Effect of the Addition of Wood Flours on the Properties of Rigid Polyurethane Foam

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ABSTRACT: The objective of this study is to investigate an appropriate process to fabricate the wood-polyurethane hybrid composites [wood-polyurethane foam (PUF)]. Rigid PUFs that contain up to 20% wood flours were successfully fabricated from polymeric 4,4-diphenylmethane diisocyanate, polyols, silicone surfactant, dibutin dilaurate/dimethylethanolamine catalysts, and distilled water (chemical blowing agent). The effects of hydroxyl value of polyols, wood flour particle size, wood flour content, isocyanate index, and water amount on the compressive property of foam were investigated. The morphology of the cell was observed with a scanning electron microscope. Wood-PUF with different densities were prepared at different water contents in the wood flours. The relationship between the compressive property and density was established following the Power law. The incorporation of wood flour improved the compressive property of PUF, whereas its tensile and flexural properties were reduced. The thermal stability of the PUF was improved with the addition of wood flour. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2902–2909, 2009

Key words: rigid polyurethane foam; wood flour; mechanical property; composites

Polyurethane foams (PUF) can be made into a large variety of products with different compositions, densities, and properties. These products are usually produced through interaction between polyols and polyisocyanates by addition polymerization with other additives, such as catalysts, surfactants, and foaming agents. Sometimes, fillers may be used to enhance the modulus and strength of the product, to increase the product density, and to reduce the cost. Polyurethane (PU) products include high-density rigid and flexible PUF, high-performance polyisocyanurate foams, energy-absorbing materials, structural products for composite core applications, machined and molded parts, and other composite products. The applications of these materials can be in the areas of aerospace, transportation, and construction. Some specific applications include tooling boards used as models for automobiles and airplanes, building models with different densities, colors, and building blocks using high-density foams.

Wood flours are low cost materials which are processed from wood residues. It is a lignocellulosic material containing natural polymers, such as cellulose, hemicellulose, lignin, and tannins. Isocyanate functional groups have been proved to form strong PU linkage and interpenetrating networks with the hydroxyl groups of wood. Isocyanate-based adhesives such as polymeric diphenylmethane diisocyanate (pMDI), PU emulsion adhesives have successfully been used as binders for oriented strand board, I-joist, and other types of engineered wood composites. Marra[1] developed a process that fibrillated wood particles of matchstick size could be carried in a foaming urethane resin to fill the cavities with a structural matrix of wood bonded at interstices by the resin. A few other patents and articles have been issued in regard to the wood-PUF composite products.[2–6] Vladkova et al.[7–9] used wood flours as fillers for rubber processing industry. Incorporating wood flours into PUF products may have many advantages. The overall cost of the wood-PUF product should be reduced thanks to the low cost of the wood flours. In addition, the incorporation of wood flours may contribute to the stiffness properties of the products. Physical-blowing agents such as chlorofluorocarbons and hydrochlorofluorocarbons are considered to be undesirable mainly because of the environmental issues. Distilled water used as chemical blowing agent has been developed and studied.[10] Distilled water reacts with diisocyanate, generating carbon dioxide, whereas polyol reacts with diisocyanate. The reaction is exothermic and the reaction heat can accelerate the foaming reaction.[11–13]

Recently, research and development of biodegradable PUF has drawn a lot of attentions. The main components for PUF include polyisocyanate and polyol. For the polyisocyanate, it would be difficult to

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TABLE I
Characteristics of the Used Materials

Materials	Supplier	Comments
pMDI	BASF	NCO% = 31.5
Polyol (GP730)	BASF	231 mg KOH/g
Polyol (GP430)	BASF	398 mg KOH/g
DBTDL	Aldrich	Catalyst
DMEA	Aldrich	Catalyst
Tegostab B8404	Goldschmidt	Surfactant
Distilled water	Laboratory	Blowing agent

address the biodegradability issue for the PUF products. For the polyol, replacement of petroleum-derived polyols with bio-based polyols can be to good option. The bio-based polyol can be derived from soybean,[14] castor oil,[15] waste paper,[16] and Palm oil.[17]

The objective of this research is to investigate an appropriate process to fabricate the wood-PU hybrid composites (wood-PUF). It is not only to broaden the market for wood utilization into a high value product, but also to reduce the overall cost of the existing PU foaming products.

