The preparation and properties of polyurethane foams reinforced with bamboo fiber sources in China

Chongpeng Qiu\textsuperscript{1,}\textsuperscript{2}, Feng Li\textsuperscript{3,}\textsuperscript{4}, Liang Wang\textsuperscript{1}, Xuelun Zhang\textsuperscript{1}, You Zhang\textsuperscript{1}, Qi Tang\textsuperscript{1}, Xiyu Zhao\textsuperscript{1}, Cornelis F De Hoop\textsuperscript{5}, Xiaopeng Peng\textsuperscript{2,}\textsuperscript{6}, Xiaojuan Yu\textsuperscript{1}\textsuperscript{*}, and Xingyan Huang\textsuperscript{1,}\textsuperscript{*}

\textsuperscript{1} College of Forestry, Sichuan Agricultural University, Chengdu, Sichuan 611130, People\textapos;s Republic of China
\textsuperscript{2} Landscape Architecture school, Chengdu Agricultural College, Chengdu, Sichuan 611130, People\textapos;s Republic of China
\textsuperscript{3} School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, United States of America
\textsuperscript{4} State Key Laboratory of Tree Genetics and Breeding, Key Laboratory of Tree Breeding and Cultivation of the National Forestry and Grassland Administration, Research Institute of Forestry, Chinese Academy of Forestry, Beijing 100091, People\textapos;s Republic of China
\textsuperscript{5} Institute of Biomass Chemistry and Technology, Beijing Forestry University, Beijing 100083, People\textapos;s Republic of China
\textsuperscript{6} Chongpeng Qiu and Feng Li are co-first authors.

E-mail: hxy@sicau.edu.cn

Keywords: polyurethane foam, bamboo fiber, \(\alpha\)-cellulose, nanocellulose

Abstract

Polyurethane (PU) foams reinforced with bamboo fiber sources in China, i.e., bamboo fiber, bamboo \(\alpha\)-cellulose fiber, and bamboo nanocellulose fiber, were prepared and their physico-mechanical properties were analyzed in this work. The bamboo fiber sources and PU foams were characterized by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscope (SEM), Thermal gravimetric analysis (TGA) and universal compression testing. The results indicated that the hydroxyl groups on the fiber surfaces were enhanced by removing non-celluloses in the preparation of \(\alpha\)-cellulose and nanocellulose. With the addition of small particle size \(\alpha\)-cellulose and nanocellulose, the cell sizes of PU foams were reduced due to more nucleating agents being introduced. The FTIR spectra confirmed that the bamboo fiber sources were involved in the foaming reaction. The PU foams with bamboo fiber sources had a higher thermal stability than neat foam, and they were satisfactory enough to be used as insulation. PU foams reinforced with 5% bamboo fiber, 3% \(\alpha\)-cellulose fiber and 3% nanocellulose fiber had better physico-mechanical performance than other foams. The reinforcement performance of 3% bamboo \(\alpha\)-cellulose fiber on PU foam was comparable with that of high-cost nanocellulose. Accordingly, bamboo \(\alpha\)-cellulose fiber was demonstrated to be a promising candidate to reinforce PU foam, which could be used in the reinforcement of foam insulation.

1. Introduction

Polyurethane (PU) foams are light weight porous materials that have promising performance characteristics of low density, low thermal conductivity, and high mechanical properties [1]. They have been widely used in packaging, cushion, automotive, furniture, and structural materials [2]. Currently, the PU foam industry is still highly dependent on petro-based chemicals with low natural degradation properties. Therefore, there has been increasing attention given to the use of biodegradable PU foams reinforced with natural fibers with a view towards economic incentives and environmental concerns [3, 4]. It has been demonstrated that the presence of natural fiber in PU foam does enhance their physico-mechanical performance [5]. Among many natural fibers, bamboo fibers have drawn particular attention due to their low-density, high stiffness, high strength and rapid growth rate, which makes them abundantly available [6, 7].

Bamboo is one of the fastest growing plants on Earth, with a peak growth rate up to 100 cm d\(^{-1}\), and it reaches maturity within 3 years [8]. The main chemical component of bamboo fiber is cellulose (45\%–50\%), and other noncellulose components are lignin, hemicellulose, pectin, tannins, etc [9]. After removing non-celluloses, pure cellulose fiber, for example, \(\alpha\)-cellulose, is obtained, and further mechanical ultrasonic
treatment can separate cellulose fiber into nanocellulose [10]. Compared with natural cellulose, nanocellulose has many extraordinary advantages, such as high strength and transparency, high surface area, etc [11]. It has been demonstrated in our previous work that the addition of nanocellulose enhanced the physico-mechanical performance of PU foams [12]. Bamboo fibers have abundant hydroxyl groups which can add the hydroxyl groups at the unsaturated sites in the reaction between polyols and isocyanate [13, 14]. With the chemical purification and ultrasonic process, the hydroxyl groups on fiber surfaces will be exposed, and more functional hydroxyl groups will be available. Apart from this, the fiber particles will be altered to smaller ones, which will be beneficial to provide higher surface area to contact and react with isocyanate, whereas, small particle size will increase the possibility of agglomeration that has a negative effect on foaming reaction [15]. Generally, the available hydroxyl groups on fiber surface and the fiber particle size will affect the physico-mechanical performance of the resulting PU foam.

