

Lightweight Biobased Polyurethane Nanocomposite Foams Reinforced with Pineapple Leaf Nanofibers (PLNFs)

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ABSTRACT: Pineapple leaf nanofibers (PLNFs) extracted from pineapple leaf fiber were used for reinforcing biobased polyurethane foam (BPU). The dispersion performance of PLNF in the foaming mixture system, nanocomposite foaming behavior, cell morphology, cell size, density, compressive strength and dimensional stability were investigated. The viscosity of the mixtures increased with increasing the PLNF content. The addition of a tiny amount of PLNF did not influence the exothermic temperature of the foam system, but reduced the expansion and gel time of the nanocomposite foams. This reduced time was found to increase the production efficiency. Scanning electron microscopy (SEM) images showed that the PLNF neither affected the cell shape nor size. While the density of the foam was not obviously altered with the addition of a small amount of PLNF, the compressive strength and dimensional stability were significantly improved.

KEYWORDS: Polyurethane foam, palm oil polyol, pineapple leaf nanofibers, physical properties

1 INTRODUCTION

Polyurethane foam (PU) is a versatile cellular material because of its excellent physical and mechanical performance. It has been widely used in different applications, such as automotive, packaging, cushioning, aircraft and insulation, as well as sandwich core production [1, 2]. In the production of conventional polyurethane foams, the main materials are derived from petrochemical refining of crude oils. With increasing concern about environmental problems and shortage of fossil resources, the renewable and biodegradable materials are being widely considered to replace the petroleum-based products. It has been found that biopolyol has suitable characteristics for polyurethane foam preparation. Due to their being a low price, abundant renewable resource, lignin, soybean oil polyol, castor oil polyol and linseed oil polyol have been used as alternative materials for PU foam preparation [3–6].

Biopolyol-based PU foams (BPUs), however, have disadvantages such as slower foaming speed and weaker mechanical properties, as compared to industrial PU foams [7]. Therefore, mechanical properties

of BPU foams should be improved to meet the usage requirements. The mechanical properties of BPU foams can be improved either by changing the isocyanate index or by adding different proportions of petrol polyol [8]. However, this increased extent of mechanical strength was limited by optimization of formulation and mass proportion. The use of reinforcement, such as nanoclay, carbon nanotubes or glass fibers, is another option to improve the mechanical properties of the bio-PU composite [9–11]. The strength and modulus can be increased several times with these kinds of inorganic additives.

Additionally, several attempts have been made to improve the mechanical properties of biobased PU foams with cellulose fibers [12–14], cellulose microfibrils [15], cellulose nanofibers [16] and cellulose nanowhiskers/nanocrystals [17–21]. From the number of references we can conclude that there are many more studies on CNC reinforced PU foam in which most of the nanocelluloses were directly added into the polyol resin after freeze-drying [16, 19–21], with only the studies of Li *et al.* dispersing cellulose nanowhiskers in the water or DMF solvents [17–18] prior to adding them into the polyol for foam preparation.

As we know, pineapples are widely cultivated in the south of China, producing around 14.00 million tonnes of fresh shoots each year. There are 30–40 leaves per shoot that remain unused after harvesting. These

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leaves are considered as by-products, and this type of by-product is also an interesting resource for development of new materials. Studies reveal that pineapple nanofiber owns the same good mechanical properties as other cellulose nanofibers, which makes it very promising material for use as reinforcement in composites intended for different applications [22–24]. Therefore, this by-product could be a potential source of nanocellulose for industrial applications.

This present work investigates the feasibility of using pineapple leaf nanofibers (PLNFs) prepared from pineapple by-product to reinforce the BPU foams. The dispersion ability of PLNF was investigated. The influence of PLNF on the BPU nanocomposite foam properties, such as PLNF dispersion ability, foaming behavior, cell morphology, density and mechanical properties, was studied.

