Processing and properties of rigid polyurethane foams based on bio-oils from microwave-assisted pyrolysis of corn stover

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Abstract: A new kind of rigid polyurethane (PU) foam was synthesized from the oil phase of bio-oils from microwave-assisted pyrolysis of corn stover. The recipes for the PU foams consisted of polyol-rich bio-oils, water as blowing agent, polyethylene glycol (PEG) as both polyol donor and plasticizer, diphenylmethane-4,4'-diisocyanate (polymeric MDI) as cross-linking agent, silicon-based surfactant, and tin-based catalyst. The mechanical properties of rigid foams were measured with universal testing machine (Instron4206). The effects of individual ingredients on the physical and mechanical properties of the foams were studied. It was found that water content, bio-oil content, and isocyanate dosage were important variables in making PU foams in terms of mechanical strength, density, and cellular structure.

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Under optimal conditions, the compression strength of the prepared PU foams reached 1130 kPa with a density of 152.9 g/L. The results show that bio-oils are potential renewable polyol sources for making rigid PU foams.

Key words: rigid polyurethane foam, PU, bio-oil, microwave pyrolysis, corn stover, physical properties
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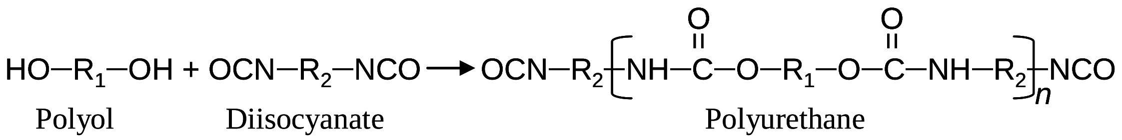
1 Introduction

Polyurethanes (PU), first synthesized in 1941, rank the fifth in production volume of plastics in the world[1]. PU products are used everywhere in people's daily lives and in engineering applications, such as automotive parts, structural materials, insulations, packaging, seating, footwear, furniture and so on. Their consumption has increased rapidly in recent years. A recent report from Freedonia Group predicted U.S. polyurethane resin demand will reach 7.6 billion pounds in 2009. One of the most important commercial PU products is PU foam. PU foams are commonly classified as flexible, semi-rigid or rigid, depending on their mechanical performances and core densities. Both flexible and rigid PU foams are the dominant global PU products and are roughly equal in market size. Flexible foams can be used in a variety of ways, such as carpet cushion, bedding, packaging, and textiles and fibers. Rigid foam is one of the most important insulating materials used today in the construction industry and is the sole insulant used in appliances such as refrigerators and freezers. Rigid foams are usually placed inside metal and plastic walls of refrigerators or between the walls in buildings as insulation to increase energy efficiency[2]. The rigid PU industry and the physics of heat transfer in cellular materials have been generally reviewed in the literature[3,4].

PU foams are polymers formed by a condensation reaction between alcohols having two or more reactive hydroxyl groups per molecule (diols or polyols) and isocyanates having more than one reactive isocyanate group per molecule (diisocyanate or polyisocyanate), as shown below.



$$\mathrm{HO{-}R_1{-}OH + OCN{-}R_2{-}NCO \longrightarrow OCN{-}R_2\left[NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}R_1{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R_2\right]_{n}NCO}$$

The raw materials of typical polyols, using a diol as a simple example, are ethylene glycol and propylene oxide. Currently, both starting materials are derived mostly from nonrenewable and dwindling petrochemical resources. To meet the need of rapidly increasing PU volume and hence polyol consumption, and due to increased concerns about the limited availability of fossil resources and the environmental problems associated with the excessive use of fossil materials, many researchers are actively searching for alternative resources as raw materials for polyols. Some researchers investigated the possibilities of converting various renewable resources such as abundant and cheap vegetable oils into polyols for polyurethane foams. While castor oil-based PU foams have existed for many years, other oil-polyols such as palm, linseed, safflower and rapeseed oil-based polyols are also known, some of which are produced on a limited commercial scale[5-7].

Other than the vegetable oils, agricultural residues such as corn stover are also potential feedstocks for bioenergy and bio-based products that could reduce U.S. dependence on foreign oils. Agricultural residues are a renewable biomass resource and easily obtainable. The amount of agricultural residues such as corn stover produced annually in the U.S. is estimated to be about 196 million tons[8]. A great deal of effort has been made to develop novel techniques to use biomass efficiently, derive environmentally-friendly materials from biomass and add value to existing agricultural products to benefit the related farming and processing industries[8,9]. Microwave-assisted pyrolysis is a novel pyrolytic process developed to conveniently and quickly process biomass into energy in the forms of syngas, charcoal and bio-oils. This new process is an environmentally-friendly technique in which energy transfer to the agricultural wastes occurs via microwave radiation[10,11]. The common way of utilizing the syngas and bio-oils obtained is combustion. This paper examines the possibility of using the bio-oils for the production of bio-based materials rather than combustion fuel. Renewable resource-based bio-oils contain a certain amount of active functional hydroxyl groups, and therefore have the potential to replace the petroleum-based polyols for manufacturing PU foams.