It’s clear that bamboo fiber and nanocellulose fiber could enhance the PU foam performance. However, the untreated bamboo fiber has a large particle size and a limited number of surface hydroxyl groups. Therefore, the untreated bamboo fiber has limited participation in the polyurethane foaming reaction. In addition, the preparation process of nanocellulose is complicated and the preparation cost is relative high. Therefore, it is necessary to increase the number of surface hydroxyl groups on the fiber while reducing preparation cost. The bamboo α-cellulose is acquired from bamboo fiber via removing non-celluloses. The size of bamboo α-cellulose fiber is smaller than untreated particles, and its surface hydroxyl groups are exposed more. The α-cellulose fiber preparation process is easier than nanocellulose. To our knowledge, there is no study on the difference effect of bamboo fiber sources, i.e., bamboo fiber, bamboo α-cellulose fiber and bamboo nanocellulose fiber on the physico-mechanical properties of PU foams.

China is endowed with rich bamboo resources, with bamboo forest areas totaling $6.4 \times 10^7$ hectares, of which 73% is moso bamboo [16]. In this study, the bamboo species *Phyllostachys heterocycla cv pubescens*, which is abundantly in Southwest China and poses excellent mechanical properties, was used. The objective, in this work, is to produce polyurethane foams reinforced with bamboo fiber sources. The novelty of this study is to apply bamboo α-cellulose fiber to reinforce PU foam in order to reduce the preparation cost of nanocellulose. The preparation process of PU foams is illustrated in figure 1.

2. Experimental

2.1. Materials

The bamboo collected in Sichuan Province, China, was air dried, ground into 40–60 mesh, and oven dried until the samples were a constant weight.

Chemicals, including toluene, ethanol, glacial acetic acid, sodium chlorite, sulfuric acid ($\text{H}_2\text{SO}_4$, 98 wt%), polyethylene glycol 400, dibutyltindilaurate, dimethicone and sodium hydroxide were purchased from Kelon Chemical (Chengdu, Sichuan, China). Polyether polyl (330 N) was supported by Dongda Wenlong Chemical
Shandong, China). Silicone foam stabilizer was purchased from Hongming Chemical (Jining, Shandong, China) and high resilience opening agent was purchased from Lanxin Chemical (Shanghai, China). Isocyanate was purchased from Tairong Chemical (Guangzhou, Guangdong, China). All chemicals were used without further purification.

2.2. Preparation of bamboo α-cellulose and nanocellulose

The preparation of α-cellulose was conducted using a standard method of ASTM D 1103–60 (1971) [17].

The isolation of bamboo nanocellulose was followed as the method mentioned by Wei et al 2019 [14]. Bamboo fibers were ground into 200–400 mesh by using ultrafine pulverizer (Chengdu, Sichuan, China). Acid hydrolysis of micro tiny cellulose (fiber length between 0.0374 mm and 0.0750 mm) was carried out to obtain nanocellulose. 80 mL of the micro tiny cellulose water suspension (22% wt) and 98 g of sulfuric acid (98% wt) were mixed in a flask by mechanical agitation at a constant temperature below 30 °C. Then, the solution was heated to 45 °C for 2 h. After the solution cooled down in a refrigerator for 12 h, the solution was centrifuged at 3500 rpm (5 min). The cellulose sedimentation was dispersed by vigorous stirring then followed by ultrasonic treatment (FS-1500, Shanghai Bioanalysis Ultrasonic Instrument Co., Ltd, Shanghai, China) for 30 min. After ultrasonic treatment, the solution was centrifuged at 5000 rpm and freeze drying (Freeze dryer SCIENTZ-10N, Xinzhi Biological Technology Co., Ltd, Ningbo, Zhejiang, China) to obtain nanocellulose.

2.3. Preparation of PU foams

PU foams were prepared by using one-step method. A typical mixture of 6 g polyol (polyethylene glycol 400), 3 g polyether polyol (330 N), catalyst (dibutyltindilaurate, 0.15 g), surfactant (dimethicone, 0.15 g), foam stabilizer (Silicone foam stabilizer, 0.15 g), and blowing agent (water, 0.10 g) was premixed with a mechanical stirrer for 40 s. Next, 10 g PMDI was added into the premixed liquid and 0, 1, 3, 5, 7% (wt%) bamboo powder, bamboo α-cellulose, and bamboo nanocellulose (calculated according to the weight of polyol) stirred with a high-speed agitator at the speed of 1000 rpm. The foams expanded freely within limit of cylinder cups (about 350 mL capacity) and cooled down overnight before testing. The PU foams with 0, 1, 3, 5, 7% (wt%) bamboo fiber, bamboo α-cellulose fiber, and bamboo nanocellulose fiber were labeled as PU0, PUB1, PUB3, PUB5, PUB7, PUα1, PUα3, PUα5, PUα7, PUN1, PUN3, PUN5, and PUN7. Each formulation was made in three replicates.

