Thermal and Structural Characterization of Nanofibers of Poly(Vinyl Alcohol) Produced by Electrospinning

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ABSTRACT: Poly(vinyl alcohol) (PVOH) was obtained from the alkaline hydrolysis of poly(vinyl acetate) (PVAc). Nonwoven membranes (mats) of PVOH nanofibers were produced by electrospinning of solutions of PVOH in water with and without aluminum chloride. The concentration of the PVOH/water solution was 12.4% w/v. The morphology of the mats was analyzed by scanning electron microscopy (SEM). The thermal properties and the degree of crystallinity of the nanofibers were measured by differential scanning calorimetry (DSC); the crystal structure of the mats was evaluated by wide-angle X-ray diffraction. The best nanofibers were obtained by electrospinning the PVOH/water solution with aluminum chloride (45% w/v) in which an electrical field of 3.0 kV/cm was applied. It was observed that the addition of the aluminum chloride and the increase in the applied electrical field decreased the number-average nanofibers diameters. The mats without aluminum chloride had higher melting temperatures and higher degrees of crystallinity than the mats with the salt. The crystal structure of the mats was found to be monoclinic; however, the mats were neither highly oriented nor have a high degree of crystallinity. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1680–1687, 2009

Key words: electrospinning; poly(vinyl alcohol); nanofibers; characterization

INTRODUCTION

Poly(vinyl alcohol) (PVOH) is a water-soluble polymer, industrially obtained by the alkaline hydrolysis of solutions of PVAc. It is used as fibers, fibers mats, membranes, films, adhesives, paper coating, and polymerization stabilizers.[1] Also, because of its biocompatibility and biodegradability, it is used in hydrogels, contact lens, body artificial components, and drug release systems.[2,3]

The industrially synthesized PVOH can have different mol % of hydroxyls groups, which is termed the degree of hydrolysis (DH) and can also have different degrees of polymerization (P_n). A PVOH with DH between 87 and 89 mol % has lower mechanical and water resistance than a PVOH with DH between 98 and 99.9 mol %. Also, the higher the DH, the higher is the amount of crystallinity. The crystalline unit cells predominant in the PVOH are orthorhombic, monoclinic, and hexagonal.[4]

These polymers have excellent chemical resistance, tension strength, and abrasion resistance. The PVOH fibers with diameters between 5 and 500 μm are spun by conventional processes like melt spinning, wet spinning, and dry spinning.[5] However, for specific applications like particle filters, membranes, nanocomposites, protective clothes, human skin coatings, and drug release systems, it is necessary that the fibers have nanodimensions. Thus, usually these fibers are produced as nanofibers mats using an electrospinning process.[6]

The electrospinning process using a polymeric solution is done by the application of an electrical tension between the solution and a ground collector. The solution is contained in a capillary tube. An electrode connected to a high-voltage supply is inserted into the polymeric solution. At the beginning of the spinning, the solution is maintained inside the capillary tube by action of its surface tension; with the increase of the applied electrical voltage, the surface of the solution drop at the exit of the capillary tube changes from hemispherical to conical, forming a cone, known as Taylor's cone. When the electrostatic forces outnumber the surface tension, an electrified solution jet is ejected from the capillary tube exit. During its trajectory from the capillary exit to the ground collector, the electrified jet loses solvent by evaporation, and the polymer solidifies. The solid polymer forms a nonwoven membrane (mats) made of polymeric nanofibers, which deposit on the ground collector metallic surface.

The nanofibers diameter is influenced by the electrospinning process variables such as solution concentration, solution surface tension, solution electrical conductivity, applied electrical voltage, capillary flow rate, distance between the capillary exit, the ground collector (working distance), etc.[6]

