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To cite this article: W Cárdenas *et al* 2016 *IOP Conf. Ser.: Mater. Sci. Eng.* **138** 012001

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Preparation of potato starch microfibers obtained by electro wet spinning

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Abstract. Starch is one of the most abundant biopolymer in nature. It has been primarily used as a thickener in the food industry. Starch is found in greater amounts in the potato tubers, which is one of the largest food productions in the region of Boyacá-Colombia. Thus, potatoes are a viable source of starch. The main objective of this study is the preparation and characterization of native starch's microfiber by electro wet-spinning technique. The parameters that were changed for each treatment were as follows: the amount of potential applied to the solution, the distance between the needle and the collector and the rate of injection of the solution in order to determine the physical and chemical properties of the membranes, conformed by potatoes starch microfiber. Diverse instrumental analysis techniques were applied. They were: Scanning Electron Microscopy (SEM) to determine the morphologies and diameters of microfibers, Fourier Transform Infrared Spectroscopy (FTIR) to determine the chemical changes, Thermogravimetric Analysis (TGA) and Differential Calorimetry Scanning (DSC) to obtain the thermal transitions and the temperatures of useful. The microfibers were analysed in order to determine their structural properties and thus define the range of application. In conclusion, potatoes starch microfibers were obtained with average diameters of 15, 17, 23 and 25 micrometres, besides the fibers presented a degradation temperature of 304 °C, indicating that fibers are available with diameters of small scale, with good thermal properties. This study will enable the implementation of the microfibers to obtain bio packaging for food products and other applications.

1. Introduction

Polymeric Nano and microfibers have been studied enough due to their characteristics which present high porosity, mechanical strength, flexibility and adhesion to other materials and high surface energy due to tiny diameters. Some other outstanding microfibers polymers' properties such as the



mechanical, physical and chemical have been reported in several papers. These exalted properties are important for the development of new materials for industrial and technological applications. One of the most used techniques for preparation in nano-microfibers is the electrospinning. This is due to the versatility to prepare continuous fibers in diverse sizes: from nano to the micro size [1, 2].

The main parameters of electrospinning are power supply of high voltage, rate of injection of the solution and distance between needle and metallic collector. The power supply of high voltage charges the polymer solution accelerating it from the needle to a collector. A jet of solution is ejected toward the metal plate due to the electric field force which is greater than the surface tension of the polymer solution. The jet of the solution is exposed to the atmosphere over the course of needle to collector, allowing the solvent to evaporate. This is to obtain solid polymer fibers with small diameters in the collector [3-5]. This technique in which fibers with small-scale diameters are formed by use of electrostatic forces, was discovered many years ago[6-8], but in the last decade research in this area has been increasing given that many studies for the production of nonwoven webs from a variety of synthetic polymers to be used in different applications such as filters, textiles, tissue scaffolds, drug delivery, sensors and nanocomposites[9-14].

Also electrospun from natural polymers such as starch and cellulose have been studied, being that these polysaccharides have rapid degradation, high biocompatibility and are not harmful to the environment. These natural polymers have been studied for the manufacture of products that replace fossil fuel-based materials [15, 16]. Starch is a major natural polymer, besides being abundant in nature, is also a great industrial utility either in the food, pharmaceutical, textile, paper, among others [17-20]. One of the main advantages for natural polymers is its easy access because there are various sources that have concentrations of more than 70% of polysaccharide. Among the most food used for the extraction of starch are corn, potatoes, barley and wheat [21-24].

In previous studies Kong, L et al [25] conducted electrospinning of starch from different sources such corn, potatoes, beans, rice and barley. They considered several grades of concentration of amylose and amylopectin, composites in which variation of concentration in the starch, offers different qualities as high heat resistance as described by Barichello et al [25]. Also Kong et al studied parameters of electro wet-spinning for obtaining corn starch fibers with diameters around 1 a 5 micrometers. Besides Kong, L et al [25-27] obtained starch microfibers the electrospinning equipment was configured to electro wet-spinning where the plate collector was immersed in pure ethanol with the final purpose of retirement of dimethyl sulfoxide dissolvent. However, they used industrial starch for electrospun microfibers and they have not been made electro wet-spinning from nature starch from the potatoes.

