Materiales

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CORN STARCH NANOFILAMENTS OBTAINED BY ELECTROSPINNING

NANOFILAMENTOS DE ALMIDÓN DE MAÍZ OBTENIDOS POR ELECTROSPINNING

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Abstract

Until today, there are not reports of nanofilaments from starch. Therefore, the aim of this research was to find the conditions for obtaining nanofilaments from natural polymers by the electrospinning process. An electrospinning prototype system built at laboratory was used. The performance of native corn starch water suspension (control), and succinated corn starch mixed with water, glycerol and surfactant were evaluated by electrospinning. Several processing parameters were critical for obtaining nanofilaments, among them were distance between needle and collector, voltage, conductivity, dielectric constant as well as water suspension viscosity. Native starch was not appropriate for obtaining nanofilaments due to particles agglomeration by retrogradation. To overcome those problems, several mixtures of succinated starch, surfactant Tween-20 and glycerol were evaluated. The viscosity was reduced from 664 cP in native starch mixture to 28 cP in succinated corn starch/Tween 20/glycerol, and the resulting low viscosity together with high dielectric constant >253 were adequated for achieving nanofilament of average diameter of 200 nm by electrospinning due to formation of Taylor's cone. Corn starch nanofilaments have several amazing characteristics making them optimal for many applications as scaffolds in regenerative medicine, thickeners and glues in other industries.
Keywords: starch, nanofilament, electrospinning.

Resumen

Actualmente, no hay publicaciones de nanofilamentos elaborados con almidón. Por tanto el objetivo de esta investigación fue encontrar condiciones para obtener nanofilamentos de polímeros naturales utilizando el proceso de electrospinning. Se utilizó almidón de maíz nativo y almidón succinatado mezclado con glicerol, surfactante y agua para elaborar las soluciones. Las condiciones críticas de procesamiento para obtener nanofilamentos fueron distancia entre aguja y colector, voltaje aplicado, flujo de solución, conductividad, constante dieléctrica y viscosidad. No fue posible obtener nanofilamentos a partir de almidón de maíz nativo debido a que se aglomera y no fluye uniformemente. Para corregir ese problema, varias suspensiones de almidón nativo y succinatado, Tween 20 y glicerol fueron evaluadas. La viscosidad en la suspensión de almidón nativo fue de 664 cP y se redujo a 28 cP en almidón succinatado/Tween 20/glicerol. El almidón succinatado, Tween 20 y glicerol permitieron condiciones para obtener nanofilamentos de diámetro de 200 nm. La baja viscosidad de 28 cP así como una alta constante dieléctrica >253 en la suspensión fueron los parámetros importantes para obtener nanofilamentos debido a que se puedo formar el cono de Taylor. Los nanofilamentos tienen potencial uso en aplicaciones como andamios en medicina regenerativa o como espesantes y adhesivos en otras industrias.
Palabras clave: almidón, nanofilamento, electrospinning.

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1 Introduction

The process that uses electrostatic forces to form fibers is called electrospinning. This process had been known for about 100 years ago, however with the advent of new electrical circuits, the electrospinning technology become again of scientific interest due to a better control in the high voltage source.

Recently, electrospinning process had taken an important interest in scientific literature, due to the ease way and versatility for making fibers with diameters in the nanoscale level. Furthermore, electrospinning process has the capability for building high porosity tissue (named scaffolds) similar to extracellular membrane for medical and food applications (Huang *et al*, 2003; Tapia Picazo *et al*, 2014). In addition, the electrospining scaffolds have good potential in the healing process and repair of skin wounds.

The electrospinning process uses a high voltage source for supplying electrical charge to the working solution (polarizability), which due to electrostatics forces, is accelerated to a collector of opposite charge. The electrostatic attraction between the polarized working solution and the collector is the main force that allows the changing from liquid to filament; this change starts with a rounded cone meniscus called Taylor's cone (Dzenis and Reneker, 1994; Sanchez *et al*, 2013), and finishes with a solid filament. When the electrostatic force exceeds the surface tension on the working material, a liquid jet is expelled from Taylor's cone, traveling through the atmosphere, allowing the solvent to evaporate, leading to deposition of solid fibers on the collector. Both the working material (mainly polymers) as well as the solvent used should have high dielectric constant, as this promotes polarization and thus the formation of nanofilaments (Won, 2004). Until today, there are not reports in the literature of nanofilaments from biopolymers such as starch because of the special conditions required to make these nanofilaments such as high surface tension and dielectric constant (Teo and Ramakrishna, 2006; Santos *et al*, 2014). The present work is one of the first that had obtained corn starch nanofilaments. A possible application of nanofilament starch is as thickener in the food industry or scaffolds for medical applications in the healing process and repair of skin wounds.

