The final liquefaction products having the hydroxyl number of 250–430 mg KOH/g and the \bar{M}_n of about 1050 can be used as the polyol component to manufacture polyurethane. A kind of polyurethane foam was prepared from liquefied wheat straw, commercial polyol, and diisocyanates in the presence of organotin catalysts and foaming agents. The polyurethane foam presented better compressive strength and thermal sta-

bility than that manufactured from diisocyanate and polyol alone. The thermal stability of PU foam was improved with the increase of [NCO]/[OH] ratio and the addition of liquefied wheat straw. The polyurethane foam presented faster biodegradation at ambient temperature than normal polyurethane foam did. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 508–516, 2009

Key words: polyurethanes; thermal properties; biodegradable; liquefaction; wheat straw

INTRODUCTION

The utilization of lignocellulosic biomass has attracted much attention because of the abundant reserves and renewable nature of the raw materials. Lignocellulosic biomass can be used to manufacture polymer materials. As lignocellulosic biomass usually presents poor processing performances, it is sometimes converted into substances that can be processed before use. A lot of conversion techniques have been proposed in the past few decades. Liquefaction is one of the useful and effective techniques.

Numerous liquefaction ways have been developed to complete the conversion. The liquefaction products having low molecular weight have been used as fuels or chemicals.^{1–3} The liquefaction products possessing moderate molecular weight and active functional groups can be used to manufacture plastics, foams, films, and adhesives.^{4–7}

Shiraishi and coworkers^{5–7} investigated the liquefaction of wood in polyols as the solvent. The resulting liquefaction products were directly used as the polyol component for manufacturing polyurethane foams without any fractionation.^{5,8} Many kinds of woods, chemically modified woods, wood wastes, and some nonwoods have been successfully liquefied.^{6,9,10}

Plant components act as a hard segment in polyurethane. They can enhance glass transition temperature, mechanical modulus, and strength of polyurethanes. The polyurethanes from woody materials were found biodegradable in soil.¹¹ Phenol-formaldehyde resin and epoxy resin^{12,13} can also be manufactured from liquefied woods and nonwoods, as well as from liquefied paper.

A large amount of phenol was used in Shiraishi et al.'s study to prevent the liquefaction intermediate from condensation. Large portions of phenol remain in the liquefied products without chemical bonding to the depolymerized fragments.¹⁰ The existence of phenol has negative effects on the processing performances of the liquefaction products; therefore, the removal of the residual phenol is necessary. The liquefaction without the addition of phenol is recommended because it can simplify the liquefaction and the post-treatment of the liquefaction products.

The performances of polyurethane foams manufactured from liquefied plant raw materials, especially those from nonwood fibers, have seldom been investigated.

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In this study, rigid polyurethane foam was manufactured from diisocyanate and liquefied wheat straw, a widely distributed nonwood fibrous raw material in China. The characteristics of liquefaction products and those of the polyurethane foams were also investigated.

EXPERIMENTAL

Materials

Wheat straw (*Triticum aestivum*) was obtained from Nanyang, Henan Province, China. It contained 40.5% of cellulose, 29.9% of hemicellulose, 17.2% of Klason lignin, and 9.8% of ash. It was milled to 28–80 mesh and oven-dried at 105°C for 24 h before use. Polyethylene glycol (PEG 400), glycerin, and sulfuric acid were of reagent grade. NE-141, the commercial name of methylene diphenylene diisocyanate (MDI), was the product of Dow Chemical Company, USA. Toluene diisocyanate (TDI) was produced by Cangzhou Dahua TDI Co., Cangzhou, China. Ditin *n*-butyl dilaurate (DBTDL), the catalyst used in polyurethane manufacturing, was a commercial product of Shanghai Minchen Chemical Co., China. Tegostab B-8433, a silicone surfactant used to stabilize the foam, was a commercial product of was a product of Goldschmidt AG, Germany. TNR410, a polyol, was a commercial product of Tianjin No.3 Petrochemical Plant, China. HCFC-141b, a foaming agent having the formula $\text{CH}_3\text{CCl}_2\text{F}$, was the commercial product of Solvay Flour GmbH, Germany. All these chemicals were used as received.

Liquefaction of wheat straw and characterization of liquefaction products

Polyethylene glycol, glycerin, and sulfuric acid were added according to predesired composition into a three-necked flask equipped with a reflux condenser and a stirrer. Wheat straw was added into the flask, which was preheated to the desired temperature. The liquefaction was conducted with constant stirring and refluxing at 130–160°C. After a defined duration, the reactor was cooled to the room temperature rapidly.

The liquefaction products were neutralized by MgO. Water produced in the liquefaction procedure was removed by vacuum evaporation. The reaction mixture was filtered to isolate the residue from the solution. The solution was concentrated by thin film evaporation at 60°C to remove volatile solvents and water. The residue was extracted with diethyl ether in a Soxhlet extractor to remove the liquid products, then air-dried, and thereafter dried in a 105°C oven. The mass of the residue was obtained.

