Rigid Polyurethane Foams Based on Activated Soybean Meal

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ABSTRACT: Soybean meal (SM), an abundant biomass resource, was used as the surrogate to partially replace polyols in rigid polyurethane foam synthesis. Compared with polyurethanes based on other soybean-based resources, such as soybean protein isolate (SPI), polyurethane foams based on activated SM showed better thermal and mechanical properties. The amount of SM in the final polyurethane foams can be as high as 30 wt % (base on the total weight of foam), which dramatically decreases the cost of the foams. The results also showed that SM played a vital role in improving the foam properties, which could be attributed to the participation of the functional groups in SM in the polyurethane foam synthesis. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4331–4338, 2012

Key words: rigid polyurethane foam; soybean meal; soybean protein isolate; modification; mechanical properties

INTRODUCTION

Polyurethane foams (PUFs) are widely used as insulating and structural materials due to their excellent thermal and mechanical properties since its discovery in 1940s.[1,2] Polyols, as one of the most important components for PUFs synthesis, are generally obtained from petroleum industry. Using naturally abundant, inexpensive, and renewable materials as surrogates for polyols has long been an important subject in the polyurethane industry. Vegetable oil polyols,[3–5] lignin,[6,7] starch,[8,9] cellulose derivatives,[10,11] tannin,[12] and polysaccharides[13] have been used to partially replace polyols to synthesize polyurethanes.

On the other hand, soybean industry provides abundant biomass that might be applied in polyurethane industry. Soybean protein isolate (SPI)[14–16] and soybean protein concentrate (SPC)[17] have been used in the preparation of soybean-based PUFs. However, these soybean-based materials are relatively expensive. Soybean flour (SF)[18] and soy dreg[19] have also been used to modify polyurethane polymers, but either SF or soy dreg was only simply dried before use without any other pretreatments, which resulted in mediocre properties of the obtained polyurethanes.

One general problem encountered in biomass modified PUFs is the efficiency of the participation of biomass in the PUFs formation process. The major components in soybean resources are soybean proteins and polysaccharides. The strong inter- and intra-molecular H-bonding in its structure made polysaccharide insoluble in water and most organic solvents, hence difficult to participate in PUFs' synthesis. Soybean proteins also have highly order structures, with many active groups such as disulfide bond ($-S-S-$), $-NH_2$, and $-COOH$ buried inside,[20] which brings many difficulties to disperse them in polyols and react with isocyanate. Indeed, when unmodified soybean proteins[14–18] were used in PUFs preparation, the protein dose was always low (about 10 wt % based on the total foam), which made little contribution to cost-cut and performance improvement of the foams. However, it is possible to modify soybean proteins to expose these groups to react with isocyanate. Many methods, such as alkali treatment, detergent treatment, and urea modification, etc., have been reported to unfold proteins and increase their solubility in organic solvents. These methods have been applied for the preparation of adhesives and films.[21] However, to the best of our knowledge, there were no reports on the synthesis of PUFs based on modified soybean proteins.

Soybean meal (SM) is an easily available, abundant by-product of soybean oil extraction industry, with a worldwide yield of 160 million tons at 2009s. The cost of SM was 30% lower than that of SF and about 65% lower than that of SPI and SPC, which makes it more attractive as a biomass resource for

PUFs. Alkali treatment and —S—S— reduction were two important methods to modify proteins in soybean biomass. Although there are several reports on the effects of pH value and sodium sulfite on the modification of SPI, SPC, and SPF,[21,22] the modification of SM and its application for PUFs preparation, as far as we know, were not reported. We herein report our results in the synthesis of PUFs using activated SM. The amount of SM in PUFs could be as high as 30 wt % based on the total foam weight, which dramatically decreases the cost of biomass-based PUFs, with little sacrifices of foam performance. The properties of the resulting foams could be adjusted in a very broad range.