2.4. Characterization of biomass fibers

The FTIR analysis was performed on a Nicolet IS10 spectrometer (Thermo Fisher Scientific, MA, USA). A small quantity of sample was covered flatwise on the detection window. Each biomass fiber was analyzed in the range of resolution from 400 cm−1 to 4000 cm−1 with a spectral resolution of 4 cm−1, and a total of 32 scans were collected.

Fiber length of biomass fibers were analyzed by Stereo microscope. The fiber length was measured by an Image-pro plus 6.0.

2.5. Characterization of PU foams

Cell morphology of PU foams were analyzed by scanning electron microscopy (SEM, JSM-6110 LV, Tokyo, Japan). Prior to analysis, the samples were gold coated. Images of cross-sections of PU foams were obtained. The average cell diameter was calculated from 50 measurements.

The FTIR analysis of PU foams was performed on a Nicolet IS10 spectrometer (ThermoFisher Scientific, MA, USA).

The densities of PU foams were determined by dividing the weight of the specimens (30 × 30 × 30 mm3) by the calculated volume, according to ASTM D 1622–08. The porosity of PU foams were calculated in SEM images using Image I software.

Thermal conductivity of PU foams was determined by using a thermal conductivity tester TC3000E (Xiaxi Electronic Technology, Xi’an, Shandong, China). The original PU foam samples, in cylindrical cups, without further processing, were used to determine thermal conductivity. A 10 min read time was performed to minimize the contact resistance errors. Ten replicates were conducted for each group.

A micro electronics universal science experiment machine RGM4100 (Chengdu, Sichuan, China) was used to measure the compressive properties of the foams, according to the ASTM D 695. Samples were placed between the two parallel plates and compressed at 10 mm min−1. The Young’s modulus was calculated by the slope of tangent of linear portion in the stress-strain profile in accordance to the method described in previous reports [12]. The compressive stress was taken from the stress-strain curves at the deformation of 10%. Ten replicates were measured for each group.

Thermogravimetric and differential thermogravimetric (TG/DTG) analysis of PU foams were conducted with NETZSCH STA 449 F5/F3 Jupiter (NETZSCH–Gerätebau GmbH, Selb, Germany) to simultaneously
obtain thermogravimetric data. Each sample (approximately 5 mg) was conducted at 30 °C to 800 °C with a constant heating rate of 10 °C min⁻¹ under a flow of 40 ml min⁻¹ of nitrogen atmosphere.

3. Results and discussion

3.1. FTIR of bamboo fiber sources

FTIR spectra of bamboo fiber, bamboo α-cellulose, and bamboo nanocellulose are shown in figure 1. The broad absorption band around 3690 cm⁻¹ corresponding to the −OH stretching vibration [18], suggesting that all bamboo fiber sources have numerous hydroxyl groups. The band at 1735 cm⁻¹ was attributed to acetyl and uronic ester groups in hemicellulose, which was absent from α-cellulose and nanocellulose, suggesting that hemicellulose was successfully removed by the alkali and bleaching treatments [12]. The absorption peaks at 1456 cm⁻¹ and 1230 cm⁻¹ corresponding to C−H deformation combined with aromatic ring vibration and the methoxyl groups in lignin [19]. It was absent from α-cellulose and nanocellulose after chemical treatments (figure 2), which indicated that lignin in fibers was removed successfully. The band at 1300 cm⁻¹ was assigned to O−H plane bending in cellulose [20], with the removal of hemicellulose and lignin, its intensity was gradually enhanced in α-cellulose and nanocellulose. Moreover, the enhancement of hydroxyl groups at 3690 cm⁻¹ was ascribed to the removal of non-celluloses as well [18]. Consequently, FTIR spectra of bamboo fiber sources evidenced that the purification process, i.e., removing non-celluloses, was successfully conducted by alkali and bleaching treatments. The removal of non-celluloses could breakdown bamboo cell walls, resulting in shorter α-cellulose fibers (reduced from 2256 μm to 1320 μm). Further ultrasonic processing provided a strong shear force to split fibers into shorter nanocellulose (0.125 μm).

