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Nanocrystalline cellulose as a reinforcing agent for electrospun polyacrylonitrile (PAN) nanofibers

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ABSTRACT

Objectives: Nanocrystalline cellulose (NCC) is a sustainable material with excellent mechanical properties and can potentially be used as a reinforcement agent. The objective of this work was to test the effects of NCC incorporation on the mechanical properties of electrospun polyacrylonitrile (PAN) nanofibers.
Methods: Eleven percent in weight of PAN (molecular weight 150 kD) in a dimethylformamide (DMF) solution was electrospun at 14.6 kV. Nonfunctionalized NCC was added to the solution at 1%, 2%, or 3 wt% (NCC/PAN). Suspensions were mixed and sonicated for 2 h before spinning. Strips (5 × 0.5 cm) were cut from the spun mat, parallel and perpendicular to the rotational direction of the fiber collection drum. Tensile tests were performed, and ultimate tensile strength (UTS), yield strength (YS; 0.3%), elastic modulus (E), and elongation at maximum stress (EMS, %) were calculated from stress–strain plots. Data were analyzed by multiple t tests and one-way ANOVA ($\alpha = 0.05$).
Results: Among all groups, samples with 3 wt % NCC loading had significantly superior mechanical properties. The fiber mats showed anisotropic behavior.
Conclusions: Regardless of concentration, the addition of NCC resulted in increased UTS, E, and YS of the nanofibers.

1. Introduction

The association between nanofibers and nanoparticles is a promising approach to expand the applications of electrospun nanofibers [1–4]. Nanocrystalline cellulose (NCC) represents renewable rod like nanoparticles abundant in nature [5,6] characterized by large surface area and outstanding mechanical properties. Several polymers make effective use of NCC's properties, mostly in film or bulk form [5]. Alginate-based films have been reported to have greater tensile modulus and strength after addition of NCC [7]. Similarly, polyurethane films show remarkably higher elastic modulus (E), tensile strength, and work of fracture after incorporation of low concentrations of NCC [8].

Recently, NCC was successfully incorporated into electrospun polymeric nanofibers with promising results for increasing tensile strength and E [9–13]. The addition of low concentrations of NCC appears to improve mechanical outcomes, but higher concentrations may compromise these properties [14,15]. NCC powder associated with polyacrylic acid nanofibers shows an increase of 35-fold in modulus and 16-fold in strength [16].

Electrospun polyacrylonitrile (PAN) nanofibers are being widely used due to their light weight, which is associated with great mechanical strength and toughness [17]. Association of PAN nanofibers with NCC has been achieved, indicating the possibility to further enhance their mechanical properties. When PAN nanofiber mats are coated with a single or double layer of an NCC suspension to produce stronger filtration membranes, the ultimate tensile strength (UTS) increases from ∼5 to almost 10 MPa with one layer and almost 14 MPa with two layers of NCC [18]. Besides, when NCC is added at 3% to PAN nanofibers and is tested as a single fiber, it shows an increase of 148% in tensile strength and 111% in E [19].

Abbreviations: ANOVA, analysis of variance; DMF, dimethylformamide; E, elastic modulus; EMS, elongation at maximum stress; FTIR, Fourier transform infrared; NCC, nanocrystalline cellulose; PAN, polyacrylonitrile; SEM, scanning electron microscopy; TEM, transmission electron microscopy UTS, ultimate tensile strength; YS, yield strength

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Apart from the few studies mentioned above, the literature is scarce regarding NCC as a reinforcing agent for PAN nanofibers. Therefore, this study aimed to investigate the effects of adding NCC to PAN nanofibers on the tensile properties of the electrospun mats. The null hypothesis was that the addition of NCC at 1%, 2%, or 3% (w/w) would not enhance tensile properties of PAN nanofiber mats.