The objective of this study was to evaluate the feasibility of preparing PU foams from bio-oils. First, bio-oils were prepared from the microwave-assisted pyrolysis of corn stover. After simple pretreatment, the bio-oils were characterized and used as polyols in the preparation of the PU foams. Then the physical and mechanical properties including density and compressive strength of the PU foams were tested. These properties are of great importance to the applications of PU foams. In PU foam production, in addition to the usual basic components of isocyanate and polyols, other ingredients such as blowing agent, catalyst, surfactant and additive are also employed to regulate the morphology of the cellular structures and consequently affect the physical and mechanical properties of the PU foams. Therefore, the effects of the amount of PEG, surfactant, catalyst, water, bio-oils and isocyanate on the properties of the PU foams were studied.

2 Materials and methods

2.1 Materials

Ground corn stover was first collected and then dried, milled and pelletized by AURI, Co-Product Lab, Waseca, MN, USA. The pellets were 0.83 cm in average diameter, 1.37−2.54 cm in average height, and 0.85 g/cm^3 in average density, and contained about 7.6% moisture content. Table 1 summarizes the main physical properties and chemical characteristics of corn stover pellets. Data are from the Phyllis database, containing information on the composition of biomass and waste[12,13]. Polyethylene glycol (PEG 400) and stannous 2-ethyl hexanoate were purchased from Sigma-Aldrich. Diphenylmethane-4, 4’-diisocyanate (polymeric MDI) was kindly provided by Dow Chemical Company. Polyether modified polysiloxane was purchased from Degussa-Goldschmidt.

Table 1 Physical properties and chemical characteristics of corn stover pellets

Component	Min	Max	Mean	DEV
Ash (wt)/%	9.82	13.51	11.63	1.31
Volatiles(wt)/%	70.24	74.79	72.57	1.33
HHV /MJ • kg^{-1}	17.9	18.53	18.28	0.21
C (wt)/%	44.77	48.02	46.61	0.77
H (wt)/%	5.41	6.14	5.68	0.21
N (wt)/%	0.59	0.74	0.67	0.05
O (wt)/%	36.99	41.42	39.54	1.57
S (wt)/%	0.06	0.1	0.08	0.02
Uronic acids(wt)/%	1.72	4.53	3.22	0.82
Arabinan(wt)/%	1.89	2.69	2.31	0.27
Xylan(wt)/%	15.99	21.61	19.13	1.36
Mannan(wt)/%	0.38	0.55	0.47	0.06
Galactan(wt)/%	0.71	0.99	0.87	0.10
Glucan(wt)/%	30.61	38.12	35.30	2.00
Cellulose(wt)/%	30.61	38.82	35.56	2.2
Hemicellulose(wt)/%	19.13	25.29	22.74	1.47
Lignin(wt)/%	17.13	21.25	18.76	1.24

2.2 Microwave-assisted pyrolysis of corn stover for bio-oil preparation

Corn stover pellets were pyrolyzed through microwave irradiation heating using a 1 kW MAS-II microwave reactor from Sineo Microwave Chemical Technology Co. Ltd (Shanghai, China). Six hundred grams of corn stover was placed in a quartz flask which was then placed inside the microwave reactor. The pyrolysis process was usually completed within 25 minutes. Temperature of the sample was monitored using an infrared optical pyrometer, and the inside chamber was viewed through an Oslon TFT LCD color monitor. The volatile pyrolyzates were condensed with a series of water-cooled columns and collected in the flasks. The condensed liquid separated into two phases after standing for two days in ambient conditions. The upper phase is a mixture of water and water soluble chemicals such as acids. The lower phase is conventionally referred to as bio-oils.

2.3 Pretreatment of bio-oil

About 15% of water was remained in the bio-oils, which was too much for the production of PU foams. A certain amount of water in the bio-oils was removed by rotation evaporation under reduced pressure at about 70−80℃. The bio-oils with reduced moisture content were directly used in the synthesis of PU foams without further treatment.

