

Influence of Adding Lignin and Wood as Reactive Fillers on the Properties of Lightweight Wood–Polyurethane Composite Foams

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Abstract

In this study, bio-based rigid polyurethane (PU) composite foams were prepared by a free-rising method, with the addition of wood particles (10 and 20 weight percent by the foam mass) and kraft lignin (5 and 10 weight percent by the polyol mass) as reactive reinforcing fillers. The resultant PU composites were evaluated for chemical structure, density, morphology, compressive properties, water uptake, and thermal stability. Fourier-transform infrared analysis confirmed the formation of characteristic urethane bonds in all foam samples. The foaming process was slowed down by the incorporation of lignin and wood particles. The apparent density of lignin-incorporated wood–PU composite foam ranged between 77 and 105 g/cm³. Compared with the neat PU foam, addition of wood particle resulted in decreased compressive properties and increased water uptake of the foams, whereas incorporation of lignin had a positive effect on the compressive properties and water resistance. In general, the PU foam sample with the incorporation of only 5 percent lignin (PUL₅) exhibited the optimal physical–mechanical properties, with the compressive strength increased by 74 percent and 24-hour water uptake decreased by 28 percent compared with the control PU foam. Thermogravimetric analysis showed that the incorporation of lignin and wood particles did not significantly affect the thermal degradation pattern of foam but rather increased the mass of char residue.

Rigid polyurethane (PU) foams are a class of highly cross-linked polymers with a closed- or open-cell structure, which are used in a wide range of applications including the automotive, construction, and insulation industries (Kur-ńska et al. 2020). As one of the most common commercial foams used in the world, rigid PU foams exhibit many characteristic properties including low apparent density, low thermal conductivity, good dimensional stability, and high ratio of strength to weight (Alinejad et al. 2019). Rigid PU foams are typically prepared by mixing an A-side polyisocyanate with a B-side polyol blend (a preblended mixture of catalysts, surfactants, blowing agents, and polyols) to form cross-linked polymer networks. Currently, both the polyisocyanate and polyols are mostly derived from petrochemical resources (Xue et al. 2014). Since the publication of the principle of green chemistry, the replacement of fossil-based raw materials by renewable or sustainable resources as starting materials has become a growing tendency with respect to environmental and economic aspects (De Luca Bossa et al. 2020). In this context, numerous studies have been aimed at using sustainable sources to improve the sustainability of the PU

products, including the use of chemicals and additives derived from bio-based feedstock (such as vegetable oil and forest biomass) in the synthesis of PU (Chen and Tai 2018).

Wood fragments and their derivatives—including wood particle, cellulosic fiber, paper waste sludge, and lignin—are the main biomass-based fillers that are applied in PU foams because of their huge availability (Rącz et al. 2009, Delucis et al. 2018b, Kairyte et al. 2018). It is known that these lignocellulosic fillers contain OH groups, which have potential to interact with isocyanate functional groups (Mosiewicki et al. 2009, Gu et al. 2013). This nature draws considerable interest to incorporate these fillers into PU

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formulations. Furthermore, the incorporation of lignocellulosic filler into petro-based PU foam results in the yielded materials exhibiting a susceptibility to fungal attack in wet environments, which is a desirable attribute for decreasing the environmental impact after disposal (Silva et al. 2010). Among these fillers, cellulose micro- and nanoparticles are produced via expensive or tedious processes, so wood and lignin particles are more favorable in terms of cost. Yuan and Shi (2009) fabricated rigid wood-PU hybrid foams, which contain up to 20 percent wood flour. They found that the incorporation of 5 percent wood flour improved the compressive modulus and thermal stability of the foam. Delucis et al. (2018a) investigated the effect of six fillers from forestry waste (wood, bark, pine cones and needles, kraft lignin, and recycled paper sludge) with variable contents (1, 5, and 10 weight percent [wt%]) on PU-based foams. Results showed that addition of 1 and 5 percent wood were the most effective among the studied compositions, with better compressive properties and lower water uptake.

Lignin is one of the three major components of plant cell walls and the most abundant aromatic polymer in nature. Annually, >70 million tons of lignin and its derivatives are produced as byproducts during the extraction of cellulose for the paper and pulp industries (Kai et al. 2016). But only a small amount of lignin is used to produce commercial materials, with the majority burned as low-grade fuel to produce energy (Matsushita 2015). Lignin is inexpensive and possesses many unique properties such as biodegradability, high thermal stability, and favorable stiffness (Thakur et al. 2014). These advantages have motivated interest in developing lignin into value-added products. Both aliphatic and phenolic OH functional groups of lignin can react with isocyanate to form urethanes, making lignin a potential candidate to replace the fossil-derived polyols for PU synthesis (Upton and Kasko 2016). Recently, several attempts have been made to use lignin, either directly or after chemical modification, as bio-polyols in the preparation of PU foams. Research by Pan and Saddler (2013) found that lignin is chemically cross-linked, not just physically trapped in the PU foam. The largest source of industrial lignin is the kraft pulping process. Li and Ragauskas (2012) synthesized a series of lignin-based rigid PU foam by replacing varying amounts of commercial polyols with oxypropylated kraft pine lignin. The obtained foams exhibited better mechanical properties than its control counterpart made from only commercial polyols. Compared with chemical derivatization, utilizing lignin without chemical modification is more economically and environmentally favorable. Several attempts have been made to replace the petroleum-based polyols directly with unmodified industrial lignins (e.g., organosolv, kraft, and alkaline lignin), but in some cases it has resulted in PU foams with inferior mechanical properties compared with foams based solely on petrochemical polyols (Pan and Saddler 2013, Xue et al. 2014). The main challenge for direct incorporation of unmodified lignin in PU foam is its aggregation and poor solubility of lignin in the polyol (Mahmood et al. 2016, Alinejad et al. 2019). In order to enhance the disaggregation, Hayati et al. (2018) dispersed low loading of lignin in polyether polyol at a temperature closer to the “softening” point of kraft lignin. Through this methodology, the resultant PU foam exhibited an improvement in compressive strength compared with the control. Currently, to the

best of our knowledge, few researches have investigated the bio-based PU composite foams prepared from both wood and lignin particles. Whether the produced PU composite foams achieve comparable properties as compared with the reference PU foams remains to be investigated.

