Cellulose nanocrystals-based nanocomposites: fruits of a novel biomass research and teaching platform

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Research and teaching of biomass and bioenergy concepts has become paramount in these trying economic times that demand alternatives to scarce and unrenewable petroleum supplies for manufacture. This article attempts to provide a review of select and highly functional biomass concepts from a United States Department of Agriculture-sponsored work 'BioSUCCEED' at North Carolina State University that focuses specifically on cellulose nanocrystals, a sustainable, robust, and potentially powerful vehicle for improved engineered composites.

Keywords: Biomass teaching programme, cellulose, mechanical properties, nanocomposites, nanocrystals.

NORTH CAROLINA University, North Carolina Agricultural and Technical State University, and the University of Tennessee have established a virtual United States Department of Agriculture centre of teaching and research that is referred to by the acronym BioSUCCEED (Bioproducts Sustainability, a University Cooperative Center of Excellence in Education. It is an instructional platform headed at North Carolina State University that attempts to disseminate current knowledge and research in biomass and bioenergy through the production of a series of modules that are available at www.biosucceed.com (www.ncsu.edu/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 technically appealing materials for high-end applications.

The use of renewables for materials applications is becoming popular 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 'cellulose nanocrystals (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 properties at very low volume fractions of the reinforcing phase, i.e. CNs. Typical reinforcement phases have included clay, hydroxyapatite and multi-walled carbon nanotubes. Recently, CNs 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[1–5]. The probability of CNs contributing to significant enhancements in the mechanical properties of a composite is high because the theoretical value of Young's modulus of pure crystalline cellulose domains[6] is about 150 GPa which, for comparison, approaches the value of steel (200 GPa). Cellulose-based microstructures offer unique opportunities due to their high stiffness/strength, hydrophilicity, biocompatibility, stereoregularity, biodegradability, chemical stability and the ability to form superstructures as well as the possibility of subsequent surface chemical modification. Depending on their origin, CNs have diameters ranging from 3 to 20 nm, with a high aspect ratio[7–9]. In spite of the abundance of cellulose as a biological raw material, its utilization as a component in composites is largely unexplored. Several uses have been identified for such nanocrystals to work as fillers of composite materials[10–14], food products (non-caloric thickening agents)[15], edible coatings[16], drug delivery agents[17], etc. Current interest in the development of sustainable bio-based economies as well as the

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emerging shortage of fossil fuels is expected to promote further study into these alternatives.

Generic isolation of cellulose whiskers in micro/nano-scale sizes

Cellulose fibrils (micro or nano size) or cellulose whiskers can be obtained from cellulose filter paper or cotton fibres. Amorphous regions at the interface of microcrystalline domains in these fibres (along the microfibril length) are easily removed by acid treatment to produce microcrystals. Cellulose microfibrils obtained by HCl hydrolysis have a rod-like shape. The cellulose whiskers are expected to have high mechanical modulus and therefore are expected to be excellent candidates in the manufacture of composite materials. The characterization of filter-paper derived cellulose whiskers has been accomplished using atomic force microscopy. The length and width of the whiskers in the present study were found to range from 0.80 to 5.3 μm; and from 0.16 to 0.51 μm (Figure 1).

Water-borne polyurethane CN composites

Now let us explore some examples of work in CN-fortified composites that has come out of our research and teaching programme. We have reported that a series of nanocomposite films with an aqueous suspension of CNs as the filler and a polycaprolactone (PCL)-based water-borne polyurethane (WPU) as the matrix can be prepared by just blending the components in water[18]. 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 the filler amount was increased from 0 to 30 wt% (Figure 2). Unfortunately, these gains can only be at the expense of reduced elongation at break over the range from 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 CN 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, 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 were prepared (Figure 3)[19]. 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 CNs. This was a promising and useful paradigmatic approach: using the nanocrystals as a template. As a result, good dispersion and strong interfacial adhesion between CNs and WPU were obtained.

