

Cellulose nanocrystals-based nanocomposites: A Fruit of the BioSUCCEED¹ Biomass Platform

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North Carolina University, North Carolina Agricultural & Technical State University, and the University of Tennessee have established a virtual USDA center of teaching & research that is referred to by the acronym *BioSUCCEED*. One of the focus areas of *BioSUCCEED* is to promulgate state-of-the-art knowledge in biomass/biomaterials for public consumption and hence hasten the advent of the biomass-based economy. Not only does biomass provide a venue for conversion to biofuels, but it can provide very technically appealing materials for high end applications.

The use of renewables for materials applications is becoming more and more in vogue these days. One of the most promising natural raw materials in this respect is cellulose, a constituent of wood and most plants. In fact, many people today are deconstructing cellulose into its elementary building blocks known as “nanocrystals,” or CNs “nanoparticles,” or “whiskers.”

One of their most promising uses is in composites. The introduction of reinforcing nanoparticles into a continuous phase to form nanocomposites has attracted a great deal of attention recently. Why? Because it can provide significant improvements in mechanical

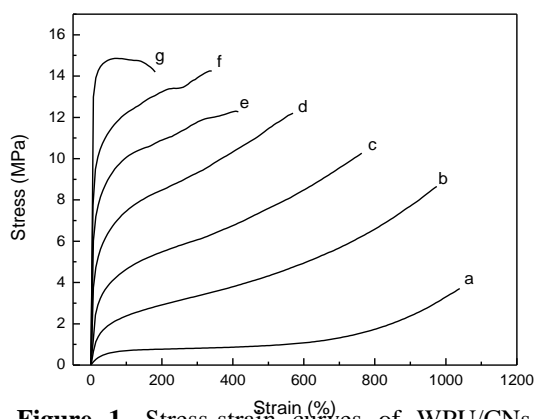


Figure 1. Stress-strain curves of WPU/CNs nanocomposite films having the following contents of CNs: a, 0 wt%; b, 5 wt%; c, 10 wt%; d, 15 wt%; e, 20 wt%, f, 25 wt%; g, 30 wt%. Reprinted with permission from ref 2. Copyright 2007 American Chemical Society.

properties at very low volume fractions of the reinforcing phase, i.e., the CNs. Typical reinforcement phases have included clay, hydroxyapatite, and multi-walled carbon nanotubes. Recently, cellulose nanocrystal have begun to steal the limelight as reinforcing materials in nanocomposites because of their low cost, high availability, renewability, nanoscale dimensions, high surface area, unique morphology, ease of chemical modification, low density, and good mechanical response to stress. The probability of CNs to contribute to big enhancements in the mechanical properties of a composite is high because the theoretical value of Young’s modulus of pure crystalline cellulose domains is about 150

¹BioSUCCEED (Bioproducts Sustainability, a University Cooperative Center of Excellence in Education) is an instructional platform headed at North Carolina State University that attempts to disseminate current knowledge and research in biomass & bioenergy through the production of a series of modules that are available at www.biosucceed.com (www.ncsu.edu/biosucceed).

GPa (*I*) which for comparison approaches the value of steel (200 GPa).

Let's explore some examples of work in CNs-fortified composites that has come out of our program. We have reported that a series of nanocomposite films with an aqueous suspension of CNs as the filler and a polycaprolactone (PCL)-based WPU as the matrix can be prepared by just blending the components in water (2). The nanocomposite films displayed a significant increase in Young's modulus and tensile strength – from 0.51 to 344 MPa and 4.27 to 14.86 MPa, respectively, when increasing the filler amount from 0 to 30 wt-% (Figure 1). Unfortunately, these gains can be at the expense of reduced elongation at break from about 1100% to 200%, paralleling what most previous studies found when developing polymer composites that use CNs as the filler.

As we know, to prepare high performance nanocomposite materials with a hydrophobic matrix and a hydrophilic CNs filler, the major issues to address are **adequate dispersion** and **strong interfacial adhesion** between the matrix and the filler. Obviously, the most ideal and effective way is through covalent attachment of the polymer to the stiff surface of CNs through bonding on the abundant hydroxyl groups on the surface of CNs. Therefore, we (3) prepared WPU/CN nanocomposites via a one-pot synthetic reaction between the exposed hydroxyl functionalities on the CN surfaces and isocyanate on the ends of the WPU prepolymer (Figure 2). The presence of the grafted WPU chains on the surface of CNs provided a crystalline environment that induced the crystallization of the WPU polymeric chains from the matrix surrounding the CNs. This was a very promising and useful paradigmatic approach: using the nanocrystals as a template. As a result, very good dispersion and strong interfacial adhesion between CNs and WPU were obtained.

