Dispersion and reinforcing effect of carrot nanofibers on biopolyurethane foams

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HIGHLIGHTS

• Semirigid castor oil based PU foams with very low bulk density (<50 kg/m³) 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

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 (≥ 180 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.
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 bio-based 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 polyester-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-CNФ-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 transpar-
fractured after immersion in liquid nitrogen for 1 min, and the resulting cross-sections were sputter coated with gold to avoid charging. The cell sizes were manually measured using SEMAfore image analysis and determined by the Feret diameter. For each material, the average cell size was calculated from >100 measurements.

2.3.2. Bulk density

The densities of the foams in kg/m$^3$ were obtained as the ratio of weight to (geometric volume) of a cubic specimen with dimensions 30 × 30 × 30 mm, according to ASTM D1622–08.

2.3.3. Percentage of closed cell content

A pycnometer, AccuPyc II 1340 (10 cm$^3$ size sample chamber), with nitrogen gas was used to determine the percentage of open cell content ($C_o$) in the foams, according to a modified version of ASTM D2856 provided by Micromeritics [23](Application Note 93). The density of solid polyurethane ($\rho_s$) was obtained from a solid polyurethane preparation without foaming agent, and then the percentage of solid (cell wall and cell strut) volume occupied in BPU foam was calculated using the following expression:

$$S_v = \left( \frac{m}{\rho_s v} \right) \times 100,$$

where m is the mass of the foam specimen, and v is the geometric volume of the related foam specimen. Thus, the percentage of closed cell content was calculated using the following equation:

$$C_c = 100 - C_o - S_v.$$

2.3.4. Porosity measurement

The porosity ($\Phi$) was calculated from the bulk density ($\rho_b$) of the foam and the solid polyurethane density ($\rho_s$), as follows:

$$\Phi = 1 - \left( \frac{\rho_b}{\rho_s} \right).$$

2.3.5. Mechanical properties

The compressive properties of the foams, were measured using a universal testing machine (Instron 4411) equipped with a 5 kN load cell and a constant load rate of 2.5 mm/min. The specimens were cut into $51 \times 51 \times 26$ mm pieces, with the thickness parallel to the foam rising direction. All samples were conditioned at 21 °C and 45% RH for at least 40 h prior to the testing. All of the tests were performed according to ASTM D1621. All measurements were performed parallel to the rising direction of the foam.

3. Results and discussion

3.1. CNF dispersion in polyol resin

Polarized optical microscopy was used to study the dispersion of the CNF in the polyol resin with and without dioxane co-solvent; the light phase is carrot nanofibers. Fig. 1a shows the mixture with some large CNF aggregates and Fig. 1c the same mixture with the co-solvent, indicating successful CNF dispersion in the polyol. Fig. 1b shows the mixture with 0.25 phr, and Fig. 1d shows the mixture with 1 phr. The mixture with 1 phr is not as well dispersed as the lower-concentration mixtures, showing some nanofiber aggregation but not at same level as in the Fig. 1a.

The co-solvent assisted method is demonstrated to be able to disperse the hydrophilic carrot nanofibers well into the hydrophobic

Fig. 1. Polarized optical microscopy images of CNF dispersion in polyol resin (light phase CNF) a) polyol and 0.5 phr CNF without co-solvent, showing CNF aggregates; b) polyol and 0.25 phr CNF with co-solvent; c) polyol and 0.5 phr CNF with co-solvent; d) polyol and 1 phr CNF with co-solvent.
polyol. The increased dispersion of the CNFs in the polyol influenced
the shear resistance force. The viscosity was slightly increased with
0.5 phr CNF and much more dramatically increased with 1 phr CNF,
from 1087 mPa·s for the polyol resin to 6102 mPa·s for polyol
resin with 1 phr CNF, which can hinder the foaming. Prolongo et al.
[24] reported similar tendency in a previous study, in which carbon
nanotubes and carbon nanofibers were dispersed in an epoxy resin:
a mixture with a higher viscosity was obtained.

3.2. Behavior of CNF-reinforced BPU foams

The appearance and microstructure of prepared BPU foam and
CNF-reinforced BPU nanocomposite foams are shown in Fig. 2. All
of the foams are white and uniform, with no obvious visual differ-
ences due to the addition of CNFs. The morphology and cellular
shape of the foams with increasing CNF content remain very similar,
as shown in Fig. 2. Most of the cells are closed cells, and of spherical
shape. Some cells in these images are brighter because of the folded
cell edge.

Fig. 3 shows more detailed images of the cell struts and cell walls
of the foams. The cell struts and cell walls of nanocomposite foams
with low proportions of CNF (0.25 and 0.5 phr) are very similar to
the neat BPU foam, indicating that these low CNF contents are very
uniformly dispersed and show good interaction with the BPU poly-
mmer, compared with 1 phr CNF, where some dots and projections
become detectable on the cell wall and a coarse surface can be seen
in the cell struts. These features can be attributed to CNFs embedded
in the cell struts and cell walls and are believed to be aggregates. In
general, the good dispersion of nanofibers in polyol resin and the
uniform distribution of nanofibers in the polymer matrix could play
important roles in improving the compressive strength and modulus
of the resulting nanocomposite foams, as will be discussed in detail
later. The cell strut area and Feret diameter distributions of BPU
foams with and without CNF are illustrated in Fig. 3.

