Electrospinning Process and Structure Relationship of Biobased Poly(butylene succinate) for Nanoporous Fibers

Connor J. Cooper,†‡ Amar K. Mohanty,*,†‡ † and Manusri Misra*,†‡†

†Bioproducts Discovery and Development Centre, Department of Plant Agriculture, University of Guelph, Crop Science Building, 50 Stone Rd E, N1G-2W1 Guelph, Ontario, Canada
‡School of Engineering, University of Guelph, Thornbrough Building, 50 Stone Rd E, N1G-2W1 Guelph, Ontario, Canada

ABSTRACT: Biobased poly(butylene succinate) (BioPBS) was electrospun to create hierarchical, highly porous fibers. Various grades of BioPBS were dissolved in one of the three solutions: chloroform, a cosolvent system of chloroform/N,N-dimethylformamide (DMF), or chloroform/dimethyl sulfoxide (DMSO). These solutions were then electrospun at room temperature to produce nanoporous micron-sized fibers. The variables investigated were the solvent system used, grade of BioPBS, concentration of BioPBS, applied voltage, and the distance between the electrodes. In determining the optimal solution and electrospinning conditions, it was found that solution properties such as the solvent system, the grade of BioPBS, and the concentration of BioPBS had a significant effect on the fiber morphology. A chloroform/DMSO cosolvent system resulted in less defect defects among fibers compared to those produced from chloroform/DMF systems, regardless of the BioPBS grade. An increase in BioPBS concentration resulted in the reduction of bead defects, which at 15 (% w/v) resulted in bead-free uniform fibers. Increasing BioPBS concentration also increased the porosity of the fibers while reducing the pore size. Dynamic mechanical analysis showed that the reduction of bead defects resulted in increased tensile strength and Young’s modulus of the electrospun fibrous nonwoven mat. The results of this study show that electrospun BioPBS fibers have high porosity at the micro- and nanoscale, resulting in a hierarchical structure that has sufficient mechanical properties for potential applications in wound healing and soft tissue engineering.

INTRODUCTION

Biodegradable aliphatic polyesters have seen an increase in popularity across a wide variety of fields, due in part to the increases in global carbon dioxide levels and immense amounts of plastic waste. Polymers such as poly(lactic acid) (PLA), polycaprolactone (PCL), poly(glycolic acid) (PGA), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and poly(butylene succinate) (PBS) are in high demand for biomedical applications such as implant devices, tissue scaffolds, and wound dressings. These polymers are ideal for these applications because of their biodegradability, biocompatibility, and high capacity for drug loading. Electrospinning has become one of the most popular methods for the preparation of micro- to nano-sized fibrous polymers. However, the electrospinnability of BioPBS, and more importantly, the relationships between process parameters and the resulting morphology and mechanical properties have not been fully described in previous research. PBS is produced by the esterification of succinic acid with 1,4-butanediol; the current industrial process utilizes approximately 54% biobased content in the production of PBS in the form of biosuccinic acid (BioSA). However, with further industrialization, BioSA can be used to produce 1,4-butanediol, which would lead to 100% biobased PBS.

Nanotechnology is a promising multidisciplinary field that combines the state-of-the-art technology with cutting-edge scientific research. Among the many methods utilized to produce materials at this scale, none have seen more widespread use than electrospinning. Electrospinning is a simplistic, cost-effective, and an adaptable method that uses an electrically charged jet of polymer solution to produce fibers with diameters ranging from micro- to nanometers. A typical electrospinning setup involves a voltage source (1−30 kV), a needle or capillary, a syringe pump, and a grounded surface for fibers to be collected on. Electrospinning is capable of producing a wide range of morphologies including hollow tubes, highly aligned fibers, and even 3D shapes. This is especially advantageous in the production of biomaterials: by adjusting solution properties, electrospinning parameters, or ambient conditions, tailorable hierarchical structures can be produced. Morphological and mechanical properties can then be matched to the desired biological environment, from advanced wound dressings to load bearing implants that encourage cell growth and osseointegration.

