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Preparation and Characterization of PVA Hidrogels Nanofibers

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Summary: Poly(vinyl alcohol) (PVA) is a biomaterial that has interesting features for applications in soft tissue replacement due to its similarities in the mechanical properties of such tissues. This paper describes the preparation and characterization of PVA fibers obtained by electrospinning and crosslinked with potassium persulfate as thermoinitiator. These PVA fibers were characterized by Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) to analyze the morphology of the spun samples. Finally, Fourier Transform Infrared Spectroscopy (FTIR) and differential scanning calorimetry (DSC) were performed and the results showed that the biomaterial was partially cross-linked, which indicates a potential use for dermal regeneration applications. The morphology of the fibers indicated that structural changes occurred in the biomaterial after thermal crosslinking.

Keywords: characterization; electrospinning; hydrogel; Poly(vinyl alcohol) (PVA); scaffolds

Introduction

Hydrogels are a class of hydrophilic polymers that is able to retain large amounts of water without dissolving its structure. Hydrogels have great potential in biomedical application due to their elastic and hydrated nature, which minimizes irritation in surrounding tissues.[1] Also, hydrogels can be cross-linked in order to form different structures with distinct physical, mechanical and chemical properties. Hydrogel polymer chains can be cross-linked either chemically or physically through covalent bonds or intermolecular forces, respectively. It should be stressed that the chemical cross-linking is an irreversible process, after which no changes in the chemical structure of the polymer chain can be made.

Poly(vinyl alcohol) (PVA) hydrogels are used in biomedical and pharmaceutical industries due to their biocompatibility, ability to swell and retain large amounts of water or biological fluid, similarity to natural tissue, low surface tension, high permeability to small molecules, low toxicity and possibility of manufacturing in various geometries. [2]

In this work, PVA fibers were obtained by electrospinning aiming the production of effective curatives for the healing of wounds and burns, which can be used to promote a physical barrier capable of preventing wound contamination by exogenous microorganisms; thus facilitating healing and minimizing the production of scars. [3,4]

In the electrospinning process, electrostatic forces cause the deposition of a viscous polymer from a positively charged electrode, which is spinned to an electrode of opposite charge. Electrospinning is a simple and efficient process for producing polymeric fibers with nanoscale diameters. This process consists in the application of high voltages in a polymeric solution that flows out of a capillary, which can be a

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syringe needle. When submitted to a strong electric field, a continuous polymer solution jet is ejected from the tip of the syringe needle, where during the jet flow the solvent evaporates, and the fibers are collected in a metal plate. For a successful electrospinning, several process and solution parameters must be adjusted.[5,6] The main process parameters are: solution flow rate, distance from the collector target, applied voltage and internal diameter of the needle. Among the solution parameters, concentration and type of solvent has strong influence on solution physical properties such as surface tension, electrical conductivity, viscosity and other rheological properties of the fluid,[5–7] which determines the formation of nanofibers. Polymeric nanofibers have great potential for applications ranging from biomedicine (tissue reconstruction, cell culture) to electronics (sensors).[7]

In the literature, there are few studies on cross-linked electrospun PVA fibers.[8,9] By producing cross-linked PVA with glutaraldehyde from electrospun fibers aiming applications in dermal regeneration and healing, it was found that the cross-linking process has promoted higher stability in the biomaterial degradation, and was also observed that the biomaterial remained stable for ten days in phosphate buffer solution (PBS), which is a time interval comparable to the wound healing rate. In another research, Yang et al.[9] performed PVA cross-linking with maleic anhydride and observed the efficiency of the cross-linking process by the fact the PVA spun membranes were not soluble when immersed in boiling water. In turn, Tang[10] observed that there was a change in the PVA morphology due to the cross-linking process.

In the present work PVA hydrogels were obtained from electrospun fibers with crosslinking with potassium persulfate. The resulting PVA system was characterized by scanning electron microscopy (SEM), scanning differential calorimetry (DSC) and Fourier Transform Infra-Red Spectroscopy (FTIR).

Experimental Part

Five aqueous solutions of 10% PVA (molar mass of 89,000–98,000) trademark Sigma-Aldrich were prepared using different concentrations of potassium persulfate (KPS) as shown in Table 1.

