**Strong and Stiff: High-Performance Cellulose Nanocrystal/Poly(vinyl alcohol) Composite Fibers**

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Supporting Information

**ABSTRACT:** The mechanical properties of rodlike cellulose nanocrystals (CNCs) suggest great potential as bioderived reinforcement in (nano)composites. Poly(vinyl alcohol) (PVOH) is a useful industrial material and very compatible with CNC chemistry. High performance CNC/PVOH composite fibers were produced coaxial coagulation spinning, followed by hot-drawing. We showed that CNCs increase the alignment and crystallinity of PVOH, as well as providing direct reinforcement, leading to enhanced fiber strength and stiffness. At 40 wt % CNC loading, the strength and stiffness reached 880 MPa and 29.9 GPa, exceeding the properties of most other nanocellulose based composite fibers previously reported.

**KEYWORDS:** nanocellulose, cellulose nanocrystal, poly vinyl alcohol, composite, fiber

Cellulose nanocrystals (CNCs) are short rigid single crystals of cellulose, generally with a width of ca. 5−20 nm and length of 100−300 nm.1 Their straight rodlike morphology is characteristic, and distinguishes them from longer, typically entangled, cellulose nanofibers (CNFs), which represent the other important member of the nanocellulose family. Cellulose is the principal component in all plants and is the most abundant renewable polymer on earth. The ideal crystalline form intrinsically possesses a very high strength (~7.6 GPa) and stiffness (~160 GPa) coupled with low density (~1.6 g/cm³).3 The other attractive features of CNCs, including biocompatibility, biodegradability, and sustainability, have stimulated a diverse range of potential applications including cosmetics, medical implants, chiral templates for inorganic materials, and green composites.

The opportunity to obtain high mechanical performance from a renewable material has recently spurred an intensive period of research for applications of CNCs as a reinforcement for polymers.3 Unfortunately, CNCs are only compatible with a few polymer matrices and usually aggregate when blended with other materials, leading to a reduction in polymer/CNC interfacial area, poor stress transfer, and stress-concentrating agglomerates.6 Surface modification, particularly covalent polymer grafting,7 can overcome the poor compatibility but the procedures are often laborious and hard to scale. An alternative approach is to make use of one of the few intrinsically compatible polymers as a matrix.8 Poly(vinyl alcohol) (PVOH) is one such suitable candidate: it does not adsorb on cellulose in water8 but its hydroxyl groups hydrogen bond copiously with those of cellulose in the dry state. However, although a range of CNC/PVOH composites have been prepared, for example by electrospinning (~50 MPa),10 cross-linking (~100 MPa),11 and liquid crystal microphase separation (0.05 N/tex),12 mechanical performance is generally inferior compared to expectations.

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In this paper, we exploit uniform CNC/PVOH suspensions to prepare high strength nanocomposite fibers via a gel spinning method, followed by hot-drawing. This approach is effective for high CNC loading fractions with excellent dispersion and alignment (Figure 1), as required for mechanically superior composite fibers.

Aqueous CNC suspensions (Figure 2a) were prepared by an established acid hydrolysis route, and mixed with PVOH. Solutions in DMSO, to form a uniform, stable spinning dope, with a final DMSO:water volume ratio of 4:1. Optical micrographs (Figure S1) show little evidence of agglomeration, due to the compatibility of the components, until the CNC content reaches around 60 wt % relative to PVOH. Nano-composite CNC/PVOH fibers were successfully produced by injecting these spinning dopes into a coaxial flowing stream of antisolvent (acetone) to induce controlled coagulation. The coflowing antisolvent was intended to increase CNC alignment during the fiber spinning process and improve fiber consistency, by confining the gel filament in a laminar flow; this approach has previously been shown to be effective for carbon nanotube-PVOH fibers.13 Around 1 mL of CNC spinning dope was coagulated and stretched during the spinning process to form a ~2 m long fiber. Fibers were dried at ambient conditions then subsequently hot-drawn at 150 °C, to a draw ratio of 6, below the CNC degradation temperature of 200 °C.14 Drawing the as-spun fiber has two effects: it condenses the fiber and increases the alignment of both the CNC and polymer in the fiber direction, as can be seen by the increased birefringence (Figure S2) and X-ray diffraction patterns (see below).15 The final CNC/PVOH composite fibers were 10 m in length (digital image, Figure 2b), with a linear density of 1.0 ± 0.1 tex (Figure 2c). Higher-magnification SEM images (Figure 2d) indicated that individual CNCs remained well dispersed in the composite at loadings up to 40 wt % CNCs. Indeed, good quality, dense, uniform fibers were obtained for the pure polymer and nanocomposites containing up to 40 wt % CNC. At 60 wt % CNC, the fibers contained obvious agglomerates and pores (Figure S3).