MATERIALS AND METHOD

Materials

The pMDI (LuPranate®M20S) and polyether polyol (PluRacol®GP730, GP430) were supplied by BASF Company. Distilled water generated in our laboratory was used as chemical blowing agent. Dibutin dilaurate (DBTDL) was used as the main catalyst, whereas *N, N*-dimethylethanolamine (DMEA) was used as cocatalyst. The surfactant, Tegostab B8404 was supplied by Goldschmidt Chemical, Canada. Southern pine wood flours were supplied by American Wood Fibers Company. The sizes of wood flour were 80 meshes, 40 meshes, and 20 meshes, respectively (denoted as A-80, A-40, and A-20). A summary of the raw materials is listed in Table I.

Viscosity measurement

The viscosity of polyol blended with wood flours was measured with Brookfield viscometer (RVTD model). The temperature was maintained at 25 ± 2°C during the measurements using a thermostatically controlled tank.

Hydroxyl number measurement

The hydroxyl number is defined as the number of milligrams potassium hydroxide equivalent to the hydroxyl content of 1.0 g of sample. The hydroxyl number analysis was performed based on the ASTM D4274-94 (ASTM, 1996). Before the analysis, wood flour was oven-dried at 105°C for 12 h.

TABLE II
Chemical Compositions of Rigid Polyurethane Foam (PUF) Blown by Water

Ingredients	php[a]
Polyether polyol	100
Tegostab B 8404	2
DBTDL	0.1
DMEA	1
Distilled water	0.5
Wood flour	Vary
pMDI	Vary

[a] Represents as parts per hundred of polyols by weight.

Experimental design and formulations

The major factors investigated for the wood-PUF product include wood flour size, wood flour content, hydroxyl value, catalyst, and surfactant. Table II shows the formulation used for the foam. For the completion of the reaction, additional pMDI (ca. 10%, NCO/OH = 1.1) was used.

Foam preparation

The PUF samples were prepared by one-pot and free-rising method. The chemical compositions are shown in Table II. The polyol, catalysts, surfactant, and blowing agent (B-side material) were added by weighing into a 200 mL disposable plastic cup and mixed with a mechanical stirrer. Wood flour was then added and mixed at 3000 rpm for 10–15 s. The mixture was allowed to degas for 120 s. PMDI (A-side material) was then added rapidly. Stirring was continued for another 10–15 s at the same rpm. The mixtures were poured immediately into a wooden mold with aluminum foil lining and the foam was allowed to rise and set at room temperature. The filler concentration varied from 0 to 20%. Figure 1 illustrates the foaming procedures.

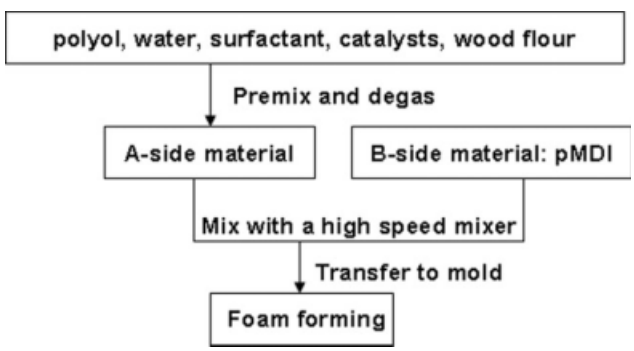

Figure 1 Procedures of polyurethane foam preparation.

Foam property characterization

Morphology

The morphology of the PUF samples was examined with a scanning electron microscope (SEM) (Zeiss EVO 50). The samples were gold coated before scanning. The accelerating voltage was 5 kV. The SEM images were taken in different areas for each sample.

Density test

The density of the PUF was determined by averaging the mass/volume measurement results of six specimens per sample following the procedure described in ASTM D1622-98 standard. Standard deviations for the density measurement were calculated.

Mechanical property test

Compression test. The compressive properties of the foams were measured using an Instron universal testing machine (model 5500) in accordance with the ASTM D1621-00 standard. Samples were cut to a size of 40 × 40 × 25 mm (width × length × thickness). The orientation is parallel to foam rise direction. The cross-head speed was 2 mm/min with a load cell of 500 kgf. The load was applied until the foam was compressed to approximately 15% of its original thickness. Six replicates per sample were tested and the results were averaged.