The cell size distribution exhibits a slightly smaller range with in-
creasing CNF content, resulting in a more uniform foam and smaller
cell size compared to the neat BPU foam. This feature is also con-
firmed by the SEM images in Figs. 2 and 3. It is possible that the CNFs act as nu-
cleating agents for the cells and therefore have a positive effect on uni-
form cell size distribution and decreased cell size.

3.3. Density, porosity and closed cell content

The densities of the nanocomposite foams are summarized in
Table 1. No significant changes in the foam density are observed with
the addition of the CNFs.

The porosity and closed cell content are also listed in Table 1. The
porosity is approximately 96% for all of the foams, and the closed cell
content is almost 90%, except for the nanocomposite foam with
0.5 phr CNF, which was slightly lower, approximately 79%.
3.4. Mechanical properties

The compressive strength and modulus of the prepared nanocomposite foams are shown in Fig. 4. The compressive strength and modulus of the neat BPU foam are 241 kPa and 3.5 MPa, respectively. These properties are very good if compared, for example, with our earlier results with palm oil based BPU foams strength 54 kPa and modulus 1 MPa [20]. The properties are further improved with the addition of CNF, the highest compressive strength and modulus was achieved at 0.5 phr CNF content. The compressive strength increased from 241 to 307 kPa and the modulus from 3.5 to 5.7 MPa. In addition, foam with higher CNF content was more ductile, possibly caused by a fiber bridging effect. However, when the proportion of CNF reached 1 phr, the compressive strength and modulus slightly decreased, though remaining higher than the native BPU foam. This slight decrease is expected to be due to aggregation of the CNF.

Siqueira et al. [22] demonstrated that nanopaper produced using carrot nanofibers exhibits excellent mechanical properties, i.e., a high elastic modulus of 13.3 GPa and high yield strength of 175 MPa. In addition, the size of cellulose nanofibers is small enough to strengthen the cell walls in the foams. The high specific surface area of cellulose nanofibers also contributes to the composite properties because of the reaction between the −OH groups of cellulose nanofiber and the isocyanate groups of pMDI. To determine the effect of density on foam modulus, the following equation for the modulus evaluation is given by Gibson and Ashby [25]. In closed cell polyurethane foam, the Young’s modulus of the foam includes three contributing factors: edge bending, face stretching and gas compression.

\[
\frac{E_s}{E_s} = \frac{\phi_\text{edge}}{E_{\text{s}}} + \frac{\phi_\text{face}}{E_{\text{s}}} + \frac{p_0(1-2\phi_s)}{E_s(1-\rho_s/\rho_s)}
\]

where \(\phi_\text{edge}\) and \(\phi_\text{face}\) are the edge bending and face stretching, respectively; \(p_0\) is the gas compression, which is negligible for the closed rigid foam. Thus, the above equation is simplified to

\[
\frac{E_s}{E_s} = \frac{\phi_\text{edge}}{E_{\text{s}}} + (1-\phi) \frac{\phi_s}{E_{\text{s}}}
\]

where \(E^*\) and \(E_s\) are the modulus of the foam and solid material, respectively; \(\rho^*\) and \(\rho_s\) are the bulk density of the foam and the density of the solid material, respectively; and \(\phi\) is the volume proportion of the solid material in the foam, \((1-\phi)\) is the remaining fraction that is in the cell faces. \(\phi\) is taken as 0.8, which is typical for rigid polyurethane foams [26]. The calculated modulus values of the foam and skeleton material (solid material) based on Eq. (5) are shown in Table 2.

The modulus of the nanocomposite foams and the estimated modulus of the solid material increases significantly with increasing proportion of CNFs up to 0.5 phr. The estimated modulus of the solid material increased by 37% for this material. This result indicates that the reinforcement of the foam modulus is not only due to the foam density but also due to the increase in modulus of the solid material.

3.5. Performance of nanocomposite foams

Fig. 5 shows how the mechanical properties of the foams of the most successful CNF reinforced BPU foams produced in this study, the 0.5 phr CNF foam, compared to commercial PU foams. The addition of the CNF brings both the modulus and the strength of the BPU based foams in line with the commercially available rigid foams. Thus, when density is considered, these nanocomposite foams show a commercially viable performance with regards mechanical properties.

Their use in a sandwich structure was also investigated by measuring the flexural stiffness of the foams with and without a skin of paper impregnated with epoxy (Fig. 6). The chart shows that the flexural properties of the foams are in line with those of rigid PU foams, as was the case for the compressive properties of the nanocomposite foam. It also shows that sandwich structure can be successfully made from the foams and that as expected, enhances the flexural modulus.

4. Conclusions

Rigid biopolyurethane foams were successfully reinforced by achieving good dispersion of carrot nanofibers (CNF) in castor oil polyol followed by a free-rising foaming method with water as blowing agent.
The addition CNFs up to 0.5 phr improved the compressive strength and modulus of the foams with no significant effect on the density, porosity or closed cell content. Estimations from the Gibson's equation showed that this improvement is due to increase of the solid material modulus when CNF is added.

The prepared BPU nanocomposite foams are very promising because this material has a high strength with a lower density compared to other many other biobased PU foams and can also compete with commercial PU foams with similar density.

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