The objective of this study is to prepare and evaluate low-density bio-based PU composite foams formulated with wood particle and kraft lignin as reactive fillers, without sacrificing the physical-mechanical and thermal properties of the material. The chemical structure, apparent density, compressive properties, water uptake, and thermal stability of the composites were investigated and compared with the pristine PU foam.

Materials and Methods

Materials

Poplar (*Populus tomentosa* Carr.) wood particles were supplied by Ningfeng Wood-Based Panels Co., Ltd. (Lianyungang, China) and sifted to pass 100 mesh. Industrial softwood kraft lignin (Indulin AT) powder, with the total content of Klason and acid soluble lignin of 93.5 percent and average particle size of 68 μm , was provided by MeadWestvaco (USA). Its weight average molar mass (M_w) was reported as 2,700 g/mol (Luo et al. 2018). The lignin, with its OH group content of 4.99 mmol/g (mmol of OH group per g dry lignin), was characterized by ^{31}P nuclear magnetic resonance (^{31}P NMR). A commercial polymeric diphenylmethane diisocyanate (pMDI; WANNATE CW20, 32 wt% NCO), with a viscosity of 150 to 250 mPa \times s at 25°C, was received from Wanhua Chemical Co., Ltd. (Yantai, China). WANOL R2438A, an amine-based polyether polyol with OH value of 385 to 415 mg (KOH)/g and viscosity of 9,000 to 17,000 mPa \times s at 25°C, was also obtained from Wanhua Chemical Co., Ltd. Glycerol was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The lignin powder, wood particles, and polyols were oven-dried at 105°C for 24 hours prior to use. Dibutyltin dilaurate and triethanolamine were purchased from Xiya Chemical Industry Co., Ltd (Shandong, China) and used as the catalysts. Polydimethyl siloxane was purchased from Fuchen Chemical Reagent Co., Ltd. (Tianjin, China) and used as surfactant. All the chemical reagents were of analytical grade and used as received. Deionised water was used as the chemical blowing agent, which could react with isocyanate, generating carbon dioxide.

Preparation of foams

Prior to preparing foam, the lignin powder was blended with WANOL R2438A and glycerol by rapidly stirring at 120°C for 2 hours to obtain the lignin/polyols dispersions. The lignin concentrations were set at 5 and 10 percent based on the mass of glycerol and WANOL R2438A. The glycerol concentration (5%) was kept constant, with respect to the mass of lignin/polyols dispersions. To ensure the completion of the reaction, the NCO/OH ratio of 1.1 was used. The weight of pMDI (W_{pMDI}) required was calculated using the following equation:

$$W_{\text{pMDI}} = \left[\sum (W_{\text{OH}} \times M_{\text{OH}}) + \left(W_{\text{H}_2\text{O}} \times \frac{2}{18} \right) \right] \times 1.1 \times \frac{42}{32\%} \quad (1)$$

where W_{OH} is the weight of WANOL R2438A, glycerol, lignin, and wood particle (g), respectively; M_{OH} is the respective number of OH groups contained in 1 g of WANOL R2438A, glycerol, lignin, and wood particle, respectively; and W_{H_2O} is the weight of water.

Three series of lignin-containing wood-polyurethane (W-PU) samples with addition of 0, 10, or 20 percent of wood particles (PUL, W_{10} -PUL and W_{20} -PUL series) were prepared, according to the formulations listed in Table 1. The corresponding PU samples containing 0, 5, or 10 percent lignin were designated as PUL₀, PUL₅, and PUL₁₀, respectively. First, the lignin/polyols dispersion, catalysts, surfactant, and water were weighed out in the required proportions into a 200-mL plastic cup and mechanically stirred at 300 revolutions/minute (rpm) for 30 seconds to obtain a homogeneous mixture. For W_{10} -PUL and W_{20} -PUL series, the wood particles were added and mixed for 30 seconds. Afterwards, predetermined pMDI was added and the resultant mixture was mechanically stirred at 1,000 rpm for 5 to 15 seconds at room temperature, quickly transferred into an open 1,000-mL plastic mold and allowed to rise freely owing to the self-generated heat. All the foam samples were left for 48 hours at ambient conditions for curing prior to further characterization.

Characterization of foams

The reactivity of foam formulations was measured in a cup foam test according to ASTM D7487-18 (ASTM International 2018) by recording the cream time, gel time, free-rise time, and tack-free time. Fourier-transform infrared (FTIR) spectra of the foam samples were recorded using a Nicolet IS10 FTIR Spectrometer (Thermo Fisher Scientific, Germany) in transmittance mode. The foam samples were ground in a mill and passed through a 100-mesh screen to obtain fine powder. Each spectrum was collected for the wavelength range of 4,000 to 400 cm^{-1} at a resolution of 4 cm^{-1} with 64 scans. Data processing was performed using Omnic v.9.2 software (Thermo Fisher Scientific).

The morphology of the foam cross-sections was observed perpendicular to the direction of foam rise using a VHX-6000 digital microscope (KEYENCE, Japan). The apparent density of foams was calculated as the ratio between the weight and geometric volume using the samples for compression test, with average values of six specimens per foam type reported.

The compressive properties of the foams were measured using an Instron 5582 universal testing machine (USA)

according to ASTM D1621-16 (ASTM International 2016). Specimens with a size of 50 by 50 by 25 mm^3 were tested in orientation perpendicular to the foam rise direction. The stress-strain curves were recorded at a crosshead speed of 2.5 mm/min. The load was applied until the foam was compressed to approximately 13 percent of its original thickness. The compressive strength was determined at 10 percent deformation or at the yield point if a yield point occurred before 10 percent deformation. Six specimens from two replicates were tested for each foam type and the results were averaged.