Flexural test. The specimens were cut to a size of 25 × 120 × 20 mm (width × length × thickness). A center-point load set up was used for the bending test with a span of 100 mm. The cross-head speed was 10.00 mm/min.

Tensile strength test. Tensile strength testing was performed in accordance with the procedure described in ISO 1926. The size of specimen was 20 × 100 × 6 mm (width × length × thickness). The gauge length was 50 mm. Five replicates per sample were measured and averaged.

Thermal property test

Thermal gravimetry analysis with differential scanning calorimetry (TGA-DSC; Setsys Evolution 1750 TGA-DSC 150) was used to measure the thermal characteristics of PUFs. An aluminum pan was used to place the sample powder inside the heating chamber and the samples were heated up to 600°C at a rate of 10°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

Experimental design and formulations

The amount of catalyst DBTDL and DMEA were adjusted to balance the reaction between the isocyanate and polyol or the isocyanate and water, respectively. The cream time was adjusted to about 10 s, 30–45 s for the gel time, and 45–60 s for the tack free time.[18] In this experiment, the cream time, gel time, and tack free time are adjusted to ca. 60 s, 90 s, and 100 s in our laboratory, respectively. Seo et al.[10] have investigated the effect of catalyst on the kinetic rate of PUF forming. There are many parameters to affect the foam forming including isocyanate index, water content, wood flour size, and wood flour content. The compressive strength and modulus are the main properties for the PUF products.

Hydroxyl value determination

The hydroxyl values of the wood flour were determined and shown in Table III. It showed that the hydroxyl values of three wood flour sizes are nearly identical. The hydroxyl group of wood flour reacts with the isocyanate. Based on the hydroxyl value, the amount of pMDI that wood flour consumes can be calculated.

Viscosity of polyol and wood flour mixture

The viscosity is a very important factor to consider for the PU foaming process. A high viscosity makes it difficult for the blending with pMDI and results in less uniform for foam forming. Figure 2 shows the effect of wood flour content and size on the viscosity of polyol/wood flour mixture. Generally speaking, the higher the wood flour content, the higher the viscosity for the polyol/wood mixture. However, when the wood flour content was lower than 10%, the adding wood flour did not seem to increase the viscosity of the mixture significantly. At the same wood flour content, the viscosity increased as the wood flour size decreased. This may be because that the smaller the wood flour size, the larger the surface area for the wood flour, and higher the viscosity for the mixture is obtained. The viscosity of GP430/wood mixture was relatively higher than that of GP730/wood mixture due to a higher viscosity of GP430. It was also found from the experiment that when 15 and 20% of wood flour were added to GP430, the viscosity of the mixture was increased too high to handle in the foaming process.

TABLE III
Hydroxyl Value of Wood Flours with Different Sizes

Wood flour	OH number (mg KOH/g)	Average value
A-80, 80 mesh size	312	311
A-40, 40 mesh size	311	
A-20, 20 mesh size	310	

