ELECTROSPUN NANOCOMPOSITE FIBERS MADE FROM POLY(VINYL ALCOHOL) AND CELLULOSE NANOFIBRILS

Eliton S. Medeiros[1,2*], Luiz H. C. Mattoso[2], Edson N. Ito[2], William J. Orts[1]

[1*]*United States Department of Agriculture, Bioproduct Chemistry and Engineering Unit, Western Regional Research Center, 800 Buchanan St., Albany, CA 94710, USA - eliton.medeiros@ars.usda.gov, eliton@cnpdia.embrapa.br*
[2]*Laboratório Nacional de Nanotecnologia Aplicada ao Agronegócio, Embrapa Instrumentação Agropecuária, Rua XV de Novembro, 1452, São Carlos-SP, 13560-970, Brazil.*

In this work, nanofibers of poly(vinyl alcohol) reinforced with cellulose nanofibrils were produced by electrospinning. The effects of process variables on morphology and addition of cellulose nanofibrils were investigated by scanning electron microscopy (SEM) and tensile tests. Thermogravimetry (TGA) and transmission electron microscopy (TEM) analyses were also carried out in order to characterize the presence, orientation and reinforcing effect of the cellulose nanofibrils. SEM results showed that fiber structure is strongly affected by the electrospinning conditions. Thinner fibers are favored by decreasing viscosity, polymer injection rate, high rotation speed and high relative humidity, whereas increasing the applied voltage favors the formation of beaded fibers. The reinforced composites had a 2.4-fold increase in their mechanical properties by addition of only 6.6 wt.% of cellulose nanofibrils without major changes in elongation at break.

Keywords: *Electrospinning, cellulose nanofibrils, poly(vinyl alcohol), nanofibers.*

Introduction

Cellulose-based fibers and agriculture biomass have received increasing attention as reinforcement agents in plastics in a wide range of composite applications [-]. The advantages of reinforcing polymers with nanoscale particles have been clearly shown for clay nanocomposites and other inorganic fillers in which the addition of nano-scale clay particles improves dimensional stability, stiffness, and higher heat distortion temperature. Natural cellulose nanofibrils (CnF) can act in a fashion similar to clay nanocomposites in reinforcing polymers, although they exhibit both advantages and disadvantages relative to clay [,]. Cellulose is the most common organic polymer, representing about $1.5x10^{12}$ tons of the total annual biomass production [] with a range of properties, including biodegradation. The promise behind cellulose-derived nanocomposites lies in the fact that the axial Young's modulus of the basic cellulose crystalline nanofibril has been reported as high as 137 GPa [], which means it rivals steel in strength and stiffness.

Electrospinning is versatile technique to produce micro and nanofibers of polymers because it provides a potential way to fabricate continuous nanofibers with different structural designs [,]. Control of process parameters allows the production of fibers with controllable properties and diameters ranging from tens of microns down to a few nanometers. A variety of materials such as engineering plastics, copolymers, polymer blends, biopolymers, and conducting polymers have been successfully electrospun to produce uniform fibrous mats [,]. The use of electrospun nanofibers includes filtration membranes, drug release systems, wound dressing and tissue engineering to chemical and biological protective clothing, sensors, and composites [,]. However, it has been reported in the literature that electrospun fibrous mats of many polymers and biopolymers possess relatively low dimensional stability and mechanical strength [-], which limits their use in some of the abovementioned applications.

In order to improve the mechanical strength of electrospun materials, a common approach used is the chemical cross-linking of the matrix [], which depends not only on its reactivity but also on its thermal stability and the biocompatibility of the cross-linking agent, therefore limiting the technique to a number of materials. Another approach that can be exploited to improve the mechanical strength is the use of reinforcing agents, for forming engineering fibrous composites. In this sense, cellulose nanofibrils are a good candidate due to its biocompatibility and high strength, which

enables the improvement of the low tensile properties of electrospun fibers while maintaining their biodegradability and biocompatibility [,]. Interestingly, cellulose nanofibrils can be coated with conductive polymers such as polyaniline providing an excellent microwave and radar absorbing material [,], thus opening up several new uses for electrospun materials in military and electronic circuit board applications.

In this work, we explore the possibility of improving the tensile properties of electrospun nanofibers of poly(vinyl alcohol), PVA, by adding cellulose nanofibrils as a reinforcing agent. The effects of process variables (applied voltage, polymer concentration and injection rate, working distance, rotation speed of the collector, and relative humidity) on morphology of the electrospun mats were investigated by SEM. The reinforcing capability of cellulose nanofibrils was investigated by tensile tests. TGA and TEM analyses were also carried out to characterize the presence and orientation, and reinforcing effect of the cellulose nanofibrils.