The molecular weight and the molecular weight distribution of the product were determined by gel permeation chromatography. The apparatus comprised a Waters 515 pump, a Waters Ultrastaygel 500Å column, and a Waters 410 RI detector. Tetrahydrofuran was used as the eluent. Narrow-distributed polystyrene was used as the standard sample to calibrate the column.

The hydroxyl number, the acid number, and the water content of the liquefaction products were measured according to ASTM D2849.

The viscosity of the liquefied product was measured at 25°C using a Brookfield viscometer (Brookfield Engineering Laboratories, Middleboro, MA) at the rotation speed 12 rpm.

Preparation and characterization of polyurethane foam

Predetermined amounts of the liquefied wheat straw, commercial polyol, DBTDL, and Tegostab B-8433 were mixed thoroughly in a paper cup. Then diisocyanate and HCFC-141b were added into the cup. Then, the mixture was stirred at the speed of 3000 rpm for 15 s. The mixture was poured immediately into a cubic paper container that was precoated with dimethicone, the releasing agent, and then was allowed to rise at room temperature. After 2-min rise, the foam was allowed to cure at room temperature for 1 h. Then, the foam was removed from the container and was cut into 50 mm × 50 mm × 50 mm specimens. The specimens were conditioned at 23°C and 50% relative humidity for 48 h, and then, the densities were determined.

The isocyanate index was calculated according to literature.⁹

The compressive strength and the density of the polyurethane foams were measured according to ASTM D-1621 and ISO 845-1988, respectively.

The glass transition temperature (T_g) of each polyurethane foam was measured by differential scanning calorimetry (DSC) on a MDSC 2910 apparatus manufactured by TA Instruments (New Castle, DE 19720). A 7–10 mg sample was first scanned to 100°C to eliminate the effect of enthalpy relaxation, thereafter cooled to –50°C and scanned again to 100°C. All scans were conducted under dry nitrogen flow of 50 mL/min at a heating or cooling rate of 10°C/min. The T_g in the second scan was defined as one-half the total change in heat capacity (C_p) occurring over the transition region.^{14,15}

The TG analysis was conducted on Perkin–Elmer (Shelton, CT 06484) Pyris 1 TGA analyzer. The sample (8–12 mg) was tested at the heating rate of 10°C/min from room temperature to 600°C under N₂ gas flow of 200 mL/min.

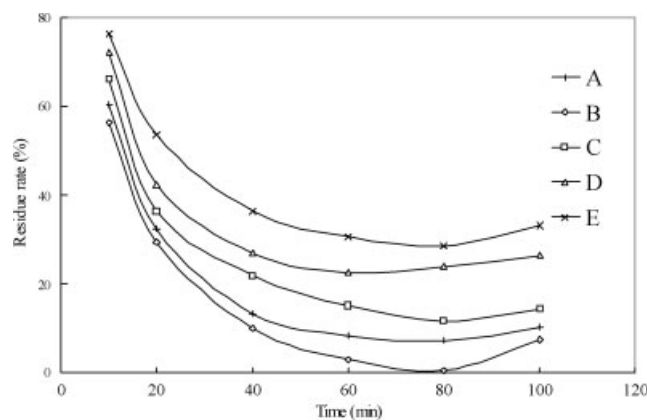


Figure 1 Effects of solvent composition on the residue rate. Temperature, 150°C; dosage of sulfuric acid, 2%: (A) glycerin : PEG 400 = 0 : 10, (B) glycerin : PEG 400 = 2 : 8, (C) glycerin : PEG 400 = 4 : 6, (D) glycerin : PEG 400 = 6 : 4, (E) glycerin : PEG 400 = 8 : 2.

The soil embedding test for testing the rate of biodegradation of polyurethane foam was conducted according to literature.¹¹ The samples were cut into specimens of 5 cm (width) × 5 cm (length) × 1 cm (thickness). The specimens were weighed and then embedded in a piece of land with a certain microorganism. Then, the samples were unearthed, respectively, at an interval of 2 weeks. The samples were carefully washed and dried. The average weight loss of each kind of sample was calculated from the data of five specimens.

