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Recent Development in Applications of Cellulose Nanocrystals for Advanced Polymer-Based Nanocomposites by Novel Fabrication Strategies

Chengjun Zhou and Qinglin Wu

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1. Introduction

Cellulose, one of the world's most abundant, natural and renewable biopolymer resources, is widely present in various forms of biomasses, such as trees, plants, tunicate and bacteria. Cellulose molecule consists of β-1, 4-D-linked glucose chains with molecular formula of $(C_6H_{10}O_5)_n$ (n ranging from 10,000 to 15,000) through an acetal oxygen covalently bonding C1 of one glucose ring and C4 of the adjoining ring (OSullivan, 1997; Samir et al., 2005). In plant cell walls, approximately 36 individual cellulose molecule chains connect with each other through hydrogen bonding to form larger units known as elementary fibrils, which are packed into larger microfibrils with 5-50 nm in diameter and several micrometers in length. These microfibrils have disordered (amorphous) regions and highly ordered (crystalline) regions. In the crystalline regions, cellulose chains are closely packed together by a strong and highly intricate intra- and intermolecular hydrogen-bond network (Figure 1), while the amorphous domains are regularly distributed along the microfibrils. When lignocellulosic biomass are subjected to pure mechanical shearing, and a combination of chemical, mechanical and/or enzymatic treatment (Beck-Candanedo et al., 2005; Bondeson et al., 2006; Filson et al., 2009), the amorphous regions of cellulose microfibrils are selectively hydrolyzed under certain conditions because they are more susceptible to be attacked in contrast to crystalline domains. Consequently, these microfibrils break down into shorter crystalline parts with high crystalline degree, which are generally referred to as cellulose nanocrystals (CNCs) (Habibi et al., 2010). CNCs are also named as microcrystals, whiskers, nanoparticles, microcrystallites, nanofibers, or nanofibrils in the liturautes, all of which are called "cellulose nanocrystals" in this review.

During the past decade, CNCs have attracted considerable attention attributed to their unique features. First, CNCs have nanoscale dimensions and excellent mechanical

properties. The theoretical value of Young's modulus along the chain axis for perfect native CNCs is estimated to be 167.5 GPa, which is even theoretically stronger than steel and similar to Kevlar (Tashiro & Kobayashi, 1991), while elastic modulus of native CNCs from cotton and tunicate reach up to 105 and 143 GPa, respectively (Rusli & Eichhorn, 2008; Sturcova et al., 2005). Due to an abundance of hydroxyl groups existed on surface of CNCs, reactive CNCs can be modified with various chemical groups to accomplish expected surface modification, such as esterification, etherification, oxidation, silylation, or polymer grafting, which could successfully functionalize the CNCs and facilitate the incorporation and dispersion of CNCs into different polymer matrices (Habibi et al., 2010). Therefore, CNCs are considered as one of the ideal nano-reinforcements for polymer matrices (including water-soluble and water-insoluble polymer systems) and have already been incorporated into many polymer matrices to produce reinforced composites (Cao et al., 2011; Kvien et al., 2005). In addition, high aspect ratio, low density, low energy consumption, inherent renewability, biodegradability and biocompatibility are also the advantages of environmentally-friendly CNCs (Siro & Plackett, 2010). Because of the growing interest in the bioconversion of renewable lignocellulosic biomass and unsurpassed quintessential physical and chemical properties of CNCs mentioned above, substantial academic and industrial interests have been directed toward the potential applications of CNCs in polymer-based nanocomposites for various fields, such as high performance materials, electronics, catalysis, biomedical, and energy (Duran et al., 2011; Mangalam et al., 2009).
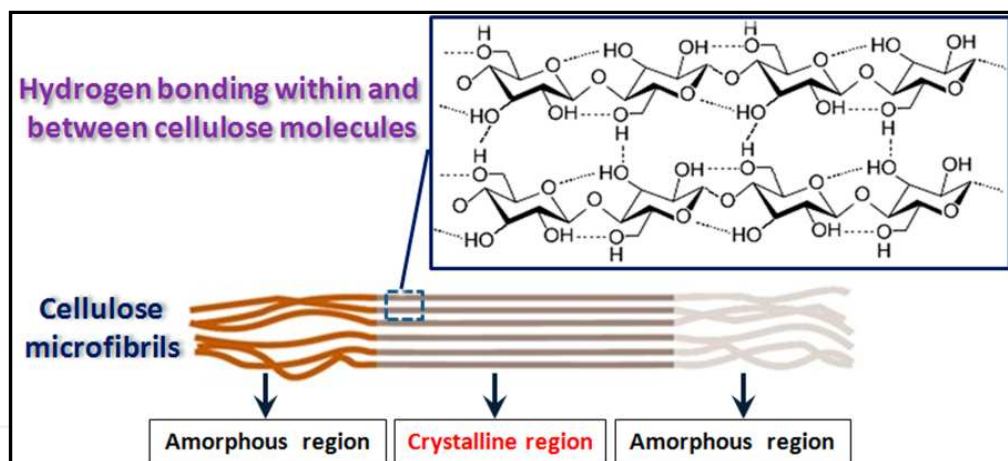
Figure 1. Scheme of interaction between cellulose molecular chains within the crystalline region of cellulose microfibrils .

