

# Preparation and Characterization of Water-Blown Polyurethane Foams from Liquefied Cornstalk Polyol

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**ABSTRACT:** Polyurethane foams were prepared from the liquefied cornstalk polyol, which was obtained by the liquefaction of cornstalk in the presence of polyhydric alcohols using sulfuric acid as catalyst. The advisable liquefaction reaction conditions were selected by investigating their influences on the properties of liquefied cornstalk polyol, taking account of the requirement for the preparation of appropriate polyurethane foams. The influences of the contents of catalysts, water, surfactant, and isocyanate on the properties of polyurethane foams were

also discussed, and feasible formulations for preparing cornstalk-based polyurethane foams were proposed. The results indicated that the foams prepared from such liquefied cornstalk polyol exhibited excellent mechanical properties and thermal properties, and could be used as heat-insulating materials. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1099–1111, 2008

**Key words:** polyurethane foams; liquefaction; cornstalk; mechanical properties; glass transition temperature

## INTRODUCTION

Polyurethane foams (PUFs) are used widely in many fields as heat-insulating, packaging, structural, flotation and load bearing materials, due to their ease of processing and unique combination of excellent thermal insulation and mechanical properties. Traditional PUFs are prepared by the polymerization of polyol with isocyanate simultaneously occurring with gas generation resulting from the chemical reaction of water or blowing agent evaporation by the exothermic reaction itself. However, the raw materials for preparing PUFs, based on isocyanate and polyol (polyether or polyester polyols), are obtained mainly from fossil resources. With increasing concern about the limited availability of fossil resources and environmental problems associated with the excessive use of fossil fuels, there has been a great deal of interest in replacing petroleum-based products with renewable and biodegradable materials. In the past time, many researchers have been

interested in using the renewable resources originating from agricultural products, such as starch, plant oils, and polysaccharides, to prepare PUFs.<sup>1–3</sup> But it would consume plenty of foodstuff resources.

Recently the conversion and effective utilization of lignocellulosic biomass as renewable resources are increasingly receiving attention for scientists. Lignocellulosic biomass as natural polymer is composed mainly of cellulose, hemicellulose, and lignin, which contain more than one hydroxyl group in the molecular chains, and can be utilized as polyol for preparing polyurethane materials. However, because of its crystal structure and three-dimensional networks, most hydroxyl groups are embedded into polymeric matrix and lose reactive activity. Nowadays, many attempts have been made to use biomass efficiently by applying chemical and biochemical techniques and derive environmentally friendly materials. Of these efforts, the liquefaction of biomass in the presence of organic solvents under moderate temperature and atmospheric pressure and its application to the preparation of polymeric materials have attracted considerable attention. There were two types of conventional organic solvents to involve the use of biomass. The first was phenols, and the resultant products were rich in phenolic hydroxyl units, and therefore they could be used to prepare adhesives, molding materials, similar to conventional phenolic resin<sup>4–8</sup>; The second was alcohols, especially polyhydric alcohols, and the resultant products could be used as polyol to prepare polyurethane materials.<sup>9–14</sup>

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By now, the research on the utilization of biomass was mainly focused on wood.<sup>6–13</sup> With the exacerbation of deforestation and aggravation of water loss and soil erosion, it is necessary to replace wood with other biomass to protect forest resources. Especially for China, which is an agricultural country, the percentage of forest cover is low. On the contrary, there are nearly  $7 \times 10^8$  tons of agricultural by-products every year, including sugar bagasse, cornstalk, wheat straw, and rice straw, which are still incinerated or discarded into nature and pollute environment. Thus, it is significant to use these agricultural castoffs efficiently for energy strategy and environmental protection. In this study, many attempts have been made using the liquefaction technique to introduce biomass components into polyurethane foams formulation as the replacement of synthetic polyol in part, using cornstalk as raw material. The changes of the properties of liquefied cornstalk polyol under different reaction conditions were investigated to get suitable properties for preparing polyurethane foams. And it was also necessary to understand the influences of the contents of catalysts, water as blowing agent, surfactant and isocyanate on the structures and properties of the foams to obtain excellent PUFs derived from cornstalk.

## EXPERIMENTAL

### Materials

Cornstalk powder (20–80 mesh) was used as raw material. It was dried in an oven at 105°C for 24 h and kept in a desiccator at room temperature before use. Polyethylene glycol (PEG,  $M_n = 400$ ), glycerin and ethylene glycol (EG) were used as liquefaction solvents. Ninety-eight percent sulfuric acid was used as catalyst. 1,4-dioxane was used as solvent to dissolve the liquefied product and determine residue content. Pyridine, phthalic anhydride, and sodium hydroxide were used to determine the hydroxyl number and acid number of liquefied product.

Besides the liquefied cornstalk polyol, the raw materials required to prepare water-blown polyurethane foams were catalysts, blowing agent, surfactant, and isocyanate. Stannous octoate (organo-tin catalyst) was used as gelling catalyst. Triethylene diamine (amine catalyst) was used as blowing catalyst after been dissolved in dipropylene glycol to 33 wt % (L-33). Organosilicon surfactant (AK-8805) was used as foam stabilizer. Distilled water was used as chemical blowing agent. Polymethylene polyphenylene isocyanate (PM-200) was used as isocyanate, and the isocyanate content was 30.9 wt %. Except cornstalk and water, the other chemicals used above in this study were of analytical reagent grades, which were obtained from commercial sources, and used directly as received without further purification.

### Liquefaction of cornstalk

The liquefaction was carried out in a three-neck flask equipped with a stirrer, reflux condenser, and thermometer. The flask charged with the mixture of liquefaction solvents (PEG, glycerin or EG) and sulfuric acid was immersed into an oil bath and preheated at a certain temperature. Quantitative cornstalk powder was then added to the flask under stirring. The liquefaction was conducted under constant stirring and reflux at the certain temperature. After the presetting time, the flask was immersed in ice-water to quench the liquefaction reaction.

### Preparation of polyurethane foams

The liquefied cornstalk polyol for preparing PUFs was obtained using PEG/glycerin (4/1, w/w) as liquefaction solvents for 180 min at 150°C, with the liquid ratio and catalyst concentration being 5/1 (w/w) and 3 wt %, respectively, and using magnesia to adjust the pH. The predetermined amounts of liquefied cornstalk polyol, catalysts, water, and surfactant were premixed thoroughly for 2 min in a paper cup with a mechanical stirrer. Afterwards, a calculated amount of isocyanate (PM-200) at a certain isocyanate index was added to the premixture. And then, the combination was stirred with a high-speed agitator at a stirring speed of 3600 rpm for 20–30 s. Immediately, the resultant mixture was poured into an open mold having the dimension of  $120 \times 120 \times 180$  mm<sup>3</sup> (length  $\times$  width  $\times$  height) and allowed to rise freely at room conditions. The obtained foams were allowed to cure at room conditions for 1 h before being removed from the mold. And all properties of the foams were measured after curing at room conditions for seven days. The isocyanate index was calculated as the follows:

$$\text{Isocyanate index} = \frac{\frac{C_{\text{PM-200}}}{42} \times W_{\text{PM-200}}}{\frac{N_{\text{LCT}}}{56,100} \times W_{\text{LCT}} + \frac{2}{18} \times W_{\text{W}}} \quad (1)$$

where  $C_{\text{PM-200}}$  and  $W_{\text{PM-200}}$  were the isocyanate content (wt %) and weight (g) of PM-200, respectively;  $N_{\text{LCP}}$  and  $W_{\text{LCP}}$  was the hydroxyl number (mg KOH/g) and weight (g) of liquefied cornstalk polyol, respectively;  $W_{\text{W}}$  was the weight of water (g).

The formulations of PUFs with the liquefied cornstalk polyol are listed in Table I.