2.4 Determination of acid value of bio-oil

A mixture of 2 g bio-oils sample and 40 mL dioxane-water solution (4/1, V/V) was titrated with a 1 mol/L NaOH to pH 8.3 using a pH-meter to indicate the end-point. Calculate acid value using the formula below.

Acid value (mg KOH/g) = (C − D) × N × 56.1/W

where C is volume of NaOH standard solution consumed in sample titration, mL; D is volume of NaOH standard solution consumed in blank titration, mL; W is sample weight, g; N is equivalent concentration of NaOH standard solution, mol/L.

2.5 Determination of hydroxyl value of bio-oil

Weigh 1 g of bio-oils sample into a 150 mL beaker. Add 10 mL of phthalic anhydride solution (dissolving 150 g phathalic anhydride in 900 mL of dioxane and 100 mL pyridine) into the beaker. Cover the beaker with aluminum foil and put the beaker into a boiling water bath for 20 minutes. After cooling down, add 20 mL of dioxane-water solution (4/1, V/V) and 5 mL of water to the beaker and then titrate with 1 mol/L NaOH to pH 8.3 by using a pH-meter to indicate the end-piont. Conduct blank titration with the same procedure. Calculate hydroxyl value by the formula below.

Hydroxyl value (mg KOH/g) = (B − S) × N × 56.1/W + Acid value

where B is volume of NaOH standard solution consumed in blank titration, mL; S is volume of NaOH standard solution consumed in sample titration, mL; W is sample weight, g; N is equivalent concentration of NaOH standard solution, mol/L.

2.6 Determination of water content of bio-oil

The water content of the bio-oils was determined using a Schott Titroline automatic Karl Fisher titrator. The residual water content of polyols is a very important parameter in PU foams formulation because of water reactivity with isocyanate groups to produce carbon dioxide, which is largely responsible for the blowing process in foam making. The amount of carbon dioxide released during the foaming process determines the final density of the foam.

2.7 Reparation of PU foam

Known amounts of bio-oils, PEG, catalyst, surfactant and blowing reagent were mixed well in a paper cup for about 30 seconds. Water was used as blowing reagent. Stannous 2-ethyl hexanoate was used as catalyst. Polyether modified polysiloxane was used as surfactant. A prescribed amount of MDI was added into the mixture, which was then stirred with a high-speed stirrer (5000 r/min) for about five seconds. After stirring, the mixture was poured immediately into another paper cup, and the foam was allowed to rise and set at ambient conditions. Finally, the foam samples were cured at room temperature for at least two days before any test was conducted. Each sample was prepared in three replicates. A typical PU foam formula was listed in Table 2. When the effects of components on the properties of PU foams were investigated, the amounts of the components added to the formulas will be indicated in the texts.

The [NCO]/[OH] ratios of the samples are calculated as follows:

$$[NCO]/[OH]ratios = [M_{iso} \times W_{iso}]/[M_{poly} \times W_{poly} + (W_{water} \times 1000/9) + (W_{poly} \times \%Moisture \times 1000/9) + W_{PEG} \times 2 \times 1000/MW_{PEG}]$$

where M_{poly} is the content of the hydroxyl group in bio-oils (hydroxyl number/56.1, the unit is mmol/g); M_{iso} is the content of the isocyanate group in isocyanate (7.9 mmol/g); W_{iso}, W_{poly}, W_{water}, W_{PEG}, are the weights of isocyanate, bio-oils, water and PEG, respectively.

Table 2 Typical PU foam formulation

Components	Addition amount/g
MDI	100
Bio-oils	60−100
PEG	0−60
Water	0−6
Catalyst	1.5−6
Surfactant	2−8

2.8 Density

Foam samples were cut for density measurement which was done according to American Society of Testing and Materials (ASTM) procedure D 1622-03.

2.9 Compressive strength

Compression tests were performed on PU foams with an Instron 4206 machine. The samples to be tested were cut using a saw into cylinders 25 mm in thick and 76 mm in diameter. The tests were carried out in accordance with ASTM D1621-04a. The two surfaces of the samples were carefully cut to be strictly parallel. Tests were performed at room temperature with a constant crosshead speed at 2.5 mm/min and the load was applied until the foam was compressed to approximately 30% of its original thickness (height). The samples were compressed in the direction parallel to the foam rising direction. The force required for 10% deformation based on the original thickness has been taken as the compression strength of the foam.