For this reason, the proposal of this paper is to obtain the starch potatoes microfibers with the technical of electro wet-spinning from the natural potatoes and special from the region of Boyacá like the variety Diacol Capiro (R12) which its high amylose gives the starch high thermal resistance, this being quite important for the preparation of new biodegradable materials[26] with the objective for industrial applications.

2. Experimental

2.1. Materials

The extraction of starch was carried out from to the potato variety Diacol Capiro, also known as R-12, cultivated in Boyacá-Colombia. The solvent for the preparation of starch solution was dimethyl

sulfoxide (DMSO, CAS: 67-68-5), being acquired from the marketing firm Merck at a concentration of 99%. Also ethanol (CAS: 64-17-5) was used. It was purchased from Sigma-Aldrich trading house at a concentration of 99.8%. The extraction of the starch is carried out following the methodology proposed by Vasanthan et al and Aristizabal et al [1, 6]. The solution obtained is allowed to settle for 12 hours and the precipitate was washed with deionized water and subjected to a drying air flow at 40 °C for 8 hours.

2.2. *Electro wet-spinning*

The equipment used for this work was the electrospinning which was configured to wet. It was constructed at Universidad Pedagógica y Tecnológica de Colombia- hereafter UPTC, (see Figure 1). The power supply used is HV 350R provided by the company Unlimited Company Amherst, the injector was provided by the company Syringe Pump Company Pump Systems Inc model NE model 4000 injector. The collector plate was immersed in a solution of ethanol-water 70:30, because this solution dissolves the DMSO and so the microfibers collected are starch with high purity. The starch solution used in electro wet-spinning process was prepared according to Kong et al [5], with a starch concentration of 10% w/w, due to starches with a percentage higher than 70% amylose are completely dissolved in DMSO in a range of 10-20% w/w of starch.

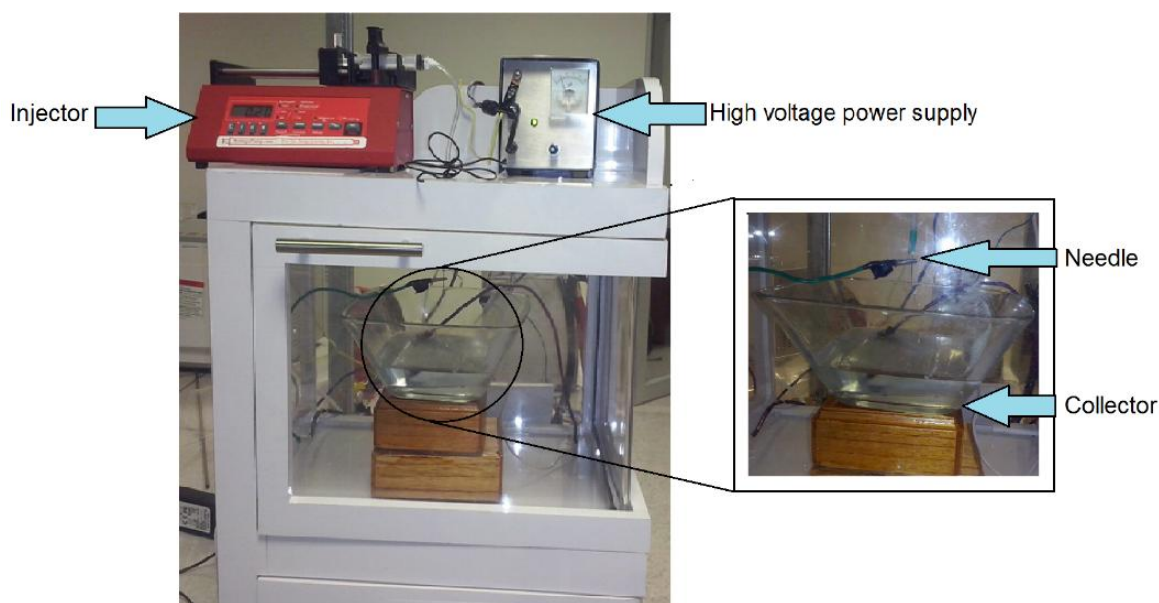


Figure 1. Electro wet-spinning equipment belonging to UPTC.