Therefore, the incorporation of CNs in WPU provided a significant improvement in the mechanical properties (Table 1). Because of its amorphous nature, WPU has a nonlinear elastic behaviour, 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 CN can largely improve the tensile properties. For a WPU/CN nanocomposite containing 2 wt% CNs, the Young's modulus and tensile

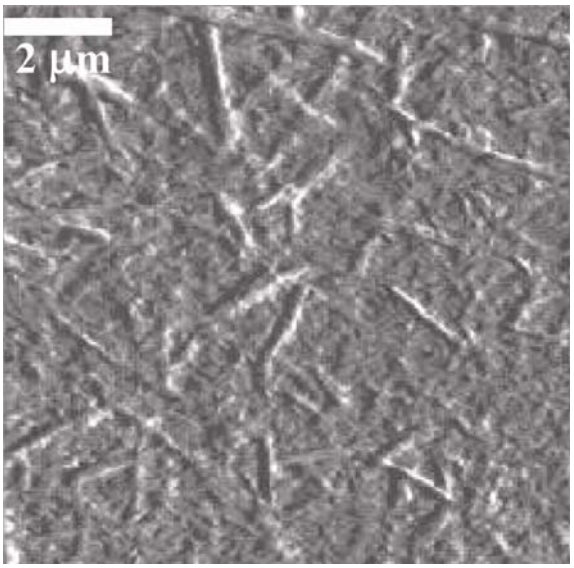

Figure 1. Atomic force microscopic images of cellulose whiskers obtained from acid hydrolysis of cellulose paper.

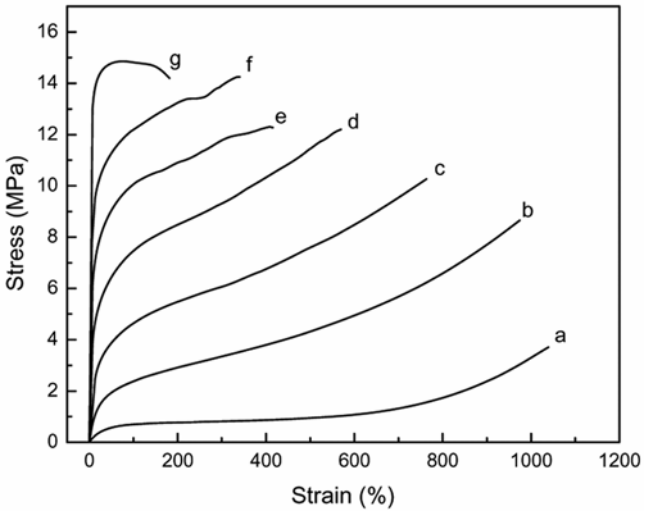

Figure 2. Stress–strain curves of water-borne polyurethane (WPU)/cellulose nanocrystal (CN) nanocomposite films having different CN contents: a, 0 wt%; b, 5 wt%; c, 10 wt%; d, 15 wt%; e, 20 wt%; f, 25 wt% and g, 30 wt%. Reprinted with permission from Kim *et al.*[2]. Copyright 2007 American Chemical Society.

