Review on cellulose nanocrystals (CNCs) as reinforced agent on electrospun nanofibers: mechanical and thermal properties

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Abstract. The growing ecological and environmental consciousness has driven efforts for development of new innovative products for various end-use applications. Nanotechnology plays an important role in the development of such products. Electrospun nanofibers which are produced from electrospinning technique are likely to be the next novel nanomaterials designated in the consumer products. Cellulose nanocrystals (CNCs) are nanoscale cellulose produced from renewable resources with strong reinforcing potential when included in a polymer matrix. Nanotechnology plays an important role in the development of such products. Electrospun nanofibers which are produced from electrospinning technique are likely to be the next novel nanomaterials designated in the consumer products. Electrospinning technique is the known prevalent technology for the manufacturing of nano-sized diameter fibers with the advanced functionalities. Various polymers have been successfully electrospun into ultrafine fibers in recent years mostly in solvent solution and some in melt. In this paper, a mini review is presented on the researches and developments related to electrospin polymer nanofibers.

1. Introduction
Nanocellulose, a unique and promising natural material extracted from native cellulose, has gained much attention for its use as biomedical material, because of its remarkable physical properties, special surface chemistry and excellent biological properties (biocompatibility, biodegradability and low toxicity) [1]. Nanocellulose can be define as nano-sectional fibers <100 nm in diameter or micronsized fibers with nano-dimensional cross-sectional structures [2]. For past decade, production of nanocellulose from biomass is gaining attention because of its mechanical and thermal properties, as well as environmental friendliness and cost-effectiveness. Review by Habibi et al., [3] and Samir et al., [4], the development of nanocellulose has attracted significant interest in the last decades due to the unique characteristics, such as high surface area-to-volume ratio, high surface area, high Young’s modulus, high tensile strength, and low coefficient of thermal expansion. Eichhorn et al., [5] in his research revealed that the specific modulus of CNCs exceeds those of common engineering materials such as steel, concrete, glass, and aluminum.

Among reported studies, CNCs have received ever-increasing interest, such as reinforced with polylactic acid (PLA) [6-10], poly-vinyl alcohol (PVA) [11-22], poly-vinyl acetate (PVAc) [23], Polycrylonitrile (PAN) [24], Poly-vinyl pyrrolidone (PVP) [25], poly-methyl methacrylate (PMMA) [26], polyethylene terephthalate (PET) [27] and etc. 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, facilitate the incorporation and dispersion of CNCs into
different polymer matrices [3] etherification, oxidation, silylation, or polymer grafting, which could successfully functionalize the CNCs and facilitate the incorporation and dispersion of CNCs into different polymer matrices. CNCs is 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 [28].

Figure 1. The TEM shows the representative morphology of the CNCs. Based on the TEM images, the CNC diameter is in the range of 6-12 nm and length between 150 and 200 nm [24].

This review is aim at presenting a summary on recent effect of cellulose nanocrystals reinforced in advanced polymer-based nanocomposites using the novel fabrication strategies for targeting electrospun nanofibers.

2. Electrospinning
2.1 Electrospinning technology
Electrospinning technique generates ultrafine electrospun nanofibers through the applied electrical force and then collects those nanofibers to form non-woven or felt-type fabrics [29-30]. The term “electrospinning”, derived from “electrostatic spinning”, was used relatively recently (in around 1994), its fundamental idea dates back more than 60 years earlier. A lab-scale electrospinning reactor unit can be straightforwardly completed by using simple laboratory apparatus consists of high voltage power supply, syringe pump and metal collector, as the basic part of the electrospinning setup component. The ultrafine electrospun nanofibers will be formed at the needle tip contained charged spinning solution, once the surface tension of the charged solution has been exceeded. The formation of those electrospun nanofibers will be deposited onto the grounded collector plate, assisted by the electrostatic interaction [31].

Figure 2. Schematic diagram to show polymer nanofibers by electro-spinning [31].
Polymer solution or melt are able to be electrospun into fibrous structure shaped by electrospinning technique with the appropriate selection of suitable solvents and optimum electrospinning working parameters. Jiang et al., [32] proved that electrospun fibers has provided additional advantages as compared to film and sheet carriers due to their nano- or submicron-scale diameter and consequent very large surface area, and, thus, are ideal as controlled release. The functional additives such as CNCs at one-dimensional (1D) range sizes are also possible to be embedded into the nano-sized diameter fibers during the process of spinning.

2.2 Electrospun nanocomposites fibers

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 [33]. CNCs have been successfully used as highly effective reinforcing nanofillers for improving mechanical properties of various electrospun polymer matrices, as summarized below.

2.2.1. Tensile properties

Mechanical properties of nanofibers are important in many practical applications. Table 1 summarized the comparison of maximum tensile stress ($\sigma_{\text{max}}$), Young’s modulus (E), and elongation at break ($\varepsilon_b$) obtained between neat PVA, neat PLA and reinforced CNC-PVA and CNC-PLA.

