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Crosslinked PVA Nanofibers Reinforced with Cellulose Nanocrystals: Water Interactions and Thermomechanical Properties

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ABSTRACT: Acid-catalyzed vapor phase esterification with maleic anhydride was used to improve the integrity and thermo-mechanical properties of fiber webs based on poly(vinyl alcohol), PVA. The fibers were produced by electrospinning PVA from aqueous dispersions containing cellulose nanocrystals (CNCs). The effect of esterification and CNC loading on the structure and solvent resistance of the electrospun fibers was investigated. Chemical characterization of the fibers (FTIR, NMR) indicated the formation of ester bonds between hydroxyl groups belonging to neighboring molecules. Thermomechanical properties after chemical modification were analyzed using thermal gravimetric analysis, differential scanning calorimetry, and dynamic mechanical analysis. An 80% improvement in the ultimate strength was achieved for CNC-loaded, crosslinked PVA fiber webs measured at 90% air relative humidity. Besides the ultra-high surface area, the composite PVA fiber webs were water resistant and presented excellent mechanical properties. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40334.

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INTRODUCTION

Film formation, processability and hydrophilicity of polyhydroxy polymers such as poly(vinyl alcohol) (PVA) make them some of the most commonly used polymers in industry.[1] They are also noted for their biocompatibility and biodegradability.[2,3] PVA has good transparency and antielectrostatic properties.[4] The hydrophilic nature of PVA is a factor in membrane permeation of water and hydrated salts. In fact, PVA-based membranes have reduced fouling by adhesion of nonpolar molecules, microbes and fulvic acids.[1] However, a major drawback for deployment of PVA in aqueous media is its high degree of swelling and solubility. This makes water stability of PVA a highly desirable property.

Due to their very high surface area-to-volume ratio nanoscale and microscale fiber membranes are very attractive in filtration media. Such sizes can confer extremely high surface cohesion that allows entrapping particles as small as the sizes of the pores.[5,6] A method commonly used to produce such fine fibers is electrospinning. Electrospinning of PVA has been studied intensely[7–9]; however, as was highlighted before, fiber webs of PVA dissolve in water, which limits their application in aqueous systems or environments with high relative humidity.[10] Modification of polyvinyl alcohol can expand end use applications[11] and crosslinking is one route to overcome water sensitivity issues. Several methods have been reported to improve the mechanical integrity of PVA membranes in water, and their selectivity in the case of salt-rejection systems.[1,12] In all the methods proposed, the main target has been to obtain three-dimensional PVA networks.[13] These include physical and chemical modification of PVA by heat treatment,[1,14] freeze–thaw to induce crystallization,[1,15] irradiation,[16] radical polymerization–peroxidisulphate,[12] and acid-catalyzed dehydration through chemical reaction with a crosslinking agent.[17] Related chemical modifications of PVA are performed by reaction of its hydroxyl groups.[14] Functional groups such as dialdehydes,[18,19] dicarboxylic acids,[4,20] or dianhydrides[21] have been used to crosslink PVA.[14] At the center of our interest is the use of simple methods of functionalization, such as those involving dicarboxylic acids. The reaction of dicarboxylic acids can occur to different extents (noting that crosslinking reactions may require acid catalysts)[22]:

1. To completion: forming two ester bonds either with the hydroxyl groups available in the same polymer (intramolecular) or with hydroxyls belonging to neighboring macromolecules, forming loop-type structures,[4]
2. by single esterification: only one extreme of the already open anhydride reacts with the one hydroxyl group and the other end becomes protonated, remaining in the acid form and,
3. to an incomplete extent: dissociation of the dicarboxylic acid, which prevents reaction.[5]

The barrier and thermal properties as well as mechanical strength of (crosslinked) fibers can be further improved by incorporation of hydrophilic fillers in the continuous polymeric matrix, such as iron oxide,[23] sodium montmorillonite clay particles,[24] and cellulose nanocrystals (CNCs).[25] Thus, incorporation of nanoparticles entails an alternative function other than filling the composite. Due to their availability, renewability, biodegradable character, and good mechanical properties, CNCs are good candidates as reinforcing phase in polymer matrices. CNC, obtained by acidic hydrolysis of cellulosic fibers, have been discussed in our previous reports to reinforce electrospun composite mats consisting of poly(caprolactone),[26] polystyrene,[27] and polyvinyl alcohol.[28]

The main goal in this work was to endow PVA and PVA-CNC fiber webs with resistance to water absorption by heterogeneous, acid catalyzed vapor-phase esterification using maleic anhydride (MA) as crosslinking agent. PVA and CNC-reinforced PVA electrospun webs were crosslinked for various reaction times. Chemical changes were monitored by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS), and cross polarization/magic angle spinning carbon solid state nuclear magnetic resonance (CP/MAS ^{13}C NMR). The solubility of the membranes in solvents of different polarities was investigated, while the effect of crosslinking on the thermal transitions of the webs was analyzed by differential scanning calorimetry (DSC). Finally, the mechanical performance of the webs was assessed by dynamic mechanical analyses (DMA) under different conditions of relative humidity.

EXPERIMENTAL

PVA with 2% residual acetyl groups (degree of hydrolysis of 98%) and molecular weight of 125 kDa was purchased from Sigma-Aldrich under trade name Mowiol 20–98. CNC were obtained by acid hydrolysis of pure, extract-free ramie fibers (Stucken Melchers GmbH & Co., Germany) as described elsewhere.[29] Briefly, after removing residual components by extraction (4 wt % aqueous NaOH solution, 80°C and 2 h), the fibers were hydrolyzed with 65 wt % sulfuric acid for 45 min at 55°C under vigorous mechanical stirring. The reaction was stopped by cooling (ice bath) and the resulting dispersion was filtered with a No. 1 glass sinter to remove unhydrolyzed fibers. The dispersion was then washed with deionized water by using successive centrifugation (12,000 rpm, 10°C, 20 min per cycle) until reaching pH neutrality. After dialysis to remove excess free acid (against water, 1 week), the CNC dispersion was sonicated and stored in a refrigerators until use. The concentration of CNC in the final dispersion was determined by gravimetry after drying. MA was purchased from Sigma Aldrich. Hydrochloric acid (HCl) was reagent grade, diluted to 0.1*N* using distilled water. Organic solvents used were acetonitrile, dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, dioxane, dimethyl sulfoxide (DMSO), pyridine, and dimethylacetamide (DMAc); all were analysis grade.

Electrospinning

Aqueous dispersions of PVA and CNC were electrospun as described in our previous work.[28] Briefly, aqueous solutions of PVA were prepared and a given volume of CNC dispersion was added to obtain a final CNC content of 15% (wt/wt) while keeping the total PVA concentrations constant at 7%. Neat PVA aqueous solutions were also prepared and electrospun for comparison purposes. Electrospinning was carried out by using a horizontal setup that included a syringe pump (Aldrich) controlled by a code to pump the dispersion contained in 10-mL disposable plastic syringes thorough a 22-G needle, 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, providing an electric field strength of 0.7 kV/cm.

