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# Effect of Moisture on Electrospun Nanofiber Composites of Poly(vinyl alcohol) and Cellulose Nanocrystals

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The effect of humidity on the morphological and thermomechanical properties of electrospun poly(vinyl alcohol) (PVA) fiber mats reinforced with cellulose nanocrystals (CNs) was investigated. Scanning electron microscopy (SEM) images revealed that the incorporation of CNs improved the morphological stability of the composite fibers even in high humidity environments. Thermal and mechanical properties of the electrospun fiber mats were studied by using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and large deformation tensile tests under controlled humidity and temperatures. The balance between the moisture-induced plasticization and the reinforcing effect of rigid CN particles was critical in determining the thermomechanical behaviors of the electrospun fiber mats. Results indicated that the stabilizing effect of the CNs in the PVA matrix might be compromised by water absorption, disrupting the hydrogen bonding within the structure. The amount of this disruption depended on the surrounding humidity and the CN loading. The reduction in tensile strength of neat PVA fiber mats as they were conditioned from low relative humidity (10% RH) to high relative humidity (70% RH) was found to be about 80%, from 1.5 to 0.4 MPa. When the structure was reinforced with CNs, the reduction in strength was limited to 40%, from 2 to 0.8 MPa over the same range in relative humidity. More importantly, the CN-loaded PVA fiber mats showed a reversible recovery in mechanical strength after cycling the relative humidity. Finally, humidity treatments of the composite PVA fiber mats induced significant enhancement of their strength as a result of the adhesion between the continuous matrix and the CNs.

## Introduction

Poly(vinyl alcohol) (PVA) is among the most commonly used synthetic polymers due to its unique properties.[1] PVA is water-soluble, easy to process, hydrophilic, and has good physical and chemical properties.[1−3] One of the most promising properties of PVA is its biocompatibility.[3] PVA is physiologically inert in terms of acute toxicity ($LD_{50}$ on rats after oral application), and it is not a skin nor a mucous membrane irritant.[2] PVA also presents remarkable barrier properties against oils and fats, aromas and perfumes, and small molecules (nitrogen, oxygen, etc.).[3,4] In addition to its biocompatibility, PVA can be biodegraded by adapted microorganisms into $CO_2$ and water, a property that makes it an environmentally friendly polymer.[2] PVA is widely used in textile, adhesive, cosmetic, food, drug, paper, and packaging industries. The main functional uses of PVA include filtration, catalysis,[5,6] membranes, optics, drug release,[7,8] enzyme mobilization,[8] tissue engineering,[9] among others.[10]

Many of the key properties of PVA, such as those mentioned above, are the result of its significant cohesive energy due to its polarity from hydroxyl groups.[11,12] However, the same characteristics that endow PVA with unique performance and hydrophilicity make it susceptible to plasticization in humid environments.[12]

The use of different reinforcing agents in composites had been growing exponentially in annual basis since the 1980s.[13] In the case of PVA-based composites, the plasticization in humid environments critically limits wider application of these materials. Ideally, a reinforcing material for the PVA composites would be found that does not impede any of its beneficial properties. A logical choice for these materials is natural fibers and products from biomass.[14,15] During the last two decades, efforts have been focused on the use of cellulose nanocrystals (CNs) as reinforcing material.[16] Earlier work introduced the concept of CNs as reinforcing phase in synthetic polymers,[17,18] and a large list of matrices has been considered for combination with CNs.[19] Relevant to the present work, CNs have been used to reinforce electrospun fibers produced from poly(ethylene oxide),[20] poly(acrylic acid),[21] polystyrene,[22] poly($\varepsilon$-caprolactone),[23] and cellulose.[24]

The presence of hydroxyl groups in CNs makes them suitable for the production of composites with polar, hydrophilic polymers such as PVA, and the benefit of improved mechanical and thermal properties has been reported in the case of cast films[25,26] and electrospun fiber mats.[27−29]

The aim of the present contribution is to study the effect of water as well as humidity treatments on the morphological integrity and the mechanical properties of electrospun PVA fibers reinforced with CNs. Water uptake and the interactions between water and the PVA matrix were considered. PVA fiber nanocomposites were conditioned under different relative humidities (RH), and scanning electron microscopy (SEM) was used to study effects on fiber morphology. Finally, measurement

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with differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were carried out to investigate the effect of fiber moisture in the thermomechanical properties.

## Materials and Methods

Poly(vinyl alcohol) (PVA) with 2% acetyl groups (degree of hydrolysis of 98%) and molecular weight of 125 kDa was purchased from Sigma-Aldrich under trade name Mowiol 20-98.

The CNs were obtained by acid hydrolysis of pure, extract-free ramie fibers (Stucken Melchers GmbH & Co., Germany) as described earlier.[30] Briefly, after removing residual additives by extraction (4 wt % aqueous NaOH solution, 80 °C, 2 h), hydrolysis was conducted with 65 wt % sulfuric acid for 45 min at 55 °C under vigorous mechanical stirring. The reaction was stopped by cooling the resulting suspension in an ice bath, and it was then filtered with a sintered glass filter (ASTM 40−60 $\mu$m) to remove unhydrolyzed fibers and finally washed with deionized water by using repetitive centrifugations (12 000 rpm, 10 °C, 20 min per cycle) until reaching neutrality. The resulting suspension was dialyzed against deionized water for a week to remove excess free acid and sonicated in order to redisperse the obtained CNs before storing them in a refrigerator. The concentration of CNs in the final dispersion was determined by gravimetry after drying.