### Measurements

#### Characteristics of the liquefied product

The residue content was used as an index of the extent of liquefaction reaction. The resultant product was diluted with a large excess (about 20 times of

**TABLE I**  
**Formulations for Water-Blown Polyurethane Foams with the Liquefied Cornstalk Polyol**

Ingredients	Parts by weight (wt %)
Component A	
Liquefaction cornstalk polyol	100
Stannous octoate	0.1–0.6
Triethylene diamine (L-33)	0–3.6
Surfactant (AK-8805)	0.5–3.5
Water	0–3.75
Component B	
Isocyanate (PM-200)	120–210

liquefied product, v/w) of dioxane/water (80/20, v/v) binary solvents, which had been recommended as the universal diluent for liquefied biomass,<sup>9–11</sup> and stirred with a magnetic stirrer for more than 4 h. Thereafter the diluted product was filtrated using filter paper under vacuum to separate residue from the liquefied cornstalk. The insoluble residue was rinsed thoroughly with dioxane/water binary solvents until colorless filtrate was obtained, and then dried in an oven at 105°C to a constant weight. The residue content, which was defined as the percent dry weight of dioxane insoluble substance versus the total cornstalk charged, was calculated as the follows:

$$\text{Residue content} = \frac{W}{W_0} \times 100\% \quad (2)$$

where  $W$  and  $W_0$  were the weights of insoluble cornstalk residue and cornstalk sample before liquefaction (g), respectively.

The acid number was measured according to the following method<sup>11,12</sup>: about 8 g liquefied product was dissolved in 100 mL dioxane/water (80/20, v/v) binary solvents. The resultant solution was titrated at room conditions with 1 mol/L sodium hydroxide solution to equivalence point using pH meter. The acid number of liquefied product in mg KOH/g was calculated as the following equation:

$$\text{Acid number} = \frac{(V_1 - V_2)C \times 56.1}{W} \quad (3)$$

where  $V_1$  and  $V_2$  were the volumes of sodium hydroxide solution consumed in the sample and blank titration (mL), respectively;  $C$  was the concentration of sodium hydroxide solution (mol/L) and  $W$  was the weight of liquefied product (g).

The hydroxyl number was measured according to GB12008.3, which referred to ASTM D 2849. About 2 g liquefied product was firstly esterified for 1 h at 115°C with 25 mL phthalic anhydride/pyridine solvents (16/100, g/mL). Then, the mixture was titrated

with 1 mol/L sodium hydroxide solution to equivalence point using pH meter to determine extra phthalic anhydride. The hydroxyl number of liquefied product in mg KOH/g was calculated as the following equation:

$$\text{Hydroxyl number} = \frac{(V_1 - V_2)C \times 56.1}{W} + \text{acid number} \quad (4)$$

where  $V_1$  and  $V_2$  were the volumes of sodium hydroxide solution consumed in the blank titration and sample (mL), respectively;  $C$  was the concentration of sodium hydroxide solution (mol/L) and  $W$  was the weight of liquefied product (g).

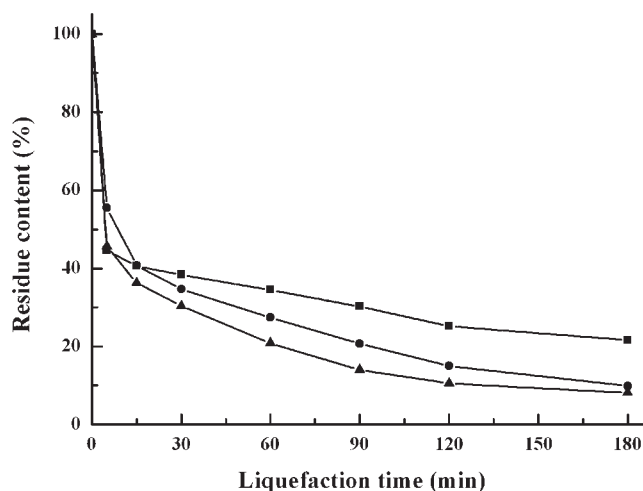
The molecular weight and its distribution of liquefied product were determined by a Waters 515 gel permeation chromatography system equipped with Ultrastaygel 500A gel columns. Measurement was performed at 40°C using tetrahydrofuran (THF) as mobile phase at a flowing rate of 1.0 mL/min. The chromatogram was monitored by a Waters 410 differential refractive index detector. The molecular weight and its distribution of the samples were calibrated with monodisperse polystyrene standards with various molecular weights.

#### Foams properties measurements

PUFs with liquefied cornstalk polyol were characterized for their molecular structures, morphologies, densities, compression strengths, dimensional stabilities, and thermal properties.

Fourier transform infrared spectra was recorded to characterize the molecule structures of the foams, liquefied cornstalk polyol, and PM-200 using RFX-65A infrared spectrometer. The foam samples were prepared in the form of KBr pellets after being dried. The liquefied cornstalk polyol and PM-200 were used as reflecting method, operated with 4 cm<sup>-1</sup> resolution. At the same time, the reaction chemistry during foaming process was monitored using ReactIR ic10 on-line infrared spectrometer. During preparing polyurethane foams, after adding isocyanate and mixing evenly, the detector was inserted into the mixture and recorded the infrared spectra at 15 s intervals.

The density of PUFs was measured according to GB 6343, which referred to ISO 845.<sup>15</sup> At first, the polyurethane foams were cut into the dimension of 50 × 50 × 50 mm<sup>3</sup> (length × width × height). After been dried under vacuum at 80°C, the specimens were weighed with precision. The densities of five specimens per sample were calculated using the weights and dimensions of the specimens and averaged.



**Figure 1** Effect of liquefaction solvents on the liquefaction of cornstalk (liquefaction solvents, ■, EG; ●, PEG; ▲, PEG/glycerin (80/20, w/w); catalyst concentration, 3 wt %; liquid ratio, 10/2 (w/w); reaction temperature, 150°C).

Stress–strain measurement of PUFs was performed under ambient conditions on CMT 7503 electronic tensile tester in accordance with GB8813, which was equal to ISO 844.<sup>15</sup> The size of the specimens was  $50 \times 50 \times 50 \text{ mm}^3$  (length  $\times$  width  $\times$  height), and the compression speed was fixed at 5.0 mm/min in the direction parallel to the foam rising direction. The compression strengths of the foam samples at 10% strain were calculated from the stress–strain curves. The compressive strengths of five specimens per sample were measured and averaged for each mechanical test.

To observe the cell structure and size of polyurethane foams, the morphology of the foams was examined with the help of XL-30 ESEM scanning electron microscope. A thin piece of foam samples (about 3-mm thickness) was carefully sliced with a sharp blade from the appropriate foam block and coated with gold on the surface before scanning. The accelerating voltage was 10 kV.

Dimensional stability measurement was performed according to GB8811, which was equal to ISO 2796.<sup>15</sup> The foam samples, whose size was  $100 \times 100 \times 25 \text{ mm}^3$  (length  $\times$  width  $\times$  height), were heated at 100°C in an oven and frozen at  $-20^\circ\text{C}$  in a refrigerator for 48 h, respectively. Then the foam samples were all taken out from the oven and refrigerator. After been kept under ambient conditions for 1 h, the dimensions of the samples were measured again. The dimensional variations of three specimens per sample were calculated and averaged.

The glass transition temperature ( $T_g$ ) was measured on Q 200 differential scanning calorimeter, using a sealed aluminum capsule. The foam samples approximately 6 mg were investigated in nitrogen atmosphere from  $-50$  to  $180^\circ\text{C}$ , at a heating rate of

$20^\circ\text{C}/\text{min}$  and nitrogen flowing rate of 50 mL/min. After a  $20^\circ\text{C}/\text{min}$  programmed cooling, the samples were reheated at the same heating rate. The  $T_g$  values were found by analyzing the DSC curves from the second runs.

Thermogravimetric analysis (TGA) was used to measure the thermal degradation of polyurethane foams. Sample weight used was 3–5 mg, and it was performed on Perkin–Elmer Pyris 1 thermal degradation tester under air atmosphere or nitrogen flowing rate of 50 mL/min by increasing the temperature from 25 to  $800^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$ . Decomposition temperature ( $T_d$ ) was determined from the TG curves and its derivative curves.