3.2. Morphology of PU foams

The SEM images of PU foams with or without bamboo fiber sources are shown in figure 3. All PU foams had well-defined and partially opened polygonal cells. The porosity of PU0.5 was higher than others, indicating that α-cellulose fiber could help to increase open cell area. The cell sizes of PU foams with bamboo fiber sources were irregular, indicating that the presence of bamboo fiber, α-cellulose fiber and nanocellulose fiber interrupted the formation of cells in the composite foams. It was observed that the cell diameters increased slightly from 821.3 μm to 1101.5 μm, as bamboo fiber was involved in the PU system, while it decreased when bamboo α-cellulose and nanocellulose were added in PU0.5 (444.1 μm) and PUN3 (445.9 μm), respectively. This was because bamboo fiber was too large to be a good nucleating agent that increases the total numbers of nucleated cells and decreases the cell sizes, while the small particle size of α-cellulose and nanocellulose had a strong nucleation effect, resulting in more numerous and smaller foam cells [21]. Moreover, the foam reinforced with α-cellulose and nanocellulose had more regular, homogeneous, dense and less distorted cell structure than PU0 and PUB, which helped increase the foam density [22–24]. This could be ascribed to the hydroxyl groups on α-cellulose and nanocellulose, which helped enhance cell structure and cell wall strength [25–27]. The high compatibility of nanocellulose fiber with the polyurethane matrix could retard the film rupturing process during film thinning.
and thus a relatively thick film could lead to a low possibility of open pore formation in the polyurethane foams. Therefore, the high surface area of nanocellulose in the polyurethane foams generated a higher number of closed cells than other formulations [28].

It can be seen from figure 3(b) that bamboo fibers were unevenly distributed in the cell walls. This result was in line with the finding reported by Chen et al [5]. It was revealed from figure 3(c) that the bamboo α-cellulose could cross the cell wall, resulting in a crack. It also could be embraced in cell walls, increasing cell wall strength. As for bamboo nanocellulose in PU foam system, it could be wrapped in cell walls and reacted with isocyanate as a hydroxyl provider [12, 29]; it also could become agglomerates and attach to the PU cell wall structure (figure 3(d)).

3.3. FTIR of PU foams

FTIR spectra of PU0, PUB3, PUα3, and PUN3 are illustrated in figure 4 and a possible chemical structure of bamboo sources reinforced PU foam is shown in figure 5. The N−H groups at 3330 cm⁻¹ corresponds to the hydrogen bonded urethane link, which indicates that isocyanate groups reacted with the −OH groups to form the −NH−COO− [30]. The absorbance at 3330 cm⁻¹ shifted to a lower peak region at 3290 cm⁻¹ as its intensity increased, which was ascribed mainly to the formation of the hydrogen bonds between hydroxyl groups on bamboo fiber sources and N−H group of PU foam [31]. It had been demonstrated in our previous works that the hydroxyl groups in biomass could be involved in the foaming reaction to build cell wall structure [12]. Moreover, the formation of the urethane linkage can be confirmed by the appearance of the signals 1715 cm⁻¹ and 1540 cm⁻¹, corresponding to C=O and C−N stretching vibration of urethane linkages, respectively [18]. No obvious absorption peak of NCO groups at 2280 cm⁻¹ were observed in FTIR spectra, indicating that the condensation polymerization between NCO groups and OH groups had been completed. The absorption peaks at 1520 cm⁻¹ and 1220 cm⁻¹ indicated the presence of isocyanurate, which was formed by the undesired reaction between isocyanate and urethane groups [25]. The absorption peak at 1702 cm⁻¹ in the carbonyl region was a response to the C−O stretching from ketone, aldehyde, and ester groups [32]. All PU foam with bamboo fiber sources had the absorption peaks at 1410 cm⁻¹, 1310 cm⁻¹, and 1080 cm⁻¹, attributing to stretching.
vibration of the intermolecular hydrogen attraction at C\_6, the bending of −\text{OH}, and the stretching vibration of C\_−\text{O}−\text{C} glyosidic ether, respectively \[33, 34\].

3.4. Physico-mechanical properties of PU foams
Table 1 presents the main PU foams’ physico-mechanical properties including density, thermal conductivity, compressive stress and Young’s modulus at 20% of stress deformation. It was noted that the density of PUB\_3 decreased by 1.2%, while those for PU\_α\_3 and PUN\_3 increased by 5.1% and 1.8%, respectively, as compared to PU\_0. This was ascribed to the fact that the cell size of PUB\_3 was larger than PU\_α\_3 and PUN\_3, caused by its weak nucleation effect on large particle size. The density of PU foams slightly increased when increasing bamboo fiber sources to 3% (\(α\)-cellulose and nanocellulose fiber) or 5% (bamboo fiber), while it declined when the fiber content was further increased. This was attributed to the biomass’ fillers increasing the dynamic viscosity of liquid mixture, which could contribute to the hindrance of blowing efficiency of foam rising \[28, 35\]. Moreover,
high biomass content could affect the reaction between polyol and isocyanate, resulting in lower foam density [36].

Compared with PU0, the thermal conductivity of PUB slightly increased by 0.2%–3.5%. This was probably attributed to the enhanced effect of thermal conductivity through solid parts. The thermal conductivity of PUB was greater than those of PUα and PUN, which was caused by the bamboo fiber size, resulting in large cell size and relatively less air medium [25]. There was no remarkable difference in thermal conductivity between PUα and PUN. This was attributed to their foam cells being uniform and small [37]. Accordingly, most of thermal conductivities listed in table 1 were lower than 50.5 m W m\(^{-1}\) K\(^{-1}\), which means they were satisfactory enough to be used as insulation foam [12].

