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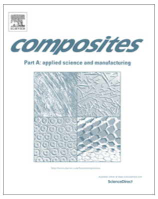

Semi-rigid biopolyurethane foams based on palm-oil polyol and reinforced with cellulose nanocrystals

Xiaojian Zhou [a], Mohini M. Sain [a,b], Kristiina Oksman [a,b,*]

[a] Division of Materials Science, Composite Centre Sweden, Luleå University of Technology, 971 87 Luleå, Sweden
[b] Centre for Biocomposite and Biomaterials Processing, Faculty of Forestry, University of Toronto, 33 Willcocks Street, Toronto M5S 3B3, Canada

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ABSTRACT

In this study, water-blown biopolyurethane (BPU) foams based on palm oil were developed and cellulose nanocrystals (CNC) were incorporated to improve the mechanical properties of the foams. In addition, the foams were compared with petroleum polyurethane (PPU) foam. The foam properties and cellular morphology were characterized. The obtained results revealed that a low-density, semi-rigid BPU foam was prepared using a new formulation. CNC as an additive significantly improved the compressive strength from 54 to 117 kPa. Additionally, cyclic compression tests indicated that the addition of CNC increased the rigidity, leading to decreased deformation resilience. The dimensional stability of BPU foams was increased with increasing CNC concentration for both heating and freezing conditions.

Therefore, the developed BPU nanocomposite foams are expected to have great potential as core material in composite sandwich panels as well as in other construction materials.

1. Introduction

Polyurethane (PU) foams as core material for sandwich composite laminates have been widely used in many applications due to their mechanical properties, light weight, versatility and insulation performance [1]. PU foams are usually prepared by the reaction of petroleum-based polyol with isocyanate. In general, catalysts, surfactants and blowing agents are employed to regulate the properties and the cell morphology. Commercial isocyanates and polyols for PU foam preparation are derived from petroleum, which is expensive and toxic, and are based on non-renewable resources. From the used raw materials, up to now, only the polyol can be partially replaced or even fully replaced using bio-polyols, especially starch polyols, sugar polyols, natural oil polyols or liquefaction products [2–5].

The most promising commercial bio-polyols used for PU foam preparation are natural oil polyols, such as soybean oil polyol [6,7], castor oil polyol [8] and palm oil polyol [9–11]. These materials are not only abundant and renewable resources, but are also easily chemically modified, resulting in excellent properties and relatively low cost [12,13]. There is, however, one distinct drawback with bio-polyols for foam preparation and that is that their low mechanical strength, cannot meet the demands of specific applications [7]. As composites are being used in an increasing number of applications, improvement in the mechanical properties is of interest. Consequently, there has been a growing interest in wood waste, clays, cellulose nanocrystals and nanofibers, nanochitin and cellulose-fiber-reinforced PU foams [14–24]. It was found that the mechanical strength and Young's modulus can be significantly improved, cell morphology and cell size distributions were optimized, and thermal behavior was influenced using very low amounts of these additives and reinforcements.

Cellulose nanocrystals (CNC) have a high surface area, high aspect (length/diameter) ratio, unique morphology, low density, high specific strength and modulus, and low coefficient of thermal expansion. Owing to these features, cellulose nanocrystals have attracted great interest during recent years [21,24–30]. Up to 10% of CNC addition in reinforced polyol-based polyurethane foams was studied by Li et al. [21]. Only few publications are found regarding the effect of nanocellulose as reinforcement for bio-polyol based PU foams, especially with regard to bio-polyol with very low hydroxyl value and functionality for PU foam preparation [19,31].

In this study, water-blown semi-rigid BPU foams were developed using a foaming formulation in the presence of a blowing agent, catalysts and surfactants. The influence of CNC on the foam performance was investigated using scanning electron microscopy

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[*] Corresponding author at: Division of Materials Science, Composite Centre Sweden, Luleå University of Technology, 971 87 Luleå, Sweden. Tel.: +46 920 49 33 71.

E-mail address: kristiina.oksman@ltu.se (K. Oksman).

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(SEM), universal compression testing and thermogravimetric analysis (TGA). A standard petroleum polyol PU foam was prepared and used as a reference foam.

2. Materials and methods

2.1. Materials

Palm oil polyol (Polygreen 3110) with 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 supplied by PolyGreen, Malaysia, and used as polyol for BPU foam preparation. Petroleum polyol (Polyol 3165) with a hydroxyl value of 165 mg KOH/g, viscosity of 350 mPa s and functionality of 3 was supplied by Perstorp, Sweden, for PPU foam preparation.

Commercial pMDI (polymeric methane diphenyl isocyanate) (ISO pMDI 92140) with –NCO content of 31%, viscosity of 250 mPa s and functionality of 2.7 was purchased from Lagotech AB, Sweden.

Freeze-dried cellulose nanocrystals (2012-FPL-CNC-043) hydrolyzed from cellulose pulp were supplied by USDA Forest Service, Madison, USA.