Received: February 23, 2018
Accepted: April 17, 2018
Published: May 23, 2018
Many biomedical applications require highly porous materials, which allows for the proper integration of cells and blood vessels, transportation of nutrients and wastes, or increased drug loading capacity.\(^\text{19}\) Materials chosen for these applications should mimic the biological environment they are meant to interact with or replace. Biological environments are often complex and hierarchical in nature with different macro-, meso-, and nanoscale structures.\(^\text{11}\) Generally, mesopores should be between 100 and 400 \(\mu m\) but can vary greatly depending on the type of tissue in question.\(^\text{11}\) Nanopores between 10 and 1000 nm are required to facilitate the transportation of nutrients and metabolic wastes.\(^\text{11}\) It is advantageous for a material to match the hierarchical structure of the biological environment it is to be used in, to improve its biocompatibility. Biodegradable and biocompatible polymers such as PCL, PLA, PGA, and their co-polymers have been successfully electrospun and are used in various biomedical applications.\(^\text{12–17}\) Similarly, the electrospinnability of PBS has also been investigated.\(^\text{18–22}\) PBS is soluble in various solvents such as chloroform (CHCl\(_3\)), dichloromethane (DCM), 1,1,1,3,3,3-hexafluoro-2-propanol, and \(\sigma\)-chlorehobenzene.\(^\text{23–25}\) However, PBS has only been successfully electrospun in CHCl\(_3\) or DCM with the addition of other cosolvents.\(^\text{18–22}\)

As PBS is often in solution in dilute concentrations, the solvent used has a significant influence on the overall solution properties, such as surface tension, boiling point, conductivity, and permittivity.\(^\text{18}\) The resulting morphology of the fibers is subsequently affected by the choice of the solvent and ambient conditions.\(^\text{26,27}\) Wannatong et al.\(^\text{28}\) investigated the effects of solvent properties on the resulting morphology of electrospun polystyrene fibers. Fiber diameter was found to decrease with increasing boiling points and density of the solvent, whereas the throughput increased with increased dielectric constant and dipole moment.\(^\text{28}\) Jeong et al.\(^\text{19}\) successfully added various cosolvents such as 2-chloroethanol (CE), 3-chloro-1-propanol (3-CP), and 1-chloro-2-propanol (1-CP) to both CHCl\(_3\) and DCM solvent systems. Klairutsamee et al.\(^\text{18}\) electrospun PBS fibers from both \(N\),\(N\)-dimethylformamide (DMF) and methanol. They also investigated the effects of adding an organic salt alkyl ammonium ethyl sulfate (AAES) on the morphology of PBS fibers. They found that the addition of salts to the solution resulted in thinner fibers, dropping from 503 to 373 nm with the addition of 0.25–1 % (w/v) AAES.\(^\text{18}\) In fact, the addition of 0.5 % (w/v) AAES to 12 % (w/v) PBS in a CHCl\(_3\) solution caused a drastic change in the fiber morphology, changing from highly beaded fibers to smooth and continuous fibers.\(^\text{18}\) This improved the electrospinnability, evident from the morphological changes, and can be attributed to an increase in solution conductivity and charge density at the jet.\(^\text{29,30}\) This ultimately increased the elongation force experienced by the fibers as the excess charge creates self-repulsion within the electric field, suppressing the axial symmetric instability,\(^\text{11}\) known as Rayleigh instability.\(^\text{11}\)

The morphology of electrospun fibers is a key determinant in both the physical and mechanical properties of the resulting product. Any anomaly or abnormality along the fiber may cause a significant decrease in strength.\(^\text{32,33}\) Much of the electrospinning literature focuses on how various parameters affect the fiber morphology.\(^\text{24–29}\) Several factors affect the electrospinning process, which can be broken down into process parameters, solution properties, and ambient conditions.\(^\text{34–40}\) Processing parameters are those that are controlled by the electrohydrodynamic setup, such as the applied electric field, electrode gap (EG), and flow rate. Solution properties include polymer concentration, viscosity, molecular weight, conductivity, and surface tension. Ambient conditions include temperature and humidity.

In this study, electrospun nonwoven mats were prepared using two different grades of BioPBS in a single solvent CHCl\(_3\) system, as well as cosolvent systems consisting of CHCl\(_3\) with dimethyl sulfoxide (DMSO) and CHCl\(_3\) with DMF. To the best of the authors’ knowledge, no report has been conducted to demonstrate the effects of DMSO on the electrospinning of PBS. The effects of using different solvent systems, BioPBS grades, BioPBS concentrations, applied voltages, and distances between electrodes on the morphological differences in fiber diameter and diameter distribution of electrospun BioPBS fibers were studied. Various polymer concentrations were prepared to determine the relationship between morphology and subsequent tensile strength and porosity. The fiber morphology and porosity were determined using scanning electron microscopy (SEM), while the tensile properties of the fibers were measured using dynamic mechanical analysis (DMA). It was found that solution properties such as solvent system, the grade of BioPBS, and the concentration of BioPBS used had a significant effect on the fiber morphology. This had a subsequent effect on both porosity and tensile properties. This study demonstrates the electrospinnability of BioPBS, capable of creating nanoporous fibers that have the potential for use in biomedical or tissue engineering applications.