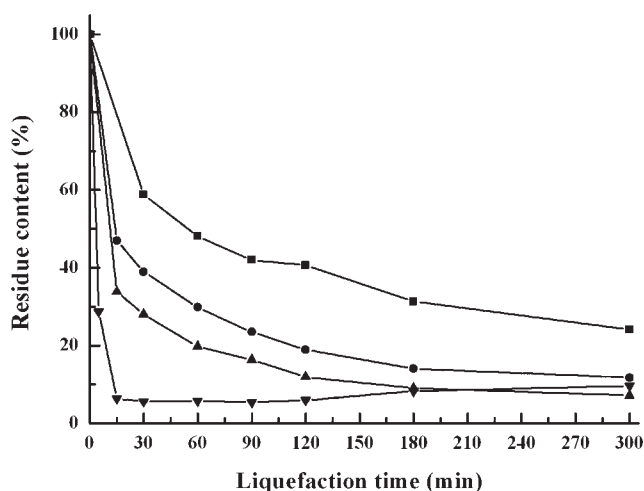
## RESULTS AND DISCUSSION

### Liquefaction of cornstalk in polyhydric alcohols and the properties of liquefied cornstalk polyol

The time-dependence of the liquefaction curves for cornstalk in different polyhydric alcohols is shown in Figure 1. With the prolongation of reaction time, the residue content decreased gradually. The whole reaction course could be divided into two stages. In the incipient stage from 0 to 30 min, the liquefaction efficiency was quite high, and nearly 60% of cornstalk was rapidly liquefied in the first 30 min; in the second stage, the residue content decreased slowly, and at last tended to balance. The rapid liquefaction stage could be attributed to the components of lignin, hemicellulose and some readily accessible cellulose, which were easily and firstly liquefied; while the second stage, which was characterized by the slow decrease of residue content, mainly depended upon the hard-to-access cellulose.<sup>11</sup> It was known that the liquefaction of cornstalk in the presence of organic solvents was a solvolysis process and solvents played important roles in the decomposition of cornstalk.<sup>8</sup> Thus, the liquefaction efficiency of cornstalk was found to vary in different liquefaction solvents. By comparison, it was realized that in the case of ethylene glycerol (EG), the liquefaction efficiency was sufficiently low and approximately one-fifth of cornstalk was left un-liquefied after 180 min. Thus, for the preparation of PUFs, PEG/glycerin (4/1, w/w) was selected as organic solvents to obtain liquefied cornstalk polyol, in which the liquefaction efficiency of cornstalk was highest.

The liquefaction reaction of cornstalk was also observed to proceed at certain reaction temperature. From Figure 2, it is obvious that the liquefaction efficiency was enhanced with the increase of reaction temperature. When the temperature was  $130^\circ\text{C}$ , the liquefaction efficiency was very low; after 300 min, there still left approximately one-fourth of cornstalk



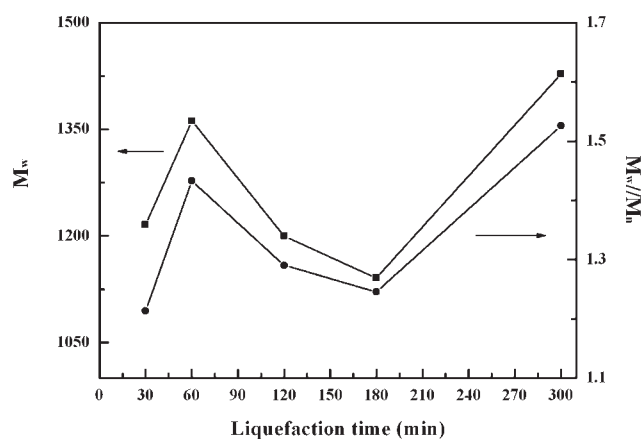


**Figure 2** Effect of reaction temperature on the liquefaction of cornstalk (liquefaction solvents, PEG/glycerin (80/20, w/w); catalyst concentration, 3 wt %; liquid ratio, 10/3 (w/w); reaction temperature, ■, 130°C; ●, 150°C; ▲, 170°C; ▼, 190°C).

unliquefied. But when the temperature increased to 150°C, the liquefaction efficiency was improved greatly, which indicated that increasing reaction temperature could accelerate liquefaction reaction. A further increase in temperature to 170°C did not improve the liquefaction efficiency significantly. However, when the temperature increased to 190°C further, almost all cornstalk was liquefied at the early stage, which may be due to pyrolysis and other side reactions at the high temperature, and prolonging liquefaction reaction decreased liquefaction efficiency instead because of promoting recondensation reaction at the same time.<sup>4,5,10,11</sup> So the liquefaction reaction was conducted best at 150°C.

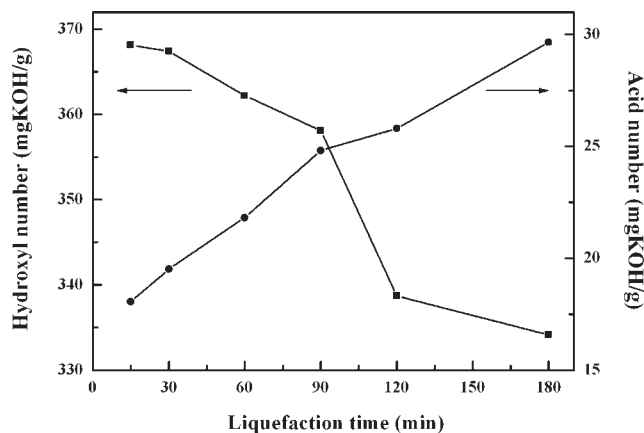
The molecular weight and its polydispersity of liquefied product also varied with the prolongation of liquefaction reaction. From Figure 3, it is observed that, at the beginning, cornstalk was decomposed into macromolecules, and so the corresponding weight-average molecular weight ( $M_w$ ) and its polydispersity ( $M_w/M_n$ ) increased. With the liquefaction reaction proceeding, the macromolecules were decomposed gradually and the  $M_w$  and  $M_w/M_n$  decreased continuously. However, after 180 min, the recondensation reaction occurred among the liquefaction solvents and decomposed cornstalk components, which resulted in the increase of  $M_w$  and  $M_w/M_n$  again.<sup>4,5</sup> From the time-course curves of residue content for cornstalk in Figure 2, it is also seen that the liquefaction efficiency almost kept balance after 180 min, which may be as the result of the balance of decomposition and recondensation.

The liquefaction of cornstalk in polyhydric alcohols was mainly alcoholysis process and the liquefied product contained abundant hydroxyl groups.



**Figure 3** Time-course of  $M_w$  and  $M_w/M_n$  of liquefied cornstalk polyol (liquefaction solvents, PEG/glycerin (80/20, w/w); catalyst concentration, 3 wt %; liquid ratio, 10/3 (w/w); reaction temperature, 150°C).

Figure 4 shows the changes of hydroxyl number and acid number of liquefied product as a function of reaction time. It is observed that, with the prolongation of liquefaction reaction, the hydroxyl number decreased gradually between 370 and 330 mg KOH/g, whereas the acid number increased gradually between 18 and 30 mg KOH/g. It revealed that there existed loss in hydroxyl groups during the liquefaction reaction, which could be attributed mainly to the alcoholysis reaction of cornstalk in polyhydric alcohols. And the oxidation and recondensation reactions among the liquefaction solvents and decomposed cornstalk components, which might take place during the liquefaction reaction, also consumed plenty of hydroxyl groups and decreased the hydroxyl number of liquefied product. The increase of acid number could be attributed to either the increase of acidic substances in the decomposed cornstalk components or the oxidation of alcohols

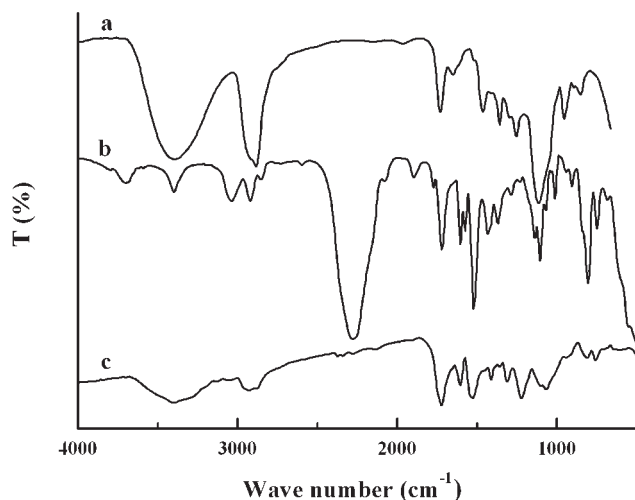


**Figure 4** Time-course of the hydroxyl number and acid number of liquefied cornstalk polyol (liquefaction solvents, PEG/glycerin (80/20, w/w); catalyst concentration, 3 wt %; liquid ratio, 10/2 (w/w); reaction temperature, 150°C).