EXPERIMENTAL

Materials

Soybean meal (SM) was supplied by Shandong Bohi Industry Co. (Qingdao, China) and its composition was shown in Table I. SM was milled and sieved through a 100-mesh sieve before use. Soy protein isolate (SPI) was supplied by Shandong Wonderful Industrial Group (Jinan, China). Other components used in the foam formulation include polymeric isocyanate (PAPI-200, from Yantai Wanhua Polyurethanes, Yantai, China), poly(ether polyol) (PEG-400, from Fuyu Chemical, Tianjing, China), catalyst (DABCO, from YanTai EDA PU Co., Yantai, China), crosslinker (triethanolamine, from China National Medicines Co., Beijing, China), and foam stabilizer (L-6865, YanTai EDA PU CO.). All the chemicals used for SM and SPI activation and hydroxyl values (OHVs) detection (ethanol, sodium hydroxide, sodium sulfite, phthalic anhydride, imidazole, pyridine) were in analytical grade and purchased from China National Medicines Co. Distilled water was used as the blowing reagent.

Activation of SM and SPI

Activated SM and SPI were prepared according to a modified method.[22] Ethanol was used instead of water as the dispersant for SM and SPI, since it swelled SM better and facilitated the unfolding process of proteins. SM or SPI has a higher dispersion ratio (in weight) in ethanol ($W_{(SPI)}$: $W_{(ethanol)}$ = 1 : 1) than in water ($W_{(SPI)}$: $W_{(water)}$ = 1 : 6 to 1 : 10).[21,22] Other factors such as pH values, the amount of reducing reagent (sodium sulfite), the reaction time, and the activation temperature, were investigated in detail to optimize the activation conditions. Orthogonal tests (L_{25} (5^6)) were carried out to investigate the independent influence of six factors, i.e., (1) doses of NaOH solution and its (2) reaction time and (3) reaction temperature; (4) doses of sodium sulfite solution

TABLE I
Ingredient in SM[a]

Ingredient	Content %
Protein	46
Polysaccharide	33
Fiber	8
Ash	4
Fat	0.5
Moisture	8.5

[a] Adapted from Shandong Bohi Industry Co., Ltd.

and its (5) reaction time and (6) reaction temperature on the activation process. The OHVs were used to evaluate the overall effects of the activation conditions. A typical activation procedure is described below:

SM powder (500 g) was dispersed in ethanol (600 mL). After stirring at room temperature (rt) for 15 min, NaOH solution (2.0 M) was added to the mixture to adjust pH value to 11. The mixture was heated up to 50°C and remained at this temperature for 3.5 h. After the mixture was cooled down to rt, sodium sulfite (15 g) was added and the resulting suspension was stirred at 35°C for 4 h. The mixture was then neutralized and ethanol was evaporated. After drying in vacuum oven, activated SM was obtained as an anhydrous powder. The activated SPI was prepared using similar procedures.

Hydroxyl values detection

The OHVs of the SM or SPI were determined using a modified ISO titration method (ISO 14900 : 2001). To an Erlenmeyer flask equipped with a condenser, were added anhydrous SM or SPI powder (m g) and 25 mL of acylating agent. The acylating agent was prepared in advance by mixing phthalic anhydride (116 g), imidazole (16 g) in pyridine (700 mL). The thoroughly mixed suspension was refluxed for 0.5 h at 115°C, then cooled to rt. The mixture was completely transferred to a beaker, and titrated with NaOH standard solution (C mol/L) until the pH value was adjusted to 8.5. The OHV was calculated according to the equation below:

$$\text{OHV} = \frac{(V_0 - V_1)\, C \times 56.1}{m} \tag{1}$$

where V_0: NaOH volume used for control sample titration (mL); V_1: NaOH volume used for SM or SPI titration (mL); C: concentration of NaOH solution (mol/L); m: the weight of SM or SPI (g). Every hydroxyl value was the mean of three test results of each sample. The deviation of each hydroxyl value of the parallel tests was lower than 1.5%.

TABLE II
Formulations for Biomass-Based PUFs Containing SM or SPI

Ingredient		Parts by weight
Component A	Polyol	100
	SM or SPI	0,35,65,100[b]
	Catalyst	0.5
	Crosslinker	0.5
	Foam stabilizer	2.0
	Water	2.5
Component B	PAPI[a]	140,150,160,170

[a] The dose of PAPI base on an isocyanate index was 120.
[b] Four different percentages of SM or SPI were used, i.e., 0, 35, 65, and 100 parts by weight, and the percentages of PAPI was adjusted accordingly, i.e., 140, 150, 160, and 170 parts by weight.