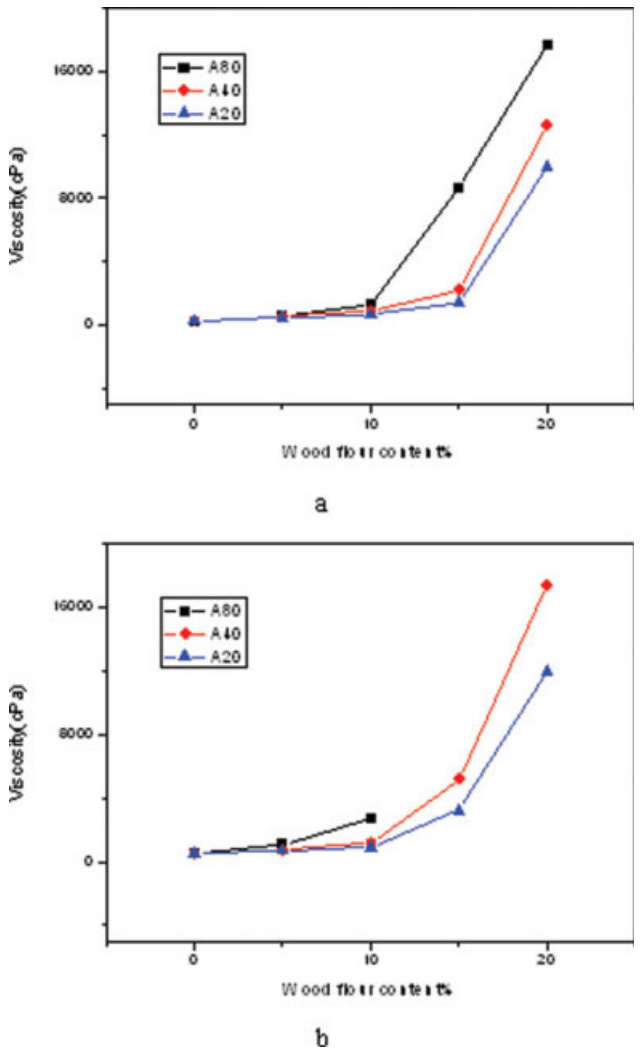

Figure 2 Viscosity of polyol/wood flour mixture as a function of wood flour content (a: GP730 polyol; b: GP430 polyol). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of hydroxyl value of polyol on compressive property

Figure 3 shows the effect of hydroxyl value on the compressive property of PUF. For the GP430 polyol (higher hydroxyl value), the compressive property of foam made from GP430 polyol was higher than that from GP730 polyol (lower hydroxyl value). As the hydroxyl value of the polyol increased, the degree of cross-linking of PUF sample would increase. Therefore, GP430 was chosen for the subsequent study.

Effect of wood flour size and content on foam density

The densities of the wood-PUF at different wood flour sizes are shown in Figure 4. The wood-PUFs presented a slightly higher density than that of pure PUF. No significant difference in density was found

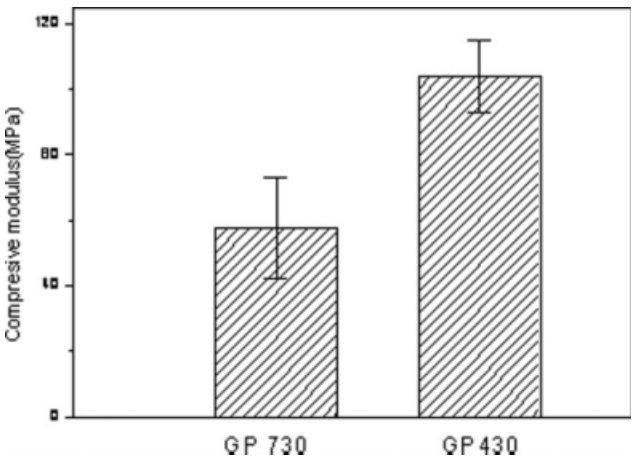

Figure 3 Effect of hydroxyl value of polyols on the compressive property of PU foams.

on the wood-PUFs fabricated from the three wood flour sizes. Figure 5 shows the effect of wood flour content on PUF density using the wood flour of A-80. As the wood flour content increased, the PUF density also increased. This may be caused by an increased viscosity of wood flour/polyol mixture when the wood flour content increases. The increased viscosity would inhibit the foam to rise, and therefore, the density of the foam increased. Also, the density of wood itself was higher than that of the foams.

Effect of wood flour size and content on compressive property

The effect of wood flour size on the compressive property is shown in Figure 6. The compressive modulus of wood-PUF was higher than that of the pure PUF. Even though no significant difference in compressive modulus was found among the three

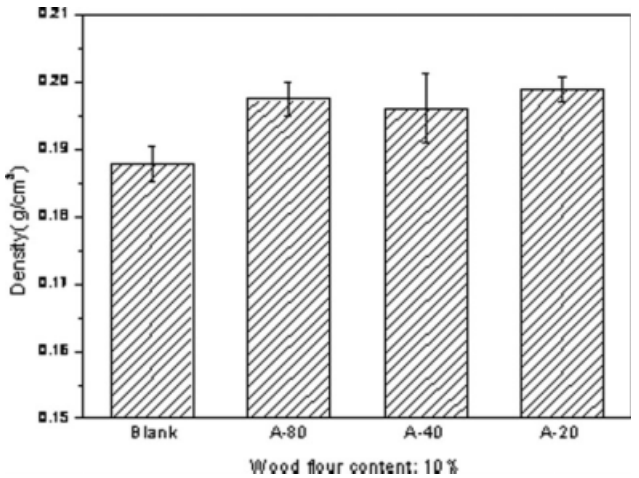

Figure 4 Effect of wood flour size on the foam density (wood flour content: 10%).