The water uptake of the foams was performed on cubic specimens (25 mm sides) with at least six replicates from two replicates. Specimens were dipped in de-ionized water for 24 hours at room temperature. The sample was taken out of water at specified time intervals and weighed after the surface water was wiped off. The water uptake of samples was reported as weight percentage gain.

Thermogravimetric analysis was carried out in nitrogen flow (40 mL/min) using a NETZSCH STA 449 F3 instrument. Approximately 10 mg of sample was analyzed at a rate of 10°C/min in the temperature range from 30°C to 750°C.

Results and Discussion

Reactivity of foam formulations

The characteristic times of foam formation were investigated using a standard cup test (Table 2). Apart from polyols, OH groups in lignin and wood were likely to react with the NCO groups of pMDI through the formation of urethane linkages during the foaming process (Fig. 1). Reactivity was decreased as the amount of lignin increased and the amount of polyols decreased in three foam series. On the other hand, reactivity was decreased as the amount of wood particle increased at the same lignin level. The slower kinetics (free-rise time and tack-free time) could be attributed to the increased viscosity of the mixture upon the addition of lignin and wood particles, or alternatively, to the increased proportion of phenolic OH groups with increasing amount of lignin added. The reactivity of phenolic OH groups in lignin was reportedly lower than that of aliphatic OH groups in the polyols (Hayati et al. 2018).

FTIR analysis

Figure 2 shows the FTIR spectra of the kraft lignin, PUL, W_{10} -PUL, and W_{20} -PUL foam series. In the spectrum of

Table 1.—Formulations and sample codes of polyurethane (PUL, with 0%, 5%, or 10% lignin) and wood-polyurethane (W_{10} -PUL and W_{20} -PUL, with addition of 10% or 20% wood particles) foam series.^a

Sample	Weight (g)							
	Lignin	Polyols	DBTDL	TEOA	PDMS	Water	Wood particle	pMDI
PUL ₀	0	100	1	0.5	2	1.5	—	119.8
PUL ₅	5	95	1	0.5	2	1.5	—	118.5
PUL ₁₀	10	90	1	0.5	2	1.5	—	116.7
W_{10} -PUL ₀	0	100	1	0.5	2	1.5	30	142.6
W_{10} -PUL ₅	5	95	1	0.5	2	1.5	30	141.1
W_{10} -PUL ₁₀	10	90	1	0.5	2	1.5	30	139.6
W_{20} -PUL ₀	0	100	1	0.5	2	1.5	60	165.5
W_{20} -PUL ₅	5	95	1	0.5	2	1.5	60	164.0
W_{20} -PUL ₁₀	10	90	1	0.5	2	1.5	60	162.4

^a DBTDL = dibutyltin dilaurate; TEOA = triethanolamine; PDMS = polydimethyl siloxane; pMDI = polymeric diphenylmethane diisocyanate.

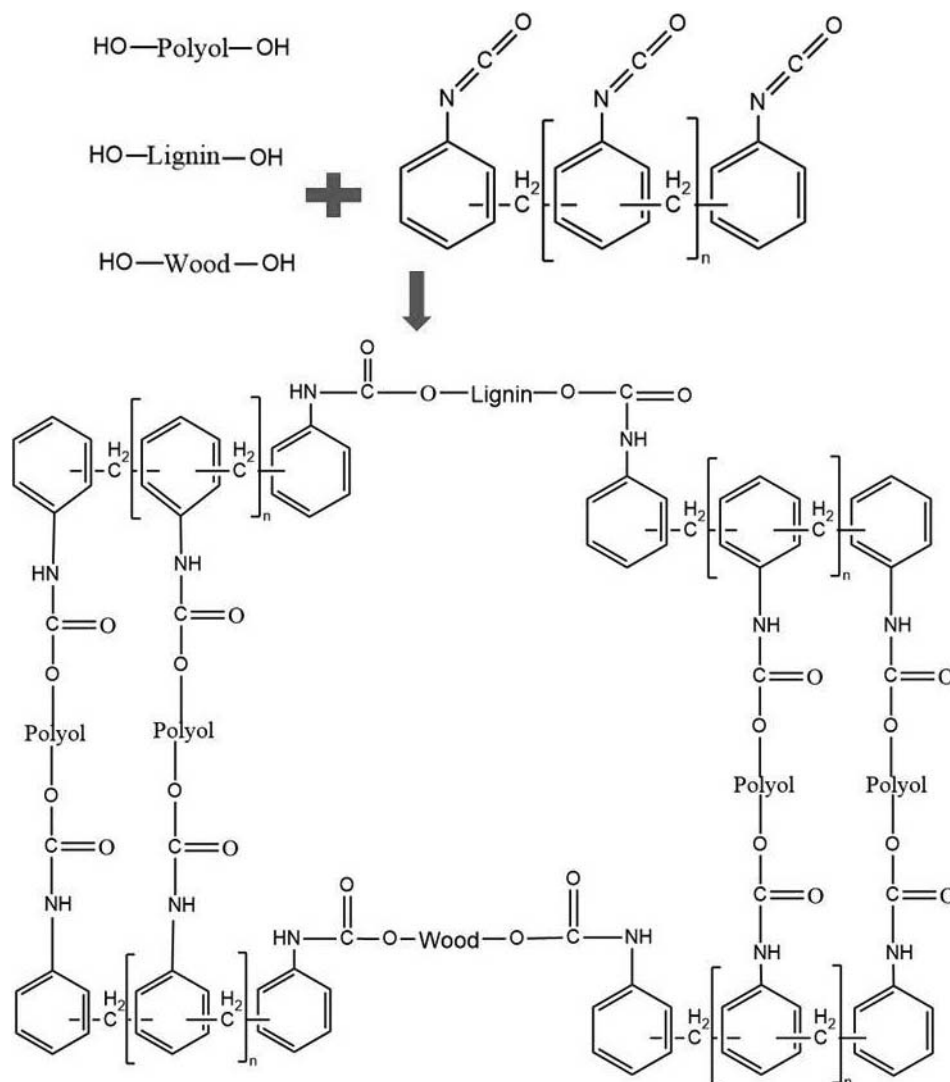


Figure 1.—Scheme of potential reactions during the foaming process.

