

Preparation and characteristics of polyurethane made with polyhydric alcohol-liquefied rice husk

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ABSTRACT: The limited availability of fossil resource is causing the urgent need to get renewable chemicals. Solvent liquefaction can convert rice husk into bio-based chemicals. Rice husk was liquefied in polyhydric alcohol catalyzed by sulfuric acid under atmospheric pressure. The viscosity, residue content, and weight average molecular weight (M_w) of liquefied rice husk were 3089 cps, 23.6% and 4100, respectively. Prolonging the liquefaction time decreased the residue content and increased the average molecular weight. Polyurethane (PU) foams were successfully prepared from the liquefied rice husk with different molar ratios of NCO to OH (NCO/OH). The mechanical properties of PU foams showed that the compressive strength in the vertical direction is higher than that in the horizontal direction. With Increase of the NCO/OH molar ratio from 1.0 to 2.0, compressive strength in the vertical direction of PU foams increased from 70.6 to 114.7 kPa at 10% strain. Thermal analysis results showed that thermal stability of liquefied rice husk-based PU resins was better than that of fossil- and liquefied wood- based PU resins. Increasing the NCO/OH molar ratio and inorganic residue of rice husk can help to increase thermal stability. © 2017 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2017**, *135*, 45910.

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INTRODUCTION

Industrial production of fuels and chemicals heavily depended on fossil resources. The limited availability of resources and the global warming relative to fossil fuel are creating the urgent need to get renewable and environmental friendly resource. Lignocellulosic biomass can be one of the most promising alternatives to replace the fossil resource.¹ Fuels and chemicals produced from various lignocellulosic materials, such as wood, bamboo, forest, or agricultural residues. Nowadays, consumption of woody materials is increasing and global number of trees decreased to ca. 52% in human history.^{2,3}

Agricultural residues are renewable, low-price, and easily obtainable biomass resource. For every ton of rice production, ca. 0.23 tons of rice husk are left as crop residues. In 2014, ca. 1.73 million tons of rice husk were produced in Taiwan according to the Council of Agriculture. A number of recent studies focused on both rice husk and the consequent utilization of rice husk ash.⁴ Analysis of rice husk from various countries indicated a chemical composition of ash 20%, lignin 22%, cellulose 38%, pentosans 18%, and other organic matter 2% on a dry basis.⁵ The ash obtained after burning the rice husk contains more than 90% silica and provides a renewable source of inorganic constituents.⁶ Rice husk ash is often added to polymer

formulations and plays the role as rigid filler. Research efforts have been devoted to exploring the use of rice husk silica in manufacture of advanced polymeric materials.^{7–9}

Solvent liquefaction could effectively convert biomass from solid into liquid. Crop residue can be utilized as an alternative to petroleum chemicals.¹⁰ Liquefaction of biomass in the presence of polyhydric alcohols was utilized in the synthesis of polyurethane (PU) resins. Liquefied bamboo shoot shell,¹¹ bagasse, and cotton stalks¹² were prepared using polyhydric alcohols and catalyzed by acid. Liquefied corn stalk,¹³ corn bran,¹⁴ and wheat straw¹⁵ were utilized in the preparation of PU foams with polyhydric alcohol as the main solvent. One patent showed liquefied rice husk was used to prepare PU foams.¹⁶ Our previous research has liquefied wood in polyhydric alcohol with acid as catalyst and reported successful application of liquefied wood for preparation of PU adhesive,¹⁷ foams,¹⁸ and films.¹⁹ These researches demonstrated that the liquefied biomass can be recommended for replacing polyhydric alcohols of PU resins. Therefore, liquefaction using renewable resources from nature would have great potential in supplying raw materials for the polymer industry. However, research paper on preparation of PU resins from partially liquefied rice husk has been scarce.²⁰

To the best of our knowledge, there has been no academic report on liquefied rice husk used in preparation of PU foam or assessment of its thermal properties. In this study, liquefaction of rice husk was prepared in polyhydric alcohol catalyzed by sulfuric acid and the properties of rice husk during liquefaction were measured. Liquefied rice husk was then blended with polymeric diphenylmethane diisocyanate (PMDI). The mechanical and thermal properties of bio-based PU foams prepared with different NCO/OH molar ratios were measured to determine the optimal conditions for PU foam preparation.

EXPERIMENTAL

Materials

Rice husk was obtained from Changhua of Taiwan. The rice husk was ground in a hammer mill, and then passed through a twenty-mesh sieve. The powder was dehydrated in an oven at 105 °C for 12 h. Polyethylene glycol (PEG-400; average molecular weight: 400), glycerin, potassium hydroxide (KOH), and sulfuric acid were reagent-grade chemicals without pretreatment. PMDI with the NCO content of 28.19% was used as isocyanate compound. Organosiloxane and dibutyltin dilaurate/1,2-ethylenediamine were used as surfactant and catalyst.