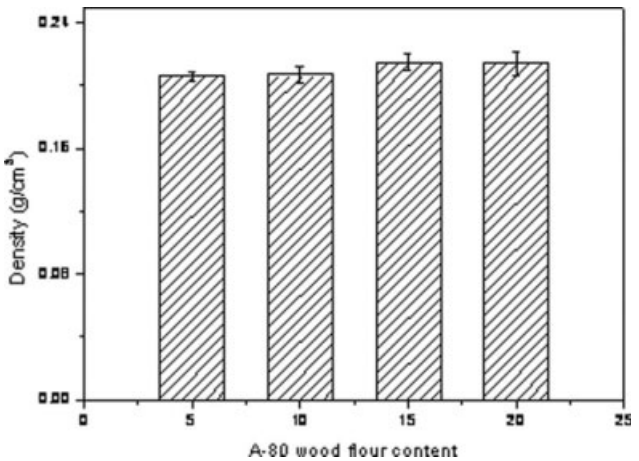

Figure 5 Effect of wood flour content on the foam density (wood flour size: A-80).

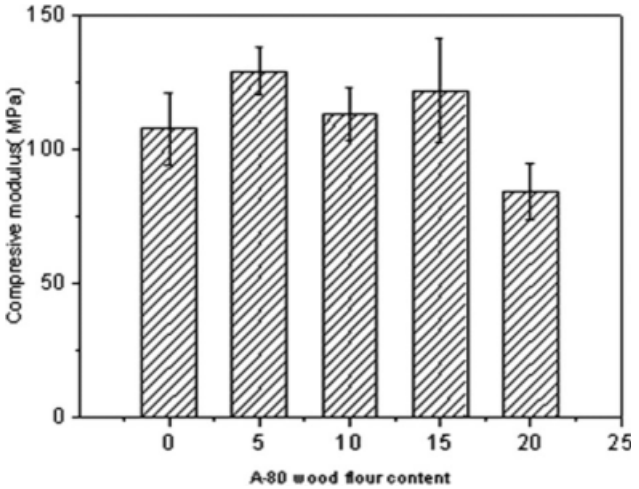

Figure 7 Effect of wood content on the compressive property of polyurethane wood foam (wood flour: A-80).

wood flour sizes, wood-PUF using A-80 wood flour appeared a highest compressive property. It may be because that A-80 wood flour has the highest surface area among the wood flour sizes used. The higher the surface area, the better the adhesion obtained between wood flours and PU.

The results for the effect of wood flour content on the compressive modulus are shown in Figure 7. The overall trend was that as the wood flour content increased, the compressive modulus of wood-PU wood foam decreased, regardless of the increased density with an increased wood flour content. However, no significant decrease was found when the wood flour content was in the range of 5–15%. This might be because of the large voids formatted in the foam structure when wood flour was incorporated. Harikrishnan et al.[19] used organically modified clay as filler to prepare PUF/clay nanocomposites. The compressive property was also reduced when the clay was incorporated. Hustad et al.[20] incorporated partially delactosed whey powder as an extender in rigid PUF. The results also showed that increasing delactosed powder decreased the compressive property and increased the open cells. It was shown in Figure 7 that the compressive modulus was increased about 19 when 5% wood flour was incorporated.

Effect of isocyanate index on compressive property

Compressive modulus of foam increased linearly as the isocyanate index increased (Fig. 8). The higher the isocyanate index, the more the opportunity for the chemical reaction between the components is obtained. In the subsequent experiment, an isocyanate index of 1.1 was used considering the cost

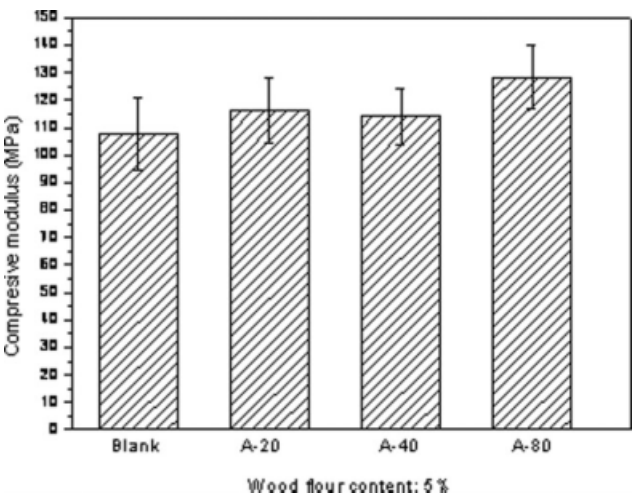

Figure 6 Effect of wood flour size on the compressive property of polyurethane wood foam (wood flour content: 5%).