The presence of nanofillers can alter the morphology of a polymer matrix as well as providing direct reinforcement; to help deconvolute these effects, polymer crystallinity and glass transition temperature (T_g) were quantified from the initial differential scanning calorimetry (DSC) heating scans (see Figure S4).3 After hot-drawing, the crystallinity of the PVOH, calculated from the heat of fusion (ΔH_m), increased steadily (Figure S4c) from 12.8 to 17.9% with increasing CNC loading. The increased PVOH crystallinity may be attributed to the dispersed, crystalline CNCs providing additional nucleation sites for PVOH during strain-induced crystallization. At the same time, the glass-transition temperature remained constant in the range of 70–72 °C. (Figure S4)

The fiber microstructure was characterized by wide-angle X-ray scattering (WAXS) to identify the crystal phases present and the degree of orientation of each component (Figure 3). Monoclinic syndiotactic PVOH has a unit cell16 with parameters a = 7.63 Å, b = 2.54 Å (parallel to the chain axis), c = 5.41 Å, and γ = 91.5°. Predominantly, CNC has a cellulose I_β structure,17 which is monoclinic with parameters a = 7.78 Å, b = 8.20 Å, c = 10.38 Å, and β = 96.5°. 1D WAXS (Figure S5) patterns of the fibers show the characteristic features of the PVOH and CNC phases. Notably, the (101), (101), and (200) planes of monoclinic PVOH and the (200) plane of monoclinic cellulose I_β crystal are observed. 2D X-ray patterns of the as-spun fibers show only approximately isotropic broad rings, indicating little preferential alignment of either PVOH or CNC (Figure S5 b-d). However, after hot-drawing, the (101) and (200) planes of the PVOH become much more intense in the equatorial region, indicating a high degree of orientation, with the fiber direction approximately parallel to the [010] direction (Figure 3a). The hot-drawn composite fibers containing 20 and 40 wt % CNC show a similar trend but with even further improved alignment. The degree of orientation of PVOH was quantified from the full width at half-maximum (FWHM) of the azimuthal intensity distribution (fitted as Lorentzian functions) of the (101) plane of PVOH at 2θ = 19.4° (Figure 3, right). The hot-drawn pure PVOH fibers showed a preferred orientation (FWHM = 39.5°) along the fiber axis, similar to those reported previously. For both hot-drawn composite fibers, the PVOH crystallite orientation increased very significantly to around FWHM = 18° (Figure 3b, c). Unfortunately, the CNC (200) peak coincides with the
tenacity and stiffness of the hot-drawn pure PVOH fibers increased to 0.3 N/tex (430 MPa) and 5.5 N/tex (8.3 GPa), respectively, at a strain to failure of 33.7 ± 0.5%. Optimized commercial pure PVOH fibers (Kuralon K–II WN2, σ = 0.6 N/tex (820 MPa), E = 17.7 N/tex (15 GPa), and e = 20%) still have better properties because of the higher draw ratios (~20) possible at higher temperatures (220 °C).19 In the current experiments, the hot-drawing temperature was limited to 150 °C due to the onset of CNC degradation.14 Nevertheless, the hot-drawn PVOH fibers containing 40 wt % CNC match the ultimate tenacity but have double the stiffness of the commercial material, with stiffness 21.1 N/tex (29.9 GPa) and a tenacity 0.65 N/tex (880 MPa) at a strain-to-failure of 5.6 ± 0.2%. Mechanical properties increased with CNC loading up to 40 wt % (CNC40/PVOH) but decreased for a CNC loading of 60 wt % due to the agglomeration effects noted above (Figure 4b, c). The increase in stiffness and tenacity for composite fibers with up to 40 wt % CNC loading can be attributed to the combined effect of increased crystallinity of the matrix and direct reinforcement by the CNCs. To explore this hypothesis quantitatively, Krenchel’s micromechanical model can be applied (eq 1).20 The model follows a rule of mixture formalism, modified for fiber length and orientation.