softwood kraft lignin, the characteristic bands of guaiacyl units at $1,270$ and $1,032\text{ cm}^{-1}$ were present, while the bands of $1,330$ and $1,117\text{ cm}^{-1}$ related to syringyl units were absent. The characteristic urethane moieties of PU are confirmed by the presence of N–H stretching vibration ($3,200$ to $3,600\text{ cm}^{-1}$), C=O stretching vibration ($1,712$

Table 2.—Characteristic times of the foam formation.

Sample ^a	Cream time (s)	Gel time (s)	Free-rise time (s)	Tack-free time (s)
PUL ₀	11	22	50	55
PUL ₅	18	24	53	68
PUL ₁₀	33	41	71	90
W ₁₀ -PUL ₀	20	30	59	73
W ₁₀ -PUL ₅	72	98	214	277
W ₁₀ -PUL ₁₀	123	164	321	380
W ₂₀ -PUL ₀	66	79	148	183
W ₂₀ -PUL ₅	100	141	255	285
W ₂₀ -PUL ₁₀	135	175	341	437

^a Polyurethane (PUL, with 0%, 5%, or 10% lignin) and wood-polyurethane (W₁₀-PUL and W₂₀-PUL, with addition of 10% or 20% wood particles).

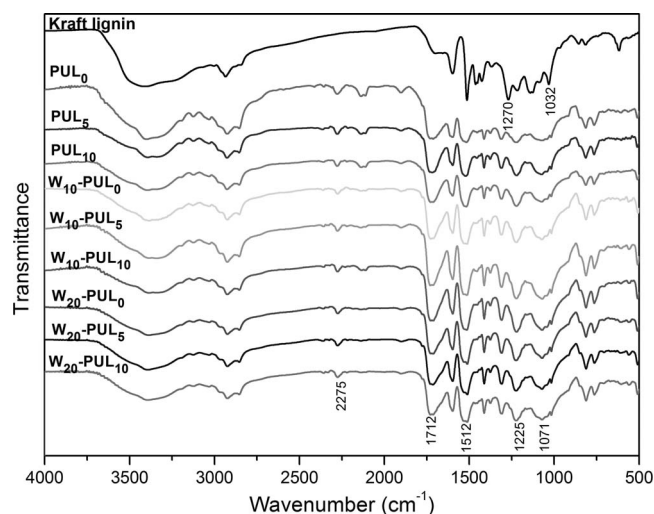


Figure 2.—Fourier-transform infrared spectra of kraft lignin, polyurethane (PUL), and wood-polyurethane (W₁₀-PUL and W₂₀-PUL, with addition of 10% or 20% wood particles) foam series.

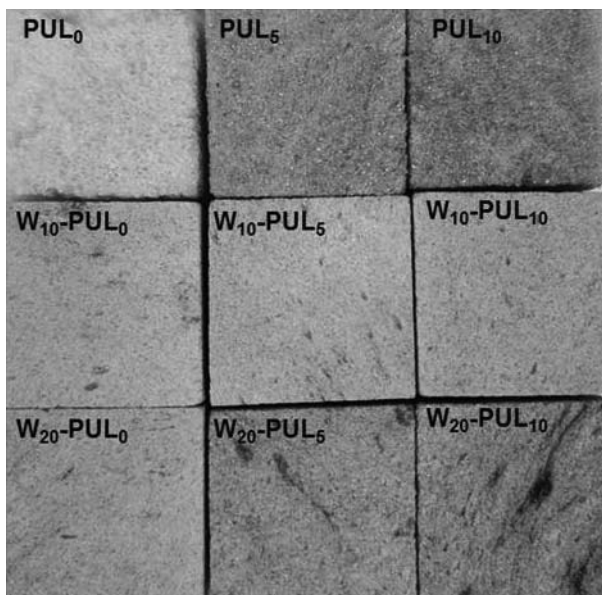


Figure 3.—Macro-scale images of PU, W_{10} -PU, and W_{20} -PU foam series with varying contents of lignin.

cm^{-1}), C–N stretching ($1,217\text{ cm}^{-1}$), and C–O stretching ($1,065\text{ cm}^{-1}$) in all foam samples (Delucis et al. 2018a, Kurańska et al. 2020). With an increase in the content of lignin, the peak of the C=O stretching vibration in PUL and W_{10} -PUL series of foams shifted from $1,713\text{ cm}^{-1}$ (hydrogen bonded C=O) to $1,727\text{ cm}^{-1}$ (free C=O) gradually, suggesting that incorporation of lignin disturbed the hydrogen bonding between NH and C=O (Luo et al. 2013). This feature indicated the interaction between lignin and pMDI. All the foam samples presented a small peak at $2,275\text{ cm}^{-1}$, which corresponded to residual NCO groups, due to molar excess of NCO groups to OH groups of approximately 10 percent. In addition, the high exotherm of

rigid foam systems can cause isocyanate trimerization (Alinejad et al. 2019), which could account for the low residual NCO content.