The electrospinning technique has been used with various polymer solutions, like poly(L-lactic acid) (PLLA) in solvents as dichloromethane, methanol, and pyridine,[7] poly(D,L-lactic acid) (PDLA) in dimethylformamide (DMF),[8] a mixture of DMF/tetrahydrofuran (THF),[9] and a mixture of chloroform (CHCl$_3$)/DMF,[10] poly(urethane-urea) in DMF,[11] poly(trimethylterephthalate) in trifluoracetic acid and methylene chloride,[12] poly(ethylene oxide) in water,[13–15] nylon 6,[16] and nylon 6.6,[17] both in formic acid, poly(ε-caprolactone) in acetone,[18] and in a mixture of CHCl$_3$/methanol.[19] PVOH has also been electrospun with various solvents.[20–29] Lee et al.[20] studied electrospun PVOH/water solutions with different P_n (1700 and 7000) changing the solution concentration, working distance, and applied voltage. They concluded that the higher the molecular weight, the better is the electrospinning. Zhang et al.[21] also electrospun PVOH in water with 0.2% w/v of sodium chloride; the increase of the solution's electrical conductivity decreased the fiber diameter. Son et al.[22] studied electrospun PVOH with NaOH and PVOH with HCl; they observed that the alteration of the solution's pH did not affect the viscosity and surface tension. In any case, the fiber diameter was lower than that of the PVOH/water solution. Other authors, Zeng et al.,[23] studied electrospun nanofibers of PVOH with bovine serum albumin and water for drugs release. Kenaway et al.[24] studied electrospun solutions of poly(ethylene-co-vinyl alcohol) in 2-propanol and water, which were used to cultivate muscles and fibroblasts cells. For electronic applications, Sui et al.[25] studied electrospun PVOH/zinc oxide composites for the use as white-light emitting diodes and white light displays. Besides these composites, PVOH/water solutions were electrospun with glioxal, a cure agent, by Ding et al.[26] The increase in the amount of glioxal decreased the mats' crystallinity and increased the mats' water resistance.

In this work, the influence of the solution concentration, addition of aluminum chloride, and the applied electrical field on the morphology and properties of electrospun PVOH nanofibers was evaluated. The properties of the solutions such as electrical conductivity, pH, and viscosity were characterized by different techniques. The nanofibers mats morphology was evaluated by scanning electronic microscopy (SEM). The thermal behavior and the degree of crystallinity of nanofibers were evaluated by differential scanning calorimetry (DSC).

The crystal structure of the mats was studied by wide-angle X-ray diffraction (WAXD).

EXPERIMENTAL

Materials

Vinyl acetate was supplied by Hexion Specialty Chemicals (Brazil), and then washed with 2% of NaOH solution, distilled under pressure, and stored at −4°C before use. Methyl alcohol, NaOH (99.9%, Merk), and aluminum chloride (Merk) were used as received. The polymerization initiator, 2,2'-azo-bis-iso-butironitrile (AIBN) was from DuPont (purity of 99.5%). In all the solutions and purifications, deionized water with electrical conductivity of 1.12 μS/cm was used.

Poly(vinyl acetate) polymerization

The polymerization of the vinyl acetate was carried out in a 2-L jacketed glass reactor, equipped with a mechanical stirring, reflux condenser, and nitrogen purging tube. PVAc was obtained by batch polymerization in a solution of methanol using AIBN as initiator at 63°C, during 4 h. The amount of reagents used for the polymerization was 683.0 g of vinyl acetate, 808.0 g of methanol, and 9.0 g of AIBN. Stirring was maintained at 200 rpm.

Poly(vinyl alcohol) synthesis

PVOH was obtained from the partial hydrolysis of the PVAc, by using a 1% solution of NaOH in methanol, with stirring for 1 h at room temperature. The concentration of the NaOH solution used in this work was similar to the one used by Moritani et al.[30,31] The obtained gel was heated at 40°C in a mixture of methanol, methyl acetate, and deionized water in the proportion of 90/1/9 v/v/v, respectively. The PVAc global conversion was determined by the ratio between the amount of solids after the end of the polymerization and the theoretical amount of solids. After the synthesis, the PVOH was washed twice with cold water, grounded and dried in an oven with air circulation at 40°C during 24 h and it was denominated as **OHP** (isotropic PVOH).

Degree of hydrolysis

The DH of the PVOH was determined measuring its degree of saponification by automatic titration using an automatic burette from Metrohm (Sweden), model 665, and by manual titration using phenolphthalein (1% w/v) as indicator. To 25 g of an aqueous OHP solution (12.4% w/v), 30 mL of a 0.1 mol/L NaOH aqueous solution was added; the whole solution was heated at 85°C for 1 h. After this, 30 mL