Preparation of Liquefied Rice Husk

For the liquefaction reaction of rice husk, glass flask equipped with a stirrer, a thermometer, and a reflux condenser was conducted. PEG-400/glycerol (9/1; w/w) with 3% sulfuric acid as catalyst were premixed as the liquefaction reagent. The mixture was stirred and heated to 90 °C by an electric heating mantle. The weight ratio of liquefaction reagent/rice husk was set at 2.5/1.0 (w/w). Next, the rice husk powder was added to the reaction system. After powder was added, the system temperature was heated to 150 °C for 90 min.

Characterization of Liquefied Rice Husk

Residue Content. Approximately 1 g of liquefied rice husk was weighed and diluted with 50 mL of dioxane. The dilution was then filtered through a G3 glass filter in vacuum. The residue was washed with excess dioxane until it became colorless, and dried to a constant weight in an oven at 105 °C. The residue content was calculated according to the following equation:

$$\text{Percentage residue} = W_R / W \times 100;$$

where W_R is the weight of residue (g) and W is the weight of rice husk (g).

Viscosity. The viscosity of liquefied rice husk was measured with a Brookfield rotary viscometer at 25 ± 2 °C.

Acid Value. Approximately 8 g of liquefied rice husk was diluted with 80 mL of dioxane and 20 mL of water, and then titrated with a 1 N KOH solution. The change in pH was monitored with a pH meter. The neutralization volume of the sample was obtained from the neutralization curve. The acid value was calculated according to the following equation:

$$\text{Acid value} = [(A - B) \times N \times 56.1] / W;$$

where A and B are the consuming volume (mL) of the KOH at the neutralization point for sample test and blank test,

respectively; N is the equivalent concentration of KOH solution, and W is the weight of liquefied rice husk.

Hydroxyl Value. Approximately 1–2 g of liquefied rice husk was charged into a 250-mL Erlenmeyer flask, followed by adding 10 mL of pyridine-acetic anhydride mixture (7/3; v/v) and gradual heating to the reflux temperature. It was boiled slightly for 20 min and then cooled to room temperature. After this, 25 mL of toluene and 50 mL of water were added, and the mixture was then titrated with 1 N KOH solution. The change in pH was monitored with a pH meter. The neutralization volume of the sample was obtained from the neutralization curve. The hydroxyl value was calculated according to the following equation:

$$\text{Hydroxyl value} = [(B - A) \times N \times 56.1] / W + \text{acid value}$$

where A and B are the consuming volume (mL) of KOH at the neutralization point for sample test and blank test, respectively; and N is the equivalent concentration of KOH solution, and W is the weight of liquefied rice husk.

FTIR Analysis. The liquefied rice husk was diluted with dioxane and filtered through a G3 glass filter. The filtrate was concentrated using a rotary vacuum evaporator at 135 °C, followed by oven drying to remove the dioxane and unreacted polyhydric alcohol. The residue solid ingredient was ground and mixed with KBr powder at a weight ratio 1:100. The FTIR spectra were obtained using a Fourier transform infrared spectrometer (Mattson Genesis II) with a diffuse reflectance accessory, a deuterated triglycine sulfate detector. The spectra were collected over the wavenumber range 4000–400 cm^{-1} at a resolution of 4 cm^{-1} .

Molecular Weight and Weight Distribution of Liquefied Rice Husk

The molecular weight and weight distributions of liquefied rice husk were determined using a Hitachi (Tokyo, Japan) L-6200A gel permeation chromatograph equipped with a Phenomenex 5 μm 100 A column (Torrance, CA) and monitored with a UV detector. Acetylation of the liquefied rice husk was conducted using acetic anhydride/pyridine (1/1; v/v). Samples were filtered through a 0.45- μm filter film to remove the residue, followed by vacuum evaporation to remove the free PEG-400/glycerol, unreacted acetic anhydride, and pyridine. The dried liquefied rice husk was redissolved in THF at a concentration of 0.1%. The injection volume of the sample was 20 μL . THF was used as the eluent with a flow rate of 1 mL/min. Monodispersed polystyrenes were used as standards for calibrating the molecular weight.

Preparation of PU Foams

For preparing PU foams, NCO/OH molar ratios for liquefied rice husk were set as 1.0, 1.35, 1.5, and 2.0. Distilled water, organosiloxane, and dibutyltin dilaurate/1,2-Ethylenediamine were added as blowing agent, surfactant, and catalyst, respectively. The 2% of blowing agent, surfactant and catalyst is based on the weight of liquefied rice husk. Next, mixed the previous mixture thoroughly with the liquefied rice husk. Then isocyanate was added under constant stirring for 30 s. The mixture was finally put into a $12 \times 12 \times 10$ cm^3 mold and the foam was allowed to rise at room temperature. After 1-min rise, the

foam was allowed to cure at room temperature for 48 h. After 2-min rise, the foam was allowed to cure at room temperature for 1 h. Finally, the foam was cut into specimens.

