Renewable natural resources reinforced polyurethane foam for use of lightweight thermal insulation

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Abstract
To obtain the energy-saving and environment-friendly lightweight bio-based thermal insulation, polyurethane matrix was incorporated with wood fiber, bamboo fiber, rice husk and liquefied polyl at different percentages (25%, 30%, and 35%). The results revealed that the apparent density for the natural fibers reinforced thermoplastic polyurethane insulation was between 105 kg.m$^{-3}$ and 178 kg.m$^{-3}$ by adding 35% of the fibers into the polyurethane matrix. The thermal conductivity of the bio-based thermal insulation ranged from 0.045 to 0.065 W.m$^{-1}$K$^{-1}$, the addition of the natural fibers increased mechanical strength. The prepared bio-based insulation showed great potential for building thermal insulations with particularly low thermal conductivity (less than 0.065 W.m$^{-1}$K$^{-1}$) and self-bearing strength.

1. Introduction
The demand of building materials is rising rapidly with the development of many countries, especially the increasing need of indoor thermal comfort is gaining more and more attention. Thermal insulation is one efficient approach to reduce the heat losses in buildings and to make the room obtain a desired temperature to improve the indoor environment quality and health condition of residents [1, 2].

Meanwhile, with the awareness of sustainable development and environment protection, people pay more attention on bio-based thermal insulations for environment-friendly and cost-effective purpose [3]. The thermal insulations derived from biomass such as agricultural straws are attracting the interest of the public, due to the hollow structure, low cost, low density as well as low thermal conductivity. The thermal radiation and conduction are the important heat transfer modes for thermal insulation [4–6], and the thermal conductivity coefficient is more often used to describe the property of insulation materials [7–10]. Research on the production of bio-insulations started in 1974 [11]. Recent studies have reported the application of biomass on the preparation of thermal insulations. Atif et al (2019) developed water resistant hemp shiv based thermal lightweight insulations, and the composites showed low thermal conductivity values of 0.051 – 0.058 W.m$^{-1}$K$^{-1}$ and relatively good compressive stress from 0.49 to 1.05 MPa [12]. Marie et al (2019) investigated the hemp shiv and corn cob residues as bio-based thermal insulation materials, and the obtained composites had thermal conductivity ranging between 0.0675 to 0.1479 W.m$^{-1}$K$^{-1}$ [13]. Dang et al (2018) manufactured an environment-friendly insulation fiberboards derived from bamboo fibers and protein-based bone glue using hot-pressing method. The fiberboards exhibited low thermal conductivity ranging from 0.0582 to 0.0812 W.m$^{-1}$K$^{-1}$ [14]. Muhammad et al (2018) studied the bio-composite based on the mixture of magnesium phosphate cement, fly ash as well as corn stalk. The results revealed that the thermal conductivity of corn stalk composites could be improved with the increment of corn stalks, and when the concentrations of corn stalk was 30%, the thermal conductivity values of two corn stalks based materials were 0.0510 and 0.0986 W.m$^{-1}$K$^{-1}$,
respectively [15]. Few studies focused on the preparation of bio-based polyurethane insulations with the addition of natural fibers.

In this study, the fibers or particles from wood, bamboo and rice husk were combined with polyurethane matrix for the manufacture of the lightweight thermal insulations. The neat polyurethane foam insulation and the polyurethane foam with liquefied rice husk were also prepared for comparison. The mechanical strength, apparent density, thermal conductivity, thermal stability and surface morphology of the thermal insulations with the addition of various natural resources were investigated for fundamental information of such bio-based thermal insulation. The results of this research may provide support for partial replacement of chemicals usages in the thermal insulation production by natural resources.

2. Experimental

2.1. Materials

Rice husks were obtained from Anhui province, China. Bamboo fibers were the processing residues from a bamboo scrimber factory located in Sichuan province, China. Wood particles were purchased from a particleboard factory located in Shandong province, China. All materials were dried to constant moisture at 103 °C. Polyethylene glycol#400, dibutyltin dilaurate, triethanolamine, simethicone were from Chron Chemicals Co., Ltd PM200 (diphenylmethane diisocyanato) was purchased from Guangzhou HONA Chemical Co., Ltd. The chemical compositions of wood particles, bamboo fibers and rice husks are shown in table 1.

2.2. Preparation of the thermal insulations

The manufacturing process of the thermal insulations was shown in figure 1. For the preparation of the neat PU foams, a mixture of 8 g polyethylene glycol#400, 0.1 g dibutyltin dilaurate, 0.1 g triethanolamine, 1.4 g simethicone and 0.4 g deionized water were premixed in a beaker with constant stirring. Then, 20 g PM200 were added into the beaker and the mixture was rapidly stirred. The PU foams were cooled to the room temperature for future use. The preparation procedure for the bio-polyols PU foam was the same as that of the neat PU foam.