2.3. *Techniques used for the characterization*

The fibers were analysed by infrared Fourier transform spectroscopy with attenuated total reflectance (ATR-FTIR). The equipment used for the analysis was the ATR-Thermo Scientific Nicolet iS5, making a total of 32 scans in a range from 4000 to 400 cm⁻¹. For the Thermal Analysis was used the DSC and TGA about the starch potatoes fibers. This technique was performed in a calorimeter SDT Q600 TGA / DSC TA Instruments. The analysis was performed with a heating rate 10 °C/min, 18 to 400 °C. For the morphological determination and for the porosity of the fibers was performed a technique with scanning electron microscopy-SEM. These micrographs were made through JEOL-JSM-7600F (Japan) equipment Tungsten filament with a voltage difference of 20.0 KV. Photographs

taken for analysis of the fibers contained increases from 60x to 650x. To carry out the estimation of fiber's diameters, the micrographs were analysed using the Image J software.

3. Results

3.1. Infrared Spectroscopy

The fibers were analysed by ATR-FTIR to observe if the electro wet-spinning process causes chemical changes in the fibers. The native starch potatoes of powder were taken as reference to the infrared spectrum and so, used to determine whether there are changes in the spectrum of the fibers. In Figure 2, the spectra obtained fibers starch and native starch powder are presented. The IR spectrum for fibers of native starch presented one band at 3289 cm^{-1} related to the OH group bending [27] and at $1148,60$; $1076,68$ and 1000 cm^{-1} corresponding to C-O-C stretching vibration of glucose [28]. The bands found between 940 and 575 cm^{-1} were attributed to the whole glucose ring stretching vibrations. The band at $1635,26\text{ cm}^{-1}$ is due to tightly bound water present in the starch [29]. The signal at $2926,59\text{ cm}^{-1}$ was the characteristic vibration of C-H stretches [30].