2. Materials and methods

2.1. Fabrication of the nanofibers and incorporation of NCC

2.1.1. Electrospinning of PAN nanofibers

To produce polymer nanofibers, a PAN powder (molecular weight [MW] = 150,000 g/mol, Scientific Polymer Products, Ontario, NY, USA) was dissolved in N,N-dimethylformamide (DMF) (Fisher Scientific, Waltham, MA, USA). PAN and DMF were weighed (Shimadzu, ATX 124, Kyoto, Japan) and mixed at a concentration of 11% (w/w) of PAN in DMF. The solution was stirred overnight at room temperature, and its viscosity was measured with a viscometer (Viscomate Model VM-10A, CBC Co., Ltd., Tokyo, Japan) prior electrospinning (viscosity range: 430–445 mPa s). The solution was then immediately transferred to a plastic syringe and placed in a Nanofiber Electrospinning Unit (NEU; Kato Tech, Japan). Electrospinning parameters were set as follows: applied voltage 14.6 kV, distance between the needle tip and the collector plate 20 cm, target speed 2 m/min (6.1 rpm), and transverse speed 1 cm/min. Syringe pump speed varied between 0.05 and 0.1 mm/min to keep a clear and visible Taylor cone. Temperature and humidity in the chamber were monitored. Air humidity was kept between 30% and 50%, and temperature varied between 24 and 27 °C. The collector plate consisted of a rotating drum manually covered with aluminum foil. Fibers were produced over a period of 48 h and collected in random mode. No attempt to achieve alignment of fibers was made. The formed fiber mat was gently removed from the collector plate and stored in a sealed plastic bag away from heat and humidity until use.

2.1.2. Incorporation of NCC

NCC was added to the 11% PAN solution in DMF at 1%, 2%, or 3% (w/w for NCC/PAN; Table 1). All the weighing was carried out on an analytical balance (Shimadzu, ATX 124, Kyoto, Japan). After the addition of NCC to PAN–DMF in a vial, the suspension was subjected to vortex mixing (Digital Vortex Mixer, Fisher Scientific, Waltham MA, USA) for 5 min at 3000 rpm. The vials containing the suspensions were next attached to a holder and sonicated for 2 h at the maximum output (Misonix Sonicator 3000, QSonica LLC, Newtown, CT, USA). After that, the vials were left for 15 min on the bench top at room temperature, and the viscosity of the suspension was measured before electrospinning according to the procedures and parameters described above. Four groups were tested and characterized (Table 2).

Table 1
Amount composition of the experimental polymer mixtures used to produce the experimental polymer mixtures (w/w).

Groups	0%	1% NCC	2% NCC	3% NCC
PAN	2.2 g	2.2 g	2.2 g	2.2 g
NCC	0 g	0.022 g	0.044 g	0.066 g
DMF	17.8 g	17.778 g	17.756 g	17.734 g
Total weight	20 g	20 g	20 g	20 g

2.2. Characterization of nanofibers and nanofiber mats

2.2.1. NCC characterization (X-ray diffraction and Fourier transform infrared [FTIR] spectroscopy)

The crystallinity of NCC was analyzed by powder X-ray diffraction (Bruker D8-Advance X-ray diffractometer, D8 Advance, Bruker, MA, USA) using an NCC powder packed in a standard Bruker sample holder and rotated. The generator was set to 40 kV and 40 mA. The machine was operated in the Bragg–Brentano configuration, with copper Kα_1 and Kα_2, nickel filter, and a LynxEye silicon strip as a detector. Additionally, NCC (Alberta Innovates, Alberta, Canada) was analyzed on a Fourier transform infrared spectrometer (IRPrestige-21 FTIR-8400S, Shimadzu, Kyoto, Japan) in attenuated total reflectance (ATR) mode. The samples were compressed against the ATR crystal and scanned 36 times at a resolution of 4 cm^{-1} within the spectra of 400 to 4000 cm^{-1}. The equipment was operated in absorbance mode with the Happ–Genzel function.

2.2.2. Tensile properties of nanofiber mats

These properties were determined (KES-G1 Kawabata, Kato Tech Co., Kyoto, Japan) at an elongation rate of 0.2 mm/s. As-spun mats were tested in two orientations: parallel and perpendicular to the rotational direction of the collector drum. Strips (5 × 0.5 cm) were cut from the mat. Five samples of each orientation from each group were tested. Displacement (mm) was calculated by dividing the time (s) required to tear the strip by the elongation rate (0.2 mm/s). Strain was determined by dividing displacement by gauge length. The load was registered in gram-force. Areal density was calculated by dividing the weight of the nanofiber (g) strips by their area in m^2.