Subsequently, 10 mL of ethyl alcohol 98% was added under stirring to 10 mL of aqueous PVA solution. An electrospinning apparatus were used, which consisted of an infusion pump (KD-100, KD Scientific), a high voltage supply (0–30 kV - Testtech), a copper plate of 90×70 mm and a syringe connected to a capillary needle for the material output. The electrospinning process was performed using a voltage of 15 kV, flow rate of 0.85 mL/h, and distance between the capillary output to the collector of 12 cm. After formation of nanofibers, the samples were thermal cross-linked in pre-heated oven at 100 °C for 20 minutes on inert atmosphere (N_2).

To characterize the morphology of the spun samples, SEM images were obtained using a JEOL (JXA 840A) coupled to EDS Noram System Six, and a Leo 440i coupled to EDS Oxford model 7060. Additionally, an optical microscope (OM) with polarized light - model GX 51 (Olympus) was also used.

Analysis in the FT-IR was also performed to check the bands regarding the C–O–C, indicating the chemical cross-linking of PVA.[9] The spectrophotometer used was Thermo Science Nicolet, model IR 100 and resolution 4 cm^{-1}. The meshes were immobilized on device, and performed analysis directly in the equipment. The behavior of the spectra was obtained by measuring the transmittance.

The thermal properties of the material were analyzed by differential scanning

Table 1.
PVA aqueous solutions, different concentrations of KPS.

Sample	1	2	3	4	5
KPS concentration (w/w)	1%	2%	3%	4%	5%

calorimetry (DSC). The experiments were conducted in inert atmosphere with conditioning at room temperature, and then heated to 270 °C, followed by two-minute isotherm. Then, the material was cooled from 270 °C to 0 °C, followed by two-minute isotherm. After these steps, a second heating from 0° to 300 °C was performed, with heating and cooling rate of 10 °C/min., with air tight sample of approximately 7 mg. The equipment used for the analysis was a differential scanning calorimeter model DSC 2920 TA Instruments.

Results and Discussion

Figure 1 shows the morphology of PVA fibers, which were formed with different KPS concentrations (w/w) before the cross-linking process. The morphology analyses were performed using SEM.

It is possible to observe through the Figure 1(a), (b) and (d) the different morphologies, showing large amount of beads connected by fiber segments. Since the electrospinning conditions were the same for all samples, this result shows that

