Morphological and Mechanical Characterization of Electrospun Polylactic Acid and Microcrystalline Cellulose

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The goal of this work was to develop a composite material, a membrane, based on polylactic acid (PLA) reinforced with cellulose microcrystalline (MCC). Membranes based on PLA were fabricated using electrospinning. The fabrication parameters, fiber morphology, and mechanical properties were analyzed. For fabrication, 12 mL of solution (12%, weight basis, of PLA in chloroform) was used and three different injector-collector distances and three voltages were employed. The fiber morphology was observed using a scanning electron microscope (SEM). To fabricate reinforced membranes using microcrystalline cellulose (MCC), an amount of 1.0%, 3.0%, and 5.0% of MCC, based on the polymer mass, was used. The MCC distribution was observed using SEM. The membranes were tested *via* tensile and tearing tests according to the corresponding ASTM D882-12 (2012) and ASTM D1938-14 (2014). It was observed that plain fibers tended to form, depending on the injector-collector distances. Additionally, microfiber porosity was observed, which was attributed to the solvent evaporation. Moreover, the addition of 1% of MCC was translated into an important increase of tensile strength, which in some cases reached a 476% increase; similar effects were observed in the tear test results.

Keywords: Polylactic acid; Microcrystal cellulose; Electrospinning; Mechanical properties; Fiber morphology; Porosity

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INTRODUCTION

Obtaining fibers and membranes based on polymers is an interesting subject of study because it shows important possibilities of application in the food, pharmaceutical, and biomedical industries (Stanger *et al.* 2005). One of the more widely used procedures to manufacturer fibers is the electrospinning technique that recently has achieved advances on an industrial scale (Mitchell 2015). The electrospinning technique is an electrostatic process where a polymeric solution is exposed to produce fibers that can be different sizes, from nanometers to micrometers (Frenot and Chronaki 2003). To obtain fibers, a syringe is loaded with a polymeric solution that is subsequently placed in a bomb where the solution flow can be controlled.

The injector's tip is exposed to a potential difference; once a drop of the solution comes out of the injector's tip, its superficial tension is defeated due to the current electric charge that allows the formation of a Taylor cone. Therefore, the increase of the electric potential causes the formation of a micro-fiber from the Taylor's cone to the fiber collector (Ramakrishna *et al.* 2005).

The solvent, which is used to prepare the polymeric solution at the moment of the fiber formation, evaporates because of the electric potential. The fabrication parameters to be controlled to accomplish the correct fibers formation are fabrication voltage, solution viscosity, and distance from the injector's tip or syringe to the collector (Bhardwaj and Kundu 2010; Rezaei *et al.* 2015). This technique is presented as an important alternative for the manufacturing of biomaterials.

Currently, the use of materials with less environmental impact is preferable, and biopolymers are an important alternative to the packing industry. These materials show interesting qualities of degradation and safety. Biopolymers share similar characteristics to conventional polymers (Niaounakis 2006). Within the group of these materials, polylactic acid (PLA), which can be compared to polyethylene terephthalate (PET) because it is a hydrophobic polymer, is a polymer that has been subjected to study by many researchers. The PLA is derived from lactic acid, and is thermostatic and compostable, produced from renewable resources, and originated from materials with a high content of starch or sugar such as corn, sugarcane, potatoes, *etc.* (Serna *et al*. 2011).

To improve the physical and mechanical properties of biopolymers, they may be reinforced with other materials, lignocellulosic in origin, such as fibers, particles, and nanoparticles. The result of this combination is a composite or biocomposite material of matrix-fiber hybrid properties (Gurunathan *et al.* 2015).

A biocomposite is made up of environmentally friendly raw materials whose physical mechanical processes vary because of the use of reinforcement material (Mohanty *et al.* 2000). Therefore, microcrystalline cellulose (MCC) can have potential use as reinforcement in biocomposite material because it is derived from renewable and environmentally friendly resources (Mathew *et al.* 2005, 2006). The MCC is derived from cellulose, reinforcing a great variety of vegetal species; they are sub products of α-cellulose extracted from wood pulp (Ardizzone *et al*. 1999). To obtain MCC, the cell wall of the fibers is divided into pieces whose sizes do not exceed a pair of microns in length. These segments are subjected to a controlled acid hydrolysis that results in two portions, one soluble in acid and the other insoluble. The insoluble fragment corresponds to approximately 17% (dry base) of microcrystal cellulose (MCC). The MCC is insoluble in water or organic solvents and is physically a fine, white, odorless powder (Das *et al*. 2010).

As previously stated, when biocomposites based on biopolymers are produced, it is important to ensure that the resulting material is eco-friendly and comes from renewable resources. Accordingly, PLA can be enhanced in its mechanical properties when it is reinforced with MCC. Diverse research has shown advances in this subject, developing biocomposites based on PLA reinforced with MCC and fabricated by means of techniques such as casting and extrusion processes. Previous research shows that the mechanical properties of PLA are effectively improved by the addition of microcrystals of cellulose (Petersson and Oksman 2006; Haafiz *et al*. 2013; Murphy and Collins 2016).

The objective of this study was to develop a composite material based on PLA reinforced with MCC. A morphological analysis was performed and then related to the fabrication parameters of the electrospinning process. Furthermore, the reinforcement contribution was observed on the mechanical properties of the final membrane. Using scanning electron microscopy (SEM), the composite and the fibers formed during the fabrication process were studied; the fibers' diameter, malformation, and flaws were also analyzed. The MCC dispersion in the membrane of fibers was also examined. Tensile and tear propagation resistance tests were performed according the ASTM standards ASTM D882 (2012) and ASTM D1938 (2014).

EXPERIMENTAL

Materials

Polylactic acid (Natureworks® 2002D; Morgan S.A, Santiago, Chile) with a molecular weight of 200,000 g/mol, density of 1.24 g/cm^3, glass transition temperature (Tg) of 58 °C, and melting point (Tm) of 153 °C was used. The MCC supplied by Merck KGaA (Darmstadt, Germany) had a grain size that measured from 1 µm to 160 µm, density of 1.5 g/cm^3, and was used as a reinforcement. The chloroform and analytical grade acetone used were supplied by Merck KGaA (Darmstadt, Germany).

Methods

Preparation of PLA, PLA-MCC solutions, and electrospinning

A total of 12 mL of solution was prepared, where 12% weight basis corresponded to PLA and 88% to the solvent (Buschle *et al*. 2007). The proportion by volume of the solvent chloroform/acetone was 2 to 1 (Dong *et al*. 2011). The PLA in pellets were dissolved in chloroform for 12 h, then acetone was added and homogenized on a magnetic plate for 1 h at room temperature. This solution was subsequently loaded in a syringe with a 0.8 mm injector of nozzle inner diameter and mounted in the electrospinning instrument (INOVENSO NE-300; Inovenso Ltd., Istanbul, Turkey) (Fig. 1).