3 Results and discussion

3.1 Characteristics of bio-oil

Bio-oils are multi-component mixtures of molecules of different sizes derived from depolymerization and fragmentation of cellulose, hemicellulose and lignin. From the data shown in Table 3, these properties were similar to those of bio-oils from other pyrolysis processes but significantly different from those of petroleum derived fuel oil[14]. Research has demonstrated that bio-oils can be used not only as fuels, but also as feedstock for making valuable chemicals. Bio-oils from common pyrolysis contain acids, alcohols, aldehydes, ethers, esters, ketones, sugars, phenols, guaiacols, syringols, furans, lignin derived phenols and extractible terpene with multi-functional groups, and almost all species of oxygenated organics[15]. The GC-MS analysis of the bio-oils from the microwave-assisted pyrolysis showed that the main compounds in the bio-oils were similar to those found in the literature[14], including 3-pentyl-furan, benzofuran, 4,7-dimethyl-benzofuran, phenol, 2-methyl-phenol, 3-methyl-phenol, 4-methyl-phenol, 2-methoxy-phenol, 4-ethyl-phenol, 3,4-dimethyl-phenol, 4-ethyl-2-methoxy-phenol, 5-ethyl-2-methoxy-phenol, 4-methyl-2-methoxy-phenol, 5-methyl-2-methoxy-phenol, 3,4-dimethoxy-phenol, 1,2,4-trimethoxyl benzene, 1-ethylidene-1H-indene, acenaphthylene, benzeneacetaldehyde, 4-methylphenyl ester, 1-phenoxy-2-propanone, 3,7,11-trimethyl-1-dodecanol, naphthalene, 6-nonynoic methyl ester, 3-(2-hydroxyphenyl)-2-propenoic acid, etc. The molecular weight of these compounds ranged from 200 to 500. The acid value and the hydroxyl value of the bio-oils were 70.12 and 78.54 mg KOH/g, respectively. The commonly used vegetable oils in the preparation of PU foams have a wide hydroxyl value range between 100 and 300. From the hydroxyl value standpoint, the bio-oils from microwave-assisted pryolysis of corn stover are a potential feedstock for PU foam synthesis. The water content of the original bio-oils was about 15%. After rotation evaporation under reduced pressure, the water content of bio-oils was reduced to about 2.0%, a level acceptable for PU foam making.

Table 3 Typical properties of bio-oils from microwave-assisted pyrolysis, conventional thermochemical conversion method and of heavy fuel oil

Properties	Microwave assisted pyrolysis bio-oil	Conventional bio-oils	Heavy fuel oil
pH value	2.87	2.0–3.8	—
Moisture content (wt)/%	15.2	15–30	0.1
Density at 20℃/g • mL^{-1}	1.25	1.1–1.4	0.94
Viscosity at 50℃/ mPa · s	60	40–100	180
Gross heating value (HHV)/MJ • kg^{-1}	17.51	16–19	40
Elemental composition (wt)/%			
C	60.66	54–58	85
H	7.70	5.5–7.0	11
O	29.21	35–40	1.0
N	2.02	0–0.2	0.3
S	0.15	0.11	1.5–4.0
Ash content (wt)/%	0.04	0–0.2	0.1
Solid content (wt)/%	0.22	0.2–1.0	1.0

3.2 Effects of different components on the density and compressive strength of PU foam

The compression set property of polyurethane foams used as load bearing materials may be the single most important property. Compression set testing is usually used to evaluate the foam morphology and network structure since it is sensitive to both features[16]. The effects of different components on the properties, particularly the density and compressive strength of the

PU foams were examined.

3.2.1 Effects of bio-oil on density and compressive strength of PU foam

Figures 1 and 2 show that as the bio-oils content increased, the compressive strength decreased. Although the foam with the lowest density was just 20% less than the other two, the compressive strength was only half of that of the strongest one, suggesting a non-linear relationship between density and compressive strength. When compared with literature data, the densities of the foam samples varied greatly, which may be attributed to the strong density-dependency of the compressive strength (σ) data of the samples. The authors divided the compressive strength (σ) by the corresponding sample density (ρ) to yield a new parameter, σ/ρ, which made comparison of the mechanical properties of the rigid PU foam easier. The highest σ/ρ value of 6.57 was obtained when 60 g bio-oils were used. Compared with the σ/ρ value ranged from 1 to 4 for most PU foams made from plant oils, it was concluded that the PU foams from microwave-pyrolysis bio-oils had better mechanical properties[17-19]. Figure 2 is the stress-strain diagram which showed the compressive strength relationship between the samples with different bio-oils content as strain went up. It seems that 60 g bio-oil in the recipe was sufficient for the production of PU foams with reasonable mechanical properties. When excessive bio-oils were added, the number of polyols and water in the recipe exceeded the number of isocyanate groups of the added MDI. The remaining un-reacted components cannot form effective bonds, resulting in reduced intensity of the foams. The increase in water due to the increase in bio-oils in the recipe is expected to promote blowing or foaming, resulting in high porosity and hence decreased density and compressive strength as discussed below.