Composite PVA−CN electrospun fibers were produced as described in our previous work.[27] Briefly, aqueous solutions of PVA were prepared, and given amounts of CNs were added to obtain a final CN content of 0, 5, 10 and 15% (w/w) while keeping total PVA concentrations constant at 7%. Electrospinning was carried out by using a horizontal setup that included a syringe pump (Aldrich) controlled by a Pump-term code to pump the dispersion contained in 10 mL disposable plastic syringes thorough 22-G needles, which was connected to a high-voltage supply unit (Series EL, Glassman High Voltage). A 30 cm diameter plate covered by aluminum foil was used as collector and placed at a working distance of 15 cm from the needle tip; the collector was connected to the negative electrode of the power supply (ground), while the needle tip was connected to the positive terminal.

**Conditioning of the Electrospun Mats.** Collected electrospun fiber mats were stored in preconditioned atmospheres with relative humidity of 0, 35, 75, or 98% RH. These % RH values were produced by using $P_2O_5$ (0% RH) or saturated solutions of $CaCl_2 \cdot 6H_2O$ (35% RH), NaCl (75% RH), and $CuSO_4 \cdot 5H_2O$ (98% RH). The electrospun mats were allowed to reach equilibrium in the respective atmosphere as confirmed by weight stabilization. In the case of 0% RH, prior to conditioning, the sample was dried in an oven at 40 °C under vacuum in order to remove any residual water.

**Humidity Cycles.** Neat PVA (no CNs) electrospun fiber mats and those loaded with 15% (wt) CNs were subjected to successive humidity cycles. The humidity cycles consisted of a drying step, in which the sample was placed in an oven at 40 °C under vacuum, followed by a humidification step, where the sample was placed in a 35% RH atmosphere. The cycle was repeated three times. Immediately after each step, the samples were stored in the respective humidity (e.g., 0% RH for dried samples and 35% RH for wet ones) until further morphological and physical characterization.

**Field Emission Scanning Electron Microscopy (FE-SEM).** The morphology of the nanofibers in the electrospun mats was studied by using a field emission scanning electron microscope (FE-SEM, JEOL 6400F) operated at an accelerating voltage of 5 kV and working distance of 20 mm. A small portion of the mat was fixed on conductive carbon tape and mounted on the support and then sputtered with a ca. 6 nm layer of gold/palladium (Au/Pd).

**Differential Scanning Calorimetry (DSC).** DSC was carried out with a TA Instruments DSC Q100. The typical procedure included heating and cooling cycles (10 °C/min rates) of ca. 10 mg of the sample in the temperature range between −50 and 180 °C. The DSC glass transition temperature ($T_g$) was taken at the onset of the glass transition endotherms.

**Table 1.** Equilibrium Moisture Content of PVA Fiber Mats Stored in Atmospheres of Different Relative Humidity (Equilibrium Moisture Is Reported as Weight Percent Rounded off to One Unit Percent)

| relative humidity (%) | neat PVA | PVA fibers loaded with CNs | | |
|---|---|---|---|---|
| | | CNs = 5% | CNs = 10% | CNs = 15% |
| 0 | 6 | 4 | 4 | 4 |
| 35 | 24 | 19 | 18 | 15 |
| 75 | 22 | 22 | 15 | 18 |
| 98 | 34 | 31 | 35 | 26 |

**Dynamic Mechanical Analysis (DMA).** DMA was performed in tensile mode (TA Instruments Q800). The measurements were carried out with 6 mm wide sample strips cut out of the corresponding electrospun fiber mats and using a gap between jaws of 10 mm. DMA measurements used a constant frequency of 1 Hz, strain amplitude of 0.03%, and a temperature range of −100 to 250 °C (heating rate of 3 °C/min).

**DMA with Humidity Control.** DMA measurements under controlled humidity were carried out with a TA Instruments Q800 equipped with an external humidity element (Kep Technologies Wetsys Setaram Instrumentation) connected to the measuring chamber. The samples were loaded to the preconditioned chamber and kept until the moisture content in the sample was stabilized before starting the measurements. Relative humidity of 10, 70, and 80% and a temperature of 30 °C were used. The minimum time for sample conditioning was set to 60 min, which is standard for these types of samples; nevertheless, in a typical experiment, equilibrium was guaranteed as determined by a stable DMA signal. Stress sweeps of the samples were done from 0 to 30 MPa or until failure.