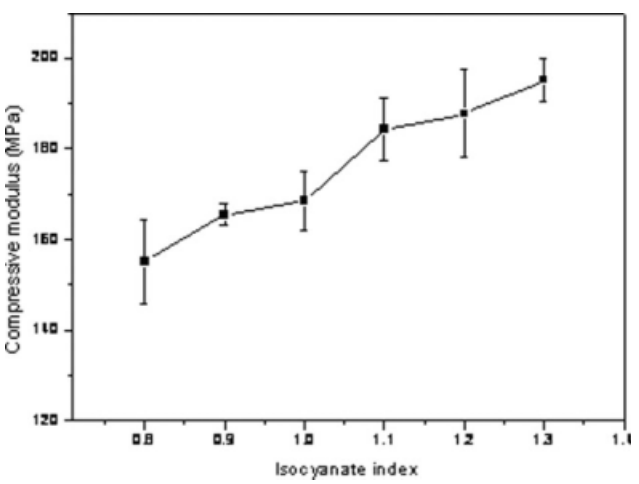

Figure 8 Effect of isocyanate index on the compressive property of polyurethane wood foam (wood flour content: 5%; wood flour size: A-80).

factor. An excess of 10% for the isocyanate was used for the side reaction consume.

Effect of water content on the wood foam density

Figure 9 shows the effect of water content on the density of wood-PUF. The amount of water varied from 1 to 3 php with an increment of 0.5 php at a wood flour (A-80 size) content of 5%. As the water content increases, the production of carbon dioxide increases, which leads to a lighter foam. Water reacts with isocyanate to form rigid PU structures in the foam, which would account for an increase in foam strength. However, the density decreases with an increase of water content, which result in a decreased compressive property (Fig. 10).

It is known that the mechanical properties of a cellular material depend on its density. A simple Power law can be used to depict the relationship between the mechanical properties (compressive property and modulus) and the density[21–23]:

$$\log\ (\text{strength property}) = \log\ A + B\ \log\ (\text{density}),$$

where A is a constant related to the temperature and physical properties of the resin and B is related to the deformation mechanics of cellular materials. The compressive property and modulus of PUF exhibited the dependence of Powder law with respect to the foam density. The slope of the plot of log (property) versus log (density) was used for the determination of the density exponent value and was calculated as 1.58 for compressive modulus as shown in Figure 11. This value was similar to those reported in the literatures.[22,23] Goods et al.[22] reported a density exponent of 1.60 for compressive modulus for water blown rigid PUF. Thirumal et al.[24] reported a density exponent of 1.72.

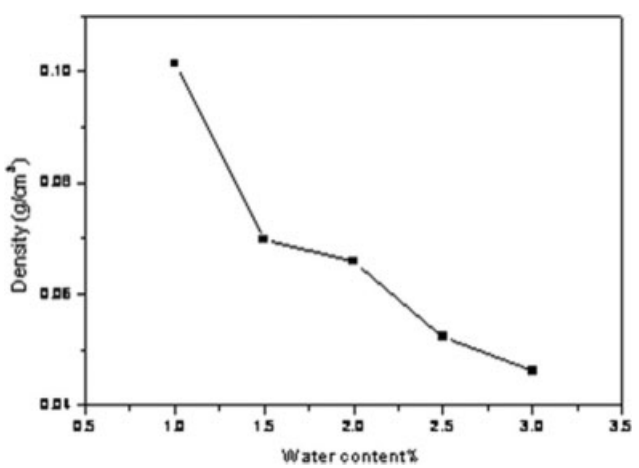

Figure 9 Effect of water amount on the density of polyurethane wood foam (wood flour content: 5%; wood flour size: A-80).