Many different approaches to fabricate polymer/CNCs nanocomposites have been reported (Eichhorn, 2011; Habibi et al., 2010; Moon et al., 2011), and most researches focused on conventional film materials (Peng et al., 2011). Recently, several non-conventional routes of producing polymer/CNCs nanocomposites have been reported, and some of the most exciting developments have been CNC-filled nanocomposite hydrogels (Capadona et al., 2009; Capadona et al., 2008; Shanmuganathan et al., 2010; Zhou et al., 2011b; Zhou et al., 2011c) and electrospun nanofibers (Lu et al., 2009; Martinez-Sanz et al., 2011; Medeiros et al., 2008; Park et al., 2007; Peresin et al., 2010b; Rojas et al., 2009; Xiang et al., 2009; Zhou et al., 2011a; Zoppe et al., 2009). These approaches could help expand novel applications of natural

biomass nanocrystals in tissue engineering scaffolds, drug delivery, electronic components and devices.

This review is aim at presenting a summary on recent development of cellulose nanocrystals applied in advanced polymer-based nanocomposites using the novel fabrication strategies for targeting nanocomposite hydrogels and electrospun fibers. Specific attentions will be given to highlight opportunities of above-mentioned nanocomposites for future research.

## 2. Nanocomposite polymer hydrogels

The nanocomposite polymer hydrogels (NPHs), referred to cross-linked polymer networks swollen with water in the presence of nanoparticles or nanostructures, are new generation materials that can be used in a wide variety of applications including stimuli-responsive sensors and actuators, microfluidics, catalysis, separation devices, pharmaceutical, and biomedical devices (Schexnailder & Schmidt, 2009). The most potential use of NPHs is for novel biomaterials in tissue engineering, drug delivery, and hyperthermia treatment because they, in comparison with conventional hydrogels, can provide improved properties such as increased mechanical strength and ability for remote controlling (Samantha A. Meenach, 2009). Because of the excellent dispersion of CNCs in water (Liang et al., 2007), the fabrication, molding, and application of hydrogels containing CNCs without modification have many advantages compared with other nanofillers such as polymer and metal nanoparticles (Saravanan et al., 2007; Wu et al., 2009). Moreover, CNCs possessed the long-term biocompatibility and controlled biodegradability, which is beneficial to further develop applications of NPHs used as biomaterials.

Nakayama et al (2004) for the first time reported cellulose-polymer nanocomposite hydrogels composed of bacterial cellulose (BC) and gelatin. Bacterial cellulose is biosynthesized by microorganisms, and displays unique properties, including high mechanical strength, high water absorption capacity, high crystallinity, and an ultra-fine and highly pure fiber (10-100 nm) network structure (Vandamme et al., 1998). By immersing BC gel in aqueous gelatin solution followed by cross-linking with N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride, high mechanical strength double-network (DN) nanocomposite hydrogels were prepared. The compressive fracture strength and elastic modulus of the obtained BC-gelatin DN hydrogel are several orders of magnitude higher than those of pure gelation gel, almost equivalent to those of articular cartilage. In addition, this double network nanocomposite hydrogels exhibits not only a mechanical strength as high as several megapascals but also a low frictional coefficient of the order of 10^{-3}. Buyanov et al (2010) have fabricated high strength composite bacterial cellulose-polyacrylamide (BC–PAM) nanocomposite hydrogels by synthesizeing PAM networks inside BC matrices. These hydrogels not only exhibit superior mechanical properties (compression strength of up to 10 MPa) and withstanding long-term cyclic stresses (up to 2000–6000 cycles) without substantial reduction of mechanical properties, but also show anisotropic behavior on both swelling and deformation. The above-mentioned reports mainly focused on the research used BC as the first nano-network, resulting in its high loading in nanocomposites. However, BC is of the high cost (about 100 times more than that of plant cellulose (Bochek, 2008)) with

the relatively low production capacity, likely limiting its potential application in hydrogels for widespread uses. Cellulose nanocrytals or nanofibers isolated from plants have lower cost and higher price-performance ratio than BC, and their size can be facilely adjusted to meet the requirement of hydrogels properties for the various applications.

By employing rod-shaped CNCs (about 10 nm in diameter and 120 nm in length) as the reinforcement nanofiller and in situ free-radical polymerizing/cross-linking acrylamide, we have successfully fabricated PAM-CNC nanocomposite hydrogels (Zhou et al., 2011b). During the gelation reaction of nanocomposite hydrogels, CNCs can accelerate the formation of hydrogels and then increased the effective crosslink density of hydrogels through the grafting copolymerization of monomer acrylamide on the surface of CNCs. Compared to the pure PAM hydrogels, the obtained nanocomposite hydrogels at a low loading level (6.7 wt%) of CNCs exhibited a dramatic enhancement in the shear storage modulus (4.6-fold) and the compression strength (2.5-fold). Hence, CNCs are not only a reinforcing agent for hydrogels, but also act as a multifunctional cross-linker for gelation. A possible mechanism for forming NPHs was proposed, as shown in Figure 2. Moreover, CNCs with smaller dimension and aspect ratios could help promote the sol-gel transition and facilitate the formation of nework of PAM-CNC nanocomposite hydrogels (Zhou et al., 2011c).