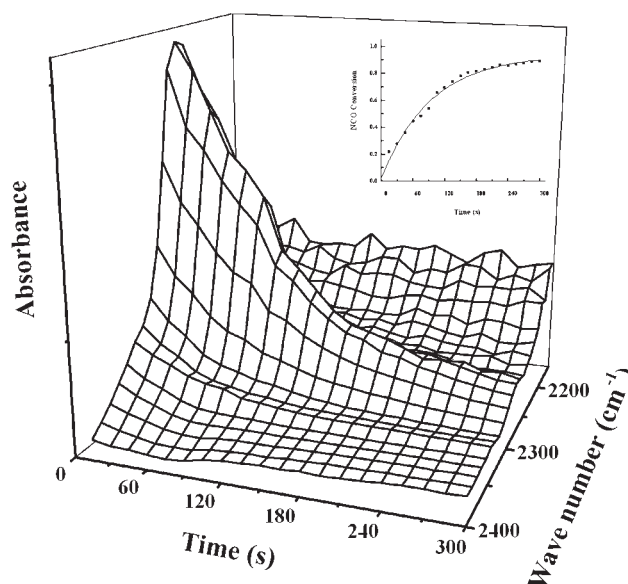
and the decomposed cornstalk components.<sup>11,13,14</sup> In combination with the analysis of the changes of liquefaction efficiency with reaction time above, the reaction time was fixed best at 180 min, when the hydroxyl number and viscosity of liquefied product with 5/1 liquid ratio were suitable for preparing PUFs.

### FTIR spectrum analysis

Figure 5 shows the IR spectra in the zone of 4000–500  $\text{cm}^{-1}$  of liquefied cornstalk polyol, PM-200 and the corresponding PUFs. From the IR spectra of (a) liquefied cornstalk polyol, the broad band at about 3400  $\text{cm}^{-1}$  was the characteristic stretching vibration of hydroxyl group, which indicated that the liquefied cornstalk polyol contained hydroxyl groups. Also (b) PM-200 contained isocyanate groups as reflected by a peak at 2270  $\text{cm}^{-1}$ . After the reaction between them to form (c) PUFs, the characteristic absorption band of isocyanate at 2270  $\text{cm}^{-1}$  disappeared, which indicated that isocyanate groups were completely consumed by the reactions with hydroxyl groups and water. On the other hand, from the IR spectra of (c) PUFs, the absorption bands at 3390, 1715, 1520, 1220  $\text{cm}^{-1}$  showed the urethane and urea linkages that were formed through the copolymerization of isocyanate groups, hydroxyl groups and water.<sup>12,16–18</sup> The bands at 3390 and 1715  $\text{cm}^{-1}$  were the characteristic stretching vibrations of amine group (N–H) and carbonyl group (C=O) of urethane and urea linkages, respectively, while the band at 1520  $\text{cm}^{-1}$  could be attributed to N–H bending vibration and C–N stretching vibration of urethane and urea groups. The band at 1220  $\text{cm}^{-1}$  was associated with the characteristic stretching vibration of C–N–H bond of urethane and urea



**Figure 5** IR spectra of (a) liquefied cornstalk polyol, (b) PM-200 and (c) polyurethane foams.

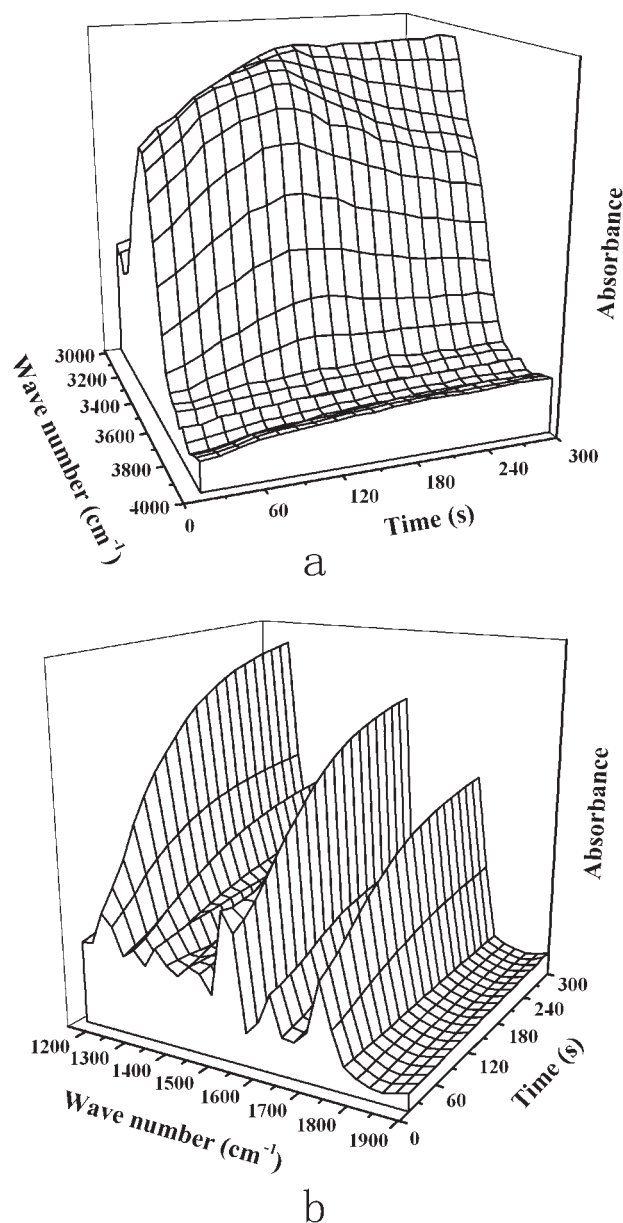


**Figure 6** Three-dimensional surface plot of isocyanate absorption band with time in the region of 2400–2150  $\text{cm}^{-1}$ .

groups. All these peaks were the characteristic bands of polyurethane, which indicated that the foams were polyurethane materials.

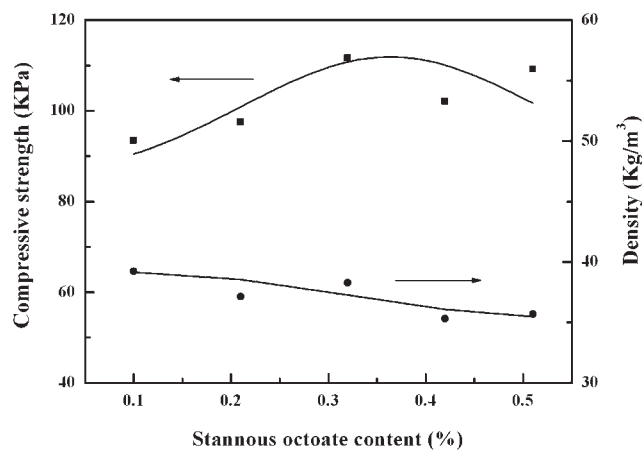
To understand the reaction process, the IR spectra obtained during foaming process is shown as a function of time in Figures 6 and 7. Several changes generally occurred for all systems. Reaction with water consumed isocyanate and produced urea groups, while reaction with hydroxyl groups from liquefied cornstalk polyol consumed isocyanate and produced urethane groups. Thus, from the two figures, a decrease in the intensity of the absorption band due to asymmetric isocyanate stretching vibration between 2400 and 2150  $\text{cm}^{-1}$  was observed clearly with simultaneous increase in the intensities of the characteristic absorption bands associated with urethane and urea groups. The conversion of isocyanate function groups could be calculated from the decay in the intensity of isocyanate absorption band with time and was shown in Figure 6. As could be observed clearly from the curve in Figure 6, the content of isocyanate groups decreased rapidly at the early stage of foaming, and then leveled off gradually, which indicated that the reaction rate during foaming process was high at first and then decreased gradually. At last, the isocyanate groups were almost depleted, and its characteristic absorption band disappeared in the IR spectra.