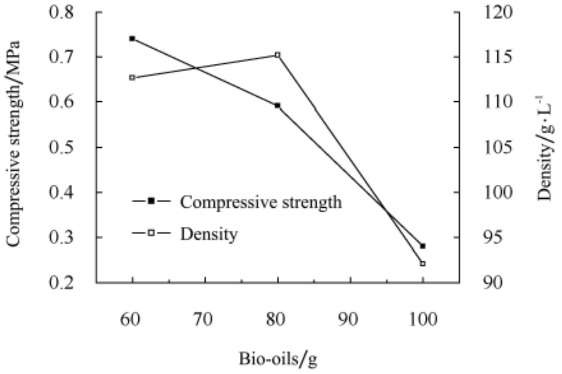


Figure 1 Effects of bio-oils content on the density and compressive strength of the PU foams (The addition amounts of water, PEG, catalyst and surfactant were 0, 50, 3, 4 g, respectively)

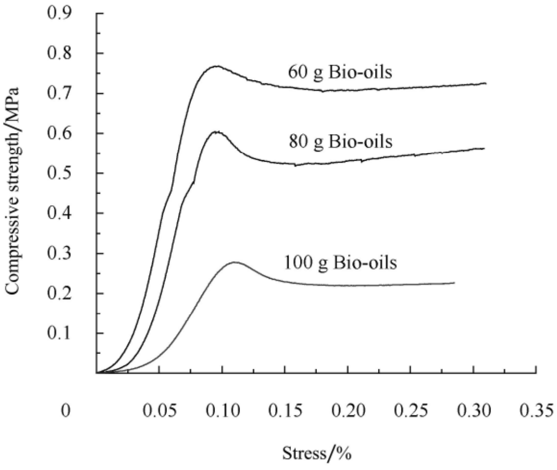


Figure 2 Compressive stress-strain diagram at different bio-oils contents

3.2.2 Effects of water on density and compressive strength of PU foam

Water, as the blowing agent, is an important component in PU foam synthesis and plays a key role in determining both the density and the compressive strength of PU foam. The effect of water on the PU foam formation reaction was investigated when the level of moisture content in the composition was varied by using different amounts of bio-oil and added water. According to Oertel[20], compressive strength decreased as water content increased, a common observation in many cellular foam systems. Increasing the water content could expand the foam volume resulting in thinner foam cell walls and larger foam cells, and therefore decreased compressive strength. As shown in Figures 3 and 4, both density and compressive strength decreased considerably as the amount of water in the compositions just increased by one unit. This phenomenon is true for all the samples. For example, the compressive strength could reach as high as 0.74 MPa without water added. However, 1 g water added could cause the compressive strength to drop to 0.38 MPa and 6 g water in the composition left the compressive strength of polyurethane foam to only 0.08 MPa. Similar phenomena had been reported in the literature[21]. Although, by adding more water, the density would also drop quickly. This means that a larger PU foam volume can be obtained at the cost of compressive strength. Therefore, adding water causes a tradeoff between the density and compressive strength.