Experimental

Cellulose nanofibrils (CnF) were obtained by acid hydrolysis of of short cellulose fiber (Whatman CF11) using 60 wt.% sulfuric acid at 60ºC, for 45 minutes. Cellulose nanofibrils were recovered as a dispersion of approximately 1.16 g/100 mL water from dialysis. These nanofibrils have average diameter (d) of 38±13 nm, length (l) of 360±60 nm, and aspect ratio (l/d) of 10±4nm, as determined by atomic force microscopy (AFM) [].

Cellulose nanofibrils were incorporated into PVA (Sigma-Aldrich, MW=30,000-70,000) by adding a previously measured amount of PVA powder to nanofibril aqueous solution at 80ºC to produce a 6.6 wt.% suspension of CnF in PVA on a dry basis. Pure PVA solutions were prepared by dissolving PVA powder directly in deionized water.

The electrospinning setup used in this study consisted of a 10 mL plastic syringe, 21G needle (i.d.: 0.84 mm), a grounded collector with controllable rotation speed, a hypodermic syringe pump (KD Scientific, USA), and a high-voltage supply (Series FC, Glassman High Voltage, Inc., USA). The effects of process variables on morphology were investigated by changing applied voltage, polymer concentration, injection rate, working distance and relative humidity. RH-controlled electrospinning experiments were carried out inside an acrylic box using saturated solutions of lithium chloride (25-30 % RH), sodium iodide (38-40%), sodium chloride (48-52%), and potassium chloride (75-80%).

Electrospun nanofibers were sputter coated with gold for 45 s and analyzed using a Scanning Electron Microscope (Model S4700, Hitachi High-Technologies, Japan) at a voltage of 2 kV. At least 50 fibers were counted in each image in order to evaluate fiber diameter distribution. Statistical analyses (t-Student) at the significance level of 0.05 were used to verify if the differences on morphology because of the changes in electrospinning parameters (voltage, rotation of the collector and polymer injection rate) were significant.

In order to characterize the electrospun composites with TEM, cellulose nanofibrils were stained with polyaniline by in situ polymerization [] followed by electrospinning. These fibers were analyzed in a Philips transmission electron microscope (Model CM 120, Philips, The Netherlands), operating at 120 kV.

Thermogravimetric measurements were performed on a Thermogravimetric Analyzer (Model TGA 2950, TA Instruments, USA). The operating conditions were: 20 mL/min nitrogen flow, 25 to 600ºC temperature range and 10ºC/min heating rate.

The tensile properties of the electrospun nanocomposites were measured with an Instron Universal Materials Testing Machine (Model 5500R, Instron Corp., USA) at ambient conditions. Tensile properties were determined using samples cut from electrospun mats, 60 mm in length, 10 mm in width and ca. 0.20 mm in thickness, at a crosshead speed of 10 mm/min. At least 10 samples were tested for both PVA and PVA/CnF composites.

Results and Discussion

Visual inspection helped determine the critical voltage (Vc) for a droplet, formed at the needle tip, to be pulled by the electric potential difference between the needle and the collector. This value increased as both polymer concentration and working distance increased. For working distances above 12 cm the critical voltage increased more rapidly at higher polymer concentrations. On the other hand, when viscosity was low the relaxation time (time necessary for stretched polymeric chains to assume a coiled conformation) decreased so that beaded fibers were obtained. At distances shorter than 11.5 cm there was not enough time for complete solvent evaporation, and the electrospun mats were composed of an interconnected network of nanofibers and beads. Therefore, based on this study, a WD of 11.5 cm and 14 wt.% PVA/CnF were chosen for further studies.