The time evolution of urethane, urea groups during foaming process could be followed by monitoring amine group and carbonyl group region of the mid infrared spectrum. Figure 7 shows the changes of the characteristic absorption bands of urethane and urea groups in the region of (a) 4000–3000  $\text{cm}^{-1}$  and (b) 1900–1200  $\text{cm}^{-1}$  of the foam samples with



**Figure 7** Three-dimensional surface plot of urethane and urea absorption bands with time in the region of (a) 4000–3000  $\text{cm}^{-1}$  and (b) 1900–1200  $\text{cm}^{-1}$ .

time. It could be observed that urethane and urea groups evolved early during foaming reaction, and the intensities of their absorption bands at (a) 3390  $\text{cm}^{-1}$ , (b) 1715  $\text{cm}^{-1}$ , (b) 1520  $\text{cm}^{-1}$ , and (b) 1220  $\text{cm}^{-1}$  increased gradually, which were normalized against that of isocyanate group. But there were no difference of the absorption bands of carbonyl group ( $\text{C}=\text{O}$ ) for urethane and urea groups, respectively, which was different from the studies previous.<sup>17,18</sup> The intensities of all characteristic bands above almost increased simultaneously, which was considered that the two reactions of isocyanate with hydroxyl groups and water, respectively, took place



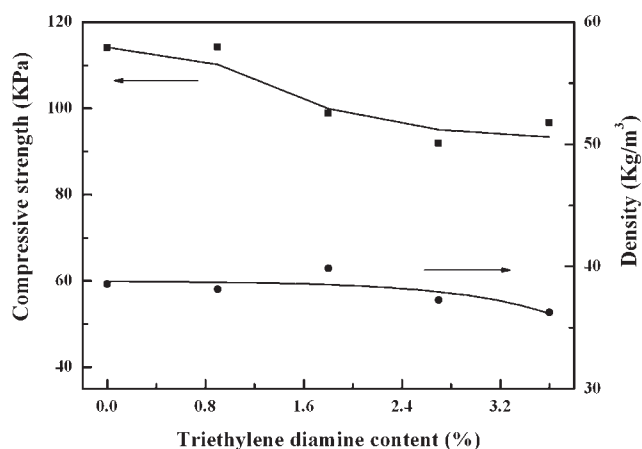
**Figure 8** Effect of gelling catalyst content on the compressive strength and density of PUFs.

simultaneously and not sequentially, as early research had suggested.<sup>18</sup>

#### Effect of catalysts content on the compressive strength and density of PUFs

Catalysts are added to accelerate the reactions of isocyanate according to the requirement and establish a balance between the networks formation and blowing reaction. In general, there are two kinds of catalysts used together, gelling catalyst and blowing catalyst. In the experiment, stannous octoate and triethylene diamine were selected as gelling catalyst and blowing catalyst, respectively.

Figures 8 and 9 show the effect of catalysts content on the compressive strength and density of the foam samples. Organo-tin catalyst catalyzes the reaction between isocyanate and hydroxyl groups mainly, and accelerates the networks formation. From Figure 8, it is observed that, when organo-tin catalyst content was low, the reaction rate was very slow and the curing reaction was not complete, and

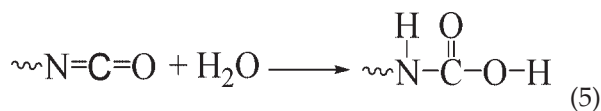


**Figure 9** Effect of blowing catalyst content on the compressive strength and density of PUFs.

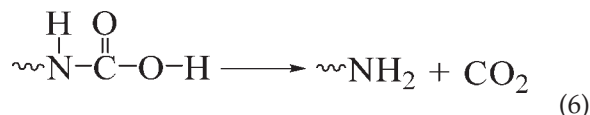
so the compressive strength of the foams was low. If there was no organo-tin as gelling catalyst, the foams were not molded. Increasing the amount of organo-tin catalyst in the foam formulations shortened gelling time, and increased the rigidity and compressive strength of PUFs.<sup>1</sup> However, when organo-tin content was superabundant (exceeding 0.4%), the abundant heat, which the reaction released because of the speedup of gelling reaction, also promoted blowing reaction, which resulted into the decrease of the compressive strength and density of PUFs instead. It is obvious in Figure 9 that, as the proportion of triethylene diamine increased, the blowing reaction was accelerated and so the compressive strength and density decreased. Even the foams would collapse because the gelling reaction was slower than the foaming reaction and the foam frameworks were not strong enough to endure the increasing cell inside pressure. So, the suitable proportion of the two kinds of catalysts was needed to balance gelling reaction and foaming reaction to prepare excellent PUFs. For the liquefied cornstalk polyol, by the experimental analysis above, the contents of stannous octoate and triethylene diamine were determined in between 0.25% and 0.40%, and between 0.5% and 1.2%, respectively.

#### Effect of water content on the properties of PUFs

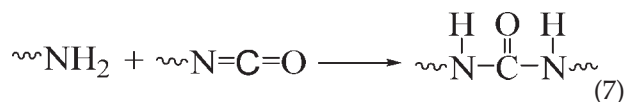
Water as chemical blowing agent reacts with isocyanate and produces carbamic acid initially.



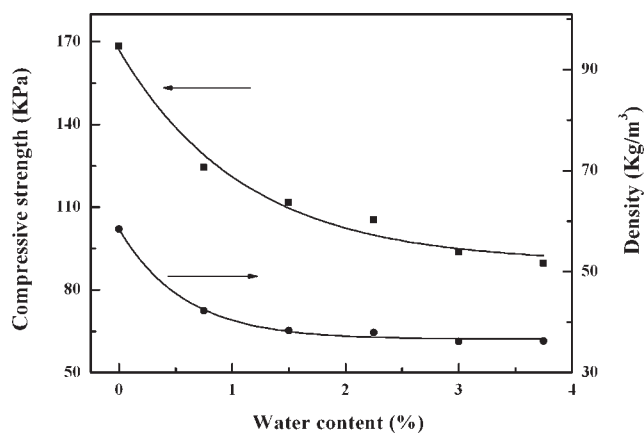
Carbamic acid is unstable and decomposes rapidly to an amine and carbon dioxide (CO<sub>2</sub>).



and then the amine also reacts with isocyanate and produces urea group.



The gas CO<sub>2</sub> diffuses to the already present air bubbles and hence the foams rise due to the increase in volume. At the same time, the viscosity of the mixture increases with polymerization and gelation. A series of experiments were performed by varying water content to investigate its effect on the compressive strength and density of PUFs, and the