TABLE I
Electrospinning Conditions

PVOH samples	Applied electrical field (kV/cm)	Room temperature (°C)	D (nm)[a] (%)	ΔD (nm) = D_{max}[b] − D_{min}[b]	Number-average fibers diameter (nm)	Room relative humidity (%)
OH1	1.5	28 ± 3	500 (52)	750	445.83	53
OH2	1.8	27 ± 3	300 (54)	750	426.95	54
OH3	2.0	26 ± 3	300 (51)	750	366.35	55
OH4	1.0	26 ± 3	500 (83)	550	539.29	53
OH5	3.0	24 ± 3	–	–	–	60
OHS1	1.5	22 ± 3	300 (58)	750	434.03	65
OHS2	1.8	29 ± 3	300 (54)	950	417.24	54
OHS3	2.0	24 ± 3	300 (68)	550	339.56	63
OHS4	1.0	24 ± 3	300 (50)	750	421.30	58
OHS5	3.0	24 ± 3	100 (47)	550	240.65	60

[a] D (nm), average fiber diameter at the highest frequency distribution.
[b] D_{max}, maximum diameter; D_{min}, minimum diameter.

of a 0.1 mol/L HCl aqueous solution was added; the titration was done with a 0.1 mol/L NaOH aqueous solution.[22,32,33] This whole procedure was done to remove the influence of the residual acidity (acetic acid) on the DH of the PVOH.

Preparation of the electrospinning solutions

The OHP was dissolved in hot water (12.4% w/v) at 85°C with stirring for 2 h. The resulting solution was named **OH**. After complete dissolution, the OH solution was cooled at 25°C. To part of the OH solution, an aqueous solution of 1% v/v of solution of aluminum chloride (45% w/v) was added. The resulting solution was denominated **OHS**.

Solutions characterization

The pH of the OH and OHS solutions was measured with a digital pH meter from Orion, model 310. The electrical conductivity was measured with a conductivimeter from Micronal (Brazil), model B330, with a Pt electrode.

The viscosity of the solutions was determined using a digital viscometer from Brookfield, model DV-E, whereas the shear rate viscosity was measured in an ARES rheometer from Rheometrics Scientific with a concentric cylinders geometry (2 mm gap). Both measurements were done at 25°C.

Solutions electrospinning

The electrospinning of the solutions was made at room temperature and humidity with a system composed of a high voltage supply (Bertan, model 30R), a grounded cylindrical collector covered with aluminum foil, and a glass syringe. The collector rotated at 25 rpm. The glass syringe had 20 mL of volume; the syringe needle was Hamilton type with 1.5 mm diameter and 30 mm length. Inside the syringe, a Cu electrode was immersed. The applied electrical tensions were 15, 18, and 20 kV during 30 min. The

working distances were 5, 10, and 15 cm. Table I shows the OH and OHS electrospinning conditions used in this work.

Nanofibers characterization

The morphology of the nanofibers was analyzed by SEM. The nanofibers mats were deposited on a double-face carbon adhesive and glued to the sample holder; silver paint was then added at the mats' borders. The sample was then gold-sputtered and analyzed using a SEM from Philips, model XL30 FEG, at 15 kV. The number-average nanofibers diameter and its distribution were calculated using the Image Pro-Plus software. The calculation of the number-average diameter was done by measuring 100–120 fibers diameters.

To study the crystal structure of the nanofibers, wide-angle X-rays diffraction measurements were done. The nanofibers mats were analyzed in a diffractometer from Siemens model D5005, operating with Cu Kα radiation, Ni filter, at 40 kV, and 40 mA. The diffractograms were deconvoluted using Origin 7.0 software and a Gaussian approximation.

The thermal transition temperatures and the degree of crystallinity were obtained by DSC in a Perkin Elmer DSC 7. Approximately 8 mg of the samples were heated between 30 and 250°C at 10°C/min; after 3 min at 250°C, the sample was cooled at the same rate. The degree of crystallinity was calculated as the ratio between the melting enthalpy of the sample and the melting enthalpy of a theoretical 100% crystalline sample (ΔHf_m^0). For the PVOH, $\Delta Hf_m^0 = 159$ J/g.[34]