2 EXPERIMENTAL

2.1 Materials

Palm oil polyol (PolyGreen 3110) with a hydroxyl value of 98 mg KOH/g, viscosity of 1660 mPa·s, functionality of 2 and acid number of 1.37 mg KOH/g, was kindly supplied by PolyGreen, Malaysia. Commercial polymeric methane diphenyl isocyanate pMDI (ISO pMDI 92140) with a functionality of 2.7, –NCO content of 32% and viscosity of 300 mPa·s was purchased from Wanhua, China. Distilled water was used as chemical blowing agent. Other chemicals and reagents, such as sodium hydroxide, nitric acid, hydrochloric acid and sulfuric acid for PLNF preparation, cosolvent (dioxane), catalyst (dibutyltin dilaurate) and surfactants (polydimethyl siloxane and silicone oil) for foam preparation, were purchased from Sigma-Aldrich, China. Pineapple leaves (see Figure 1a) were harvested at a farm in the south of China.

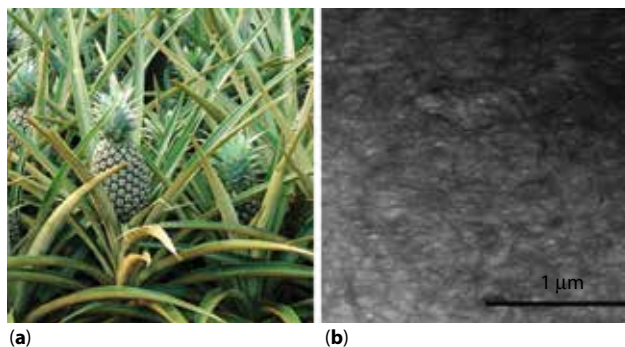


Figure 1 (a) Photographic image of pineapple leaves; (b) TEM image of PLNF.

2.2 Preparation of Cellulose Microcrystallites

Pineapple leaf nanofibers (PLNFs) were produced at lab scale as follows. Briefly, the pineapple leaf was cut and ground into cottonlike fiber. Next, 100 g fibers were treated with 2000 mL alkali (2% NaOH) solution at 80 °C for 3 h under mechanical stirring; then the pulp was transferred to a 2000 mL nitric acid (3%) solution under mechanical stirring while applying the same conditions. After each treatment, the pulp was thoroughly washed with deionized water until a neutral pH was reached. After that, the pulp was soaked in 2000 mL hydrochloric acid (5%) solution at 95 °C for 1.5 h under the same stirring speed. The cellulose powder was obtained by centrifuging several times under neutral conditions and vacuum drying. Next, 50 g of cellulose powder was treated with 60% sulfuric acid (fiber-to-liquor ratio 1:20) in a beaker at 60 °C under mechanical stirring for a period of 40 min. The PLNF was obtained by centrifugation at 12000 r/min, dialysis for 1 week and freeze-drying steps.

2.3 Preparation of Nanocomposite Foams

The PLNF was initially dispersed in a cosolvent solution then mixed with polyol for 5 min; the extra cosolvent was evaporated under heat and mechanical stirring. Then, the catalysts, surfactants and water were added under vigorous mechanical agitation and homogenized for 30 s. Afterwards, the pMDI was added over 20 s with the same stirring speed. The nanocomposite foam was obtained within a few seconds. Neat polyurethane foams without PLNF were prepared using a similar foaming process. The resulting foams were then removed from the foaming cup after 5 min and allowed to post-cure at room temperature for 1 week prior to the sample cutting process. A schematic diagram of the foaming process and the foam formulation is shown in Figure 2 and Table 1, respectively. The parts of each component are designated as phr (parts per hundred rubbers); the isocyanate index was maintained at 1.0 for all foams prepared.

2.4 Characterization

2.4.1 Characterization of PLNF

The characteristics of PLNF were investigated by TEM (transmission electron microscopy). Briefly, a tiny amount of PLNF was dispersed in distilled water by ultrasonication, and then a drop of PLNF suspension was dropped onto the surface of a clean copper mesh and allowed to dry. The size and morphology of PLNF

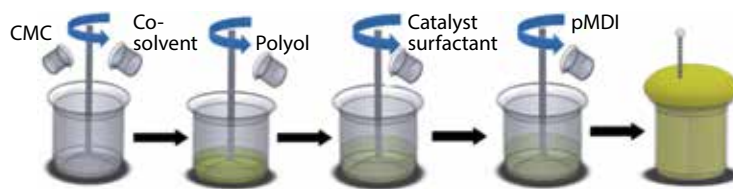


Figure 2 Schematic diagram of the laboratory-scale foaming process of the BPU nanocomposite foams.