### RESULTS & DISCUSSION

#### Solution Properties. Solvent System

Under ambient conditions (19–21 °C, 55–65% relative humidity), BioPBS was not electrospinnable in CHCl\(_3\). The low boiling point of CHCl\(_3\) compared to other solvents (Table 1) resulted in rapid evaporation of the solvent at the tip of the needle. This evaporation prevented the formation of a Taylor cone (circled in Figure 1a) and eventually led to a build-up of BioPBS at the tip of the needle, circled in Figure 1b. Although the electrospinning process can be conducted without the formation of a Taylor cone, a Taylor cone is required to produce continuous defect-free fibers.\(^\text{41}\) To reduce the evaporation rate of the solution, solvents with lower vapor pressures and high boiling points were added to CHCl\(_3\) to form a cosolvent system. DMSO and DMF were chosen as cosolvents because both possess high boiling points and low

| solvent | dielectric constant | boiling point (°C) | surface tension (mN/m) | viscosity (mPa/s)\(^\text{44}\) | vapor pressure (MPa) | Hansen solubility parameter (aMPa\(^b\)) \(^\text{44}\) |
|---------|---------------------|--------------------|------------------------|------------------------|--------------------|------------------------|
| CHCl\(_3\) | 4.8 | 61.0 | 27.16 | 0.57 | 22.26 | 19.0 |
| DMSO | 46.6 | 189.0 | 43.7 | 2.0 | 0.093 | 26.7 |
| DMF | 36.7 | 153.0 | 35.0 | 0.82 | 0.507 | 24.9 |

\(^\text{a}\)Reported at 25 °C. \(^\text{b}\)Hansen solubility parameter of PBS = 20.3 (MPa\(^b\)).\(^\text{44}\)
vapor pressures compared to CHCl₃, as shown in Table 1. However, BioPBS is insoluble in both DMSO and DMF, which can be attributed to the differences in Hansen solubility parameters between BioPBS and DMSO or DMF. The total Hansen solubility parameters given in Table 1 are based on three bond energies: dispersion, polar, and hydrogen bonds, which contain information about the intermolecular interactions of the solution. These three parameters can be used as coordinates for a point in three-dimensional space, known as Hansen space. The closer the substances are to each other in Hansen space, the more likely they are to dissolve each other. This is an approximation only, and there are limitations to using this method such as not accounting for parameters varying with temperature, molecular bonding being more complicated than three parameters, molecular size and shape, and dipole, electrostatic, and metallic interactions.

As PBS is not soluble in either DMSO or DMF, a cosolvent system is needed. When more than 10% of DMF (results not shown) or DMSO was added to both grades of BioPBS dissolved in CHCl₃, gelation rapidly occurred as the solution cooled to room temperature. Figure 2 shows the gelation of BioPBS in different fractions of DMSO/CHCl₃ as the solution was cooled to room temperature. Solutions of 30, 40, and 50% DMSO/CHCl₃ and DMF/CHCl₃ solidified before the solution could return to room temperature. 20% co-solvent systems returned to room temperature as a liquid but solidified shortly after, restricting the time available for electrospinning to approximately 1 h. This limitation in processing time would severely hinder the solution’s practical and industrial potential. Incredibly large throughputs would be needed to produce macroscale products. Conversely, a continuous production method could be utilized instead of a batch process to overcome this limitation. However, 20% cosolvent systems were not used further in this study. Both 10% DMSO/CHCl₃ and DMF/CHCl₃ sufficiently reduced the evaporation rate of the solution, allowing the formation of a Taylor cone.

With the amount of cosolvent chosen to be 10%, both the solvent system and BioPBS grade that resulted in the best morphology could be selected. Both DMSO and DMF cosolvent systems showed an outward effect on the morphology regardless of which BioPBS grade was used. Figure 3 shows a drastic change in the morphology from beaded fibers to continuous smooth fibers between film grade solutions using DMF (Figure 3a) and DMSO (Figure 3b). A similar but less drastic change can be seen in injection grade solutions where a transition from beaded to nonbeaded fibers was not observed. However, the frequency of the beads was drastically decreased in DMSO (Figure 3d) compared to DMF (Figure 3c). This morphological change can be attributed to the changes in surface tension and conductivity of the solutions between DMF and DMSO cosolvent systems. Table 2 summarizes solution properties measured in this study for single solvent CHCl₃ solutions, cosolvent systems, as well as FO solutions at 5, 10, and 15 (w/v) BioPBS concentration. The conductivity of both the film and injection grade BioPBS increased when DMSO was used compared to DMF (Figure 4c), which could partially explain the improved morphology observed in DMSO solvent systems compared to DMF. More importantly, the differences in surface tension observed between DMF and DMSO were more profound in film grade solutions (11.9 mN/m) compared to injection grade solutions (5.13 mN/m). This further explains why a more drastic change in morphology was observed in DMSO cosolvent systems compared to DMF. Surface tension is a function of the polymer solution, including the solvent; various solvents can be used to adjust the surface tension of the solution. In general, low surface tension encourages the electrospinning process to occur in lower electric fields, which is advantageous for many reasons including the reduction of processing costs.
Table 2. Solution Properties (Complex Viscosity, Conductivity, and Surface Tension) of Various Solutions, Measured at 23 °C, Prepared for Electrospinning