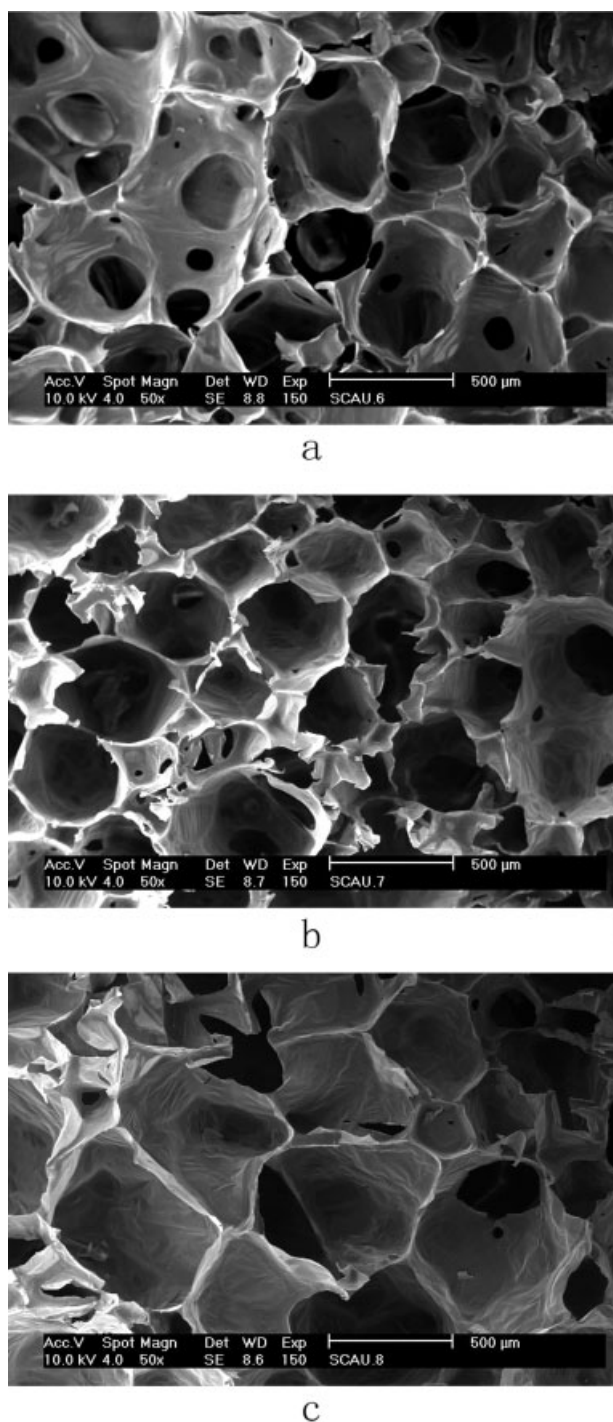


**Figure 10** Effect of water content on the compressive strength and density of PUFs.

results were summarized in Figure 10. As shown in the figure, more water was added while keeping the isocyanate index constant, the more carbon dioxide was generated and filled the foam system, which made the foam volume increase. Therefore, increasing water content decreased the foam density. The liquefied cornstalk polyol contained small quantity of water, and when no other water was added, the foam density was highest. With the increase of water content from 0 to 3.75%, the density of PUFs decreased from 58.4 to 36.3 kg/m<sup>3</sup>. But when water was superabundant, especially more than 3%, the more gas CO<sub>2</sub> was generated and the temperature of foam body was higher due to the exothermic reaction, which resulted in that the foams expanded more rapidly and were larger. And also the foam internal pressure was higher than air pressure because of the acceleration of the diffusion of gas CO<sub>2</sub> inside the foam cells. As a result, the foam molecular chains were tightened and did not relax in time during foaming process. With the decrease of the foam temperature, the foams began to shrink because of the relaxation of the tightened polyurethane molecular chains. Generally, the density of cellular materials is the main factor for determining their mechanical strength. As the density of cellular materials decreases, the mechanical strength also decreases.<sup>15,19,20</sup> From the figure, it is obvious that when water content increased from 0 to 3.75%, the compressive strength of the foam samples decreased from 168.3 to 89.5 KPa. To get PUFs with excellent mechanical properties, the water content should be added below 1.5%.

In general, for cellular materials, the mechanical properties not only depend on the rigidity of polymeric matrix, but also relate to the cell morphology, which reveals important information such as cell shape and domain size. Thus, in the present study, the micrographs of cross-sectional surfaces of the foam samples with different water content, which





**Figure 11** Scanning electron micrographs of PUFs with different water content [(a) 0%; (b) 1.5%; (c) 3%].

were observed in the free-rising direction with scanning electron microscopy (SEM), are shown in Figure 11. As seen in the figure, the higher was the water content, the larger was the average cell size of the foams. And so the foams became less dense, which resulted in the decrease of the foam density. As water content increased from 0 to 3%, the cell size increased from 417 to 625  $\mu\text{m}$ . This phenomenon could be the result of more active generation of gas

$\text{CO}_2$  with the increase of water content.<sup>20</sup> Without additive water, the cell size was inhomogeneous, and the cell strut was thick. With the increase of water content, it was evident from the foam micrographs that the cell size became more uniform and similar, and the cell strut became thinner, which might be as a result in the decrease of compressive strength of PUFs.

Table II shows the results of dimensional stability of PUFs with different water content at low temperature ( $-20^\circ\text{C}$ ) and high temperature ( $100^\circ\text{C}$ ), respectively. From a comparison of the dimensional stability among the foam samples with three different kinds of water content, it was found that an increase in water content decreased the dimensional stability. Especially at high temperature ( $100^\circ\text{C}$ ), the dimensional variations were much higher than that at low temperature ( $-20^\circ\text{C}$ ) for the same foam samples. At low temperature, the changes in dimensions of all the foam samples were less than 0.5%; on the contrary, the dimensional variations at high temperature were more than 1% when water content was higher. On the other hand, after been pretreated at different temperatures, especially at high temperature, almost all the foam samples were expanded, which might be as a result of the close cell structure. When the foam samples were heated at  $100^\circ\text{C}$ , the diffusion of gas  $\text{CO}_2$  inside the foam cells, which did not diffuse out of the foams, would accelerated. And so the foam internal pressure would increase, which resulted in the internal pressure of the foams being higher than air pressure.<sup>2,21</sup> If the foam frameworks were not strong enough to balance the pressure difference between the inside and outside of the foams, a permanent deformation of the foams occurred. Especially for the foam samples with higher water content, they were distorted more easily at high temperature because the cell strut was thinner, and gas  $\text{CO}_2$  inside the foams was more. And so, when the water content was 3%, the dimensional variations of the foam samples were more than 2% at high temperature.

The glass-transition temperatures ( $T_g$ ) of the foam samples with different water content measured by DSC are shown in Figure 12. At the first scan, the DSC curves (a,b,c) appeared single broad endothermic bands in between 50 and  $100^\circ\text{C}$ , which was associated with the enthalpy relaxation phenomena due to the short-range order. It could be interpreted that the DSC endothermic bands near  $75^\circ\text{C}$  were due to dissociation of hard segment-soft segment hydrogen bonds.<sup>22</sup> The corresponding rescanned curves (d,e,f) showed no such endothermic phenomena, because no aging time below the hard segment glass transition was allowed for the ordering to take place. The hard segment glass transition was observed within the broad endothermic zone in the

TABLE II  
Effect of Water Content on the Dimensional Stability of PUFs

Water content (%)	Dimensional variations (%)					
	-20°C			100°C		
	Length	Wide	High	Length	Wide	High
0	0.01	0.04	-0.29	-0.54	-0.44	1.23
1.5	0.08	-0.02	-0.06	1.39	1.45	0.11
3	0.45	0.33	-0.27	2.42	2.44	1.84

rescan curves. Note from Figure 12 that when water content increased from 0 to 3% while keeping the isocyanate index constant, the  $T_g$  values of the foam samples increased slightly from 87.8 to 94.6°C, respectively. Distilled water as chemical blowing agent reacts with isocyanate to generate carbon dioxide and polyurea, which is known to have more powerful acting-force of hydrogen bonds and more cross bonds among molecular chains.<sup>20,23</sup> Therefore, with the increase of water content, the ratio of polyurea to polyurethane in polyurethane molecular chains increased, and the flexibility of molecular chains could decrease and the  $T_g$  of the foams might increase.