Table 1 Formulation of the neat BPU and nanocomposite foams.

Components	Parts of component (phr)	Role
Polyol	100	Base of resin
Dioxane	20	Cosolvent
Dibutyltin dilaurate	2.75	Catalyst
Polydimethyl siloxane	1	Surfactants
Silicone oil	2.25	
Water	4.5	Blowing agent
pMDI	100	Reactive pre-polymer
PLNF	0.5, 1, 2	Reinforcements

were studied using TEM (H-7650, Hitachi, Japan) at acceleration voltage of 80 kV. The dispersion ability of the PLNF in polyol resin mixture was studied using a polarized optical microscope (Nikon Eclipse LV 100V, Japan). The viscosity of PLNF and polyol resin mixture was measured using a vibro viscometer (SV-10, 0.3–10 000 mPa·s, Japan) at 25 °C.

2.4.2 Characterization of Nanocomposite Foams

The foams were characterized for their foaming behavior, bulk density, cell morphology, cell size, compression behavior and dimensional stability after polishing. All measurements were made in the direction parallel to the foaming rise direction.

2.4.2.1 Foaming Behavior

The cream time (from pouring the isocyanate into the polyol blend until initiation of foaming), end of rise time (from pouring the isocyanate into the polyol blend until full expansion of foaming) and tack-free time (from pouring the isocyanate into the polyol blend until the skin of the foam was no longer sticky when lightly touched) were recorded during the course of the foaming process. The exothermic nature

of the foaming system was monitored using a normal thermometer, which was inserted into the foaming system while the foam was rising (Figure 2).

2.4.2.2 Microstructure

Microstructure of nanocomposite foams was studied using scanning electron microscopy (SEM) (JEOL JSM-6460LV, Japan) at an acceleration voltage of 10 kV. The samples were frozen at –25 °C and cut into 10 × 10 × 5 mm specimens then coated with gold prior to scanning to avoid charging. The cell size of the foams was manually measured using SEM Afore image analysis and defined by Feret diameter [14]. For each specimen, the average cell size was calculated by 100 measurements of individual cells for equal surface area.

2.4.2.3 Density

The bulk density of nanocomposite foams was measured according to ASTM D1622-08. The foams were cut into cubic shape with dimensions 30 × 30 × 30 mm and measured using a digital vernier caliper with a precision of 0.01 mm and weighed using an analytical balance with a precision of 0.0001 g. The bulk density of the foams in kg/m³ is defined as the ratio of weight/volume. The density of each sample was determined considering the average value of five specimens.

2.4.2.4 Mechanical Properties

The nanocomposite foams were tested in compression, using a universal testing machine (Instron 4206) equipped with a 500 N load cell and a constant load rate of 2.5 mm/min, according to ASTM D1621. The foams were cut into 51 × 51 × 26 mm samples, and the thickness was parallel to the rising direction. All samples were conditioned at 21 °C and 45% RH for at least 40 h prior to testing. The reported compressive strength was taken at a 10% deformation level, and the compressive modulus was obtained from the initial slope of the stress-strain curve. The testing was ended while the deformation reached 40% of the sample thickness. Seven replicates for each formulation were tested and the average value was reported with standard deviation.

2.4.2.5 Dimensional Stability

The dimensional stability was calculated as volumetric swelling at 70 °C and volumetric shrinkage at -25 °C, respectively, using the following equation:

$$V = \frac{V_2 - V_1}{V_1} \times 100 \quad (1)$$

where V_1 is the original foam volume before heating or freezing and V_2 is the final volume after conditioning for 24 h. The length, width and thickness of the samples were measured using a vernier caliper with 0.01 mm. The original sample dimensions were 51 × 51 × 26 mm, and the samples were conditioned at 25 °C for 24 h before being transferred into controlled conditions, 70 °C and -25 °C, respectively, for 7 days.

