



Dispersion and reinforcing effect of carrot nanofibers on biopolyurethane foams



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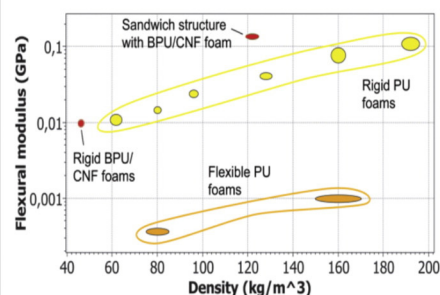
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HIGHLIGHTS

- Semirigid castor oil based PU foams with very low bulk density ($<50 \text{ kg/m}^3$) were successfully prepared.
- Carrot nanofibers were used as reinforcement to improve cell wall rigidity.
- Prepared nanocomposite foams are performing in the level of commercial PU foams.
- Foams were shown to be excellent core for biocomposite laminates.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, carrot nanofibers (CNF) were used to enhance the performance of biobased castor oil polyol polyurethane nanocomposite foams. A method of dispersing CNF in the polyol was developed and the foam characteristics and CNF reinforcing effect were studied. Co-solvent-assisted mixing resulted in well-dispersed CNF in the polyol, and foams with 0.25, 0.5 and 1 phr CNF content were prepared. The reinforced nanocomposite foams displayed a narrow cell size distribution and the compressive strength and modulus were significantly elevated and the best compressive strength and modulus were reached with 0.5 phr CNF. Similarly, the modulus of the solid material was also significantly increased based on theoretical calculations. When comparing the foam performance, compressive strength and stiffness as a function of the density, the nanocomposite foams performs as commercial rigid PU foam with a closed cell structure. These results are very promising and we believe that these foams are excellent core materials for lightweight sandwich composites.

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1. Introduction

During the past 10–15 years, the utilization of bioresources to prepare polyurethane (PU) foams has attracted attention because of the

increasing concerns about environmental problems, replacement of fossil resources and the low price and abundant supply of natural vegetable oils and biomass by-products [1–7]. However, the prepared biobased polyurethane (BPU) foams are not yet suitable for commercial applications because they do not meet the industrial standard requirements for compression strength ($\geq 180 \text{ kPa}$) [1,4]. Therefore, enhancing the properties of BPU foam has been and continues to be of interest. Many different strategies have been used to improve the properties of the foams.

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One strategy is to use different vegetable oils with different reactivity, where the polyol is modified to a higher hydroxyl value factor [3,4]. Another is the optimization of the isocyanate index [5]. However, the resulting increase in mechanical strength is limited by the optimization of the formulation and mass proportion. Different reinforcements, to improve the mechanical properties of the foams, have also been tested [8–15]. Gu et al. [9] tested hardwood pulp and Silva et al. [10] cellulose residue from pulp industry but the use of these fibers did not result in improved mechanical properties. Mosiewicki et al. [12] added wood flour, 5, 10 and 15 wt% into the castor oil based PU, but the mechanical properties of the foam decreased with the increased wood flour content. Zhu et al. [8] used cellulose fibers with a smaller size and reported an increase of compressive strength of soy-oil based foam from approx. 110 kPa to 170 kPa. Luo et al. [15] used lignin as reactive reinforcement in BPU foams and showed that the addition of 10 wt% lignin improved the foam structure as well as its mechanical properties.

Nano-sized reinforcements have also been of interest, since their small size should allow reinforcement of the cell walls and struts of the foam resulting in better compressive and flexural properties. Zhu et al. [8] reported that the use of surface modified montmorillonite nanoclay into a soy-oil BPU foam improved its mechanical properties however it increased the density of the foam. Biobased nanoreinforcements such as cellulose nanofibers [16] and nanocrystals [17–21] have also been tested. Typically the cellulose nanomaterials used have been freeze-dried and then mixed with the polyol. However, it is difficult to disperse the dried nanocellulose into the hydrophobic polyol. Several procedures have been tested to improve the dispersion. Li et al. [17] dispersed freeze-dried cellulose nanowhiskers (crystals) first in dimethylformamide (DMF) solvent by sonication and then combined this mixture with polyol and the solvent was removed using vacuum. Improved compression strength and stiffness as well as a more homogenous cell size and improved thermal stability were reported. To avoid freeze drying of the nanocellulose and the use of the solvent, the same authors [18] directly mixed aqueous nanocellulose suspension and polyol, followed by removing the water under vacuum, and then mixed in other foaming components. This procedure resulted in better dispersion and further improved properties. Cordero et al. [21] used a combination of sonication and homogenization processes to disperse the cellulose nanocrystals (CNC) in a polyol but unfortunately they did not report any compressive strength or modulus values for the prepared foams. However in the attempts to disperse the nanocelluloses in polyol, detailed information of the dispersion of nanocellulose in polyol has not been shown in these studies [16–21].

