

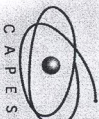
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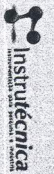
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FOREWORD

It is a great pleasure for us to welcome all the participants of the **XII International Macromolecular Colloquium and the 7th International Symposium of Natural Polymers and Composites**. We are very pleased with your contributions which are very important to the success of the Meeting. During this time, researchers will have the opportunity to initiate and enhance fruitful interactions among different institutions around the world working in the field of Polymer Science and Technology. We hope this Meeting will also offer a good opportunity to improve the research on the field of natural polymer-based materials and composites developed in Brazil.

Without your participation and specially the contribution of those presenting the 30 lectures, 34 oral sessions and 411 posters it would not be possible to organize this Meeting. We would like to acknowledge also the support from BRASKEM, CAPES, CNPq, FAPERGS, FAPESP, Petrobras and PROPESQ-UFRGS and the participation of the exhibitors dpUnion, Instrutécnica, Polimate and Reoterm.

We wish all the participants lots of interesting discussions and important stimulus for their further work and a pleasant stay in Gramado.

Organizing Committee



PEO/COLLAGEN BLENDS OBTAINED BY ELECTROSPINNING

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Hybrid biomaterials are proposed as one of the promising future directions in biomaterials research in the development of new materials. The electrospinning (E-spinning) technique was used successfully to fabricate nanofibers from different proportions of the semicrystalline polymer poly (ethylene oxide) (PEO) and collagen. Scanning electron microscopy (SEM), Fourier Transform infrared spectroscopy, rheology and conductivity techniques were performed to characterize the resulting electrospun fibers in comparison with pure PEO. By choosing water as the solvent in this study the observed fibers were 300-400 nm in diameter for both cases with broader distribution and revealed a well-defined Gaussian distribution. From SEM for pure PEO mats non woven were showed some nanofibers not continuous could be attributed its partial crystalline. However for all blends nanofibers a fairly long and high degree of linearity was observed. The process outlined herein provides a convenient, non-toxic, non-denaturing approach for the generation collagen-containing nanofibers with unique properties in various applications, such as biological sensors.

Introduction

Hybrid biomaterials are proposed as one of the promising future directions in biomaterial research in the development of new materials [1], such as nanofibers by electrospinning. These nanofibers provide a starting point for fabricating future nanodevices with unique electronic, optoelectronic, electrochemical, and electromechanical properties [2]. Collagen (COL) is a biodegradable, renewable and anionic natural polymer. The most abundant form of collagen isolated from adult connective tissues, such as skin, tendon, and bone is type I collagen. This material is a complex structure, consisting mainly of two $\alpha 1(I)$ chains and one $\alpha 2(I)$ chain, each slightly more than 1000 amino acids long, that are organized as a triple helix and stabilized primarily by hydrogen bonds. A single molecule of type I collagen has a molecular mass of 285 kD, a of around 14 and 3000 Å of width and length, respectively [3]. To verify the influence of the addition of a polymer in the property of the collagen, poly(ethylene oxide) (PEO) was used.

PEO is a semicrystalline polymer that has a wide variety of applications, such as biomaterials including scaffolds, drug delivers and conductive fibers [1]. PEO is non-toxic, chemically stable in acidic solution, and when of sufficient molecular weight is capable of forming electrospun fibers [4].

Blends of collagen can be a material applied as biomaterial in the medicine field, and electrostatic fiber spinning, or "electrospinning". Electrospinning has been extensively explored as a simple and versatile

technique to produce micro and nanofibers from polymer because it provides a potential way to fabricate continuous nanofibers [5] with different morphology and properties. This is a process that uses an electric field to control the formation and deposition of polymeric fibers [4,7-9]. Thus, this process is remarkably efficient, rapid, and inexpensive [7, 8]. In this technique, a polymer solution is injected with a high electrical potential. At a critical voltage, the charge drop begins to overcome the surface tension of the polymer source, forming an electrically charged jet. The jet within the electric field is directed toward the grounded target, during which time the solvent evaporates and fibers are formed [10]. Electrospinning produces a single continuous fibers that collects on the grounded target as a nonwoven fabric [9, 11]. Electrospinning technique has attracted great attention because polymer nanofibers with high surface-to-volume ratio can be fabricated by using this technique [8-11]. Polymer nanofibers have a broad range of applications such as tissue engineering [7, 11-19], biosensor [18-19] and drug delivery [9, 14, 15].