Foam formulations

The properties of SM (or SPI)-based PUFs were studied at several SM (or SPI) concentration levels: 0%, 10%, 20%, and 30% (weight percentage), while other factors, such as catalyst, foam stabilizer, blowing agent (water), and crosslinker were kept constant. In each formulation, the isocyanate index was kept at a constant value (120), and the dose of PAPI was adjusted according to the total OHVs of the polyol, water, and SM (or SPI). Six parallel foams were produced for each formulation. The details of the foam formulations were shown in Table II.

Preparation of SM (or SPI)-based PUFs

SM (or SPI)-based PUFs were prepared according to the classical procedure. Polyol, SM (or SPI), catalyst, foam stabilizer, water, and crosslinker (component A) were added into a plastics container and stirred at 2500 rpm for 3–5 min. Polymeric isocyanate (component B) was then rapidly added to component A and stirred at same speed for 10–20 s. The mixture was poured immediately into a wooden mold to foam at rt. After curing at rt for 30 min, the foam was removed from the mold and aged at 35°C for 24 h. Two different molds were designed: A, 350 × 350 × 20 mm size mold for thermal conductivity measurement, B, 200 × 200 × 100 mm size mold for the measurement of other properties.

Foam properties measurements

The density of the foams was determined according to ISO 845 : 2006. Compressive strength was measured at 10% deformation ratio according to ISO 844 : 2004 on an electronic universal testing machine (TY8000, Tianyuan Instrument Co. Ltd, Jiangdu, China). The sample size was 50 × 50 × 50 mm for each test and the final compressive strength was the

mean of three parallel tests. Thermal conductivity was measured using a double guarded hot plate apparatus (DRH-300, Xiangyi Instrument Co., Ltd, Xiangtan, China) according to ISO 8302 : 1991. Foams with a specific size (300 × 300 × 20 mm) were used. The final thermal conductivity was the mean of six tests results of each sample. Dimension stability tests were carried out at two sets of temperature and relative humidity (75°C, 5% RH and 40°C, 90% RH) for 14 days, respectively. At least three parallel samples were tested for the thermal and humid aging tests.

Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra of the samples were recorded on a Fourier-transform infrared spectrometer (1600, Perkin-Elmer Co., Wellesley, MA, USA). The samples were taken randomly from the foams, and the data were collected at rt over 16 scans with a resolution of 4 cm^{-1}.

The samples for scanning electron microscopy (SEM) analysis were dried overnight in a vacuum oven. The cross section of the samples was coated with gold for SEM analysis (S-4800, Hitachi, JAPAN).

RESULTS AND DISCUSSION

Activation of SM

As shown in the experimental section (Table I), SM mainly consists of proteins (46%) and polysaccharides (33%). Many functional groups, such as —NH$_2$, —OH, —SH in these proteins and polysaccharides could act as nucleophiles to react with isocyanate. Theoretically, these functionalities could be considered as the equivalents of hydroxyl groups in polyols. However, these groups are generally deeply buried in the quaternary structure of proteins by forming strong H-bonding, or covalent disulfide bond (—S—S—), which impeded the utilization of these functionalities.

The activation (modification) of the soybean-based biomass is an important step toward the full utilization of the functionalities in these materials. The major goal of the activation process is to unfold the proteins in these soybean-based biomass, weaken the H-bonding inside the quaternary structures, and break —S—S— linkage in the proteins. It was believed that more hydrophilic functionalities could be exposed to the outside environment after activation, which improved the dispersity of SM in polyol and increased the amount of SM in the foam. Alkali (NaOH) treatment and —S—S— reduction (Na$_2$SO$_3$ treatment) were used to activate SM, and the orthogonal test results of the activation are shown in Table III. Generally, higher OHV was obtained after activation compared with that of inactivated SM