Specific stress, in g/Tex, was given by the following equation:

$$\mathbf{Stress}\ (\mathbf{g/Tex}) = [\mathbf{Force(g)/sample\ width\ (mm)}] / \left[\mathbf{Areal\ density}\ (\mathbf{g/m^2})\right] \tag{1}$$

Engineering stress in MPa was calculated by the following equation:

$$\mathbf{Stress}\ (\mathbf{MPa}) = \mathbf{9.8} \times \mathbf{Stress(g/Tex)} \times \mathbf{density\ of\ material(g/cc)} \tag{2}$$

UTS, E, yield strength (YS), and elongation at maximum stress (EMS) were calculated from stress–strain plots.

2.2.3. Morphological characterization of nanofiber mats and NCC

The characteristics of PAN nanofibers and PAN with NCC nanofibers were first examined under a light microscope (Nikon Eclipse LV100 Optical Microscope, Tokyo, Japan). Samples of all fiber mats were further examined by scanning electron microscopy (SEM; S-238ON, Hitachi, Tokyo, Japan) at an acceleration voltage of 10 kV. Randomly selected areas of each mat were cut into 5 × 5 mm squares and mounted on a stub with carbon tape (n = 3). The stubs were coated with platinum/palladium (Pt/Pd) with an ion sputter coater (Hitachi E-1030 Ion Sputter Coater, Hitachi, Tokyo, Japan). One random image (at 10,000 × magnification) per group was selected to measure fiber diameter. Fifteen measurements were performed (in ImageJ, NIH, USA) per image, and average fiber diameter was determined.

NCC particles were examined by transmission electron microscopy (TEM, JEOL, JEM-1400, Tokyo, Japan) following a previously described method [9].

2.3. Statistical analysis

Student *t* tests were conducted to compare the tensile properties of nanofiber mats in the parallel and perpendicular orientation. One-way analysis of variance (ANOVA) was carried out to evaluate the effect of an increased concentration of NCC on each mechanical property of the nanofiber mats. Differences in the average fiber diameter were investigated by one-way ANOVA. The Mann–Whitney *U* test was performed instead of the *t* test in cases of non-normal distributions. A level of significance of $\alpha = 5\%$ was set for all statistical analyses. SigmaPlot software (Systat Software, San Jose, USA) was used for these analyses.

3. Results

3.1. NCC characterization (X-ray diffraction and FTIR spectroscopy)

The FTIR spectra confirmed the nature of the NCC used in the study when compared to the FTIR library database for cellulose (Fig. 1). X-ray diffraction (Fig. 2) spectra indicated the crystalline arrangement of NCC.

3.2. Tensile properties of the nanofibers mats

Overall, the incorporation of NCC resulted in a significant enhancement of all tensile properties. PAN nanofibers with and without NCC showed anisotropic behavior with superior properties in the perpendicular direction (Table 2). When 3% NCC was added to the fibers, there was a significant (80% and 62%) increase in the UTS of the mats when tested in the parallel and perpendicular direction, respectively. Furthermore, when 3% NCC was added to the nanofibers, although not statistically significant, a 114% and 80% increase in E was observed in the parallel and perpendicular orientation, respectively. YS manifested a linear increase as the NCC was added at greater concentrations. When 3% NCC was added, a significant increase (in YS) of 216% for parallel and 148% for the perpendicular orientation was observed. EMS was higher in the parallel orientation.

3.3. Morphological characterization of the nanofiber mats and NCC

SEM images revealed randomly oriented fibers in all the groups. Occasional beads were observed in groups with the addition of NCC (Fig. 3). Some fibers appeared to merge in double formation in group 2% NCC. Fiber diameters were similar among all the groups, except for the 2% NCC group (Table 3). TEM showed NCC particles (Fig. 4) with an average length of 173 nm (range: 113 to 246 nm) and average diameter of 12 nm (range: 8 to 15 nm).