3 RESULTS AND DISCUSSIONS

3.1 Pineapple Leaf Nanofibers (PLNFs) Analysis and Dispersion

The obtained PLNF appeared as a very light, white powder, the diameter of PLNF was between 5–20 nm as measured using TEM and the length is estimated to be around 500–700 nm (Figure 1b). More characteristics of these cellulose microcrystallites were described elsewhere by Huang *et al.* [25]. This kind of cellulose microcrystallite can be used to reinforce the cellular foams if it is well dispersed in the resin mixture matrix. The reason for this is that the homogeneous dispersion of nanocellulose will lead to a large interfacial area between the reinforcement and matrix, which is critical to enhance the mechanical properties of the

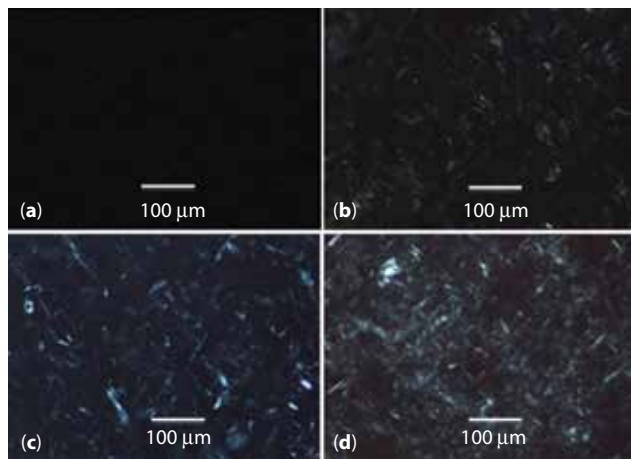


Figure 3 Optical polarized microscopy images of redispersion behavior of PLNF in the polyol resin mixture: (a) polyol; (b) polyol with 0.5 phr PLNF; (c) polyol with 1 phr PLNF; (d) polyol with 2 phr PLNF.

final composites. Figure 3 shows the dispersion ability of nanocellulose as studied by means of microscopy: Figure 3a shows the pure polyol resin and Figure 3b–d shows the polyol resin mixture with 0.5, 1 and 2 phr PLNF, respectively. As can be seen, a homogeneous dispersion of PLNF in the hydrophobic polyol resin was obtained. A similar dispersion level was confirmed in a previous study [26].

As expected, the addition of PLNF increased the viscosity of resin mixture, and a higher viscosity can be acquired for the resin with higher percentage of PLNF compared to the neat polyol. As can be seen in Figure 4, the viscosity was significantly increased from 2632 mPa·s for neat polyol to 9807 mPa·s for the resin with 2 phr PLNF. A similar tendency was also reported in another study [27] in which carbon nanotubes and nanofibers were dispersed in epoxy resin, and the obtained mixture exhibited the highest viscosity.

3.2 Foaming Behavior

Table 2 illustrates the cream time, rise time and tack-free time of neat foam and nanocomposite foams with different concentrations of PLNF. It is obvious that the rise time and tack-free time of nanocomposite foams are significantly shortened compared to those of the neat BPU foam. This is probably attributed to cellulose, which can be reacted with -NCO group in pMDI, leading to accelerated expansion and gel rate of the BPU

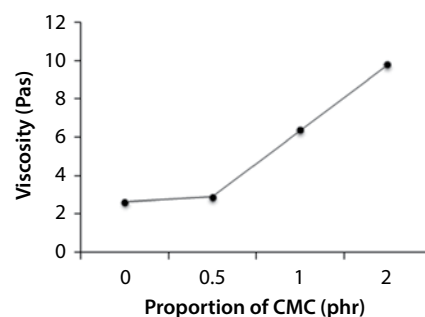


Figure 4 The effect of the PLNF proportion on viscosity of the polyol resin mixture.

Table 2 Foaming time of the BPU nanocomposite foams with different concentrations of PLNF.