Spagnol et al (2012a) synthesized superabsorbent nanocomposite hydrogels based on poly(acrylamide-co-acrylate) (PAM-AA) and CNCs by free-radical aqueous copolymerization, and focused on the investigation of pH-responsiveness and cation-sensitivity character of NPHs. Swelling capacity and swelling-deswelling behavior of PAM-AA/CNC nanocompoiste hydrogel exhibited high pH-sensitivity and reversible pH-responsiveness properties. Furthermore, the swelling measurement in different salt solutions showed that the swelling capacity of NPHs in $MgCl_2$ and $CaCl_2$ solutions are much lower than that in NaCl and KCl solutions and distilled water. The swelling–deswelling process of NPHs was alternatively carried out between sodium and calcium solutions, suggesting a swelling-deswelling pulsatile behavior. It was reported that the pH and salt responsive behavior also occurred in superabsorbent nancomposite hydrogels based on CNCs and chitosan-graft-poly(acrylic acid) copolymer (Spagnol et al., 2012b).
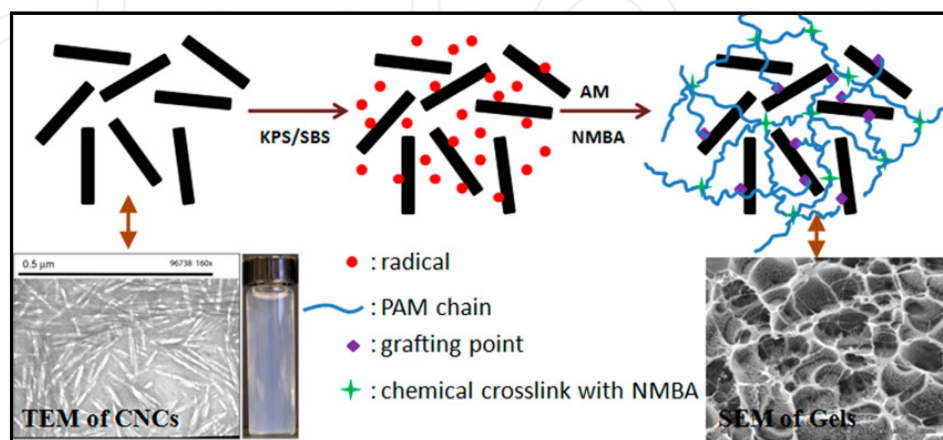
Figure 2. Scheme of the gelation mechanisms of PAM–CNC nanocomposite hydrogels. Reprinted with permission from (Zhou et al., 2011b) Copyright 2011 Elsevier.

PAM and its derivative hydrogels have been of great interest for developing applications in tissue engineering because of their non-toxic and biologically inertness, capability for preserving their shape and mechanical strength, and convenient adjustability of mechanical, chemical and biophysical properties (Zhou & Wu, 2011; Zhou et al., 2011d). Recently, we investigated the proliferations of dental follicle stem cells on PAM hydrogel and PAM/CNC nanocomposite hydrogel by alamarBlue® assay. As shown in Figure 3, the cell proliferations on PAM-CNC nanocomposite hydrogels were significantly higher than on the PAM hydrogels at days of 7 and 10, indicating that CNCs could help accelerate the proliferation of stem cells likely because the embedded nanocrystals formed an extracellular matrix-like microstructure in the hydrogel to promote cell-matrix interactions by providing more binding sites for cell adhesion and proliferation. This suggests that CNCs reinforced nanocomposite hydrogel systems showed improved cell biocompatibility and are suitable substrates used as cell carriers and traditional bone-defect repair and bone tissue engineering.
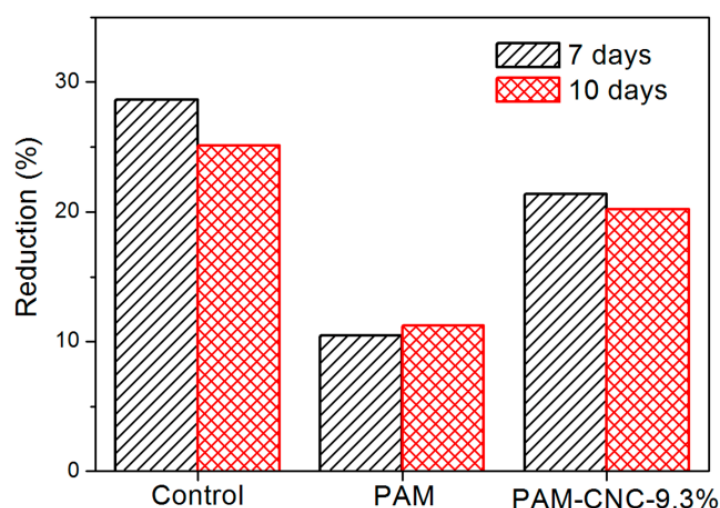
Figure 3. Reduction in expression of dental follicle stem cells for pure PAM hydrogels and PAM-CNC nanocomposite hydrogels with 9.3 wt% of CNCs at 7 and 10 days.

Aouada et al (2011) reported a simple, fast, and low cost strategy for the synthesis of nanocomposites by directly immerseing dry polyacrylamide-methylcellulose (PAM-MC) hydrogels into CNC aqueous suspensions. The CNCs were effectively anchored into the hydrogel network to provoke the increase in rigidity of the hydrogel networks and the decrease in pore sizes and the formation of three dimensional well-oriented pores. The incorporation of CNCs improved the crystallinity, and the mechanical and structural network properties of nanocomposite hydrogels without negatively impacting their thermal and hydrophilic properties. The value of the maximum compressive stress increased to 4.4 kPa for nanocomposite hydrogels from 2.1 kPa for pure PAM-MC hydrogels. Because of their biodegradability and biocompatibility, these reinforced nanocomposite hydrogels are promising materials for different technological applications, especially in agricultural applications, such as a carrier vehicle for agrochemical controlled release, such as pesticides (Aouada et al., 2010) and nutrients (Bortolin et al., 2012).

