Site Selective Modification of Cellulose Nanocrystals with Isocyanate for Adhesion Applications

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Introduction

Polyurethanes and related materials such as urethaneureas, are important and versatile in achieving adhesion in a variety of applications including coatings, sealants, and structural adhesives. This talk will review recent work in incorporating cellulosic nanomaterials into urethane-based materials through attachment of an isocyanate moiety onto the surface of cellulose nanocrystals (CNCs). Previous studies of isocyanate-modified CNCs have used hexamethylene diisocyanate or methylene diisocyanate, and generally have resulted in direct chain extension of the CNCs prior to introduction into a polyol matrix. This is undesirable as it leads to aggregation of CNCs prior to formation of a composite within a urethane framework. The procedure outlined in this talk provides a route to functionalize CNCs with isocyanate prior to their covalent addition to the polymer matrix.

Isophorone diisocyante (IPDI) is part of a class of aliphatic isocyanates used in polyurethanes, and are well-known for resistance to abrasion and UV degradation. The unequal reactivity of the two isocyanate groups in IPDI monomer was exploited to yield modified cellulose nanocrystals (CNCs) that retain an unreacted isocyanate functionality. The modified CNCs showed improvements in the onset of thermal degradation by 35 °C compared to the unmodified CNCs. Polyurethane composites based on the IPDI-modified CNCs and a trifunctional polyether alcohol were synthesized and compared to those using unmodified CNCs. CNC dispersion was superior when the modified CNCs were utilized, and resulted in transparent composites at loadings of up to 5% CNC with increases in the tensile strength and work of fracture of over 200% compared to the neat matrix.

Experimental

Freeze dried CNCs (FD-CNCs) were provided by the U.S.D.A. Forest Products Laboratory and used as received. IPDI was purchased from Sigma Aldrich at 98% purity and used as received. Polyether polyol was provided by Bayer MaterialScience (LHT-240, Molecular Weight=700 g/mol). Isocyante catalysts, DBTDL and DABCO**,** were purchased from Sigma Aldrich and used as received.

Surface Modification

The FD-CNCs were first mixed with DMSO solvent by magnetic stirring for 30 minutes. The concentration of CNC in DMSO was approximately 3 wt.%. DBTL was then added to the IPDI at 60 °C and allowed to stir for 5 minutes. The FD-CNC/DMSO suspension was added drop-wise to the stirring IDPI/DBTDL mixture with a separatory funnel. The reaction proceeded overnight in a flask with N_2 inlet and outlet ports. The reaction was run in excess of IPDI at a weight ratio of IPDI to CNC of 67:1. After the reaction, the mixture was washed with toluene and centrifuged 3 times. The toluene was poured off, and the CNCs were either mixed with triol for composite synthesis, or allowed to dry in a vacuum oven overnight. An identical procedure was applied to produce the m-CNCs using DABCO as the reaction catalyst.

Polyurethane Film Preparation

Composites were synthesized with both m-CNCs and um-CNCs at loadings of 1 and 5 wt.%, and DBTDL was used as the reaction catalyst for

both the m-CNC preparation and the polyurethane film formulation. All polymers were synthesized with a 1:1 stoichiometric ratio of –NCO from IPDI and –OH from triol. Other experimental details are covered in a recent publication.[1]

Results and Discussion

Figure 1 shows ^{13}C NMR analysis, which gave insight into the selectivity of two isocyanate catalysts, DBTDL and DABCO. The spectrum for the um-CNC represented a typical solid state ^{13}C NMR spectra for crystalline cellulose. Changes to the NMR spectra associated with the IPDI modification were observed. In addition, it was possible to observe differences in the m-CNC spectra depending on the type of catalyst used for the preparation.

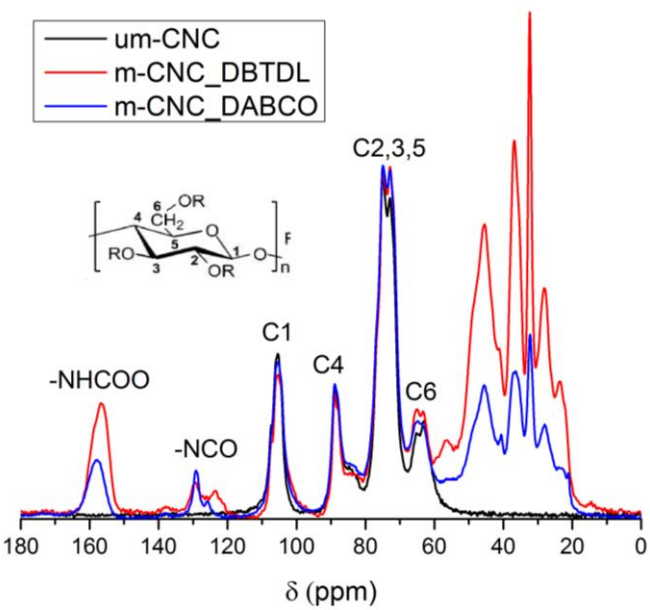

Figure 1. ^{13}C NMR spectra for um-CNCs and m-CNCs catalyzed with DBTDL and DABCO.