Composite foams	Cream time (s)	Rise time (s)	Tack free time (s)
BPU	30	170	220
BPU-0.5PLNF	31	136	185
BPU-1PLNF	30	137	192
BPU-2PLNF	32	142	190

nanocomposite foams. This has been demonstrated in Zhao's thesis [28], which revealed that the isocyanate can be reacted with the cellulose. Therefore, the addition of PLNF can save the production time and increase the efficiency.

The exothermic temperature of the foaming system is illustrated in Figure 5. It is clear that the addition of PLNF did not affect the exothermic temperature. As is known, the source of heat generated was the exothermic reaction between the water and isocyanate. Therefore, a similar temperature is obtained if the same amount of water is added, as shown in Figure 5.

3.3 Foam Images and Microstructures

The obtained foams and their microstructures are shown in Figures 6 and 7, respectively. As such, a white, very uniform foam was obtained; however, different proportions of the PLNF addition in BPU foam had no large visual difference on the foam appearance (Figure 6) or cellular morphology (Figure 7), which is in accordance with our previous study [26]. In order to demonstrate the PLNF trend of reinforcement, high magnification SEM was used to investigate the foam cell wall and strut features, but in vain.

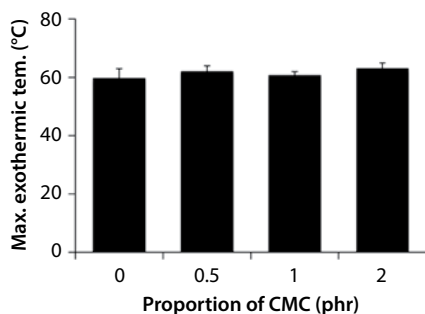


Figure 5 Maximum exothermic temperature produced during the BPU nanocomposite foams preparation.

3.4 Density and Mechanical Properties

The bulk density is listed in Table 3. The density was slightly increased with increased PLNF proportion. This is due to the viscosity increase (Figure 4), which resulted in the difficulty of CO₂ gas generation between the water and pMDI.

The compressive strength and modulus are summarized in Table 3; it can be observed that the compressive strength and modulus increased significantly with addition of PLNF. The highest compressive strength of the foams was obtained at 0.5 phr PLNF. The compressive modulus was continuously increasing with higher amounts of PLNF. To determine the effect of density on the composite mechanical properties, the normalized compressive strength was calculated as the ratio of compressive strength divided by density, as shown in Table 3. The normalized compressive strength of foam increased with increasing

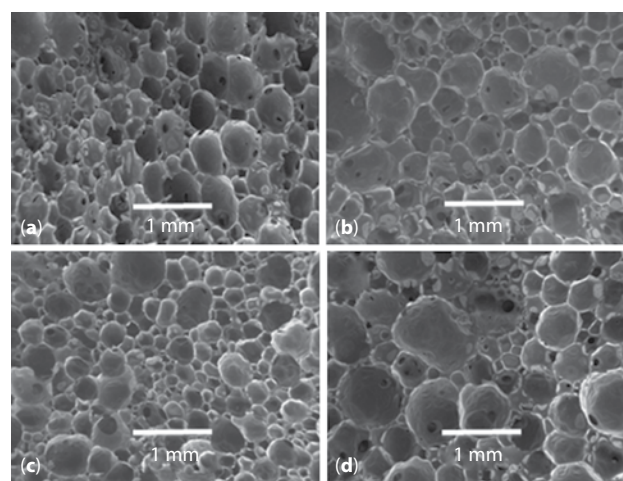


Figure 7 SEM images of the BPU nanocomposite foams: (a) neat BPU; (b) BPU – 0.5 phr PLNF; (c) BPU – 1 phr PLNF; (d) BPU – 2 phr PLNF.