Vapor-Phase Esterification

Typically, electrospun fiber webs of neat PVA or PVA loaded with 15% of CNC were placed in a container along with a small amount of MA (1–2 g) and a few drops of HCl placed in a separate vial. The container was sealed from the ambient moisture and placed in an oven at 80°C. Esterification was produced via heterogeneous reaction during given times (15–120 min). Immediately after reaction, the sample was cured for 30 min in an oven at 120°C. This same procedure, but in the absence of MA, was applied to samples that were used as reference.

Fiber Morphology

The morphology of the untreated and crosslinked webs as well as the respective web reference (processed in absence of MA) were investigated before and after 24 h immersion in water by imaging under a field emission scanning electron microscope (FE-SEM, JEOL 6400F). For sample preparation a small portion of the fiber webs were fixed on conductive carbon tape and mounted on the solid support and then sputter-coated with about 6 nm layer of gold/palladium (Au/Pd). FE-SEM was operated at an accelerating voltage of 5 kV and working distance of 20 mm.

Physical Integrity of the Electrospun Webs

The effect of the crosslinking treatment on the dissolution or erosion of the electrospun fibers was tested by immersing the fiber webs in water or organic solvents of different polarity. Webs cut into 0.5 inch squares were submerged in the respective solvent under agitation for periods of time, from 2 h to 1 day; the physical integrity of the webs was monitored by visual inspection. The organic solvents used in these tests were methanol, acetonitrile, DMF, THF, chloroform, dioxane, DMSO, pyridine, and DMAc.

Extent of Esterification

ATR-FTIR was used to verify the extent of esterification reaction in the respective electrospun fiber webs. The samples were dried overnight in an oven at 105°C and then analyzed in a FTIR (Nicolet) spectrometer used in ATR mode. All spectra were collected with a 2 cm^{-1} wavenumber resolution after 128 continuous scans. To exclude any effect of nonreacted, free MA and also to check the reversibility of the reaction, the samples were washed extensively and repeatedly using acetone and deionized water before and after collecting the multiple ATR-IR spectra. The FTIR data were normalized with respect to the CO signal, which was expected not to change during esterification reactions. Each sample was measured by triplicate.

Solid-State NMR

Freeze-dried ramie CNC, powder PVA, fiber webs of esterified PVA reinforced with CNC (15%) as well as the respective reference samples were analyzed with natural-abundance cross polarization/magic angle spinning carbon solid state nuclear magnetic resonance (CP/MAS ^{13}C NMR). The experiments were performed at 23°C with a Bruker 500 MHz Ultrashield spectrometer equipped with a solid-state Avance II$^{\mathrm{TM}}$ console. A 3.2 mm Bruker E-Free$^{\mathrm{TM}}$ MAS probe was used in all experiments. The operating frequencies of proton and carbon were 500.2802 and 125.8109 MHz, respectively. Conventional ramp-CP/MAS with a 2 ms contact time was used for ^{13}C solid-state NMR measurements. The sample-containing rotors were spun at 6.7 kHz, and the 90° pulse was 3 μs. ^{13}C Chemical shifts were calibrated by using the carbonyl carbon resonance of crystalline glycine as an external reference at 176.03 ppm. The obtained data were normalized and analyzed quantitatively.

Surface Chemical Composition

The surface chemical composition of the untreated and esterified electrospun PVA fiber webs (neat or loaded with 15% CNCs) was determined by using an AXIS 165 high resolution XPS operated with monochromated irradiation at 100 W. The samples were placed in the spectrometer and evacuated overnight to stabilize vacuum conditions. All samples were measured at three locations on the surface (analysis area of ca. 1 mm^2) and the average values reported. Elemental surface compositions were determined from low-resolution scans recorded with 80 eV analyzer pass energy and 1 eV step. Nominal cellulose contents were determined from carbon high-resolution spectra recorded on the C 1s region using 20 eV analyzer pass energy and 0.1 eV step. In the curve fitting procedure for C 1s, symmetric Gaussian components with Shirley background were used.[30,31] The binding energy scale was shifted using the C—C component of the C 1s, at 285.0 eV. Whatman filter paper (100% of cellulose) was used as an *in-situ* reference and as reference material for cellulose. No sample deterioration due to X-rays and ultra-high vacuum was detected.

Thermal Properties

The extent of reaction and its effect on the thermal behavior of the fiber webs reinforced with CNC was studied by DSC. Thermograms were acquired with a TA Instruments DSC Q100. The typical procedure included heating and cooling cycles (10°C/min rates) of about 10 mg of the sample in the temperature range between −25°C and 230 or 250°C for neat PVA and CNC-loaded PVA webs, respectively. The temperature was cycled twice to remove any effect of thermal history.

Mechanical Properties

Samples before and after crosslinking with MA were cut as 6 mm-wide strips and secured with jaws using 10 mm gap distance. The samples were cut from larger fiber webs collected after a long-enough electrospinning time so that the thickness of the electrospun web was appropriate for accurate DMA and respective sensitivity limits. Strain-stress experiments in tensile mode were performed using a TA Instruments Q800 dynamic mechanical analysis (DMA) equipped with a humidity chamber connected directly to the DMA system. Samples before and after crosslinking during given reaction times were analyzed following the same procedure. The samples were loaded on the DMA humidity chamber, which was stabilized at the chosen relative humidity before starting any measurements. Relative humidity of 50 and 90% were chosen to investigate the effect of crosslinking on the mechanical properties of the webs. Stress sweeps of the samples were performed between 0 and 30 MPa or until failure of the probe. The temperature was kept constant at 30°C in all the experiments.

RESULTS AND DISCUSSION

Effect of Water on the Morphology of Composite PVA Nanofibers

Figure 1 includes SEM images of electrospun fiber webs produced from PVA and CNC-loaded PVA before and after immersion in water. Here, we consider fibers esterified via MA crosslinking (120 min) and reference fiber webs that were subjected to the same (crosslinking) procedure but in the absence of MA. For reference, images of the corresponding dry samples (before immersion) are also included. In this latter case, it can be observed that compared to the neat PVA, the PVA nanofibers containing CNC were of better quality in terms of diameter (and diameter distribution) and uniformity (Figure 1, original fibers in dry condition). This suggests that CNCs endow the PVA solutions with better electrospinnability. This is possibly due to better molecular interactions that lead to increased polymer entanglement and more uniform flow and fiber formation upon solidification and crystallization. The systems that were crosslinked for 120 min maintained their structure even after 24 h water immersion under vigorous agitation. Importantly, it was noted that features such as high surface area and porosity were preserved.[32] We note that coaxial electrospinning can

