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Poly(lactic acid) has been electrospun into submicron fibers with embedded cassava starch matrix. The fibers had average fiber diameters between 140 and 680 nm. The starch content varied from 10 to 20% in total solids. Water contact angles were measured on sheets of these fiber materials and correlated with the fiber size and starch content. Water contact angles varied from 80 to 120° which shows that the fiber composition can control the mat properties from hydrophilic to hydrophobic. The results also showed variation in the average fiber diameters alone did not always affect sheet wettability. These results show the importance of the relationship between the electrospun fiber sheet topography and material composition to the wettability of polysaccharide electrospun nanofibers.

Keywords: polymer composite; electrospinning; poly(lactic acid); starch; surface

1. Introduction

Electrospun fibers have been widely studied for use in a number of applications due to the process simplicity, the ability to control fiber characteristics, and wide range of materials that are spinnable by this technique.[1–2] Biomedical applications in particular take advantage of electrospun nanofibers for use such as tissue scaffold, wound dressing, and drug delivery.[3] For these applications, control of the surface wettability, biocompatibility, and biodegradation are significant factors.[4] The concept is to make tissue scaffold articles to replace or augment the natural extracellular matrix, when body healing function is unable to perform efficiently as in situations of drastic skin burn, trauma wound, and diabetic wound. By introducing electrospun tissue scaffold as a platform for targeted cells to adhere and grow, once cells have been proliferated and ready for implant, the article is then transferred to the target wound and the scaffold undergoes a disintegration period and is directed out of the body. Medicine and other materials can also be easily mixed to create electrospun composite nanofibers, thus making it a good candidate for medical applications.[4]

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Tissue engineering is an interdisciplinary field that can be viewed from different perspectives. It has been reported by many papers of the specificity of materials for making tissue scaffold due to material compatibility and intrinsic properties of articles from specific fabrication process.[3,5,6] The selection of the polymer and control of the average fiber diameter are the most common approaches to influence the properties of the electrospun fiber mats. The material of nanofibers for medical application, mainly tissue scaffold application, mostly involves limited type of synthetic biodegradable polymers such as poly(lactic acid) (PLA), polycaprolactone, and poly(glycolic acid) due to the approval from the Food and Drug Administration to be used in commercialized products. But the development in the field is not limited to these synthetic materials, natural biodegradable polymers, such as composites of chitosan, collagen, and cellulose, were reported to be successfully house targeted by cells on composite substrates of these materials. As previously stated about the specificity of the material in this application, methods to adjust article properties after the material has been selected are article post-treatment and methods of fabrication, which result in specific article physical structure. [7–9] Options of physical modification of electrospun fiber sheet are varying fiber diameter and collection time of electrospun fibers on substrate. These factors affect sheet thickness and roughness that has been reported to have an effect on surface wettability,[10] one of many properties that is greatly important for tissue scaffold applications.[11]

For the purpose of optimization, understanding the effect of processing parameter and material composition to article properties, such as wetting behavior and biotoxicity, are important, as it is unclear about the optimum wetting behavior of tissue scaffold that enhance the ability for cell-growing mechanism. In author's previous work, a broader range of composite nanofiber diameter and characteristics between starch and poly(lactic acid) were created [12] and evaluation on biotoxicity and cell-growing behavior were performed.[13] Both human fibroblast and mouse fibroblast cells were successfully grown on composite substrate. The wetting behavior of the electrospun mat can be quantified through CA-Measurement. The dependence of water contact angle on polymer/composite composition and the fiber diameter have been noted in the literature [6,14], but a systematic study has not been reported. This paper presents results of an experimental study of water contact angles from electrospun PLA and cassava starch (CS) composite fiber mats through fabrication conditions. Information from this investigation will be used for tailoring tissue scaffold surfaces in order to enhance and control cell-growing behavior (Figure 1).

2. Experimental

2.1. Experimental setup

A single nozzle electrospinning process was used to make the fiber mats in this study. A high-voltage power supply (Gamma High Voltage, ES60P-10 W) was attached to a metal syringe with gauge number 24, as metal nozzle, above a metal collector at various gap distances. Polymer solutions were pushed to a metal nozzle by a mechanical pump (Multi-Phaser, NE-4000).

