NANOCELLULOSE/POLY VINYL ALCOHOL FIBRES : A GREEN RENEWABLE HIGH PERFORMANCE COMPOSITE

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Abstract

Cellulose nanocrystals (CNC) are promising candidates as stiff fillers in green, renewable, high performance composites, owing to their intrinsic high strength and stiffness. However, historically CNC materials have had low mechanical properties due to CNC aggregation, poor alignment, and low loading fractions. Here, high loadings of water-soluble CNCs are well dispersed in poly vinyl alcohol (PVOH) to form coagulation spinning dopes for composite fibres. The final fibres contain high CNC loading (up to 60 wt. %) while mechanical behaviour is heavily dependent on CNC loading, with tensile strengths approaching the GPa scale at high loadings. The alignment and crystallinity of CNCs and PVOH along the fibre axis was measured by 2D X-ray scattering to account for these differences. This work provides a possible strategy to the challenging question of preparing practical, high performance, green and renewable composites.

1. Introduction

Cellulose nanocrystals (CNCs) are needle-like nanorods of a ~10 nanometers in width and 50-1000 nm in length, depending on the source of cellulose.[1] Highly crystalline CNCs are typically obtained from cell walls through acid hydrolysis of fibres derived from plant cells.[2] CNCs have been subject to numerous research efforts, both from fundamental and applied perspective. In addition to their biocompatibility, biodegradability, and sustainability, CNCs possess useful material properties, including high strength and modulus coupled with low density.[3] CNCs have inspired a broad range of proposed applications including cosmetics,[4] medical implants,[5] and eco-friendly mechanical composites.[6]

Despite the significant advantages of CNCs, composites combining CNCs with polymer matrices are often disappointing due to poor dispersion of the nanofiller.[7, 8] Poor interaction between hydrophilic CNC and hydrophobic polymer matrices and limited set of solvents for

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suspensions hinder the dispersion of fibrils.[9] Another specific challenge is to control the crystal structure of the matrix in order to maximise the macroscale properties of bulk nanocomposites.[10] In an effort to overcome these challenges, researchers have utilised a wide variety of polymer matrices and cellulosic nanomaterials, with different processing strategies.[11] However, mechanical properties of CNC/polymer composites, especially in terms of tensile strength and Young's modulus, have often been limited.[12, 13]

Here, we present a straightforward fabrication of high performance CNC composite fibre with desirable highly aligned structure. Hydrated, water soluble CNCs were synthesized with sulfuric acid hydrolysis, as reported recently.[14] Well-dispersed CNCs enabled higher cellulose loading in the composites without the decrease in mechanical properties typically associated with agglomeration. The high performance CNC composite fibre was produced by a combination of wet-spinning and post-processing.

2. Experimental

2.1 Materials

Whatman 1 filter paper was obtained from Whatman, GmbH, Dassel, Germany. Sulfuric acid (96%), poly vinyl alcohol (PVOH) (Moiwol® 56-98, M_W ~195,000, 98.0-98.8 mol% hydrolysis) and dimethyl sulfoxide (DMSO) (≥99.9%) were obtained from Sigma Aldrich, United Kingdom. Deionised water (DIW, 99.5% purified), and acetone (99.5 %) were purchased from VWR chemicals (VWR UK, United Kingdom)

2.2 CNC Preparation

CNCs were prepared from cotton-based Whatman 1 filter paper using an established procedure.[15] 10 g of finely ground Whatman 1 filter paper was hydrolyzed in 175 mL of 64% w/w sulphuric acid at 45 °C for 45 min. The hydrolysis was quenched by the addition of 1800 mL of Milli-Q water and the resulting suspension was then washed by centrifugation until the pH of the supernatant was >1. The rest of the impurities were removed by dialyzing over deionized water for 7 days.[14]

2.3 Wet Spinning

The prepared CNC/PVOH spinning dopes were wet-spun into an acetone through a 24 gauge cannula with syringe injection pump (KDS 100, KDS Scientific), which resulted in coagulation and fibre formation (solid).

2.4 Post Processing

A series of high temperature treatment and drawing experiments was applied to wet-spun fibres to control macroscale fibre properties.

2.5 Characterization

The cross-sectional morphologies of fibre were observed by scanning electron microscopy (SEM, Leo1525 Gemini, Carl Zeiss AG, Acceleration voltage = 5 kV). The fibre samples were 10 nm thick gold coated with sputtering device (EMITECH-K550), operating at a pressure of 7×10^{-2} bar. The crystal structure of fibre was obtained from bundles of parallel fibres by using wide angle X-ray diffractometer (WAXD, Rigaku D/MAX-2500) with *CuKa* radiation (λ= 1.54056 Å), operated at 18 kW. The fibre specimens were mounted perpendicular to the X-ray beam. Diffraction patterns of fibres were recorded with a connected image plate system. Tensile properties of composite single fibres, were prepared following British standard (BS ISO 11566:1996). Fibres were loaded on card holders, with gauge lengths 15 mm ± 0.5 mm, using an epoxy adhesive (50/50 hardener to resin, Araldite Rapid Adhesive, Bostik Findley Ltd., United Kingdom). The specific tensile properties of single fibre were determined with a 20 N force sensor on a Linkam TST 350 tester with 1 mm/min crosshead speed at 64% relative humidity. At least 10 samples from different locations were measured for each sample to check the heterogeneity of samples.