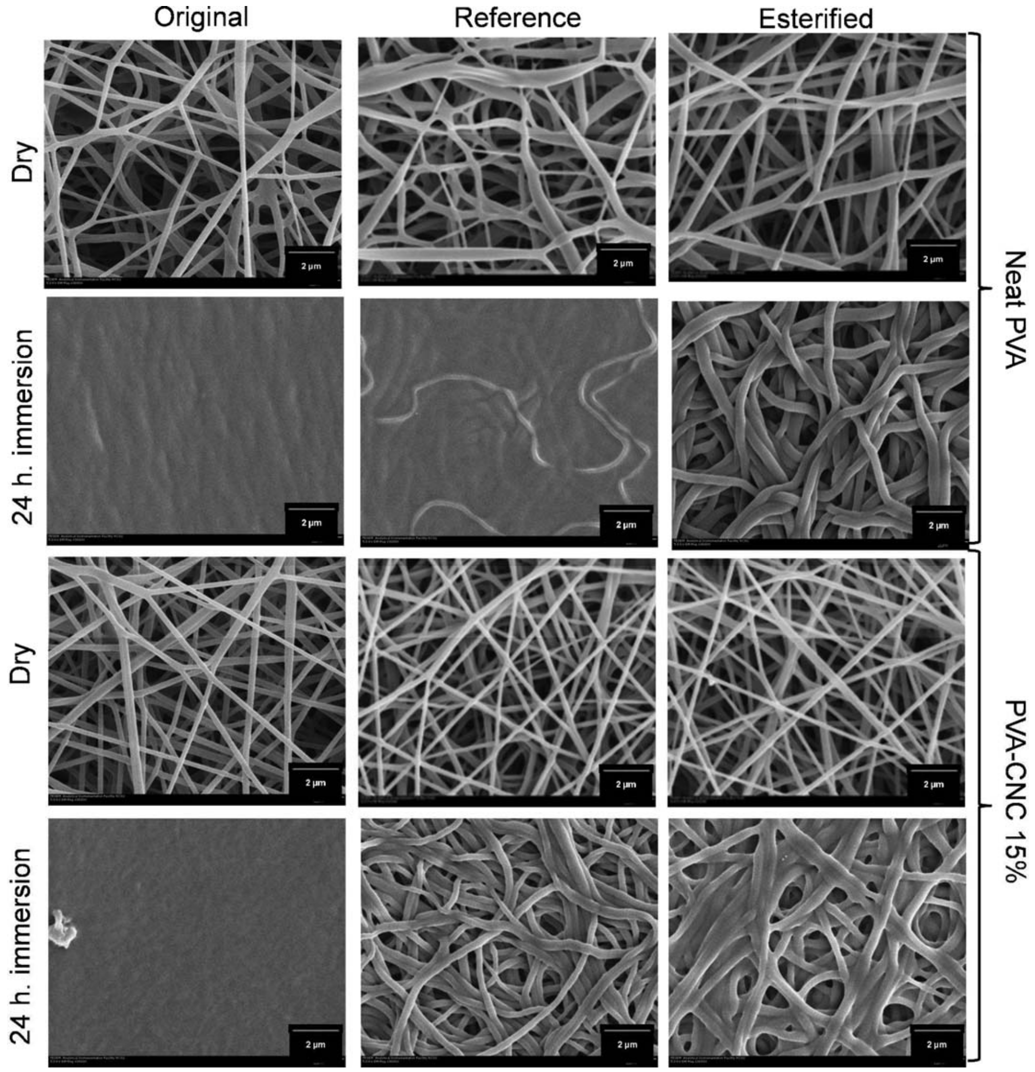

Figure 1. SEM micrographs of electrospun fibers produced from neat PVA and CNC-loaded PVA (15% CNC concentration) before (dry) and after immersion in water (24 h). The webs shown include "original" (left column); treated in the absence of MA (reference, middle column) and crosslinked in the presence of MA (esterified, far right column).

provide alternative protocols for generating similar advanced fiber materials, including the possibility of incorporating binder shells on the PVA nanofibers that can improve their water resistance and mechanical properties.[33,34]

In the case of fibers obtained from neat PVA, neither the "Original" nor the "Reference" samples preserved their structural integrity after immersion in water since a fused, continuous PVA film was observed. This makes evident that the heat treatment applied in the reference sample was not sufficient to stabilize the fiber mat. The crosslinked or esterified fiber webs were resistant to water upon immersion, albeit extensive fiber swelling was observed.

As was the case of untreated PVA fibers, the composite (PVA-CNC) fibers fused after water immersion; however, the fiber samples that were subjected to heat treatment (reference samples) showed distinctive morphological integrity. The crosslinked fibers also kept their initial fiber morphology even though swelling did occur. Besides the effect of crosslinking, the observed improvement in structural integrity in the wet state can be explained by interactions and hydrogen bonding network formed between PVA chains of the matrix and the reinforcing CNCs.[35,36]

Physical Integrity of PVA Fiber Webs in Water and Organic Solvents

The physical integrity of the electrospun fibers was determined by immersion in water under vigorous agitation. As a reference, the test included a web sample that was treated in the absence of crosslinking agent. The samples exposed to MA during the shortest reaction time (15 min) gelified and almost immediate disintegrated in water. PVA webs subjected to crosslinking for more than 15 min presented good physical and mechanical integrity when exposed to water, with the best results observed for the samples crosslinked during 120 min (Figure 2).

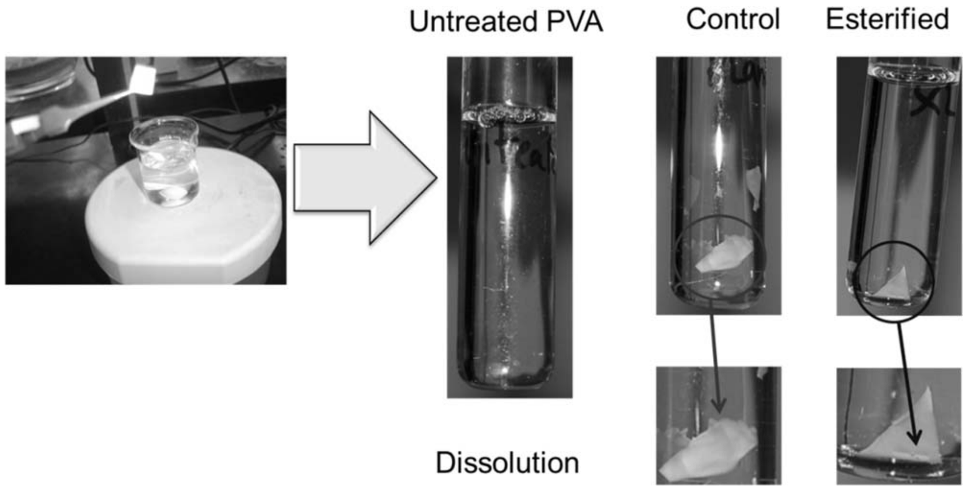

Figure 2. Fiber webs (small square samples, left) were immersed in water. The images show test tubes containing webs immersed in water for 24 h that correspond to the following systems: a neat PVA fiber web ("untreated PVA," which was fully dissolved) (left); a reference web produced after treatment in the absence of MA ("control," center) and fiber a web that was previously crosslinked for 120 min with MA ("esterified", right).