4. Discussion

On the basis of our findings, we rejected the null hypothesis. Literature comparing methods for NCC incorporation into PAN is limited. In our study, spray-dried NCC was mixed with PAN solutions, followed by a rigorous protocol of sonication. Fibers were expected to contain estimated and known amounts of NCC (NCC at 1%, 2%, and 3% [w/w] of PAN was used to produce the solutions). Previously, PAN nanofibers that were coated after spinning with aqueous suspensions of NCC yielded an increase of 100% in tensile strength with one layer of NCC and a further 40% increase when two layers were applied [18]. Such results must be interpreted with caution because the amount of NCC in a single or double layer could not be precisely determined. It was evident from the study, however, that a further increase in tensile strength would be expected with an increased amount of NCC added to the fibers. In our study, we evaluated addition of known amounts of NCC into a polymeric solution prior to spinning; this approach could provide a better understanding of the relation between NCC concentration and the respective changes in the tensile properties. It was evident from our findings that increased amounts of NCC resulted in

Table 2
Tensile properties of the experimental nanofiber mats.

	UTS - MPa (SD)		E - GPa (SD)		YS - MPa (SD)		EMS - % (SD)	
Fiber Groups	**PAR**	**PER**	**PAR**	**PER**	**PAR**	**PER**	**PAR**	**PER**
0% NCC	10.68 (1.96)^{C}	14.60 (0.99)^{C*}	0.14 (0.05)^{B}	0.34 (0.11)^{B*}	1.74 (0.23)^{C}	3.88 (0.49)^{B*}	39 (10)^{B*}	16 (1)^{B}+
1% NCC	17.47 (1.40)^{A}	19.39 (3.32)^{B}+	0.38 (0.18)^{A}	0.72 (0.18)^{A}+	5.72 (0.99)^{A}	8.65 (1.64)^{A*}	54 (4)^{A*}	23 (2)^{A}
2% NCC	14.84 (0.87)^{B}	21.02 (2.53)^{AB*}	0.25 (0.02)^{AB}	0.52 (0.21)^{AB*}	3.56 (0.16)^{B}	8.97 (0.74)^{A*}	60 (4)^{A*}	26 (4)^{A}
3% NCC	19.30 (0.97)^{A}	23.62 (1.36)^{A*}	0.30 (0.08)^{AB}	0.61 (0.09)^{AB*}	5.50 (0.23)^{A}	9.65 (1.14)^{A*}	56 (3)^{A*}	26 (2)^{A}

Different letters (one-way ANOVA) indicate significant difference between the values for each property and orientation ($p < 0.05$). * (t-test) or + (Mann-Whitney) indicated significant differences between PAR and PER for each NCC concentration for each property. Abbreviations: PAR: Parallel to rotatory drum axis; PER: Perpendicular; UTS: Ultimate tensile strength; E: Elastic modulus; YS: Yield strength; EMS: Elongation at Maximum Stress. n=5 for all groups.