3. Electrospun nanocomposite fibers

Electrospinning is a highly versatile technique to generate continuous 1D polymeric fibers with diameters ranging from several micrometers down to 100 nanometers or less through a high voltage charged polymer solutions or melts (Reneker & Yarin, 2008). Electrospun nanofibrous materials possess a variety of interesting characteristics such as small dimension, large specific surface area, wide-range porosity, unique physicochemical property, and excellent flexibility for chemical/physical surface functionalization. Hence, electrospun nanofibrous materials not only are being used in research laboratories but also are increasingly applied in industry (Greiner & Wendorff, 2007). Their application includes, but is not limited to, optoelectronics, sensors, catalysis, filtration, energy-related materials and medicine. Electrospun polymeric nanofibers, however, are not sufficiently strong for many applications because of low molecular chain orientation along the fiber long-axis resulting from low stretching forces in the process of fiber formation (Ayutsede et al., 2006). During the past several years, a large number of studies have been conducted to improve mechanical properties of electrospun polymeric nanofibers. Incorporating nanoparticles into polymer matrices is one technique that has been developed and used as one of the most effective methods for reinforcing electrospun nanofibers (Hou et al., 2005; Lu et al., 2009). As one of the strongest and stiffest natural biopolymers, CNCs have been successfully used as highly effective reinforcing nanofillers for improving mechanical properties of various electrospun polymer matrices, as summarized in Table 1. Moreover, research effort has been focused on increased dispersion of CNCs in the matrix, improved alignment of CNCs along the fiber length, tailored CNC-matrix interfacial properties (Moon et al., 2011). According to the origination of polymer (i.e. synthetic and natural polymer), this section will concentrate on the processing of electrospun nanocomposite fibers and the effect of CNCs on their mechanical properties.

3.1. CNCs reinforced synthetic polymer

Due to the excellent dispersion property of CNCs in water, the first report of electrospun nanocomposite fibers was to electrospin water-soluble PEO and CNCs from BC. Highly crystalline rod-like CNCs with a high aspect ratio and specific area (420 ± 190 nm in length and 11 ± 4 nm in width) were incorporated into the electrospun PEO fibers with a diameter of less than 1 μm. Well-embedded CNCs were aligned and partially clustered inside the fibers. Compared with the electrospun PEO fibrous mats, the tensile modulus, tensile strength and elongation of electrospun nanocomposite fibrous mats containing 0.4 wt% of CNCs were increased by 193.9%, 72.3% and 233.3%, respectively, indicating that the existence of CNCs effectively improved the mechanical properties of the electrospun mats.

The dispersion of CNCs in electrospun fibers could be improved by tailoring the geometrical dimensions (length, L, and width, w) of CNCs, which can be controlled by adjusting the source of the cellulosic material and the conditions of fabrication. Recently, wood-based CNCs with a diameter of 10 ± 3 nm and a length of 112 ± 26 nm were processed into electrospun PEO fibers (Zhou et al., 2011a). Figure 4 shows that rod-shaped CNCs without obvious aggregation are well-dispersed in the as-spun nanofibers. Decreasing

aspect ratio can facilitate a better dispersion of CNCs within polymer matrix. When the CNC content was increased from 0 to 20 wt %, E_{max} and σ of nanocomposite fibrous mats increased from 15.2 to 38.3 MPa and from 2.50 to 7.01 MPa, respectively, whereas ε_b decreased markedly from 200 to 106 %. In addition, improving dispersion of CNCs within the fibers could also be achieved by adopting some pre-treatment and processing methods on electrospinning solution, such as sonication (Martinez-Sanz et al., 2011).

| Matrix	CNC origin and size	ϕ_{CNC} wt%	E_{max} %Increase	σ %Increase	ε_b %Increase	Reference
PEO	Bacteria, 11 ± 4 nm in w, 420 ± 190 nm in L	0–0.4	+193.9	+ 72.3	+233.3	(Park et al., 2007)
PAA	Cotton	0–20	+ 3441.1 + 7633.9[a]	+1455.2 + 5658.6[a]	- 73.5 - 99.9[a]	(Lu & Hsieh, 2009)
PEO	MCC, 10 ± 3 nm in w, 112 ± 26 nm in L	0–20	+ 152.0 + 392.1[b]	+ 180.4 + 240.8[b]	- 47.0 - 37.5[b]	(Zhou et al., 2011a)
PEO	Cotton, 5–10 nm in w, 40–100 nm in L	0–20	+ 190.5	+ 377.5	- 33.5	(Zhou et al., 2012b)
PEO	Tunicate, ~ 20 nm in w, ~ 2 μm in L	0–15	+ 98.8[c]	—	—	(Changsarn et al., 2011)
PVA	Ramie, 3–10 nm in w, 100–250 nm in L	0–15	+ 270.9[c]	—	—	(Peresin et al., 2010b)
PCL	Ramie, 3–10 nm in w, 100–250 nm in L	0–7.5	+ 64.3 + ~40[c]	+ 37.2 —	+ 49.0 —	(Zoppe et al., 2009)
PS	Paper, 10–20 nm in w, 200 nm in L	0–9	+ ~60[c]	—	—	(Rojas et al., 2009)
PMMA	Bacteria, 15–20 nm in w, 0.3–8 μm in L	0–20	—	—	—	(Olsson et al., 2010)
PMMA	Wood, ~17 nm in w, 190–660 nm in L	0–41	+ 17[d]	—	—	(Dong et al., 2012)
PLA	MCC, 92 ± 3 nm in w, 124 ± 35 nm in L	0–10	+ 37.0	+ 30.2	-1.4	(Xiang et al., 2009)
EVOH	Bacteria, lower than 30 nm in w	0–8	—	—	—	(Martinez-Sanz et al., 2011)
PLA	Cotton	0–12.5	—	+161.9	—	(Ramirez, 2010)
Silk	Bark, 25–40 nm in w, 400–500 nm in L	0–4	+ 300.3	+ 208.0	- 55.6	(Huang et al., 2011)