2.2. Material

PLA in pellet form (Nature Works LLC, PLA 2002D) and commercial CS powder were used as the polymer and starch particles. Three analytical grade liquids were used for

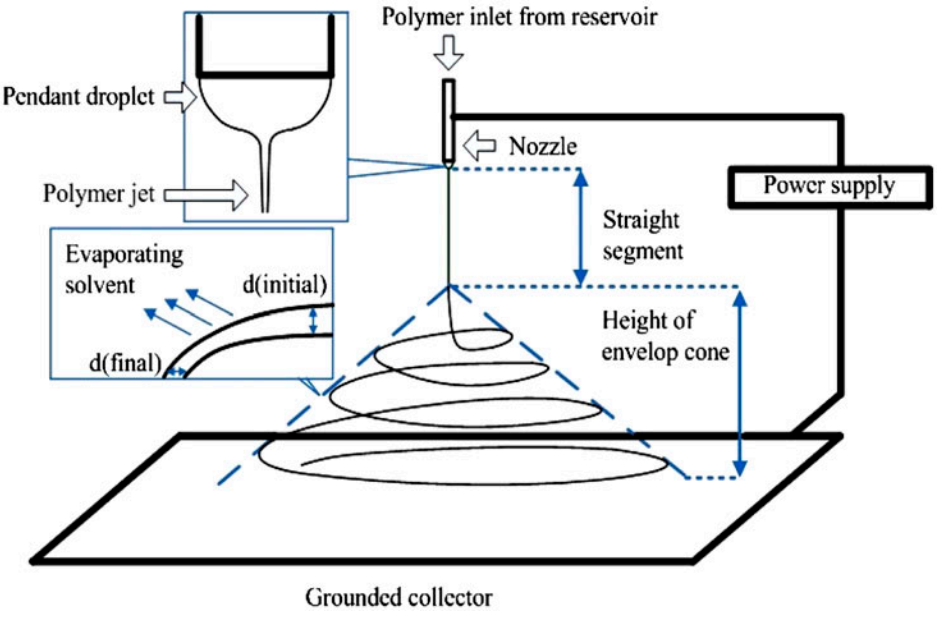

Figure 1. Single nozzle electrospinining schematic diagram. [2]

the solvents: dichloromethane (DCM) for dissolving PLA, dimethylsulfoxide (DMSO) for dissolving CS, and methanol as a conjugant to blend the DCM and DMSO solutions into a homogeneous electrospinning solution.

2.3. Solution preparation method

PLA/DCM and CS/DMSO solutions were prepared separately by adding solvent at specific amounts as indicated in Table 1, in concentrations indicated by mass in grams of solid per 100 ml of solvent. Homogeneous spinnable mixed solutions were achieved by mixing solutions and conjugated solvent in a vortex mixer [12] at room temperature for 2 min.

2.4. Measurement and characterization

Scanning electron microscope (SEM, JEOL, JSM-6400) images were used to measure the average fiber diameters by collecting the fiber diameter and length of each individual fiber that appears in SEM images and applying log normal length weight distribution to calculate the average fiber diameter and frequency distribution.[15,16]

Water (CA-Measurement, DataPhysics, DataPhysics OCA20) was used to determine water contact angle or wettability of fiber sheet of different conditions by using 1 µl drop of distilled water. The measurements were taken on more than five replicates and averaged.

Atomic force microscope (AFM, SII, SPI3800N/SPA400) was used to measure surface roughness of electrospun fiber sheet and reported as a roughness root mean square, R_{ms}.[17] Not less than five replicates of measurement from 10×10 µm scanning area [18] were used for the analysis.

Table 1. Solutions preparation and operating conditions.

Solution preparation								
Starch content in total solid	10.7%			12.7%		18.3%		
PLA/DCM (concentration, volume)	25.0% w/v, 1.0 ml			20.0% w/v, 1.0 ml		15.0% w/v, 1.0 ml		
Starch/DMSO (concentration, volume)	1.0% w/v, 2.5 ml			1.0% w/v, 2.5 ml		1.0% w/v, 3.0 ml		
Conjugated solvent (material, volume)	Methanol, 1.0 ml			Methanol, 1.0 ml		Methanol, 1.0 ml		
Resulted formula	A, B, C			D		E, F, G, H		
Operating conditions								
	A	B	C	D	E	F	G	H
Voltage difference (kV)	25.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Nozzle distance to collector (cm)	25.0	25.0	20.0	25.0	25.0	20.0	20.0	25.0
Electric field strength (kV/cm)	1.0	0.8	1.0	0.8	0.8	1.0	1.0	0.8
Polymer flow rate (μl/min)	8.0	10.0	10.0	8.0	8.0	8.0	10.0	8.0
Time period to collect (min)	3.0							