![Figure 1. Manufacturing process of the thermal insulations with the addition of bio-polyols and natural resources.](image)

**Table 1. Chemical compositions of wood fibers, bamboo fibers and rice husks.**

| Material type | Holocellulose (%) | Lignin (%) | Ash (%) | Toluene-ethanol extractives (%) |
|--------------|------------------|-----------|--------|---------------------------------|
| Wood fibers  | 73.76 ± 0.48     | 24.85 ± 0.82 | 1.66 ± 0.02 | 5.25 ± 0.17                     |
| Bamboo fibers | 68.16 ± 1.02     | 25.97 ± 0.42 | 2.52 ± 0.03 | 6.79 ± 0.49                     |
| Rice husks   | 64.95 ± 1.03     | 23.06 ± 0.17 | 14.13 ± 0.01 | 1.93 ± 0.08                     |
by replacing 50% of polyethylene glycol #400 with the liquefied polyols. The preparation of the bio-polyols was according to the method in a previous research [16]. The insulation with bio-polyols was designated as the LP foam insulation.

The preparation of natural resources reinforced bio-insulations was the same as the neat PU foam. The difference was that before the addition of the PM200, different proportions of natural resources (25%, 30% and 35%) were added into the premixture as stated above. After thoroughly mixing, 20 g PM200 were added into mixture with rapid stirring. The bio-thermal insulations were cooled to room temperature for curing. The thermal polyurethane insulations with the addition of wood particles, bamboo fibers, and rice husks were designated as WF PU foam, BF PU foam and RH PU foam insulation, respectively.

2.3. Mechanical strength
Samples for the compressive strength determination were cut with the size of 15 × 15 × 23 mm. Before the test, all the specimens were conditioned at 20 °C until reaching a constant mass. Specimens were then placed between the two parallel plates in order to have a homogeneous displacement and pressure. The test was conducted at a constant displacement of 25 mm.min⁻¹. The test was performed in triplicates and the average values of three specimens were recorded.

2.4. Apparent density
All the specimens for the apparent density determination were placed at the room temperature until reaching a constant mass. Six specimens for each group were prepared and tested. The apparent density (kg.m⁻³) was calculated with the formula below:

\[ \rho = \frac{W}{abc} \]

Where a, b, c (m) and W (kg) is the length, width, thickness, and the weight of the specimen, respectively.

2.5. Thermal conductivity
Thermal conductivity was conducted using a portable thermal conductivity meter (TC 300E, Xiaxi Ltd, Xian, China). Specimens were analyzed by introducing the thermal conductivity sensor inside the samples. Three specimens of each insulation group were determined at the room temperature.

2.6. Thermal stability
The thermal gravimetric analysis was performed with a thermal analyzer (Netzsch 409 PC, synchronous analyzer). Each sample of 3 mg was heated from room temperature to 800 °C with the heating rate of 10 °C.min⁻¹. The flow rate of the carrier gas (high-purity N₂) was 60 ml.min⁻¹.

2.7. SEM analysis
Scanning electron microscopy (SEM) was conducted using a scanning electron microscope (JSM-7500F, JEOL Ltd, Tokyo, Japan) to characterize the morphology of the neat PU foam insulation and the bio-thermal insulation. All the tested samples were coated with gold using a sputter coater (MC1000, Hitachi Ion Sputter) prior to the test.

3. Results and discussion

3.1. Physical-mechanical properties of the insulation
In order to evaluate the feasibility of the wood particles, bamboo fiber, rice husks and liquefied polyl on the reinforcement of the PU foams, the apparent density, compressive strength, thermal conductivity of the neat PU foams and the natural resources reinforced PU foams were determined, and the results are presented in figures 2–4. As shown in figure 2, the apparent density of all the reinforced PU foams insulation exhibited an increment trend with the addition of the natural resources, the LP PU foam insulation showed similar apparent density value to the neat PU foam insulation (41.861 kg.m⁻³). The apparent density of rice husk PU foam insulation exhibited the highest values, which could be ascribed to the smaller size of the rice husks employed.

The mechanical properties of the polyurethane foams could be influenced by various factors, such as apparent density, cell structure characteristics and the type of filler. Strength requirement such as compressive strength of the building insulation is considered very important. The incorporation of wood particles, bamboo fibers and rice husks significantly improved the compressive strength of the thermal foam insulation. As the addition of the fillers increase, the compressive strength of all the PU foams were significantly increased, which showed similar trend to that of the apparent density. For comparison, the RH PU foams insulation exhibited the highest compressive strength, indicating that the rice husks had good interfacial compatibility combined with
polyurethane matrix. The compressive strength of LP PU foams was relatively low compared to the natural fibers reinforced foam insulation. This is mainly because natural fibers possessed internal mechanical strength and improved integral strength of the foams [17].

The thermal conductivity of the PU foams is related to the thermal factors such as convection heat transfer, radiation heat transfer, and the conduction of solid and air contribute. The thermal conduction is related to the structure and density of PU foam, while the radiation is affected by the cell size of the PU foam [18]. Generally, for the heat transfer evaluation on the PU foams, the convection and radiation heat transfer can be neglected [8]. In this present study, the thermal conductivity was determined and discussed for the natural fiber reinforced PU foams.