RESULTS AND DISCUSSION

Factors influencing the liquefaction of wheat straw

In this work, the residue rate R is used to evaluate the efficiency of the liquefaction. R is defined as follows:

$$R (\%) = (\text{mass of residue} / \text{mass of wheat straw}) \times 100\%$$

It was reported that the solvent composition, the liquid ratio, the type of acid catalyst, the reaction time, and the temperature have significant influences on the compositions and the performance of the liquefaction products.⁹

Figures 1 and 2 illustrate the residue rate of wheat straw liquefaction as a function of reaction time. All the curves are similar to that reported by Yao et al., but wheat straw liquefies faster than paper or wood.^{9,16} Faster liquefaction of wheat straw than that of paper is probably due to the existence of lignin in wheat straw. Anyway, the liquefaction of wheat straw produces more residue than that of wood or paper because of the high content of ashes. As reported in literature, the rapid liquefaction relied on lignin and hemicelluloses existing in wheat straw, whereas cellulose mainly affected the slow

liquefaction stage.⁹ Relatively loose structure of wheat straw leads to easier soakage of wheat straw by liquefying agent, which favors rapid liquefaction. The residue rate decreased rapidly in the starting 60 min indicating that the lignin and hemicelluloses were being liquefied. When major part of wheat straw components was liquefied, relatively high concentration of liquefaction fragments easily led to the recondensation, and the residue rate began to increase.¹⁷ To reduce the residue content, the reaction time should not exceed 90 min.

It was found that increasing the content of polyethylene glycol in the liquefying reagent could accelerate the liquefaction and reduce the residue rate. However, the use of pure PEG 400 as the liquefaction solvent did not result in the lowest residue rate. The lowest residue rate was achieved when the liquefying solvent containing 80% of PEG 400 and 20% of glycerin was adopted, which is consistent to literature.^{9,17} The low residue rate is probably derived from the good permeability of glycerin into the wheat straw, and the dissolution of the wheat straw was accelerated.

The residue rate was found sensitive to the liquid ratio. The residue rate was high when the liquid ratio was below 3 indicating that the liquefaction was incomplete. This is probably because the liquefying solvent cannot penetrate into the wheat straw thoroughly in that case and the components of wheat straw are difficult to dissolve. Too high concentration of liquefaction product also increases the possibility of recondensation between the liquefaction fragments and formation of residue.⁹ Increasing the liquid ratio promotes the liquefaction and reduces the viscosity of the liquefaction products. However, the increase in liquid ratio cannot continuously improve the liquefaction efficiency when the liquid ratio is high enough. The liquid ratio of 5 : 1 is

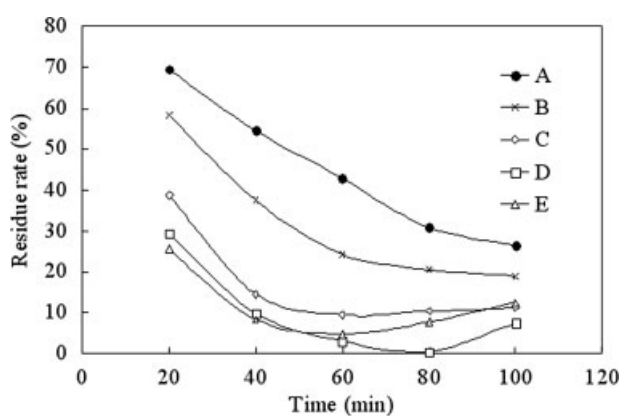


Figure 2 The influence of temperature on the residue rate. Glycerin : PEG 400 = 2 : 8, Liquid ratio 5 : 1, Acid content 2%. (A) 120°C; (B) 130; (C) 140°C; (D) 150°C; and (E) 160°C.

TABLE I
Influence of Reaction Time on Molecular Weights of Liquefaction Products

Sample	Reaction time (min)	M_{p1}	M_{p2}	Area _{p1} : Area _{p2}	\bar{M}_n	\bar{M}_w	$d = \bar{M}_w/\bar{M}_n$
1	40	1340	1070	2.13	1020	1200	1.18
2	60	1400	1060	2.10	1050	1260	1.20
3	90	1450	1040	2.12	1040	1270	1.22

PEG 400 : glycerin = 8 : 2, liquid ratio 5 : 1, acid content 2%, temperature 150°C.

proved enough to achieve high liquefaction efficiency.

Sulfuric acid catalyzes the liquefaction of wheat straw. However, lignin fragments recondense easily in acidic medium and the residue was thus formed. It was found that low residue rate and fast liquefaction were achieved when the dosage of sulfuric acid was 2%.

Figure 2 shows the impact of temperature on the residue rate. At 130°C, the residue rate reduced with time during the whole liquefaction procedure indicating that the condensation is not remarkable. When the temperature was 160°C, the residue rate decreased at the early stage of the reaction but then increased indicating that both degradation and condensation occurred rapidly at high temperature. The lowest residue rate was achieved at 150°C.

Molecular weight and molecular weight distribution

The data of GPC analysis indicate that each liquefaction product comprised of two major fractions with different molecular weights. The chromatograms of the three products presented similar shape and position indicating that the three products had similar molecular weight distribution. The data of molecular weight distributions of these products are shown in Table I where M_{p1} and M_{p2} represent the peak molecular weight of high molecular weight fraction and low molecular weight fraction, respectively. The data showed that the components with different molecular weights dissolved at a similar rate during the liquefaction procedure. Prolonging the reaction time only increased the yield of liquefaction products.