Morphology of foams

The macro-scale images for PUL, W_{10} -PUL, and W_{20} -PUL foam series with different amounts of lignin are illustrated in Figure 3. With incorporation of lignin, foam color became darker brown and the surface became rough. W_{20} -PUL₅ and W_{20} -PUL₁₀ samples exhibited agglomerates of lignin in their foam structures. The transmission optical micrographs of the foams cut perpendicular to the blowing direction are shown in Figure 4 and the corresponding average cell sizes are summarized in Table 3. The reference PUL₀ foam displayed regular closed-cell structure and smooth surface texture. With the addition of lignin and wood particles, the cellular shape became more heterogeneous and irregular along with extra formation of large cells, which was indicated by the increased relative standard deviation for average cell size (standard deviation divided by mean value). This alteration in cell morphology was attributed to the fact that the lignin and wood particle affected the process of cell nucleation in the preparation of foam (Zhu et al. 2018). The average cell size in W_{10} -PUL and W_{20} -PUL series was smaller than PUL series at the same lignin content. This is due to the fact that addition of wood particle made it difficult to effectively blend with pMDI, resulting in less expandable foams. In all three series, as the lignin content increased from 0 to 10 percent, the cell became more irregular and larger. Large cracked cells were present in W_{10} -PUL₁₀, W_{20} -PUL₅, and W_{20} -PUL₁₀, suggesting the combined use of lignin and wood particles at high contents was disadvantageous for the cell structure.

Apparent density

In foam composites, the density is an imperative parameter that affects the mechanical properties of foams (Thakur et al. 2014). The apparent density values of PUL,

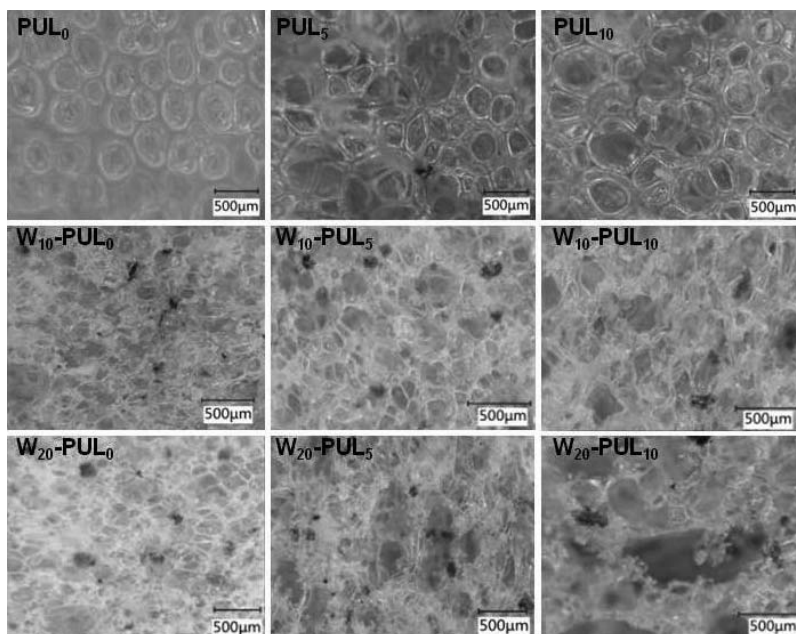


Figure 4.—Morphology of cross-sections of PU, W_{10} -PU, and W_{20} -PU foam series containing varying contents of lignin.

Table 3.—Average cell size, apparent density, and compressive properties of polyurethane (PUL, with 0%, 5%, or 10% lignin) and wood–polyurethane (W_{10} -PUL and W_{20} -PUL, with addition of 10% or 20% wood particles) foam series containing varying contents of lignin.

Sample	Average cell size (μm)	Apparent density (kg/m^3)	Compressive strength (kPa)	Compressive modulus (MPa)
PUL ₀	324 ± 27	160 ± 11	362 ± 30	11.2 ± 2.6
PUL ₅	327 ± 34	109 ± 5	633 ± 50	11.1 ± 1.6
PUL ₁₀	377 ± 49	91 ± 3	593 ± 18	8.5 ± 1.1
W_{10} -PUL ₀	199 ± 38	105 ± 14	270 ± 34	5.4 ± 0.5
W_{10} -PUL ₅	217 ± 46	81 ± 9	251 ± 16	5.4 ± 0.6
W_{10} -PUL ₁₀	239 ± 51	64 ± 4	199 ± 8	4.5 ± 0.4
W_{20} -PUL ₀	148 ± 24	88 ± 13	103 ± 12	2.2 ± 0.3
W_{20} -PUL ₅	300 ± 51	79 ± 17	107 ± 5	2.4 ± 0.4
W_{20} -PUL ₁₀	274 ± 79	77 ± 8	119 ± 9	2.7 ± 0.5

W_{10} -PUL, and W_{20} -PUL foam series are summarized in Table 3. In comparison with the control PUL₀, all other samples incorporating wood particles had decreased density. In all three series, the density of the resultant foam decreased with increasing lignin content from 0 to 10 percent. For W_{10} -PUL series, the density of control W_{10} -PUL₀ foam was approximately 105 g/cm³, and decreased by 39 percent when the polyether polyol was replaced by 10 percent with lignin. This trend was in agreement with previous studies by Pan and Saddler (2013) and Xue et al. (2014), where a reduction in the density of PU foam was reported with increasing lignin content. These studies attributed the density reduction to alteration of cellular structure of the foam. Accordingly, introducing lignin resulted in the cellular structure more irregular and the cell size increased, as shown above, which reduced the mass per unit volume.

Compressive properties of foams

The compressive strength and modulus of PUL, W_{10} -PUL, and W_{20} -PUL foam series are reported in Table 3. Density and cellular structure are the two most important parameters affecting the mechanical properties of the PU foams (Luo et al. 2013). The compressive strength and modulus decreased with wood particle increasing from 0 to 20 percent. In W_{10} -PUL series, both compressive strength and modulus decreased with the reduced density. However, in PUL series, replacing polyol with 5 percent lignin increased the compressive strength of the foam by about 74 percent. Further increasing lignin content from 5 to 10 percent resulted in slight reduction of the compressive strength. In W_{20} -PUL series, increase of lignin content did not result in notable changes in compressive properties.