RESULTS AND DISCUSSION

Solutions characterization

The PVAc global conversion was found to be 84.1%, with 38.3% of solids. The DH of the PVOH was 94 mol %. The OH and OHS solutions have electrical
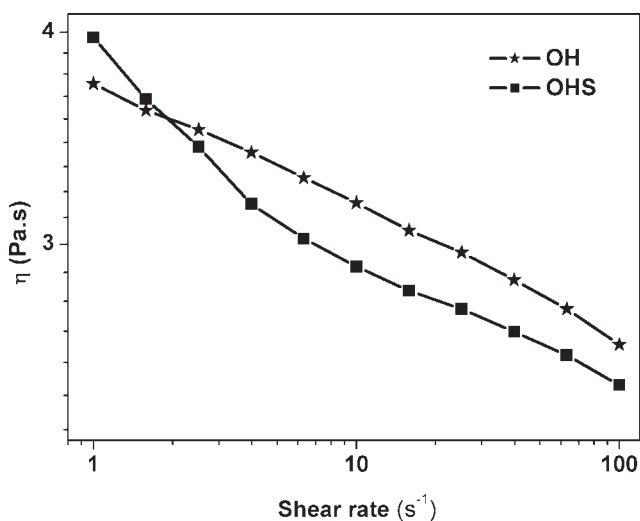
Figure 1 Shear rate viscosity of the OH and OHS solutions at 25°C.

conductivity of 0.77 and 3.29 mS/cm, pH of 5.47 and 3.75, and viscosity of 4000 and 3000 cPs, respectively. Figure 1 shows the shear rate viscosity at 25°C.

It can be observed that the OHS solutions are more acidic and had lower viscosity but a much higher electrical conductivity than the OH solutions.

Regarding their shear viscosities, it is observed that even when the shear rate was increased, the viscosity of the OHS solution was lower than that of the OH solution, both being highly pseudoplastic; that is, the salt plasticized the OH solution. No formation of gel was observed.

Solutions electrospinning

Influence of the aluminum chloride on the nanofibers diameters

The effect of the addition of the aluminum chloride to the PVOH solution can be visualized by comparing the micrographs of the electrospun nanofibers OH1 to OHS1, OH2 to OHS2, OH3 to OHS3, and OH4 to OHS4, as shown in Figure 2. The processing conditions used to obtain the OH5 mats were not adequate to obtain nanofibers, because the solution solidified in the needle; consequently, no nanofibers of the OH5 solutions were obtained. However, solution OHS5 was electrospun successfully. Figure 2 also shows a micrograph of sample OHS5.

The nanofibers' diameters distributions are also shown in these figures. It can be observed that the nanofibers without salt have higher average fiber diameters (D) than the nanofibers with salt, as shown in Table I. That is, the addition of the aluminum chloride decreased the nanofibers' average diameters, as expected, because of the increase in the electrical conductivity of the solution. This

increase in electrical conductivity promoted higher ions mobility in the solution. This higher mobility associated to the applied electrical voltage increased the elongational forces, which resulted in thinner jets and lower fibers diameters.[9,35] This behavior was also observed by other authors.[9,16,21]

Regarding the average nanofibers diameter it can be observed that conditions OHS5 produced the smallest nanofibers of all electrospinning conditions.

Influence of the applied electrical field on the nanofibers diameters

It can be observed that, in the case of both kind of solutions (OH and OHS), the increase in the applied electrical field decreased the average nanofibers diameter, as expected.

Analyzing the morphology and diameters distribution of the nanofibers to find the best electrospinning conditions, which would produce (i) nanofibers with the smallest diameter, (ii) nanofibers with the narrowest diameters distribution, and (iii) nanofibers without defects (drops and junctions), it can be observed that

- Condition OHS5 produced nanofibers with the smallest diameter;
- Conditions OH4, OHS3, and OHS5 produced nanofibers with the narrowest diameters distribution; and
- Conditions OH3, OHS3, OH4, OHS4, and OHS5 produced nanofibers without junctions and drops.

Therefore, it can be concluded that best electrospinning conditions were the OHS5 conditions, which produced the smallest fibers diameter, with the narrowest diameters distribution and without defects.