TABLE II
Molecular Weights Distribution of the Liquefaction Products Obtained at Different Temperatures

Sample	Temperature (°C)	\bar{M}_n	\bar{M}_w	$d = \bar{M}_w/\bar{M}_n$
1	130	900	1040	1.15
2	140	940	1120	1.19
3	150	1020	1200	1.18
4	160	1540	1950	1.27

PEG 400 : glycerin = 8 : 2, liquid ratio 5 : 1, H₂SO₄ content 2%, reaction time 40 min.

The molecular weight distribution, however, had little change.

The influences of temperature on the molecular weight distribution of the liquefaction products are shown in Table II. The data indicate that enhancing the temperature resulted in wider molecular weight distribution. This is because enhancing temperature could promote the decomposition of the wheat straw components and the recondensation of the liquefaction intermediates simultaneously. Both high molecular weight products and low molecular weight products are thus formed.

Infrared spectra of liquefied wheat straw

The infrared spectra of the wheat straw, the liquid product, and the residue are shown in Figure 3. The major bands of cellulose and lignin can be observed in the infrared spectrum of wheat straw. The band at 830 cm⁻¹ represents the bending of aromatic C—H. The bands at 1510 cm⁻¹ and 1600 cm⁻¹ represent the aromatic ring of lignin. The bands at 1035, 1110, and 1160 cm⁻¹ represent the C—O stretching of cellulose. The infrared spectrum of the liquefaction product (Curve B) is similar to that of the wheat

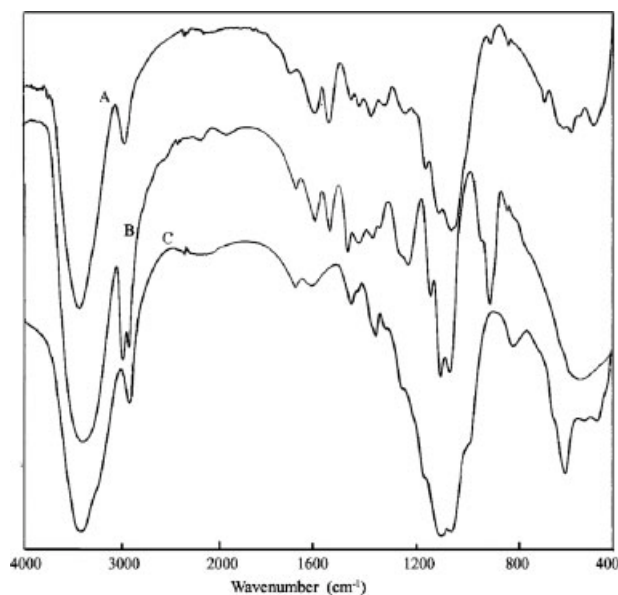


Figure 3 Infrared spectra of wheat straw, liquefaction product, and residue. (A) wheat straw; (B) liquefaction product; and (C) residue obtained at 90 min.

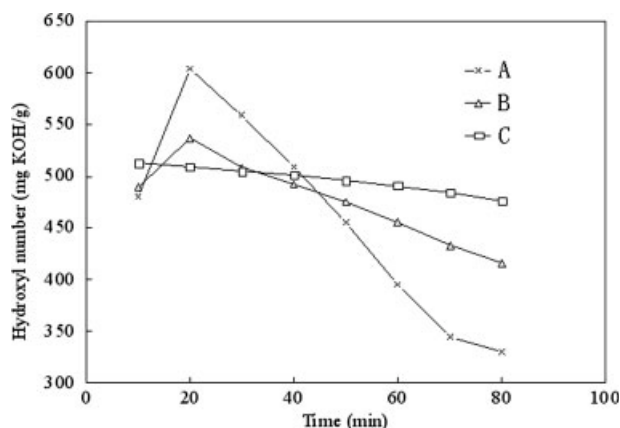


Figure 4 Variations of hydroxyl numbers of liquefied wheat straw and solvent as a function of time. (A) Liquefied wheat straw in 8 : 2.PEG 400 : glycerin mixture. (B): liquefied wheat straw in 6 : 4 PEG 400 : glycerin mixture. (C) 8 : 2 PEG 400-glycerin mixture.

straw. The major bands representing carbohydrates and lignin can be observed indicating that the both lignin and cellulose in wheat straw were transferred into the liquid phase.

The infrared spectrum of the residue (Curve C) presents less fine structure. The bands at 1510 and 1600 cm^{-1} representing the aromatic rings of lignin were weaker than that of wheat straw indicating that lignin content in the residue was lower than that in the raw material. Similarly, the main bands representing cellulose in the spectrum of the residue were also weaker than that in wheat straw indicating that only a small portion of cellulose is reserved in the residue. A band was observed at 1735 cm^{-1} in the spectrum of the residue, which could be assigned to ester-carbonyl groups of uronic acid esters in hemicellulose.¹⁸ No band was found at 1735 cm^{-1} in the starting mixture indicating that the esters were formed from the reaction between the acid and cellulose or hemicellulose during the liquefaction procedure. The esters could be dissolved in the solvent for liquefaction so that the 1735 cm^{-1} band also appeared in Curve B. The bands at 1600 and 1510 cm^{-1} were weakened indicating that the lignin content was reduced. The bands at 1035, 1110, and 1160 cm^{-1} in the IR spectra of the residue were also intensive, which indicates that the contents of cellulose and hemicellulose in the residue were high.