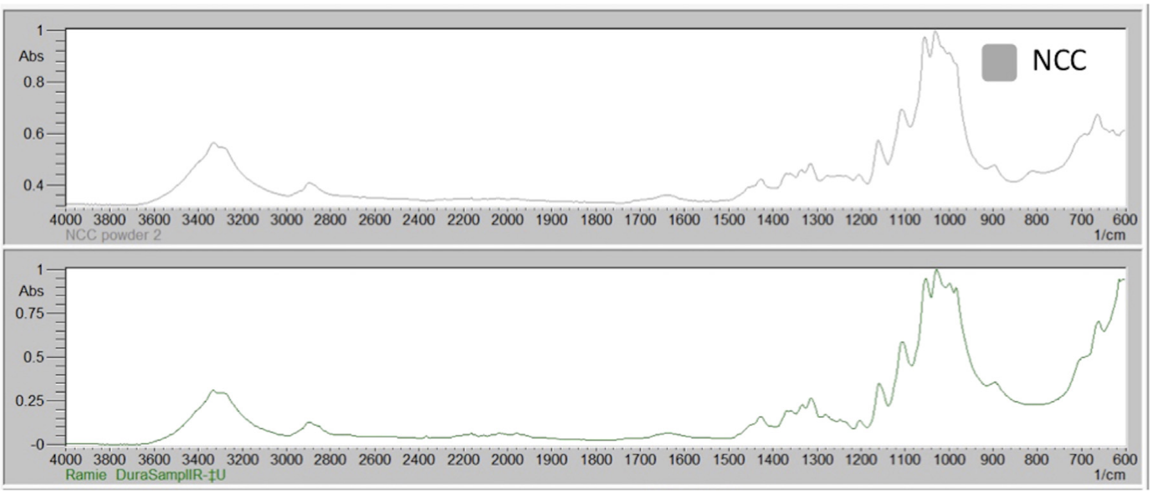

Fig. 1. The FTIR spectrum of the NCC powder used in the study (top) as compared to the FTIR database for cellulose (bottom).