Figure 1 shows SEM images of the electrospun nanofibers obtained to investigate the effect of injection rate on morphology. It can be observed that the number of beads and fiber irregularity increased as injection rate increased from 2 to 8 μL/min. During electrospinning, a polymeric solution is forced through a syringe pump to form a droplet at the needle tip, and the high voltage potential induces free charges into the solution. These charged ions move in response to the applied electric field toward the electrode of opposite polarity, consequently transferring tensile forces to the polymer liquid. At a fixed WD, and keeping the applied voltage constant, higher injection rates supply more polymer solution to be stretched by the electric field, thus provoking an unbalance between the volume of polymer accumulated and the electrostatic charges necessary to overcome surface tension and viscoelastic forces. As a result, charge density is not enough to stretch these droplets completely and break them into fibers, which causes large bead formation and some thin fibers instead of completely fibrous mats.
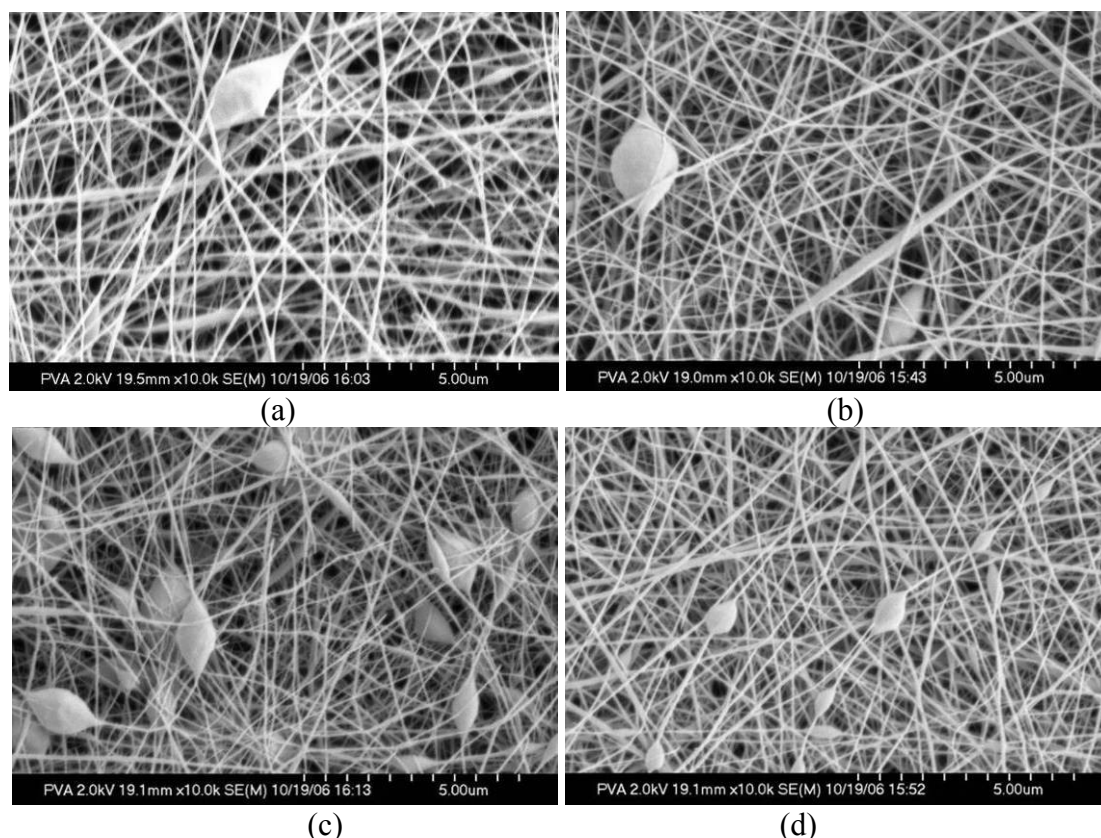

Figure 1 – Effect of injection rate on morphology of PVA/CnF electrospun nanofibers using a voltage of 21 kV and a working distance (WD) of 11.5 cm. (a) 2 μL /min; (b) 4 μL /min; (c) 6 μL / min, and (d) 8 μL/min.