Thermal transitions of the nanofibers by DSC

Figures 3 and 4 show the DSC thermograms and heating and cooling runs, respectively, of the OHP sample and of all the electrospun nanofibers. Table II shows the water vaporization temperature ($T_{eb,water}$), the PVOH melting point (T_m), the PVOH crystallization temperature (T_c), the PVOH melting enthalpy (ΔH_m^0), the PVOH crystallization enthalpy (ΔH_c^0), and the degree of crystallinity of the nanofibers obtained by DSC for all PVOH samples. Because of the superposition between the water evaporation peak and the glass transition temperature (T_g), this last one was not determined in the majority of the mats. However, it is known that the T_g of PVOH is around 85°C.[36]
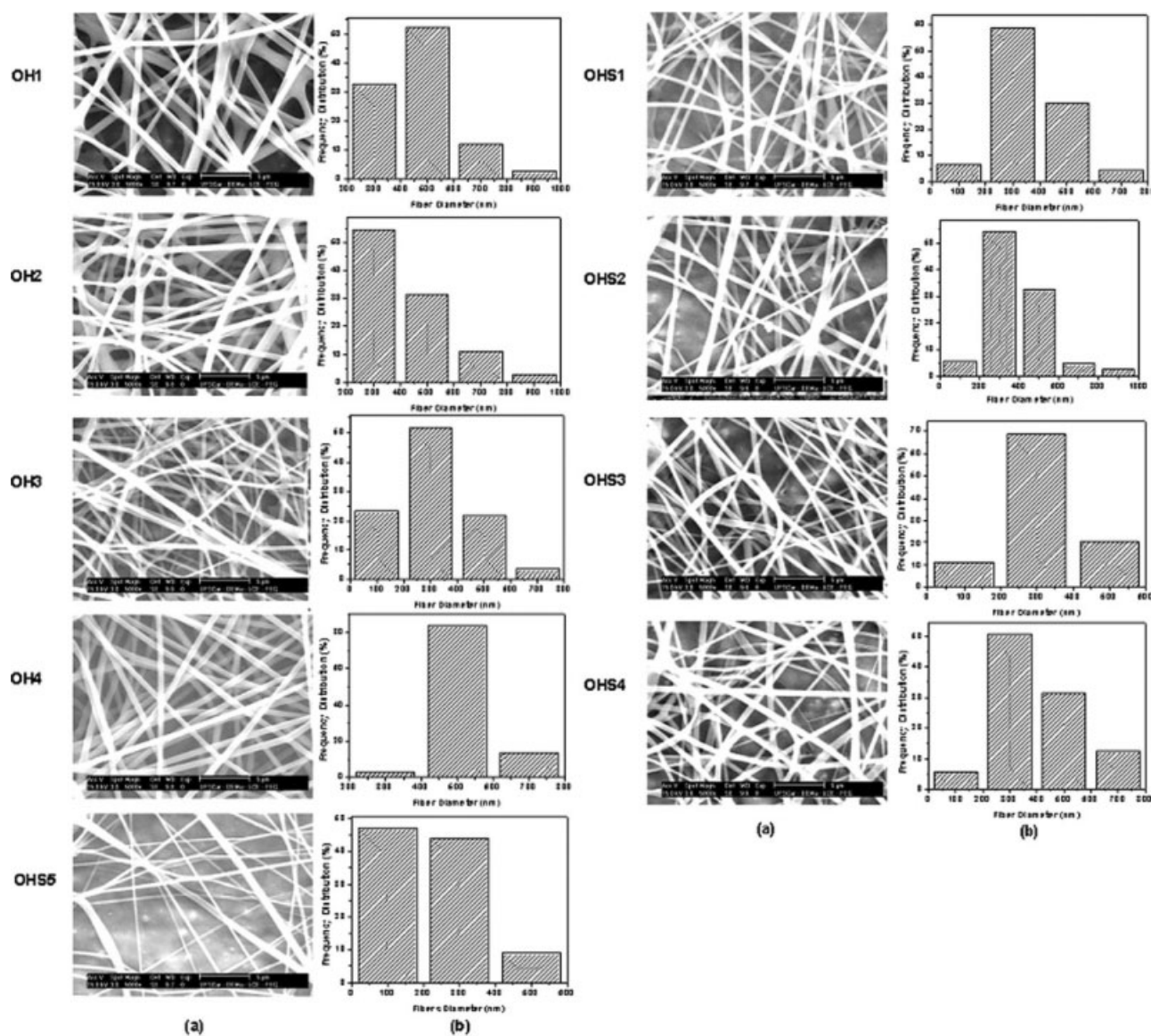
Figure 2   (a) SEM micrograph and (b) diameter distributions of the nanaofibers of the OH1–OH4 and OHS1–OHS5 mats.
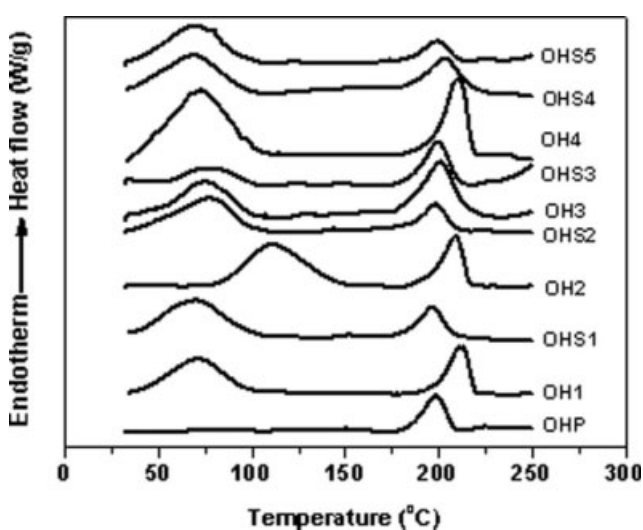