To further clarify the effect of introducing lignin and wood particles, the normalized compressive strength and modulus (i.e., dividing the compressive strength and modulus of each specimen by its respective density) were calculated in a similar way to the previous studies (Luo et al. 2013, Hayati et al. 2018; Fig. 5). Introducing wood particle decreased the specific compressive properties of the resultant foams. This is attributed to the addition of wood particle causing deficiency in the foam cellular structure and thus weakening the stability and strength of the structure (Pan and Saddler 2013). In all three series, both normalized compressive strength and modulus exhibited a statistically significant increase when lignin content increased from 0 to 5 percent, suggesting that substituting partial polyol with lignin enhanced the rigidity of foam. Further increasing

lignin content from 5 to 10 percent resulted in a slight decrease in normalized compressive properties except for normalized strength of PUL series, which slightly increased following lignin incorporation at 10 percent, whereas the difference in normalized compressive values between 5 percent and 10 percent lignin content for the three series was insignificant. In general, PUL₅ sample exhibited the optimal compressive properties, with normalized compressive strength of 5.9 MPa/(g·cm⁻³) and normalized compressive modulus of 97 Mpa/(g·cm⁻³).

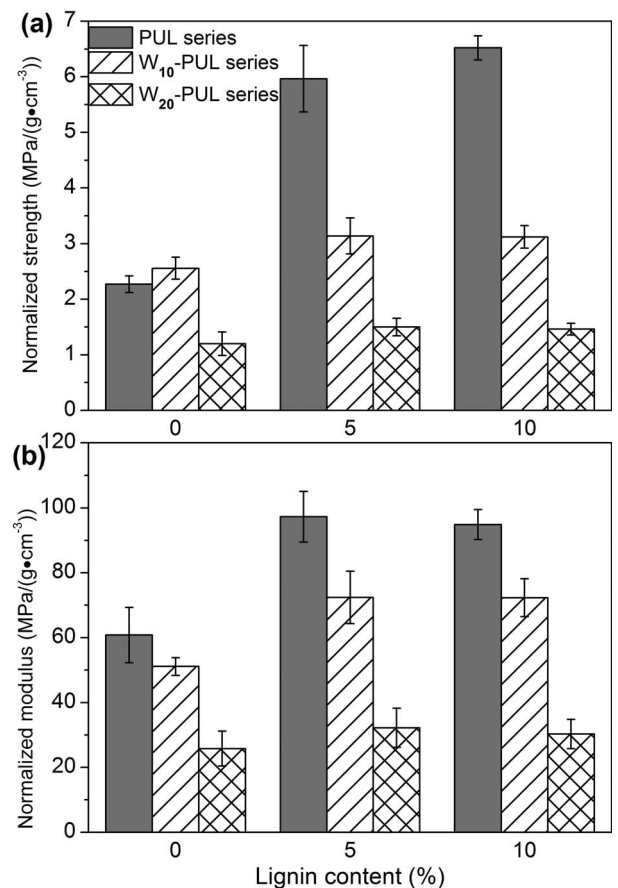


Figure 5.—(a) Normalized compressive strength and (b) normalized compressive modulus of PU, W_{10} -PU, and W_{20} -PU foam series containing varying contents of lignin.

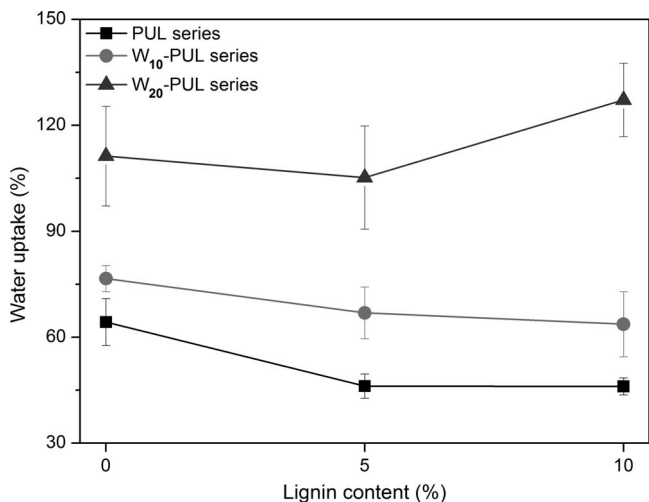


Figure 6.—Water uptake of PUL, W₁₀-PUL, and W₂₀-PUL foam series containing varying amounts of lignin.

Water uptake of foams

Water uptake values of foams after 24 hours in water immersion at room temperature are shown in Figure 6. The control PUL foam exhibited water uptake of 64 percent. Increasing the wood content increased water uptake of the foams. This phenomenon was due to the irregular cellular structure of W-PU samples with lots of voids that held more water inside. On the other hand, when polyol was replaced with lignin at 5 percent, the water uptake for all three foam series was reduced. The water uptake of PUL₅, W₁₀-PUL₅, and W₂₀-PUL₅ was reduced by 28, 13, and 5 percent compared with PUL₀, W₁₀-PUL₀, and W₂₀-PUL₀, respectively.

Thermal stability of foams

Thermogravimetric analysis was conducted to evaluate the influence of lignin and wood particles on the thermal stability of foams. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the foams are shown in Figure 7. Lignin exhibited a broad degradation profile, with the maximum rate of decomposition at 375°C. All the foam samples were thermally stable up to 200°C. After that, an intense thermal degradation quickly occurred in the range of 200°C to 400°C, dominated by the degradation of the polyol component, urethane bond, and wood particle (Xue et al. 2014, Zhu et al. 2018). The second decomposition step at around 400°C to 500°C was mainly attributed to the decomposition of other remaining structures after the initial degradation step, such as diisocyanate and lignin aromatic rings (Tavares et al. 2016). Above 600°C, mass loss for foams was considerably smaller. In general, all foam samples exhibited similar thermal degradation behavior and the incorporation of lignin and wood particles did not significantly affect the pattern.