The effect of applied voltage on morphology of PVA/CnF electrospun nanofibers was carried out by fixing both WD at 11.5 cm and polymer injection rate at 2μL/min and then changing the applied voltage from 12 to 25 kV. SEM micrographs of the nanofibers electrospun at 12, 15, 18, 21 and 25 kV are shown in Figure 2. It can be seen that the number of beads increased significantly as applied voltage increased, while fibers were thinner at both low and high voltage, although for the higher voltages very thick fibers are also present. At the lowest voltage, the electrical field is presumably not strong enough to stretch the fibers, whereas at the highest voltage the intense electric potential difference pulls the droplets, perhaps in a non-uniform way, thus forming both thin and thick fibers, as well as beads. This non-uniformity broadens the distribution of fiber diameters. At intermediate values, between 15 and 21 kV, fiber diameter reaches an optimum value of 80 ± 10 nm, i.e., a narrow fiber diameter distribution with no beads.
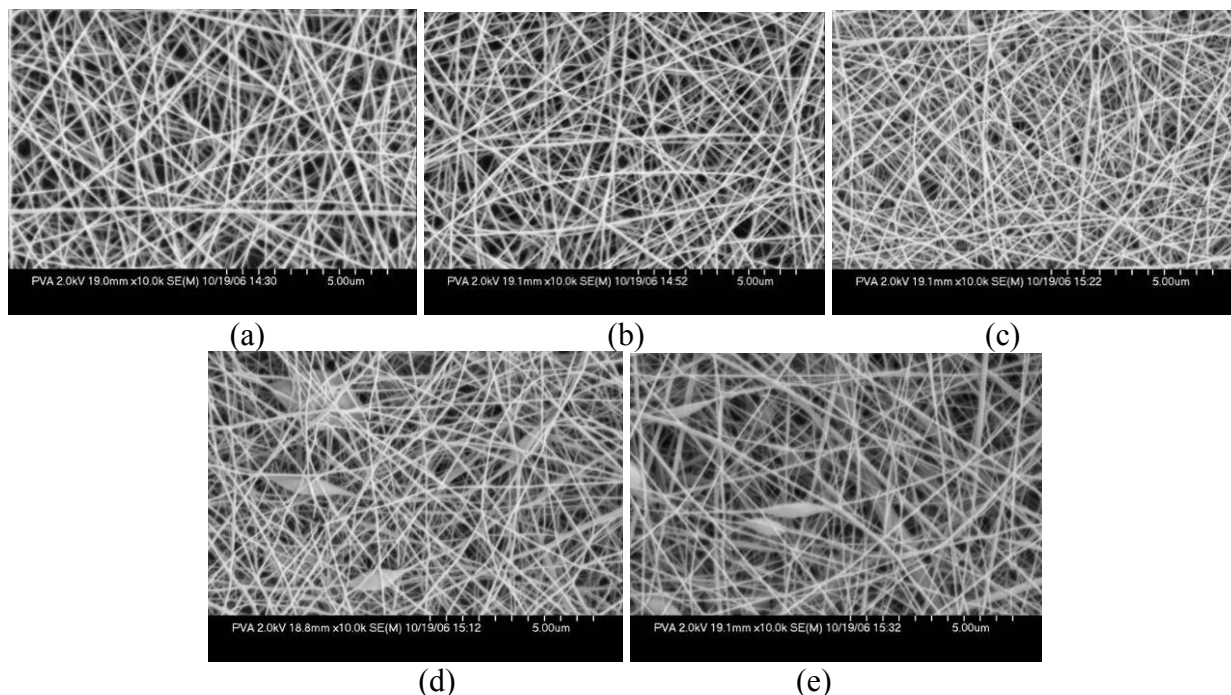

Figure 2 − Effect of voltage on morphology of PVA/CnF electrospun nanofibers using an injection rate of 2 μL/min and a working distance (WD) of 11.5 cm. (a) 12 kV; (b) 15 kV; (c) 18 kV; (d) 21 kV and (e) 25kV.