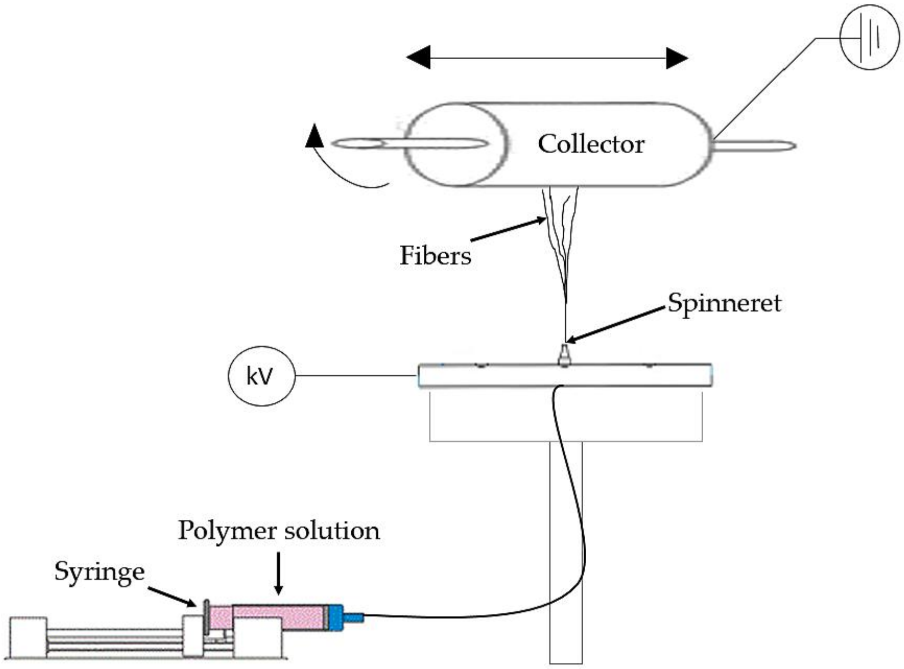

Fig. 1. Set up of electrospinning apparatus, configuration of ascendant vertical fabrication

The electrospinning equipment was calibrated with three fabrication distances and voltages. The distances from the injector to collector were 15 cm, 18 cm, and 20 cm. The voltages used were 22 kV, 24 kV, and 26 kV. The solution flow was estimated at 0.2 mL/h (Haroosh *et al.* 2011). The collector used was a drum rotatory collector (Inovenso Ltd., Istanbul, Turkey).

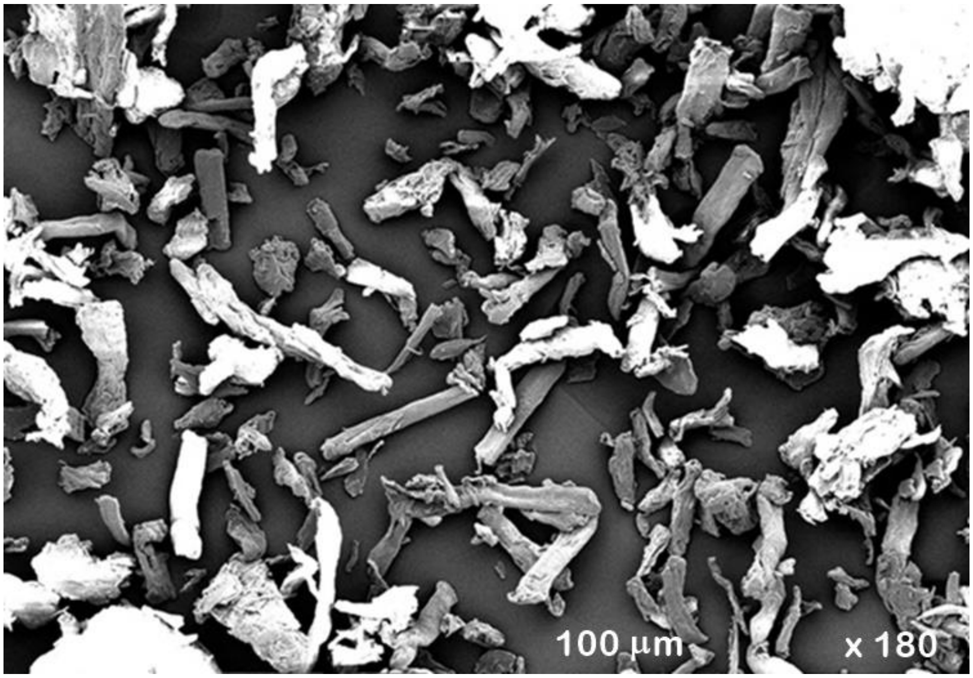

Fig. 2. Microcrystalline cellulose

The PLA-MCC solution was prepared as previously described with the addition of MCC in 1%, 3%, and 5% based on polymer weight. The MCC are shown in Fig. 2. After homogenization of PLA and acetone, the corresponding MCC for each experiment was added and then homogenized continuously for 1 h at room temperature. Once well mixed, the solution was loaded in a syringe and then into the electrospinning machine.

Morphological characterization

The morphology of the membranes and distribution of MCC were observed using a JEOL JSM- 6610LV SEM (Jeol Ltd., Tokyo, Japan) with an accelerating voltage of 5 kV, where the samples were previously gold coated for 30 s (Denton Vacuum, New York, USA). The fiber diameter in the membrane was measured using ImageJ- Image Processing and Analysis in Java software (National Institutes of Health, version 1.46r, Bethesda, MD, USA).

Mechanical characterization

The tensile and tear strengths of the membranes were measured with a universal testing machine (Model Z020; Zwick Roell, Zwick Roell Group, Ulm, Germany). The tensile tests were performed in accordance to the ASTM D882 (2012) standard. Tear propagation resistance tests were performed in accordance to the ASTM D1938-14 (2014) standard.

Statistical analysis

The mechanical properties were analyzed using a factorial general design with two factors and two response variables: Tensile strength (MPa) and Tear propagation resistance (N) (Table 1). An analysis of variance (ANOVA) was performed with a level of confidence $\propto = 0.05$. The software Design Expert (Stat-Ease, version 10, Minneapolis, USA) was used.