The reference (control) fiber webs (heat treated in the absence of MA) exhibited delamination and some resistance to dissolution. This is ascribed to the effect of heat stabilization. However, this was noted to be temporal; permanent stability was observed only in the case of crosslinked samples. These observations can be explained by the effect of more complete esterification reaction followed by heat curing, which enhances the alignment of PVA polymer chains by removal of water molecules and causes the formation of polyenes.[4] The solubility of the PVA fiber webs that reacted for 120 min with MA was also tested after immersion in organic solvents (Table I). Upon crosslinking, the electrospun PVA webs were not only insoluble in water, but also in low polarity solvents, indicating the successful crosslinking of polymer chains with MA. Similar results were observed for fiber webs loaded with CNCs.

Extent of MA Esterification in Composite PVA Fibers

The esterification after vapor-phase reaction with MA of the electrospun fiber webs was studied via ATR-FTIR. The spectra collected for PVA and CNC-loaded PVA before and after MA crosslinking during different times are shown in Figure 3. Peaks corresponding to the typical O—H and C—H stretching (2910–2942 cm^{-1}) were characteristic in the spectra of neat PVA [Figure 3(a)]. Strong resonance absorption was observed between 3000 and 3600 cm^{-1} due to stretching of intermolecular and intramolecular hydrogen bonds. These signals overlapped with the absorbance of water. Bending of the O—H, C—H, and CH_2 groups was observed in the region of ~1430–1446 cm^{-1}, while the strong band observed at 1096 cm^{-1} corresponded to C—O

Table I. Solubility of PVA Fiber Webs Crosslinked for 120 min

Solvent	Fiber web solubility
DMSO	Slightly soluble
DMAc	Slightly soluble
DMF	Insoluble
Acetonitrile	Insoluble
Pyridine	Slightly soluble
Methanol	Insoluble
Dioxane	Insoluble
Chloroform	Insoluble
THF	Insoluble

Different solvents were used and listed in order of reduced polarity (according to the polarity index in Ref. 37).

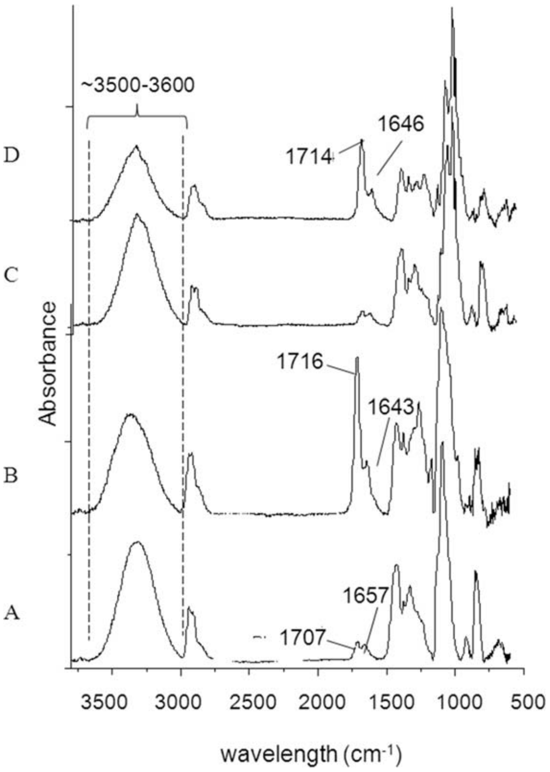

Figure 3. ATR-IR spectra of electrospun fibers webs of neat PVA before (A) and after crosslinking reaction (B). Included are also samples of PVA loaded with CNC that were unreacted (C) or crosslinked (120 min; D).

stretch and also O—H bending. Finally, the skeletal signals appeared as a medium intensity bands in the region from 850 to 916 cm^{-1}. Two peaks of low intensity appeared between 1600 and 1750 cm^{-1} and were assigned to C—O and C═O stretching from the residual acetyl content (2%) present in the PVA matrix.[38,39] In the case of PVA loaded with CNC [Figure 3(c)], the same characteristics peaks corresponding to PVA were observed. Changes in shape and intensity of the main signals were evident, indicative of a hydrogen bond network formed between CNC and the PVA molecules.[28]

When the samples were reacted with MA, the most significant changes in the spectra [Figure 3(b,c)] included the increase in the intensity of the peaks between 1610 and 1710 cm^{-1}. According to the proposed mechanism of reaction between PVA and MA, changes in the characteristic bands of C═O, C═C, C—O—C, and COOH are expected to occur. The shifts observed in this region can be attributed to the conjugation of these signals.[5] A decrease of intensity and change in shape of the spectra was noted in the peak corresponding to O—H (~3000–3600 cm^{-1}), which corresponded to the consumption of OH during the esterification reaction.

The ratio of peak heights corresponding to carbonyl and hydroxyl, before and after washing out excess MA from the sample was used to follow the time-evolution of the reaction. The results for both, neat PVA and PVA loaded with CNC are shown in Figure 4. In this figure, λ_{OH} and $\lambda_{C=O}$ are the absorbance of the hydroxyl groups at ~3315 cm^{-1} and carbonyl groups at ~1716 cm^{-1}, respectively.

The number of carbonyl groups was lowest for samples that underwent short reaction times. In both cases, fiber webs of neat PVA and CNC-reinforced PVA, a progressive increase in the absorbance ratio ($\lambda_{C=O}/\lambda_{OH}$) was observed. This is due to the contribution of the esters formed upon crosslinking. In the case of the reference samples that were subjected to longer treatment times, the relative absorbance intensity $\lambda_{C=O}/\lambda_{OH}$ for neat PVA and CN-loaded PVA increased by 86 and 60%, respectively. The lower relative intensity in the presence of CNC can be attributed to the lower availability of the hydroxyl groups to react with MA due to the hydrogen bonding network formed between the PVA chains and the CNCs. The interactions when the CNCs are present in the PVA polymeric matrix become more complex as these components interact and hydroxyl groups become less available.[35] The reversibility of the crosslinking reaction for PVA noted as the difference in the relative intensity C═O/OH before and after the washing step is about 10%, which can be attributed to residual MA deposited on the fiber webs. The standard error was observed to be higher in the case of CNC-loaded PVA than for the PVA fiber webs.

Chemical and Surface Chemical Composition of Composite PVA Nanofibers

Electrospun fiber webs of CNC-loaded PVA were analyzed by XPS to study the changes in surface chemical composition before and after crosslinking reactions. Electrospun PVA fiber webs and a sample consisting of cotton (pure cellulose) were also analyzed. XPS peaks from carbon C1s (C—C, C—O, C═O, and O—C═O) and oxygen O1s were easily measured in all cases. Table II includes the relative concentrations of O, C, and O/C ratio. The concentrations of carbonyl and carboxylic groups calculated after deconvolution of high resolution C1s are also included.

From the XPS analysis no trace of cellulose was detected in the topmost layer (ca., 10 nm) of the CNC-loaded PVA fiber webs, before or after crosslinking. This was expected because there is no evidence of CNCs located on the surface of the fibers (the CNCs are likely present inside the electrospun fibers). Both PVA and CNC are hydrophilic and interact by means of H-bond networks. Such system is strong enough to overcome the rather high shear forces of the electrospinning process as well as to keep the CNC homogeneously distributed inside the fibers.