TABLE III
Orthogonal Experiment Test Results of OHVs of Activated SM

| Factors | NaOH treatment | | | Na$_2$SO$_3$ treatment | | | Hydroxyl value (mgKOH/g) |
	pH	Time (h)	Temperature (°C)	Dose[a] (%)	Time (h)	Temperature (°C)	
Batch 1	8	1	30	1	1	25	92.5
Batch 2	8	2	40	2	2	35	100.6
Batch 3	8	2.5	50	3	3	40	98.6
Batch 4	8	3	60	4	4	50	97.5
Batch 5	8	3.5	70	5	5	60	93.4
Batch 6	9	1	40	3	4	60	113.4
Batch 7	9	2	50	4	5	25	114.6
Batch 8	9	2.5	60	5	1	35	121.6
Batch 9	9	3	70	1	2	40	101.2
Batch 10	9	3.5	30	2	3	50	98.9
Batch 11	10	1	50	5	2	50	118.1
Batch 12	10	2	60	1	3	60	100.3
Batch 13	10	2.5	70	2	4	25	116.2
Batch 14	10	3	30	3	5	35	98.9
Batch 15	10	3.5	40	4	1	40	100.8
Batch 16	11	1	60	2	5	40	99.6
Batch 17	11	2	70	3	1	50	131.2
Batch 18	11	2.5	30	4	2	60	98.7
Batch 19	11	3	40	5	3	25	100.8
Batch 20	11	3.5	50	1	4	35	138.6
Batch 21	12	1	70	4	3	35	121.5
Batch 22	12	2	30	5	4	40	99.8
Batch 23	12	2.5	40	1	5	50	102.3
Batch 24	12	3	50	2	1	60	100.9
Batch 25	12	3.5	60	3	2	25	118.6
K$_1$	96.52	109.02	97.76	106.98	109.40	108.54	
K$_2$	109.94	109.30	103.58	103.24	107.44	116.24	
K$_3$	106.86	107.48	114.16	112.14	104.02	100.00	
K$_4$	113.78	99.86	107.52	106.62	113.10	109.60	
K$_5$	108.62	110.06	112.70	106.74	101.76	101.34	
R	17.26	10.20	16.40	8.90	11.34	16.24	

[a] The amount of Na$_2$SO$_3$ was based on the dose of SM. K$_i$ (i = 1,2,3,4,5) represents the average of the OHVs for each factor at different levels. R refers to the difference between the highest and lowest K value.

(84.5 mgKOH/g), suggesting that more nucleophilic functionalities in SM were exposed to outside environment via the activation process.

The results of the orthogonal tests were analyzed using conventional intuitive and range data analysis methods.[23,24] K value and R value were used to evaluate the effect of each level and factor on activation. K value is the average of OHVs for each factor at every level and is used to evaluate which level is the optimal level. For each factor, the largest K refers to the optimal level. For instance, for the influence of the doses of NaOH solution, it was shown in Table III that when the pH value was adjusted to 11, the largest K value was obtained (K$_4$, 113.78). So pH 11 is the optimal level for the doses of NaOH solution. R value is the difference between the highest and lowest K value for each factor, and is used to determine which factor(s) is (are) the most important factor(s) in the activation process. Larger R reflects stronger influence of the corresponding factor on the activation. As shown in Table III, The temperature of Na$_2$SO$_3$ treatment, the doses of NaOH solution and

its reaction temperature showed more significant influence on the OHVs (R = 16.24, 17.26, and 16.40, respectively). Based on intuitive and range data analysis, the best conditions for SM activation were (1) alkali treatment at pH = 11 for 3.5 h at 50°C, followed by (2) reduction with 3% Na$_2$SO$_3$ solution for 4 h at 35°C. A separate activation test was then performed at this optimized condition, and an OHV of 142.7 mgKOH/g was obtained. Activation of SPI at the same conditions gave an OHV of 124.3 mgKOH/g, which was also much higher than the OHV of inactivated SPI (81.3 mgKOH/g).

Performance of SM-based and SPI-based PUFs

SM-based and SPI-based PUFs were prepared according to the classical procedure. The influence of foam formulations on the properties of the foams such as density, compressive strength, thermal conductivity, and dimension stability was investigated in detail. A least-significant difference (LSD) was applied to compare the means of the properties of

TABLE IV
Density of Foams Containing SM and SPI

Density (kg/m³)		Biomass (%)			
		0	10	20	30
SM	Activated	49.8ᵃ	60.5ᵃ	64.3ᵇ	67.6ᶜ
	Inactivated		59.3ᵃ	61.3ᵃ	63.8ᵇ
SPI	Activated	49.8ᵃ	60.1ᵃ	62.4ᵃ	65.3ᶜ
	Inactivated		59.3ᵃ	60.8ᵃ	63.7ᵇ

Means with the same superscripts are not significantly different at 5% level.

the foams obtained from different treatments and different types of biomass (SM, SPI).