Table 1. Design of the Experiment

Factors	Levels			
MCC (%)	0	1	3	5
Fabrication Voltage (kV)		22	24	26
Response Variables	Tensile strength (MPa)			
	Tear propagation resistance (N)			
Number of specimens tested = 5				

RESULTS AND DISCUSSION

Morphology

The membrane fibers' morphology has been found to have a dependence on the manufacturing voltage and injector-collector distance (Zhenyu and Ce 2013). Additionally, these variables, as well as the impulse of the incoming fibers to the collector, have influence on the fiber's diameter (Ki *et al*. 2005). The SEM images for membranes manufactured with an injector-collector distance of 15 cm and voltages of 22 kV, 24 kV, and 26 kV (Fig. 3), displayed ribbon-shaped microfibers, flat wide microfibers, and thick polymeric layers. The latter could have been the result of a collision between the microfiber and the collector due to the short injector-collector distance and the strong attractive force generated by the electrostatic field allowing fiber flaws (Wu *et al*. 2010). As expected, an increasing voltage resulted in a reduction in the fibers' diameter, where the higher Coulomb force and the stronger electric field encouraged a further microfiber stretching (Megelski *et al*. 2002).

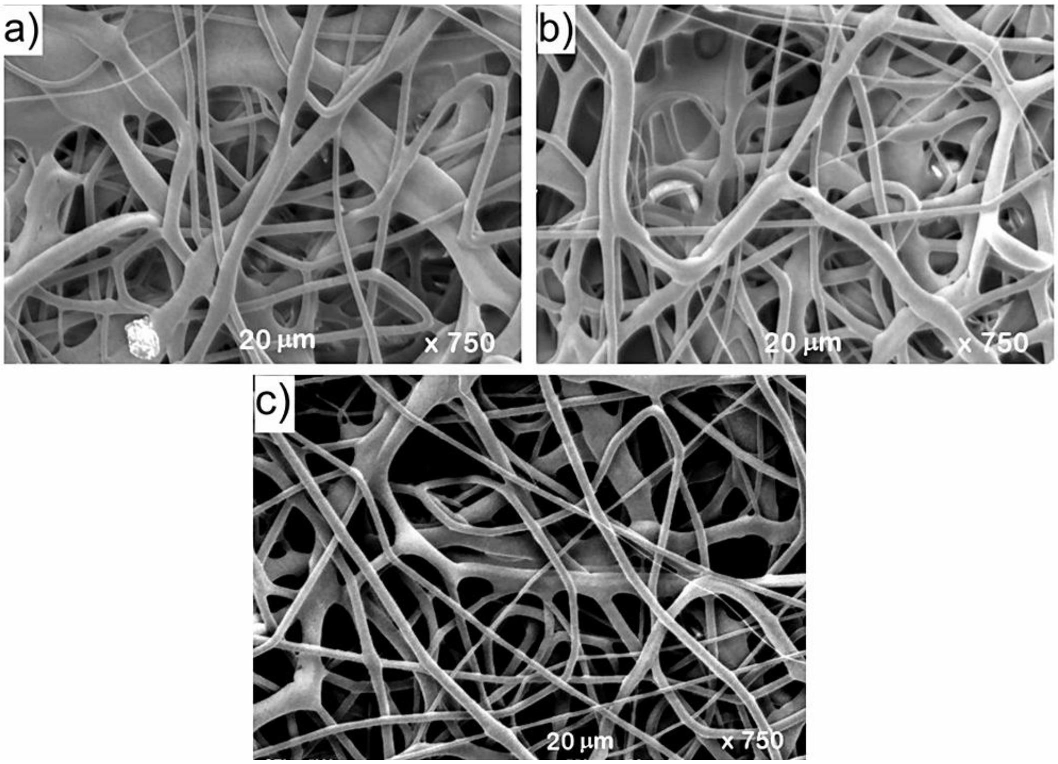

Fig. 3. SEM images of membranes manufactured based on PLA using electrospinning with 15 cm injector- collector distance and voltages: a) 22 kV; b) 24 kV; and c) 26 kV

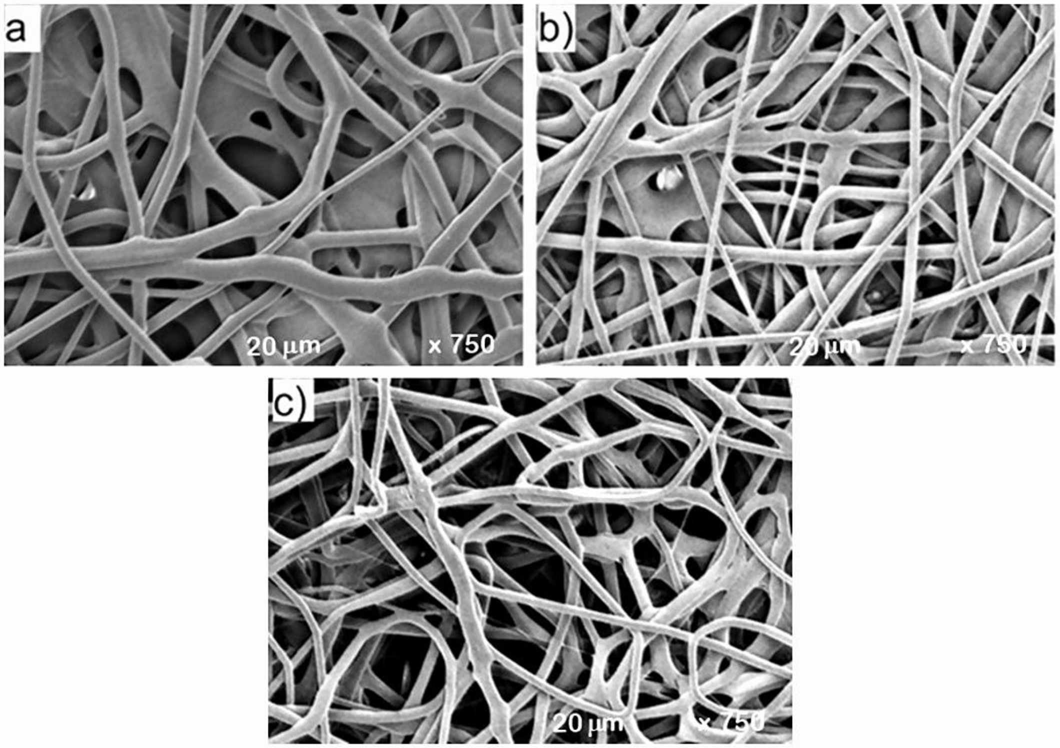

Fig. 4. SEM Images of membranes manufactured based on PLA using electrospinning with 18 cm injector-collector distance and voltages: a) 22 kV; b) 24 kV; and c) 26 kV

