

Conductivity and Crystallinity of Polyethylene Oxide/Polyaniline Microfibers Obtained by Electrospinning

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ABSTRACT

In this paper we present results concerning the processing and characterization of polyaniline microfibers obtained by the electrospinning technique. The electrospinning technique is used to produce micro and nano fibers, this technique uses an electric field to stretch the jet of the polymer and thus produce fibers, which are deposited on a collecting plate. The continuous fibers production will form some like a membrane. The fibers provide a large surface area due to their small diameter, therefore, interesting commercial and scientific application could be considered. In this study, fibers from a solution made of polyethylene oxide and polyaniline were obtained. Chloroform was used as solvents for these polymers. The fibers obtained were characterized by scanning electron microscopy, x-ray diffraction and electrical conductivity. These results indicate that the diameters of the composite fibers are on the micrometric range, the conductivity thereof is that of a semiconductor material and the degree of crystallinity corresponds to a semi-crystalline material.

Keywords: Polyaniline, Polyethylene Oxide, Microfibers, Crystallinity, Conductivity.

RESUMEN

En este trabajo se presentan resultados concernientes al procesamiento y caracterización de microfibras de polianilina obtenidas por la técnica de electrohilado. La técnica de electrohilado es usada para producir micro y nanofibras, esta técnica usa un campo eléctrico para estirar el chorro del polímero y así producir las fibras, las cuales son depositadas sobre un plato colector. La producción continua de fibras llega a ser en forma de una membrana. Las fibras proveen una gran área superficial por su pequeño diámetro y esto tiene un gran interés comercial y sus aplicaciones científicas son consideradas. Se ha usado cloroformo como solvente para estos polímeros. Las fibras obtenidas son caracterizadas por microscopía electrónica de barrido, difracción de rayos x y conductividad eléctrica. Los resultados indican que los diámetros del compósito de fibras están en un rango micrométrico, la conductividad muestra un comportamiento de un material semiconductor y el grado de cristalinidad corresponde a un material semicristalino.

Palabras clave: Polianilina, Oxido de polietileno, Microfibras, Cristalinidad, Conductividad.

1. Introduction

The electrospinning is a versatile and non-expensive method for producing micro and nanofibers with different compositions, which have multiple applications in tissue engineering, biomaterials, electric engineering, controlled drug delivery, filtration, materials science as well as smart textiles [1-4].

A strong electric field, of the order of some kV, 15-30 kV, is applied between two opposite poles,

being one of them by the needle of the injection system and the other one metal plate (collector). In this way micro and/or nanofibers will be deposited on the collector, forming in some cases, a fabric with specific texture, color, and density.

The polymer solution, previously prepared, is loaded into the syringe injection, using an inert plastic tube, which is connected to a needle. An infusion pump attached to the plunger of the

syringe creates a pressure and a constant flow through the tube, which is transmitted to the polymer solution in the needle. By the effect of polarization caused by the electric field, the solution is thrown out as a stream toward a conductive surface connected to ground (usually a metal screen), located a distance 5-30 cm away from the needle [5-6]. During the formation of the jet (Taylor's cone), the solvent is gradually evaporated and the product obtained is deposited in the form of a composite non-woven as a micro and/or nano fibers with diameters between 50 nm and 10 microns.

During the last 25 years, electrically conductive polymers such as polyacetylene, polythiophene, polypyrrole and polyaniline have been intensively studied due to the combination of their electrical properties typical of metals and the physical properties of plastic polymers. Potential applications of such polymers are: electromagnetic interference shielding, corrosion protection, electrostatic discharge protection, energy storage, electrochromic devices, among others [7]. In this paper electrospinning technique has been used to form microfibers of Polyethylene oxide/Polyaniline composite, whose properties can be tailored by changing, among others, the concentration of the used polymers and the degree of doping of the polyaniline.