[a], tensile properties of crosslinked nanocomposite fibrous mats; [b], tensile properties of heterogeneous nanocomposite fibrous mats; [c], Dynamic mechanical analysis (DMA) storage modulus of nanocomposite fibrous mats; [d], nano-DMA storage modulus of individual nanocomposite fiber.

w, width of CNCs; L, length of CNCs; ϕ_{CNC}, loading range of CNCs in composites; E_{max}, max Young's modulus of nanocomposite mats; σ, max tensile stress at yield for nanocomposite mats with E_{max}; ε_b, elongation at break for nanocomposite mats with E_{max}.

Acronyms: PEO, poly(ethylene oxide); PVA, poly(vinyl alcohol); PAA, poly(acrylic acid); PCL, poly(ε-caprolactone); PLA, poly(lactic acid); PS, polystyrene; EVOH, Ethylene–vinyl alcohol copolymer; PMMA, poly(methyl methacrylate);

Table 1. Summary of the experimental results of the reviewed publications involving origin and size of CNCs, and mechanical properties of electrospun nanocomposite fibers/mats.
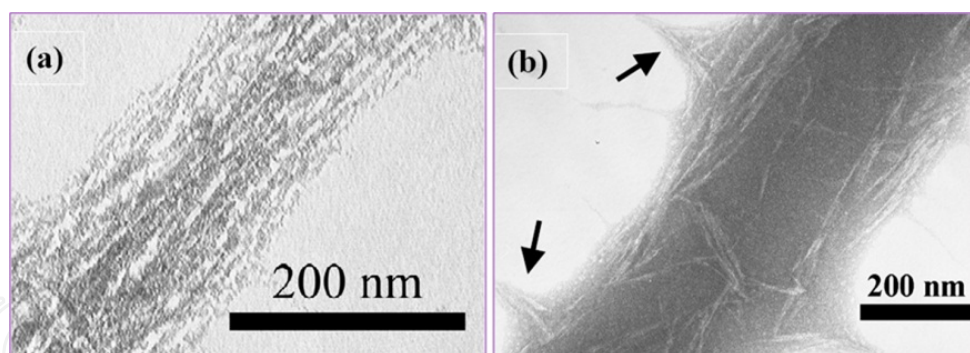
Figure 4. TEM micrographs of PEO/CNC nanocomposite fibers with 20 wt% CNC loading electrospun from 5 wt% (a) and 7 wt% (b) solutions. (arrows pointing to typical secondary nanofibers). Reprinted with permission from (Zhou et al., 2011a) Copyright 2011 American Chemical Society.

For the hydrophobic polymer systems, CNCs should firstly be well-dispersed in organic solvent (such as DMF, N,N′-dimethylformamide; THF, tetrahydrofuran) before electrospinning because solution-based processing of nanocomposite nanofibers require good dispersability of both CNCs and polymer in one common solvent. Direct ultrasonication of freeze-dried CNCs is a facile method to prepare electrospinning solution (Xiang et al., 2009), and the redispersion of CNCs could be improved by conducting surface modification on CNCs (Zoppe et al., 2009) and adding additves. Rojas et al (2009) obtained fibers with smooth surface using solely THF as a solvent to electrospin PS containing surfactant-dispersed CNCs. The addition of non-ionic surfactant to the PS-CNC suspensions improved their stability, minimized (or prevented) the presence of beads in the resulting fibers, and promoted the nano-reinforcement of CNCs on PS fibers. However, the directly re-dispersed CNCs cannot form stable suspension at high loading leverls because the hydrophilic nature of cellulose and the strong hydrogen bonding interactions between CNCs. Olsson et al (2010) reported a two-step solvent exchange method to replace the water of CNC suspension by acetone, followed by further replacement through DMF/THF solvent in the same manner. A high degree of dispersion of CNCs was obtained for a variety of CNC contents and the aggregation of CNCs up to 7 wt% was greatly suppressed because CNCs were aligned and rapidly sealed inside PMMA matrix during the continuous formation of electrospun fibers. Moreover, the direct solvent exchange from water to organic solvent conducted by vacuum rotary evaporation was also used to disperse CNCs (Dong et al., 2012; Zoppe et al., 2009) .