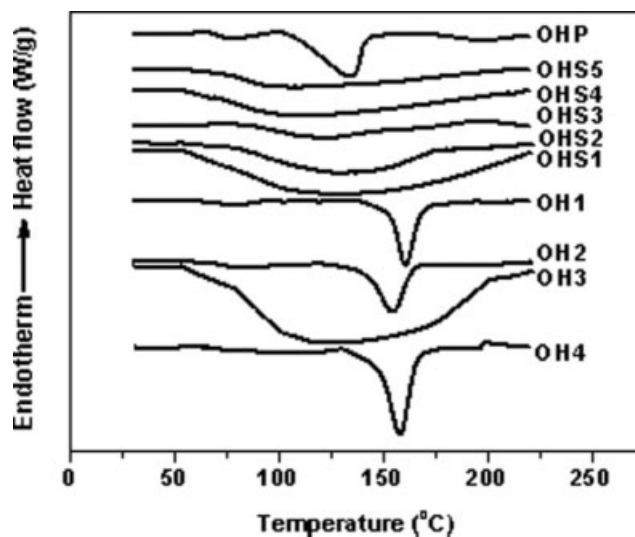**Figure 3**   DSC thermograms of the heating run of the iso-tropic OHP sample and of all PVOH mats.

Figure 4   DSC thermograms of the cooling run of the iso-tropic OHP sample and of all PVOH mats.

TABLE II
Thermal Transitions and Degree of Crystallinity of the PVOH Nanofibers

PVOH Sample	$T_{eb,water}$ (°C)	T_m (°C)	ΔH_m^o (J/g)	T_c (°C)	ΔH_c^o (J/g)	Degree of crystallinity by DSC (%)
OHP	–	199	42.48	134	−14.60	26.7
OH1	71.5	211	52.00	161	−15.65	32.7
OH2	111.8	209	45.88	155	−26.43	28.9
OH3	74.8	201	39.47	125	−8.44	24.8
OH4	73.5	210	58.62	158	−24.06	36.9
OHS1	69.9	197	27.02	128	−15.64	17.0
OHS2	77.9	199	23.02	130	−18.21	14.5
OHS3	78.4	200	24.64	124	−4.26	15.5
OHS4	69.3	203	42.48	112	−13.11	26.7
OHS5	69.6	200	28.70	106	−5.40	18.1

The thermograms of the heating run of the nanofibers mats exhibited one endotherm before the melting peak, attributed to water evaporation. Sui et al.[25] also correlated this endotherm to water loss of the processed mats from PVOH/water solutions. They observed that in the gel form (hydrogels), this endotherm also appeared and it was broader than the melting endotherm. In Figure 3, it can be observed that in all the mats, this endotherm is also broader than the melting endotherm.

The percentage of vaporized water (X_{H_2O}) was calculated from eq. (1):[37]

$$X_{H_2O} = \frac{m}{m_T} \times 100 \qquad (1)$$

where m is the vaporized water mass (kg); m_T is the DSC sample mass (kg). The vaporized water mass was calculated from the DSC enthalpy of vaporization (ΔH_v), $\Delta H_v = m (c\Delta T + L)$, where ΔT is the end vaporization temperature – initial vaporization temperature $= T_{end} - T_{initial}$; c is the specific heat capacity of the water, 4190 J/kg K; $L =$ latent heat of vaporization of water $= 2.26 \times 10^6$ J/kg; Table III shows the ΔT, ΔH_v, and X_{H_2O} calculated values of all the PVOH mats.

It can be observed that the X_{H_2O} values varied from 0.90 to 4.30%; that is, all the mats contained residual water.