Therefore, the incorporation of CNs in WPU provided a very significant improvement in the mechanical properties (shown in Table 1). Because of its amorphous nature, WPU has a nonlinear elastic behavior, possesses a low tensile strength of 4.4 MPa, a low Young's modulus of 1.7 MPa, and a high elongation at break of about 1048%. CNs had a profound effect on the tensile properties. It was evident that even a small amount of CNs can largely improve the tensile properties. For a WPU/CN nanocomposite containing 2 wt-% CNs, the Young's modulus and tensile strength are about 220% and 40%, respectively, higher than those for a pure WPU film. In the nanocomposites, generally, the Young's modulus and tensile strength are significantly increased compared to neat WPU. The Young's modulus increases with the CNs loading level, reaching the highest value of 107.4 MPa at 10 wt-% loading of CNs, approximately 60-fold higher than for the matrix. The largest improvement for the tensile strength reached 9.7 MPa for the nanocomposites loaded with 10 wt-% of CNs. In contrast to conventional filled polymer systems, the increase of strength carries a price: it is attained at the expense of ductility. The values of elongation at break of the WPU/CN nanocomposites increase with an increase of CNs content in the range of 0-4 wt-%, reaching a maximum value of 1355% for the WPU/CN-4.

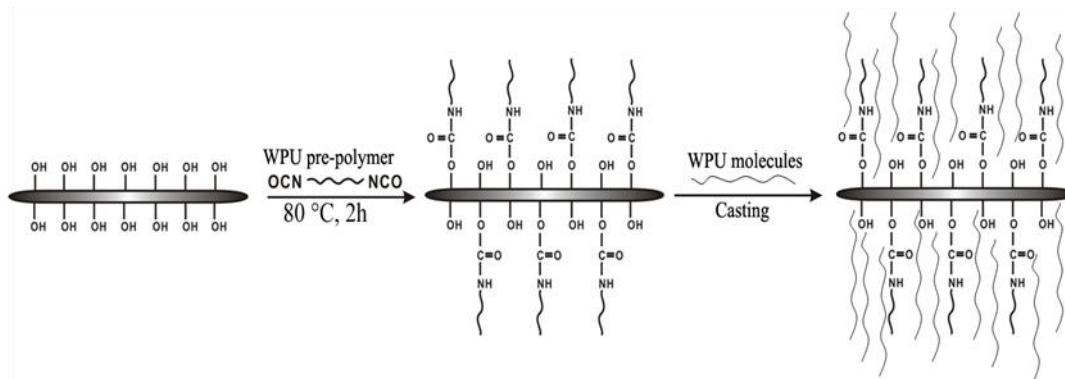


Figure 2. This work demonstrated that cellulose nanocrystal (CN)-grafted waterborne polyurethane (WPU) chains provided crystalline domains on the surface of the CNs. These domains expedited the crystallization of the polycaprolactone soft segments in the WPU/CN nanocomposites. This co-crystallization phenomenon induced the formation of a co-continuous phase between the matrix and filler which significantly enhanced interfacial adhesion (From ref 3, Reproduced by permission of the Royal Society of Chemistry).

Table 1. Mechanical properties of WPU and the WPU/CN nanocomposites obtained from tensile tests: Young's modulus (E), Tensile strength (σ_B), and Elongation at break (ϵ_B). Reprinted with permission. (From ref 3, Reproduced by permission of the Royal Society of Chemistry).

Sample	E (MPa)	σ_B (MPa)	ϵ_B (%)
WPU	1.7 ± 0.2	4.4 ± 0.2	1049.5 ± 30.6
WPU/CN-2	5.4 ± 1.3	6.3 ± 1.2	1273.3 ± 36.4
WPU/CN-4	22.5 ± 2.3	7.5 ± 0.8	1355.2 ± 60.3
WPU/CN-6	41.4 ± 1.8	8.9 ± 1.1	1027.2 ± 25.9
WPU/CN-8	55.6 ± 3.6	9.4 ± 0.5	827.1 ± 30.4
WPU/CN-10	107.4 ± 6.2	9.7 ± 0.6	626.6 ± 13.2

Cellulose nanocrystal-filled nanofibers. Electrospinning is a versatile method to manufacture fibers with diameters from several micrometers down to 100 nm or less through the action of electrostatic forces. Generally, processing parameters such as the voltage and distance between the spinning tip and the collector, the properties (conductivity, viscosity, density, surface tension, etc.) of the spinning solution and its flow rate can affect the result of the spinning process. For a good discussion on electrospinning of renewables, we published an article on this same area that we recommend to all interested (4). Various simultaneous phenomena taking place during spinning when loading the polymer suspension with CNs make it

difficult to control and to draw a clear-cut correlation between operational conditions and the properties of the produced micro- or nanofibers.

Polycaprolactone (PCL)/CN electrospun nanofibers have been prepared in a DMF-dichloromethane solvent system (Figure 3). The incorporation of CNs into PCL produces minimal changes on the morphology and porosity, but increase the diameter of the fibers around 2-fold. Interestingly, a significant improvement in the mechanical properties of the nanofibers after CNs reinforcement was observed.

Magalhães et al. (4) reported for the first time how a co-electrospinning technique can be used to overcome the issue of orienting cellulose nanocrystals in a neat cellulose matrix. Eucalyptus-derived cellulose was dissolved in N-methyl morpholine oxide (NMMO) at 120°C and diluted with dimethyl sulfoxide (DMSO) and used in an external concentric capillary needle as the sheath (shell) solution. At the same time, a cellulose nanocrystal suspension obtained by the sulfuric acid hydrolysis of sisal bleached and cotton fibers was used as the core liquid in the internal concentric capillary needle. The core-in-shell fibers also showed better mechanical properties than the pure cellulose fibers.