The aim of this study was to determine the operating conditions of an electrospinning system to obtain corn starch nanofilaments and the effect of surfactant (Tween 20 and glycerol) in processing.

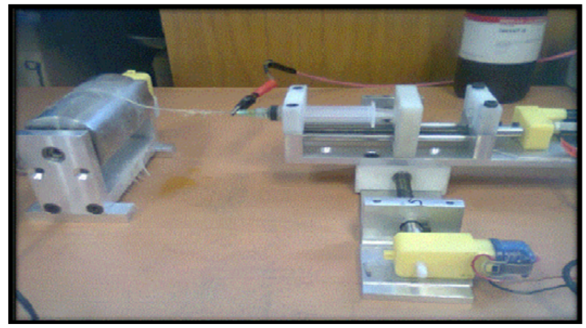

Fig. 1. Electrospinning system built in CICATA-IPN Unidad Querétaro, Mexico.

The parameters to evaluate will be the distance between needle and the collector, the applied high voltage, the flow of the working solution, the viscosity, the capacitance and the conductivity of the solution. Size and physical properties of the nanofilaments will be evaluate using SEM micrographs.

2 Materials and methods

2.1 Electrospinning system

The electrospinning system was built specially for this research in CICATA-IPN Unidad Querétaro (Fig. 1). The system has an Ultravolt High Voltage source Model 30A24 with a range of 0 KV to 30 KV, a home-made syringe pump with flow that has ranges between 0.01 to 0.3 mL/min, a linear actuator with a speed of 0.1 to 1 cm/min which move syringe pump in a linear way and a drum collector with an angular speed of 1 to 10 rpm.

2.2 Electrical conductivity measurements

Conductivity was calculated from electrical resistance. Electrical resistance was measured using a LCR Hi Tester HIOKI Model 3532-50 (Japan). The sample cell has a 1.9 cm length L, 0.9 cm width W and 0.6 cm height H. Conductivity was calculated using the equation (1) (Serway and Beichner, 2002).

$$Conductivity = (1/R) * (L/(W * H)) \quad (1)$$

Where R is the electrical resistance (ohms); L,W and H are the Length, Width and Large respectively of the measurement cell (units in cm). Conductivity units are Siemens/cm.

2.3 Dielectric constant measurements

The dielectric constant was calculated using the equation (2). Capacitance was measured using a LCR Hi Tester HIOKI Model 3532-50 (Japan) at a frequency of 1000 Hz. The sample cell has a 1.9 cm length L, 0.9 cm width W and 0.6 cm height H. (Serway and Beichner, 2002; Ireta Moreno *et al*., 2010)

$$Dielectric\ \ constant = C/(8.85x10-12)*(L/W*H) \tag{2}$$

Where C is the capacitance units in Farad; L,W and H are the cell dimensions units in cm.

2.4 Viscosity measurement

Viscosity was determined using a rheometer (Anton PaarPhysica MCR 101, Austria) with a set-up of concentric cylinders. The test was conducted at a constant deformation speed of 100 s-1 and a temperature of 22°C, which are similar conditions to those reported by Yuliarti *et al*., (2011). The viscosity was reported in centipoise (cP), and the measurements were performed in triplicate.

The aqueous suspensions used were prepared with water:native starch 100:7.5; water:native starch:glycerol 100:7.5:5; water: succinated starch 100:15; water:succinated starch:Tween 20, 100:15:5 and water:succinated starch:Tween20:glycerol 100:15:5:5. w/w.

2.5 Nanofilament diameter

To study the nanofilaments morphology and diameter, an ESEM (Philips model XL30, Philips Research Laboratories, Eindhoven, the Netherlands) with a beam of 15-20 kV (50μA), gaseous secondary electron (GSE) detector was used. The images were taken at 2500X and 10,000X, 1.1 mBar and a spot size of 4.5.

2.6 Electrospinning processing parameters

The electrospinning processing parameters are: a) distance between needle and collector (cm) b) the applied High Voltage (Volts) c) syringe Flow (ml/min) d) Electrical conductivity (ohm * cm)$^{-1}$, dielectric constant (no units) and e) viscosity (cP).