The infrared spectra suggest that condensed carbohydrates are the major component in the residue. However, the data of contents of Klason lignin in the residue do not support this opinion. The content of Klason lignin in the wheat straw was 17.2%, but the lignin content in the residue increased to 59.8% at the time 60 min. One reasonable explanation to this result is that the residue contained many kinds of acid-insoluble substances other than Klason lig-

nin. Actually, the dehydration of carbohydrates also results in acid insoluble residues. These residues are sometimes calculated as Klason lignin.

As the liquefied wheat straw is a complicated mixture, it is difficult to characterize the liquefaction product simply by spectrophotoscopic methods.

Acid number and hydroxyl number

The acid number of the reaction mixture at the beginning of the liquefaction was measured to be 15 mg KOH/g. The value increased to 28 mg KOH/g at the time 90 min. The increase in acid number can be attributed either to the increase of acidic substances or to the oxidation of the carbohydrates and lignin during the liquefaction.¹⁹

The hydroxyl numbers of the final liquefaction products varied in the range of 250–430 mg KOH/g, which depended on the solvent composition, as shown in Figure 4. In Experiment A, the hydroxyl number of the reaction mixture at 10 min was 480 mg KOH/g. Then, the hydroxyl number increased rapidly and reached the maximum value at 20 min. The increase is probably due to the cleavage of ester or ether linkages between the lignin units. After that, the hydroxyl number decreased slowly because of the dehydration and/or the oxidation reaction of the liquefied carbohydrates.⁵ The hydroxyl number was measured to be 352 mg KOH/g at 90 min, which is in the suitable range for preparing polyurethane foams. Curve B indicates that the hydroxyl number could be reduced by increasing the PEG 400 content in the mixed solvent because the content of free hydroxyl in PEG is low. The maximum hydroxyl number is reduced indicating that the ester linkages were not cleaved so completely as in Experiment A. In Experiment C, the control test, no wheat straw was added into the solvent. The

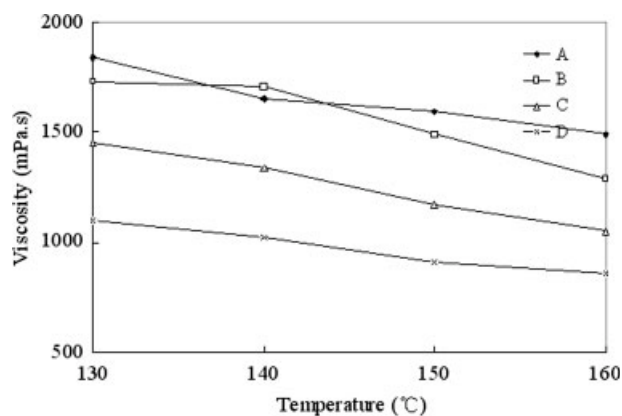


Figure 5 Viscosities of the liquefaction products obtained at different temperatures. (A) PEG 400 : glycerin = 10 : 0; (B) PEG400: glycerin = 8 : 2; (C) PEG400 : glycerin = 6 : 4; (D) PEG400 : glycerin = 4 : 6.

TABLE III
The Effect of Organotin Dosage on the Density of Polyurethane Foam

Organotin dosage (%)	1.0	1.5	2.0	2.5	3.0	3.5
Density (kg/m ³)	40.1	32.6	30.48	29.8	32.0	32.3
Compression strength (kPa)	110	120	120	112	124	109

hydroxyl number was found to decrease slowly. These experiments indicate that the peak value of the hydroxyl number was derived from the degradation of wheat straw.

Viscosity of the liquefaction products

Figure 5 shows the variation of the viscosity of liquefied wheat straw-based polyols with reaction time. The viscosity was found to depend on the composition of the liquefying agent. The viscosities of the liquefied wheat straw are feasible to manufacture polyurethane foam.

Suitable condition of preparation of polyurethane foams

Polyurethane foam was prepared from polyols and diisocyanates catalyzed by organotin or amines. Liquefied biomass can be used as the polyol component because it comprises the skeleton and active functional groups of polyols. As the "bio-polyol" was prepared from the by-product of sugar refinery, its price was lower than that of the "petro-polyol."

Density and compressive strength are two major indexes to evaluate the performances of the PU foams. In this work, the contents of the catalyst, the stabilizer, the foaming agent, and isocyanate were optimized to enhance the performances of foams.