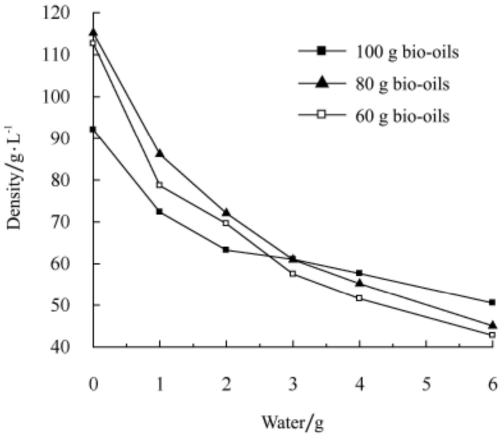


Figure 3 Effect of water content on the density of PU foams

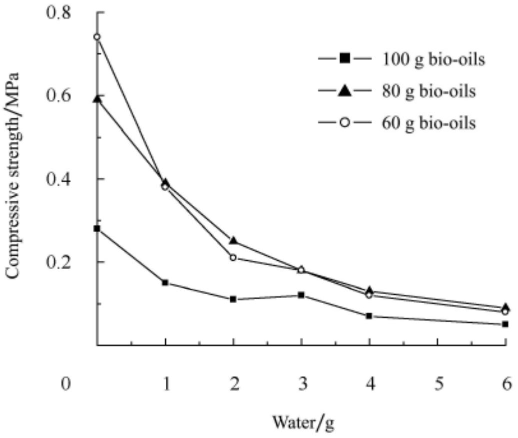


Figure 4 Effect of water content on the compressive strength of PU foams

3.2.3 Effects of PEG on density and compressive strength of PU foam

The polyurethane foams made from bio-oils with MDI were quite brittle and became powder-like materials when pressed. It is found that adding a certain amount of PEG to the recipe greatly improved the PU foam quality. PEG is a polyether polyol and a plasticizer used in the polymer industry. Like other petroleum-based polyols such as glycerin, diethylene glycol (DEG) and Voranol 490 polyether polyol, PEG was used in making vegetable oil-based PU foams[4,5,19]. The bio-oils-based PU foams with PEG exhibited greater mechanical strength with higher flexibility than those without PEG. The original density and compressive strength of PU foams using PEG as the only polyol is shown in Table 4. If no water was added, the mixture could not blow well to form foam, once again demonstrating the importance of water in the physical and mechanical properties of the PU foams. The average density and average compressive strength of the foams would reduce by half when an additional 1 g water was added. PU foam made from pure PEG with 1 g water added showed a compressive strength less than half of that for PU foam made from 60 g bio-oil without added water. In fact, 60 g bio-oils contained 1.2 g of water which was a little more than the amount of water (1 g) that was added to the PEG foam formula. The bio-oil foam had a greater compressive strength than the PEG foam, suggesting that the type of polyol is as important as water in terms of mechanical strength.

Table 4 Properties of PU foam from PEG

Isocyanate: Water: PEG: Catalyst: Surfactant	Average Density /g • L^{-1}	Average Compressive Strength/MPa	Strain /%	NCO:OH
100 : 1 : 50 : 3 : 4	80.43	0.32	10	2.07
100 : 2 : 50 : 3 : 4	47.52	0.12	10	1.58

Figure 5 shows that the density and compressive strength of the PU foams increased with the increase of PEG. Tanaka et al.[19] reported the similar result where both PEG and DEG were used as additives in their PU foam formulas. However, the main object of this research is to either improve or maintain the property of the PU foams by replacing the PEG with bio-oils as much as possible. Therefore, a large amount of PEG in the formula is not preferred. Considering the mechanical

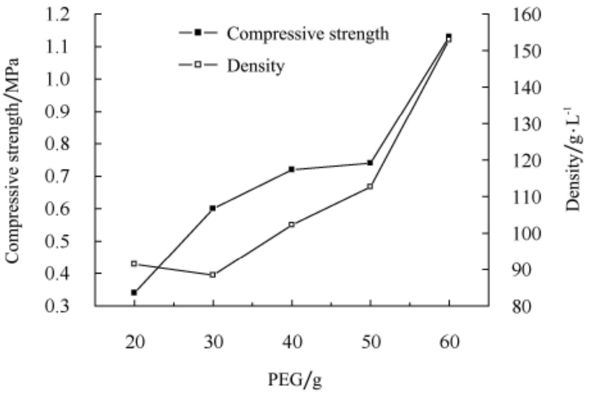


Figure 5 Effects of PEG content on the density and compressive strength of PU foams

property enhancement by and cost of PEG, it is concluded that 40−50 g PEG would be suitable for the rigid polyurethane foam synthesis. Of course, the amount of PEG should be varied with different desirable PU foams properties.

3.2.4 Effects of isocyanate on density and compressive strength of PU foam

Samples with different isocyanate contents and a constant bio-oils content of 60 g were used to investigate the role of isocyanate in the density and compressive strength of the PU foam. The data were plotted in Figure 6. The density of the PU foam increased as the isocyanate increased. When the isocyanate content was at 180 g, the density reached 150 g/L, which was a fairly high density for foams. However, the compressive strength behaved quite differently from the density. The compressive strength increased at first until it reached a peak, but then it began to decrease at 100 g isocyanate with the NCO/OH ratio of 1.56. Other reports also confirmed that the compressive strength was improved with the increase of the NCO/OH ratio from 1.1 to 1.3[17]. The compressive strength was only 0.03 MPa when 180 g isocyanate was added. Therefore, either too much or too little isocyanate used would reduce the compressive strength. The existence of any un-reacted components in the foams, either isocyanate or bio-oils, may act as plasticizer which softens the cell structure of the foams. Research shows that maximum compressive strength was achieved at a 60:100 ratio of bio-oils to isocyanate. This ratio was used for preparing samples used in the subsequent experiments.