2. Materials and methods

The polymer solution was prepared by using polyethylene oxide of 900,000 wt%, polyaniline 46,000 wt% and camphorsulfonic acid (CPSA) as dopant. Chloroform was used as solvent at a concentration of 10% by weight. For the electrospinning process the solution was prepared at room temperature, by dissolving the polymer in the solvent. The solution, containing polyaniline and polyethylene oxide was submitted to magnetic stirring during 2 hours in order to homogenize the mixture. The optimal parameters found for the production of the fibers were:

Polymer concentration: 10% weight.

Applied voltage: 12 kV.

Flow rate: 2 ml / hour.

Distance from the needle to the collector plate: 15 cm.

Inner diameter of the needle: 0.6 mm.

For the collection of the fiber, a rotating device was designed. The fibers are deposited in the form of membrane or non-woven mesh as shown in figure 1.



Figure 1. Polyaniline fibers obtained by electrospinning.

The morphology of the obtained fibers was observed by using a field-emission scanning electron microscopy FEI-Sirion operated at 2 kV and different magnifications. In order to make some rough calculation of the degree of crystallinity a Siemens diffractometer, model D-500, with the $K\alpha$ cobalt radiation (wavelength of 1.77 Å) was used. The degree of crystallinity can be estimated by considering two characteristics of the diffraction pattern, on the one hand the diffraction peaks associated to the crystalline contribution, on the other hand the whole diffraction pattern, the wide bands related to the amorphous part of the fibers and also the diffraction peaks [8-9]. In both cases the area under the curve must be determined, because the fraction of crystallinity, χ_c , is given by the following equation:

$$\chi_c = \frac{I_c}{I_c + I_a} \quad (1)$$

where I_c is the intensity of the crystalline region and I_a the respective one to the amorphous contribution.

Electrical resistance was measured according to the two-point method. A Hewlett-Packard 6281A DC power supply was used to apply a voltage, and the current through the sample was measured with a Keithley 2420 electrometer. Several resistance measurements were carried out in range 0-9 volts. Average values are considered and reported.

3. Results and discussion

3.1 Scanning Electron Microscopy

In figure 2, it can be seen that the fibers form such a kind of web, just like a so called composite non-woven web. There are some beads which correspond to liquid solution droplets formed through the mesh structure. At higher magnification, see figure 3, the diameter of the fibers can be estimated. There it can be observed that the diameters varies in the range 1.36 - 3.61 μ m.

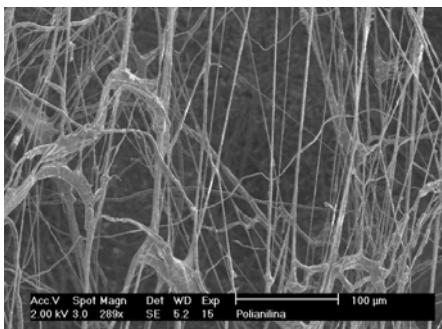


Figure 2. SEM image of electrospun polyethylene oxide / polyaniline 289x.

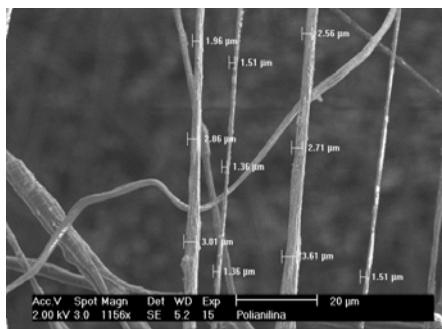


Figure 3. SEM image of electrospun polyethylene oxide / polyaniline 1156x, measurement of diameters.

3.2 X-Ray Diffraction

Figure 4 shows the XRD pattern of the fiber. The crystalline character of the fiber is observed through the well defined diffraction peaks which are located at $2\theta=22.32^\circ$ and $2\theta=27.09^\circ$ associated to polyethylene oxide component [10]. Figure 5 depicts the integrated intensity of the whole pattern, considering both crystalline and amorphous contributions. The area under the curve, i.e. the integrated intensity was obtained by fitting each diffraction peak to a gaussian curve [8-9], as shown in figure 6 and 7, together with the respective value of the integrated intensity. Then the crystallinity was calculated giving a value of 34.27 %, which can be considered as a low crystallinity value.