Small changes in the relative O and C atomic concentrations were observed as the reaction (crosslinking) time was increased. However, when analyzing the C1s high-resolution spectra

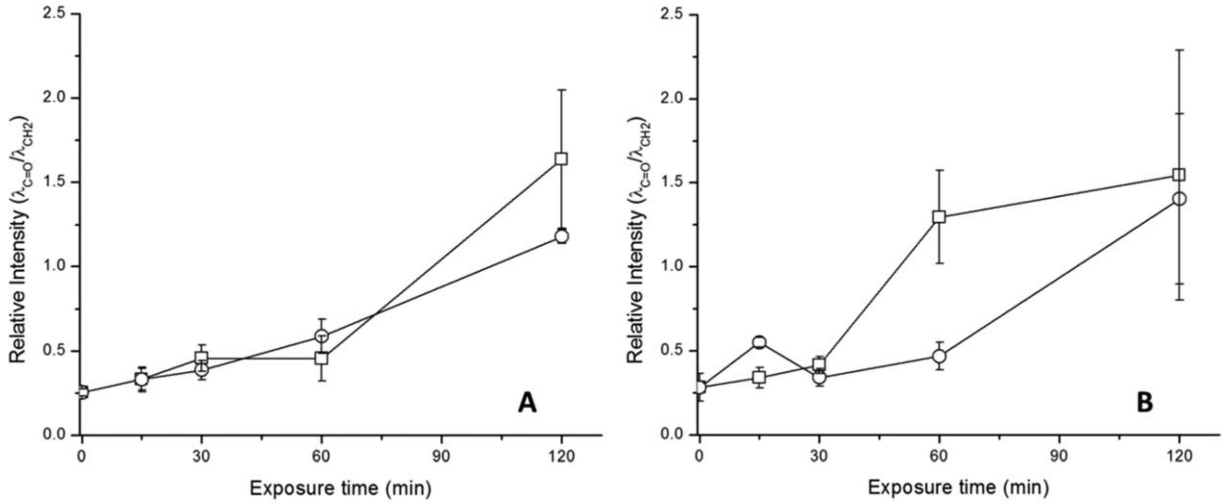

Figure 4. Relative absorbance intensity $\lambda_{C=O}/\lambda_{OH}$ as a function of reaction time for fibers electrospun from PVA solutions without (A) and with 15% CNC loading (B) (before (-□-) and after (-○-) washing).

Table II. Relative Atomic Concentrations (atom %) of Oxygen and Carbon as well as the O/C Ratio of Crosslinked (x-Linked) Fiber Webs of CNC-Loaded PVA and Unmodified PVA

Sample	O1s	C1s	O/C	C—C	C—O	C=O	COO
Cellulose	41.8	58.2	0.72	6.3	74.8	17.9	1.1
PVA fiber web	31.4	68.6	0.46	49.8	46.1	2.7	1.4
PVA/CNC fiber web	30.8	69.2	0.45	50.9	44.8	3.0	1.3
x-Linked PVA/CNC (30 min)	29.1	70.9	0.41	51.9	42.3	2.8	3.0
x-Linked PVA/CNC (60 min)	31.7	68.3	0.46	48.2	44.8	2.5	4.5
x-Linked PVA/CNC (120 min)	29.7	70.3	0.42	49.9	40.6	2.1	7.4

The surface concentration of carbonyl and carboxylic groups relative to the total carbon signal obtained after deconvolution C1s spectra are also included. Cellulose from cotton was used as a reference.

(Figure 5), the relative concentration of carbonyl groups increased significantly, from 1.3% for the untreated fiber web to 7.3% after reaction with MA for 120 min. This observation is in agreement with IR spectroscopy data, which showed an increase in the amount of carbonyl groups produced upon reaction between PVA and MA.

Solid-state ^{13}C CP/MAS NMR analyses were performed for freeze-dried CNC and electrospun fiber webs produced from neat PVA and CNC-loaded PVA (Figure 6). A sample reacted with MA during short times (30 minutes) was also considered to elucidate the likelihood of each of the possible reactions presented in the introduction and discussed further in Figure 7. Additionally, information about the tacticity of the PVA polymer and unequivocal evidence of the presence of CNC in the electrospun samples was obtained from ^{13}C CP/MAS NMR data. The NMR spectra for neat PVA [Figure 6(a)] reveal a sharp peak corresponding to CH_2 and the three characteristic peaks of CH (I, II, and II between 60 and 80 ppm). These spectra correspond to either atactic, syndiotactic or a mixture of both, as studied by Kobayashi et al.[40] In the case of freeze-dried ramie CNC, characteristic peaks were observed for the different carbons present. Starting from the lower resonance region of