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3. Results & Discussion

To create a high performance CNC composite fibre with desired microstructure (Figure 1), the CNCs were synthesised from H_2SO_4 hydrolysis of cellulose to give rigid rods of crystalline cellulose with uniform width (7 nm) and polydisperse length (50-300 nm, mean length c.a. 120 nm). Synthesised CNCs were dissolved in deionized water at varying concenctrations. Pure CNC dispersions at 20 mg mL^{-1} form a nematic liquid crystal (LC) phase, which is confirmed from previous research.[16] Spinning dopes with a wide range of CNC loadings (20 wt.% and 40 wt.%) were prepared through mixing pre-prepared aqueous solutions of PVOH (30 mg mL^{-1}) and CNC. To the best of our knowledge, 40 wt.% loading of CNC is the highest CNC loaded cellulose/PVOH composites.

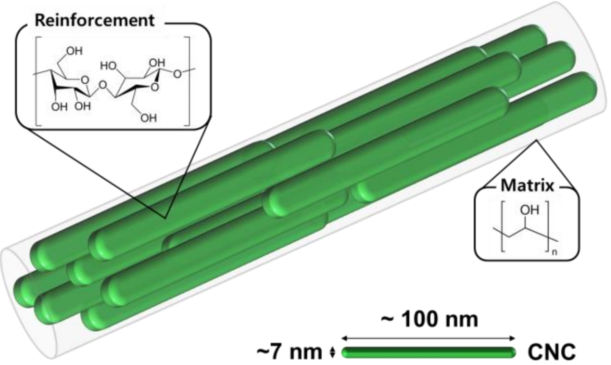

Figure 1. Illustration of controlled microstructure of CNC fibre

The aqueous dopes were injected through 10 mL h^{-1} into acetone coagulation bath, leading to destabilization and coagulation of the PVOH and CNCs into a gel-like, ribbon-shaped fibre. The fibres were removed from the coagulation bath and dried ambiently, to give fibres ~130 by ~80 µm (typically ~2 meter in length). The fibres were subsequently stretched along the fibre axis at constant drawing ratio (600 %) at 160 °C . After stretching, the final CNC/PVOH composite fibres were 10 meters in length, with a uniform ribbon-shaped fibre of ~40 µm by ~20 µm (Figure 2).

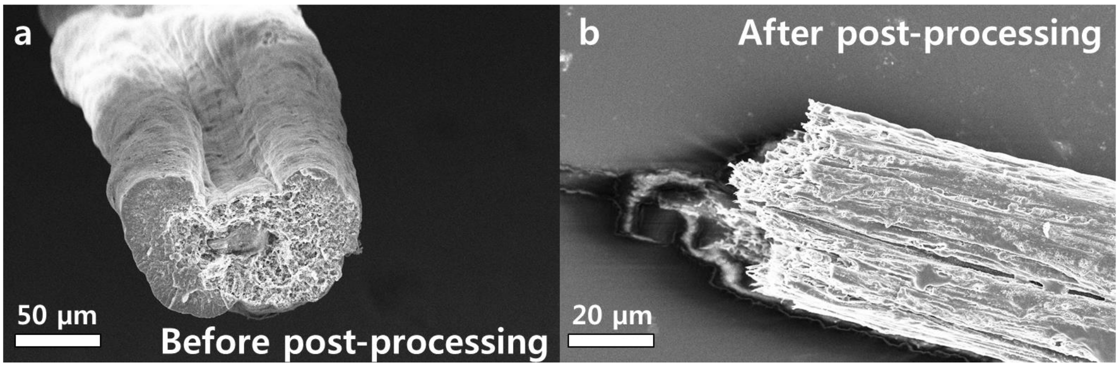

Figure 2. Fibre microstructure images of 40 wt.% CNC/PVOH fibre (a) before, and (b) after post-processing.