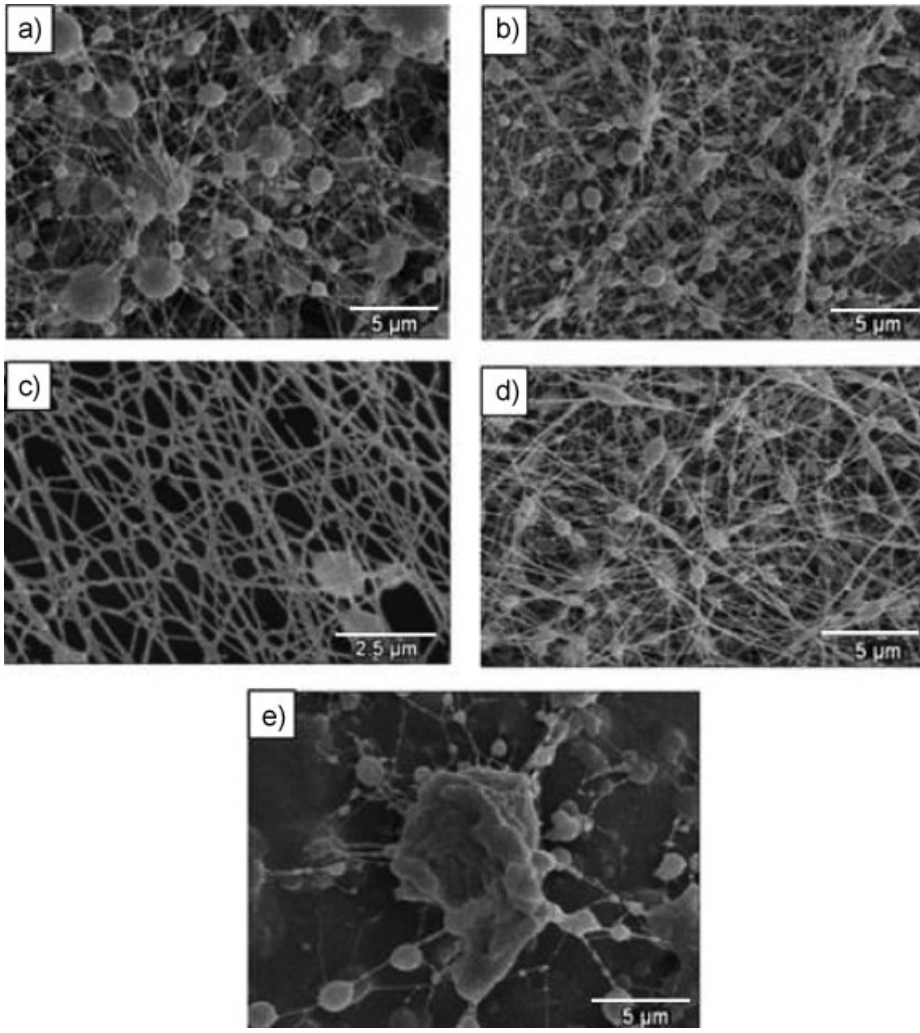

Figure 1.
SEM images (x 5000): (a) Sample with 1% KPS (w/w), (b) Sample with 2% KPS (w/w), (c) Sample with 3% KPS (w/w), (d) Sample with 4% KPS (w/w), (e) Sample with 5% KPS (w/w).

the the amount of KPS affected the solution properties such as viscosity, surface tension and electrical conductivity leading to different morphologies. Further studies are necessary in order to elucidate the effect of the solution properties in the formation of the fibers.

It can be seen in Figure 1(c) fibers without the presence of bead clusters, indicating that this concentration and parameters produced the meshes with better morphology.

Figure 2 shows SEM images of sample 3 (Table 1, Figure 1c), indicating the morphology of PVA fiber and diameters of nanofibers formed by electrospinning, before the thermal cross-linking process. It can be seen that the fibers have a preferential alignment and the fiber diameters are approximately between 90 nm and 184 nm.

Figure 3 shows SEM images of the electrospun PVA fibers after thermal cross-linking process of sample 3. The thermal cross-linking process has lead to an increase in the fiber diameter, where the values were between 189 nm and 7.8 μm. Also, it can be observes the occurrence of clusters among the fibers, which caused the loss of nanopores and increased the biomaterial density.

Figure 4 shows images obtained through OM of PVA spun nanofibers after the thermal cross-linking process. Figure 4(a) shows the orientation of nanofibers and Figure 4(b) shows the surface appearance formed by the meshes.

Figure 5 shows the FT-IR spectrum of PVA spun fiber after the cross-linking process. It is possible to observe the formation of the band of C–O–C group at 1190 cm^{-1} and the band of C=O group at 1649 cm^{-1} and C–O at 1093 cm^{-1}, which indicates the chemical cross-linking of the material.[9]