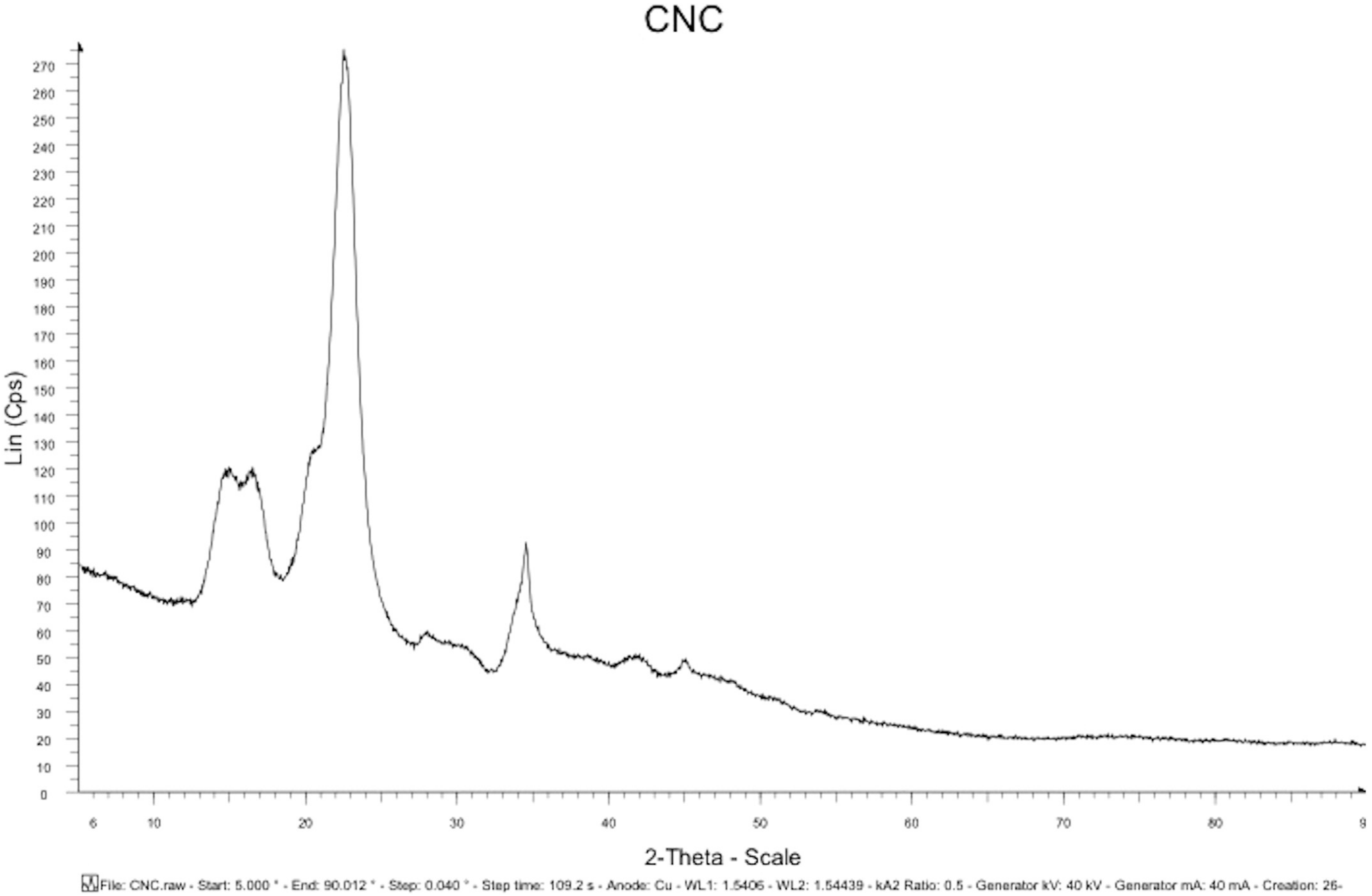

Fig. 2. X-ray diffraction analysis of the NCC powder used in the study. The diffraction pattern shows constructive interference that satisfies Bragg's law. Sharp peaks indicate that NCC atoms were organized into a crystalline structure.

overall enhancement of tensile properties, albeit apparently not in a linear fashion.

In our control group (0% NCC), we tested electrospun nanofibers produced from 11 w% PAN solutions. The results on the control group differ widely from our own previous findings about PAN nanofibers [20]. Previously, we used 7% w/w PAN in DMF, and the results on tensile properties were higher than the ones reported here for 11% w/w PAN/DMF (ca. UTS:24 MPa, E:1 GPa, YS:19 MPa). Such differences when tested by the same protocol can be explained by the fact that 7% PAN yielded fibers with an average diameter of 170 nm in the previous study, whereas the fibers in the present study (11% PAN) were on average 400 nm in diameter. Electrospinning theory suggests that reduced polymer concentration will render solutions less viscous, thus resulting in fibers with a smaller diameter, which in turn are expected to yield better mechanical properties [21]. We originally attempted to include NCC into 7% PAN solutions, but no consistent and reproducible fibers were obtained. We tested several other polymer concentrations before achieving reproducible patterns at 11% PAN. It is unclear why NCC could not be added to lower concentrations of PAN–DMF solutions, and such research is beyond the scope of the present study.

Our findings corroborate our previous report on the anisotropic behavior of the randomly oriented fiber mats [20]. Although the reasons for anisotropy are not fully understood, it is helpful to realize that orientation plays a role in the properties, and this knowledge may be useful when applications are designed. The difference between the parallel and perpendicular orientation can be explained by the nature of the whipping movement in the electrospinning process [22]. Because greater strength is seen when fibers are tested under tensile stress and unidirectionally [23], it is likely that the fiber is deposited in a way that most of the orientations are displaced longitudinally toward the long axis of the collector drum. When tested perpendicularly to the rotational axis of the drum, fibers are being pulled along their long axis and therefore show increased strength.

YS, tensile modulus, and tensile strength were all increased by the addition of NCC at all the different concentrations. Groups 1% NCC and 3% NCC showed fiber diameter that was similar to that of the control group. This result suggests that the enhanced properties were due to the presence of NCC and not to the reduced fiber diameter. Reinforcement mechanisms of action of NCC in polymeric systems can be explained by different models that suggest that at low volume fractions, exponential increases in mechanical properties can be observed [5]. The percolation effect is one of the models that are used to explain how NCC reinforces structures of composites [24]. In this model, the formation of a highly connected rigid network is crucial so that the nanoparticles can exceed mechanical properties of conventional composites. To elicit such an effect, a certain minimum amount of NCC is needed that—depending on the shape, size, aspect ratio, and orientation of particles and interactions between them—will attain a percolation threshold. To provide conditions for formation of the percolation network, it is necessary to provide sufficient time and space so that the particles can engage in interfacial interactions [25]. Electrical measurements have confirmed the presence of such a network in composites containing NCC [26]. Considering that in this study, UTS, E, and YS were higher in all NCC-containing fiber groups, it can be assumed that the threshold necessary to form the percolation effect was achieved, although we did not attempt to determine it.