The thermogravimetric parameters, including initial thermal decomposition temperature (T_0 , temperature for 5% weight loss), maximum decomposition temperature (T_{max}), and char residue at 700°C are summarized in Table 4. Lignin incorporation slightly increased the T_0 for three foam series. The T_{max} increased after the introduction of 5 percent lignin; however, after further increasing the lignin content from 5 to 10 percent, the T_{max} slightly decreased. Furthermore, all three foam series demonstrated a marked increase of char at 700°C with respect to the pristine PUL₀. As lignin content increased from 0 to 10 percent, the char residue increased by 18, 67, and 34 percent for PUL, W₁₀-PUL, and W₂₀-PUL series, respectively. These results indicated that thermal stability of the foams was enhanced by using lignin as bio-polyol.

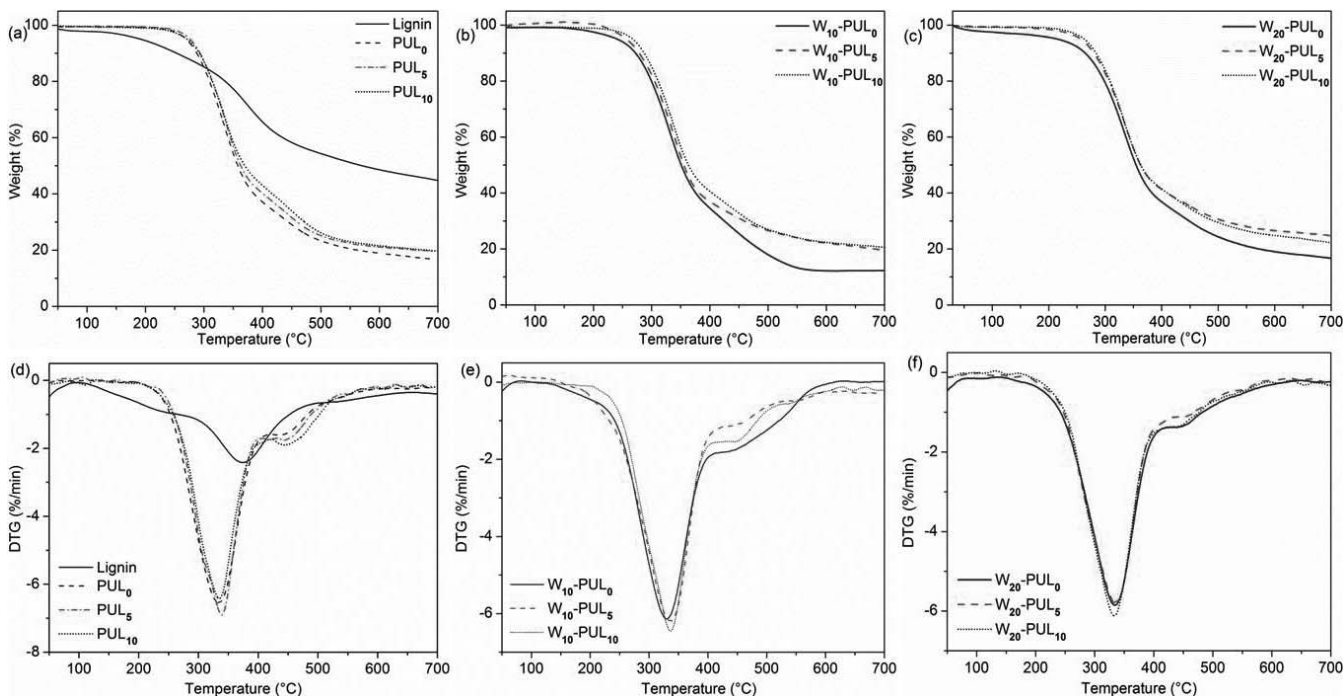


Figure 7.—(a, b, c) Thermogravimetric analysis and (d, e, f) derivative thermogravimetric (DTG) curves of the PUL, W₁₀-PUL, and W₂₀-PUL foam series with varying lignin contents.

Table 4.—Thermogravimetric parameters of polyurethane (PUL, with 0%, 5%, or 10% lignin) and wood–polyurethane (W₁₀-PUL and W₂₀-PUL, with addition of 10% or 20% wood particles) foam series samples containing varying contents of lignin.

Sample	T ₀ (°C)	T _{max} (°C)	Char residue (%)
Lignin	183.2	374.6	44.8
PUL ₀	268.0	334.4	16.6
PUL ₅	273.9	339.1	19.5
PUL ₁₀	267.7	333.9	19.6
W ₁₀ -PUL ₀	243.1	329.6	12.3
W ₁₀ -PUL ₅	254.0	337.3	19.5
W ₁₀ -PUL ₁₀	264.8	336.6	20.6
W ₂₀ -PUL ₀	203.7	333.7	16.6
W ₂₀ -PUL ₅	253.2	334.7	24.7
W ₂₀ -PUL ₁₀	259.6	333.2	22.2

Conclusions

This article reports a simple and efficient strategy to prepare bio-based PU composite foam by the incorporation of kraft lignin and wood particle as reactive reinforcing fillers. With the introduction of these fillers, the apparent density of foam was decreased and the cellular shape became more heterogeneous and irregular along with formation of large cells. Compared with the neat PU foam, incorporation of 10 and 20 percent wood particle negatively affected compressive strength and water resistance, whereas replacing commercial polyol with 5 percent lignin improved these properties. However, further increasing the lignin content from 5 to 10 percent did not result in notable changes. Thermal stability of W–PU foams was improved by the incorporation of lignin. Wood particle can be used conditionally as a filler of PU foam, only when a certain amount of lignin is used at the same time. The results of this study help to promote the utilization of abundant natural biopolymers, especially industrial lignin, in the synthesis of PU composite foam.

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Literature Cited

Alinejad, M., C. Henry, S. Nikafshar, A. Gondaliya, S. Bagheri, N. Chen, S. K. Singh, D. B. Hodge, and M. Nejad. 2019. Lignin-based polyurethanes: Opportunities for bio-based foams, elastomers, coatings and adhesives. *Polymers* 11(7):1202.