## Results and Discussion

**Morphology of PVA−CN Nanofiber Mats.** Electrospun PVA fibers were produced following the experimental conditions optimized and stated in previous reports; the average diameter of the neat PVA fibers was ca. 235 nm, and CN loading induced a significant reduction in fiber diameter, down to ca. 188 nm in the case of 15% CN loading. Preliminary experiments to determine the stability of the electrospun fibers to humidity consisted of exposing fiber mat samples to different relative humidity and determining the equilibrium moisture content (see Table 1).

In Table 1, the equilibrium moistures at 75% RH for neat PVA and PVA with 10% of CNs were unexpectedly lower than those at 35% humidity. However, this difference was within the experimental error; the standard deviation in these (gravimetric) measurements was 5.4% moisture units. An increase in moisture of the composite fiber mat with the % RH was a consistent trend for a given CN loading. Most importantly, the presence of CNs in the fibers was observed to reduce, to some extent, the water uptake by the composite PVA fiber mats.

The effect of the water absorbed on fiber morphology after conditioning at different relative humidity was also studied. Figure 1 shows SEM micrographs for electrospun fibers obtained from neat PVA and from PVA with 15% CN loading after storage at 0 and 98% RH. Neat PVA fibers stored in dry conditions, with typical diameters in the submicrometer scale, swelled as the surrounding humidity increased. During sample preparation and FE-SEM imaging, the relative humidity was obviously different than that used during conditioning; nevertheless, the fibers stored in humid atmospheres tended to fuse together, and such state remained the same upon FE-SEM imaging, clear evidence of the effect of water absorption. Only small changes in morphology were observed when the fiber mats

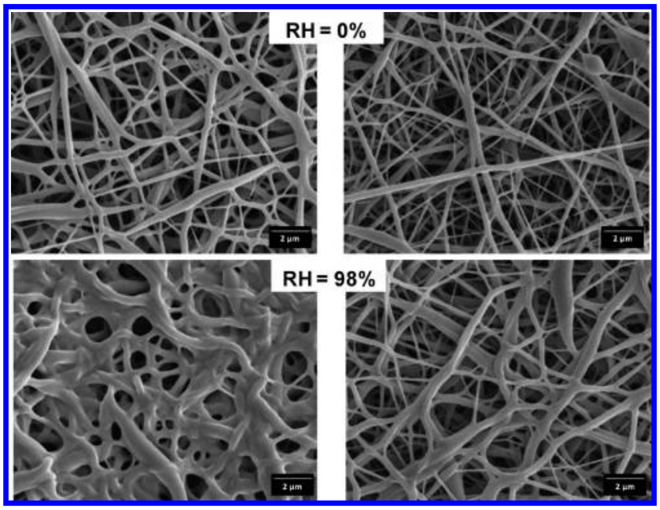

**Figure 1.** FE-SEMs of electrospun neat PVA fibers (left) and loaded with 15% of cellulose nanocrystals (right) after equilibration at two different conditions of relative humidity, 0 and 98%, as indicated.

were exposed to relative humidities of up to 75%. However, at 98% RH, the change in morphology was more clearly observed. The average diameter of PVA fibers loaded with 15% CN increased from 140 (standard deviation of 70 nm) to 230 nm (standard deviation of 130 nm) after conditioning at 0 and 98% RH, respectively. As shown in Figure 1, there was a large variation in fiber diameter, even compared to data reported earlier by the authors.[27] This was mainly due to differences in the pumping conditions in the present electrospinning setup; however, the trend clearly indicated an increase in diameter with % RH. Remarkably, the influence of relative humidity during conditioning on the morphology of the nanofibers was less significant when the PVA fibers were loaded with CNs, as also shown in Figure 1. Such observation also applies to lower CN loadings (5 and 10% CN, not shown). This improvement in fiber morphological stability can be explained by the interactions and distribution of water molecules between PVA and reinforcing CNs. Hydrogen bonding is expected to exist due to the large density of hydroxyl groups. On the other hand, water molecules in PVA fibers after equilibrium with the respective humidity can be weakly or strongly bonded to the polymer chains.[31] In the presence of CNs, the interactions become more complex; PVA chains, CNs, and water molecules become involved in pair interactions.[31] The hydroxyl groups present on the surface of CNs are expected to form a hydrogen-bonded network with the PVA, decreasing the availability of hydroxyl groups to bind with weakly bound water molecules. Therefore, this effect is hypothesized to be a leading reason for the higher stability to humidity brought about CNs in PVA fibers when conditioned in humid environments.

**Glass Transition Temperature of the PVA-Based Fiber Mats.** The effect of the humidity on the glass transition temperature ($T_g$) was investigated by thermal analyses. Differential scanning calorimetric analyses were carried out with neat PVA electrospun fibers at different CN loadings and after conditioning at different relative humidity. Figure 2 shows the variation in $T_g$ after conditioning at 0, 35, and 75% RH for various CN loadings. Detection of the glass transition temperature for samples conditioned at 98% RH was not possible because the exothermal peaks overlapped with the broad exothermal corresponding to the melting of water present in the sample.