For statistical analysis, a p-value less than 0.050 indicates significant differences among factors were observed.[19]

3. Results and discussion

Electrospun composite nanofibers were fabricated, and their average fiber diameters were determined at least twice to find a representative average fiber diameter for each condition. Then, fiber mats were prepared and randomly selected for water contact angle and surface roughness measurement for a fair comparison. It was found that allowing electrospun fiber to collect on a metal collector for longer times created a sheet of fiber with different surface characteristics.[20] Thus, it was essential to specify the time of fiber collection for each measurement to reduce variations. Electrospun fiber sheet roughness characteristics and water contact angle have been statistically measured and are reported in Table 2.

3.1. Effect of fabrication condition on fiber characteristics

The fabrication conditions of this study were limited to avoid complexity. The key parameters to control the spinnability of electrospun polymer jet, the voltage difference, the polymer flow rate, and the nozzle to collector distance, were adjusted within a limit so that all fibers exhibit smooth and round features as they are common fiber feature for fibrous tissue scaffolds. The study of the fabrication factor controlling the fiber characteristics has been widely studied and documented, but its influence is varied and specific to the type of material. Due to the scope of this work, which aims to evaluate the effect of fiber sheet surface characteristics through wettability by applying statistical tools to assist in interpretation; this study will omit a detailed analysis of fiber fabrication conditions influencing fiber sheet characteristics (Figure 2).

Table 2. Fiber characterization results, average ± error.

	A	B	C	D	E	F	G	H
Starch content (%)	10.7	10.7	10.7	12.7	18.3	18.3	18.3	18.3
Average fiber diameter ($\times 10^2$ nm)	2.8 ± 1.2	3.2 ± 1.5	6.7 ± 2.8	3.0 ± 1.4	1.4 ± 0.5	1.6 ± 0.7	2.5 ± 0.9	2.6 ± 0.8
Apparent water contact angle (degree)	111.0 ± 8.5	102.6 ± 2.7	105.5 ± 6.7	115.4 ± 6.5	105.8 ± 5.6	111.2 ± 2.2	88.0 ± 6.0	91.0 ± 2.5
R_{ms} value ($\times 10^2$ nm)	5.2 ± 2.4	2.2 ± 0.4	2.1 ± 0.7	1.8 ± 0.5	2.5 ± 0.7	1.7 ± 0.5	1.9 ± 0.5	2.1 ± 0.4