| Nanocomposites     | $\sigma_{\text{max}}$ (MPa) | E (MPa)       | $\varepsilon_b$ (%) | References |
|--------------------|-----------------------------|---------------|---------------------|------------|
| PLA                | 82.2 ± 6.6                  | 3455 ± 158.0  | 5.0 ± 1.1           | [7]        |
| PLA/CNC            | 118.5 ± 16.5                | 3852 ± 241.0  | 51.1 ± 11.3         |            |
| PLA–PHB            | 6.0 ± 1.0                   | 210 ± 30.0    | 50 ± 10.0           |            |
| PLA–PHB–CNC1       | 16.0 ± 2.0                  | 230 ± 10.0    | 50 ± 5.0            |            |
| PVA                | 2.6 ± 1.1                   | 0.8 ± 0.2     | 294 ± 101.0         | [8]        |
| 3CNW/PVA           | 3.8 ± 0.1                   | 1.1 ± 0.3     | 343 ± 84.0          | [14]       |
| 7PVA               | 4.97 ± 0.12                 | 31.9 ± 0.3    | 271 ± 13            | [15]       |
| 7PVA/CNC-20        | 6.71 ± 0.25                 | 53.9 ± 1.4    | 86 ± 7              |            |
| MPLA               | 1.6 ± 0.4                   | 7.8 ± 3.1     | 51.8 ± 3.8          |            |
| MPLA/CNC           | 10.8 ± 1.7                  | 135.1 ± 10.4  | 44.0 ± 5.1          | [22]       |

Mujiga-Garcia et al., [7] indicated that the improvements are assumed to be due to the alignment of the CNC along to the fiber axis. A very large tensile strength improvement was observed for PLA/CNC compared to neat PLA, which can be considered as an evidence of a flexible interface between PLA/CNC and the PLA matrix and allowed this high stretching which is resulting to higher maximum strength. According to Huan et al., [15] PVA/CNC nanofibers became more uniform and finer with increased CNC content due to the synergetic effect of electric conductivity, interfacial tension, and viscosity of electrospinning solutions. It was also found that thermomechanical and mechanical properties of both types of nanofibrous mats were enhanced as a result of the addition of CNCs to the PVA polymer matrix. This was ascribed to the efficient stress transfer from PVA to CNCs originating from the strong percolation network interactions held by hydrogen bond in the nanofibers and the ordered arrangement of electrospun nanofibers in the nanofibrous mats.
Figure 3 shows a scheme of the tensile fracturing of electrospun mats based on SEM photographs. At the beginning, the mats were stretched in macroscopic view and most fibers in mats hardly moved attributed to the cohesion between fibers, which determined 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. At this stage, single fiber has the same tensile behaviour as the cast films as mentioned above. However, the rupture of individual fibers one by one did not influence the tensile properties of the whole mats, resulting in larger elongation at break for electrospun mats compared with the cast films. At the maximum tensile stress level, most fibers were necked and broken, leading to the final rupture of mats [15].

2.2.2. Thermal properties of biocomposites
Thermal properties of electrospun PVA, PLA and reinforced CNC/PVA, CNC/PLA nanofiber are summarized in Table 2. Maximum thermal degradation temperature ($T_{\text{max}}$) is referring to the decomposition temperature corresponding to the maximum weight loss.

| Nanocomposites     | $T_{\text{max}}$ ($^\circ$C) | References |
|--------------------|-------------------------------|------------|
| PLA                | ~370.0                        | [7]        |
| PLA/CNC            | ~385.0                        |            |
| PLA–PHB            | 335.0                         | [8]        |
| PLA–PHB–ATBC–CNC1  | 340.0                         |            |
| 7PVA               | ~220.0                        |            |
| 7PVA/CNC-20        | ~275.0                        | [15]       |
| PLA                | 351.8                         |            |
| PLA/CNC            | 357.5                         | [21]       |
| MPLA               | 348.0                         |            |
| MPLA/CNC           | 353.6                         | [22]       |

In general, Table 2 shows that the maximum temperature of nanocomposites increased with increased CNC content. As studied by Shi et al., [21] and Zhou et al., [22] indicated that the incorporation of CNCs in matrix improved the heat resistance of composites. Huan et al., [15] reveals that the char yield of electrospun PLA/CNC nanocomposites mats increased with increased CNC content. The char yield is directly correlated to the potency of flame retardation for the composites. Char yield is usually defined as the percentage (%) of solid amount you obtain at end of pyrolysis. Increased char formation can limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction, and inhibit the thermal conductivity of the burning materials. Moreover, the increased crystallinity could also improve the $T_{\text{max}}$ of the composites [34]. Therefore, the increase of $T_{\text{max}}$ of PLA/CNC nanocomposites...
mats was mostly attributed to the char formation and increased crystallinity in nanocomposites. According to Dong et al., [26], the influence of CNCs on the thermal transitions of PMMA could be explained by interactions between the hydroxyl groups of CNCs and the carbonyl groups of PMMA. Hydrogen bonding interactions between hydroxyl and carbonyl groups have been widely used to facilitate miscibility of polymer blends, in which hydrogen bonding was found to have a significant effect on the thermal properties of polymer blends. The hydrogen bonding interactions between CNCs and PMMA could also facilitate the dispersion of CNCs in PMMA/DMF solutions.

3. Conclusions
Electrospinning is a simple method to produce nano scale fibers both in laboratory and industrially. Different kinds of artificial and natural polymers have been successfully electro spun into small and fine fibers. In the last decade the number of researches about this method and its applications has increased and this demonstrates the importance of electrospinning. In the review, it is shown that CNCs have a distinct advantage for improving mechanical properties of both nanocomposite hydrogels and electrospun nanocomposite fibers/mats. The molecular interactions of CNCs and matrix chains could be beneficial to the mechanical and thermal properties of electrospun nanocomposites. This review also indicates that the nanocellulose has a great potential for application in reinforcing polymers. Even though there is numbers of studies related to nanocomposites containing CNC, 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.

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