Density

Rigid foams need to have a density higher than 30 kg/m³ to keep adequate strength to bear certain load for commercial applications, such as pipe insulation and refrigerator insulation. The density of the plastic foam is determined by the weight and volume of the plastics matrix and the gas trapped in the foam cells.[18]

The densities of PUFs containing SM and SPI at different weight percentage levels were listed in Table IV. It is reasonable that the density of the foams increases when the doses of biomass increases while the blowing conditions remained the same. Statistical analyses using LSD rules with 95% confidence showed greater difference in the density between the control foam and foams containing biomass up to 20%. The foams prepared from activated SM and SPI have higher densities than those prepared from inactivated ones. This might be due to the higher concentration of functional groups in activated SM and SPI, which react with PAPI forming more compact structures as compared to those in inactivated SM and SPI. At the same biomass weight
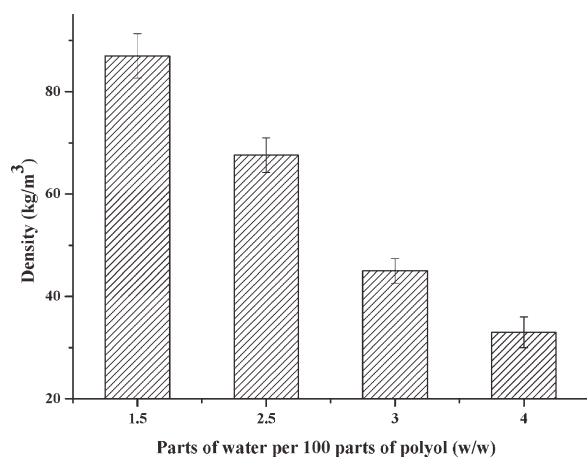

Figure 1 Effect of water content on the density of foams containing 30% activated SM.

TABLE V
Compressive Strength of Foams Containing SM and SPI

Biomass(%)	Compressive strength (kPa)			
	Activated SM	Inactivated SM	Activated SPI	Inactivated SPI
0	186ᵃ	186ᵃ	186ᵃ	186ᵃ
10	241ᵃ	212ᵃ	232ᵃ	208ᵃ
20	287ᵇ	231ᵃ	241ᵃ	218ᵃ
30	348ᶜ	242ᵃ	262ᵇ	221ᵃ

Means with the same superscripts are not significantly different at 5% level.

percentage, SM-based PUFs have higher densities than SPI-based ones, which can be attributed to a more compact structure due to the presence of fibers and polysaccharides in SM.

The density of the foams could be adjusted by changing the amount of blowing agent. Figure 1 shows the decrease of the foam density with the increase of water content. When the water content (weight ratio) went up to four parts per 100 parts of polyol, the density of the foam could be lowered to 33 kg/m³. However, when the water content exceeded three parts per 100 parts of polyol, the obtained foams exhibited small holes at the surface and large holes and flaws inside, which led to worse thermal performance (i.e., higher thermal conductivity) of the foams. On the other hand, when the water content was too low (less than 1.5 parts per 100 parts of polyol), foams with much higher density (>85 kg/m³) were formed, which dramatically increased the cost. Thus the water content was controlled at 2.5 parts per 100 parts of polyol to keep a balance between performance and cost.

Compressive strength

The compressive strength of rigid PUFs should be higher than 100 kPa for commercial applications. The compressive strength of a foam is defined as the maximum compressive stress level that the foam can withstand for a very short time at a fixed point in the compression loading cycle.[25]

Table V lists the compressive strength of PUFs containing SM and SPI at 10% deformation with compressive loading direction parallel to the foam-rising direction. The compressive strength increased with the increase of biomass content (both for SM and SPI) in the foams, as shown in Table V. The LSD test shows that foams containing 30% activated SM had significantly greater compressive strength than that of the control. Moreover, the foams containing activated SM and SPI showed higher compressive strength than those containing inactivated SM and SPI. For instance, the compressive strength of PUFs with 30% activated SM is 348 kPa, while that with 30% inactivated SM is

TABLE VI
Thermal Conductivity of Foams Containing SM and SPI

Biomass (%)	Thermal conductivity (w/m·k)			
	Activated SM	Inactivated SM	Activated SPI	Inactivated SPI
0	0.0246[a]	0.0246[a]	0.0246[a]	0.0246[a]
10	0.0252[a]	0.0280[a]	0.0263[a]	0.0291[b]
20	0.0259[a]	0.0292[b]	0.0276[a]	0.0302[b]
30	0.0265[a]	0.0312[c]	0.0286[a]	0.0321[c]

Means with the same superscripts are not significantly different at 5% level.