In all cases, the $T_g$ values, between 40 and 80 °C, were consistent with those reported by the PVA manufacturer.[2] For neat PVA, as expected, the $T_g$ decreased with increasing relative humidity as a result of the plasticizing effect of water and the increased amount of weakly bounded water molecules.[26] In contrast, the presence of CNs counteracted the plasticizing effect of water; that is, the rigid reinforcing phase acted as an antiplasticizer as reported in PVA-based cast films.[26,32] A restriction in the mobility of polymer chains, especially in the amorphous regions, is expected to occur due to the strong hydrogen-bond interactions between the CNs and the PVA chains. The competitive interactions between hydroxyl groups of the surface of the CNs and those in the PVA matrix and the selective partitioning of water molecules between the bulk and the CNs are expected to impact the mobility of amorphous chains in the vicinity of matrix crystallites coating the reinforcing CN particles. Such effects have been verified in water-free systems loaded with plasticizers that have low or no affinity with CNs, as reported in the literature.[33,34] In such systems, a net increase of $T_g$ was observed and explained by the migration of the plasticizer molecules from the reinforcing agent interface to the bulk matrix.[34]

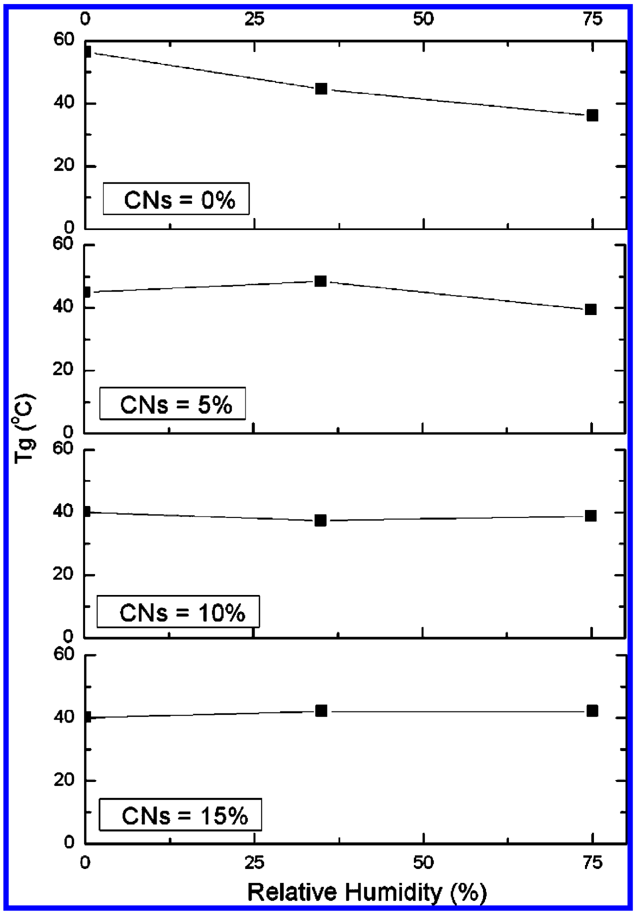

**Figure 2.** Glass transition temperature of PVA electrospun fibers mats loaded with different amounts of CNs and conditioned at different relative humidity.

**Mechanical Properties of PVA−CN Nanofiber Mats.** Previous work demonstrated that the incorporation of CNs in dry PVA electrospun fibers induced a significant improvement of mechanical properties.[27,28] However, the complex and strong interactions that exist between PVA chains, water molecules, and CNs in less dry composites are expected to influence markedly their mechanical properties and, as will be shown later, may compromise their performance. Therefore, a leading question relevant to this subject pertains to the role of the CN reinforcing phase.

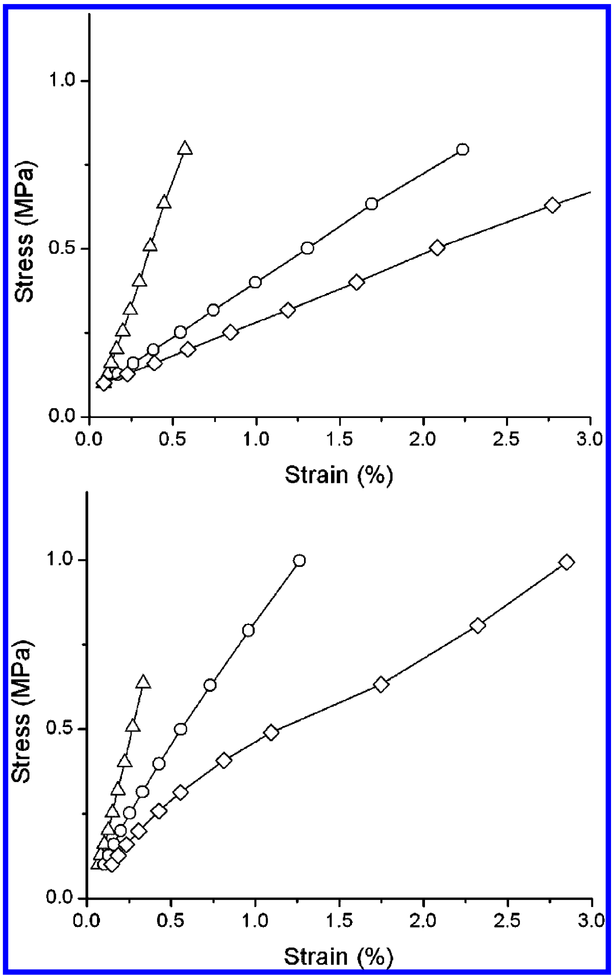

**Figure 3.** Stress/strain curves of neat unfilled (top curves) and filled (with 15% CNs, bottom curves) PVA electrospun fibers equilibrated at relative humidities of 10 (△), 70 (○), and 80% RH (◇).