Liquefied wheat straw contains free hydroxyls and ether linkages as well as lots of rigid structural units that derive from lignin. However, the liquefied wheat straw cannot replace all the polyols produced from petroleum. TNR410', an aliphatic polyether polyol that was usually used in rigid polyurethane foam, was added in this study. The polyol-diisocyanate ratio should be controlled in a proper range. Too low dosage of diisocyanate results in a decrease in urethane concentration in polyurethane networks. In the experiments, liquefied wheat straw can replace ~ 40% of polyols to prepare polyurethane foam.

DBTDL, an organotin catalyst, was used to catalyze the reaction between -NCO and -OH groups during the curing process of polyurethane foam. The catalysts' effects on the density and compression strength of polyurethane foam are shown in Table III.

The density of polyurethane foam was reduced to a minimum value at the organotin dosage 2.5%, but the compressive strength had little change.

Tegostab B-8433, a silicone surfactant, was used to stabilize the polyurethane foam. Suitable dosage of the stabilizer was 0.5–2.0%. Too less dosage of stabilizer could not stabilize the polyurethane foam, and too much stabilizer made the foam collapse. The density of the foam depends on the surfactant dosage.

Although sometimes reported being used in foaming of polyurethane, water is not considered a good foaming agent because it consumes too much isocyanate and results in heterogeneous foaming. Water foaming also releases too much heat and the quality of the foam is difficult to control. To obtain rigid foam with good performance, a chlorofluorocarbon, which is a substitute of CFC, was used in this experiment. Suitable dosage of HCFC-141b was 1.6%.

Structural characterization of polyurethane foam

Figure 6 illustrates the IR spectra of the polyurethane foam prepared from liquefied wheat straw and TDI (Sample A) and MDI (Sample B). As liquefied wheat straw was a complicated mixture, the IR spectra give mixed bands of various components of the polyurethane sample. The two polyurethane samples give similar IR spectra. The wide band at 3410 cm⁻¹ represents stretching vibration of N—H. The bands at 1702 and 1730 cm⁻¹ represent the stretching vibration of hydrogen-bonded carbonyl groups between N—H and C=O groups of urethane linkages and "free" carbonyls, respectively. The bands at 1530 and 1220 cm⁻¹ can be attributed to the $\delta(N-H)$ and $\nu(C-N)$. The bands at 1510 and

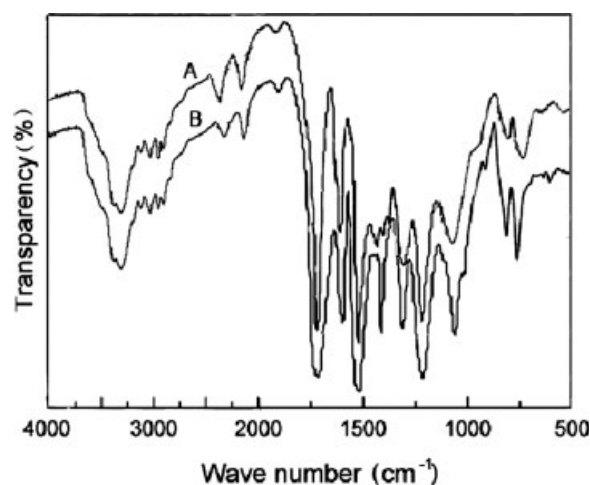


Figure 6 IR spectra of polyurethane foam. (A) from polyol and TDI; (B) from polyol and MDI.