In this study, biodegradable polymer blends were developed from PEO/Collagen fibres by electrospinning (E-spinning) technique.

Experimental

The collagen fiber was extracted from bovine hides were supplied by NovaProm Food Ingredients Ltda (Lins, SP, Brazil). This sample was used without any chemical treatment.

Collagen was prepared by suspensions containing 2 g of collagen in 30 ml of distilled water, adjusting the pH with glacial acetic acid around pH 3,5. This acid was chosen after the mass of the suspension was completed to 100 g with distilled water. The suspensions were then agitated at room temperature for 60 min and centrifuged at 13000 rpm for 10 min at 15 °C. The protein contents in the suspensions before centrifugation (total protein) and in the supernatant (soluble protein). The solubility was expressed as the ratio of soluble protein to total protein in the suspension as a percentage (g of soluble protein/100 g of total protein) [6].

PEO contains a nominal molecular weight of 900000 g.mol⁻¹ was obtained from Aldrich. To prepare solutions for electrospinning, weighted 4% wt of PEO, and mixed in ultrapure water (18 MΩ.cm⁻¹) and vigorously stirred for several hours at room temperature until complete dilution. The blend ratios of PEO/collagen were controlled through varying the relative volume ratios of each component as 100/0, 80/20, 60/40, 20/80 and 0/100. The blend solutions were spun into fibers using a home made electrospinning equipment.

Perkin Elmer FTIR spectrometer was used for obtaining a spectrum of PEO, collagen fibers and PEO/Collagen fibers. The measurements were performed at room temperature by casting on Si-substrate and 42% humidity. The FTIR measurements was spectral range from 400 to 4000 cm⁻¹, resolution of 2 cm⁻¹ and superpositioning of 64 scans.

Viscoelastic properties of the polymers and blends were measured with a MCR 301 rheometer (Paar Physica, Messtechnik, Stuttgart, Germany) at 25 °C. Truncated cone-plate geometry (1°, 75 mm diameter) was used, in which the truncated cone had a gap of 0.05 mm between the flat surfaces of both elements. The viscosity of the polymeric solutions was carried out at 0.001-100 s⁻¹ shear rate.

Solution conductivity determined using a conductivity flow cell Horiba conductivity meter model ES-12E.

Scanning electron micrographs (SEM) analysis was performed using Zeiss DSM 960 computerized microscope operated between 10 and 20 kV on samples containing a thin layer (ca. 15 nm) of gold sputter-coated. The average diameter was determined using digital image analyses (Image J). A minimum of 100 measurements were used to determine the diameter.

Results and Discussions

Scanning electron microscopy (SEM)

Figure 1 shows SEM micrographs of the electrospun fibers from pure PEO and PEO/Collagen fibers (80:20, respectively) and their diameter distribution. In both cases the nanofibers, are almost uniform with some beads on a string morphology. The formation of beads has been attributed to jet instability, which presumably

is reduced upon increasing solution viscosity with the addition of high molecular weight PEO. This observation is consistent with the results by Huang et al [3]. The diameter of the electrospun fibers in both cases resembles a Gaussian distribution. The average diameter lies for pure PEO and PEO/Collagen at 350 and 400 nm, respectively with broader distribution (Figure 1c and 1d). Figure 1b, fibers were showed fairly long, a high degree of linearity were observed. The length of this nanofibers appears to be nearly several hundreds micrometers. However, this is not surprising because E-spinning can straightforwardly produce long continuous fibers up to millimeters in length [2]. SEM images from pure PEO (Figure 1a) solution were showed long fibers but not continuous. This could be attributed a partial crystalline of the PEO. After, collagen addition nanofibers were showed long and continuous. Significantly, fibers could not be formed from pure collagen solution, but were observed after addition of PEO.