We showed in an earlier study [22] that carrot nanofibers (CNF), separated from residue from raw juice production, have similar and even better mechanical properties to many other cellulose nanofibers. These carrot nanofibers have been shown to be more easily re-dispersible, are low in cost and can be separated more energy efficiently than many other raw materials. These reasons make carrot nanofibers very interesting and promising material for use in the strengthening of biopolymer composites [22].

In this study, the dispersion ability of carrot nanofibers with different concentrations in polyol resin was studied. Furthermore, the effect of the CNF concentration for the foam morphology; cell size distribution, porosity and closed cell content were studied. The compressive mechanical properties of the prepared foams were measured, and the modulus of the solid material in the foam was calculated. Finally, the foam performance was compared with commercial PU foams.

2. Experimental

2.1. Materials

A castor oil polyol, Jagropol-400, Jayant Agro-Organics Ltd., India, with a hydroxyl value of 350 mg KOH/g, a viscosity between 700 and 1100 mPa·s, and a functionality of 3 was used. A commercial isocyanate,

4,4'-polymeric methane diphenyl isocyanate, (ISO pMDI 92140) with a functionality of 2.7, a –NCO content of 32% and a viscosity of 250 mPa·s, was purchased from Lagotech AB, Sweden.

A catalyst, *N,N*-dimethylcyclohexylamine (DMCHA) was purchased from VWR, Sweden. A polyether-modified polysiloxane surfactant, TEGOSTAB® B8433, was purchased from Evonik, Denmark. Distilled water was used as a blowing agent.

Carrot nanofibers (0.5 wt% concentration in water) consisting of mainly cellulose, were separated from bleached raw juice residue. The preparation of carrot nanofibers and their characteristics are described elsewhere by Siqueira et al. [22].

2.2. CNF dispersion and nanocomposite foam preparation

2.2.1. CNF dispersion in polyol resin

In general, the water in CNF dispersion directly influences the foaming process, and the aqueous dispersion of CNFs in polyol is difficult. Therefore, a co-solvent, dioxane, was used to assist CNF dispersion in polyol resin. This co-solvent assisted method was carried out at increased temperature and high shear to form a mutually miscible system of water, CNFs, dioxane and polyol, from which the volatiles (water and dioxane) were gradually removed, transferring the CNFs from the water phase to the polyol phase, to obtain well-dispersed CNFs in polyol. In this method, one third of the polyol and CNF suspension were mixed using an Ultra-Turrax homogenizer at 10,000 rpm for 5 min. The water-CNf-polyol mixture was then transferred onto a hotplate (with magnetic stirrer) set at a temperature of 70 °C and stirring at a constant speed of 600 rpm. The water was slowly evaporated and gradually replaced with dioxane. It was observed that in the presence of dioxane, which is miscible with both water and polyol, a relatively transparent mixture is formed at high temperature and shear stirring. This transparency implies that the components of system are compatible with each other, and the high temperature and shearing ensured that the CNFs remained dispersed even when the volatiles were removed. After 2 h, the remaining polyol was added in three equal portions at intervals of 1 h. During this period, the dioxane added was twice the amount of the polyol. Then, the temperature was increased to 90 °C to evaporate the remaining water and dioxane from the mixture under stirring. Finally, a transparent dispersion was achieved, indicating good dispersion of the CNFs in the polyol, which was confirmed by optical microscopy. This CNF dispersion was used to prepare nanocomposite foams.

2.2.2. Preparation of nanocomposite foams

The basic formulation of the BPU foams was castor oil polyol, catalyst 1 phr, surfactant 2 phr and water as blowing agent 3.5 phr. The amount of different components in phr (per hundred resin) is based on the polyol weight. To this basic formulation, dispersions of CNF at different concentrations (0.25, 0.5 and 1 phr) were mixed using mechanical stirring at room temperature for 30 s. Then, the pMDI was added and stirred for a further 20 s. The neat BPU and BPU-nano-composite foams were obtained within a few seconds. The foams were removed from the mold after 30 min and cured under ambient room conditions for 1 week prior to sample preparation. The pMDI index (moles of NCO groups/mol of OH groups) was adjusted to 1 for each of the foams.

2.3. Characterization

The dispersion of the CNFs in the polyol mixture was studied using a polarized optical microscope, Nikon Eclipse LV 100V (Japan). The viscosity of the CNF and polyol resin mixture was measured at 25 °C using a Vibro viscometer SV-100 (0.3–10,000 mPa·s), Japan.

2.3.1. Cell morphology

The microstructure of the foams, parallel to the rising direction, was studied under a scanning electron microscope (SEM) (JEOL JSM-IT 300LV, Japan) using an acceleration voltage of 10 kV. Foams were

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