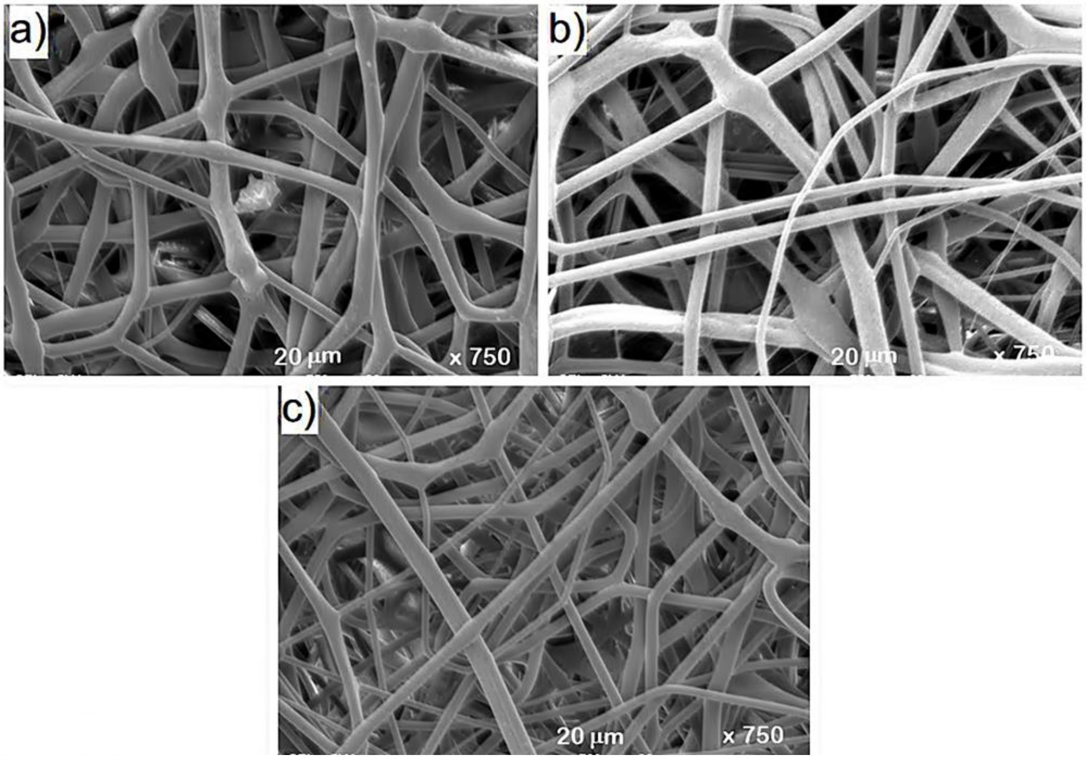

Fig. 5. SEM Images of membranes manufactured based on PLA using electrospinning at a 20 cm injector-collector distance and voltages: a) 22 kV; b) 24 kV; and c) 26 kV

The fibers showed imperfections when the injector-collector distance was set to 18 cm (Fig. 4). However, increasing distance allowed a microfiber symmetry as well as a longer time for the microfiber to reach the collector, which turned into a microfiber stretching (Kang *et al*. 2010). As mentioned before, an increase in voltage is related to the fiber's stretching and diameter reduction (Dzenis 2004).

Homogeneous microfibers were observed when an injector-collector distance of 20 cm was used (Fig. 5), though flawless smooth fibers were only achieved when a manufacturing voltage of 26 kV was used. Thus, the latter and the former were selected as the optimal manufacturing conditions for these experimental membranes. Smooth homogeneous microfibers (constant diameter) were expected as the outcome of electrospinning membrane manufacturing (Li *et al*. 2015).

Table 2 shows a summary of the morphological analysis of manufactured membranes with electrospinning and its respective fabrications conditions. The fabrication variables and morphological features of fibers were observed using SEM.

Table 2. Morphology of Electrospinning Membranes and Its Fabrication Conditions

Injector-collector (cm) Distance	Voltage (kV)	Morphology
15	22	Flaws
	24	Flaws
	26	Microfibers – Flaws
18	22	Flaws
	24	Microfibers – Flaws
	26	Microfibers – Flaws
20	22	Heterogeneous fibers
	24	Microfibers
	26	Plain fibers

Microfiber diameter was measured in membranes with flawless fiber formation (Fig. 6). Following the Xie *et al.* (2014) method, 100 random diameter measurements were taken using the ImageJ software so that an average could be estimated along with a representative histogram (Xie *et al*. 2014). Figure 6 shows the manufacturing conditions of the studied membranes corresponded to an injector-collector distance of 20 cm and voltages of 22 kV, 24 kV, and 26 kV.

Fiber diameter variation is shown in Fig. 6. When the manufacturing voltage was set to 22 kV, microfibers exhibited an average diameter of 3.81 µm, which was higher than the 3.50 µm that was obtained for 24 kV and 26 kV. As stated before, increasing voltages implied stronger electric fields and increased microfiber stretching, and therefore fiber diameter reduction. However, when membranes were manufactured at 24 kV and 26 kV, their composing fibers showed no further diameter reduction; hence it can be argued that the microfiber reaches its maximum stretching at 24 kV and remains constant for higher voltages such as 26 kV, which was similar to results from Megelski *et al*. (2002). Smooth fibers were achieved when membranes were produced using a 1%, 3%, and 5% MCC addition.

The fiber in the membranes manufactured with MCC are shown in Fig. 7, where MCC with significant different sizes were observed. Furthermore, a significant amount were attached to the fibrillar surface. A favorable particle dispersion along each of the fibers was observed, with proportional separation distances among the fibers.