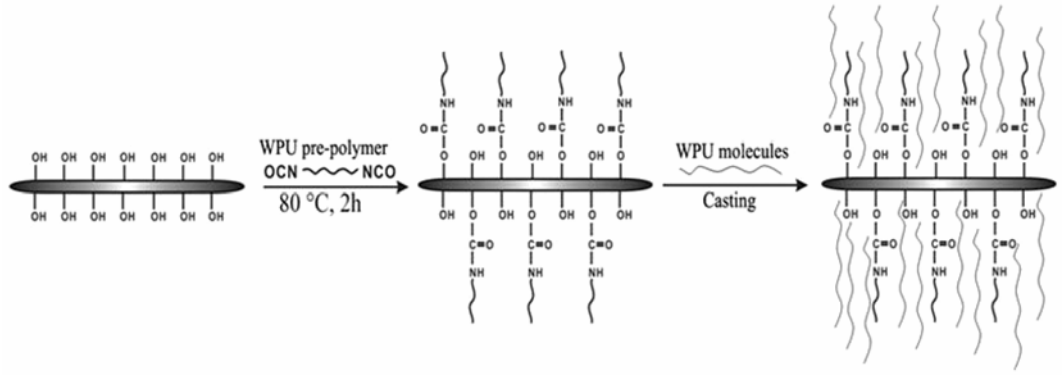

Figure 3. This work demonstrated that CN-grafted WPU chains provided crystalline domains on the surface of the CNs. These domains expedited the crystallization of the polycaprolactone (PCL) soft segments in the WPU/CN nanocomposites. This co-crystallization phenomenon induced the formation of a co-continuous phase between the matrix and the filler, which significantly enhanced interfacial adhesion. (From Magalhães *et al.*[19]; reproduced with permission of the Royal Society of Chemistry.)

Table 1. Mechanical properties of water-borne polyurethane (WPU) and WPU/cellulose nanocrystal (CN) nanocomposites obtained from tensile tests: Young's modulus (E), tensile strength (σ_B), and Elongation at break (ε_B). (From Magalhães *et al.*[19], reproduced with 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

strength were 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 loading level of the CNs, reaching the highest value of 107.4 MPa at 10 wt% loading of CNs, approximately 60-fold higher than that for the matrix. The largest improvement for the tensile strength reached 9.7 MPa for the nanocomposites loaded with 10 wt% of the CNs. In contrast to conventional filled polymer systems, the values of elongation at break of the WPU/CN nanocomposites increased with an increase in CN content in the range of 0–4 wt%, reaching a maximum value of 1355% for WPU/CN-4.

CN-filled nanofibres

Electrospinning is a versatile method to manufacture fibres with diameters from several micrometres 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. A good discussion on electrospinning of renewables can be found in Magalhães *et al.*[20]. Various simultaneous phenomena taking place during spinning when loading the polymer suspension with CNs make it difficult to control and draw a clear-cut correlation between operational conditions and properties of the produced micro- or nanofibres.

PCL/CN electrospun nanofibres have been prepared in a DMF-dichloromethane solvent system (Figure 4). The incorporation of CNs into PCL produces minimal changes in the morphology and porosity, but increases the diameter of the fibres about two-fold. Interestingly, a significant improvement in the mechanical properties of the nanofibres after CN reinforcement was observed.

Magalhães *et al.*[20] reported 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 at 120°C and diluted with dimethyl sulphoxide, and used in an external concentric capillary needle as the sheath (shell) solution. At the same time, a CN suspension obtained by the sulphuric acid hydrolysis of sisal bleached and cotton fibres was used as the core liquid in the internal concentric capillary needle. The core-in-shell fibres also showed better mechanical properties than the pure cellulose fibres.

Electrospun CNs in water-soluble polymer polyvinyl alcohol (PVA) have been reported[21]. Ultrathin cross-sections of the obtained nanocomposites consisted of fibres with maximum diameters of about 290 nm for CN loadings up to 15% (Figure 5). 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