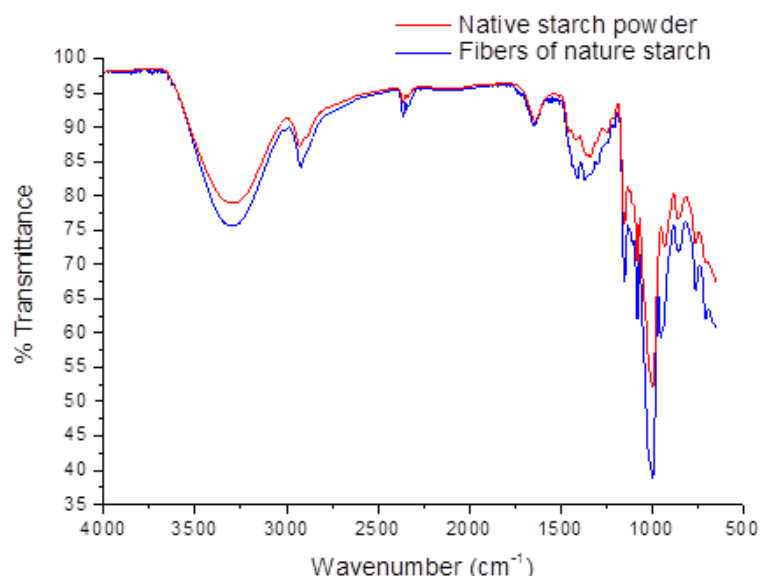


Figure 2. Infrared spectrum of the fibers potato starch and potato starch powder

For the of native starch, the IR spectrum presents the band of the OH group bending at $3296,59\text{ cm}^{-1}$. The C-O-C stretching vibration of glucose presents signals at $1148,15$; $1077,83$ and 1000 cm^{-1} and the bands attributes to the glucose ring stretching vibrations are between 937 - 580 cm^{-1} . At $1652,15\text{ cm}^{-1}$ is the bound water present in the starch and the band characteristic vibration of C-H stretches is found at $2921,93\text{ cm}^{-1}$. As shown in Figure 2, the electrospun fibers of native starch do not present chemical changes to the native starch powder. The bands found in both spectra are described in Table 1. Given the similarity of the signals obtained, we can confirm that the starch does not undergo chemical changes as a result of electro wet-spinning.

Table 1. Signals encountered in the infrared spectrum of the fibers of native starch and starch.

Starch Fibers (cm^{-1})	Native Starch (cm^{-1})	Type of vibration
3289,08	3296,59	Stretch wáter
2926,59	2921,93	C-H stretching
1635,26	1652,15	O-H bending
1148,60; 1076,68 y 1000	1148,15; 1077,83 y 1000	Stretch C-O-C

3.2. Thermal Analysis- TGA

To observe the thermal properties belonging to the starch potatoes fibers an analysis of TGA was conducted and the results are shown in Figure 3.

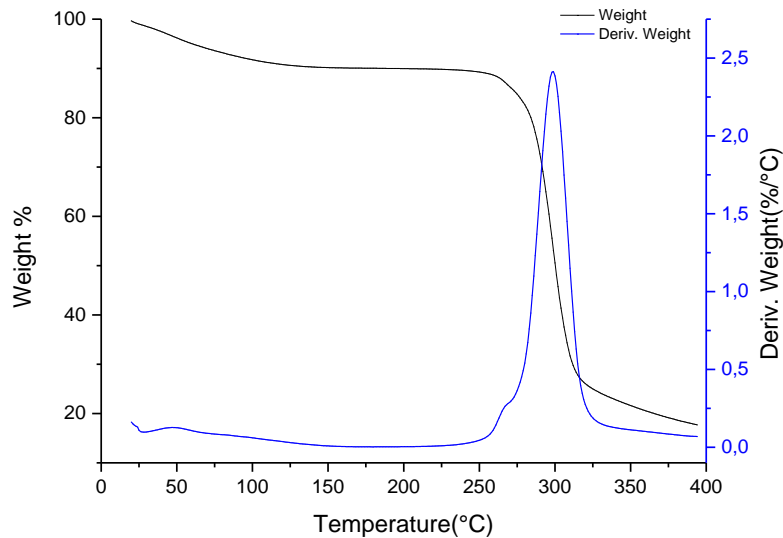


Figure 3. TGA diagram of starch potatoes fibers

In thermogravimetric analysis, the loss in mass due to volatilization of the degradation products is monitored as a function of temperature. It is possible to observe the loss of humidity of starch potatoes microfibers at 100°C corresponding to 11% of loss of total weight. After evaporation, the weight of the fibers stay constant until 250°C, where it is observed the beginning of loss of the weight of the fibers that correspond to the beginning of decomposition temperature of the starch fibers. The blue line observed in the figure, correspond to the derivative of weight in function of temperature. Here the temperature of fast degradation of fibers at 304°C can be seen. The fast loss of weight occurred at 315°C, in this transition point the fibers have lost near of 60% as compared with the initial weight. This analysis indicates the maxim temperature for usefulness (250°C) that must be considered for the design of elements with this material.

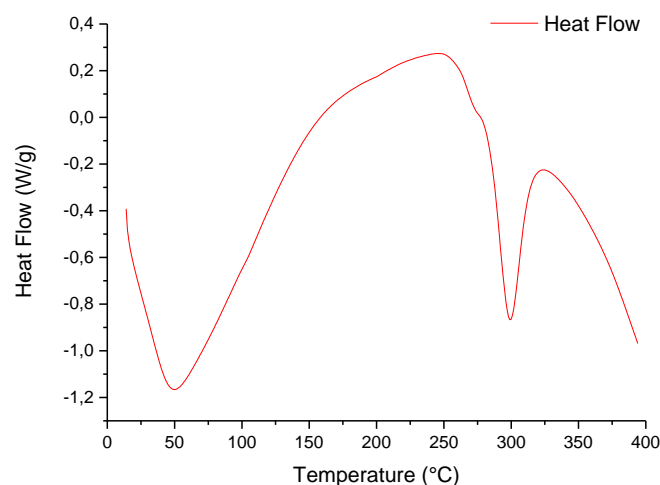


Figure 4. DSC of starch potatoes fibers.