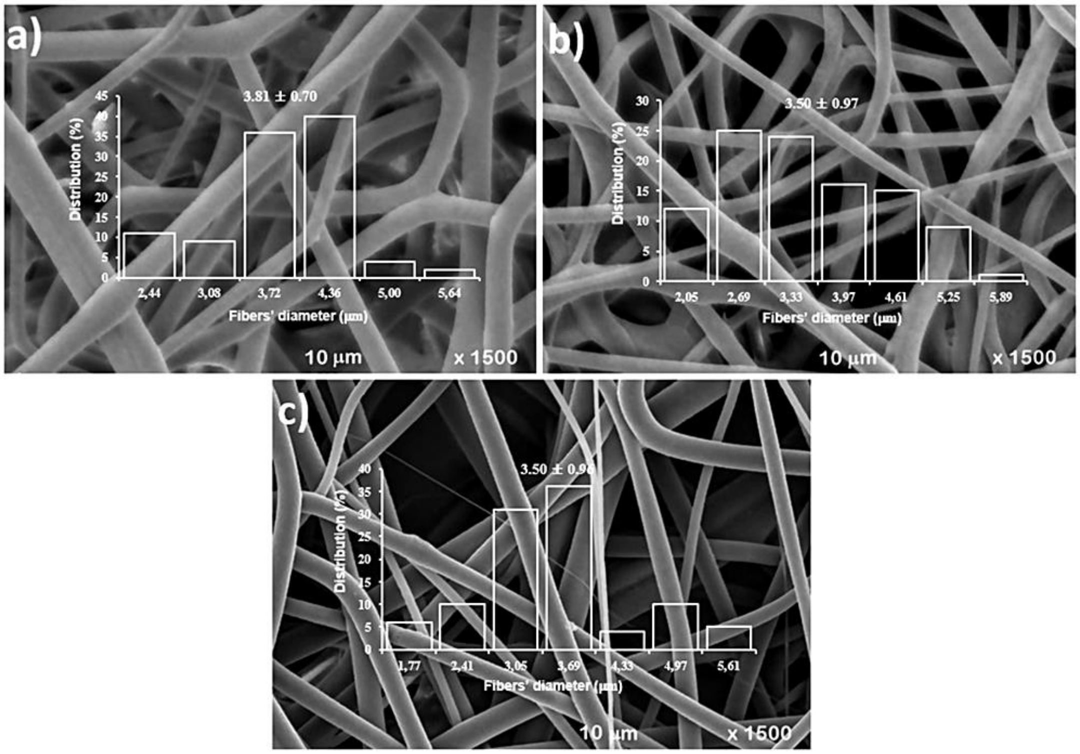

Fig. 6. Microfibers' diameter distribution in membranes based on PLA, manufactured with 20 cm injector-collector distance and fabrication voltages: a) 22 kV, b) 24 kV, and c) 26 kV

The MCC particles, with similar dimensions compared to the fiber diameter, were attached to the fibers. Moreover, MCC of larger sizes may have been transported to the collector during the manufacturing process. The MCC whose size exceeded the microfiber transportation capacity; *i.e.*, those who could not be transported to the collector during the manufacturing process, could be part of the unfinished fibers that became residual drops during the electrospinning process, due to their size and weight.

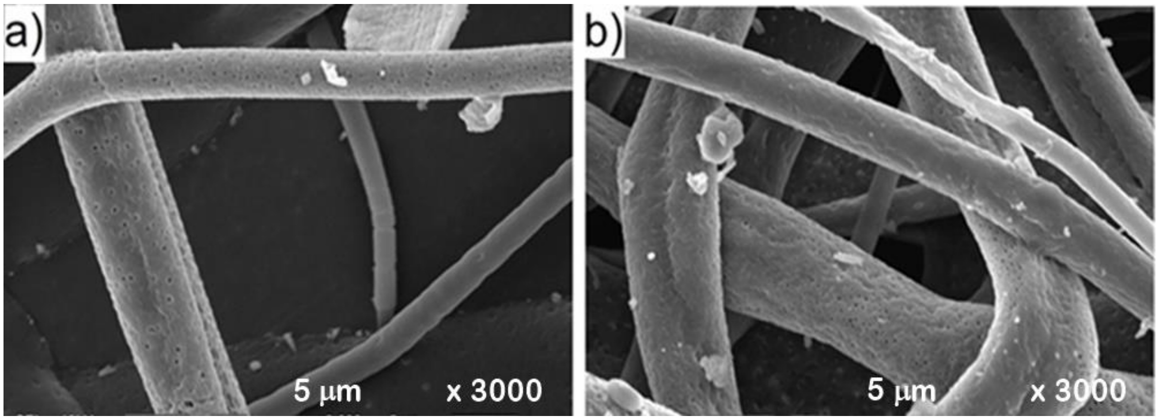

Fig. 7. PLA microfibers reinforced with MCC: a) addition of 1% MCC and b) 3% MCC

Quick solvent vaporization left micropore formation within the fiber's body (Fig. 8); the manufacturing voltage during the electrospinning process triggered the solvent dissipation, *i.e.*, separation from the polymer. Chloroform-acetone solvents used for polymer dilution had a high degree of volatility that along with the manufacturing voltage promoted the solvent's vaporization, which allowed pores formation; similar observations were reported by Buschle *et al*. (2007) and Li *et al.* (2015).

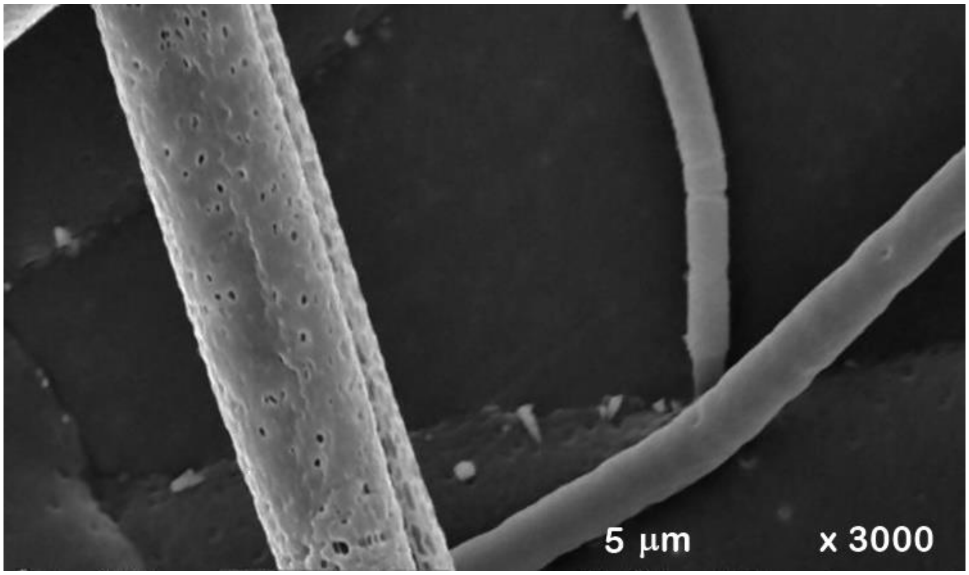

Fig. 8. Porosity in the microfiber's structure

Mechanical Analysis

Membranes with smooth fiber surface, with MCC addition (1%, 3%, and 5%) and manufactured at an injector-collector distance of 20 cm and 22 kV, 24 kV, and 26 kV voltages, were subjected to a tensile strength and tear propagation resistance testing. This guarantees smooth fibers and membranes, without non-desirable defects, for mechanical properties (Dzenis 2004).