A high degree of alignment of crystalline matrix and reinforcements is desirable to maximize mechanical performance. The fibre microstructure was characterised by two-dimensional wide angle X-ray diffraction (2D WAXD). During the post-processing, the amorphous PVOH chains are rearranged into ordered crystalline form with mechanical stretching at elevated temperature, above T_g. In addition, the existing alignment of CNCs help to crystallise polymer chains along the fibre axis as the initially formed gel solidifies, increasing the crystallinity of matrix and strength of composites through tailoring the microstructure. 2D XRD characterization (Figure 3) supports the strong effects of

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both post-processing and CNC reinforcement. 2D diffraction patterns of controlled samples demonstrate that as-spun PVOH is isotropic. It is clearly shown that a mechanical stretching induces a higher degree of orientation of polymer matrix in fibres (Figure 3a and b) along the fibre axis. The 2D diffraction pattern of CNC/PVOH composites illustrates the impact of CNC presence, and the increased degree of orientation of polymer matrix versus pure, drawn polymer; comparing the diffraction patterns indicates an increase in PVOH matrix orientation in both (101) and (200) planes in the presence of CNCs (Figure 3c).

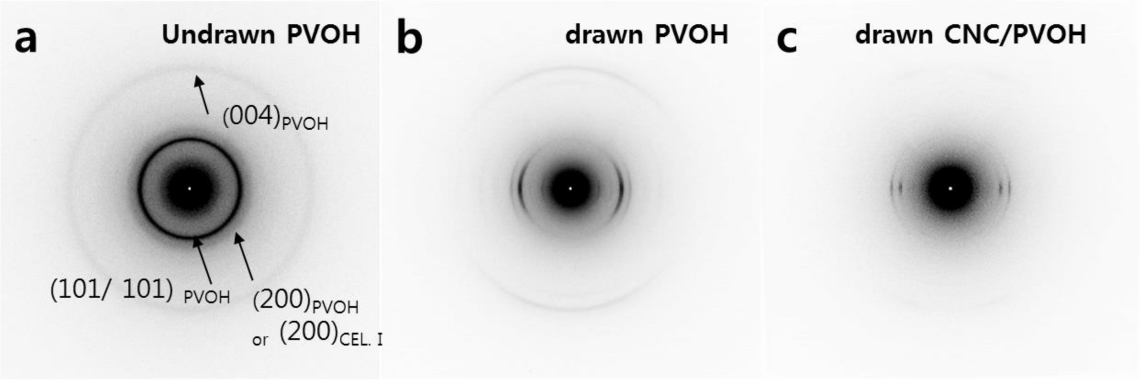

Figure 3. 2D-XRD diffractograms of (a) undrawn PVOH fibres, (b) drawn PVOH fibres, and (c) drawn CNC/PVOH composite fibres (40 wt.%)

The tensile properties of the CNC/PVOH composite fibre were measured with a 20N force sensor on a Linkam TST 350 tester with 1 mm/min crosshead speed at 64% relative humidity. CNC/PVOH composite fibre showed significantly increased yield strength and Young’s modulus for all fibres, comparing with PVOH fibre (Figure 4). The 40 wt.% of CNC/PVOH showed the highest Young’s modulus (29.6 ± 4.2 GPa) and tensile strength (0.85 ± 0.06 GPa) with a strain-to-failure of 5.6 ± 0.2 %. Clearly, the incorporation of CNC into the PVOH matrix increased the tensile strength and Young’s modulus, which indicates that the PVOH fibre become tougher and more resistant to deformation in the presence of CNC.

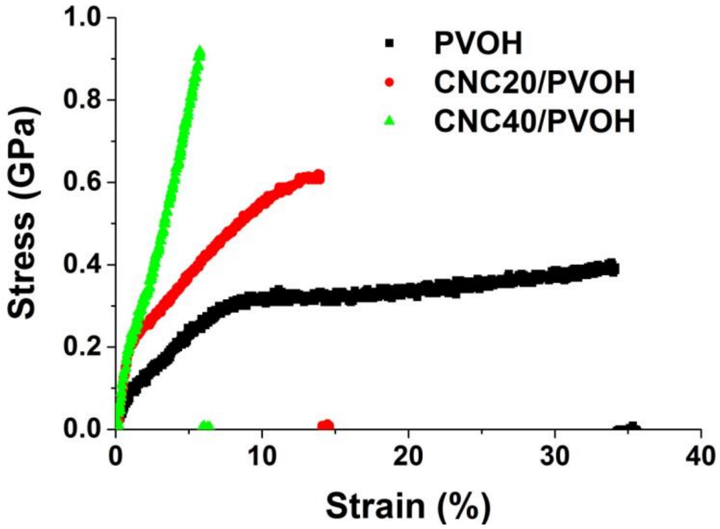

Figure 4. Mechanical performance of CNC/PVOH composite fibre

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4. Conclusion

We prepared high performance CNC/PVOH composite fibre through wet spinning and post-processing. The water-soluble liquid crystalline CNC enables better CNC/PVOH interfacial interaction and improve their compatibility, and this allows a homogeneous dispersion of CNC in the PVOH matrix up to 40 wt.%. From 2D X-ray scattering, the PVOH matrix is found to be aligned along the fibre axis by mechanical stretching in the presence of CNCs, enhancing the mechanical performance. The dramatic improvements in mechanical properties of this composite fibre offer great promise for a number of applications, previously limited by poor mechanical performance.

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