Measuring Properties of PU Foams

The compressive strength and density of PU foam specimens were measured according to ASTM D-1621 and ISO 845:1988, respectively. The apparent density of PU foam was measured according to ASTM D 1622-03. The size of the test specimens was $5 \times 5 \times 5 \text{ cm}^3$. The density was calculated by the weight and the volume of the specimen. The apparent densities of three specimens were measured, and then the average values are reported. The compressive strength was measured using the universal testing machines (Shimadzu EZ TEST-500N) with loads both vertical and horizontal to the rising directions of PU foam specimens. The crosshead speed of compression was set at 0.5 cm/min.

Water absorption and water retention of PU foams were used a modified method from previous study.²¹ PU foam specimens with dimensions of $2 \times 2 \times 2 \text{ cm}^3$ were used for water immersion testing. The water immersion testing was carried out by dipping the specimens into water, and measuring the rate of water absorption and water retention after 7 days at room temperature. Water absorption (%) and water retention (g/cm^3) could be calculated as follows: Water absorption (%) = $(W_1 - W_0)/W_0 \times 100$ and water retention (g/cm^3) = W_1/V_0 ; where W_0 , W_1 , and V_0 denote initial weights, wet weights and volumes of PU foams, respectively.

Method of weight retention follows previous investigation.²² PU foam specimens with dimensions of $1 \times 1 \times 1 \text{ cm}^3$ were used for weight retention after water and ethanol immersion. The specimens were immersed into 600 mL of water and ethanol at 50 and 25 °C for 1 h followed by vacuum oven drying at 60 °C and calculating weight retention.

Three specimens were tested for each experiment.

Measuring Thermal Properties of PU Foam

Thermogravimetric analysis (TGA) of PU foam was performed using a Perkin-Elmer Pyris 1. The PU foam powder was kept in a platinum sample pan and heated to 700 °C from room temperature at a heating rate of 10 °C/min. The real-time weight loss as a function of temperature was recorded during the experiment.

RESULTS AND DISCUSSION

Characteristics of Liquefied Rice Husk

The chemical composition of rice husk on a dry basis has been reported as inorganic matter ca. 20% and other organic matter ca. 80%.⁵ Analysis of rice husk in Taiwan also revealed composition of inorganic ash 15.8%. Figure 1 shows variations in viscosity and residue content of liquefied rice husk during liquefaction. The weight ratio of PEG-400/glycerol to rice husk was 2.5/1.0. The results indicated that both viscosity and residue content decreased rapidly in the first 15 min of liquefaction and then leveled off. The residue contents of liquefied rice husk were 42.5 and 30.1% at the beginning and 15 min of liquefaction, respectively.

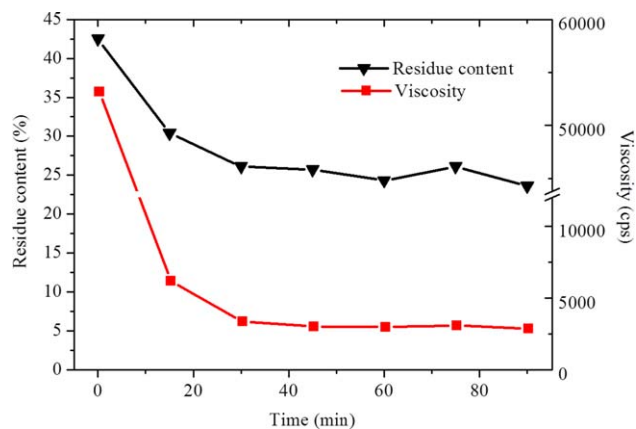


Figure 1. Variations of residue content and viscosity of rice husk during liquefaction. [Color figure can be viewed at wileyonlinelibrary.com]

The viscosity, residue content, and water content of liquefied rice husk were 3089 cps, 23.6 and 4.1% at 90 min of liquefaction. The heartwood and sapwood of liquefied *Cryptomeria japonica* yielded 21.4 and 17.5% residual content under the same reaction conditions.²³ The heartwood and sapwood of liquefied *C. Japonica* showed viscosities of 5920 and 4910 cps, respectively. A high residue of liquefied rice husk indicated that the residue contained inorganic matter and caused re-condensation.^{24,25} Weight ratio of liquefaction reagent/rice husk was at 2.5/1.0 (w/w). Therefore, the ash of liquefied rice husk is approximately 4.5%. Previous studies demonstrated rice husk ash also used as filler for increasing the thermal stability of PU and wood composites because the ash obtained after burning the rice husk contains more than 90% silica.^{8,9} Rice husk ash provides a renewable source of inorganic constituents. In addition, liquefied rice husk of low viscosity is more preferable in the manufacture PU resins.