It was noteworthy that the maximum compressive strength and Young’s modulus of PUB were observed in the PUB3, which was probably attributed to the enhancement from bamboo fiber wrapped in foam cell wall. However, with further increasing bamboo fiber content from 5% to 7%, the mechanical values were reduced, which was ascribed to the high viscosity undermining foam processing [15, 38]. The maximum mechanical properties of PU foams reinforced with bamboo α-cellulose and nanocellulose fibers were found in PUα3 and PUN3. This could be ascribed to the good distribution of α-cellulose and nanocellulose in the PU system at low content, as well as the hydroxyl groups reacting with isocyanate contributing to form three-dimensional crosslinked polyurethane groups, increasing the cell strut area and crosslinking density [12]. Apart from this, the interactions between nanocellulose and polyurethane hard segments (urethane and urea) could reinforce the cell wall strength [39]. Besides, the high strength of purified fiber could facilitate the cell skeleton to endure greater compression stress [31]. However, adding excessive biomass could remarkably increase the rheological property, thereby resulting in an inadequate reaction [10, 24]. Furthermore, higher concentration of nanocellulose resulted in agglomeration that became the stress concentrators and point of failure for PU foams [40]. It was worth noting that the maximum compressive stress and Young’s modulus of PUα and PUN was higher than that of PUB. This was partially because the available hydroxyl groups exposed on the surface of bamboo fiber were fewer than those on α-cellulose and nanocellulose, contributing to the reduction of the formation of hard segments in the foaming reaction of PU foams [37]. Notably, the compressive strength of PUα3 (236.3 KPa) was greater than those of PUN3 (175.3 KPa) and PUB3 (166.5 KPa). The highest Young’s modulus of PUB, PUα and PUN increased more than 3.7 times, 4.6 times and 5.0 times, respectively, by adding 5% of bamboo fiber, 3% α-cellulose and 3% nanocellulose in PU matrix, as compared with PU0. Comprehensively, the addition of α-cellulose fiber in PU foams did have better physicio-mechanical properties than adding bamboo fiber, and it was comparable with high-cost nanocellulose fiber.

3.5. TG/DTG analysis of PU foams
The thermal degradation behaviour of the PU foams was evaluated by TG/DTG analysis. As observed in figure 6, the degradation of the PU foams was divided into four stages. The first weight loss peak at 100 °C corresponded to the evaporation of moisture [41]. The second decomposition peak between 120 °C and 363 °C was attributed to the depolymerization of urethane bond and the decomposition of cellulose, hemicellulose in the PUB3 and α-cellulose in the PUα3 and PUN3 [42, 43]. The third decomposition peak between 363 °C and 467 °C was attributed to the chain scission of polyol backbone and lignin in the PUB3 [44], and the last decomposition peak from 467 °C to 551 °C was probably ascribed to the decomposition of organic chains, which was mainly governed by cleavage of urea groups [15]. All residues at 800 °C of PU foams with bamboo fiber sources were

### Table 1. Physico-mechanical properties of PU foams with or without bamboo fiber sources.

| Simple ID | Density (Kg m\(^{-3}\)) | Thermal conductivity (W m\(^{-1}\) K\(^{-1}\) × 10\(^{-3}\)) | Compressive stress at 20% deformation (MPa) | Young’s modulus (KPa) |
|-----------|-----------------|-----------------|-----------------|-----------------|
| PU0       | 80.9 ± 1.9      | 48.4 ± 1.4      | 143.6 ± 16.5    | 323.4 ± 8.1     |
| PUB1      | 84.3 ± 2.7      | 50.1 ± 1.7      | 140.2 ± 23.7    | 182.1 ± 4.1     |
| PUB2      | 79.9 ± 2.7      | 48.5 ± 1.5      | 145.3 ± 12.5    | 356.1 ± 3.6     |
| PUB3      | 82.1 ± 3.4      | 51.0 ± 1.2      | 166.5 ± 15.8    | 1207.5 ± 9.7    |
| PUB4      | 81.7 ± 5.3      | 49.1 ± 1.3      | 118.5 ± 23.8    | 588.4 ± 5.3     |
| PUα1      | 81.2 ± 4.9      | 48.4 ± 1.4      | 131.2 ± 23.5    | 1072.9 ± 11.8   |
| PUα2      | 85.1 ± 5.1      | 49.5 ± 1.1      | 236.3 ± 42.3    | 1472.5 ± 17.7   |
| PUα3      | 74.3 ± 1.9      | 47.5 ± 1.3      | 123.4 ± 8.5     | 771.5 ± 3.9     |
| PUα4      | 78.9 ± 1.9      | 48.0 ± 1.6      | 114.7 ± 15.8    | 218.5 ± 1.3     |
| PUN1      | 79.6 ± 6.4      | 47.9 ± 2.8      | 156.7 ± 23.6    | 1028.2 ± 7.2    |
| PUN2      | 82.4 ± 4.3      | 48.4 ± 0.5      | 175.3 ± 26.6    | 1624.8 ± 21.1   |
| PUN3      | 77.0 ± 6.2      | 48.5 ± 2.1      | 144.9 ± 28.8    | 953.5 ± 13.3    |
| PUN4      | 76.2 ± 3.8      | 48.9 ± 1.9      | 115.3 ± 24.4    | 639.0 ± 5.1     |
higher than PU0. This was because the introduction of biomass into PU foam decomposed to coke and ash [45]. The weight loss of PU0 between 120 °C and 363 °C was 52.3%, and those for PUB3, PUα3 and PUN3 were 51.6%, 47.7%, and 52.2%, respectively. Moreover, the maximum weight loss rate at around 320 °C of PU foams with bamboo fiber sources were lower than PU0, suggesting that the thermal stability of PU foams with bamboo fiber sources were higher than neat foam.