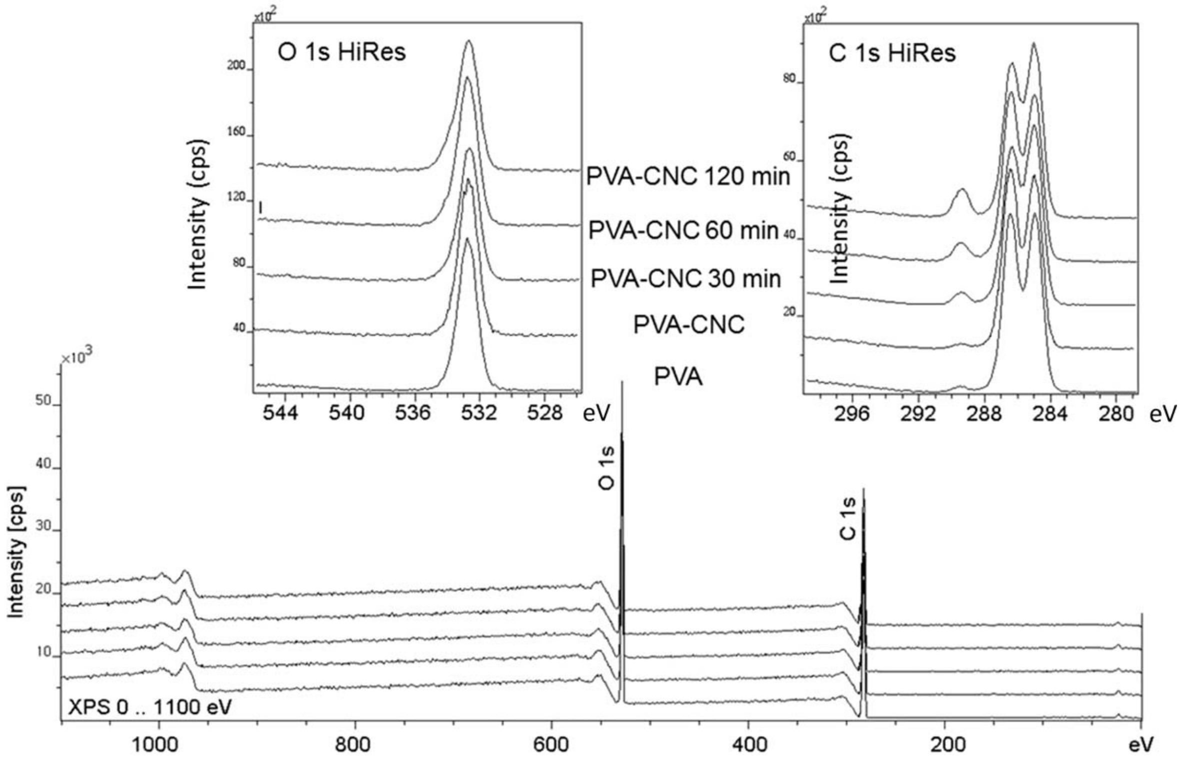

Figure 5. XPS spectra for PVA composite fiber webs. The top panel includes O1s and C1s high resolution XPS spectra of PVA and CNC-loaded PVA electrospun fibers before and after crosslinking during different reaction times, as indicated. The bottom panel includes the corresponding survey spectra (arbitrarily displaced in the intensity axis keeping the same order as shown in the high resolution spectra). Note: spectra for the PVA fibers are displayed in the bottom and those for CNC-loaded PVA fibers after crosslinking for 120 min (PVA-CNC 120 min) are the topmost spectra (samples corresponding to 30 and 60 min esterification are in between).

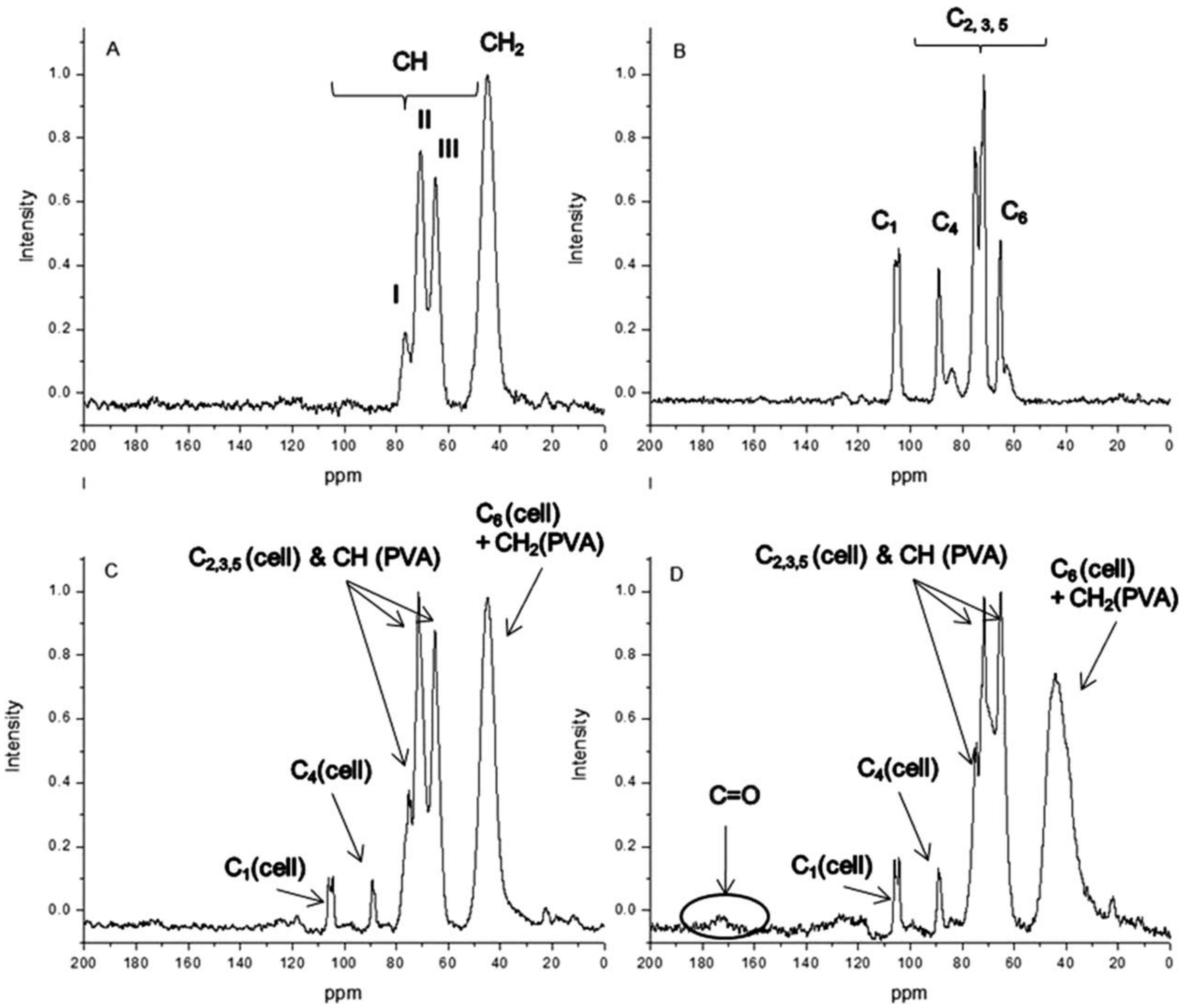

Figure 6. CP/MAS ^{13}C NMR spectra for electrospun PVA fibers (A), CNC (B), CNC-loaded PVA fibers (untreated, no MA reaction; C), and crosslinked CNC-loaded PVA fibers (30 min reaction time with MA; D).

the spectra, C_6 resonance peak appeared as a single sharp peak in the region of 65 ppm, followed by a triad of signals corresponding to C_2, C_3, and C_5 between 70 and 80 ppm. The signal at 90 ppm was assigned to C_4 and finally C_1 appeared around 107 ppm as a sharp peak.[41]

The peaks detected for PVA fibers and CNCs were also present in the spectra corresponding to CNC-loaded PVA fiber webs [Figure 6(c)]. A small, distinctive signal around 175 ppm appeared in the CNC-loaded PVA fiber webs after the reaction with MA. Such signal is attributed to the formation of ester bonds between the polymeric matrix and the MA.

The possible esterification reactions that occurred in the present system are indicated in Figure 7, as was also succinctly mentioned in the Introduction. It is expected that chemical changes took place via dehydration between the anhydride group present in the MA and the PVA hydroxyl groups, thus crosslinking was achieved through acid catalyzed esterification and bond formation upon thermal activated reaction.[13]

Thermal Transitions of Esterified PVA Composite Nanofibers

The thermal transitions of the fiber webs after different reaction times was studied via DSC in order to elucidate further the nature of crosslinking of PVA-based fiber composites with MA. Crosslinked polymers typically show an increase in their glass transition temperature due to the restriction in polymer chain mobility as a consequence of bond formation.[42] In addition, the samples obtained after crosslinking reactions, fiber webs heat-treated in the absence of MA were run as reference. In general, the thermal transitions observed in the first thermal cycle were rather difficult to interpret due to the thermal history of the samples. In fact, the thermal behavior of the electrospun fibers is affected by the orientation of the polymer chains during the spinning process, which is likely lost after the first heating cycle. In passing, we indicate the possibility of further reaction after the first DSC heating scan, if allowed to rest for some period of time after the DSC scan.