Acid value is related to the degradation degree of the acetyl group from lignocellulosic materials. The hydroxyl value can be employed to indicate the amount of hydroxyl groups present in the liquefied lignocellulosic materials. For the polyhydric alcohol-liquefied wood, the hydroxyl value decreases with increase in etherification between the solvent and wood components.^{26,27} The acid value and hydroxyl value of liquefied rice husk were 18.9 and 198.6 mg-KOH/g, respectively. On the other hand, the heartwood of liquefied Japanese cedar had acid value and hydroxyl value of 21.8 and 315.0 mg-KOH/g,²³ respectively. In our previous research,^{17,23} Japanese cedar, Taiwan acacia, and China fir were liquefied in PEG-glycerol co-solvent. Acid number of liquefied Taiwan acacia and China fir is 25.6 and 38.0 mg KOH/g. Liquefied wood was used directionally as polyol for application of PU adhesives. The results demonstrated that the strength of liquefied wood-based PU adhesives could fit the requirement of the CNS 11031 standard and PU foams were successfully prepared from raw liquefied wood. Liquefied wood-based PU showed the high structural stability. Therefore, we also used directly liquefied rice husk as polyol for preparation of PU foam. Moreover, the discrepancy in results can be attributed to the lower amount of organic matter present in liquefied rice husk.

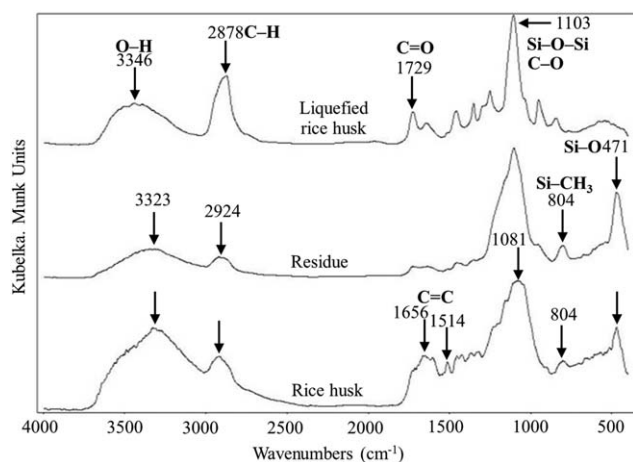


Figure 2. FTIR spectra of rice husk, liquefied rice husk and its residue.

FTIR Spectra of Liquefied Rice Husk

The FTIR spectra of rice husk reported by Daifullah *et al.*²⁸ displayed three bands, around 3400, 1080, and 460 cm^{-1} . The broad band around 3400 cm^{-1} was attributable to the existence of surface hydroxyl groups and chemisorbed water. The siloxane band appeared around 1080 cm^{-1} due to Si—O—Si formation and the sharp band near 460 cm^{-1} was due to the metal halogen bond. Kamath and Proctor²⁹ indicated that the FTIR band of rice husk at 3000–3600 cm^{-1} was attributed to the O—H stretching of the silanol group (Si—OH). The predominant absorbance band between 800 and 1400 cm^{-1} was due to siloxane bonds (Si—O—Si) and the network vibration modes were attributed to the highly compact polymer network.²⁹ Chang *et al.*³⁰ also demonstrated that the FTIR bands of rice husk ash around 1098, 801, and 470 cm^{-1} correspond to amorphous silica. Yamada and Ono³¹ indicated that strong bands observed at 1507 and 1603 cm^{-1} might be attributable to the aromatic compounds of lignin. Boeriu *et al.*³² demonstrated that carbohydrate originating vibrations are associated with other vibrations in the spectral region 1000–1300 cm^{-1} .³² Moreover, FTIR band of polysaccharides at 1035 cm^{-1} appears as a complex vibration associated with the C—O, C—C stretching and C—OH bending.

Figure 2 shows the FTIR spectra of the rice husk, liquefied rice husk, and residue of liquefied rice husk. FTIR spectrum of rice husk reflects the chemical structure of lignocellulose and silanols. On the other hand, FTIR bands of carbohydrate are found at 1000–1300 cm^{-1} in the residue. These results suggested that the residue comprised mainly inorganic silica-based materials. The rice husk had a strong and broad absorption band at 3000–3500 cm^{-1} . After liquefaction, this absorption decreased significantly, implying that the hydroxide group in woody components could react with polyhydric alcohol during liquefaction. The absorption band at 2850–2950 cm^{-1} was attributed to the C—H and CH_2 of aliphatic hydrocarbon. The band at 2850–2950 cm^{-1} of rice husk increased significantly after liquefaction, suggesting that PEG 400 and glycerin had reacted with rice husk and reflected to the structure of liquefied rice husk. The absorption at 1729 cm^{-1} for liquefied rice husk was attributed to the C=O stretching vibration that is characteristic of

un-conjugated ketones, aldehydes, and carboxyls. Lignocellulose was oxidated and formed a new aldehyde group or carboxyl group in their structure after liquefaction. The band at 1081 cm^{-1} was attributed to the stretching vibration of C—O of lignocellulose and Si—O—Si of rice husk. The band at 471 cm^{-1} was attributed to the amorphous silica and decreased significantly after liquefaction, indicating that liquefied rice husk comprised mainly organic materials. The results indicated that 1081, 804, and 471 cm^{-1} are attributable to amorphous silica of rice husk. The FTIR result showed that end of silica in silanol groups (Si—OH) and syloxane groups (Si—O—Si) in rice husk residue and the liquefied rice husk. Kang *et al.*³³ indicated that silanol groups of substituting surface can react with isocyanate and form urethane linkage (S—NCO) on silica particles. Therefore, silanol groups of rice husk residue might help to reactivity of PU foams.