As shown in Table 2, the initial decomposition temperature (IDT) of PUα3 was higher than the other bamboo fiber reinforced PU foam. In addition, the degradation temperature of PUα3 at 10% (T10%) and 50% (T50%) of weight loss, were greater than other PU foams, suggesting that α-cellulose fiber presented a better enhancement for the thermal stability of PU foams than bamboo fiber and nanocellulose fiber. The first maximum decomposition temperature (T1max) and the second maximum decomposition temperature (T2max) of PU foams reinforced with bamboo fiber sources were higher than those of PU0. This was ascribed to the addition of biomass contributed to stronger noncovalent intermolecular interactions between unreacted hydroxyl groups and urethane cross-linking moieties. Moreover, the hydroxyl groups in bamboo fiber sources could enhance the cross-linking density in PU foams [46, 47].

4. Conclusions

Bamboo fiber sources, i.e., bamboo fiber, bamboo α-cellulose fiber and bamboo nanocellulose fiber, were used to reinforce polyurethane (PU) foam in this work. The hydroxyl groups in bamboo α-cellulose and nanocellulose were enhanced by removing non-celluloses. PU foams reinforced with bamboo fiber had a larger cell diameter than neat foam, while the foams having α-cellulose and nanocellulose had more numerous and smaller foam cells due to their small particle size nucleating effects. PU foams reinforced with 5% bamboo fiber, 3% α-cellulose fiber or 3% nanocellulose fiber had better physico-mechanical performance than other foams, suggesting that the bamboo fiber sources did have a strong reinforcement effect for PU systems. This result was partially ascribed to the reaction between the hydroxyl groups on bamboo fiber sources and the PU foam matrix. The thermal stabilities of PU foams were increased by introducing bamboo fiber sources. Moreover, PU foam

| Sample | IDT/°C | T10%/°C | T50%/°C | T1max/°C | T2max/°C | Residue at 800/°C |
|--------|--------|---------|---------|----------|----------|------------------|
| PU0    | 249.3  | 280.7   | 351.3   | 323.1    | 397.1    | 12.8%            |
| PUB3   | 230.8  | 276.8   | 349.5   | 324.5    | 398.3    | 13.7%            |
| PUα3   | 247.0  | 287.8   | 362.1   | 329.5    | 403.2    | 13.2%            |
| PUN3   | 225.5  | 274.1   | 351.1   | 325.3    | 399.3    | 13.3%            |

IDT, T10%, T50%, T1max and T2max means initial decomposition temperature, 10% weight loss temperature, 50% weight loss temperature, the first maximum decomposition temperature and the second maximum decomposition temperature, respectively.

Figure 6. TG/DTG analysis of PU0, PUB3, PUα3, and PUN3.
reinforced with 3% α-cellulose had comparable physico-mechanical properties as compared with high-cost nanocellulose fiber reinforced foams. Accordingly, bamboo α-cellulose fiber, was demonstrated to be a promising candidate to reinforce PU foam. The future work should be focused on the modification of α-cellulose fiber to obtain a higher reinforcement performance.

Acknowledgments

This work was partially supported by the Natural Science Foundation of China (No. 31770622), the Foundation of Key Laboratory of Pulp and paper Science and Technology of Ministry of Education of China (KF201909), and the USDA Forest Service’s Wood Innovation Funding Opportunity Program, Agreement 15-DG-11083150-054. Additional support was provided by the Key Research and Development Project of Sichuan Science and Technology Plan Projects (Grant # 2020YFSO357).