The effect of rotation speed of the collector on morphology of PVA/CnF electrospun nanofibers was observed by fixing WD at 11.5 cm, polymer injection rate at 5μL/min, and applied voltage at 15 kV, and then changing rotation speed from 200 to 1,000 rpm (Figure 3) showed that the increase in collector rotation resulted in more uniform and thinner fibers, potentially due to the higher stretching level imposed on them. At speeds over 1,000 rpm the overhead stirrer vibrated excessively, which made further experiments difficult. This shows that a rotating target can be used, not only to control fiber alignment, but also to control fiber diameter; the ultimate choice is dependent on the end use of the electrospun mats. Despite being less efficient than the methods reported by Pan et al. [] and Li et al. [] in which nearly 100% uni- and bidirectionally aligned nanofibers can be obtained, this electrospinning setup does not need to be modified in order to impart a certain degree of orientation to the mats. Indeed, aligned electrospun nanofibers of polyacrylonitrile by high speed rotating method, similar to the setup used in this work but using higher speed, has been reported as an efficient method to prepare unidirectionally aligned carbon precursor fibers [].
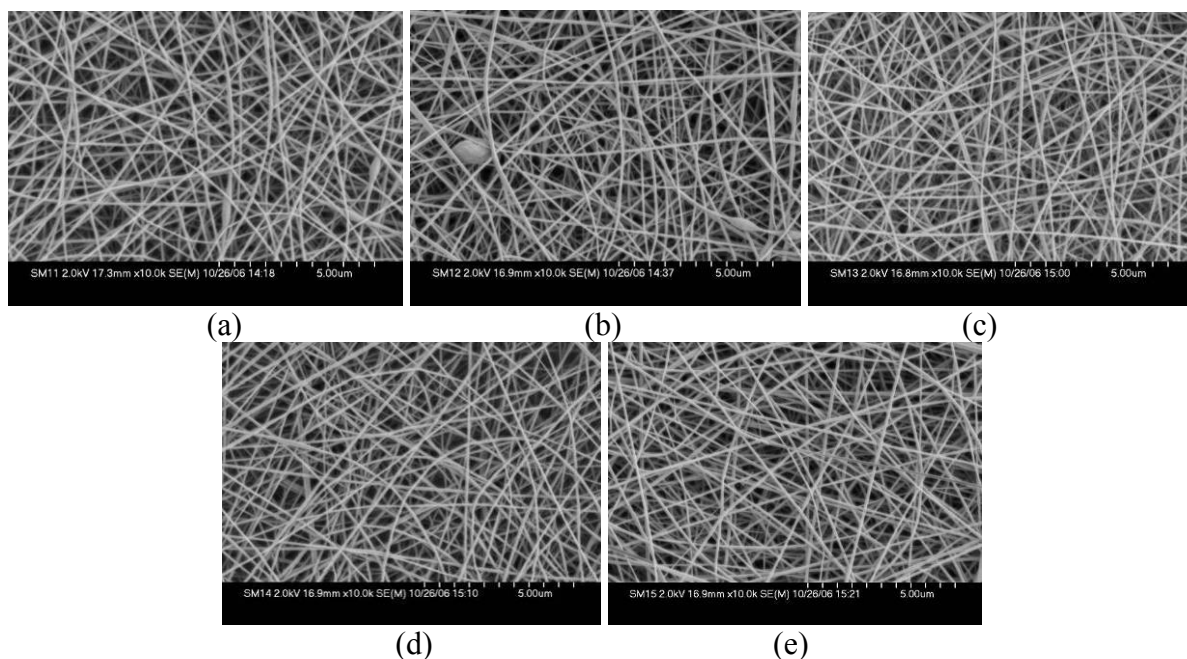
(a)   (b)   (c)