Molecular Weight Distribution of Liquefied Rice Husk

Figure 3 shows the variations in molecular weight distribution of liquefied rice husk during liquefaction. Liquefied rice husk comprised two major fractions of high- (Peak H) and low- (Peak L) molecular weights, respectively. Kurimoto *et al.*³⁴ also reported that the molecular weight distribution curve of liquefied wood was divided into two ranges. Prolonging the liquefaction time increased the fraction of high molecular weight. Kobayashi *et al.*²⁵ suggested the high-molecular-weight fraction appeared because the degraded derivatives from the beginning of wood liquefaction reacted with polyhydric alcohol and recondensed with acidic condition. Table I lists the M_w , number average molecular weight (M_n), and polydispersity (M_w/M_n) of liquefied rice husk at different times during liquefaction. As can be seen, the total M_n and M_w ranged from 890 to 1280 and 2200 to 4100, respectively, during liquefaction. Prolonging the liquefaction time increased the total molecular weight and polydispersity approximately. The M_w of Peak L and Peak H ranged from 1480 to 1970 and 9800 to 12,100, respectively during liquefaction. With increase in liquefaction time, Peak H increases significantly while Peak L increases only slightly. At the beginning of liquefaction, the areas of Peak L and Peak H were 48.9 and 50.1%, respectively. However, the areas of Peak L and Peak

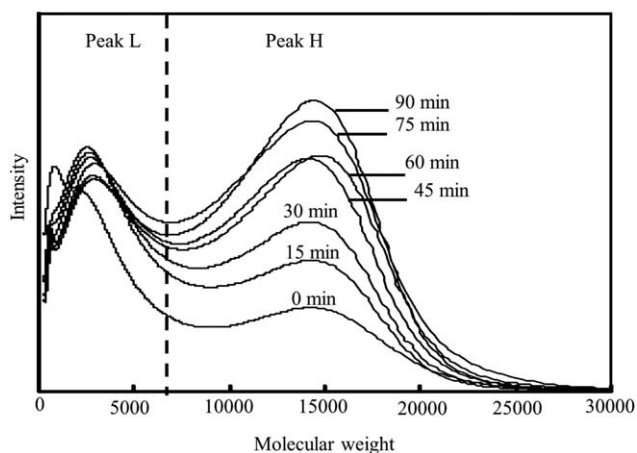


Figure 3. Variations in molecular weight distribution of liquefied rice husk during liquefaction.

Table I. Molecular Weights of Liquefied Rice Husk during Liquefaction

Time (min)	Peak L				Peak H				Total		
	M_n	M_w	M_w/M_n	Area (%)	M_n	M_w	M_n/M_n	Area (%)	M_n	M_w	M_w/M_n
0	820	1480	1.81	49.9	8300	9800	1.19	50.1	890	2200	2.52
15	960	1770	1.84	44.1	10,300	11,400	1.11	55.9	1080	2900	2.64
30	980	1840	1.87	38.8	10,600	11,900	1.12	61.2	1120	3400	2.86
45	1030	2020	1.97	32.5	10,100	11,400	1.13	67.2	1210	3700	3.05
60	930	1830	1.95	30.4	11,000	12,200	1.11	69.6	1120	3700	3.31
75	930	1830	1.96	27.4	10,900	12,100	1.11	72.6	1170	4000	3.42
90	1040	1970	1.91	28.2	10,900	12,100	1.11	71.8	1280	4100	3.22

Table II. Water Absorption and Solvent Resistance of PU Foams made with Liquefied Rice Husk

NCO/OH ratio	Density (kg/m ³)	Water absorption (%)	Water retention (g/cm ³)	Weight retention (%)	
				Water	Ethanol
1.0	38	1393	0.46	95.4	92.8
1.35	43	713	0.27	97.6	97.4
1.5	47	652	0.21	96.4	98.1
2.0	65	364	0.17	98.7	99.5

H became 28.2 and 80.1%, respectively, at 90 min of liquefaction time. In other words, during liquefaction, the area of Peak H increases while that relative area of Peak L decreases. Kurimoto *et al.*³⁴ tested six wood species through liquefaction using PEG-glycerol co-solvent and indicated the polydispersities of liquefied wood were 24.2–35. Liquefied wood-based PU films showed rigid mechanical properties because of higher area percentage of Peak H as crosslinking agents. Hence, increasing Peak H can help the mechanical properties of PU foams.

