



The preparation and characterization of polyurethane reinforced with a low fraction of cellulose nanocrystals

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ABSTRACT

Cellulose nanocrystals (CNC) produced from renewable cellulosic feedstocks have been used in polymer reinforcement, resulting in significant enhancements to mechanical properties. In this study, a series of CNC reinforced polyurethane (PU) nanocomposites were manufactured and tested for their rheological, thermo-mechanical, mechanical and abrasion properties. First, stable polyol-CNC suspensions were prepared using a combination of water and 1,3-propanediol as dispersing solvent. These suspensions were then combined with isocyanates to produce CNC reinforced PU samples. Rheological testing of the uncured polyol-CNC-isocyanate liquid suspension indicated the formation of a pervading network between CNC particles. The thermo-mechanical properties of the CNC reinforced nanocomposites were significantly improved compared to unreinforced PU, as measured by differential scanning calorimetry and dynamic mechanical analysis. With the addition of 0.5% CNC by weight to the PU resin, the glass transition temperature increased 10 °C. Furthermore, this CNC reinforcement of the PU resin yielded an increase in the tensile strength, Young's modulus, elongation at break, and abrasion resistance of approximately 30%, 55%, 70%, and 40%, respectively. These increases are likely due to a combination of increased cross-linking density within the PU network, arising from PU-CNC molecular interactions, and the reinforcing effect of the CNC.

1. Introduction

Since their discovery, cellulose nanocrystals (CNC) have attracted significant attention due to their exceptional mechanical properties, their large aspect ratio, and their origins in abundant cellulosic biomass. These properties make them excellent candidates as reinforcements in multifunctional biobased nanocomposites [1–3]. However, in order to produce effective nanocomposites, homogeneous dispersion of CNC into the polymer matrix is essential. In practise, it is found that CNC tends to agglomerate in the majority of organic solvents and polymer matrices due to its high surface area and large inter-particle attraction. Such agglomeration issue poses a major challenge for nanocomposite production, usually resulting in poor mechanical properties due to non-uniform stress distributions within the composite material.

CNC is typically prepared by acid hydrolysis of cellulose fibers using either sulfuric acid or hydrochloric acid [3]. For CNC produced through

sulfuric acid hydrolysis, water is the preferred processing medium due to the contribution of negatively charged sulfate groups (OSO_3^-) which facilitate the formation of stable aqueous CNC suspensions. These suspensions can be mixed with hydrosoluble polymers; then after evaporating the water, films can be obtained that retain the excellent CNC dispersion [4–7]. However, this method is only applicable to hydro-soluble polymers which severely limits its application [8–10].

Recently, it has been found that CNC can be dispersed in polar organic solvents, such as dimethylformamide (DMF) or dimethylsulfoxide (DMSO), by vigorous mixing and intensive ultrasonic treatment [11–15]. This approach offers a potential method to incorporate CNC into hydrophobic polymer matrices such as polyurethanes (PU) through incorporating CNC into the polyols. The chemistry of PU is complicated by the inclusion of many components other than the major building blocks of polyols and isocyanates, such as catalysts, chain extenders, surfactants and water (in the case of PU foam) etc. However, the polyol structure is critically important in determining the properties of the

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final PU. For example, Marcovich et al. [12] studied nano-reinforced PU by incorporating CNC into petroleum polyether polyols using DMF as a medium, and then further reacting the mixture with polymeric diphenylmethane diisocyanate (pMDI). They reported that the tensile modulus of the PU increased significantly at very small reinforcement loadings, and that a reaction occurred between the CNC and isocyanate leading to an increase in the glass transition temperature (T_g) of the PU matrix. However, the use of DMF is very limited for large scale operations due to potential toxicity issues. In addition, due to the high boiling point of DMF (153 °C) as well as the strong hydrogen bonding between the N atom of the DMF molecules and hydroxyl group of the CNCs, it is difficult to be removed completely using conventional drying process. The solvent residue will have detrimental effects on the properties of the final materials. Most recently, Curtis et al. [16] found that a stable 1,3-propanediol-CNC suspension could be achieved through solvent exchange with water, and that CNC could be efficiently dispersed into canola oil based polyols after removal of 1,3-propanediol under reduced pressure. From this study, transmission electron microscopy (TEM) showed that individual CNC particles were homogeneously dispersed within the PU matrix. The addition of only 0.5% CNC by weight resulted in an increase in the T_g of the PU nanocomposite by 6 °C compared to the pure PU. Furthermore, the Young's modulus and Taber abrasion resistance also increased by approximately 10% and 25%, respectively. Unfortunately, during this process water had to be removed from the diol-CNC aqueous suspension prior to mixing with the canola based polyols, since these types of polyols are relatively hydrophobic and immiscible with water (forming emulsions). In contrast, petrochemical based polyether polyols can often absorb up to 15% water by weight [17]. As such, the need for a water removal step in the PU-CNC nanocomposite production process could possibly be eliminated, ultimately simplifying the procedure and reducing production costs. Furthermore, this allows for the production of stable polyol-CNC blends which can potentially be substituted directly into a large number of applications which currently use petrochemical based PU formulations.