\[
E = \eta_{II}V_{II}E_{II} + V_{m.a}E_{m.a} + V_{m.c}E_{m.c}(V_{II} + V_{m.a} + V_{m.c} = 1)
\]

where \(E_{II}, E_{m.a}, \text{ and } E_{m.c}\) are the moduli of the CNC (120 GPa), amorphous matrix (3.75 GPa), and crystalline matrix (25.5 GPa), and \(\eta_{II}\) and \(\eta_{I}\) efficiency factors relating to fiber orientation and length, respectively; the equation has been modified to treat the crystalline and amorphous PVOH components separately, to account for the changing levels of crystallinity between samples (see Appendix 1 in the Supporting Information for full derivation). The volume fractions are determined from weight fractions and the material densities (1.26 g/cm³ for amorphous PVOH, 1.34 g/cm³ for crystalline PVOH and 1.6 g/cm³ for CNC)20 and the degree of PVOH crystallinity, which was determined by DSC (Figure S4). Orientation factors for the PVOH crystals determined from the (101) peaks for the hot-drawn PVOH (Figure 3), and composite fibers containing 20 and 40 wt % CNC, were calculated to be 0.73, 0.83, and 0.84, respectively. The orientation efficiency factor of CNC was assumed to be the same as the degree of orientation of the PVOH as more detailed analysis was precluded due to peak overlap. The fiber length factor was calculated using the shear-lag model using the measured CNC length distribution from previous work.20 To be consistent with volume fraction terms used in the model, and the known moduli of the constituent phases, the stiffness of the composite fibers was normalized by area rather than linear density. The model predictions are in reasonably good agreement with the measured moduli (Figure 4c). The divergence at the highest CNC content correlates with the onset of CNC agglomeration. The general fit for the nanocomposite fibers containing well dispersed CNCs, suggests that both CNC reinforcement and matrix crystallinity (which is also affected by the CNC loading fraction) do indeed play a role. For example, the relative increase in stiffness (31.6 GPa) obtained for the sample containing 40 wt % CNC, above the value of the pure PVOH fiber (6.5 GPa), is attributed partly to the stiffening contribution of the CNCs (26.6 GPa) and partly to the increase in stiffness (from 12.8 to 17.9%) contributing an increase in stiffness of 5.0 GPa.
The stiffness and strength of the new CNC/PVOH fiber exceed the properties of other nanocellulose-based fibers reported in the scientific literature (Figure 4d). Strikingly, our new fibers are approximately 10 times stronger than previous CNC composite fibers. Interestingly, their performance is quite similar to optimized commercially available, pure cellulose fibers, including Cordenka EHM ($\sigma=900$ MPa and $E=38$ GPa) and Lyocell A ($\sigma=624$ MPa and $E=31.2$ GPa), while exceeding those of Viscose ($\sigma=260$ MPa and $E=9.3$ GPa), both in terms of stiffness and ultimate tensile strength.

Because of the lower density of PVOH ($\sim 1.26$−$1.34$ g/cm$^3$) compared to pure cellulose (1.5 g/cm$^3$), the CNC40/PVOH fibers even outperform Cordenka EHM in terms of specific ultimate tensile strength (0.62 GPa cm$^3$/g versus 0.60 GPa cm$^3$/g). The ductile PVOH matrix also offers a higher elongation at break (5.5% versus 4.6%). Although single-walled carbon nanotubes are reported to offer greater reinforcement in PVOH fibers, because of their superior mechanical properties, they are not renewable, are less environmentally benign, and are harder to process than CNCs. The relative success of the CNCs can be attributed to their excellent hydrogen-bonding compatibility with PVOH.

Interestingly, the presence of the CNCs appears to dramatically improve the polymer microstructure, even under relatively modest drawing conditions. The size and stiffness of the CNCs is expected to assist their orientation by shear, due to longer rotational relaxation times. The coaxial flow coagulation spinning process appears to be very effective at orienting both components. Once oriented, the CNCs encourage the nucleation of PVOH crystals, increasing both polymer crystallinity and orientation. Despite the lower crystallinity of PVOH in this composite, compared to commercial PVOH ($\sim 50$−$60\%$), the higher fiber stiffness shows that the CNCs are contributing effectively. The overall improvement in properties is thus likely to be a combination of improved polymer microstructure and direct reinforcement by the CNCs. The results obtained are extremely promising, and offer considerable scope for further optimization of constituents and processing conditions. To date, the development of CNC composites has been hampered by the poor mechanical performance obtained in most cases. The high performance obtained here demonstrates that further development is warranted. The highly aligned, high loading CNC reinforced fibers may have direct relevance to biomedical applications due to their biocompatibility. In addition, they could be readily combined with a suitable (renewable) matrix to create a new generation of hierarchical composites.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b11578.

Detailed experimental procedures, optical microscopic images, DSC thermograms, XRD diffraction patterns, tenacity-strain curves, and SEM images (PDF)
REFERENCES