As can be seen from figure 3, the neat PU foams and LP PU foams showed a low thermal conductivity. While the thermal conductivity of the WF PU foams, BF PU foams and RH PU foams was relatively high. The thermal conductivity values of the natural fiber reinforced PU foams were in the range of 0.045–0.065 W.m⁻¹K⁻¹, revealing that the thermal conductive capacity of the fiber reinforced PU foam was simultaneously increased as the compressive strength was improved. The thermal conductivity of RH PU foams was the highest. It was ascribed to smaller cells with thick walls that realized more heat transfer, as smaller size of the rice husks also improved their interfacial compatibility with the PU matrix [5]. However, based on the qualification that a material is qualified as insulating material when its thermal conductivity is less than 0.1 W.m⁻¹K⁻¹ [19], the slight increase in the thermal conductivity values of the natural fiber reinforced PU foams induced by the
addition of the fibers will not affect their application as thermal insulators since their thermal conductivity values were still much smaller than 0.1 W.m$^{-1}$K$^{-1}$. For comparison, the natural fiber reinforced PU foams in this research has lower or comparable thermal conductivity values with the bio-based thermal insulations as reported in previous researches [12–15, 20].

### 3.2. Microstructure of the foam insulation

The microstructure of the neat PU foam and the LP PU foams exhibited a honeycomb structure and the cells were well assembled (figure 5). The bamboo fiber reinforced PU foam insulation still showed good cell structure, and the fibers had good interfacial adhesion with the polyurethane cell walls. The addition of wood particles induced alteration in the cell assembles, resulting in the formation of un-integrity cells. The microstructure of the foam insulation revealed that the natural fibers might play as framework providing support strength for the whole material. Meanwhile, the original honeycomb structure of the PU foam rendered the low thermal conductivity values of the insulation samples. Therefore, the good incorporation of the mechanical supporting fibers as skeleton into the honeycomb structure polyurethane foams as matrix generated strong strength at low density for the fiber reinforced PU foam insulation.

**Figure 4.** The thermal conductivity of the neat PU foam insulation, LP foam insulation and the natural resources reinforced foam insulations.

**Figure 5.** Microstructure of (a) the neat PU foam insulation, (b) LP foam insulation, (c) WF PU foam insulation, (d) BF PU foam insulation, and (e) RH PU foam insulation.
3.3. Thermal stability of the insulation

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the neat PU foams and the reinforced PU polyurethane foams are shown in Figure 6. The DTG curves of the neat PU foam insulation showed there were two main degradation stages, with the maximum mass loss temperature at 351 °C and 513 °C, respectively. The first stage of degradation occurred between 150 °C and 400 °C, which was related with the dissociation of urethane bonds in polyurethane foam. The second stage of degradation occurred between 400 °C and 600 °C ascribing to the decomposition of polyol soft segments in polyurethane foam [21].

The thermal characteristics of RF PU foam, BF PU foam and WF PU foam were similar. All the natural fiber reinforced PU foam insulation presented one main stage of degradation between 250 °C and 500 °C. Compared with the neat PU foam insulation, the incorporation of rice husks, bamboo fibers and wood particles shifted to a lower temperature when the mass loss was below 5%, which may be ascribed to the losses of moisture existing in the inherent structure of the natural fibers [22–24]. The result was consistent with the previous research of Mosiewicki et al (2009) [11]. The char yield of RH PU foam insulation was the highest, which was ascribed to high content of minerals such as Si, Ca, Mg, Mn in rice husk, which was difficult to decompose [25–28].

As for the LP PU foam, two main degradation stages were observed in the DTG curves, with the maximum mass loss temperature at 341 °C and 416 °C, respectively. Similar to the neat PU foam, the decomposition of the rigid segments in polyurethane resulted in the first degradation stage of LP PU foam. The temperature corresponding to the second maximum mass loss was lower than the neat PU foam, which could be explained...
that the liquefied polyols contained many hydroxyl-containing components with relatively low molecular weight, which was easier to decompose than the neat PU foam.

4. Conclusions

In this work, the lightweight thermal polyurethane insulations with wood and bamboo fibers, rice husks were prepared. As the addition content of the natural fibers into the PU matrix resulted in the significant increase in compressive strength. The thermal conductivity values of the fiber reinforced PU foams were in the range of $0.045 - 0.065 \text{ W.m}^{-1}\text{K}^{-1}$, revealing that the thermal conductive capacity of the fiber reinforced PU foam was suitable for application as building thermal insulation with improved compressive strength. The SEM images demonstrated the original honeycomb structure of the PU foam rendered the low thermal conductivity values of the insulation samples. The thermal stability analysis showed that compared with the neat PU foam, the biothermal insulations with the addition of bio-polyols and natural fibers were both difficult to decompose with high char residue content.

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