In our study, fiber mats were tested as-spun without any further fiber treatment or fiber alignment. It has been shown that alignment of NCC within the fiber [4,9] and post-treatment heat [16] can increase the crosslinking of the hydroxyl groups of NCC with the polymeric

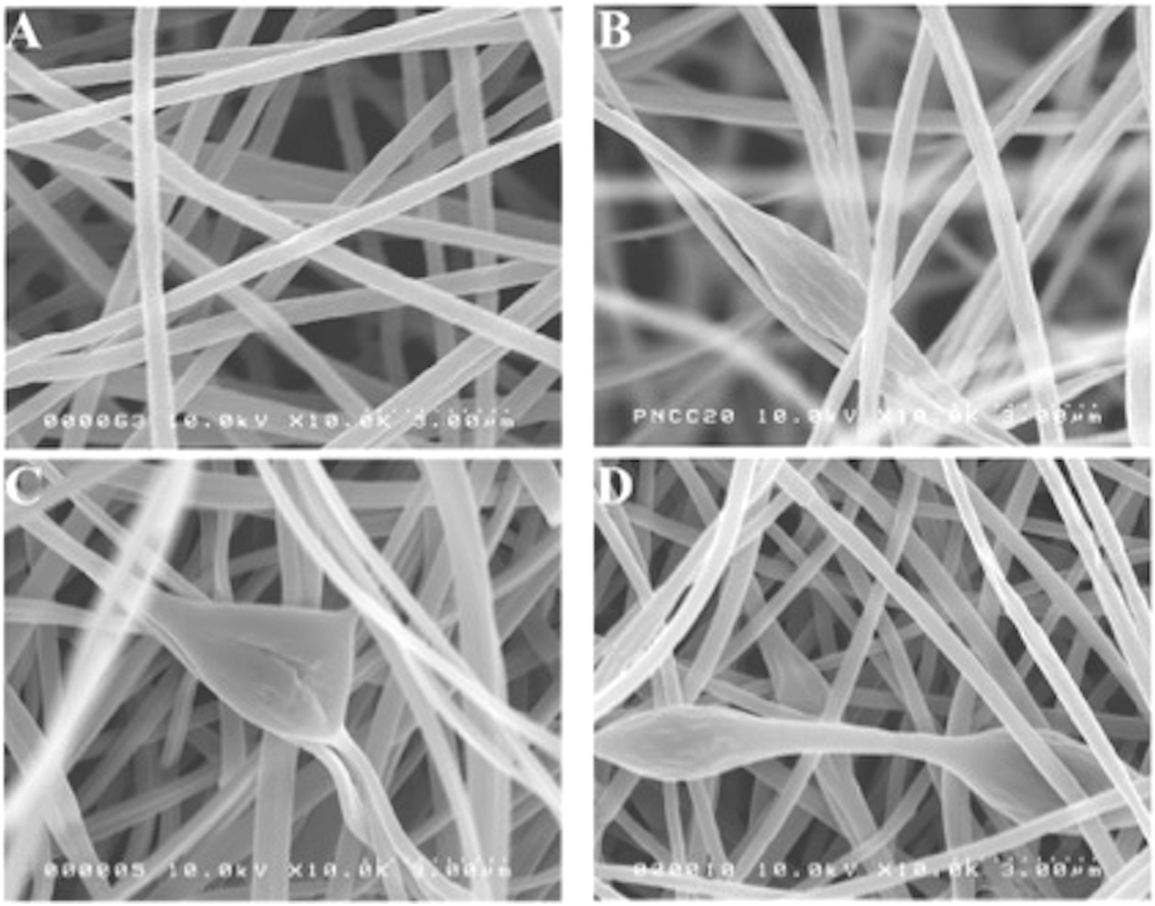

Fig. 3. Representative SEM images of the nanofiber mats (A = 0% NCC; B = 1% NCC; C = 2% NCC; D = 3% NCC). The fibers were randomly distributed and had similar diameters among all the groups. A few beads were observed in the groups where NCC was added.