(d)   (e)

Figure 3 – Effect of rotation speed of the collector on morphology of electrospun fibers. (a) 200 rpm; (b) 400 rpm; (c) 600 rpm; (d) 800 rpm; and (e) 1000 rpm. Experimental conditions: WD=11.5 cm; V=15 kV; PVA (14 wt.%) and CnF (6.6 wt.%).

The effect of RH on fiber morphology of electrospun PVA/CnF nanofibers studied by controlling moisture inside the electrospinning box with saturated solutions is shown in Figure 4. It can be observed that both fiber diameter and packing density are strongly affected by changes in RH. Whereas lower RH favored an open structure (low density of fibers per unit area), higher RH values favored the formation of a more closed structure with thinner diameters. The average fiber diameter of the electrospun PVA/CnF composites ranged from 30 to 200 nm, which lies in the range reported in the literature for electrospun fibers of pure PVA, i.e., from 87 to 2,000 nm, but most of the works reported a narrower distribution between 200 and 800 nm [,]. When RH increases, the conductivity of the medium increases because of both polarization of the air due to the high applied electric field with ozone formation (this phenomenon can be detected easily by the ozone odor in the electrospinning box) and because of formation of conductive "paths" due to water dipoles across the working distance. This reduces the stretch on the fibers, but also splits them as a consequence of the formation of secondary jets that ultimately cause a reduction in fiber diameter. On the other hand, when RH is low the rate of solvent evaporation can be so high that it generates a rapid increase in polymer viscosity and the polymer chains are not able to undergo voltage-induced stretching, therefore increasing fiber diameter. This effect, which is also likely induced by the static buildup on the acrylic box, was corroborated by excessive clogging at the tip of the needle during the electrospinning at 25-30% RH and by the formation of spider web-like structures throughout the box, which are characteristic features of high rate of solvent evaporation.
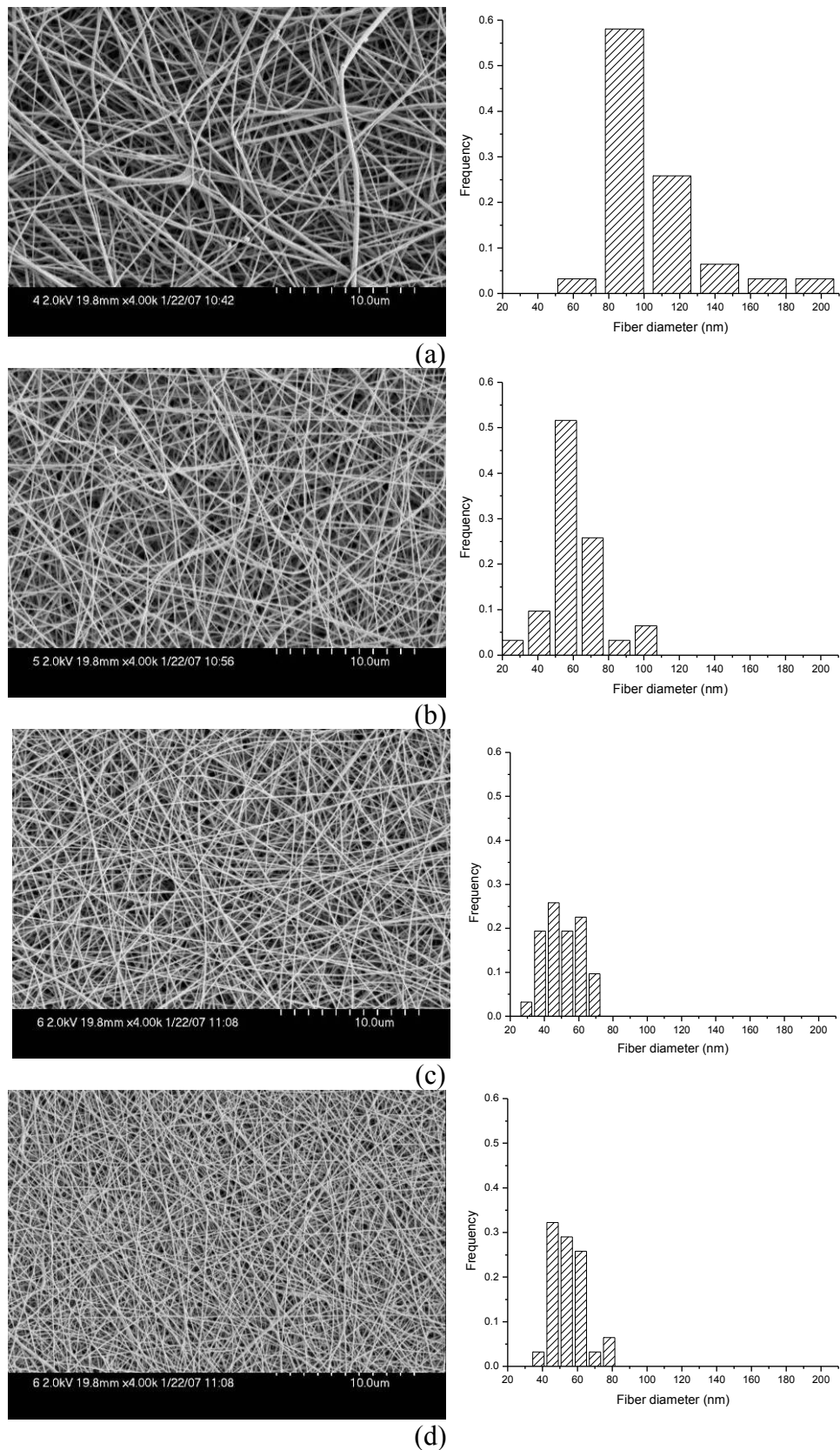
(a)

(b)

(c)

(d)

Figure 4 – SEM micrographs (left) and distribution of fiber diameters (right) of PVA nanofibers electrospun at: (a) 25-30 (b) 38-40, (c) 48-52 and (d) 75-80% RH.

In order to characterize the presence, orientation and reinforcing effect of the cellulose nanofibers, TGA, TEM and tensile properties were measured. TG curves (Figure 5) show that the thermal events associated to PVA/cellulose composites are intermediate between the pure components;

results which are corroborated by TEM analyses (Figure 6) showing cellulose nanofibers in the core and sticking out from electrospun PVA nanofibers. Atomic force microscopy (AFM) measurements of these nanofibrils [] showed that they have an average diameter (d) of 38±13 nm, length (l) of 360±60 nm, and an aspect ratio (l/d) of 10±4nm, therefore in agreement with the dimensions of the cellulose nanofibrils in Figure 6.
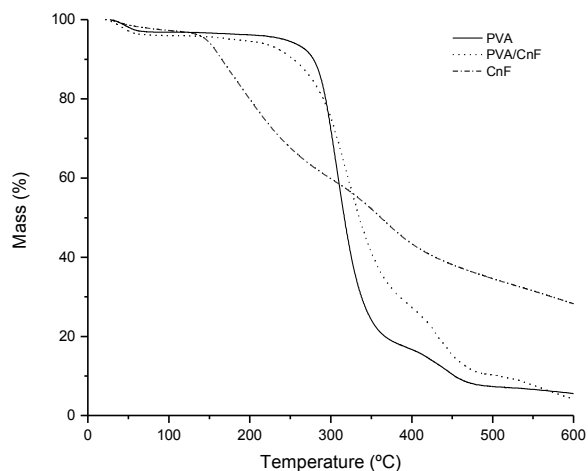