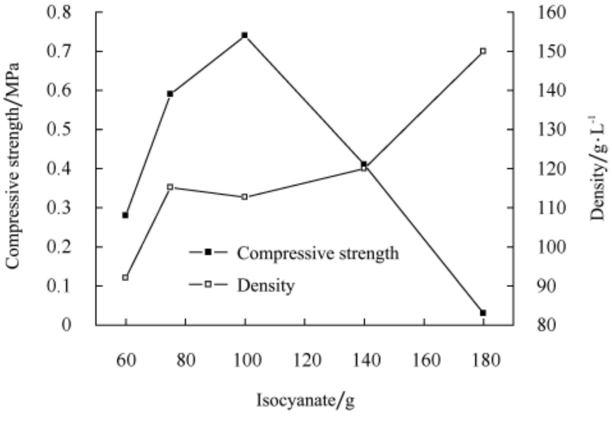


Figure 6 Effects of isocyanate content on the density and compressive strength of PU foams

3.2.5 Effects of catalyst and surfactant on density and compressive strength of PU foam

There are two kinds of chemical reactions that occurred in the foaming process. One is the blowing reaction between isocyanate and water, which produces carbon dioxide that blows the reaction mixture and forms foam. The other is crosslink formation, which is the reaction between isocyanate and hydroxyl groups of the polyols. Both reactions are exothermic[22]. Tertiary amines are catalysts for both the blowing and network formation, whereas organometallic catalysts such as tin catalyst promoted mainly isocyanate-hydroxyl reactions and were considered as “gelation catalysts”[23,24]. Surfactants were used to reduce interfacial tension between monomers and the aqueous phase, ensuring proper mixing of all ingredients prior to the onset of polymerization. It can also stabilize the cell walls by lowering the surface tension between the cells and prevent their coalescence, resulting in smaller cells uniformly distributed over the network. Adding appropriate amounts of catalyst and surfactant can help reactants to react under optimal gelling and blowing conditions. The final cellular structure is a balance between the crosslink formation and the blowing reaction. Samples prepared with different catalyst and surfactant contents were studied. In Figures 7 and 8, it can be seen that though more catalyst and surfactant may lead to higher density and higher compressive strength, the differences were not so obvious especially in the compressive strength when the amount of catalyst and surfactant exceeded 3% and 4% respectively. The research by Guo et al.[17] showed that too much catalyst would decrease the compressive strength. This may be due to the fact that the catalysts they used belong to tertiary amines. The catalyst used in this study was organometallic catalyst, which is known to promote crosslink reaction and thus enhance the structure of the foam. The results showed that catalyst at 3% was sufficient for the reaction. A sufficient amount of surfactant is necessary to form microcells with proper rigidity. However, excess surfactant would act as plasticizer and thus decrease mechanical strength. From our experimental data, foam strength showed no decrease at high amounts of surfactant in the experiment range, indicating that the surfactant used was not in excess.

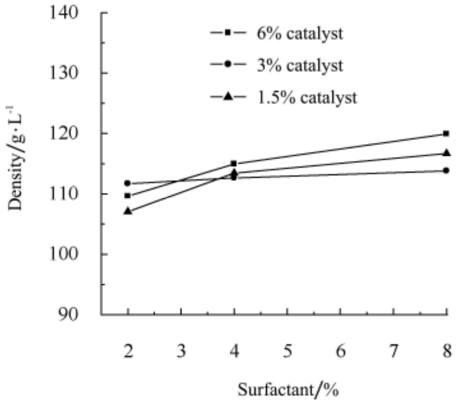


Figure 7 Effects of catalyst and surfactant content on the density of PU foams

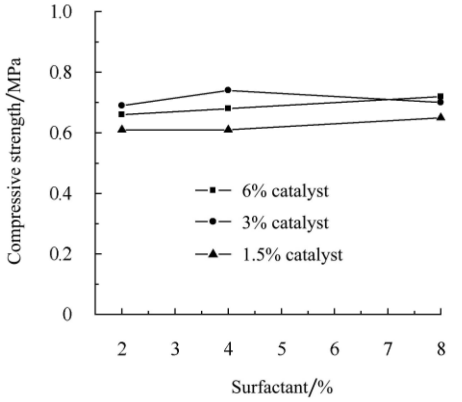


Figure 8 Effects of catalyst and surfactant content on the compressive strength of PU foams