2.7 Experimental methodology

The methodology followed in this study was: 1) Preparation of the solution to deposit; 2) Obtaining parameters for nanofilaments such as the distance between the needle and collector, the applied voltage, solution flow, viscosity, conductivity; 3) Measurement of nanofilament diameter with SEM micrographs.

3 Results

Native corn starch during gelatinization in water showed a high viscosity value as is shown in table 1. This condition was contrary to the required viscosity for some microparticles or microfilament applications. According to various authors, the ideal carrier used to produce microparticles should have low viscosity at high solid levels and high solubility (Reineccius 1989; Murúa-Pagola *et al*., 2009; Rodriguez-Marin *et al*, 2013), so, in the present study starch suspensions with different viscosities from water suspensions of succinated starch, the detergent Tween 20 and glycerol were evaluated as carriers in the formation of microfilaments.

Table 1 shows the processing parameter found for the starch water suspensions. The native corn starch showed a relatively high viscosity 664.85 cP compared to the modified starch water suspensions (26 cP). The glycerol, as a plasticizer, increases the fluidity of the solution as indicate in table 1 where native corn starch with glycerol decrease viscosity to 299 cP. However, that viscosity value was not enough for getting nanofilaments. The addition of glycerol also increased the conductivity of the native corn starch water suspension. The values of conductivity agree with those reported by other authors (Morales-Sánchez *et al*., 2009). Table 1 shows that Tween 20 helps by increasing the dielectric constant and reducing the viscosity in the water suspension. In addition, the starch modification and chemical compounds used to make the water suspension carrier affected some electrical properties (Table 1). The dielectric constant agrees with the value found here measured at frequency of 1000 Hz. Other authors had reported dielectric constant of 50 for corn starch evaluated at microwaves frequency range (2.5 GHz) (Tsoubeli *et al*., 1995). The succinated corn starch had a dielectric constant of 220 while native corn starch had a dielectric constant of 76. So, with an increase in the dielectric constant value, the electrostatic forces enhanced the charge of the succinated starch water suspensions, which allowed the formation of nanofilaments.

Table 1. Electrospinning process parameter values used for obtain corn starch nanofilaments.

Water suspension	Solvent	Viscosity cP	Dielectric constant	Conductivity Ω^{-1} cm^{-1}	Distance collector to needle	High voltage KV DC cm	Nanofilament
Native Corn starch	water	664	76	5.69×10^{-4}	4-12	6-9.5	No, sparged
Native Corn starch with glycerol	water	299	82	6.93×10^{-4}	4-8	6-10	No, sparged
Corn starch Sodium succinate	water	28	220	7.38×10^{-4}	4-8	6-10	No, sparged
Corn starch Sodium succinate / Tween 20	water	26	253	7.82×10^{-5}	4-8	6.0-8.5	yes
Corn starch sodium succinate/ glycerol/ Tween 20	water	30	260	5.02×10^{-4}	4-10	7.2-15.9	yes

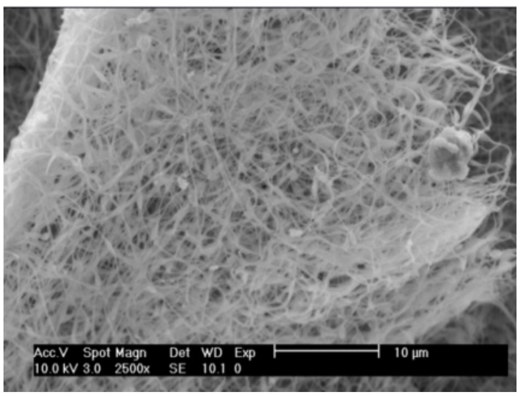

Fig. 2. SEM micrograph of nanofilament of sodium succinate corn starch with glycerol and Tween 20 deposited in the collector.

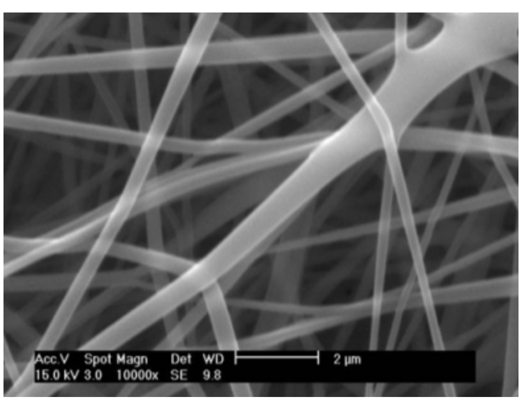

Fig. 3. SEM micrograph of nanofilaments of sodium succinate corn starch with glycerol and Tween 20 (enlarged).