The alignment of CNCs along the fiber is also an important factor to determine the axial strength of electrospun nanocomposite fibers reinforced with CNCs. Considering CNCs can be aligned under the high electrostatic fields (Habibi et al., 2008), the electrospinning process could facilitate alignment of CNCs along the fiber long-axis. Usually, the alignment of CNCs was observed by scanning electron microscope (SEM) (Dong et al., 2012; Olsson et al., 2010) and TEM (Changsarn et al., 2011; Lu & Hsieh, 2009; Park et al., 2007; Zhou et al., 2011a). Figure 4 presents typical TEM pictures of CNC aligned parallel inside/along the longitudal axis of nanocomposite fibers. Interestingly, Figure 4b shows that CNCs dispensed in electrospun fibers had radial anisotropy or a skin-core morphology, in which CNCs in the core are oriented more randomly, while ones in the skin have a higher degree

of orientation. Dong et al (2012) investigated the orientation of CNCs embedded in electrospun PMMA/CNC fiber by solvent-etching PMMA from nanocomposite fibers with drops of THF, and discovered highly aligned CNCs along the fiber axis, as shown in Figure 5. Besides the high electrostatic fields, the high alignment of CNCs along the polymer fiber could also be attributed to the shear forces in the liquid jet and the orientation of polymer chains during electrospinning process, and the nanoscale confinement effect (Chen et al., 2009).
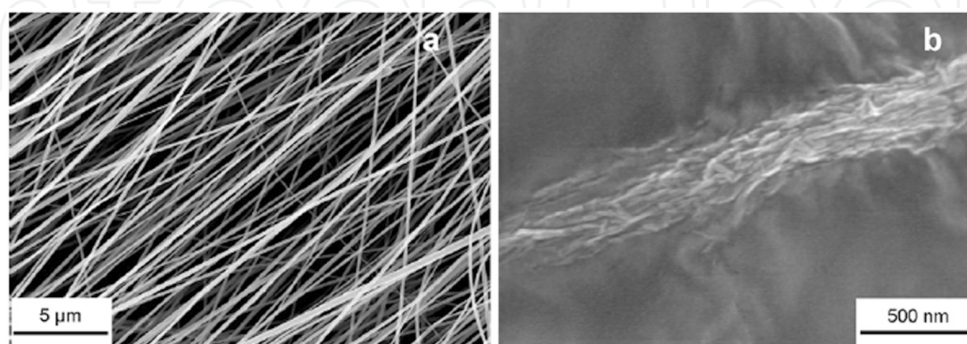

Figure 5. SEM of (a) alignment of PMMA/CNC fibers with 33 wt% of CNCs and (b) alignment of CNCs along fiber long-axis revealed by solvent etching. Reprinted with permission from (Dong et al., 2012) Copyright 2012 Elsevier.

It is well known that the improved interface between nanofillers with polymer matrix is beneficial to the mechanical properties of polymer-based nanocomposites (Zhang et al., 2010; Zhou et al., 2012a; Zhou et al., 2008b; Zhou et al., 2008c). For hydrophilic polymers, the hydrogen bonding between CNCs and polymer matrix play a very important role in determining polymer-CNC interaction. Peresin et al (Peresin et al., 2010b) reported CNC-reinforced nanocomposite fibers produced via electrospinning of poly(vinyl alcohol) (PVA) with two different concentrations of acetyl groups. The hydrogen bonding between PVA and CNCs was confirmed by observing the band between 3550 and 3200 cm^{-1} in Fourier transform infrared spectra (FTIR). The higher the hydrolysis degree of PVA (i. e. more –OH group in PVA chain), the stronger the PVA-CNC interaction, which was also observed by FTIR spectra. To confirm the effect of the hydrogen bonding, DMA in tensile mode was used for mechanical analysis. The storage modulus of nanocomposite fibrous mats showed a steady increase with increased CNC content from 0 to 15% loading. The storage modulus was 15.45 MPa for pure PVA mats and rose to 57.30 MPa at 15 wt% CNC loading. It was concluded that the observed strength enhancement in CNC-loaded PVA mats mainly is related to the reinforcing effect of the dispersed CNCs through the percolation network held by hydrogen bonds.

In addition to strong hydrogen bonding, covalent bonding also provides a means for enhancing polymer-nanofiller interface to achieve optimal composite properties (Zhou et al., 2008a). To produce greater reinforcing effect from CNCs in electrospun nanocomposite fibers, Lu & Hsieh (2009) fabricated electrospun PAA-CNC nanocomposite fibers. The interfacial interactions between CNCs and PAA could be further improved by heat-induced esterification between the CNC surface hydroxyls and PAA carboxyl groups, which produce covalent crosslinks at the PAA-CNC interfaces, render the nanocomposite fibrous mats insoluble in