Basic Properties of PU Foams

This study used liquefied rice husk as raw material of polyhydric alcohol, PMDI as isocyanate, water as blowing agent and organosiloxane as surfactant. The preliminary test results showed that the PU foams were incompletely reacted and cured. Dibutyltin dilaurate was used as catalyst, but the PU foam collapsed and shrank, showing that the blowing rate was too rapid while the drying rate was too slow, thus yielding unstable PU foam structure. After modifying the formulation and using 1,2-Ethylenediamine as catalyst instead, successful preparation of PU foam with stable structure was achieved.

Table II displays the water absorption and solvent resistance of PU foams made with liquefied rice husk at different NCO/OH molar ratios. The densities, the water absorption and solvent resistance of liquefied rice husk-based PU foams are similar with liquefied wood-based PU foams²³ and soybean oil-based PU foams.³⁵ As can be seen, with increasing NCO/OH molar ratio, the density of PU foams increased while their water absorption and water retention decreased. Hence, increasing NCO/OH molar ratio can help strengthen the network structure of PU foam because isocyanate is the crosslink agent in curing reaction. Semsarzadeh and Navarchian³⁶ also demonstrated

similar results. The properties of water absorption and solvent resistance are similar with liquefied wood-based PU foams.²³

Mechanical Properties of PU Foams

In this study, the vertical and horizontal direction defined by rise direction of PU foams.³⁷ Figure 4 shows the stress-strain curves obtained by compression testing of PU foams made with liquefied rice husk as can be seen, the compressive stress in the vertical direction is higher than that in the horizontal direction because press was not used in the manufacture of the PU foams. Kurimoto *et al.*³⁸ indicated the mechanical properties of PU films made with liquefied wood depended upon the NCO/OH ratio used. Table III summarizes the compressive strength of PU foams at various NCO/OH ratios. As can be seen, the densities and compressive stress of PU foams increased by 10 and 25%, respectively, with increasing NCO/OH molar ratio. The results could possibly result in a higher crosslinking density with increasing NCO/OH molar ratio which accounts for the improvement in mechanical properties. At NCO/OH molar ratios 1.0 and 1.5, the strain (98 kPa) in the horizontal direction

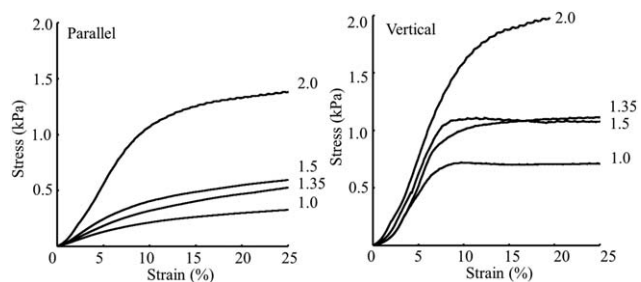


Figure 4. Stress–strain curves of PU foam made from liquefied rice husk. 1.0, 1.35, 1.5, and 2.0 are molar ratios of NCO/OH.

Table III. Compressive Strength of PU Foams made with Liquefied Rice Husk

NCO/OH	Densities (kg/m ³)	Direction ^a	Compressive strength (kPa)		Strain (%) (98 kPa)
			At 10% strain	At 25% strain	
1.0	38	Vertical	70.6	74.5	4.6
1.35	43		121.5	114.7	4.2
1.5	47		95.1	99.0	4.0
2.0	65		114.7	131.3	4.8
1.0	38	Parallel	23.5	34.3	35.6
1.35	43		33.3	51.9	16.8
1.5	47		22.5	37.2	17.4
2.0	65		90.2	120.5	4.0

^aRise direction of PU foams.

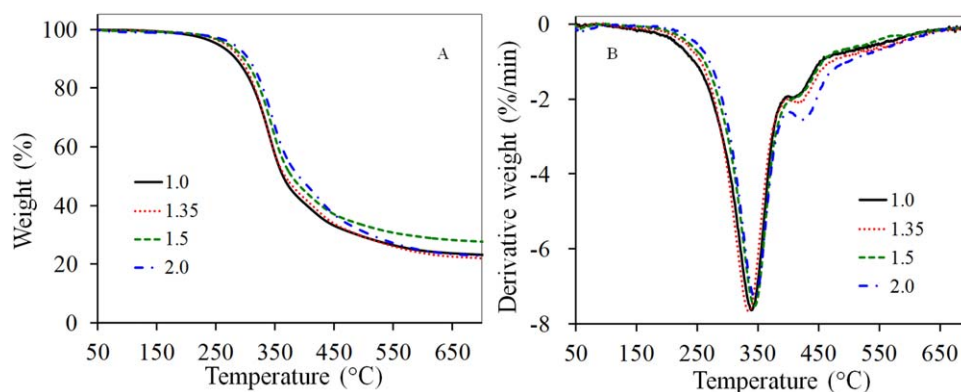


Figure 5. TGA curves of PU foams made with liquefied rice husk. 1.0, 1.35, 1.5, and 2.0 are molar ratios of NCO/OH. [Color figure can be viewed at wileyonlinelibrary.com]

is higher than that in the vertical direction. The strain of horizontal direction decreased from 35.6 to 4.0% and also depended upon NCO/OH molar ratio. However, the strain of vertical direction was 4.0–4.8%. Taken together, the results indicated better compressive strength in the vertical direction than in the horizontal direction. The compressive strength in the vertical direction of liquefied rice husk-based PU foams are similar with soybean oil-based rigid PU foams.³⁵