Laboratory-grade chemical agents such as catalysts (triethylamine and dibutyltin dilaurate) and surfactants (polydimethyl siloxane and silicone oil) were obtained from VWR and Sigma Aldrich, Germany. Distilled water was used as blowing agent.

2.2. Foaming process

The foams were prepared according to the process presented in Fig. 1. First, the polyol and the CNC were mixed for 2 min under mechanical stirring in a plastic beaker. When the mixture became homogeneous, catalysts and surfactants were added and mixed for 30 s, and then pMDI was added and vigorously stirred for 20 s. The blowing agent (water) was added in the last step, and mixed for 10 s with the same stirring speed, and then the foaming began after a short time. Finally, white, semi-rigid foam was obtained within a few seconds. Neat polyurethane foams were prepared using a similar foaming process in the absence of CNC. The foam was removed from the foaming beaker after 1 h and allowed to post-cure at room temperature for 1 week prior the characterization.

The formulations used are shown in Table 1 and to ensure the index for the foam formulation was maintained at 1.5, 126 and 150 phr of pMDI was used for BPU and PPU respectively. In the formulation it is assumed that the water, added as blowing agent, will also react with pMDI and thus is included in the calculation of the –NCO/–OH index. BPU foams are based on the bio-polyol with pMDI and PPU foams are based on the petroleum polyol with pMDI. The parts of each component are based on per hundred parts of the polyol, designated as phr. Thus, BPU0, BPU1, BPU2, BPU4 and BPU8 are referred to as 0, 1, 2, 4 and 8 phr of CNC.

Foams were characterized in terms of foaming behavior, bulk density, surface morphology, cell size, compression behavior, dimensional stability, water uptake and thermal stability. It is noted that all the measurements were made in the direction parallel to the foaming rise direction.

Table 1
Foaming formulation for semi-rigid BPU nanocomposite foams and PPU foam.

Components	Parts of component (phr)	Role
Polyol	100	Base of resin
pMDI	$126\ (150_{PPU})$	Reactive prepolymer
Triethylamine	2	
Dibutyltin dilaurate	2.6	
Polydimethyl siloxane	5	Surfactant
Silicone oil	5	
Water	4	Blowing agent
CNC	1, 2, 4, 8	Reinforcement
Index (–NCO/–OH)	1.5	Both materials

2.3. Characterization

The cream time (the time from pouring the isocyanate into the polyol blend until initiation of foaming), end of rise time (the time from pouring the isocyanate into the polyol blend until full expansion of foaming) and tack-free time (the 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 foaming process.

The foams were cut into squares measuring 25 × 25 × 25 mm using a sharp knife. Samples were carefully weighed using an analytical balance with a precision of 0.0001 unit and the dimensions were measured using a digital vernier caliper with a precision of 0.01 unit. The bulk density of the foams in kg/m^3 was simply calculated as a weight/volume ratio. The density of each sample was ascertained using the average value of five specimens.

Samples were frozen at $-25\,^{\circ}C$, cut into 10 × 10 × 5 mm pieces with a sharp knife and coated with gold prior to the morphology study using scanning electron microscopy (SEM), JEOL JSM-6460LV, Japan with an acceleration voltage of 10 kV. The cell size was defined by feret diameter (the longest distance between any two points along the cell boundary in one cell) [20]. The cell sizes were manually measured using SEMAfore image analysis. For each specimen, the average cell size was calculated by averaging several tens of individual cells.

The compressive strength of the foams was tested using a universal testing machine (Instron 4411) equipped with a 500 N load cell. The testing was carried out with a constant crosshead speed of 2.0 mm/min and decompression was done at the same rate when the deformation reached 40% of the original thickness. Then, the foam was recompressed when the crosshead reached the initial position. Four repetitions of the cyclic loading for each sample were carried out. The maximum compressive strength (when the deformation reached 10% at the first cycle) and stress–strain curve behavior for all cyclic curves were evaluated. The specimen dimensions were 50 × 50 × 25 mm, the thickness was parallel to foam rising direction, and the samples were conditioned at 20 °C and in 23% RH for 24 h prior the testing. Three samples for each formulation were measured and the average value is reported.

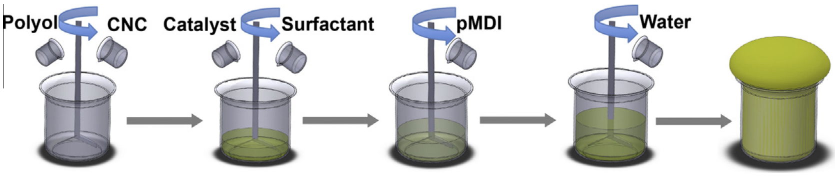

Fig. 1. Schematic diagram of the lab-scale foaming process of BPU foam and nanocomposite foams. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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