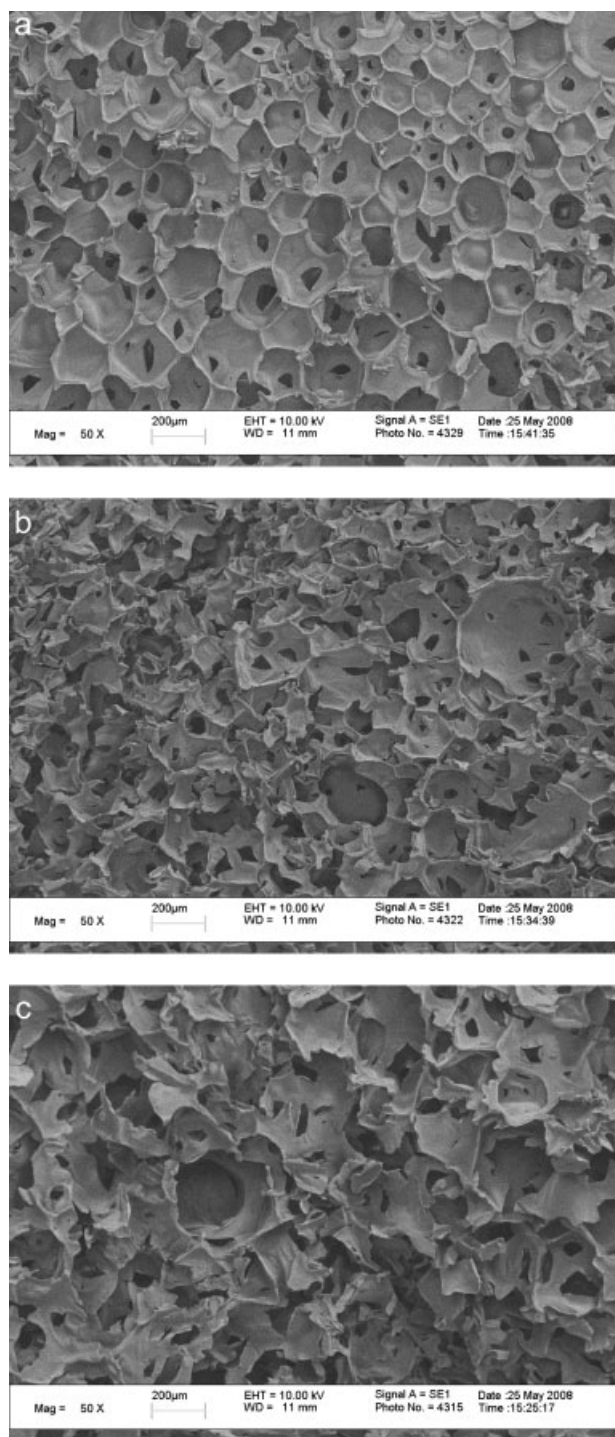


Figure 7 SEM images of polyurethane foam.

1600 cm^{-1} are derived from the aromatic rings of lignin. The bands at 2270 cm^{-1} in all FTIR spectra of the polyurethane samples prepared from different diisocyanates represent the excess -NCO group of diisocyanates. The bands at 1640 and 1636 cm^{-1} can be attributed to the stretching vibration of carbonyl groups of allophanates corresponding to polyurethane-diisocyanates.

Figure 7(a,b) show representative scanning electron micrographs (SEM) images of the polyurethane foam manufactured from liquefied wheat straw and TDI while Figure 7(c) shows that from liquefied wheat straw and MDI.

The pore diameter of polyurethane foam containing 15% of liquefied wheat straw in the polyol component varied in the range between 150 and 230 μm . The surface of the foam was found to be smooth. Increasing the content of liquefied wheat straw to 30% in polyol component resulted in the inhomogeneous surface and irregular pore shape, as shown in Figure 7(b). Some wrinkles were found on that from liquefied wheat straw and MDI (Fig. 7(c), showing the extent of homogeneity and microphase separation).

In a normal procedure of polyurethane manufacture, diisocyanates act as the hard segments, whereas polyols act as the soft segments. However, in this experiment, the liquefied wheat straw did not act as a normal polyol because of its special structure, and the diisocyanate does not act as a typical hard segment. MDI possess a relatively higher symmetric structure than TDI. The symmetric structure favors the formation of an ordered phase. Furthermore, MDI is more reactive than TDI because of steric hindrance and conjugative structure. It was reported that asymmetric diisocyanate, e.g., TDI, can improve the compatibility between the hard and soft segments, and the use of symmetric MDI in the preparation of polyurethane foam favors the microphase separation.²⁰

Mechanical properties of polyurethane foams

The compressive strength and the density of the foam prepared from the mixed polyol and MDI varied in the range of 130–250 kPa and 29.8–56.2 kg/m^3 , respectively, as listed in Table IV. It was observed that the foam density decreased with the increase in isocyanate index, i.e., the $[\text{NCO}]/[\text{OH}]$ ratio. The minimum foam density was achieved when the isocyanate index was 1.5. Similarly, the compressive

TABLE IV
The Effect of Isocyanate on the Properties of Polyurethane Foam

Isocyanate index	1.2	1.3	1.4	1.5	1.6
Density (kg/m^3)	56.2	43.1	36.2	33.3	34.6
Compressive strength (kPa)	169	185	212	195	192
Glass transition temperature ($^{\circ}\text{C}$)	31.7	37.2	43.5	52.6	55.3

Content of liquefied wheat straw in the mixed polyol component is 40%.

TABLE V
The Effect of Content of Liquefied Wheat Straw on the Properties of Polyurethane Foam

Liquefied wheat straw content (%)	0	10	20	30	40	50
Compressive strength (kPa)	173	192	206	208	195	183
Glass transition temperature (°C)	-6.5	13.8	32.7	48.5	52.6	55.6

strength reached the maximum when the isocyanate index was 1.4. To balance the requirement of compressive strength and foam density, the isocyanate index should be controlled in the range of 1.4–1.5.