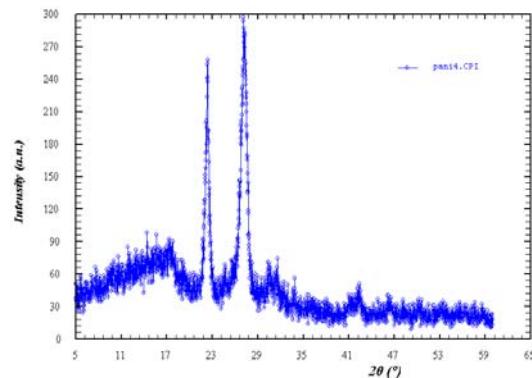


Figure 4. XRD pattern of electrospun polyethylene oxide / polyaniline.

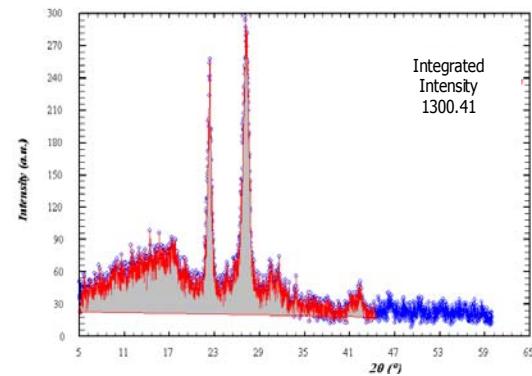


Figure 5. Integrated intensity amorphous portion and crystalline portion.

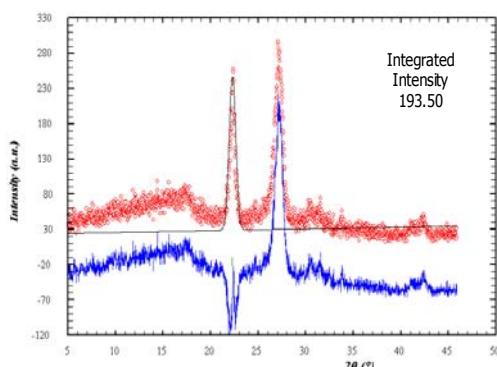


Figure 6. Integrated intensity peak 1.

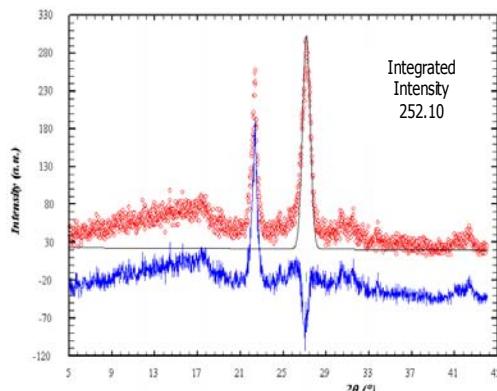


Figure 7. Integrated intensity peak 2.

3.3 Electrical conductivity

Figure 8, shows the I-V curve of PEO/PANI. The conducting composite fibers showed an ohmic behavior for voltages between 0-9 volts. The calculated electrical conductivity of fibers was 95389.30 μ S.

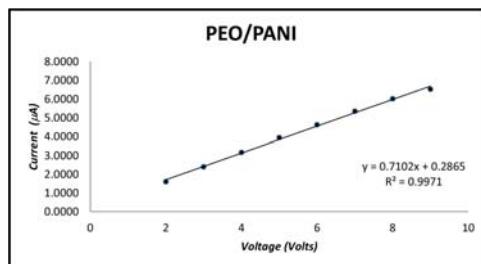


Figure 8. Voltage vs. current oxide polyethylene / polyaniline microfibers.

4. Conclusions

From the results obtained in this work have the following conclusions:

The orientation of the fibers, in the non-woven web, depends on the way they are collected. According to the liquid jet is stretched and the solvent was evaporated, the fiber diameter can be substantially reduced. The conductivity of the composite of PEO/PANI varies depending on the level of doping of the polyaniline. The low percentage of crystallinity is due to the semicrystalline character of the polymers used to form the composite.

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