#### Effect of surfactant content on the properties of PUFs

In the preparation of PUFs, surfactant is used to lower surface tension and stabilize cell windows before the solidifying of polyurethane matrix. And also, the surfactant content influences the cell morphology and properties of PUFs. Figure 13 shows the micrographs of cross-sectional surfaces of the

foam samples with different surfactant content. With the increase of surfactant content from 0.5% to 3.5%, the cell size of the foam samples decreased from 468 to 256  $\mu\text{m}$ . It was due to that an increase in surfactant content not only decreased surface tension and thus helped increase the number of air bubbles introduced during mixing, which served as the starting point for the growth of foam cells, but also prevented the coalescence of the foam cells during foaming process.<sup>24,25</sup>

At the same time, the surfactant content also influences the compressive strength and density of PUFs. From Figure 14, it is observed that the density of the foam samples decreased at first, and then increased on the contrary with the increase of surfactant content. Without surfactant, the cell structures collapsed before the gelling reaction could stabilize the foams during foaming process, and so the density was higher. But the cell size was especially large, which also influenced the compressive strength partially and resulted in that the compressive strength of PUFs without surfactant was lower slightly than that of the foams with 0.5% surfactant. With the increase of surfactant content, the foam cells became stable and the foams expanded upwards, and so the density of the foam samples decreased gradually. However, when the surfactant content exceeded 3%, the cell windows were more stable and the ratio of close cell structure increased, which resulted in that the foam body was prone to thermal expansion resulting from the acceleration of the diffusion of gas  $\text{CO}_2$  inside the foam cells due to the exothermic reaction during foaming process. Afterwards cold shrinkage occurred because of the relaxation of the tightened foam molecular chains, and the foam density increased instead. Meanwhile, the changes of the compressive strength showed the same tendency with the increase of surfactant content from 0.5% to 3.5%, which may be in close relation to the density of PUFs. Balancing the morphology and mechanical properties, the surfactant content was selected in between 1.5% and 2.5%.

The effect of surfactant content on  $T_g$  of the foam samples is shown in Figure 15. It is seen that the  $T_g$  of the foam samples decreased as the amount of

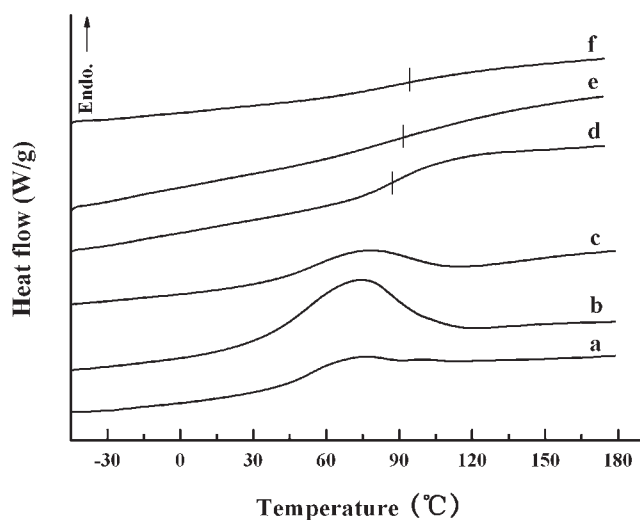
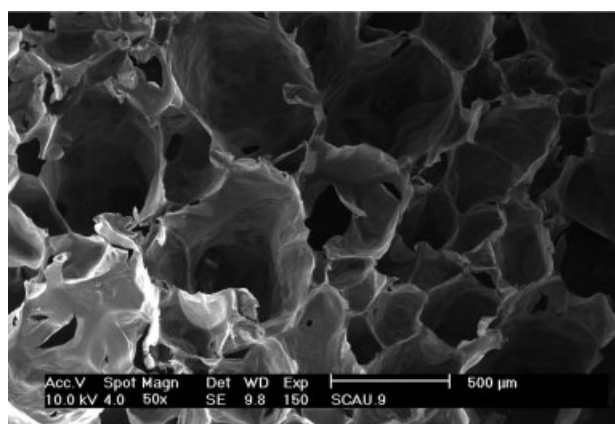
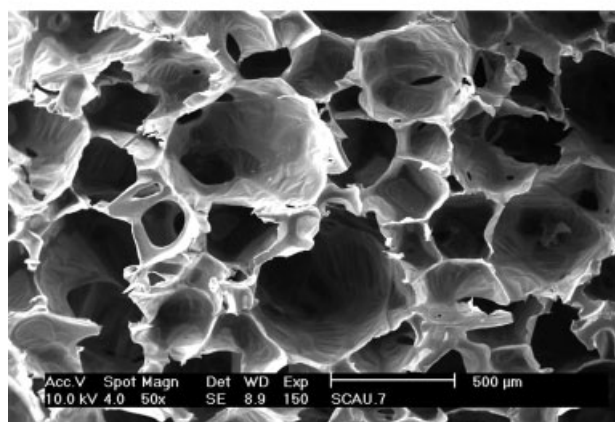


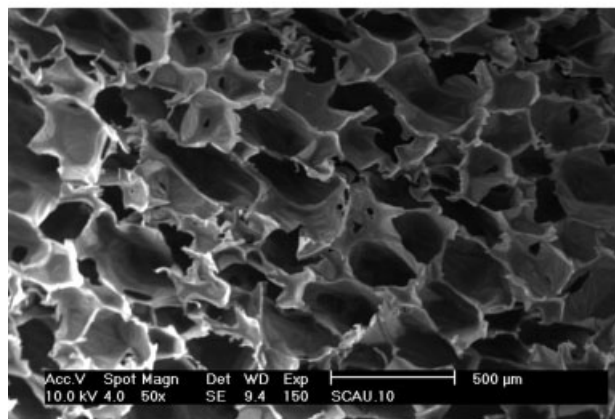
Figure 12 Effect of water content on  $T_g$  of PUFs [(a,b,c) the first scan of PUFs with 0, 1.5, 3% water, respectively; (d,e,f) the rescan of PUFs with 0, 1.5, 3% water, respectively].



a



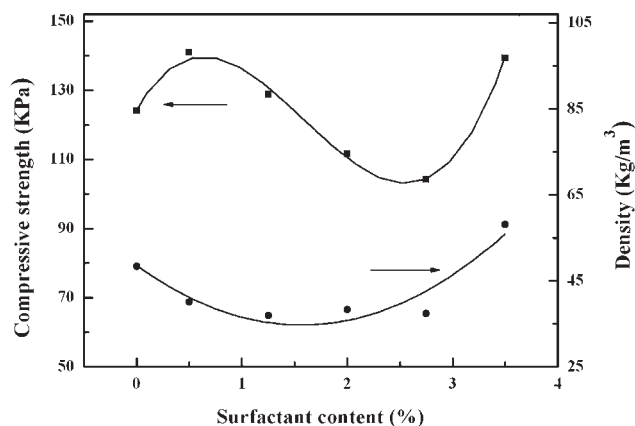
b



c

**Figure 13** Scanning electron micrographs of PUFs with different surfactant content [(a) 0.5%; (b) 2%; (c) 3.5%].

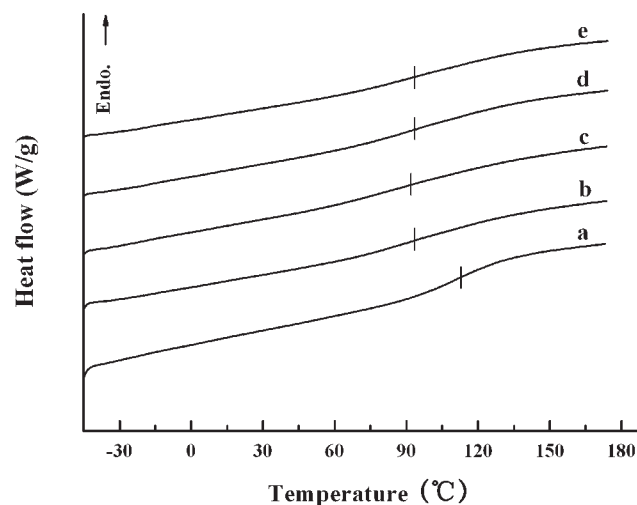
surfactant increased. Especially when surfactant content increased from 0 to 0.5%, the  $T_g$  values decreased from 112.5°C to 93.5°C greatly, which might be attributed to the plasticizing effect between the two miscible components of PUFs.<sup>3,20</sup> But with a further increase in surfactant content, the  $T_g$  values of the foam samples kept constant around 93°C.