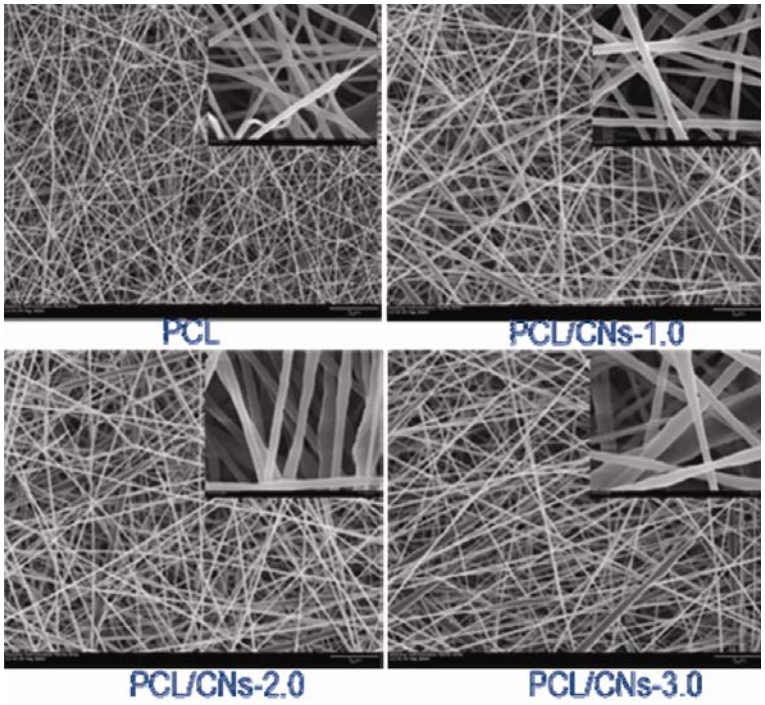

Figure 4. Field emission scanning electron microscopic (FESEM) images of PCL and PCL/CN electrospun fibres.

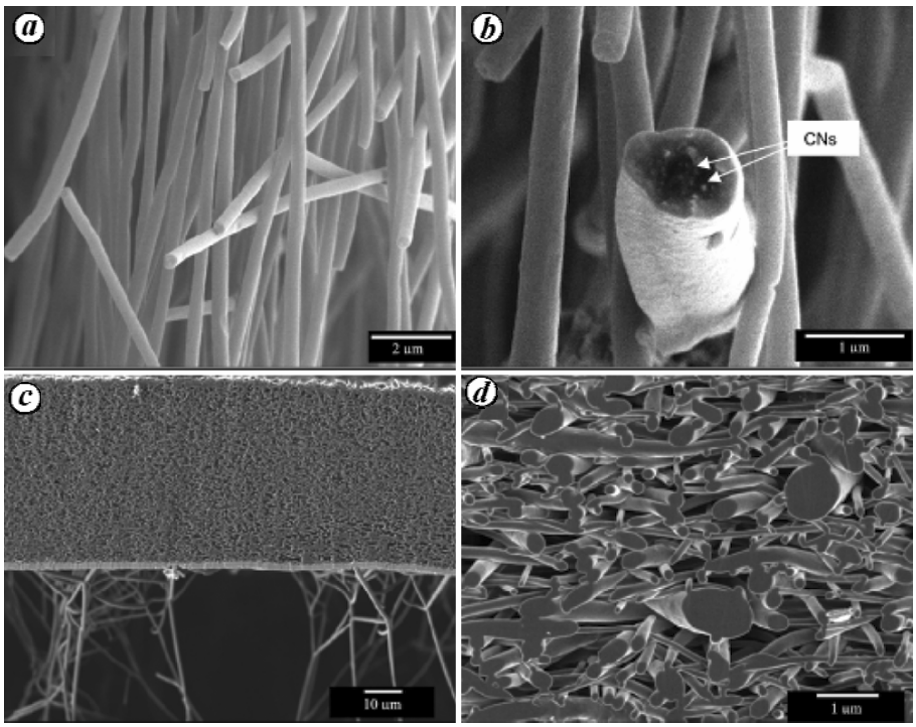

Figure 5. Cryo-SEM (***a, b***) and variable pressure, ultrahigh resolution FESEM photomicrographs in transversal cross-sections (***c***, ***d***) of electrospun polyvinyl alcohol (PVA)-98 loaded with 15% CNs. The bright thin layers observed at the top and bottom in (***c***) are from a copper tape used to protect the sample and to facilitate cross-section by 5 kV Ar^+ ion polishing. The straggling fibres (ca. 1 μm diameter) in (***c***) are not related to the PVA fibre mat. Bar sizes are as follow: ***a***, 2 μm; ***b***, 1 μm; ***c***, 10 μm and ***d***, 1 μm. Reprinted with permission from Zoppe *et al.*[5]. Copyright 2010 American Chemical Society.

of the nanocomposite mats increased significantly as a consequence of the reinforcing effect of CNs by the network held by hydrogen bonds. Other successful studies in this area include CNs dispersed in polystyrene and dissolved in tetrahydrofuran[4] and poly(acrylic acid) in ethanol[22].

Conclusion

The knowledge base in biomass and 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 at NCSU to highlight the amazing potential of CNs for various transformations. In sum, we have learned that CNs are an attractive material to incorporate into composites because they can introduce tremendous strength gains and provide us with highly versatile chemical functionality.

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