In figure 4 it is possible to observe the energy absorptions that presents the native starch potatoes fibers with the increase of the temperature. Here the gelatinization temperatures of starch potatoes microfibers can be seen which are endothermic signals. The first signal appeared at 50°C, where the first stage of absorption of enthalpy energy of 81.16J/g is presented. This energy is absorbed by the fibers of starch for the dissociation of amylose (amorphous part) present in the starch. The second endothermic peak appeared at 303°C with enthalpy energy of 120 J/g. It occurs when this energy break the amylopectin bound. When the process increases the temperature, the fibers absorb the heat and generate the dissociation of amorphous phase (amylase). When the temperature is increasing, this generates the melting of a second component of starch potatoes, known, in this case, as amylopectin. The easy dissolution of amylase starch potatoes fibers at a low temperature happen because the hydrogen bonds are not that strong, while the bond of amylopectin is most stable, therefore it required higher temperature. Figure 4 confirms what is reported in several papers. It is to say that starch potatoes Diacol capiro (R-12) presents a high temperature resistance [26], so it is a good candidate for the fabrication of biodegradable material and industrial applications that require temperature above 100 C°.

3.3. Morphological analysis

The Morphological analysis of the fibers was carried out to four treatments of fibers. The Electro wet-spinning parameters used are shown in Table 2. In Figure 5 it is showed the micrograph taken to 4 treatments mentioned.

Table 2.Parameters used in the 4 treatments.

Parameters	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Voltage (Kv)	10	10	8	8
Rate injection (ml/h)	2	2	2	4
Distance needle-collector (cm)	8	6	6	6

In figure 5 it can be observed that all fibers obtained present roughness, cross-linking and agglomerations in some areas. This can indicate the effects of electro wet-spinning process because despite the variety of possible conditions, the contact of the jet of solution of starch with the ethanol, in the moment of deposition in the collector, does not generate completely the solidification and then the fibers were still wet and it creates the cross-link between the fibers. On the other hand, the agglomerations are evidence of the no continuity in the process. Therefore some polymers leave the needles with major o less volume.

In the first treatment, it is possible to denote that the fibers are fused. This could be due to the presence of solvent in the time of deposition that was not evaporated completely in the process of spinning, as consequence of high voltage. In the fibers of second treatment, it can be observed roughness, inhomogeneous in the size of the diameter and defined fibers. In contrast with the first treatment, here the process had less time and therefore, the fibers are thicker (25 micrometers) than the first treatment (17 micrometers).