Table 3
Average diameter of the fibers. nm (SD).

Groups	0% NCC	1% NCC	2% NCC	3% NCC
Mean (SD)	400 (47) ^{B}	422 (88) ^{B}	596 (199) ^{A}	388 (41) ^{B}
Range	327–502	307–560	261–828	288–450

Different letters (one-way ANOVA) indicate significant difference between the values ($p < 0.05$), n = 15.

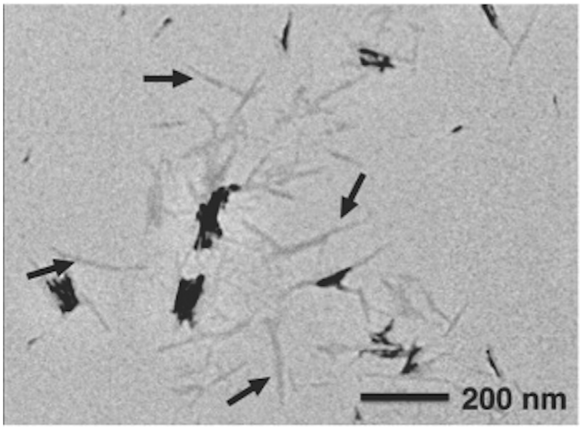

Fig. 4. A TEM image of the NCC used in the study. The NCC particle has a rod like appearance with a length close to 200 nm and a diameter ~12 nm.

matrix and further enhance the mechanical properties. Although we did not explore these approaches, it is practically helpful that we were able to demonstrate significant improvements in tensile properties of the fibers by simple addition of NCC at low concentrations. Care was taken to investigate and characterize the NCC used in the study. The TEM images were possible only after several attempts. The protocol described here is based on other studies [9]. Nevertheless, it was possible to identify the particle only when uranyl acetate [27] was added into the aqueous suspension. Given that agglomeration was identified in our TEM images, a reasonable suggestion for future work is to subject the suspension of NCC to sonication before applying it to the TEM grid. Although TEM analysis was difficult, it successfully illustrated the particles used in the study and confirmed their morphological features as expected. The presence of NCC in the fibers could not be confirmed by SEM. Because the fiber diameter far exceeded the size of the particles, it is possible that the particles were embedded in the fibers and were not visible on the surface. The presence of NCC in the fibers, and more importantly, the effects of their presence could be demonstrated here by means of the marked differences in the tensile properties.

SEM findings revealed the presence of beads in the fibers when NCC was added. It is generally accepted that fewer beads are expected as viscosity of the mix increases [28]. This did not seem to be the case in our study because beads were observed in the NCC groups without significant changes in viscosity. The presence of beads has been anecdotally associated with poor fiber production, contrary to ideal targets in electrospinning [29], which dictates that the fiber surface be defect-free, and beads are considered defects. Contrary to that principle, our study indicates that the presence of beads did not compromise mechanical properties. In fact, beads were found in a larger number and size (data not shown) in the group with 3% NCC, which resulted in the best mechanical properties. It thus appears that the suggested shortcoming, i.e., the presence of beads, is only cosmetic but not functional. We were not able to find any study that has shown any functional deterioration of nanofibers owing to the presence of beads. This fact necessitates future research to clarify the role of beads in nanofibers.

The reinforcement effect of NCC in PAN can be useful for future research on fiber-reinforced composites for applications in dentistry [17]. Considering that PAN is one of the main polymers used as a precursor of carbon fibers, having a raw material that can be made stronger using an eco-friendly filler may bring carbon fibers to a new performance level. Moreover, NCC has been proved to be a good carrier of drugs [30]. Future research may be focused on the bioactivity of composite structures with fibers containing NCC.

5. Conclusions

The addition of NCC resulted in an increase in the UTS, E, and YS of PAN nanofibers. Fibers showed anisotropic behavior, with higher strength and E in the perpendicular orientation.

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Ethical approval

This study did not involve human subjects or laboratory animals; therefore, no ethical approval was required.

Conflict of interest

The authors declare that they have no conflicts of interest.

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