Thermal Properties of PU Foams

TGA was performed under inert gas flow to investigate the thermal stability of PU foams. Figure 5 shows TGA and DTG curves of PU foams made with liquefied rice husk. As can be seen, for all PU foams studied, the thermal degradation started at

approximately 287 °C and could be divided into two stages. The first stage of weight loss occurred between 280 and 380 °C, the peaks moved toward high temperature with increasing NCO/OH molar ratio. Therefore, increase in thermal stability of PU foams with increasing NCO/OH molar ratio. Previous studies demonstrated that urethane (200 °C) and urea (250 °C) linkages are thermally weak links in the structure of PU resins.^{39,40} As mentioned above, thermal stability of liquefied rice husk-based PU foams was better than fossil-based PU resins. Table IV summarizes TGA thermo-analysis parameters at various NCO/OH ratios. Notably, weight retention of liquefied rice husk-based PU foams all exceeded 22.1% at 700 °C. In contrast, weight retention of ethylene glycol (EG)-based and liquefied wood-based PU resin was lower than 10% at 700 °C.¹⁹ The results also

Table IV. TGA Thermo-analysis Parameters of PU Foam made with Liquefied Rice Husk

NCO/OH molar ratios	First stage			Second stage			Weight retention at 700 °C (%)
	Onset (°C)	Peak (°C)	End (°C)	Onset (°C)	Peak (°C)	End (°C)	
1.0	287	339	374	413	424	459	23.1
1.35	288	333	371	397	424	451	22.1
1.5	296	342	377	413	432	449	27.6
2.0	300	344	380	401	435	454	22.7

demonstrated liquefied rice husk-based PU showed the higher thermal stability than EG- and liquefied wood-based PU resin at the first stage. Inorganic residue of rice husk can help increase thermal stability of liquefied biomass-based polymers.

CONCLUSIONS

In this investigation, rice husk was liquefied in PEG-400/glycerol cosolvent with the weight ratio of solvent to rice husk as 2.5/1, and using sulfuric acid as catalyst. The liquefaction temperature of the mixture was heated to 150 °C and was maintained for 90 min for the liquefaction reaction. The residue content and viscosity of liquefied rice husk were 23.6% and 2888 cps, respectively. The M_w , M_n , and M_w/M_n of liquefied rice husk were 1284, 4137, 3.22, respectively. The liquefied rice husk was blended with PMDI, organosiloxane, 1,2-Ethylenediamine, and water to prepare the PU foam specimens. Results showed that both mechanical and thermal properties of PU foams were influenced by the molar ratio of NCO/OH. In addition, the higher the molar ratio of NCO/OH, the better the compressive strength and thermal stability are. Moreover, the thermal stability of liquefied rice husk-based PU foams was better than fossil- and liquefied wood-based PU resins because of the inorganic residue of rice husk.