The electrospinning was done at room temperature, below the T_g of the PVOH; therefore, no crystallization would be expected. However, the PVOH was dissolved in water, which could have decreased the T_g of the PVOH; also the formation of strong intermolecular hydrogen bonds in the PVOH allowed an easy alignment of the macromolecules by the elongational flow during electrospinning. All these factors could have contributed for the crystallization of the PVOH mats.

During the DSC heating run, no cold crystallization was observed. Therefore, the melting endotherm was attributed to the melting of the crystals formed during the electrospinning.

It can be observed that the mats without salt had higher melting temperatures and higher degrees of crystallinity than the mats with salt. This result indicates that the electrospun nanofibers obtained from the solutions without salt had more perfect crystallites (higher melting point) and in a higher amount than the mats with salt. It seems, thus, that in the solution without salt, the PVOH macromolecules had more freedom and fewer entanglements, being more easily extended, which allowed the forming of more perfect crystals. After melting, the crystallization of the PVOH without salt occurred earlier than the isotropic PVOH, sample OHP. This acceleration of the crystallization can be a consequence of improper melting. On the other hand, the addition of salt seemed to hinder the crystallization of the PVOH macromolecules. Also PVOH cure could have occurred. It is known that glioxal,[26,38] aluminum chloride, aluminum sulfate,[38] and lithium chloride[39] are cure agents for PVOH and also that a plasma or a heating treatment can cure this polymer.

Crystalline structure of the nanofibers by WAXS

In this work, the degree of crystallinity of all samples was determined by DSC and not by WAXS measurements. The DSC values were more accurate, because the presence of orientation in the calculation

TABLE III
Amount of Vaporized Water in the PVOH Mats

PVOH mat	$\Delta T = T_{end} - T_{initial}$ (K)	ΔH_v (J/g)	X_{H_2O} (%)
OH1	57.30	65.17	2.70
OH2	66.60	91.94	3.60
OH3	43.08	72.53	3.00
OH4	46.01	109.69	4.30
OHS1	60.80	69.86	2.80
OHS2	65.40	74.47	2.90
OHS3	50.50	72.40	0.90
OHS4	55.50	61.09	2.40
OHS5	56.30	82.38	3.30

of the % of crystallinity by WAXS interfered on those results.

Figure 5 shows the X-ray diffractogram of the isotropic PVOH (OHP sample). The diffractogram was indexed using the monoclinic unit cell of PVOH, with $\alpha = \lambda = 90°$ and $\gamma = 91.7°$ and lattice parameters $a = 7.81$ Å, $b = 2.52$ Å, and $c = 5.11$ Å.[36] The positions of the diffraction peaks with $2\theta = 11.6°$, $19.4°$, $22.5°$, $32.1°$, and $40.5°$ are characteristics of a monoclinic crystal structure.

Figure 6(a) shows the WAXS diffractograms obtained for the PVOH mats; it is observed that the mats' diffractograms have diffraction patterns similar to the OHP sample, indicating also a monoclinic structure. The peaks intensity, however, is smaller than that of the OHP sample.

It is known that, in general, the crystallographic planes that contribute to the crystallinity of a material can be the same that the ones that contributed to the crystalline molecular orientation. Thus, the diffraction peaks that are accounted for crystallinity can be the same that the ones that are accounted for crystalline orientation. Because the nanofibers were extremely small and very difficult to handle, it was not possible to measure the crystalline molecular orientation.

However, if a mat is reduced to an isotropic powder by grinding in liquid nitrogen, the crystalline molecular orientation can be drastically reduced[40] and the remainder diffraction peaks can be correlated only to crystallinity.