Figure 5 – TG curves of electrospun nanofibers of PVA and PVA reinforced with cellulose nanowhiskers, and cellulose nanowhiskers.
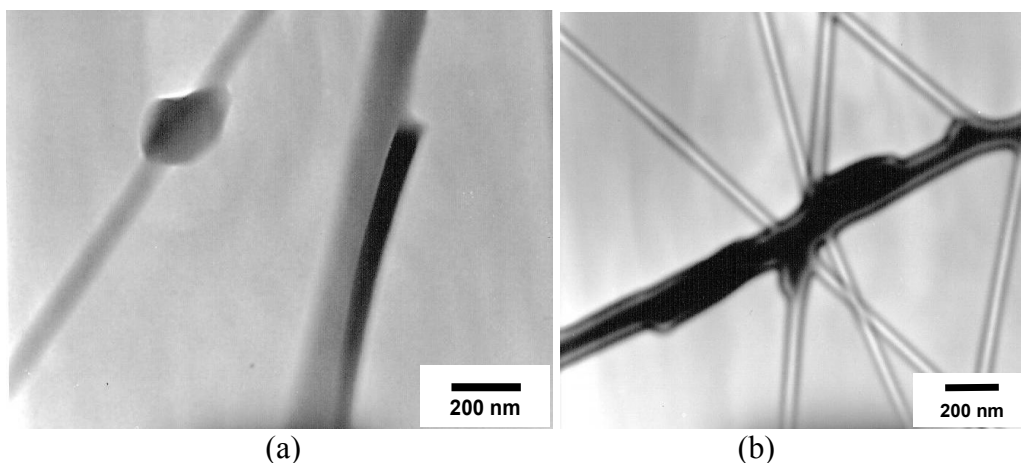

| (a) | (b) |

Figure 6 – TEM micrographs of electrospun PVA/CnF nanofibers. (a) Detail of a stained cellulose nanofiber (dark areas) protruding from an electrospun PVA nanofiber, and (b) in the core of electrospun PVA nanofibers.

The mechanical properties of the electrospun nanofibers of PVA/CnF were compared to nanofibers of PVA electrospun in the same experimental conditions. The results of the mechanical tests are summarized in Table I and typical stress-strain curves of electrospun nanofibers of PVA and PVA reinforced with cellulose nanofibers are illustrated in Figure 7. It can be observed that Young's modulus and tensile strength of reinforced composites increased by ca. 240 % by addition of only 6.6 wt.% of cellulose nanofibers without major change in elongation at break. A similar behavior was found by Petersson and Oksman [] with poly(lactic acid) nanocomposites reinforced with microcrystalline cellulose in which the addition of cellulose reduced elongation at break by 16% as a result of incorporation of 5 wt.% of cellulose. In contrast, addition of the same amount of bentonite, a layered silicate, caused a reduction of 75 %.
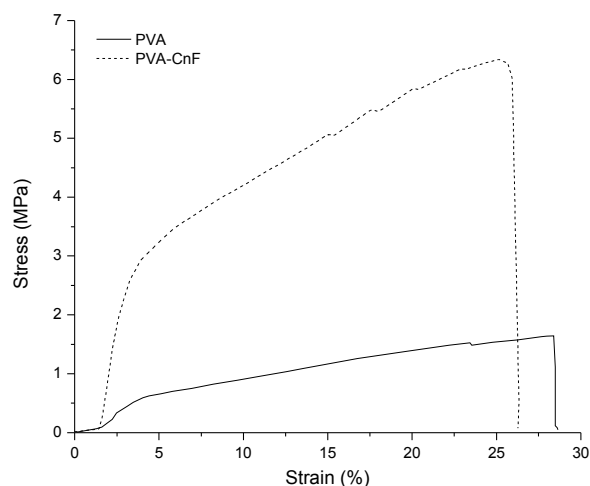
Figure 7 – Typical stress-strain curves of electrospun nanofibers of PVA and PVA reinforced with cellulose nanofibers.

Table I – Mechanical properties of electrospun nanofibers of PVA and PVA reinforced with cellulose nanofibrils.

	PVA	PVA-Cellulose
Young's Modulus, E (MPa)	45 ± 17	108 ± 18
Tensile stress, σ m (MPa)	2.0 ± 0.6	4.8 ± 1.2
Elongation at break, εm(%)	26 ± 5	25 ± 4

The strong interactions between these hydrophilic components helps explain the increase in both Young's modulus and tensile strength without significantly reducing the elongation at break. Furthermore, the polarity of both components due to the presence of hydroxyl groups is one of the factors that may have contributed to improve the compatibility between nanofibers and matrix, thus, promoting a more efficient load transfer from matrix to fibers in a way similar to traditional fiber reinforced composites [,].