Hence, the first objective of the current study is to improve on our previous reported CNC dispersion method by eliminating the water removal step. The second objective is to test the hypothesis that the CNC dispersion method developed for bio-based polyols is also applicable to the more widely used petrochemical polyether polyols. Ultimately, these will be tested through making CNC reinforced PU nanocomposites.

A simplified dispersion method was tested in which 1, 3-propanediol was used as a co-solvent to improve the solubility of the polyol with water. After removing both the water and 1, 3-propanediol under reduced pressure, a stable polyol-CNC suspension could then be achieved. Finally, a series of PU-CNC nanocomposites with high solid content PU resins and various CNC concentrations were prepared directly from polyol-CNC suspensions and pMDI without the addition of a solvent. The rheological behaviors of the polyol-CNC-MDI suspensions were characterized, and the thermo-mechanical, mechanical and abrasion properties of the resulting PU-CNC nanocomposites were evaluated.

2. Materials and experimental methods

2.1. Materials

The polyether polyol used in this study was Carpol® GP-725 which was obtained from Carpenter Co. (Richmond, VA, USA). The hydroxyl number of this polyol was 240 mg KOH/g, and water content was 300 ppm as provided by the supplier. The aromatic pMDI (Mondur MRS, NCO content of 31.5%) was sourced from Covestro Co. (Pittsburgh, PA, USA). The 1,3-propanediol was purchased from DuPont Tate and Lyle (USA). CNC was prepared from softwood pulp using a sulfuric acid hydrolysis process, and was reported in detail in our previous work [16]. The CNC was supplied as a homogenous

aqueous suspension with concentration of 10.3% by weight. This suspension was a CNC slurry taken directly from the CNC extraction process, prior to any drying processes. Note that all the percentages presented in this work are based on weight.

2.2. Preparation of CNC-polyol suspensions

The aqueous suspension of CNC (10.3%) was diluted with 1,3-propanediol to a CNC concentration of 2% using ultrasonication. Varying amounts of the H₂O-1,3-propanediol-CNC (H₂O-1,3 PD-CNC) suspension were then mixed with the GP 725 polyol (based on the target CNC concentration in the final PU-CNC nanocomposites), and excess water and 1,3-propanediol was simultaneously removed using a wiped-film evaporator (WFE) at low pressure. For example, a GP 725 polyol-CNC suspension having a final concentrations of 1.6% CNC was prepared by mixing 80 g of GP 725 polyol with 64 g of 2% H₂O-1,3 PD-CNC suspension then evaporating water and 1,3-propanediol using WFE. The water content of such prepared GP725-CNC suspensions was ~250 ppm as determined by the Karl Fischer titration method. The 1,3-propanediol residues in the GP725-CNC suspensions were shown by gas chromatography to be all < 1%. This procedure was found to produce homogenous suspensions of GP 725 polyols-CNC that were stable and ready for polyurethane nanocomposite production, without the use of solvents.

2.3. Preparation of PU-CNC suspensions and nano-composites

PU-CNC suspensions with various concentrations of CNC were prepared by weighing suitable amounts of GP 725 polyol-CNC and pMDI in a plastic container (based on an NCO/OH ratio of 1.1/1.0), mixing thoroughly for 3 min, and placing the mixture in a vacuum oven at 50 °C for 3–5 min to remove bubbles. GP 725 polyol-CNC-MDI mixtures with various CNC concentrations (0.25, 0.5, 0.75, 1.0 and 2.0% by weight) were prepared. Rheological measurements were then performed on the unreacted suspensions.

The NCO/OH ratio used to determine the relative amounts of GP 725 polyol-CNC and pMDI was calculated based on the hydroxyl number of pure polyol (240 mg KOH/g). This was found to be almost identical to the estimated hydroxyl number of 239 mg KOH/g for the GP 725 polyol-CNC suspension having the highest concentration of CNC (3.2%). This latter estimate was calculated based on 2.8 ± 0.3 mmol of reactive hydroxyl groups per gram of CNC, as reported by Pei et al. [15].

PU-CNC nanocomposite films were prepared by pouring the PU-CNC suspension into a mold and degassing. Afterwards, the sample was cured for approximately 24 h at 50 °C then post-cured for 24 h at 100 °C to complete the reaction. Transparent GP 725 PU-CNC nanocomposite samples with various CNC concentrations (0.25, 0.5, 0.75 and 1.0% by weight) were successfully prepared. Pure PU coatings (unreinforced) and PU containing 1% 1,3-propanediol additive in the polyol were also prepared as a control using the same procedure.

2.4. Characterization

Viscoelastic properties of the uncured liquid suspensions were measured using an AR2000 Advanced Rheometer. Due to the thermo-setting nature of the material, disposable plates (25 mm diameter) were used as the test geometry. Measurements were performed in oscillatory shear configuration at a fixed temperature of 25 °C. A linear viscoelastic response characterized the entire range of strain amplitudes used in this work. Measurements took approximately 12 min. for each sample.

Modulated differential scanning calorimetry (MDSC) measurements were carried out on a DSC Q100 (TA Instruments, DE, USA) and dynamic mechanical analysis (DMA) measurements were carried out on a DMA Q800 (TA Instruments, DE, USA), following the protocol from our previous work [16].

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