Preliminary tensile tests were carried out to evaluate mechanical properties at large deformation in different relative humidity conditions. Stress/strain curves of unfilled and CN-loaded PVA electrospun fiber mats were obtained at 10, 70, and 80% RH, as shown in Figure 3. The data were obtained from fiber mats collected by electrospinning during an appropriate time to produce fiber mat thicknesses suitable for DMA measurements within its sensitivity limits. The films were all even and smooth with negligible variations in thickness as measured by a digital micrometer. While these humidity values are different than those discussed in earlier sections, they were the ones that were practical in the conditions of use of the respective instrument. Values of the Young's modulus derived from the initial slope of the stress−strain plots and the respective ultimate strain are summarized in Table 2 for fiber mats reinforced with CNs and tested under different equilibrium moistures. It is worth noting that regardless the moisture content of the fiber its modulus was always greater for the CN-loaded composites.

Due to the plasticizing effect of water, unfilled and CN-filled PVA nanofiber mats showed, as expected, an important decrease in the tensile strength; also, a significant increase of the ultimate strain was observed as the moisture in the fiber increased (from 10 to 70% RH). However, the relative reduction in tensile strength was more evident in the case of neat PVA fiber mats, about 80% reduction (from 1.5 to 0.4 MPa) compared to the more limited reduction of 40% when the fibers were loaded with 15% CNs (from 2 to 0.8 MPa).

**Table 2.** Values of Young's Modulus and Ultimate Strain of Electrospun PVA Fiber Mats with and without Reinforcing CN (at 15% Loading) Measured at Different Conditions of Relative Humidity[a]

| | Young's modulus (MPa) | | ultimate strain (%) | |
|---|---|---|---|---|
| % RH | 0% | 15% | 0% | 15% |
| 10 | 1.5 | 2.0 | 0.57 | 0.33 |
| 70 | 0.4 | 0.8 | 2.63 | 1.26 |
| 80 | 0.2 | 0.3 | 3.70 | 2.85 |

[a] Note: The data reported in this table were obtained after averaging several measurements. The standard deviation in the collected data was 5%, and each data point was collected for 2 s after equilibrium was reached.

The ultimate strain increased with moisture content, by about 460%, for neat PVA fiber mats, while in the case of a CN-filled system, such increase in strain was 380%. These observations together with the behaviors noted before for the tensile strength support evidence of the plasticizing effect of water molecules. Water softens the polymer matrix, inducing a reduction in strength and an increase in elasticity. However, the presence of CNs limits the absorption of water because, relative to PVA, cellulose is less hygroscopic; also, because of their rigid nature, CNs offset the plasticizing effect of water. Overall, the observations presented so far support evidence that CNs form a strong hydrogen-bond network with PVA decreasing the number of available hydroxyl groups that bind with the weakly bonded water molecules. At extreme moisture content, for equilibrium with environments with relative humidity higher than ca. 80% RH, water molecules are expected to disrupt such a network and therefore the effect of CNs is screened out.

To confirm the explanations presented before and also to test the reversibility in the strength performance of the composite fiber mats upon water absorption, neat PVA fiber mats and PVA fibers loaded with 15% of CNs were exposed to humidity cycles, from 80 to 0% RH. The DMA with incorporated humidity controller was used in experiments in which stabilization of the system was allowed for 60 min per cycle. The shifts in the storage modulus and the elongation were recorded continuously as the relative humidity was changed (see Figure 4). It can be observed that, when the surrounding humidity increased, the modulus of the neat and CN-reinforced PVA fiber mats decreased. This change was accompanied by an increase in the elongation resulting from the plasticizing effect of water.

Both unloaded and CN-loaded PVA nanofibers fully and reversibly recovered the storage modulus when the humidity was cycled between 0 and 80% RH. However, only the unloaded PVA fiber mats reversibly recovered their original shape (elongation) after humidity cycles; deformation of CN-filled PVA mats occurred irreversibly in the first humidity cycle (80 to 0% RH) probably due to the absorption of strongly bonded water molecules located at the interface between the reinforcing CNs and the PVA matrix chains. After the first cycle, the elongation was recovered reversibly. This distinctive behavior of the composite PVA fiber mats is believed to be a consequence of water-induced reorganization of PVA chains at the CN−PVA interface. In order to shed more light about this phenomenon, the composite fiber mats were subjected to complete drying (under vacuum) to ensure complete removal of the water molecules and then were studied according to the experiments explained in the following discussion.