The remarkable improvement in mechanical properties by addition of cellulose nanofibers has also been found by Orts et al []. The authors reported that for extruded starch plastics, the addition of cotton-derived fibrils at a concentration of 10.3 wt.% increased Young's modulus by 5-fold relative to a control sample with no cellulose reinforcement. Moreover, this increase in tensile properties, especially maximum load and tensile strength, depended not only on the shear-induced alignment of the fibers but also on the type of polymer matrix, implying that complex interactions are involved in the reinforcing capability of the nanofibers.

This increase in Young's modulus and tensile strength is much more accentuated than in traditional fiber reinforced composites where a relatively modest increase in these properties is attained only by using comparatively much higher amounts of reinforcements. Indeed, Young's modulus of the basic cellulose crystalline fibrils has been reported as 137 GPa, but in order to fully exploit its potential as reinforcements detailed investigation of the cellulose nanofiber-polymer interface is required [].

Conclusions

Nanofibers of poly(vinyl alcohol) reinforced with cellulose nanofibers were successfully produced by electrospinning. The morphology of the electrospun nanofibers (electrospun mats) was strongly affected by the electrospinning conditions, i.e., the effect of applied voltage, polymer concentration and injection rate, tip-to-collector distance, and relative humidity. Thinner fibers are favored by decreasing polymer concentration and injection rate, increasing rotation speed of the collector and

relative humidity, whereas increasing the applied voltage favors the formation of beaded fibers. The balance between all these variables is the key to accurately controlling the morphology and the final properties of the electrospun mats. The reinforced composites had their Young's modulus and tensile strength increased by ca. 240 % by addition of only 6.6 wt.% of cellulose nanofibers without major changes in elongation at break due to the good interaction between PVA and cellulose nanofibers during the compounding step. These results show that addition of cellulose nanofibrils to electrospinning solution of PVA is an efficient method to improve the mechanical strength of electrospun nanofibrous mats.

Acknowledgements

References

1. T. Subbiah; G.S.Bhat; W.Tock R.; S.Parameswaran; Ramkumar S.S.; *J. Appl. Polym. Sci*. 2005, 96, 557.
2. S. Ramakrishna; K. Fujihara; W. Teo; T. Lim; Z. Ma, *An introduction to Electrospinning and Nanofibers*, World Scientific Publishing, Singapore 2005.
3. H. Pan; L. Li; L.Hu; X. Cui; Polymer, 2006, 47, 4901.
4. H.Jiang; Y.Hu; Y.Li; P.Zhao; K.Zhu; W.Chen; *J. Control. Rel*. 2005, 108, 237.
5. W.J.Orts; J.Shey; S.H.Imam; G.M.Glenn; M.E.Guttman; J.F.Revol, *J. Polym. Environ.* 2005, 13, 301.
6. H. Hovhannisyan; H.Matnishyan; A.Vardanyan; A.Hakhumyan; L.Abrahamyan, *proceedings of the 34th European Microwave Conference,* 2004, 2, 793.
7. V. Favier; H. Chanzy; J.Y. Cavaille*, Macromolecules,* 1996, 28, 6365.
8. L. H. C. Mattoso; D. A. Baker; J. Avloni; D. F. Wood; W. J. Orts,; *Proceedings of the 41st International Symposium on Macromolecules, Rio de Janeiro*, Brazil, 2006.
9. H. Fong; I. Chun; D.H. Reneker, *Polymer,* 1999, 40, 4585.
10. R. Jaeger; M. M. Bergshoef; C. M. I. Batlle; S. Holger; G. J. Vancso, *Macromol. Symp.* 1998, 127, 141.
11. W.K. Son; J. H. Youk; T. S. Lee; W. H. Park; *Mat. Letters,* 2005, 59, 1571.
12. E.S. Medeiros; L.H.C. Mattoso; R. Bernardes-Filho; D. F. Wood W.J. Orts, *Colloid Polym. Sci.* 2008, 286, 1265.
13. D. Li; Y. Wang; Y. Xia, *Adv. Mat*. 2004, 16, 361.
14. L. Petersson; K. Oksman, *Comp. Sci. Tech.* 2006, 66, 2187.
15. E.S. Medeiros; L.H.C. Mattoso; P.A. Sreekumar; K. Joseph; in: S. Thomas; L.A. Pothan, Eds. *Natural Fibre Reinforced Polymer Composites*, Philadelphia, Old City Publishing Co. In press.
16. E.S. Medeiros; J.A.M. Agnelli; K. Joseph; L.H. Carvalho; L.H.C. Mattoso, *Polym. Comp.* 2005, 261, 11.