Figure 6 shows the DSC curve of the PVA spun fiber after thermal cross-linking

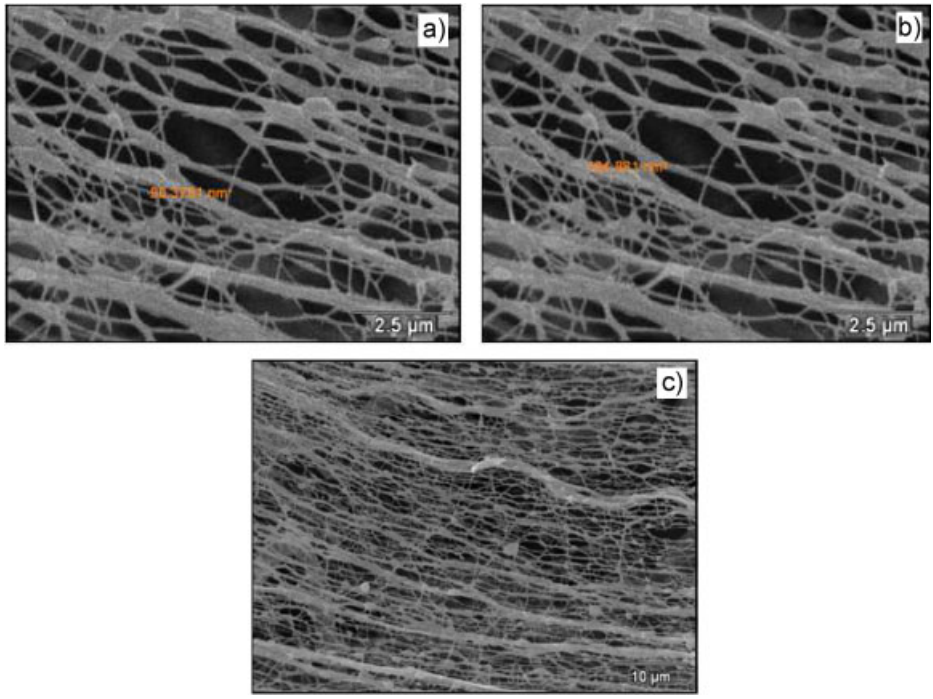

Figure 2.
SEM images of PVA fiber spun before thermal cross-linking process: (a) and (b) with magnification of 5000x; and (c) with magnification of 1000x.

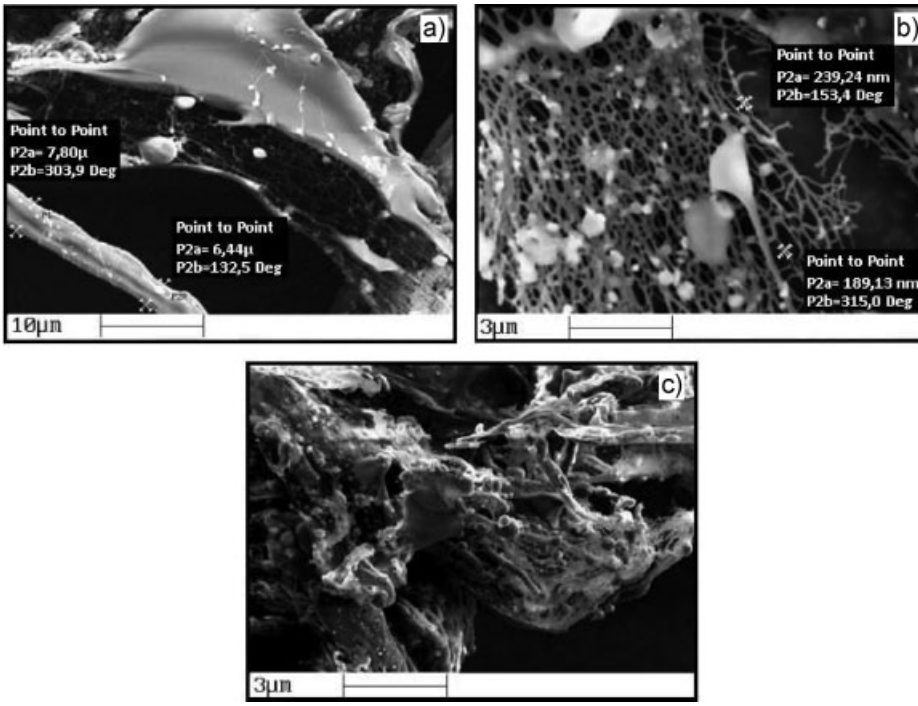

Figure 3.
SEM images of spun PVA fiber after thermal cross-linking process: Sample (a) and (b) show increase in the fiber diameter, sample (c) increased the biomaterial density. The magnification of the SEM images are: a) 3000x, b) 11350x and c) 898x.

process. It can be observed that two endothermic events and one exothermic event occurred in the first heating, which indicates that the biomaterial was partially cross-linked. However, in the second heating it can be observed the total cross-linking due to the absence of endothermic reaction peak. The presence of hydrophilic domains may provide greater ability to absorb liquids exuded by the wound.

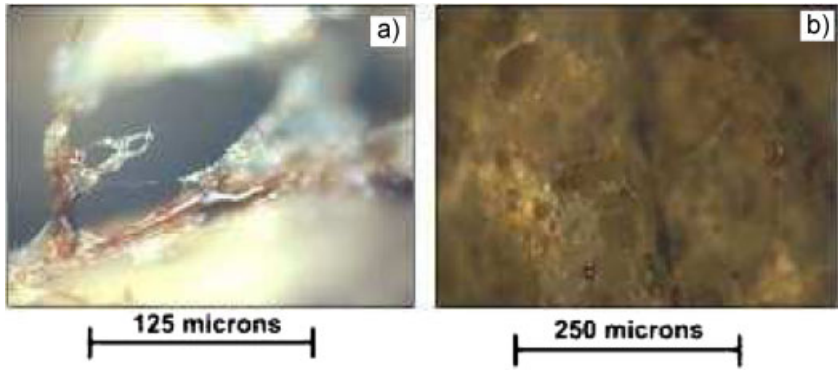

Figure 4.
OM images of PVA spun fiber after thermal cross-linking process with magnification scale (1000x): (a) orientation of fibers can be visulized and (b) shows the surface appearance of meshes.