DMA temperature ramps were carried out in order to analyze further the effects observed previously. The ramps were conducted in linear tensile mode, after conditioning the samples at corresponding given relative humidity, from room temperature

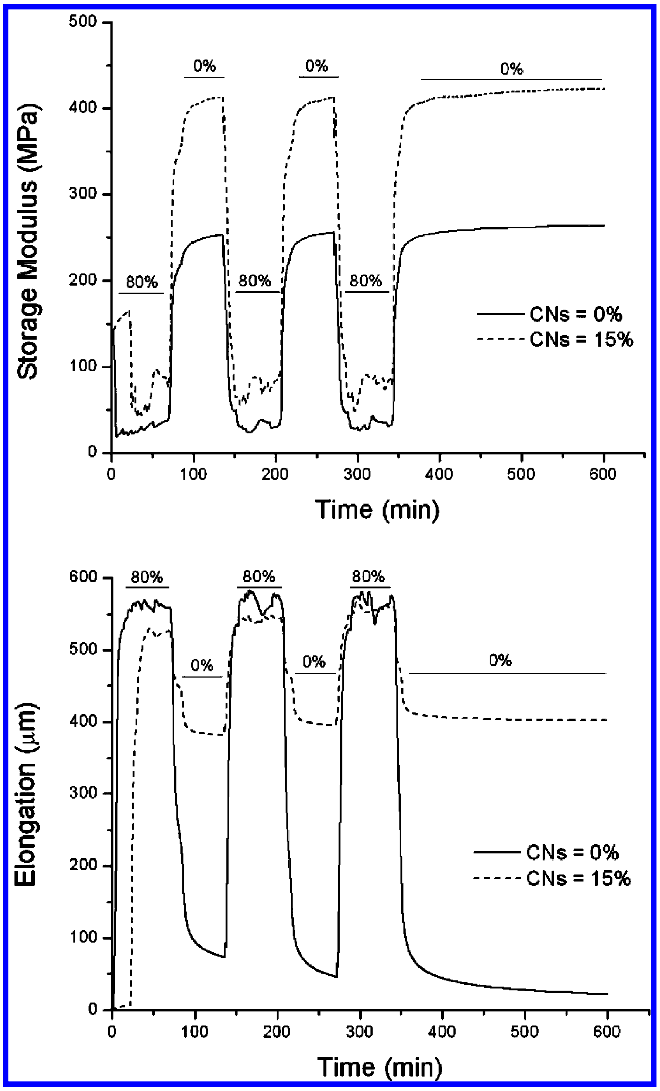

**Figure 4.** Variation of the storage modulus (top) and elongation (bottom) of unfilled and 15% CN-loaded PVA fiber mats after cycling the relative humidity from 80 to 0% RH (runs were performed at constant 25 °C).

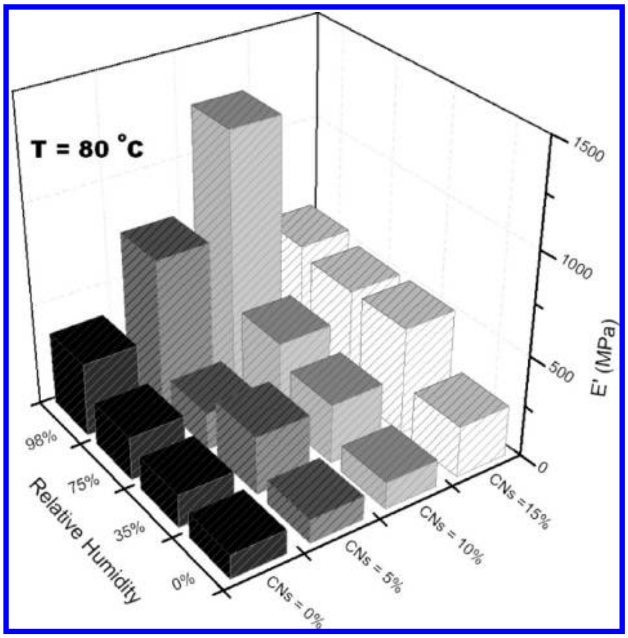

**Figure 5.** Storage modulus of electrospun nanofiber mats loaded with different amounts of CNs after stabilization at different relative humidity (0, 35, 75, and 98%) and with temperature maintained at 80 °C.

up to the melting temperature of PVA polymer. It was found that the variation with temperature of the storage modulus (not shown here) displayed the typical behavior of partially crystalline polymers. The values of the storage modulus at 80 °C, above the $T_g$ of PVA, obtained from DMA curves for different relative humidity and CN loadings are reported in Figure 5.

At 80 °C, water molecules were partially removed and hydrogen bonding between PVA chains and weakly bonded water was disrupted. Therefore, competition for formation of hydrogen bonds with water (strongly bonded water molecules) was expected to exist between the PVA chains and CNs.