First, both m-CNC spectra showed new peaks in the δ=160 to 120 ppm range, and in the δ=50 to 20 ppm range when compared to the um-CNCs. Peaks in the δ=50 to 20 ppm region were due the hydrocarbons present in the IPDI, specifically: –CH_2– from the aliphatic IPDI ring (δ= 45.5 ppm), the tertiary carbon (δ=36.9 and δ=32.3 ppm), and the –CH_3 groups (δ=28.0 and δ=23.5 ppm). The peaks in the δ=160 to 120 ppm region represented the urethane (δ=158.0 – 156.8 ppm) and isocyanate (δ=129.2 – 123.4 ppm) functionality on the CNC particle.

Two distinct peaks were observed in the solid state NMR spectra for the isocyanate. From solution NMR, it is known that the primary isocyanate group (δ = 122.22 ppm)[3] has a lower chemical shift compared to the secondary isocyanate site (δ = 122.98 ppm).[3] The primary isocyanate was positioned at 121.9 ppm and the secondary isocyanate at 123.8 ppm. The secondary peak also showed a stronger absorbance in this spectra, and the ratio of the secondary to primary peak intensity was 1.50. In order to compare the relative quantities of primary and secondary isocyanates in the solid state ^{13}C NMR spectra, however, the peak area should be considered. This information was used to infer the selectivity of the two catalysts. First, the CNCs modified using the DABCO catalyst indicated two isocyanate peaks at 125.8 and 129.4 ppm, and the CNCs modified using the DBTDL catalyst indicated isocyanate peaks positioned at 123.5 and 129.2 ppm. Based on the values established by solution NMR for the assignment of primary and secondary isocyanate peaks, it was assumed that the peak at approximately 124 ppm corresponded to the primary isocyanate, and that the peak at approximately 129 ppm corresponded to the secondary isocyanate. Given the relative area under the curve of the primary and secondary isocyanate peaks, it was apparent that the DABCO catalyst preferentially reacted the primary isocyanate.

The mechanical performance of the composites compared to the neat matrix was assessed with tensile testing. The elongation at break for all samples tested ranged from 160 to 190%, although all measurements fell within the error ranges of each other, so no change in this property was observed with CNC addition. The data for tensile strength at break is given in Figure 2, with error bars representing confidence intervals of 95%. As a general trend, the samples containing m-CNC performed better than samples containing um-CNC at the same concentrations. For

example, at a 1 wt.% concentration, the m-CNC composite had improved tensile strength and work of fracture by 42% compared to the um-CNCs. This trend was more apparent for the 5 wt.% samples, with a 163% increase in tensile strength, and a 132% increase in the work of fracture for the m-CNC composites. In fact, the 1 wt.% m-CNC samples performed better than the 5 wt.% um-CNC samples. Therefore, less of the modified material is needed to achieve a similar or improved mechanical performance when compared to the unmodified particles. Most significantly, the 5 wt.% m-CNC sample improved the tensile strength by 226%, and the work of fracture by 257% when compared to the neat matrix.

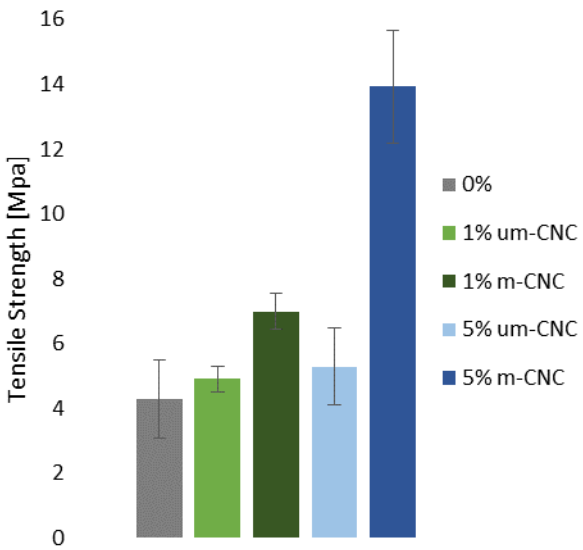

Figure 2. Tensile strength for neat polyurethane and polyurethanes containing 1 and 5% um-CNC or m-CNC.

Since the elongation at break was similar for all samples tested, it is possible that one of the mechanisms of reinforcement was due to the stiffening of the matrix by the CNC particles. While the tensile test standard chosen for this study did not allow for quantitative determination of elastic modulus, the initial slope of the stress-strain curves suggested that it was increased with increasing CNC loadings.

Conclusions

The reaction of freeze dried CNCs with IPDI was optimized to yield modified cellulose particles with a high surface coverage of the difunctional monomer. The pendant primary isocyanate group was then used as a route to facilitate covalent bond formation with a polyurethane elastomer, resulting in a significant improvement in the tensile properties at 5 wt.% m-CNC compared to the neat matrix. Some advantages of this modification scheme were made apparent by a marked improvement in onset temperature for thermal degradation and nanoparticle dispersion in the selected polymer matrix, two highly sought after features concerning cellulose nanomaterials. Additionally, this functionalization method may serve as a platform for the addition of other desirable functional groups and/or as a means for increasing compatibility with a range of organic solvents and polymers.

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References

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