Thus, to separate the diffraction peaks accounted for crystallinity from the diffraction peaks that are accounted for orientation, the mats were grinded in liquid nitrogen and their WAXS diffractrograms were measured. The diffractogram of the mats as
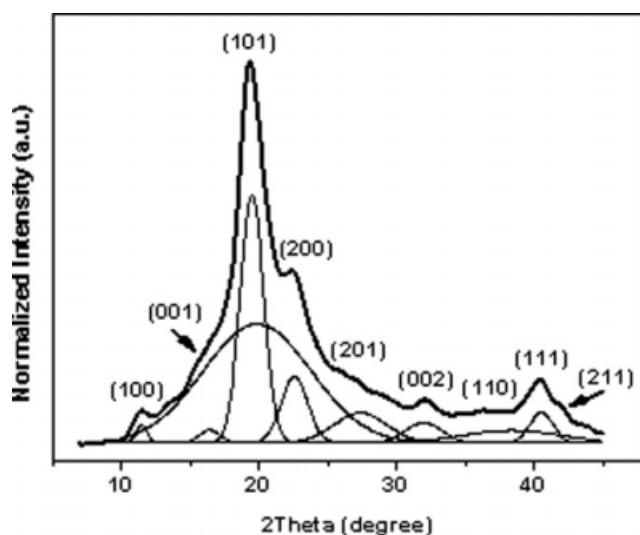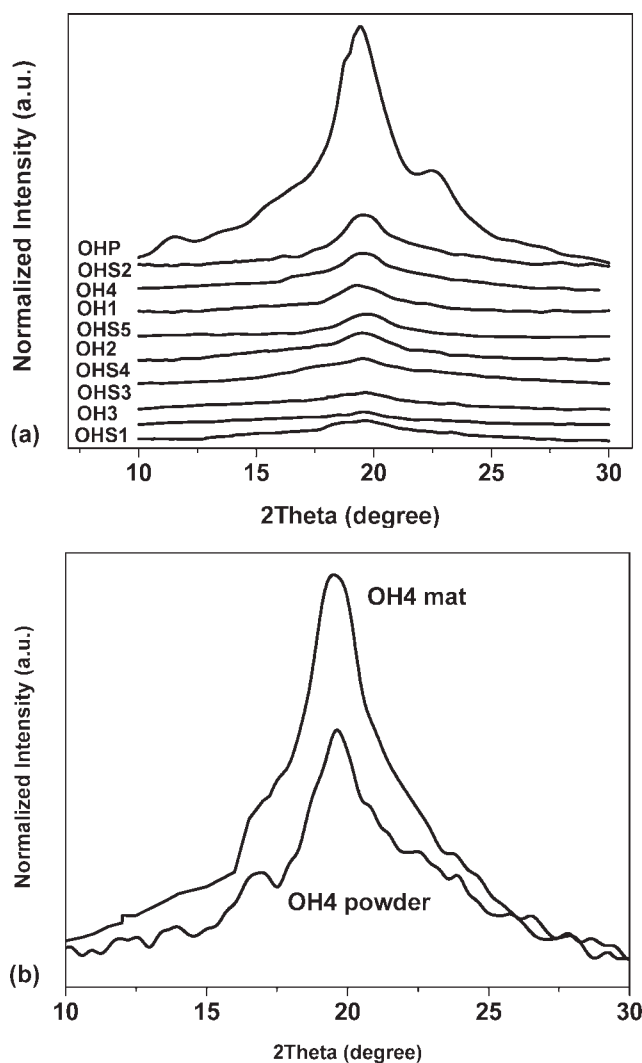

(a)

(b)

Figure 6 X-ray diffractograms (a) of the OHP sample and of all PVOH mats and (b) of the OH4 sample, as a mat and as a powder.

powder was obtained using a rotator sample holder rotating at 60 rpm. Figure 6(b) shows the diffratrogram of the OH4 mat compared with the OH4 powder. A reduction in intensity of the diffraction peaks in the OH4 powder can be observed, showing that the mats' diffraction peaks embody crystallinity and orientation.

Thus, no % of crystallinity could be calculated from the diffractograms. Because the peaks intensities of the mats were very small when compared with the OHP sample, it was concluded that the mats were neither highly oriented nor have a high degree of crystallinity.

CONCLUSIONS

Nanofibers of PVOH were produced by electrospinning of a 12.4% w/v PVOH/water solution with and without aluminum chloride. The best nanofibers

Figure 5 Indexed and deconvoluted X-ray diffractogram of the OHP sample (isotropic PVOH).

(the smallest average diameter, the narrowest diameters distribution and without defects) were obtained by electrospinning a PVOH/water solution with aluminum chloride (45% w/v) in which an electrical field of 3.0 kV/cm, at room temperature, with 60% humidity was applied.

It was observed that the addition of the aluminum chloride and the increase in the applied electrical field decreased the nanofibers' average diameters.

All the mats contained residual water; the mats without aluminum chloride had higher melting temperatures and higher degrees of crystallinity than the mats with the salt. The crystal structure of the mats was monoclinic; however, the mats were neither highly oriented nor have a high degree of crystallinity.

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