At any given relative humidity, CNs induced a significant increase in the elastic modulus of the fiber composite, which corroborated the reinforcing abilities of CNs, as was also reported in the case of water-free PVA composite nanofibers.[27] A unique effect was observed at high relative humidity (i.e., 98%); by loading the composite with CN, up to levels of ca. 10% in weight, a significant increase in the elastic modulus was observed; however, at higher loadings, beyond 10%, a drop in the mechanical strength occurred. Therefore, there is a threshold in CN loading for improved mechanical properties, and such effect could be related to the competition between water molecules and added CNs and PVA matrix for establishing hydrogen bonds. In moist fibers, for loadings above 10% CN, the effect of the reinforcing phase was screened by the dominant plasticizing effect of water.

On the other hand, samples conditioned at 80 °C under higher relative humidity induced an increase in the elastic modulus, for all CN loadings tested. At the relatively high temperature of 80 °C, the weakly bonded water molecules, which act as plasticizer, were partially removed and hydrogen bonding with PVA chains was disrupted; in such cases, the reinforcing effect of CNs was more clearly observed. These results support the previous hypothesis that strongly bonded water is likely to be located at the interface between CNs and PVA chains and contributed largely to the percolation network between matrix−matrix and filler−matrix systems, which enhance the strength of the fiber composites. The trends observed are in line with previous reports dealing with cast films of PVA reinforced with cotton nanocrystals.[26]

**Effect of Humidity Cycles on the Properties of Composite PVA Fiber Mats.** It is well-known that humidity cycles induce the formation of irreversible or partially reversible hydrogen bonds upon removal of water from cellulosic pulp or paper, the so-called “hornification” effect.[35] Drying may cause shrinkage of cellulose fibers, but it has some beneficial effects, such as a more intensely bonded structure, higher dimensional stability, and higher adhesion between fibers. Similar concepts can be applied to other hydrophilic polymer systems, such as PVA, which has a large density of hydroxyl groups and forms a rich hydrogen-bond network. Therefore, it was considered of practical significance to study the effect of humidity cycles on the structure and physical properties of PVA electrospun fiber mats.

The morphology and mechanical properties of PVA fiber mats were investigated after each of three total humidity cycles. The as-produced fibers were first dried in an oven at 40 °C under vacuum and then humidified in 35% RH at room temperature, and this humidity cycle was repeated three times.

SEM images for different samples are presented in Figure 6 for neat and CN-loaded PVA electrospun fibers. It can be easily observed that the fibers kept their integrity and nanofibrillar

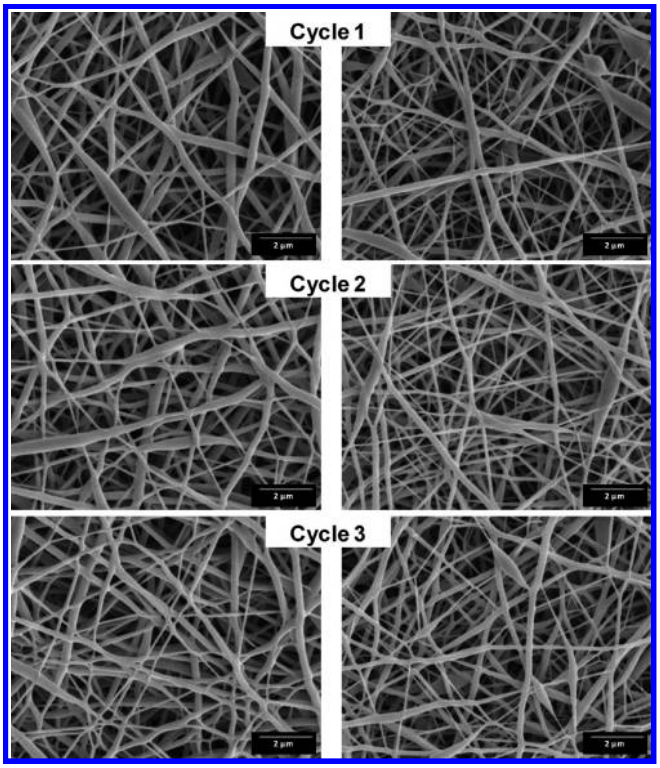

**Figure 6.** SEM images of neat (left) and 15% CN-loaded (right) electrospun PVA fiber mats after the respective humidity cycles.