3.2.6 Relationship between ratio of OH to NCO and compressive strength

Another interesting variable was the ratio of OH to NCO since reactions between OH groups and NCO groups are the principal reactions governing the formation and properties of PU foam. Any excess (unreacted) OH or NCO may weaken the structure, as mentioned earlier. Furthermore, type of OH may also play an important role in the reactions. For example, too much OH from water may create an overblown structure of the foam with a very large volume and thin cell walls characterized by weak mechanical strength. While isocyanate was the only compound contributing to NCO, a number of compounds contributed to the number of OH and the functions of OH may vary with the sources. For example, there were OH-containing chemicals and water in the bio-oils; the added water and PEG also contained OH groups. As mentioned earlier, non-water OH groups are expected to participate in polymerization which should strengthen the cellular structure of the foam while OH from the added water and biooil water may act as a blowing agent and weaken mechanical strength. Figure 9 shows that when the amount of added water was varied while keeping other compounds constant, an increase in OH/NCO simply decreased the compressive strength. This indicates that an increase in OH/NCO within the range studied only decreased the mechanical strength when such an increase is due to increased water. On the other hand, when the increase in OH to NCO ratio is due to an increase in PEG or decrease in NCO, the mechanical strength increases linearly with the increase of OH to NCO ratio (Figure 10). The data in both Figures 9 and 10 suggest that the mechanical strength could be further increased by increasing the amount of OH from bio-oils or PEG.

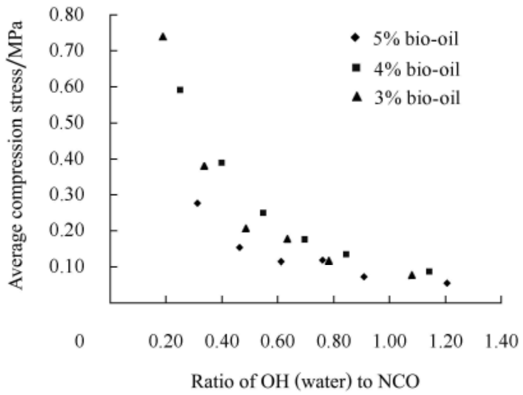


Figure 9 Relationship between ratio of OH (from water) to NCO and compression stress. OH change was due to the change in the amount of added water and moisture content in the bio-oil

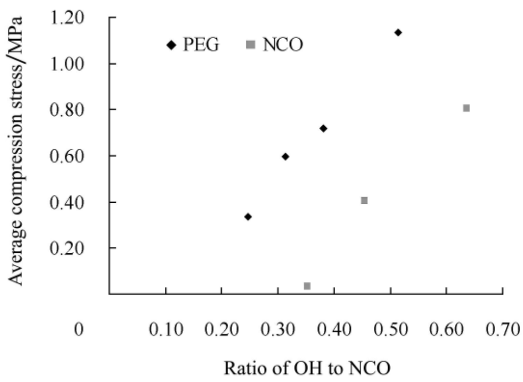


Figure 10 Relationship between ratio of OH (from PEG) and NCO and compression stress. PEG: OH/NCO ratio change was due to the change in the amount of PEG. NCO: OH/NCO ratio change was due to the change in the amount of isocyanate

4 Conclusions

The oil phase of the bio-oil from microwave-assisted pyrolysis of corn stover was found to have a reasonably high hydroxyl value and was therefore considered a good source of bio-poyols. The bio-polyols were crosslinked in the bio-oil using isocyanate to form polyurethane (PU) foams. The effects of the bio-oil, isocyanate, PEG, water, catalyst and surfactant on the densities and compressive strength of the PU foams were investigated. Water was found to be a very important variable in making PU foams from the bio-oil. The results showed that while water was necessary to blow the mixture and gave a foamy structure, the mechanical strength (compressive stress) decreased with increasing water content in the recipes. Increasing bio-oils from 60 g to 100 g was found to decrease the mechanical strength, which may be attributed to the effect of water (contained in the bio-oil) on the density and cellular structure. The density increased with the increase of isocyanate while the compressive strength increased first then decreased with the increase of isocyanate. PEG seems to be a good hydroxyl group donor and helps strengthen the foam structure. Though the amount of catalyst and surfactant also influenced the foam properties, their effects were less important compared with the other components. The densities and compressive strength of synthesized PU foams ranged from 42 g/L to 152 g/L and 0.03 MPa to 1.13 MPa, respectively. The PU foams obtained were comparable or even better in terms of compressive strength than the PU foams from plant oils[5,6,17,18,25,26]. Bio-oil based PU foams with different densities and compressive strengths can be prepared by manipulating the foam formulation.

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