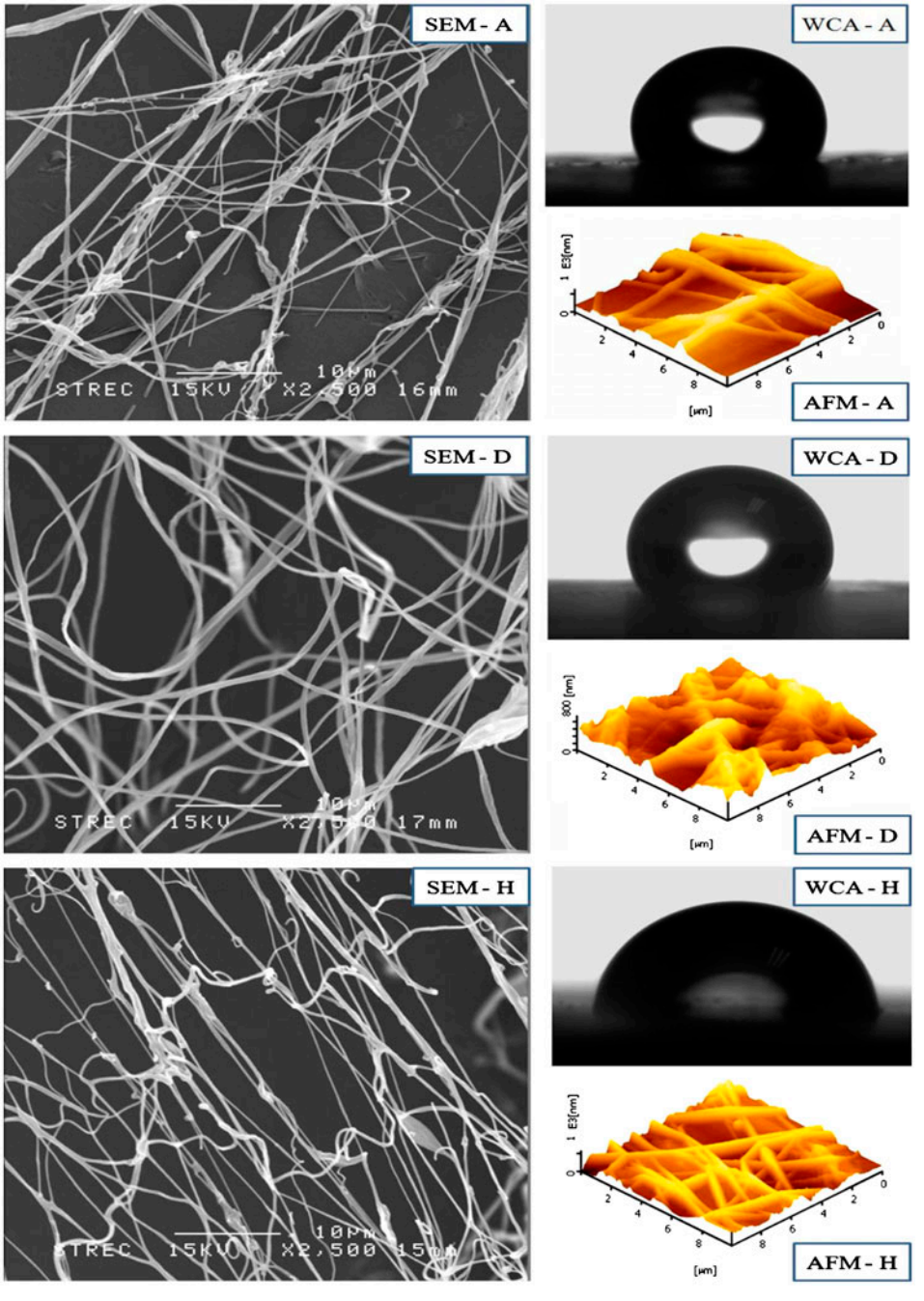

Figure 2. Selected condition of scanning electron micrographs, water contact angle image, and atomic force microscopic images.

3.2. *Effect of fiber characteristic and material composition to wettability*

The group of samples [A, D, G, and H] was compared by one sample *t*-test statistic to determine the difference among samples average fiber diameter. A hypothesis of this test was set that this group had average value of 275 nm as a representative average diameter, $H_0 = 275$ nm. Statistical calculation showed that p-value $= 0.974 > 0.050$ which indicated no evidence of significant differences between average fiber diameters in this group, or the average fiber diameter was statistically equal in size. Therefore, it was possible to use this set of data to evaluate the starch content effect on wettability. Statistical comparison showed significantly different water contact angles between fibers of different amounts of starch, for composite fibers of average fiber diameter within the range of 250–300 nanometer [A, D, G or H], p-value $= 0.000 < 0.050$. This result coincided with other studies reporting that hydrophilic material addition causes water contact angle to decrease.[11,14]

By compiling selected conditions [A, B, C, E, G, and H] into two-stage nested design, starch content was a fixed factor with three average fiber diameters as a random factor for each starch content as shown in Figure 3(A). This diagram was designed to compare group of data with similar starch content to evaluate the influence of fiber diameter on fiber mats wettability.

Statistical analysis showed no significant difference of water contact angle (p-value $= 0.132 > 0.050$), but there was a difference of water contact angle from different average fiber diameters within each starch content group [A–C] and [E, G, H] as both yield p-value $= 0.000 < 0.050$ analysis was contradictionary in itself but can be explained by selecting new groups of data and studying the effect of average fiber diameter separately. At starch content 10.65% in total solid [A–C], there was no significant difference between water contact angles (p-value $= 0.105 > 0.050$) when varying