ASTM International. 2016. Standard test method for compressive properties of rigid cellular plastics. ASTM D1621-16. ASTM International, West Conshohocken, Pennsylvania.

ASTM International. 2018. Standard practice for polyurethane raw materials: Polyurethane foam cup test. ASTM D7487-18. ASTM International, West Conshohocken, Pennsylvania.

Chen, Y. C. and W. Tai. 2018. Castor oil-based polyurethane resin for low-density composites with bamboo charcoal. *Polymers* 10(10):1100.

De Luca Bossa, F., C. Santillo, L. Verdolotti, P. Campaner, A. Minigher, L. Boggioni, S. Losio, F. Coccia, S. Iannace, and G. C. Lama. 2020. Greener nanocomposite polyurethane foam based on sustainable polyol and natural fillers: Investigation of chemico-physical and mechanical properties. *Materials* 13(1):211.

Delucis, R. d. A., W. L. E. Magalhães, C. L. Petzhold, and S. C. Amico. 2018a. Forest-based resources as fillers in biobased polyurethane foams. *J. Appl. Polym. Sci.* 135(3):45684.

Delucis, R. d. A., W. L. E. Magalhães, C. L. Petzhold, and S. C. Amico. 2018b. Thermal and combustion features of rigid polyurethane biofoams filled with four forest-based wastes. *Polym. Compos.* 39(S3):E1770–E1777.

Gu, R., M. M. Sain, and S. K. Konar. 2013. A feasibility study of polyurethane composite foam with added hardwood pulp. *Ind. Crops Prod.* 42:273–279.

Hayati, A. N., D. A. C. Evans, B. Laycock, D. J. Martin, and P. K. Annamalai. 2018. A simple methodology for improving the performance and sustainability of rigid polyurethane foam by incorporating industrial lignin. *Ind. Crops Prod.* 117:149–158.

Kai, D., M. J. Tan, P. L. Chee, Y. K. Chua, Y. L. Yap, and X. J. Loh. 2016. Towards lignin-based functional materials in a sustainable world. *Green Chem.* 18(5):1175–1200.

Kairyte, A., M. Kirpluks, A. Ivdre, U. Cabulis, S. Vėjelis, and G. Balčiūnas. 2018. Paper waste sludge enhanced eco-efficient polyurethane foam composites: Physical–mechanical properties and microstructure. *Polym. Compos.* 39(6):1852–1860.

Kurańska, M., J. A. Pinto, K. Salach, M. F. Barreiro, and A. Prociak. 2020. Synthesis of thermal insulating polyurethane foams from lignin and rapeseed-based polyols: A comparative study. *Ind. Crops Prod.* 143:111882.

Li, Y. and A. J. Ragauskas. 2012. Kraft lignin-based rigid polyurethane foam. *J. Wood Chem. Technol.* 32(3):210–224.

Luo, S., J. Cao, and A. G. McDonald. 2018. Cross-linking of technical lignin via esterification and thermally initiated free radical reaction. *Ind. Crops Prod.* 121:169–179.

Luo, X., A. Mohanty, and M. Misra. 2013. Lignin as a reactive reinforcing filler for water-blown rigid biofoam composites from soy oil-based polyurethane. *Ind. Crops Prod.* 47:13–19.

Mahmood, N., Z. Yuan, J. Schmidt, and C. Xu. 2016. Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review. *Renew. Sustain. Energ. Rev.* 60:317–329.

Matsushita, Y. 2015. Conversion of technical lignins to functional materials with retained polymeric properties. *J. Wood Sci.* 61(3):230–250.

Mosiewicki, M. A., G. A. Dell’Arciprete, M. I. Aranguren, and N. E. Marcovich. 2009. Polyurethane foams obtained from castor oil-based polyol and filled with wood flour. *J. Compos. Mater.* 43(25):3057–3072.

Pan, X. and J. N. Saddler. 2013. Effect of replacing polyol by organosolv and kraft lignin on the property and structure of rigid polyurethane foam. *Biotechnol. Biofuels* 6(1):12.

Rácz, I., E. Andersen, M. I. Aranguren, and N. E. Marcovich. 2009. Wood flour–recycled polyol based polyurethane lightweight composites. *J. Compos. Mater.* 43(24):2871–2884.

Silva, M. C., J. A. Takahashi, D. Chaussy, M. N. Belgacem, and G. G. Silva. 2010. Composites of rigid polyurethane foam and cellulose fiber residue. *J. Appl. Polym. Sci.* 117(6):3665–3672.

Tavares, L. B., C. V. Boas, G. R. Schleder, A. M. Nacas, D. S. Rosa, and D. J. Santos. 2016. Bio-based polyurethane prepared from Kraft lignin and modified castor oil. *eXPRESS Polym. Lett.* 10(11):927–940.

Thakur, V. K., M. K. Thakur, P. Raghavan, and M. R. Kessler. 2014. Progress in green polymer composites from lignin for multifunctional applications: A review. *ACS Sustain. Chem. Eng.* 2(5):1072–1092.

Upton, B. M. and A. M. Kasko. 2016. Strategies for the conversion of lignin to high-value polymeric materials: Review and perspective. *Chem. Rev.* 116(4):2275–2306.

Xue, B.-L., J.-L. Wen, and R.-C. Sun. 2014. Lignin-based rigid polyurethane foam reinforced with pulp fiber: Synthesis and characterization. *ACS Sustain. Chem. Eng.* 2(6):1474–1480.

Yuan, J. and S. Q. Shi. 2009. Effect of the addition of wood flours on the properties of rigid polyurethane foam. *J. Appl. Polym. Sci.* 113(5):2902–2909.

Zhu, S., K. Chen, J. Xu, J. Li, and L. Mo. 2018. Bio-based polyurethane foam preparation employing lignin from corn stalk enzymatic hydrolysis residues. *RSC Adv.* 8(28):15754–15761.