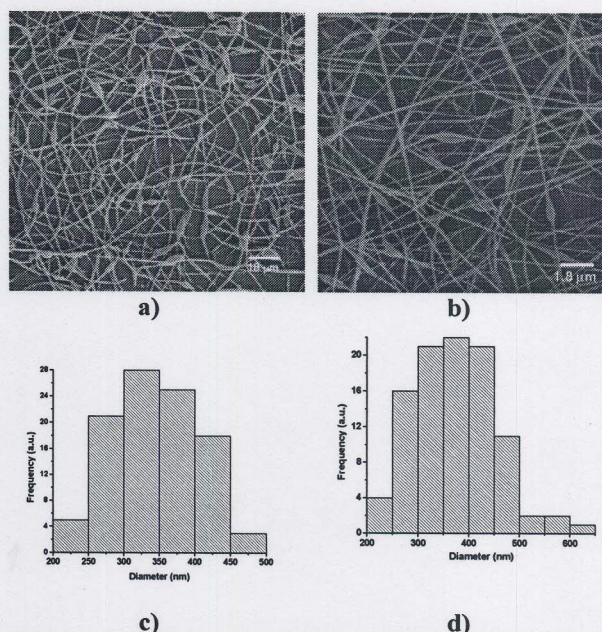


Figure 1 – Electron scanning micrograph and histogram of the PEO/Collagen blends by electrospinning. a) PEO ; b) 80/20 PEO/Collagen blend; c) PEO histogram; d) PEO/Collagen (80/20) blend histogram.

Fourier Transformed (FTIR)

Figure 2 shows the FTIR spectrum of the PEO, Collagen fibers and PEO/Collagen fibers by casting.

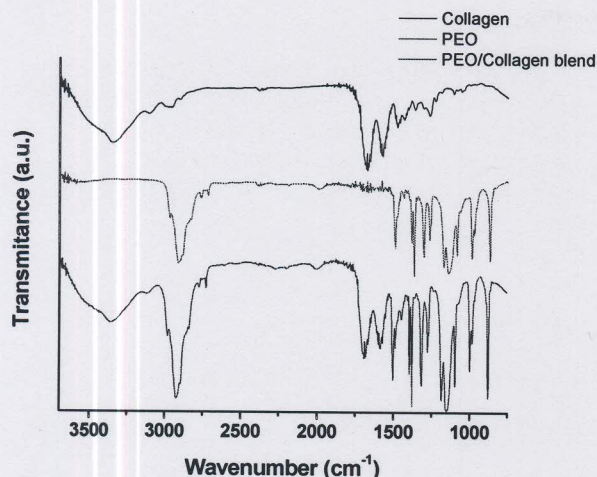


Figure 2 – FTIR spectra for a) PEO, b) Collagen and c) PEO/Collagen fiber (80:20) blend by casting.

In this study PEO assignments in FTIR were attributed according Kim et al. based in a molten state [2]. The vibrational bands of the semicrystalline PEO are observed at 1467 and 1455 cm^{-1} correspond to CH_2 bending. The bands at 1411 and 1341 cm^{-1} to a CH_2 wagging motion. At 1358 cm^{-1} to the mixed motion of CH_2 wagging and C-C stretching, 1278, 1240, and 1235 cm^{-1} bands to CH_2 twisting. At 1144 cm^{-1} to the mixed motion of C-C and C-O-C stretching. At 1093 cm^{-1} band should be C-O-C stretching. The band at 1060 cm^{-1} to the mixed motion of CH_2 rocking and C-O-C stretching. The bands at 961 and 947 cm^{-1} to CH_2 rocking, and the 842 cm^{-1} band to CH_2 bending. The FTIR for collagen was showed (Figure 2a) 1654 cm^{-1} ($>\text{C}=\text{O}$ group stretching) and bands around 1550 cm^{-1} as resulting of N-H bonds deformation (in-plane) and C-N stretching. A wide band around 3300 cm^{-1} should be attributed to a possible O-H stretching of the collagen (treonine, serine and hidroxiproline). The bands around 1400 cm^{-1} could be attributed pirrolidinic rings presents in the proline and hidroxiproline of collagen structure [1].