TABLE IV
Tensile and Flexural Properties of Blank Polyurethane Foam and Wood Foam Filled with 5%, A-80 Wood Flour

	Flexural property		Tensile stress
	MOR (MPa)	MOE (MPa)	(MPa)
Pure PU foam	2.88 ± 0.14	52.84 ± 2.58	2.19 ± 0.10
wood-PU foam	2.50 ± 0.20	50.30 ± 3.08	1.72 ± 0.22

Tensile and flexural properties of wood foam

The tensile and flexural properties of pure PUF and wood-PUF are shown in Table IV. The incorporation of wood flour reduced the tensile and flexural properties, even though the density of wood-PUF was increased slightly. The incorporation of wood flours might weaken the interfacial compatibility between PU and wood flour, which results in a reduction of tensile and flexural properties.

Thermal analysis of wood foam

Figure 12 shows the thermal stability of pure PU and wood-PUF. As shown in this figure, the TGA curves display a two-step degradation mechanism for both the pure PU and wood-PUF. The first-step degradation (rapid degradation stage) was initiated at 300°C and terminated at 357°C regardless of the formulation types. The second-stage degradation was a slow stage for both pure PU and wood-PUF. In this stage, the degradation process was continuous, but was not very obvious in the weight decrease. Comparing with the curves of pure PUF, the incorporation of wood flour resulted in an improvement of thermal stability.

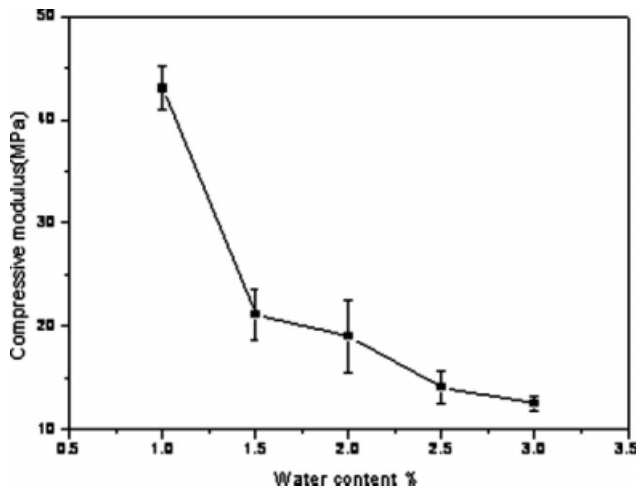

Figure 10 Effect of water content (as blowing agent) on the compressive modulus of polyurethane wood foam (wood flour content: 5%; wood flour size: A-80).

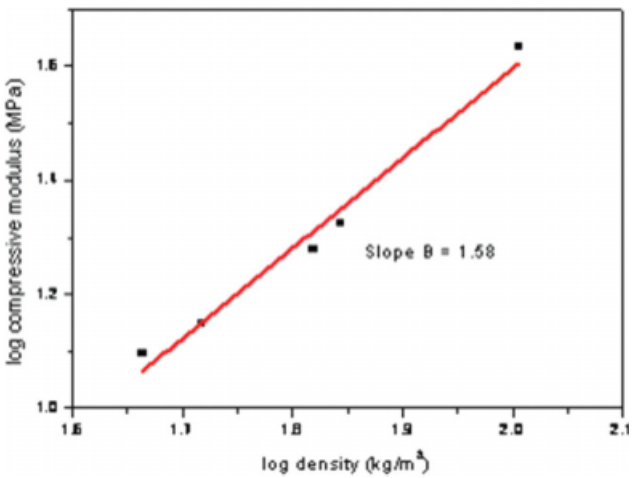

Figure 11 Compressive modulus versus density for the polyurethane wood foam blown with water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

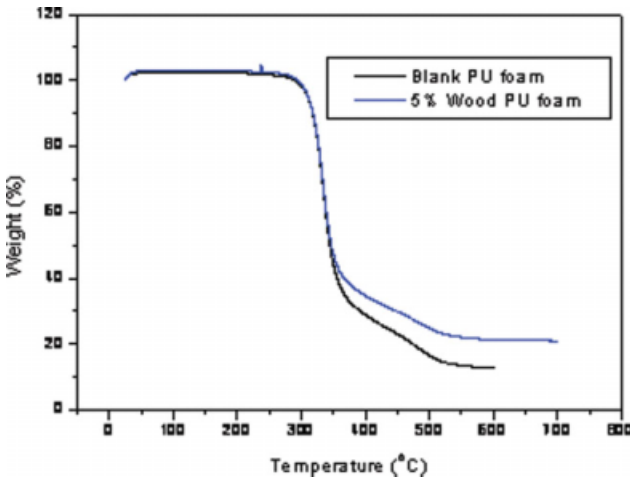

Figure 12 Weight loss curves of polyurethane wood foams as a function of time from thermogravimetric analysis (TGA). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Morphology