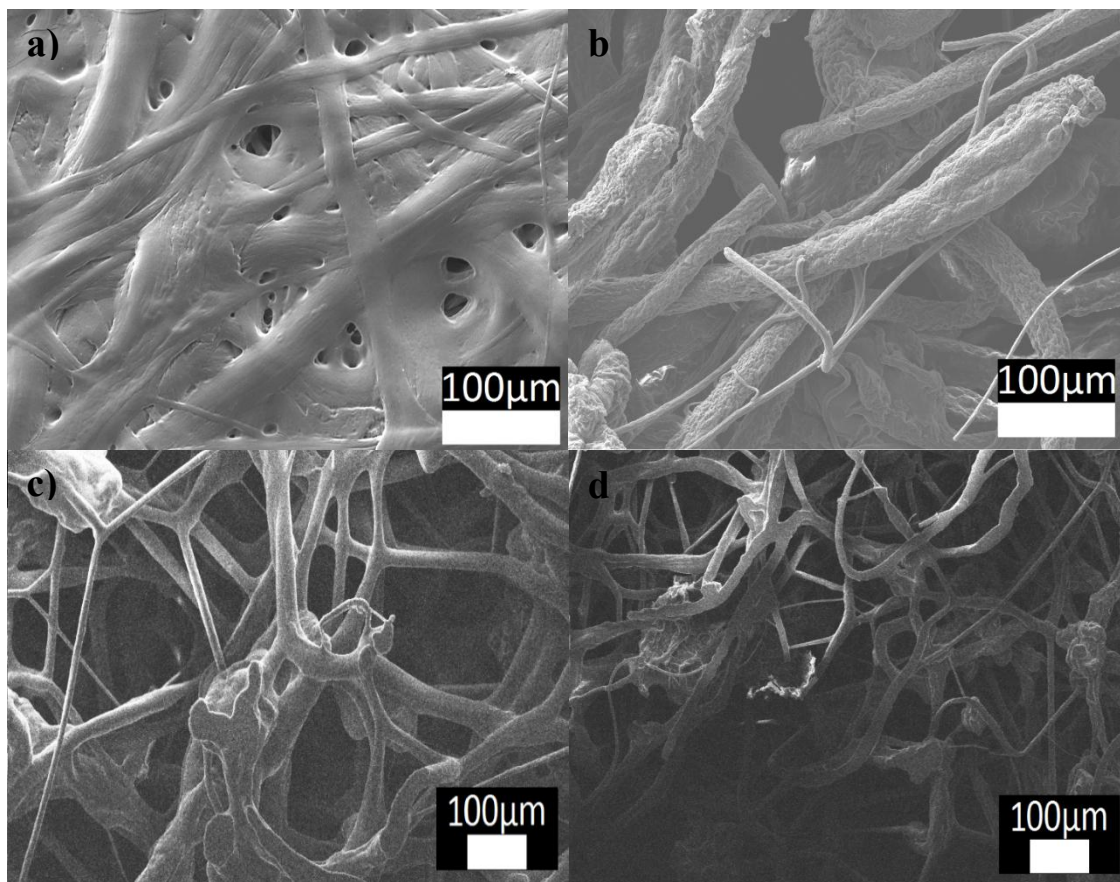


Figure 5. Micrograph of SEM starch potatoes fibers taken at the Instituto de Investigaciones en Materiales IIM of UNAM, a) treatment 1 (250X), b) treatment 2 (250X), c) treatment 3 (200X), d) treatment 4 (100X).

The fibers of the third treatment presented similar characteristic to second treatment such as continuous and defined fibers. Also it is possible to observe that the diameters of fibers in this treatment are more homogeneous, interlinking and smaller (15 micrometers) in comparison with the second treatment. This is explained because of the decrease of the voltage that allowed the jet of the solution to leave the capillary with less force and more time in the spinning. The fibers of the fourth treatment are similar to the third in the homogeneity in the diameters, the interlinking and they presented an increase in the diameters (25 micrometers). This is possible due to the increase in the rate of injection.

In studies carried out by Kong et al [31] with industrial corn starch, they obtained fibers with diameters between 1 and 5 micrometers, with a smooth morphology and homogeneous diameters. The difference with our results in the inhomogeneous morphology is due to the starch potatoes variety, Diacol Capiro (R12), presents different concentrations of amylose and amylopectin in comparison with starch corn. In consequence, it is generated a change in the viscosity of polymeric solution. In addition, these two components (amylose and amylopectin) influence in the starch thermal properties which was showed in the TGA. Another reason for this difference in diameter is due to the fact that our ethanol had a percentage of water that caused a time of solidification of fibers different.

The treatment with more homogeneity was treatment 3 and although the studies of Milasius et al [32] obtained fibers (125 nanometers) thinner in the order of nanometers, the fibers in our work were obtained from natural starch potatoes with voltage in the order of 6-8 Kv, while Milasius et al used voltage in the order of 75 Kv. They also used polyvinyl alcohol such dissolvent with addition with ethanol and collected the fibers with drum.