Changes in the behavior of the samples were only observed after crosslinking during 15 min, as noted by a slight decrease in the glass transition temperature (T_g), from 87 to 77°C [Figure

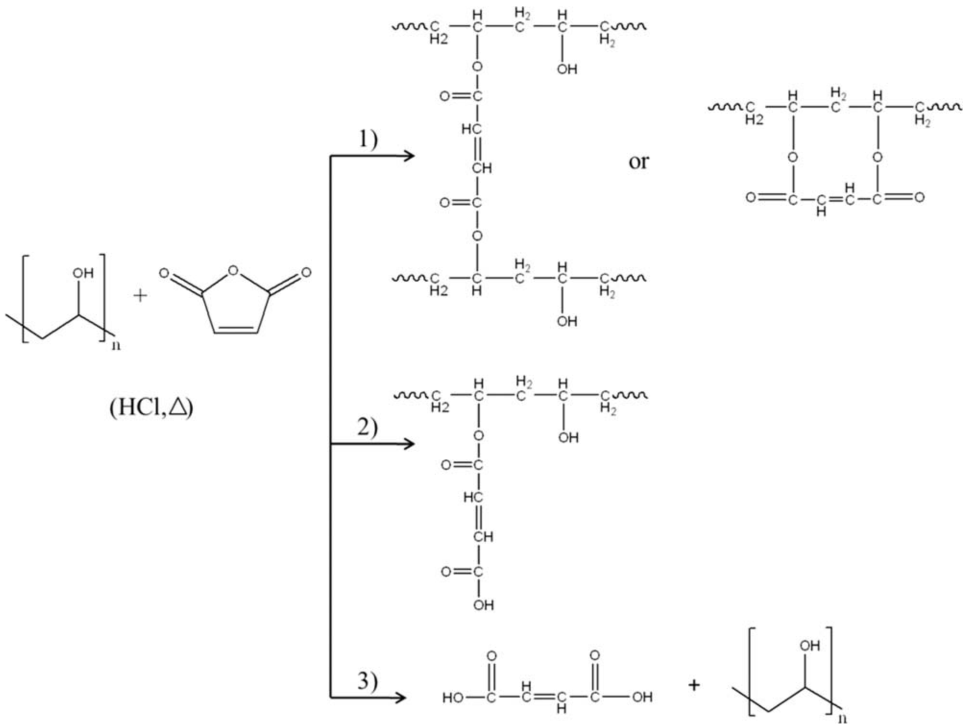

Figure 7. Possible reactions upon treatment of PVA with MA: formation of two ester bonds either with hydroxyl groups present in the same molecule (intramolecular) or with hydroxyls belonging to neighboring molecules (1),[4] single esterification of one end of the open anhydride reacting with one hydroxyl group and the other end becomes protonating and remaining in the acid form (2) and, dissociation of MA without reacting, remaining in the dicarboxylic acid form (3).[5]

8(a)]. Additionally, both transitions corresponding to melting and crystallization were reversible and appeared clearly in two consecutive thermal cycles (data not shown). Fiber webs exposed to heat for longer periods of time (in absence of MA crosslinking agent), presented very similar melting (T_m), and cold crystallization (T_{cc}) temperatures. As mentioned earlier, heat treatment contributes to the stabilization of the system by elimination of water molecules, producing physical crosslinking of the polymer chains.

After removal of the thermal history (second heating cycle), and upon reaction times long enough to produce significant changes in the polymer (from 30 to 120 min), neither melting nor crystallization transitions were observed in the thermograms (data not shown). Only second-order transitions were observed, which indicate glass transitions due to the molecular reorganization, in this case due to chemical modification. Similar behavior was reported as evidence for crosslinking reaction on PVA fiber aggregates using glyoxal as crosslinking agent.[8]

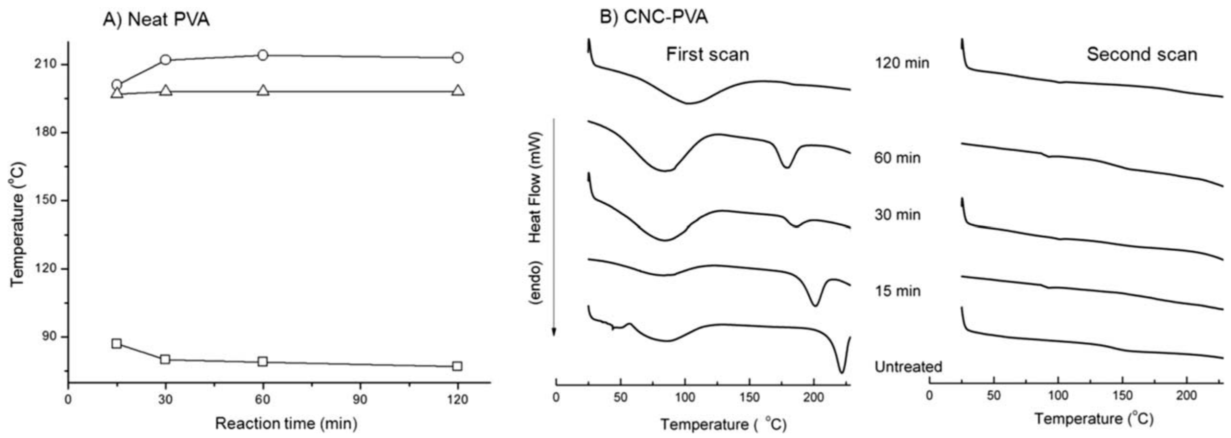

Figure 8. DSC transition temperatures [T_g (-□-), T_{cc} (-Δ-), and T_m (-○-)] recorded in the first heating cycle of fiber webs electrospun from neat PVA followed by MA reaction during different times (A). The effect of reaction time during crosslinking with MA and the irreversibility of the thermal transitions are shown for composite CNC-PVA fibers, at different reaction times (first and second scans, as indicated; B).