water, and make mats to be more thermally stable and far more superior tensile properties. The Young's modulus and tensile strength of mats were significantly improved with increased CNC loadings in the nanocomposite fibers by up to 35-fold and 16-fold, respectively, with 20 wt% CNC loading, as shown in Figure 6. It is more impressive that the crosslinked nanocomposite fibrous mats with 20 wt% CNC exhibited 77-fold increase in modulus and 58-fold increase in strength, respectively. Moreover, the synergies of polymer crosslinking network and CNC's reinforcement could also improve the mechanical properties of nanocomposite fibrous mats. Recently, we reported UV-initiated crosslinking of PEO nanofibers in the presence of CNCs, which was performed with pentaerythritol triacrylate as both photo-initiator and crosslinker (Zhou et al., 2012b). With increased CNC content up to 10 wt%, the maximum tensile stress and Young's modulus of the crosslinked PEO/CNC composite fibrous mats increased by 377.5 and 190.5% than those of uncrosslinked PEO mats, and 76.5 and 127.4% than those of crosslinked PEO mats, respectively.
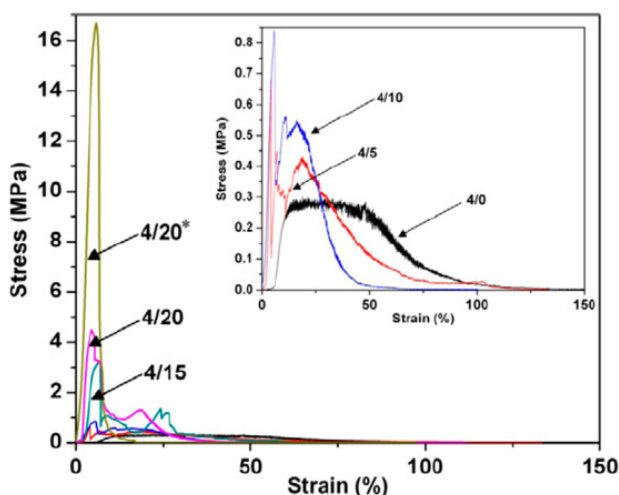

Figure 6. Stress-strain curves of electrospun PAA/CNC nanocomposite fibrous mats at different CNC loadings. * represents crosslinked samples. Reprinted with permission from (Lu & Hsieh, 2009) Copyright 2009 IOP Publishing.

Due to the fact that the electrospun mats are non-woven fabrics, their mechanical properties are influenced by several factors including composition, morphology and structure of individual fiber, the interaction between fibers, orientation of fibers, and porosity of mats. An nano-indentation study was performed on single sub-micron PMMA/CNC fibers in the transverse direction to explore the reinforcement of CNCs on single nanocomposite fibers, which showed a modest increase in the mechanical properties with increasing CNC content, about 17% improvement in nano-DMA storage modulus with the loading of 17 wt% CNCs (Dong et al., 2012). In addition to the reinforceing effect of CNCs on fibers, it was also found that the addition of CNCs could reduce electrospun fiber diameters and improved fiber uniformity attributed to the enhanced electric conductivity of electrospinning solutions in the presence of CNCs. This tends to increase the mechanical properties of mats because smaller fiber diameters yield higher overall relative bonded areas between fibers by increasing its surface area, bonding density, and distribution of bonds (Olsson et al., 2010; Peresin et al., 2010b; Zhou et al., 2011a). Moreover, the orientation of nanocomposite fibers

within mats also influence greatly on the mechanical properties of mats (Wang et al., 2011). Alignment of electrospun nanocomposite fibers reinforced with CNCs has been achieved by many techniques, including by running the fibers over a hollow spool with high rotation (Olsson et al., 2010), an aluminium frame with openings (Changsarn et al., 2011), a rotating mandrel covered with aluminium foil (Dong et al., 2012). Figure 5a shows the morphology of one-dimensional aligned fibers of PMMA/CNC. Furthermore, the more sufficient contact and stronger bonding between fibers could also lead to the improvement in mechanical properties of fibrous mats. It was found that humidity treatments on the PVA/CNC nanocomposite fibrous mats induced significant enhancement of strength as a result of the increased contact area and enhanced adhesion between the fibers (Peresin et al., 2010a). The heterogeneous fibrous mats composed of rigid–flexible bimodal PEO/CNC nanocomposite fibers was demonstrated to be higher in mechanical properties than their homogeneous counterparts (Zhou et al., 2011a). The reinforced mechanism was illustrated by morphology observation of the tensile process, as shown in Figure 7. With increased strain, the tensile stress of unaligned electrospun fibrous mats increased sharply at the beginning, and then increased slowly over a relatively long period of strain followed by the final rupture (Gomez-Tejedor et al., 2011). At the beginning of tensile process, the mats were stretched in a macroscopic view and most fibers in mats hardly moved attributed to the cohesion between fibers, which could determine Young's modulus of mats. When most fibers in mats reached the tightened form, yield of mats appeared, at which the interaction points among fibers were broken. With further increase of tensile strain, the fibers in mats were drawn out to highly align along the tensile direction. However, the rupture of individual fibers one by one did not influence the tensile properties of the whole mats, resulting in a large elongation at break for electrospun mats. At the maximum tensile stress level, most fibers were necked and broken, leading to the final rupture of mats.
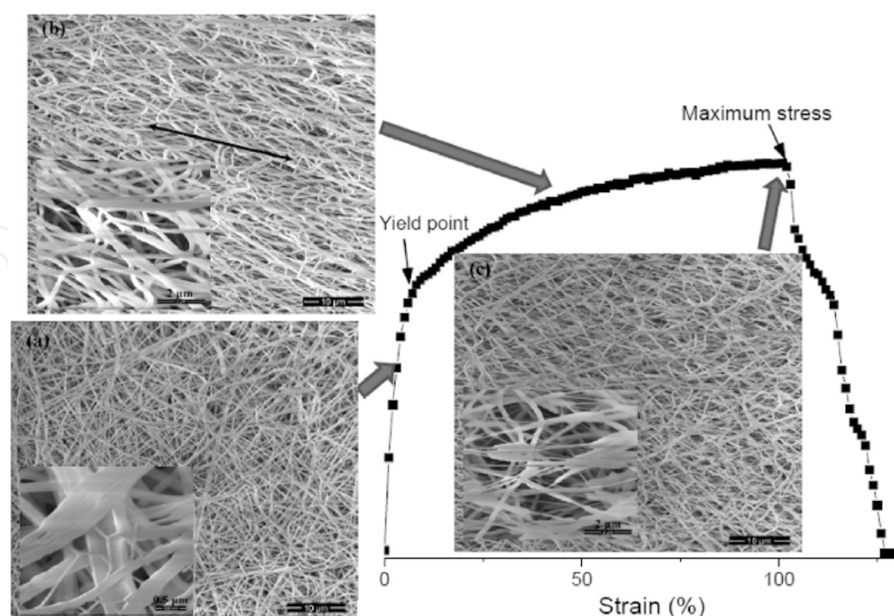
Figure 7. Morphology observation of the tensile process on PEO/CNC nanocomposite fibrous mats with 20 wt% CNC loading electrospun from 7 wt% solutions. Reprinted with permission from (Zhou et al., 2011a) Copyright 2011 American Chemical Society