Table 3. ANOVA and p-Values for the Response Variables for Tensile Resistance and Tear Propagation Resistance

Factor	**p*-Value = 0.05**	
	Tensile Strength (MPa)	**Tear Resistance (N)**
Model	< 0.0001	< 0.0001
A % MCC	< 0.0001	< 0.0001
B Voltage	0.0078	< 0.0001
AB	< 0.0001	< 0.0001
R^2	0.8826	0.7662
R^2 - adjusted	0.8557	0.7126
Note: *p-Value < 0.05 indicated that the model was significant; *p-Value > 0.05 indicated that the model was not significant		

The tensile strength results, as well as tear resistance, showed that the p-value was < 0.005, (Table 3), indicating that the model was significant. The normal probability of residuals for the response variables agreed with the normality assumption. Moreover, no significant changes were observed, nor outlier data from the samples. The variability proportion of each response was explained by the statistical model through the R^2 value. It was also observed that in the adjusted R^2 value, the number of factors present in the model was correct, which confirmed the validity of the ANOVA test. For both response variables, the percentage of MCC and manufacturing voltage and their interactions were significant.

Tensile Strength

The membrane's tensile tests are shown in Fig. 9. Manufactured membranes with MCC addition featured a better performance against tensile stress compared to those without MCC. The increase of mechanical properties under tensile conditions could be a consequence of the MCC reinforcement and the potential adhesion between the PLA matrix and MCC bond that helps to better transfer stress.

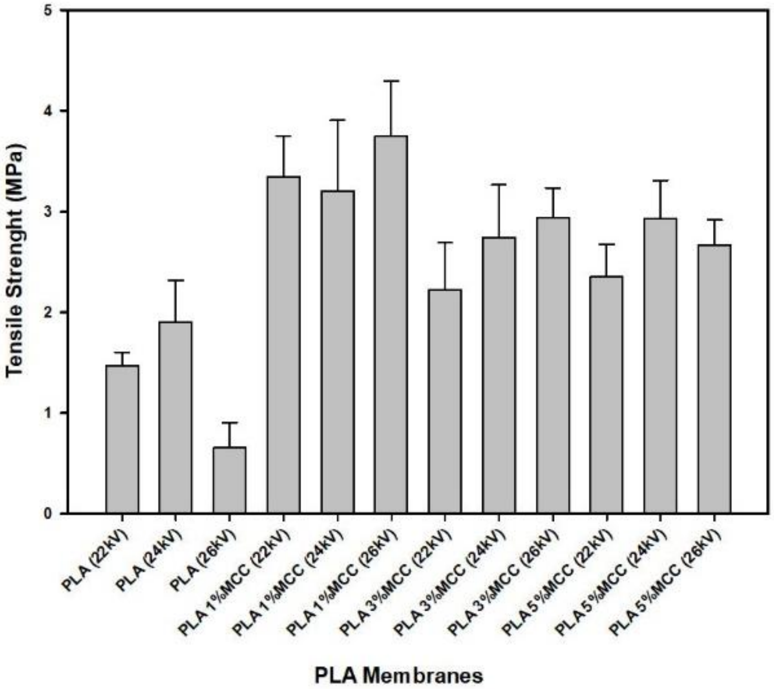

Fig. 9. Tensile strength results; mean value and 95% confidence interval

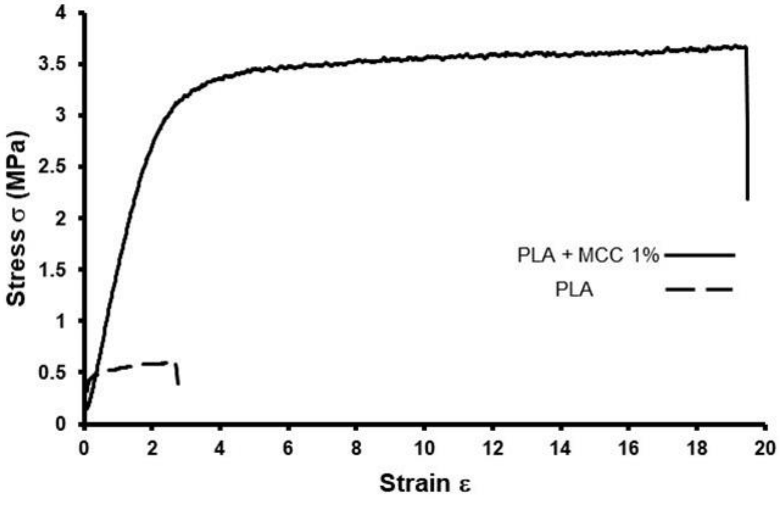

Fig. 10. Stress-strain curves for PLA and PLA + MCC 1% membranes, manufactured at 26 kV and 20 cm injector-collector distance

Figure 10 shows the stress-strain behavior of the fabricated membranes based on PLA with 1% MCC, 20 cm injector-collector distance, and 26 kV. A significant change was observed in the mechanical properties due to the MCC addition. Table 4 shows the results of the tensile strength and strain during the test.

Table 4. Tensile Strength, Percentage of Elongation (ε), and Tear Resistance of the Membranes

Solution	Injector-collector (cm) Distance	Voltage (kV)	Tensile Strength		ε		Tear Resistance	
			MPa	SD	%	SD	N	SD
PLA	20	22	1.47	0.21	2.83	1.1	0.23	0.06
		24	1.99	0.19	3.15	0.93	0.20	0.05
		26	0,65	0.2	3.39	1.06	0.19	0.06
PLA + MCC 1%	20	22	3.34	0.65	19.12	3.92	0.34	0.06
		24	3.2	1.13	40.18	7.82	0.45	0.10
		26	3.75	0.87	19.98	0.19	0.40	0.07
PLA + MCC 3%	20	22	2.22	0.74	15.42	4.38	0.37	0.10
		24	2.74	0.84	16.56	0,81	0.34	0.06
		26	2.94	0.47	49.58	5.76	0.65	0.11
PLA + MCC 5%	20	22	2.35	0.51	16.23	2.00	0.45	0.07
		24	2.93	0.6	22.63	0.15	0.34	0.10
		26	2.67	0.4	23.19	3.69	0.52	0.09

*SD: standard deviation

Nevertheless, it was observed that 1% MCC performed better than 3% and 5% MCC addition. According to Pirani *et al.* (2013) and Abdulkhani *et al.* (2015), an increase in the amount of particles in the membrane may be related to a decreasing of the tensile properties of the material. When the MCC addition is greater than 1%, particles tend to fill a greater surface area, being able to agglomerate or occupy spaces into the polymeric matrix (Pirani *et al.* 2013; Abdulkhani *et al*. 2015). Additionally, from a theoretical point of view, a smaller diameter resulted in a greater number of fibers and consequently higher tensile resistance. However, in this case, the size of MCC was not homogeneous, which could have caused a variation in the mechanical behavior. Table 5 shows the percentage of increasing mechanical properties in tensile and tear in the PLA membranes reinforced with MCC and PLA membranes without reinforcement.