The cross-sectional surfaces of PUF samples observed with SEM are shown in Figure 13. The cellular structures were observed in the free-rising direction of the foam. When a 5% wood flour was added, the cell size nearly maintained the same. When the water content was increased from 0.5 to 1.5–3%, the cells were not uniform. And in most cases, the cells were broken. The cells were much larger and broken probably because of the non-uniform distribution of moisture (an inherent impurity in polyols) for the blowing agent. As the water content further increased from 1.5 to 3%, the cell size

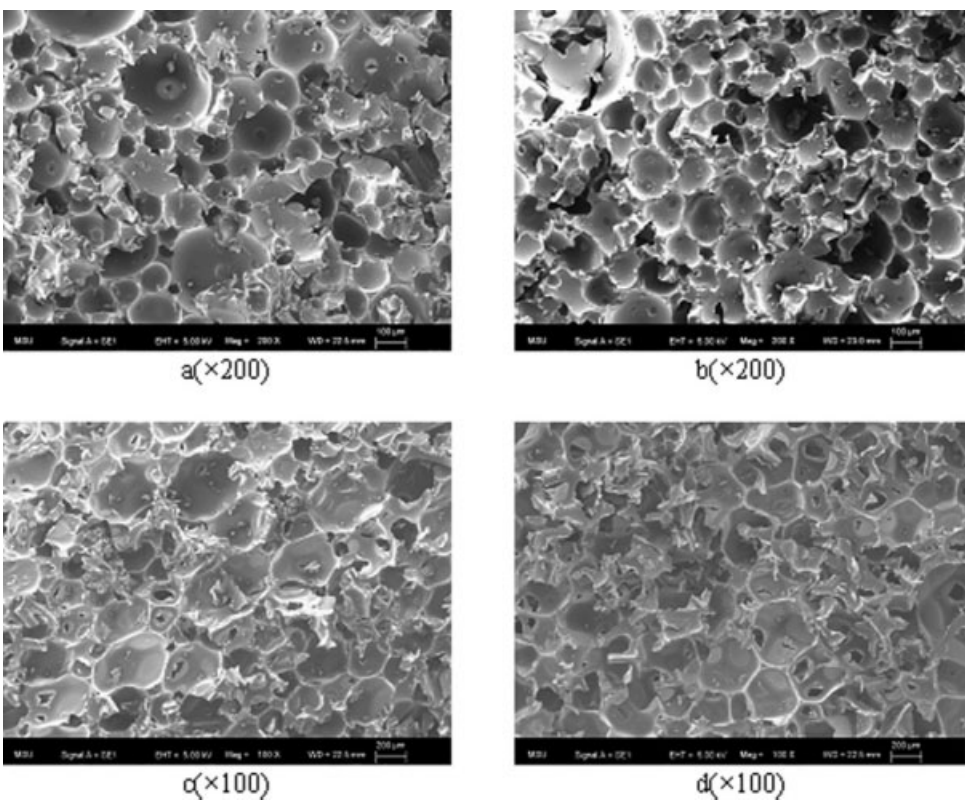

Figure 13 SEM micrographs of polyurethane wood foams: (a) blank polyurethane foam, without wood, water content is 0.5%, (b) 5% wood flour content, A-80 size wood flour, water content is 0.5%, (c) 5% wood content, A-80 size wood flour, water content is 1.5%, (d) 5% wood content, A-80 size wood flour, water content is 3%.

changed slightly because the excess of carbon dioxide came out through the broken cell wall.

CONCLUSIONS

Rigid PUF reinforced with wood flour content up to 20% can be successfully fabricated. An incorporation of 5% wood flour in PUF improved the compressive modulus for about 19%. The size of wood flours (20–80 meshes) did not show a significant effect on the compressive modulus of the foam. The morphology of the cells changed slightly with the incorporation of 5% wood flour. The relationship between the compressive modulus and density followed the Power law. The incorporation of wood flour resulted in a reduction of tensile and flexural properties, but an improvement of thermal stability of the foam.

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