242 kPa. This again can be attributed to the higher crosslink density when activated SM and SPI were incorporated into the foam, since more functional groups in activated SM and SPI react with PAPI. Interestingly, at the same biomass content level, SM-based PUFs showed better compressive strength than SPI-based ones. For example, the compressive strength of PUFs with 20% activated SM is 287 kPa, while that with 20% activated SPI is 241 kPa. This might be due to the presence of other components in SM. Both SM and SPI have proteins, but polysaccharide components in SM might act as mechanical supporting materials hence contributed more to the strength of the foam structure.

Thermal conductivity

PUFs are one of the best commercially available insulation materials due to their good thermal insulating properties, low moisture-vapor permeability, high resistance to water absorption, relatively high mechanical strength, and low density.[2] Generally, the higher density and the smaller size of the cells in PUFs indicate the lower thermal conductivity.

The effects of the SM and SPI on the foam's thermal conductivity were shown in Table VI. The thermal conductivity of the foam increased slightly with the increase of the amount of SM and SPI in the formulation. This is due to the increase of polymer phase in the foams, which had 10 times or more thermal conductivity than that of gas phase.[26] However, statistical analysis using LSD rules with 95% confidence showed no significant difference in the thermal conductivity between the control and the foams containing activated SM and SPI. On the other hand, the thermal conductivity of the foams containing activated SM and SPI was lower than that of the foams containing inactivated SM and SPI. For example, thermal conductivity of PUFs containing 30% activated SM is 0.0265 w/m·k, while that containing 30% inactivated SM is 0.0312 w/m·k. This might be due to the smaller and denser cells formed in the foams containing activated SM and SPI, since more groups reacted with isocyanate after activation. Moreover, foams containing SM showed lower thermal conductivity than foams containing SPI. For example, thermal conductivity of PUFs containing 30% activated SM is 0.0265 w/m·k, while that containing 30% activated SPI is 0.0286 w/m·k. This might be attributed to the presence of the polysaccharide of SM, which prefers to form cells with smaller size.
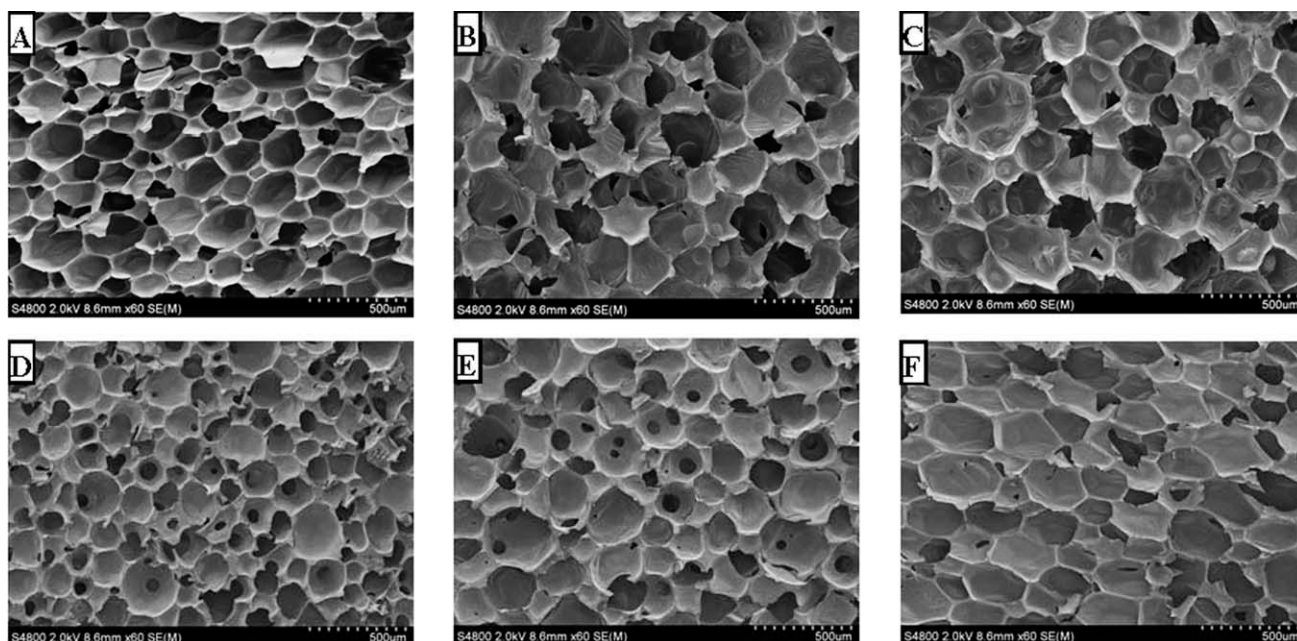