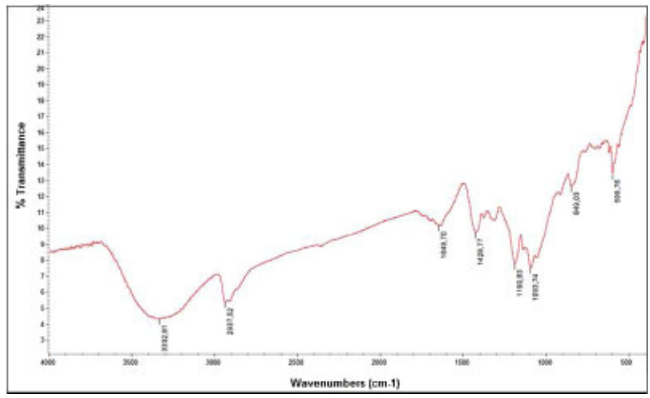

Figure 5.
FT-IR spectrum of the PVA spun fiber sample after thermal cross-linking process.

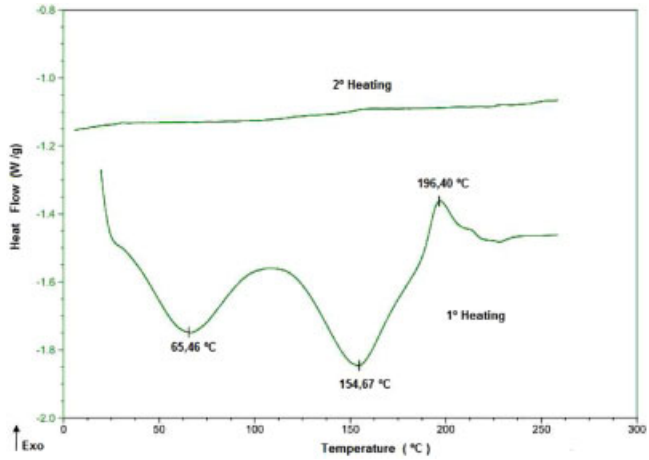

Figure 6.
DSC curves of PVA spun fiber after thermal cross-linking process.

Conclusion

Fibrous meshes of PVA were obtained by electrospinning from solution of PVA in aqueous solution, where the mesh from 3% w/w aqueous solution of KPS presented the best morphology, since it was mainly composed of fibers. After thermal cross-linking the sample morphology presented changes, which was evaluated through SEM. It was found that thermal cross-linking process had an influence in the fiber diameter, where the fibers presented an increase in their diameter and the presence of clusters was also observed. Cross-linking was verified through FT-IR spectrum, whereas the DSC thermogram showed that the material was partially cross-linked. Total cross-linking process was completed during the second heating cycle of the DSC experiment.

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[1] A. Kishida, Y. Ikada, *Hydrogels for biomedical and pharmaceutical applications*, Marcel Dekker, Japan **2002**.
[2] P. Bártolo, *Stereolithography materials, processes and aplications*, Springer New York Dordrechet Heidelberg, London **2011**.
[3] X. Liu, et al. *J. Bio. Mat.Res.* **2010**, *94A*, 499.
[4] Y. O. Kang, *J. Biomed. Mater. Res.* Part B, **2009**, 568.
[5] J. F. Cooly, U.S. Patent 692,691 (**1902**).
[6] W. J. Morton, U.S. Patent 705,631 (**1902**).
[7] Q. P. Pham, U. Sharma, A. G. Mikos, *Tissue Eng.* **2006**, *12*, 1197.
[8] J. H. Yang, et al. *J. Appl. Polym. Sci.* **2011**, *120*, 2337.
[9] E. Yang, X. Qin, S. Wang, *Mater. Lett.* **2008**, *62*, 3555.
[10] C. Tang, et al. *Macromolecules.* **2010**, *43*, 630.