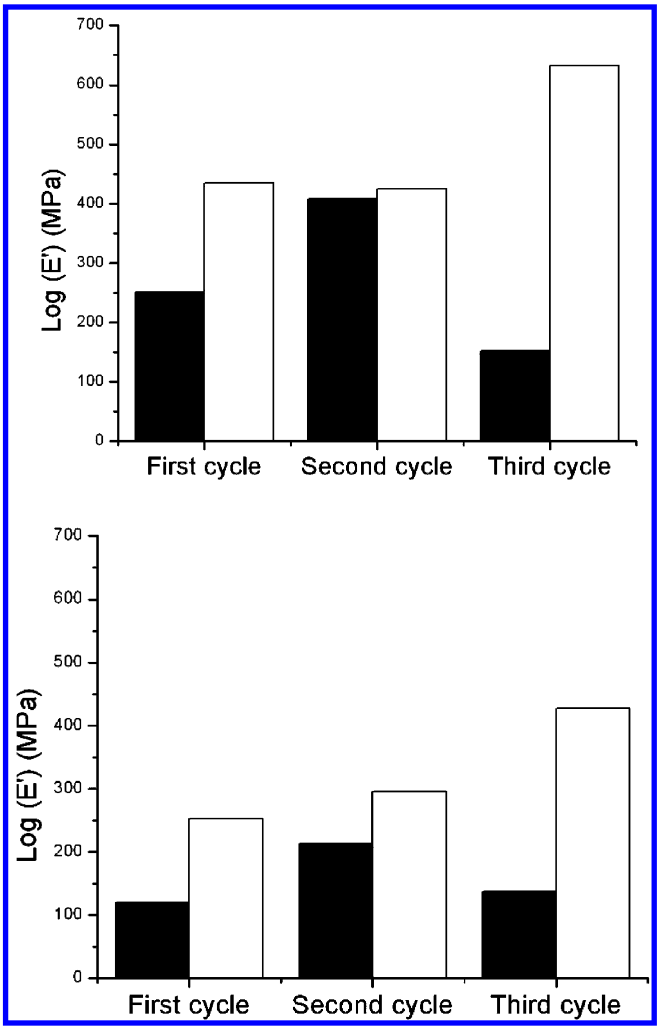

**Figure 7.** Storage modulus measured at 30 °C (top) and 80 °C (bottom) at 0% RH for neat (filled bar) and 15% CN-loaded (unfilled bar) PVA electrospun fiber mats after each successive humidity cycle.

morphology. Corroborating previous results, we observed that the average fiber diameter was maintained in the submicrometer range; in dry conditions, the average diameters were ca. 190 and 160 nm for the unloaded and 15% CN-loaded PVA, respectively. The samples were analyzed by using DMA after each cycle. It was observed that the trends for the storage modulus as a function of temperature (not presented here) were similar to those of neat PVA fibers, which confirmed that no molecular changes occurred during the humidity cycles. The storage moduli at 30 °C (below $T_g$) and 80 °C (above $T_g$) obtained after each cycle are presented in Figure 7.

The storage modulus of neat PVA nanofiber mats increased from about 200 to 400 MPa after the first humidity cycles and dropped after the last, third cycle. This is in contrast to the continuous increase in storage modulus observed in the case of CN-loaded PVA fiber mats upon humidity cycles. These results indicate that, upon water absorption−desorption, new hydrogen bonds are created between chains in neat PVA fiber mats, inducing an increase in contact area that enhance the adhesion between the fibers. However, after reaching a maximum contact area, the modulus dropped because of the restricted mobility of PVA chains under stress, resulting from physical aging phenomenon. As suggested by Padanyl,[36] in the case of absorption−desorption of water by cellulosic fibers in paper, a physical change at the molecular level occurs during time in the amorphous or partially amorphous regions. This time-dependent change, defined as “physical aging”, induces a gradual change in macromolecular packing as the equilibrium free volume state is approached. The presence of moisture affects strongly this equilibrium state, and by alternating water absorption and desorption cycles, thermodynamic reorganization occurs until the material reaches an equilibrium state. In the presence of CNs and after the three humidity cycles, PVA fiber mats did not reach equilibrium: compared to neat PVA, the modulus of CN-loaded PVA fiber mats kept increasing due to their respective limited water absorption. In addition, the humidification cycle increased the water concentration in the CN−PVA matrix interface, and after the removal of water molecules, the flexible hydrogen bonds between PVA chains and/or between PVA and water molecules were replaced mainly by stiffer CN−PVA bonds, which enhanced the strength of the composite. Moreover, the difference in the suprastructure of PVA and CNs makes the tacticity of hydrogen bonds between PVA chains and CNs different than between PVA macromolecules, which influences their free volume equilibrium. In summary, the potential of using humidity cycles to improve fiber−fiber and/or fiber−CN adhesion and consequently to enhance the physical properties of the composite fibers was highlighted, but further studies are required to unveil the molecular basis for the observed behaviors. Finally, no attempt was made to relate the observed phenomena to mechanosorptive behaviors, but similar concepts can be applied to the system under study due to its hygroscopic nature; molecular mobility, physical aging, material-specific interfiber mechanisms, and sorption-induced stress gradients are all factors that are expected to affect the performance (for example, strength and creep behavior) of composite fibers after humidity cycling.

## Conclusions

Electrospun fiber composites based on PVA were conditioned in air at different levels of relative humidity. It was observed that the resultant equilibrium moisture content in the fibers affected markedly their properties and mechanical performance. The addition of cellulose nanocrystals stabilized the system against water absorption and improved the morphological and thermomechanical properties of the fiber composites. A reversible behavior in terms of mechanical strength and elongation took place when the fiber composites were cycled between low and high relative humidity. This observation was explained in terms of hydrogen bonding: the plasticizing and anti-plasticizing effect of water and CNs, respectively, and their key roles in defining the mechanical functions of related composites. The results presented here support evidence of the efficient stress transfer between CN and PVA polymer chains in composite electrospun fibers, both in dry and in moist conditions.

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