The compressive strength of the same kind of polyurethane foam was found to increase with the content of liquefied wheat straw in the polyol component, as shown in Table V. The liquefied wheat straw comprises modification products of cellulose, hemicelluloses, and lignin. The rigid, net-like structure of lignin favors the increase in crosslinking density of the polyurethane macromolecules. It is reported that the stiffness, the strength, and the thermal stability of polyurethane improve with the addition of liquefied plant biomass.²¹ The compressive strength, however, began to decrease when the content of "bio-polyol" in the mixed polyol exceeded 30%. Possible reason was that too high content of hard segments in the foaming mixture

Several samples of polyurethane foam were prepared from same polyol components but different diisocyanates under same foaming conditions to compare the properties of the polyurethane foam. The data in Table VI indicate that MDI gives higher compression strength and modulus of the polyurethane foam than same dosage of TDI.

Thermal stability of polyurethane foam

TG analysis was used to evaluate the thermal stability of the polyurethane foams. The TG curves of the polyurethanes containing different dosages of liquefied wheat straw are shown in Figure 8.

TABLE VI
Mechanic Performances of Polyurethane Foam Prepared from Different Diisocyanates

Diisocyanate	MDI		TDI	
Liquefied wheat straw content (%)	10	30	10	30
Compressive strength (kPa)	192	208	168	185
Elastic modulus (MPa)	2.56	3.64	2.02	3.16

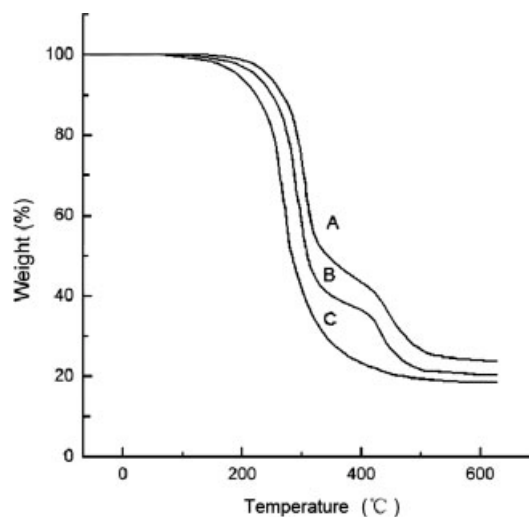


Figure 8 TGA curve of the polyurethane foams manufactured from different raw materials.

Polyurethane is thought to be relatively thermally unstable primarily because of the presence of urethane bonds, and the degradation usually starts at the urethane bond at temperature between 150 and 210°C, depending on the type of substituents on the isocyanate and polyol side.

Polyurethane without addition of liquefied wheat straw was found to decompose at about 165°C and lost 5% of its initial weight at 180°C. The temperature at which the polyurethane presents the highest decomposition rate was 256°C. The polyurethane sample within which 35% of liquefied wheat straw was added gives two weight loss stages in the TG curves. The first step of decomposition appeared at ~ 215°C and can be attributed to the decomposition of pyranose rings and isocyanate, and the second step appeared at 400–500°C and may be attributed to the decomposition of lignin and other difficultly breaking parts. As shown in TG curves, the temperature of the first and the second step of decomposition shift to the high temperature side with increasing the content of liquefied wheat straw. The data indicate that the thermal stability is significantly improved by the hard segments, especially by the addition of liquefied wheat straw.

The glass transition temperature (T_g) was calculated by DSC and the data were found to increase with the isocyanate index, as shown in Table V. When the isocyanate index increased, the glass transition was changed to a transition within a broad temperature range from that within a narrow temperature range. It has been found that polyurethane foams with highly branched or crosslinked structure required more thermal energy to initiate chain movements. The addition of liquefied wheat straw or increasing the isocyanate index results in the

TABLE VII
Weight Loss of Polyurethane Foam in Embedding Test

Content of liquefaction product (%)	Weight loss at different time (%)		
	3 months	6 months	9 months
0	4.2	6.4	12.2
28	6.2	11.8	16.0
46	9.0	14.5	17.2

increase in crosslink density and reduces the mobility of the main chain of polyurethane molecules. The thermal stability of the polyurethane foam is thus improved.

Biodegradation of polyurethane foam

Table VII illustrates the weight loss of three polyurethane samples prepared from liquefied wheat straw and polyhydric polyols in embedding tests. The weight loss of the three samples prepared from liquefied wheat straw-based polyols increased with time. The data show that the biodegradation of polyurethane foam was accelerated by the addition of liquefied wheat straw. Experimental data show that the biodegradation of polyurethane foam was accelerated by increasing the content of liquefied wheat straw in the polyurethane foam.

CONCLUSIONS

Wheat straw can be liquefied at 130–160°C in the polyethylene glycol-glycerin mixture catalyzed by sulfuric acid. The liquefaction product is suitable to be used as the polyol component in preparing polyurethane foams. The rigid polyurethane foam was prepared by mixing the liquefaction product, polyol TNR-410 with MDI in the presence of DBTDL as the catalyst, HCHC-141b as the foaming agent, and other additives. The thermal stability of the polyurethane foam was improved by the addition of

liquefied wheat straw. The morphology of the polyurethane foam was influenced by the dosage of liquefied wheat straw. The polyurethane foam was biodegradable.

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