Electrospun CNs in water soluble polymer polyvinyl alcohol have been reported by Peresin et al. (5). Ultrathin cross-sections of the obtained nanocomposites consisted of fibers with maximum diameters of about 290 nm for CN loadings up to 15% (Figure 4). The electrospinning process did not affect the structure of the PVA polymer matrix, but its degree of crystallinity increased significantly together with a slight increase in the corresponding melting temperature. More importantly, the elastic modulus of the nanocomposite mats increased significantly as a consequence of the reinforcing effect of CNs by the network held by hydrogen bonds. Other successful work in this area includes CNs dispersed in polystyrene and dissolved in THF (6) and poly(acrylic acid) in ethanol (7).

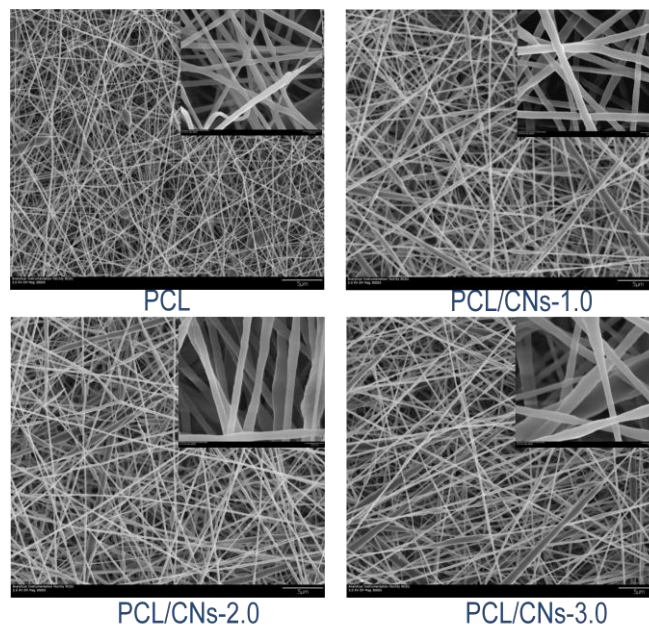


Figure 3. The FESEM images of PCL and PCL/CNs electrospun fibers.

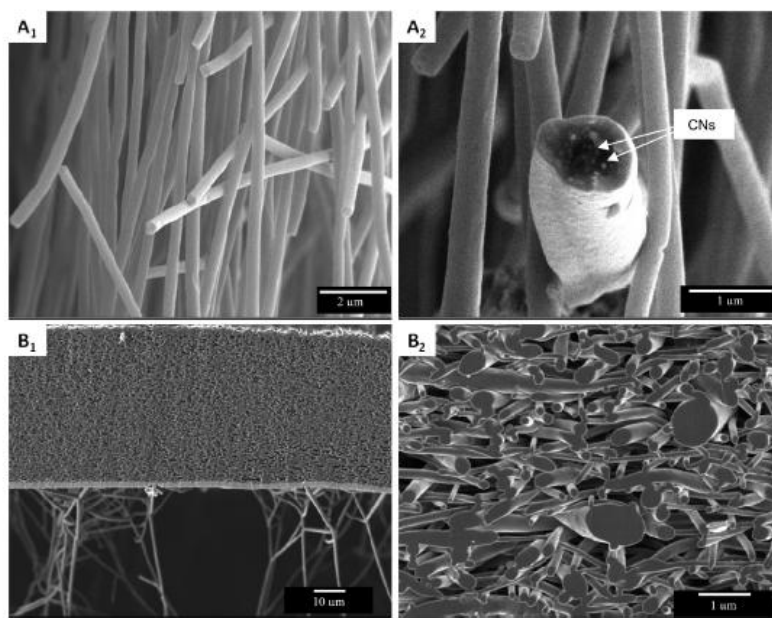


Figure 4. Cryo-SEM (A1 and A2) and variable pressure, ultrahigh resolution FE-SEM micrographs in transversal cross-sections (B1 and B2) of electrospun PVA-98 loaded with 15% of CNs. The top and bottom, bright thin layers observed in B1 are from a copper tape used to protect the sample and to facilitate cross-section by 5 kV Ar⁺ ion polishing. The straggling fibers (ca. 1 μm diameter) in the same image are not related to the PVA fiber mat. Bar sizes in each image are as follow: A1) 2 μm , A2) 1 μm , B1) 10 μm , and B2) 1 μm . Reprinted with permission from ref 5. Copyright 2010 American Chemical Society.

Conclusions

The knowledge base in biomass & bioenergy will continue to expand as the pressure of a dwindling petroleum economy continues to loom. Although many focus on biofuels, biomaterials remain a little plumbed and often ignored forum for teaching and research. This article attempts to provide select information from our Group here at NCSU to highlight the amazing potential of cellulose nanocrystals for various transformations. In sum, we have learned that cellulose nanocrystals are an attractive material to incorporate into composites because they can introduce tremendous strength gains and highly versatile chemical functionality.

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