ORCID iDs

Xingyan Huang https://orcid.org/0000-0001-8622-5320

References

[1] Nguyen H D, Thuy Mai T T, Nguyen N B, Dang T D, Phung Le M L, Dang T T and Tran V M 2013 A novel method for preparing microfibrillated cellulose from bamboo fibers Advances in Natural Sciences Nanoscale & Nanotechnology 4 15016
[2] Saffar T, Bouaffi H, Braghiorli F L, Magdouli S, Langlois A and Koubaa A 2020 Production of bio-based polyol from oxycarboxylated pyrrolidin for rigid polyurethane foam application Waste Biomass Valor 11 6411–27
[3] Joshi S V, Drzal L T, Mohanty A K and Arora S 2004 Are natural fiber composites environmentally superior to glass fiber reinforced composites? Composites Part A: Applied Science and Manufacturing 35 571–6
[4] Abdul Khalili H P S, Bhat A H and Irena Yusra A F 2012 Green composites from sustainable cellulose nanofibrils: A review Carbohydr Polym 87 963–79
[5] Chen S and Jiang Y 2018 The acoustic property study of polyurethane foam with addition of bamboo leaves particles Polym Composite 39 1370–81
[6] Linul E, Linul P, Valea C, Marsavina L and Silaghi-Perju D 2018 manufacturing and compressive mechanical behavior of reinforced polyurethane flexible (PUR) foams iop Conference 416 012053
[7] Osorio L, Trujillo E, Van Vuure A W and Verpoest I 2011 Morphological aspects and mechanical properties of single bamboo fibers and flexural characterization of bamboo/ epoxy composites J Reinf Plast Compo 30 396–408
[8] Ramle S F M, Ahmad N A, Rawi N F M, Zahidann N S and Geng R B 2019 Physical properties and soil degradation of PLA/ PBAT blends film reinforced with bamboo cellulose IOP Conf. Ser.: Earth Environ. Sci. 596 012021–7
[9] Abdul Khalili H P S, Bhat I U H, Jawaed M, Zaidon A, and Hadi Y S 2012 Bamboo fibre reinforced biocomposites: A review Mater Design 42 353–68
[10] Huang X, De Hoop C F, Xie J, Hse C, Qi J and Hu T 2017 Characterization of bio-based polyurethane foams employing lignin fractionated from microwave liquefied switchgrass Int. J. Polym. Sci. 2017 1–8
[11] Chen W, Yu H, Liu Y, Chen P, Zhang M and Hai Y 2011 Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments Carbohydr Polym 83 1804–11
[12] Huang X Y, De Hoop C F, Xie J, Li C, Wu Q, Boldor D and Qi J Q 2017 High bio-content polyurethane (PU) foam made from bio-polyl and cellulose nanocrystals (CNCs) via microwave liquefaction Mater Design 138 11–20
[13] Noreen A, Zia K M, Zubier M, Tabasum S and Zahoor A R 2016 Bio-based polyurethane: An efficient and environment friendly coating systems: A review Prog. Org. Coat. 91 25–32
[14] Wei J, Yang Z, Sun Y, Wang C, Fan J, Kang G, Zhang R, Dong X and Li Y 2019 Nanocellulose-based magnetic hybrid aerogel for adsorption of heavy metal ions from water J. Mater. Sci. 54 6799–18
[15] Gu R and Sain M M 2013 Effects of wood fiber and microlyaf on the performance of soy-based polyurethane foams J. Polym. Environ. 21 30–8
[16] Li F, Qiu C P, Zhang X L, Tan R W, de Hoop C F, Curole J P, Qi J Q, Xiao H, Chen Y Z and Xie J L 2020 Effect of biomass source on the physico-mechanical properties of polyurethane foam produced by microwave-assisted liquefaction Bioresources. 15 7034–47
[17] ASTM D 695 1972 Standard Test Method for Alpha-Cellulose in Wood, (West Conshohoken USA: ASTM international)
[18] De Haro J C, Allegretti C, Smit A T, Turri S, D’Arriago P, Griffinii G et al 2019 Bio-based polyurethane coatings with high biomass content: tailored properties by lignin selection Acs Sustain Chem. Eng. 7 11700–11
[19] Isachenko A I, Ayari V V, Melikhin A O, Garshver A V, Volkov P A and Dimitrienko S G 2019 Polyurethane foam modified with borohydride: preparation and possibilities of using for synthesis of gold nanoparticles and their nanocomposites IOP Conf. Ser.: Mater. Sci. Eng. 704 12001–7
[20] Xie J, Hse C, Li C, Shupe T F, Hu T, Qi J and De Hoop C F 2016 Characterization of microwave liquefied bamboo residue and its potential use in the generation of nanofibrillated cellulosic fiber Acs Sustain Chem. Eng. 4 3477–85
[21] Li J, Jiang J, Xu J, Xia H and Liu P 2016 Branched polyols based on oleic acid for production of polyurethane foams reinforced with bamboo fiber Iran. Polym. J. 25 811–22
[22] Gama N V, Soares B, Freire C S R, Silva R, Neto C P, Barros-Timmons A and Ferreira A 2015 Bio-based polyurethane foams toward applications beyond thermal insulation Mater Design 76 77–85
[23] Shao H, Zhang Q, Liu H, Guo W and Shupe T F 2020 Renewable natural resources reinforced polyurethane foam for use of lightweight thermal insulation Mater. Res. Express 7 055302