Figure 2 Scanning electron micrographs of biomass-based plastic foams. (A) Foam containing 30% activated SM, (B) foam containing 30% activated SPI, (C) foam containing 30% inactivated SM, (D) foam containing 20% activated SM, (E) foam containing 10% activated SM, and (F) control.

TABLE VII
Dimension Stability of PUF Foams Containing SM and SPI

Volume change (%)	Activated SM (%)				Inactivated SM (%)				Activated SPI (%)				Inactivated SPI (%)			
	0	10	20	30	0	10	20	30	0	10	20	30	0	10	20	30
At 75°C and 5% RH conditions																
Day 1	0.15	0.21	0.38	0.36	0.15	0.41	0.87	0.78	0.15	0.28	0.61	0.60	0.15	0.65	0.98	1.15
Day 7	0.39	0.78	0.53	0.46	0.39	0.91	1.12	0.98	0.39	0.82	0.62	0.78	0.39	1.21	1.22	1.18
Day 14	0.98	0.87	0.95	0.81	0.98	1.05	1.15	1.21	0.98	0.94	1.08	1.02	0.98	1.11	1.17	1.22
At 40°C and 90% RH conditions																
Day 1	0.71	0.63	0.76	0.82	0.71	1.02	0.97	1.31	0.71	0.86	0.92	1.11	0.71	1.21	1.39	1.75
Day 7	0.89	0.98	0.78	0.86	0.89	1.35	1.23	1.22	0.89	0.96	1.05	1.13	0.89	1.51	1.65	1.98
Day 14	1.23	1.12	1.05	1.12	1.23	1.67	1.58	1.48	1.23	1.25	1.35	1.27	1.23	1.98	2.13	2.05

Scanning electron micrographs of six typical foams clearly showed the change of the cell number and size with different biomass in the foams, as shown in Figure 2. Foam containing 30% activated SM [Fig. 2(A)] has the largest number of cells compared with the other two (foams containing 30% activated SPI [Fig. 2(B)] and 30% inactivated SM [Fig. 2(C)], and the cells are the smallest and in more uniformed sizes. This is in accordance with the observation that foams containing activated SM have the best thermal insulating properties among the biomass-based polyurethanes. On the other hand, although the cell size increased and the cell number decreased with the decrease of the amount of activated SM in PUFs [Fig. 2(A,D–F)], it did not lead to a thermal conductivity increase. Instead, the thermal conductivity decreased (Table VI). This might be due to the change of polymer phase in the foams,[26] which contributed more to the thermal conductivity. More SM in the polymer phase gave a better conductivity in polymer phase, which led to worse thermal insulation property.

Dimension stability

A key requirement for rigid foam, especially for low-density foam, is the ability to maintain its shape and size, i.e., to be dimensionally stable through its life, which may range from a couple of years to over 50 years under a wide variety of environmental conditions.[27] So the dimensional stability of SM-based PUFs was tested and compared with SPI-based foams. Table VII shows the volume change of the foams at two test conditions: 75°C and 5% RH and 40°C and 90% RH, respectively. As shown in Table VII, the foams with biomass showed similar dimensional stability with conventional PUFs (control) at 75°C and 5% RH conditions. The volume change increases with the increase of aging time, but all are less 1.3%. The foams containing activated SM and SPI showed smaller volume change than those containing inactivated SM and SPI, which might be due to their denser structures and higher compressive strength. For example, the volume change of PUFs with 30% activated SM and SPI are 0.81% and 1.02% at 14 days, respectively, while that with 30% inactivated SM and SPI are 1.21% and 1.22%. Moreover, foams containing 30% activated SM showed better long-term dimensional stability (0.81% volume change) compared with conventional PUFs (0.98% volume change), as shown in Table VII.