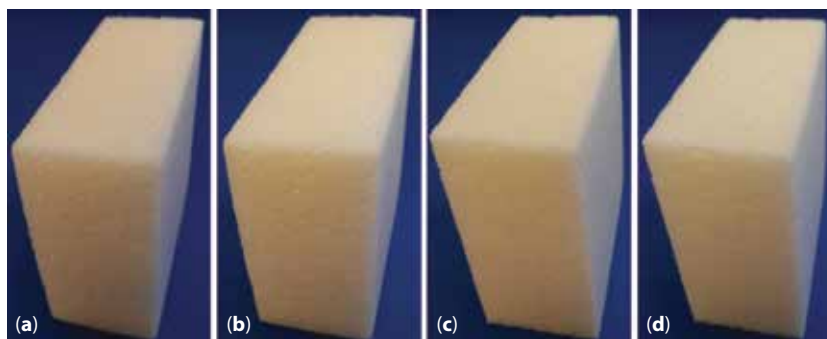
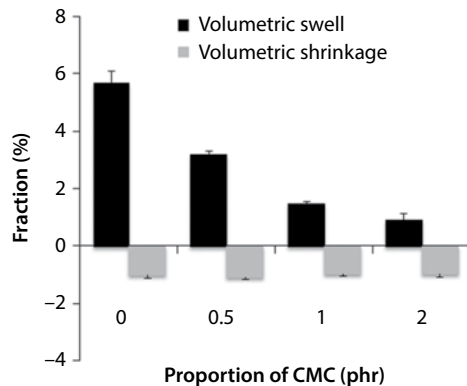


Figure 6 Photographic images of the BPU nanocomposite foams: (a) neat BPU foam; (b) BPU – 0.5 phr PLNF; (c) BPU – 1 phr PLNF; (d) BPU – 2 phr PLNF.

Table 3 Main characteristics of BPU nanocomposite foams with different proportions of PLNF.

Composite foams	Density (kg/m ³)	Cell size (μm)	Compressive strength (kPa)	Compressive modulus (kPa)	Normalized Compressive strength (kPa/kg m ⁻³)
BPU	46 ± 1	438	55 ± 3.2	2356 ± 27	51
BPU-0.5PLNF	45 ± 1	467	74 ± 2.8	2673 ± 17	59
BPU-1PLNF	48 ± 2	454	68 ± 2.0	2719 ± 13	57
BPU-2PLNF	51 ± 2	463	70 ± 2.1	2890 ± 25	57

**Figure 8** Dimensional stability of neat BPU foam and BPU nanocomposite foams with different proportions of PLNF at heating and subzero conditions.

the proportion of PLNF. Thus, this improvement of mechanical properties is not attributed to the foam density, but to the reinforcement in the cell wall and increase of the cell strut area. This also has been demonstrated extensively in our previous studies [21, 26]. Moreover, the cellulose provides –OH groups to react with –NCO group in isocyanate to form covalent bonding, which is another potential reason for increasing the mechanical strength.

3.5 Dimensional Stability

Dimensional stability is defined as volume swelling and volume shrinkage at 70 °C and –25 °C, respectively, for 7 days (Figure 8). BPU foams with PLNF exhibited lower volume swelling value, indicating that the addition of PLNF improved the dimensional stability at the heat condition. However, the dimensional stability of BPU foams with PLNF did not improve at the subzero condition; on the contrary, it even became inferior to that of the neat BPU foam. This is not consistent with our previous study, in which both volume swelling and shrinkage were improved with CNC addition [21]. This is probably because of the different production processes of PLNF and CNC, which will be the focus of our concern in the future. It is worth noting that the absolute value

of volume shrinkage at –25 °C was lower than the volume swelling at 70 °C by comparing both sides of the x-axis for BPU foams. This indicates that the BPU foams prepared in this work had better subzero resistance than heat resistance.

4 CONCLUSIONS

Lightweight biobased polyurethane nanocomposite foams reinforced with pineapple leaf nanofibers (PLNFs) have been successfully developed in this work. Tiny amounts of PLNF can be well dispersed in the polyol resin mixture. The PLNF addition did not affect the foaming temperature, but the foaming rate. Small loading of PLNF offered water-blown nanocomposite foams with superior mechanical properties and dimensional stability, the highest compressive strength and an increase in modulus of 35% and 23%, respectively, compared with the control foam. Therefore, the prepared foams in this work are promising based on their mechanical properties and renewable resources, and can possibly be used for applications such as sandwich composite core layer.

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