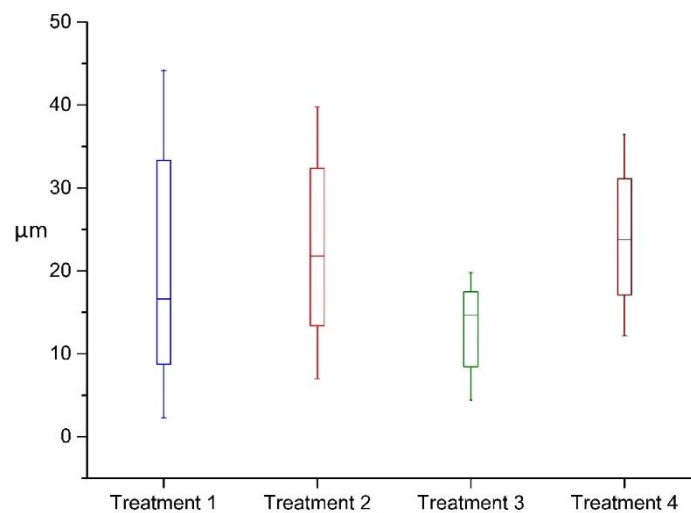


Figure 6. Boxplot about 4 treatments.

The analyses of diameter of starch potatoes fibers was measure by software ImageJ and the results are shown in figure 6 with the boxplot, where the upper diameters, the average and the lower diameter of the fibers in each treatment are represented. In figure 6 it can be observed that the third treatment with a voltage of 8 Kv, distance between needle and collector of 6 cm and rate of injection of 2 ml/h, presented the lowest diameter average (15 micrometer) and lowest variation (among 5 y 20 micrometers) in comparison with other treatments.

The treatment 1 showed a mean diameter of 17 micrometer, similar to the treatment 3, but showed a more variation (3 - 44 micrometers). This difference in the variation may be due to the fact that the first treatment used higher voltage (10 Kv) with distance 8 cm generate more mobility of the fibers in the path between needle and collector and as a consequence the fibers are deposited in several places of the collector and it generates the variation of diameters of fibers.

The treatment 4 (8 Kv, 6 cm and 4 ml/h) generates an average diameter of 25 micrometers that exceeds the others treatments. Here the only difference in the treatment is in the increase of rate of injection of 2 ml/h, which demonstrates the influence of the rate injection about the diameter of starch potatoes fibers. Such influence may explain that higher rate injection causes major volume of the solution in the needle, therefore the force generated by the field electric does not decrease diameter of jet generating an increase in the diameter of the fibers deposited in the collector. However, in this case the variation of diameters is lower in comparison with the treatment 2, this is due to more voltage that makes the polymer accelerates toward to collector. Then, the fibers are deposited faster and dispersed without enough time for stretching.

4. Conclusions

This study proves that native potato's fibers from the Region of Boyacá Colombia, with diameters in the size of micrometers can be obtained. It also shows the effect of the three parameters used in the

electro wet spinning, being the parameters of the third treatment the one that showed homogeneous continuous fibers, and high interlinking. It also notes that the deposition and washing with ethanol for the separation of solvent of the fibers, in the electrospinning process, was fundamental to obtain fibers. It was also noted that after the electrospinning, the fibers do not showed a change in the chemical structure as evidenced with the FTIR. Besides that, the test of DSC and TGA evidence that the fibers show a high resistance to heat (304°C is the maxim temperature of degradation), which is of quite important for the use of this material in the industry. Because the maxim temperature for useful found for the starch potatoes microfibers was 250°C that must be considered for design of elements with this material

5. Acknowledgments

The present study was carried out under the cooperation agreement between UPTC - IIM-UNAM and it was supported by the projects PAPIIT-UNAM/IN108930, CONACYT/ CNPq174247 in México and the projects at UPTC with SGI codes: 1573 y 1769 in the UPTC-Colombia.

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