The same trend was found under more humid conditions, as shown in Table VII. However, the changes in volume of all foams were larger than that under less humid conditions. This might be caused by the moisture absorbed in the foams under humid
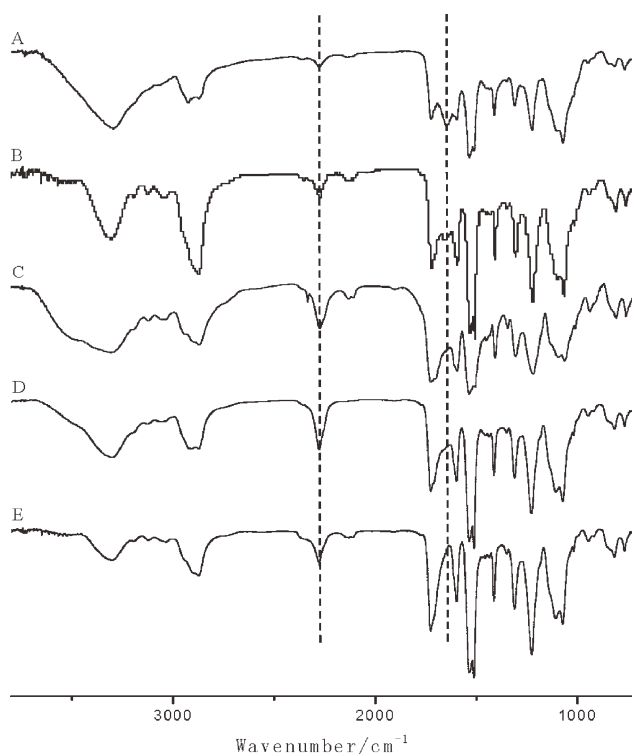

Figure 3 FT-IR spectra of the (A) 30 wt % SM-based PUF, (B) 30 wt % SPI-based PUF, (C) mixture of control-2 and 30 wt % SPI powder, (D) mixture of control-2 and 30 wt % SM powder, and (E) control-2. The control-2 was prepared according to the same formulation as A and B.

conditions. The rigid PUF will absorb moisture to equilibrate the water vapor pressure in the surrounding atmosphere.[28] More moisture adsorption might induce larger deformation, since it plasticized the PUFs and weakened the strength of foam.

Evidence for SM and SPI participation in PUFs formation

In order to study whether SM or SPI participated in the reaction with PAPI or just acted as a filler in the foam, IR analysis of the obtained PUFs were conducted. Five samples for IR analysis were prepared: A (PUF prepared with 30 wt % SM), B (PUF prepared with 30 wt % SPI), C (mixture of control-2 with 30 wt % SPI powder), D (mixture of control-2 with 30 wt % SM powder) and E (control-2). The control-2 was prepared according to the same formulation as A and B. The results were shown in Figure 3.

Two distinct characters were observed. First, the peak at 2278 cm^{-1} showed up in the spectrum of sample C and D, which is assigned to free isocyanate ($-$NCO) group, was barely seen in that of sample A and B. Given that the component ratio of sample A and B are the same, it clearly indicated that more $-$NCO groups were consumed when SM and SPI were used in the polymerization. Secondly, a new absorption peak around 1640 cm^{-1} only appeared in the spectrum of sample A and B, which could be assigned to the carbonyl stretch of urea functionality ($-$HNCONH$-$). This indicated that the amino groups in SM and SPI reacted with PAPI. As a conclusion, SM and SPI at least partially participated as a reactant in the synthesis of PUFs.

CONCLUSIONS

SM-based PUFs were prepared and compared with the control foam and SPI-based ones. The incorporation of SM, especially activated SM, had great influences on the foam properties. The foams containing activated SM showed higher compressive strength, lower thermal conductivity, and better dimension stability compared with those foams containing activated SPI, inactivated SM, and inactivated SPI. PUFs containing 30% SM showed similar thermal conductivity, better compressive strength (348 kPa), and better long-term dimensional stability (0.81% volume

change at 70°C and 5% RH for 14 days) as compared to PUFs control. FT-IR and SEM analysis revealed that SM participated in the PUFs synthesis and played a vital role in improving foam properties. Given the worldwide abundance of SM, SM-based PUFs might become a more environmental-friendly surrogates for conventional PUFs.

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