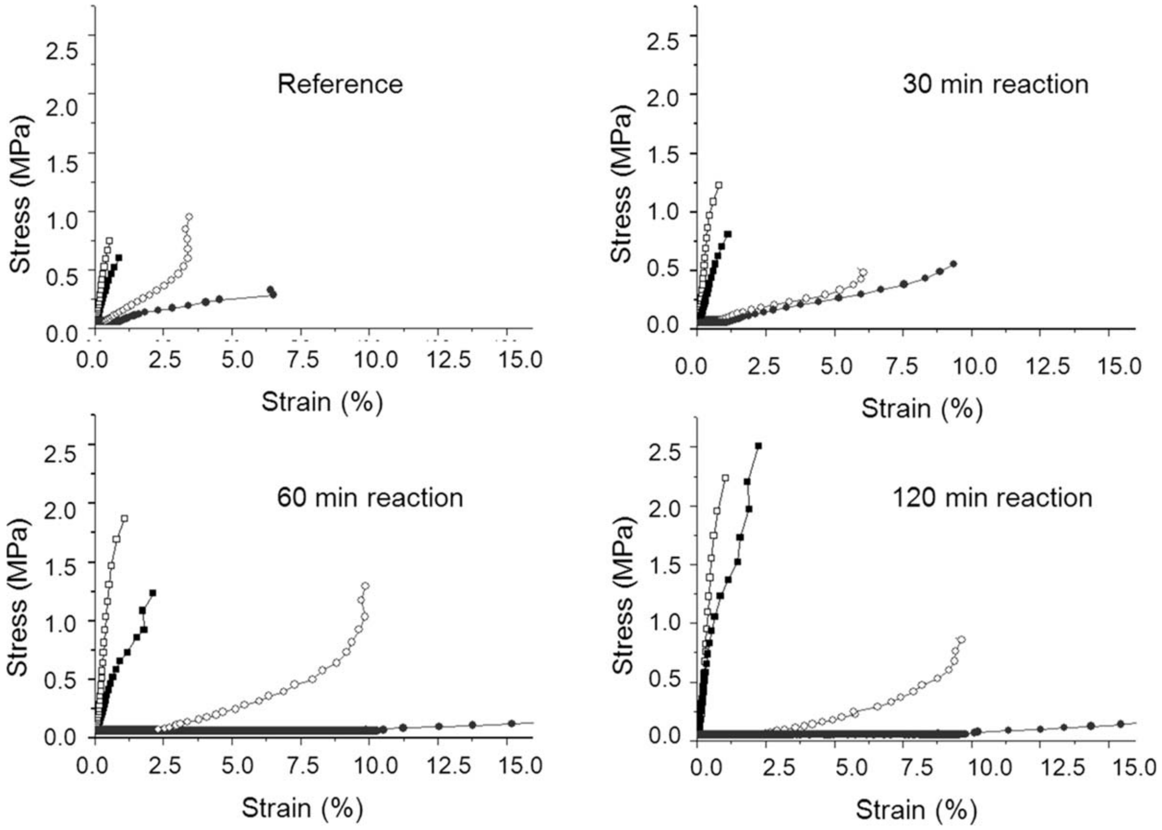

Figure 9. Stress-strain curves for fiber webs produced from neat PVA (filled symbols) and CNC-loaded PVA (15% CNC loading, open symbols); 50 and 90 %RH conditions were used in the tests: upper (squares) and bottom (circles) profiles in each frame, respectively. The reference sample was treated in the absence of MA. Results corresponding to samples that were subject to crosslinking with MA during 30, 60, and 120 min are included, as indicated.

The thermal behavior of PVA fibers loaded with CNCs was distinctively different. Figure 8(b) shows the thermograms corresponding to two consecutive temperature scans for the electrospun fiber webs of PVA loaded with CNC, untreated and modified with MA during different reaction times. As reported previously, CNC-loaded PVA shows a glass transition (T_g) that varies from 40 to 80°C, depending on the storage conditions and the thermal history of the sample.[28] For samples treated with MA, the T_g peak possibly associated with the vaporization of water present in the sample became a broader endotherm with a temperature onset around 64°C, in all the cases. An irreversible transition was observed for electrospun PVA loaded with CNC, which can be attributed to the melting of the PVA matrix at 221°C, which correlates to those reported in our previous work.[28] However, this nonisothermal transition shifted to lower temperatures with the increasing reaction time, until complete fusion with the lower transition for the sample treated during 120 min. This behavior has been reported by several authors in systems involving PVA as result of the disruption of the crystal structure due to chemical crosslinking of the polymer chains.[43] Additionally, the thermogram corresponding to the second heating scan [Figure 8(b), right] showed smooth transitions that can be ascribed to the glass transition. The transitions observed were irreversible and in presence of CNC cold crystallization of the PVA matrix did not occur. This indicates that an enhanced nucleation in the PVA crystallinity accompanied by a new transcrystalline phase occurred when CNCs were present in the matrix. The changes in interphases and crystallinity of semicrystalline polymers induced by reinforcing agents in composites and related mechanisms have been widely discussed,[44] including the case of PP reinforced with CNC.[45]

Mechanical Properties of Esterified PVA Composite Nanofibers

We demonstrated the reinforcing effect that CNC loading has on electrospun fibers, resulting in electrospun fiber webs with improved mechanical performance.[26,28] Moreover, we studied the plasticizing effect of water molecules in such composites, and the counter effect produced by the presence of CNC by testing the mechanical properties of these materials at different relative humidity.[35] As evidenced by the results discussed so far and judging by the higher structural stability of the crosslinked fiber webs, it is expected that this effect can be improved further in the case of CNC-loaded electrospun PVA fibers. Tensile tests were performed at two different relative humidity values (50 and 90% RH). Figure 9 includes the stress/strain curves corresponding to fiber webs obtained from electrospinning of neat PVA (top) and the corresponding CNC-loaded systems (bottom) after crosslinking with MA during different times. A reference sample obtained after treatment (120 min) in the absence of MA is also included.

The crosslinking reaction time for the unmodified PVA fiber web tested at 50% RH produced a clear increase in the ultimate strain (or strain at break). The crosslinked material was much less brittle than the unmodified one and there was an improved response as the time of reaction (crosslinking) was increased. Similar effects were observed for the same set of samples when tested at high relative humidity (90% RH); in this case, the material showed a significantly lower tensile strength, in agreement with our previous findings.[36] Following the same trend as what was found at lower RH, the ultimate strain increased with the crosslinking time; the crosslinked PVA fiber web became considerably elastic, to the point of not breaking at the maximum strain used (note the low tensile strength after 30 min reaction time). It can be speculated that in the case of crosslinked material, the softening effect of water was augmented due to limited interaction by hydrogen-bonding with the crosslinked PVA molecules. Note that this effort only considered MA but polycarboxylic acids such as citric acid, butanetetracarboxylic acid, and others may open further opportunities for increased esterification profiles.

As expected, the presence of CNC in the composite fiber webs improved the tensile strength and ultimate strain, particularly at high RH. As an example, the ultimate strength of fiber webs after CNC loading and crosslinking measured at 90 and 50% RH increased up to about 82 and 34%, respectively. Remarkably, the improvement with CNC-loading was observed at longer crosslinking times. When compared with the performance of neat PVA fiber webs measured at 90% RH, CNC-loaded webs were still elastic but maintained their (high) tensile modulus.

CONCLUSIONS

Acid-catalyzed heterogeneous crosslinking with MA of PVA and CNC-loaded PVA electrospun fibers were found to be insoluble in water and nonpolar solvents (120 min reaction time). FTIR, XPS, and solid-state NMR indicated that esters bonds were created in the fiber webs. The thermal transitions of the PVA-based fiber webs, with and without CNC loading, changed significantly upon crosslinking, confirming the reactions not only on the surface but in the bulk of the fibers. The crosslinking was effective in improving the physical integrity of the PVA-based electrospun fibers. The ultimate strength of fiber webs after CNC loading and crosslinking measured at 90 and 50% RH increased up to about 82 and 34%, respectively. Overall, these results show promise in the applications of such systems in sensors, selective permeable membranes and other materials that require physical, thermal, and mechanical integrity under humid conditions.

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