3.2. CNCs reinforced natural polymer

With increasing environmental consciousness about petroleum-based polymer materials, development of fully biodegradable, eco-friendly, and sustainable, bio-based nanocomposites have attracted more and more attention both in the academic and industrial fields (Kim & Netravali, 2010; Oksman et al., 2006). The so-called "green" composites are derived from natural resources including plant or animal origin (Khalil et al., 2012). Some researchers have successfully used CNCs as highly effective reinforcing nanofillers to fabricate electrospun bio-nanocomposite fibers from various biopolymers such as PLA (Li, 2010; Ramirez, 2010; Xiang et al., 2009), cellulose and its derivative (Herrera Vargas, 2010; Magalhaes et al., 2009), silk (Huang et al., 2011), and lignin (Ago et al., 2012).

PLA is such typical bio-based aliphatic polyester produced by polymerization of lactic acid, which is originated from renewable natural resources such as corn, starch, and molasses. The electrospun PLA/CNC nanocomposite fibers were widely reported because PLA possessed excellent physical properties of transparency, high elastic modulus, and high melting temperature. Xiang el al (2009) incorporated CNCs into electrospun PLA fibers, and found that Young's modulus and strength of obtained nanocomposite mats with 1 wt% loading of CNCs were improved by approximately 37 and 30 %, respectively. Besides the reinforcement of CNCs on PLA fibers, Ramírez (2010) also investigated the cytocompatibility of the PLA/CNC nanocomposite fibrous mats used as scaffold. After one week of cell culture, confocal microscopy indicated that the cells grown on the PLA/CNC nanocomposite mats were confluent and very well aligned along the fibers while cells cultured on pure PLA mats were not as confluent as in the developed nanocomposite mats. This demonstrates the feasibility of the PLA/CNC nanocomposite fibrous mats as a potential scaffold for bone tissue engineering.

Magalhães et al (2009) reported a electrospun fully-cellulosic core-in-shell nanocomposite fibers consisting of regenerated cellulose (type II and amorphous) in the shell and CNCs in the core, which were fabricated by the co-electrospinning technique. Wood-based 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 CNC suspension obtained by the sulphuric acid hydrolysis of sisal bleached and cotton fibers was used as the core liquid in the internal concentric capillary needle. It was found that the formation of individual fiber could be promoted by precisely controlling the voltage and flow rate to decrease the shell-to-core volume ratio. The novel core-in-shell nanocomposite fibers also showed better mechanical properties than the pure electrospun cellulose II fibers.

4. Conclusion and perspectives for the future

In the review, recent development on applications of cellulose nanocrystals in nanocomposites fabricated by two novel strategies, i.e., gelation and electrospinning is presented. It is shown that CNCs have a distinct advantage for improving mechanical properties of both nanocomposite hydrogels and electrospun nanocomposite fibers/mats.

The obviously reinforced effect of CNCs could help facilitate the potential applications of CNC-filled nanocompsite as advanced function materials.

CNCs reinforced hydrogels have been reported widely, and their properties, mainly mechanical properties, have been investigated. With the increased requirement for the multifunctional properties, nanocomposite hydrogels from CNCs and other stimuli-responsive polymer would be further developed. Various nanocomposite hydrogels reinforced with CNCs can be designed to become fast temperature, pH, and salt sensitive for controllable drug delivery system. Futhermore, using CNCs to reinforce natural polymer-based hydrogels could endow many favorable properties such as hydrophilicity, biodegradability, biocompatibility, low cost, and non-toxicity, resulting in applications of nanocomposite hydrogels in tissue engineering.

For the electrospun nanocomposite fibers containing CNCs, most studies focus on their fabrication, morphology, mechanical and thermal properties. There are still several major challenges for the further development of CNC-reinforced nanocomposites fibers. These include surface modification and homogeneous dispersion of CNCs, interface and alignment characterization of CNCs within individual electrospun nanocomposite fiber, analytical model for mechanics of single nanocomposite fiber, and assembly and effect of nanocomposite fibers within mats. More importantly, it is very worthwhile to exploit the functional characteristics and properties of CNC-filled nanocompsite fibers/mats to create new and specific applications such as energy-related materials, sensor, barrier films, and tissue engineering scaffolds.

Author details

Chengjun Zhou and Qinglin Wu
School of Renewable Natural Resource, Louisiana State University Agricultural Center,
Baton Rouge, Louisiana, USA

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5. References

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