Figure 2-3 shows the micrograph of filaments of corn starch sodium succinate with glycerol and tween 20 deposited on the collector. It was observed nanofilament with a diameter average of 200 nm.

4 Discussion

Based on the observations of the starch suspensions used as carriers for electrospinning experiments, it can be suggested that the major factor that determines whether or not the modified starch mixture suspension will form nanofilaments was the low viscosity and high dielectric constant (Table 1). It was impossible to obtain nanofilaments from native corn starch because gelatinized corn starch formed agglomerates of high viscosity that were deposited over collector. The deposited material was indeed particles instead of nanofilaments (Fig. 4). It is well known that for electrospinning it is necessary to have a homogenous solution without agglomerates. Some authors indicated that the incorporation of bulky succinate group to hydrophilic starch molecules confers surface-active properties to the modified starch giving a hydrophobic character to starch and weakens the internal bonding that holds the granules together (Bhosale and Singhal, 2006, Ponce-Reyes *et al*, 2014). These modifications disrupt the hydrogen bonding and reduce re-agglomeration of particles in the system. Therefore, to avoid starch agglomerates and to have appropriated water suspension mix with good performance for electrospinnig, corn starch was modified with sodium succinate.

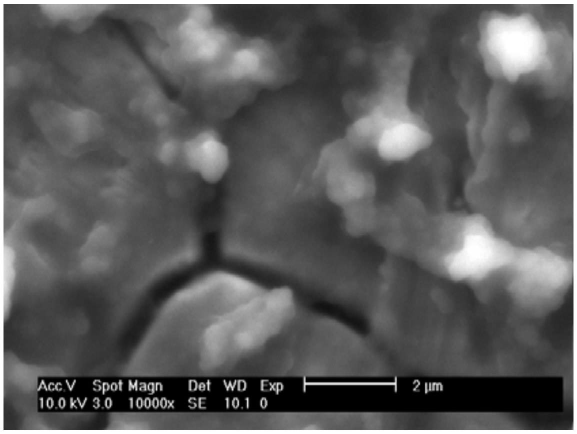

Fig. 4. SEM micrograph of gelatinized native corn starch deposited in the collector.

Then, the succinated corn starch was mixed with glycerol and detergent Tween 20. This approach work very well since was possible to obtain the nanofilament.

In addition, the starch modification and chemical compound in the water suspension carrier affected some electrical properties (Table 1). While a dielectric constant near 80 governs the strength of electrostatic interactions in aqueous solution, a higher dielectric constant was related to higher starch molecules polarization. The succinated corn starch mixed with Tween 20 has a different dielectric constant than native starch which allows more polarizability because there are radicals that increase electrostatic charge forces between the solution in the syringe pump and the drum collector. Table 1, shows that mixture containing the Tween 20 made good quality nanofilaments, this fact can be explained due to the effect of Tween 20 which is a nonionic polyoxyethylene detergent with surfactant effect that reduced the interfacial tension between liquid and solid in the system and enhancing the formation of the Taylor's cone. So, when Tween 20 was together with succinated corn starch, two effect were detected: one effect was the increase of dielectric constant (253) which enhanced the electrostatic deposition and the second effect was the reduction of surface tension manifested by the low viscosity in the starch mix suspension.

Conclusions

The electrospinning process can be used to produce corn starch nanofilaments. However, it was impossible to use direct native corn starch for obtaining nanofilaments because gelatinized corn starch formed high viscous agglomerates in form of particles instead of nanofilaments that were deposited on the collector.

Native corn starch was modified with sodium succinate and mixed with glycerol and a detergent Tween 20 for obtaining nanofilaments with an average diameter of 200 nanometers.

Succinated corn starch/Tween 20/glycerol had a low viscosity which helped in the formation of Taylor's cone and a high dielectric constant that improved the polarizability for the electrospinning process.

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Nomenclature

R	electric Resistance, ohms.
C	electric Capacitance, Farad.
L, W, H	physical dimensions, cm.

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