REFERENCES

1. Binder, J. B.; Raines, R. T. *J. Am. Chem. Soc.* **1979**, *131*, 2009.
2. Bais, A. L. S.; Lauk, C.; Kastner, T.; Erb, K. *Ecol. Econ.* **2015**, *119*, 326.
3. Crowther, T. W.; Glick, H. B.; Covey, K. R.; Bettigole, C.; Maynard, D. S.; Thomas, S. M.; Smith, J. R.; Hintler, G.; Duguid, M. C.; Amatulli, G.; Tuanmu, M. N.; Jetz, W.; Salas, C.; Stam, C.; Piotta, D.; Tavani, R.; Green, S.; Bruce, G.; Williams, S. J.; Wiser, S. K.; Huber, M. O.; Hengeveld, G. M.; Nabuurs, G. J.; Tikhonova, E.; Borchardt, P.; Li, C. F.; Powrie, L. W.; Fischer, M.; Hemp, A.; Homeier, J.; Cho, P.; Vibrans, A. C.; Umunay, P. M.; Piao, S. L.; Rowe, C. W.; Ashton, M. S.; Crane, P. R.; Bradford, M. A. *Nature*. **2015**, *525*, 201.
4. Sun, L.; Gong, K. *Ind. Eng. Chem. Res.* **2001**, *40*, 5861.
5. Chandrasekhar, S.; Satyanarayana, K. G.; Pramada, P. N.; Raghavan, P.; Gupta, T. N. *J. Mater. Sci.* **2003**, *38*, 3159.
6. Della, V. P.; Kühn, I.; Hotza, D. *Mater. Lett.* **2002**, *57*, 818.
7. Kalapathy, U.; Proctor, A.; Shultz, J. *Bioresour. Technol.* **2000**, *73*, 257.
8. Costa, A. P. O.; Silva, R. B.; Gerbase, A. E.; Petzhold, C. L. *J. Appl. Polym. Sci.* **2012**, *123*, 1370.
9. Fuad, M. Y. A.; Zaini, M. J.; Jamaludin, M.; Ishak, Z. A. M.; Omar, A. K. M. *J. Appl. Polym. Sci.* **1994**, *51*, 1875.
10. Kim, S.; Dale, B. E. *Biomass Bioenergy*. **2004**, *26*, 361.
11. Ye, L.; Zhang, J.; Zhao, J.; Tu, S. *Bioresour. Technol.* **2014**, *153*, 147.
12. Hassan, E. B. M.; Shukry, N. *Ind. Crops Prod.* **2008**, *27*, 33.
13. Yan, Y.; Pang, H.; Yang, X.; Zhang, R.; Liao, B. *J. Appl. Polym. Sci.* **2008**, *110*, 1099.
14. Lee, S. H.; Yoshioka, M.; Shiraishi, N. *J. Appl. Polym. Sci.* **2000**, *78*, 319.
15. Chen, F.; Lu, Z. *J. Appl. Polym. Sci.* **2009**, *111*, 508.
16. Lin, X. Y.; Liang, S. E.; Wang, J. H.; Tian, C. R.; Huang, Y. X. *Chin. Pat.* 102617821 (**2012**).
17. Lee, W. J.; Lin, M. S. *J. Appl. Polym. Sci.* **2008**, *109*, 23.
18. Yu, C. Y.; Lee, W. J. *Polym. Degrad. Stab.* **2014**, *101*, 60.
19. Lee, W. J.; Kuo, E. S.; Chao, C. Y.; Kao, Y. P. *Holzforchung.* **2015**, *69*, 547.
20. Rozman, H. D.; Yeo, Y. S.; Tay, G. S.; Abubakar, A. *Polym. Test.* **2003**, *22*, 617.
21. Yao, Y.; Yoshioka, M.; Shiraishi, N. *J. Appl. Polym. Sci.* **1996**, *60*, 1939.
22. Lee, W. J.; Chen, Y. C.; Wu, C. C.; Juan, Y. M. *J. Appl. Polym. Sci.* **2009**, *113*, 1257.
23. Chin, W. S.; Lee, D. G. Q. *J. Chin. For.* **2007**, *41*, 40.
24. Yamada, T.; Ono, H. *J. Wood Sci.* **2001**, *47*, 458.
25. Kobayashi, M.; Asano, T.; Kajiyama, M.; Tomita, B. *J. Wood Sci.* **2004**, *50*, 407.
26. Lee, W. J.; Chang, K. C.; Sung, I. C.; Chen, Y. C. Q. *J. Chin. For.* **2006**, *39*, 517.
27. Kurimoto, Y.; DOI, S.; Tamura, Y. *Holzforchung.* **1999**, *53*, 617.
28. Daifullah, A. A. M.; Girgis, B. S.; Gad, H. M. H. *Mater. Lett.* **2003**, *57*, 1723.
29. Kamath, S. R.; Proctor, A. *Cereal Chem.* **1998**, *75*, 484.
30. Chang, F. W.; Yang, H. C.; Roselin, L. S.; Kuo, W. Y. *Appl. Catal. A Gen.* **2006**, *304*, 30.
31. Yamada, T.; Ono, H. *Bioresour. Technol.* **1999**, *70*, 61.
32. Boeriu, C. G.; Bravo, D.; Gosselink, R. J. A.; van Dam, J. E. G. *Ind. Crops Prod.* **2004**, *20*, 205.
33. Kang, S.; Hong, S. I.; Choe, C. R.; Park, M.; Rim, S.; Kim, J. *Polymer.* **2001**, *42*, 879.
34. Kurimoto, Y.; Koizumi, A.; DOI, S.; Tamura, Y.; Ono, H. *Biomass Bioenergy.* **2001**, *21*, 381.
35. Guo, A.; Javni, I.; Petrovic, Z. *J. Appl. Polym. Sci.* **2000**, *77*, 467.
36. Semsarzadeh, M. A.; Navarchian, A. H. *J. Appl. Polym. Sci.* **2003**, *90*, 963.
37. Hu, Y. H.; Gao, Y.; Wang, D. N.; Hu, C. P.; Zu, S.; Vanoverloop, L.; Randall, D. *J. Appl. Polym. Sci.* **2002**, *84*, 591.
38. Kurimoto, Y.; Takeda, M.; Koizumi, A.; Yamauchi, S.; DOI, S.; Tamura, Y. *Bioresour. Technol.* **2000**, *74*, 151.
39. Chattopadhyay, D. K.; Webster, D. C. *Prog. Polym. Sci.* **2009**, *34*, 1068.
40. Ravey, M.; Pearce, E. M. *J. Appl. Polym. Sci.* **1997**, *63*, 47.