Table 5. Percentage Increase in Tensile and Tear Resistance

Fabrication (kV)	PLA	Percentage Increase in Tensile Strength (%)			Percentage Increase in Tear (%)		
		PLA + MCC 1%	PLA + MCC 3%	PLA + MCC 5%	PLA + MCC 1%	PLA + MCC 3%	PLA + MCC 5%
22	1.47	127	51	59	47	60	95
24	1.99	60	37	47	125	70	70
26	0.65	476	352	310	110	242	173

Tear Propagation Resistance

The material behavior under a tear propagation resistance test (Fig. 11) showed a positive reinforcing contribution compared with the pure PLA membranes (Table 4). Moreover, it was observed that increased MCC addition contributed to a tearing resistance increment (Table 5).

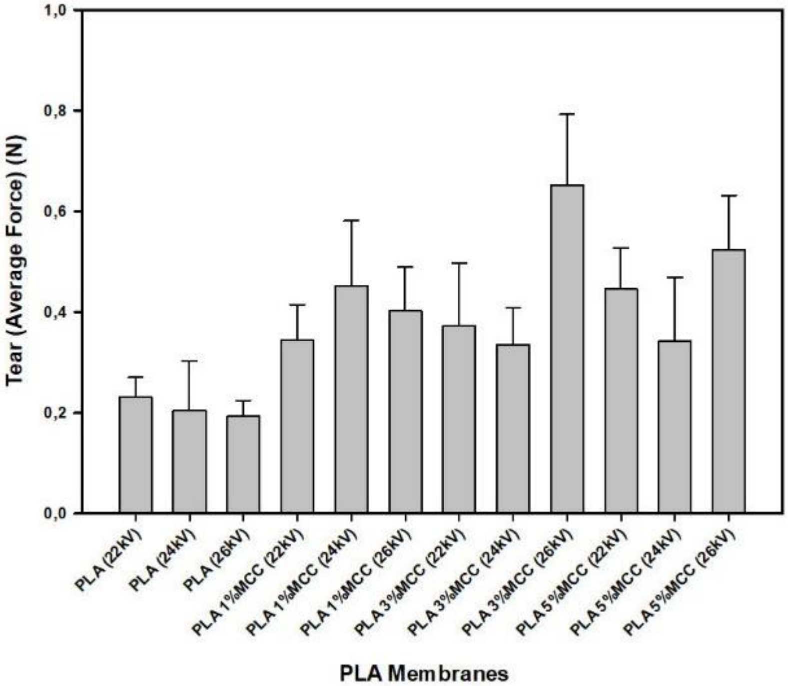

Fig. 11. Tear strength results; mean value and 95% confidence interval

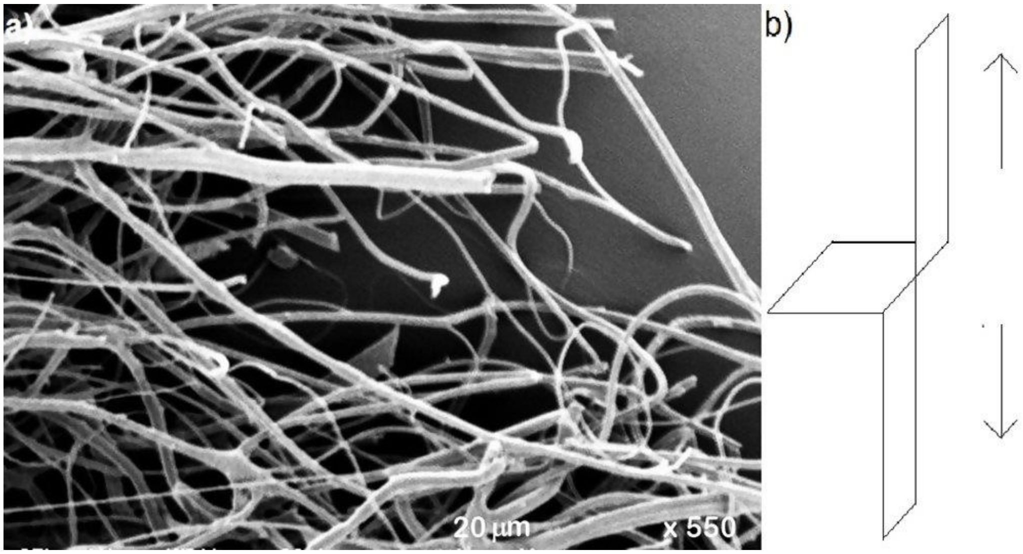

Fig. 12. a) SEM Image of the break zone after the tear resistance test and b) test specimen during the tear resistance test

Figure 12a shows the fracture zone of the material where there was evidence of a large number of microfibers in different layers and the presence of MCC in the fibers, which increased its mechanical properties, making the material difficult to fracture. In contrast, and due to the MCC particle size variability, there may have been some fibers bonded to the larger particles, which may have contributed to the resistance to tearing. Figure 11b shows the sample position for the tear propagation resistance test, where it was evident that the fracture zone was equivalent to the thickness of the sample.

CONCLUSIONS

1. This study demonstrated that the addition of 1%, 3%, and 5% MCC particles acted as PLA reinforcement, improving the mechanical properties of the final membrane.
2. For some fabrication conditions (MCC 1% and 26 kV), the reinforced membranes showed an increase of 476% in tensile strength compared to the pure PLA membranes.
3. Moreover, it was observed that when the added MCC was greater than 1% the tensile mechanical properties decreased. In contrast, regarding tearing stresses results, adding more MCC enhanced the material's properties. Finally, MCC is a material that may be used in membranes that can be utilized in the food packaging industry.

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REFERENCES CITED

Abdulkhani, A., Hosseinzadeh, J., Dadashi, S., and Mousavi, M. (2015). "A study of morphological, thermal, mechanical and barrier properties of PLA based biocomposites prepared with micro and nano sized cellulosic fibers," *Cellulose Chemistry and Technology* 49, 597-605.

Ardizzone, S., Dioguardi, F. S., Mussini, T., Mussini, P. R., Rondinini, S., Vercelli, B., and Vertova, A. (1999). "Microcrystalline cellulose powders: Structure, surface features and water sorption capability," *Cellulose* 6(1), 57-69. DOI: 10.1023/A:1009204309120

ASTM D882-12 (2012). "Standard test method for tensile properties of thin plastic sheeting," ASTM International, West Conshohocken, PA.