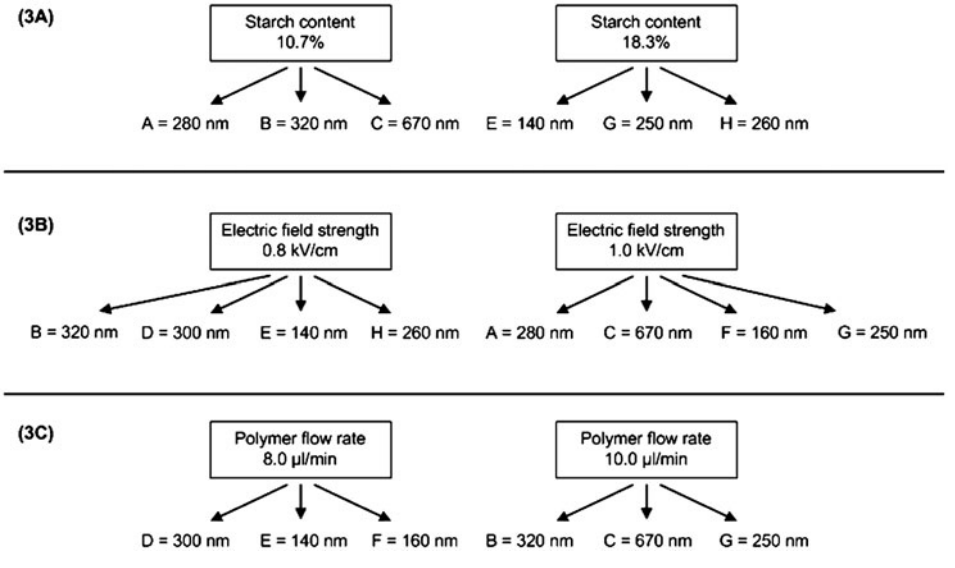

Figure 3. Two-stage nested design data compilation diagram with average fiber diameter (A) group with similar starch content (B) group with similar electric field strength (C) group with similar polymer flow rate.

average fiber diameters. At starch content 18.27% in total solid [E, G, and H], there was significant difference between water contact angle for varying average fiber diameter (p-value = 0.000 < 0.050). This indicated that the effect of fiber diameters on water contact angles could be recognized as it was statistically significant for certain starch content.

3.3. *Effect of fiber characteristic and material composition to fiber sheet characteristic*

It is well known how electrospinning process operating condition controls dimension and characteristic of electrospun fibers.[1] Studies of voltage difference and polymer mass flow rates showed a direct effect on fiber characteristic through the relation between electric current formed from ionic conduction and polymer solution viscosity and electric resistivity.[21,22]

As the electric field strength draws charged liquid jet toward a collector, differences in magnitude might affect the amount of fiber and fiber sheet characteristics. By compiling all data [A through H] into two-stage nested design pattern as shown in Figure 3(B) where electric field strength magnitude was a fixed factor and each have four random factors of average fiber diameters, statistical analysis showed no significant difference of R_{ms} between groups of electric field strength, p-value = 0.526 > 0.050. This diagram was designed to compare group of data with similar electric field strength to evaluate the influence of fiber diameter on fiber mats surface roughness. It can be concluded that there was statistically significant difference of R_{ms} between average fiber diameters p-value = 0.000 < 0.050.

While higher polymer solution delivery rate to nozzle causes change in fiber size, this might be an indirect effect to fiber sheet surface characteristic. To verify this assumption, similar compilation of data as to the study of electric field strength in case [B–G] where polymer solution flow rate was a fixed factor and three average fiber diameters, was nested to form two-stage nested design pattern, as shown in Figure 3(C). This diagram was designed to compare group of data with similar polymer flow rate to evaluate the influence of fiber diameter on fiber mats surface roughness. Statistical results showed no significant difference of R_{ms} between groups of polymer mass flow rate to nozzle, p-value = 0.946 > 0.050.

Difficulty of separating the effect of operating condition from their influence on fiber characteristic and fiber sheet characteristic could be identified by using statistical tools. Our studies showed that these range of operating conditions and material used did not have significant influence on fiber sheet characteristics as it had been assumed earlier.

4. Conclusion

Physical modification of electrospun fiber does not always affect fiber sheet wettability, which was determined by measuring water contact angle. It was found that at a certain range of materials combination, fiber diameter does not have a statistically significant effect on water contact angle. It is important to understand these effects in order to give an accurate adjustment to product properties and use as a guideline for future studies of wettability of electrospun fiber sheets.

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