**Figure 14** Effect of surfactant content on the compressive strength and density of PUFs.

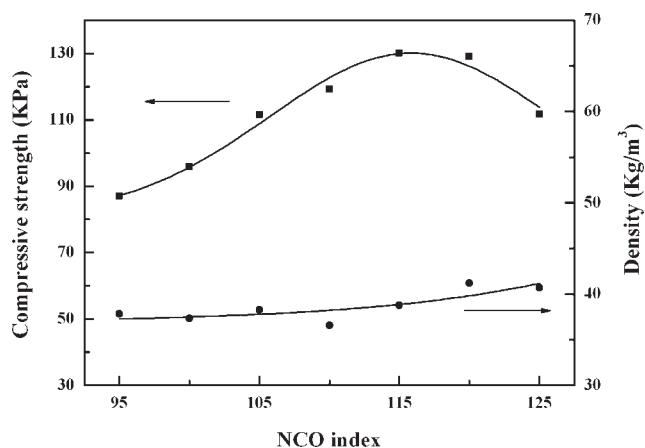
### Effect of isocyanate content on the properties of PUFs

To investigate the effect of PM-200 content on the properties of PUFs, the isocyanate (NCO) index was varied from 95 to 125. Figure 16 shows the effect of the amount of PM-200 on the compressive strength and density of the foam samples. The molecular structure of polyurethane is known to be composed of soft-segment and hard-segment, and the urethane ( $-\text{NH}-\text{CO}-\text{O}-$ ) and urea ( $-\text{NH}-\text{CO}-\text{NH}-$ ) groups belong to hard-segment. When isocyanate content was less (the NCO index was less than one), the isocyanate was absent to react completely with hydroxyl groups and water, which resulted in decreasing the crosslinking degree, and so the compressive strength of the foam samples was lower. With the increase of  $-\text{NCO}/-\text{OH}$  molar ratio, the crosslinking degree and weight percent of hard segment in polyurethane molecular chains increased,



**Figure 15** Effect of surfactant content on  $T_g$  of PUFs [(a) 0%; (b) 0.5%; (c) 2%; (d) 2.75%; (e) 3.5%].





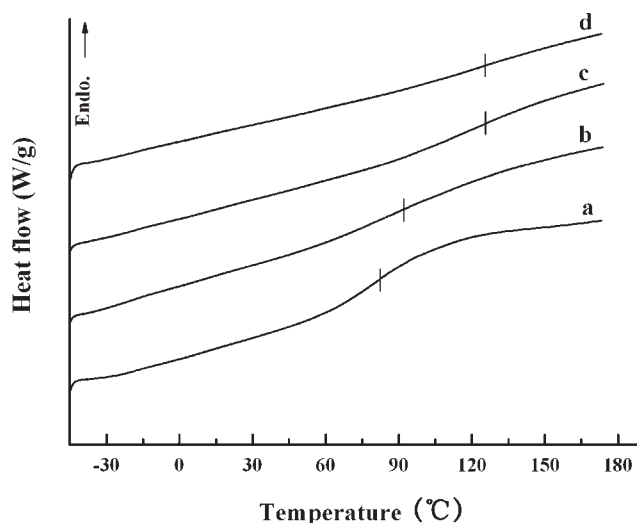
**Figure 16** Effect of isocyanate index on the compressive strength and density of PUFs.

and its compressive strength also increased gradually. When the NCO index was more than one, superfluous PM-200 could react with the formed urethane and urea groups, generating allophanate and biuret, respectively, which introduced additional three-dimensional networks and hydrogen bonds to the foam molecular chains.<sup>20,23</sup> Therefore, as the NCO index increased sequentially, it was suggested that the increase of compressive strength might be attributed to the increase of crosslinking degree and acting-force of hydrogen bonds among polyurethane molecular chains. But excessive isocyanate resulted in the decrease of compressive strength instead because of the incomplete curing reaction of isocyanate. However, comparing the compressive strength from the diagram, the density increased slightly with the increase of NCO index. So the NCO index should be kept in between 110 and 120.

In the same way, as the increase of weight percent of hard segment and crosslinking degree in polyurethane molecule chains, the flexibility of molecular chains decreased and the  $T_g$  of PUFs increased. As shown in Figure 17 for the rescanned DSC curves of PUFs, the  $T_g$  values of the foam samples increased from 82.3 to 125.7°C when the isocyanate index increased from 95 to 125, respectively.

### Thermogravimetric analysis

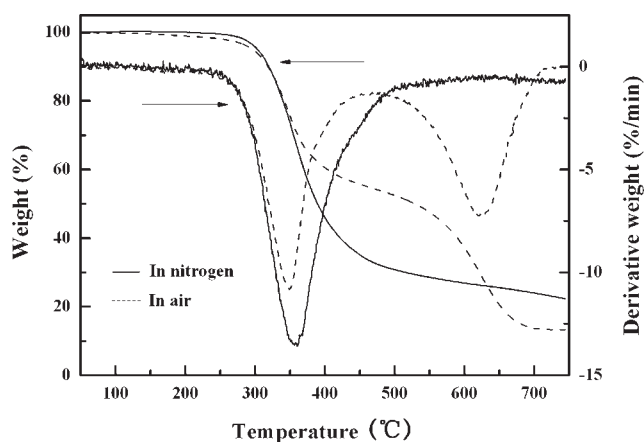
Polyurethane foams are mainly used as heat-insulating materials, and their thermal behavior is very important. For the cornstalk-based foams, the thermal decomposition was investigated by thermogravimetric analysis (TGA) in nitrogen and air at the heating rate of 20°C/min, and the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of typical foam samples with 1.5% water were plotted as shown in Figure 18. By comparing the thermal and thermo-oxidative behaviors, the decomposition



**Figure 17** Effect of isocyanate index on  $T_g$  of PUFs [(a) 95; (b) 105; (c) 115; (d) 125].

of the foam samples in nitrogen was different from that in air. The TGA curves of the foam samples showed only single weight loss stage in nitrogen atmosphere, whereas there were two main weight loss stages occurring during decomposition in air atmosphere, which indicated the degradation mechanism in air was much more complex than that in nitrogen.

Whatever the atmosphere, the thermal characteristics at first stage appeared to be similar and presented the same degradation rate. The samples did not show obvious weight loss until the temperature rose to 250°C, and the rate of weight loss began to increase gradually to a maximum at about 350°C. This suggested that the first weight loss stage in air had the same thermal degradation mechanism with the decomposition in nitrogen, which might be the characteristic of the decomposition of urethane bond and polyol backbone.<sup>3,14,26</sup> Attentively, the single



**Figure 18** TG and DTG curves of PUFs with 1.5% water in nitrogen and air.



DTG peak in nitrogen indicated there was a random sequence distribution in the foam backbone to the decomposition of the foams, because no distinct peak representative of the thermal decomposition of polyol and isocyanate was observed during the thermal decomposition of PUFs in nitrogen. The difference was that the initial degradation temperature and the temperature at the maximum degradation rate in nitrogen were higher slightly than that in air. In nitrogen atmosphere, slight weight loss was observed after the samples were heated above 500°C, when there had around 30% foam residue left un-decomposed. Different from the decomposition in nitrogen, however, in air there was a second weight loss stage which appeared between 550 and 700°C with a maximum rate of weight loss at about 620°C. The second stage, which had more than 10% residue at 750°C, appeared to be thermo-oxidative nature of the foams since it did not exist in nitrogen atmosphere. All of these indicated that the polyurethane foams derived from cornstark exhibited excellent thermal stability like conventional polyurethane foams.

### CONCLUSIONS

The liquefaction of cornstark was conducted in the presence of polyhydric alcohols under moderate temperature and atmospheric pressure. By analyzing the time-course of the properties of liquefied product under different reaction conditions, the liquefied cornstark polyol was obtained under the selected reaction conditions, which was suitable for preparing polyurethane foams. At the same time, the polyurethane foams were prepared by the copolymerization of liquefied cornstark polyol and isocyanate using water as blowing agent. The contents of catalyst, water, surfactant and isocyanate were optimized by investigating their influences on the structures and properties of cornstark-based polyurethane foams. Such polyurethane foams prepared from the liquefied cornstark polyol had excellent mechanical properties and thermal properties, which could be used as heat-insulating materials. It not only utilized

the agricultural castoffs efficiently but also protected environment to prepare polyurethane foams using agricultural by-products as raw materials in replacement of fossil resources.

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