ASTM D1938-14 (2014). "Standard test method for tear-propagation resistance (trouser tear) of plastic film and thin sheeting by a single-tear method 1," ASTM International, West Conshohocken, PA

Bhardwaj, N., and Kundu, C. (2010). "Electrospinning: A fascinating fiber fabrication technique," *Biotechnology Advances* 28(3), 325-347. DOI: 10.1016/j.biotechadv.2010.01.004

Buschle, G., Cooper, J., Xie, Z., Wu, Y., Waldrup, J., and Ren, X. (2007). "Release of antibiotics from electrospun bicomponent fibers," *Cellulose* 14(6), 553-562. DOI: 10.1007/s10570-007-9183-3

Das, K., Ray, D., Bandyopadhyay, N. R., and Sengupta, S. (2010). "Study of the properties of microcrystalline cellulose particles from different renewable resources by XRD, FTIR, nanoindentation, TGA and SEM," *Journal of Polymers and the Environment* 18(3), 355-363. DOI: 10.1007/s10924-010-0167-2

Dong, Y., Chaudhary, D., Haroosh, H., Sharma, V., and Thomas, B. (2011). "Functionally electrospun PLA/tubular clay nanocomposites for the potential application of drug delivery," in: *Nineteenth International Conference on Processing and Fabrication of Advanced Materials (PFAM XIX)*, University of Auckland, Auckland, New Zealand, pp. 836-846.

Dzenis, A. (2004). "Spinning continuous fibers for nanotechnology spinning continuous fibers for nanotechnology," *Science* 304(5679), 1917-919. DOI: 10.1126/science.1099074

Frenot, A., and Chronakis, I. (2003). "Polymer nanofibers assembled by electrospinning," *Current Opinion in Colloid and Interface Science* 8, 64-75. DOI: 10.1016/S1359-0294(03)00004-9

Gurunathan, T., Mohanty, S., and Nayak, S. (2015). "A review of the recent developments in biocomposites based on natural fibres and their application perspectives," *Composites Part A: Applied Science and Manufacturing* 77, 1-25. DOI: 10.1016/j.compositesa.2015.06.007

Haafiz, M. K., Hassan, A., Zakaria, Z., Inuwa, I. M., Islam, M. S., and Jawaid, M. (2013). "Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose," *Carbohydrate Polymers* 98(1), 139-145. DOI: 10.1016/j.carbpol.2013.05.069

Haroosh, H. J., Chaudhary, D. S., and Dong, Y. (2011). "Effect of solution parameters on electrospun PLA/PCL fibers," in: *Chemeca 2011: Engineering a Better World*, Sydney, Australia, pp. 1525-1534.

Kang, H., Zhu, Y., Jing, Y., Yang, X., and Li, C. (2010). "Fabrication and electrochemical property of Ag-Doped SiO_2 nanostructured ribbons," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 356(1–3), 120-125. DOI: 10.1016/j.colsurfa.2010.01.009

Ki, C. S., Baek, D. H., Gang, K. D., Lee, K. H., Um, I. C., and Park, Y. H. (2005). "Characterization of gelatin nanofiber prepared from gelatin-formic acid solution," *Polymer* 46(14), 5094-5102. DOI: 10.1016/j.polymer.2005.04.040

Li, Y., Lim, C. T., and Kotaki, M. (2015). "Study on structural and mechanical properties of porous PLA nanofibers electrospun by channel-based electrospinning system," *Polymer* 56, 572-580. DOI: 10.1016/j.polymer.2014.10.073

Mathew, A. P., Oksman, K., and Sain, M. (2005). "Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC)," *Journal of Applied Polymer Science* 97(5), 2014-2025. DOI: 10.1002/app.21779

Mathew, A. P., Oksman, K., and Sain, M. (2006). "The effect of morphology and chemical characteristics of cellulose reinforcements on the crystallinity of polylactic acid," *Journal of Applied Polymer Science* 101(1), 300-310. DOI: 10.1002/app.23346

Megelski, S., Stephens, J. S., Bruce, C. D., and Rabolt, J. F. (2002). "Micro- and nanostructured surface morphology on electrospun polymer fibers," *Macromolecules* 35(22), 8456-8466. DOI: 10.1021/ma020444a

Mitchell, G. R. (2015). *Electrospinning Principles, Practice and Possibilities*, RSC Polymer Chemistry Series, Cambridge, United Kingdom. DOI: 10.1039/9781849735575-FP001

Mohanty, A. K., Misra, M., and Hinrichsen, G. (2000). “Biofibres, biodegradable polymers and biocomposites: An overview,” *Macromolecular Materials and Engineering* 276–277, 1-24. DOI: 10.1002/(SICI)1439-2054

Murphy, C. A., and Collins, M. N. (2016). “Polylactic acid biocomposite filaments with improved mechanical properties,” *Society of Plastics Engineers* Online, 1-3. DOI: 10.2417/spepro.006652

Niaounakis, M. (2006). *Biopolymers: Applications and Trends*, Elsevier Inc., Plastics Design Library (PDL), Chadds Ford, PA, USA.

Petersson, L., and Oksman, K. (2006). “Biopolymer based nanocomposites: Comparing layered silicates and microcrystalline cellulose as nanoreinforcement,” *Composites Science and Technology* 66(13), 2187-2196. DOI: 10.1016/j.compscitech.2005.12.010

Pirani, S., Abushammala, H., and Hashaikeh, R. (2013). “Preparation and characterization of electrospun PLA/nanocrystalline cellulose-based composites,” *Journal of Applied Polymer Science* 130(5), 3345-3354. DOI: 10.1002/app.39576

Ramakrishna, S., Fujihara, K., Teo, W., Lim, T., and Ma, Z. (2005). *An Introduction to Electrospinning and Nanofibers*, World Scientific Publishing Co., Ton Tuck Link, Singapore. DOI: 10.1142/5894

Rezaei, A., Nasirpour, A., and Fathi, M. (2015). “Application of cellulosic nanofibers in food science using electrospinning and its potential risk,” *Comprehensive Reviews in Food Science and Food Safety* 14(3), 269-284. DOI: 10.1111/1541-4337.12128

Serna, C., de Rodríguez, S. A., and Albán, A. (2011). “Polylactic acid (PLA): Properties and applications,” *Revista Ingeniería y Competitividad* 5(1), 16-26. DOI: 0123-3033

Stanger, J., Tucker, N., and Staiger, M. (2005). *Electrospinning*, Smithers Rapra Technology, Shawbury, United Kingdom.

Wu, Y., Dong, Z., Wilson, S., and Clark, R. L. (2010). “Template-assisted assembly of electrospun fibers,” *Polymer* 51(14), 3244-3248. DOI: 10.1016/j.polymer.2010.04.039.

Xie, J., Mao, H., Yu, D. G., Williams, G. R., and Jin, M. (2014). “Highly stable coated polyvinylpyrrolidone nanofibers prepared using modified coaxial electrospinning,” *Fibers and Polymers* 15(1), 78-83. DOI: 10.1007/s12221-014-0078-2

Zhenyu, L., and Ce, W. (2013). *One-Dimensional Nanostructures Electrospinning Technique and Unique Nanofiber*, Springer Heidelberg, New York, USA. DOI: 10.1007/978-3-642-36427-3

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