The formation of an interface in PEO/Collagen fibers blends is not surprising since there existing significant potential for hydrogen bonding between the ether oxygen of PEO a protons of the amino and hydroxyl groups in collagen. However, the nature and extent of hydrogen bonding, and as a consequence the presence an interface, will depend not only on the concentration of the polymer components in the blend, but also on whether the polymer chains are configured either in an amorphous or crystalline state.

Rheology

The rheograms in the figure 3 shown the viscosity as a function of shear rate for pure polymer solutions as well as blend compositions. Both curves have been plotted over a log-log scale with shear rate ranging from 0.001 s^{-1} - 100 s^{-1} .

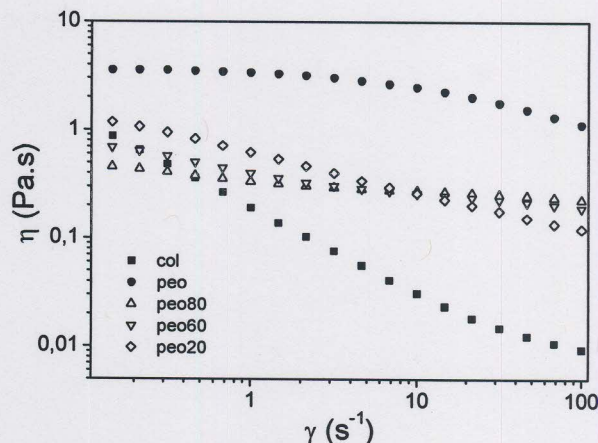


Figure 3 – Collagen, PEO and PEO/collagen (80:20, 60:40 and 20:80, respectively) solutions rheology.

It is observed that the flow and viscosity curves are straight lines indicating that the Ostwald-de-Waele equation (Power law model) is a suitable model for the representation of the data. The power law model

$$\tau = K\gamma^n$$

where τ is the shear stress and γ the shear strain, was fitted to the observed rheological data.

The increase in the viscosity of the polymeric blends and progressive decrease of the zero shear viscosity of blend solution with the increase of weight fraction of PEO is observed. The flow curves by pure PEO solutions reflect a Newtonian fluid behavior. The pseudoplastic behavior is observed in pure collagen and blend solutions. Both PEO and collagen are well miscible with 1 wt% acetic acid solution to form one phase solutions.

Conductivity

Figure 4 shows an increasing the concentration of PEO in the PEO/Collagen fibers blend increased conductivity.

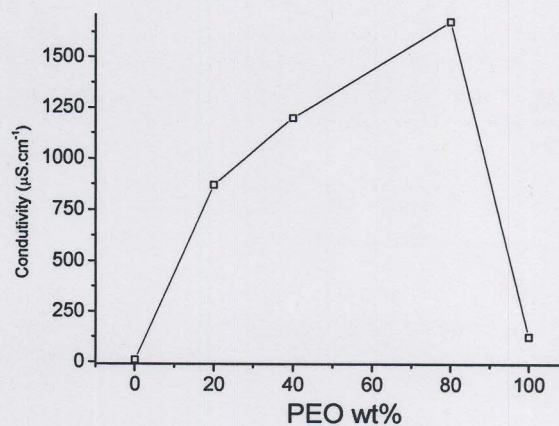


Figure 4 – Collagen, PEO and PEO/collagen solutions conductivity.

Likewise, solution conductivity was also found to influence fiber formation it was confirmed by SEM images (image does not presented) When an electric field is applied to an electrolyte-containing aqueous polymer solution, field induced ion movement carries the solution along by an additional viscous drag force. This phenomenon enhances jet stability and, as a consequence, reduces bead formation. These observations are consistent with the results by Huang et al [3].

Conclusions

In the present study the electrospinning process was successfully used to fabricate polymer nanofibers containing PEO and collagen. Finally, the hybrid electrospinning was showed great provides and potential as a convenient and simple technique for the fabrication of blends to future nanodevices. A possible mechanism for the interaction at pH 3.5 involves an affinity between the ether oxygen of PEO a protons of the amino and hydroxyl groups in collagen leading to the formation of the COOH group and the dedoping of PEO.

Aknowledgements

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