[24] Aladejana J T, Wu Z, Fan M and Xie Y 2020 Key advances in development of straw fibre bio-composite boards: an overview Mater. Res. Express 7 12005–19
[25] Li B, Zhou M, Huo W, Cai D, Qin P, Cao H and Tan T 2020 Fractionation and oxypropylation of corn-stover lignin for the production of bio-based rigid polyurethane foam Ind Crop Prod 143 111887
[26] Campanella A, Bonnaille I M and Wool R P 2009 Polyurethane foams from soyoil-based polyols J. Appl. Polym. Sci. 112 2567–78
[27] Jabber L Y, Grumo J C, Alguno A C, Lugubgan A A and Capangangan R Y 2019 The effect of cellulose fibers on the formation of petroleum-based and bio-based polyurethane foams Key Eng. Mater. 803 371–6
[28] Sung G and Kim J H 2017 Influence of filler surface characteristics on morphological, physical, acoustic properties of polyurethane composite foams filled with inorganic fillers Compos. Sci. Technol. 146 147–54
[29] Kumari S, Chaushan G S and Ahn J H 2016 Novel cellulose nanowhiskers-based polyurethane foam for rapid and persistent removal of methylene blue from its aqueous solutions Chem. Eng. J. 304 728–36
[30] Wang F, Lu M, Zhou S, Lu Z and Ran S 2019 Effect of fiber surface modification on the interfacial adhesion and thermo-mechanical performance of unidirectional epoxy-based composites reinforced with bamboo fibers Molecules 24 2682
[31] Zhang S, Sun K, Liu H, Chen X, Zheng Y, Shi X, Zhang D, Mi L, Liu C and Shen C 2020 Enhanced piezoresistive performance of conductive WPU/CNT composite foam through incorporating brittle cellulose nanocrystal Chem. Eng. J. 387 120415
[32] Gomez-Serrano V, Valenzuela-Calahorro C and Pastor-Villegas J 1996 FT-IR study of rockrose and of char and activated carbon J. Anal. Appl. Pyrol. 4 335–64
[33] Haafiz M K M, Hassan A, Zakaria Z and Inuwa I M 2014 Isolation and characterization of cellulose nanowhiskers from oil palm biomass microcrystalline cellulose Carbohydr Polym 103 119–25
[34] Mandal A and Chakrabarty D 2011 Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization Carbohydr Polym 86 1291–9
[35] Czlonka S, Sienkiewicz N, Strąkowska A and Strzelec K 2018 Keratin feathers as a filler for rigid polyurethane foams on the basis of soybean oil polyol Polym. Test. 72 32–45
[36] Stanzione M, Oliviero M, Cocca M, Errico M E, Gentile G, Avella M, Lavorgna M, Buonocore G G and Verdolotti L 2020 Tuning of polyurethane foam mechanical and thermal properties using ball-milled cellulose Carbohydr Polym 231 115772
[37] Jin X, Li J, Zhang R, Jiang Z and Qin D 2020 Fabrication of high-performance bamboo–plastic composites reinforced by natural halloysite nanotubes Molecules 25 22359
[38] Klemm D, Kramer F, Moritz S, Lindstrom T, Ankerfors M, Gray D and Dorris A 2011 Nanocelluloses: a new family of nature-based materials Angew. Chem. Int. Ed. Engl. 50 5436–66
[39] Cordero A I, Mamaly J, Fortunati E, Kenny J M and Chiacciarelli L M 2015 The role of nanocrystalline cellulose on the microstructure of foamed castor-oil polyurethane nanocomposites Carbohydr Polym. 134 110–8
[40] Ivdre A, Mucci V, Stefani P M, Aranguren M I and Cabulis U 2016 Nanocellulose reinforced polyurethane obtained from hydroxylated soybean oil IOP Conf. Ser.: Mater. Sci. Eng. 111 120111
[41] Tian H, Liu Z, Zhang M, Guo Y, Zheng L and Li Y C 2019 Bio-based polyurethane, epoxy resin, and polyolefin wax composite coating for controlled-release fertilizer Acs Appl Mater Inter 11 5380–92
[42] Yang H, Yan R, Chen H, Lee D H and Zheng C 2007 Characteristics of hemicellulose, cellulose and lignin pyrolysis Fuel 86 1781–8
[43] Zapata B, Balmaseda J, Fregoso- Ortiz E and Torres–García E 2009 Thermo–kinetics study of orange peel in air J. Therm. Anal. Calorim. 98 309–15
[44] Zhang X, Wang F and Keer L M 2015 Influence of surface modification on the microstructure and thermo-mechanical properties of bamboo fibers Materials 8 6597–608
[45] Swain S N, Rao K K and Nayak P L 2005 Biodegradable polymers; part II: thermal degradation of biodegradable plastics cross-linked from formaldehyde–soy protein concentrate J. Therm. Anal. Calorim. 79 33–8
[46] Huang X, De Hoop C F, Xie J, Hse C, Qi J and Hu T 2017 Bio-based polyurethane foam insulation from microwave liquefaction of woody underbrush BioRes. 12 8160–79
[47] Kairytė A, Kremsenas A, Vaitkus S, Czlonka S and Strąkowska A 2020 Fire suppression and thermal behavior of bio-based rigid polyurethane foam filled with biomass incineration waste ash Polymers-Basel 15 683