| grade-solvent | complex viscosity (Pa·s) | conductivity (μS/cm) | surface tension (mN/m) |
|---------------|--------------------------|----------------------|------------------------|
| neat CHCl₃    | 5.732 × 10⁻² ± 2.83 × 10⁻³ | (<1.0 × 10⁻⁵)⁴¹     | 30.55 ± 0.414          |
| FF            | 0.213 ± 4.5 × 10⁻³       | 0.0275 ± 5 × 10⁻³   | 7.200 ± 0.887          |
| FO            | 0.229 ± 0.0115           | 0.0475 ± 9.6 × 10⁻³ | 19.10 ± 2.21           |
| FC            | 0.256 ± 0.0114           | 0.0003 ± 5 × 10⁻⁴   | 28.88 ± 2.15           |
| IF            | 0.138 ± 1.2 × 10⁻³       | 0.0475 ± 9.6 × 10⁻³ | 11.86 ± 1.67           |
| IO            | 0.156 ± 2.7 × 10⁻³       | 0.07 ± 0.018        | 16.99 ± 0.68           |
| IC            | 0.178 ± 0.0104           | 0.0003 ± 5 × 10⁻⁴   | 28.61 ± 1.87           |
| FO-1S         | 0.229 ± 0.0135           | 0.0475 ± 9.6 × 10⁻³ | 19.10 ± 2.22           |
| FO-10         | 0.075 ± 1.75 × 10⁻³      | 0.19 ± 0.02         | 15.32 ± 2.32           |
| FO-5          | 0.0170 ± 1.06 × 10⁻⁵     | 0.41 ± 0.01         | 5.892 ± 1.87           |

“FF-film in DMF, FO-film in DMSO, FC-film in CHCl₃, IF-injection in DMF, IO-injection in DMSO, IC-injection in CHCl₃, and FO-15 film in DMSO with a BioPBS concentrations of 15%. Surface tension of CHCl₃-water = 31.66.⁴⁵”

Many researchers have investigated how choice of solvent effects on the resulting fiber morphology, specifically its dielectric constant and boiling point. Wannatong et al.²⁸ investigated several different solvents with various properties such as density, dielectric constant, and boiling point, and their effect on electrospun polystyrene fibers. They measured the productivity of fiber production (number of fibers per square meter per time) and found that the fiber productivity increased as the dielectric constant of the solvent increased. It was also found that as the boiling point of the solvent increased the diameter of fibers decreased.²⁸ Casasola et al.⁴⁶ found a similar relationship between the fiber diameter of electrospun PLA fibers and the boiling point of the cosolvent in a two solvent system; as the boiling point of the co-solvent increased, fiber diameter decreased. DMSO has a higher boiling point relative to DMF (Table 1), using solvents with higher boiling points results in lower rates of evaporation. This allows the polymer jet to retain its viscoelastic properties longer, resulting in longer exposure to stretching forces, producing smaller diameter fibers.³⁰ This further explains the improved morphology observed when electrospun from DMSO cosolvent systems compared to DMF.

The dielectric constant (ε) of the solvent system also affects the resultant fiber morphology.¹⁸,²⁸,³⁰,⁴⁶ Both cosolvents used in this study have a higher ε relative to CHCl₃, which could explain the improved electrospinnability observed by the addition of either DMF or DMSO to CHCl₃. Furthermore, DMSO has a higher ε relative to DMF, which could also explain the differences in morphology observed in Figure 3. An increase in ε results in an increase in solution conductivity.¹⁸,³⁰,⁴⁷ This results in more self-repelling charges on the surface of the polymer jet, increasing the Coulombic stretching force resulting in a stronger elongation force.¹⁸ A decrease in solution conductivity will result in insufficient elongation of the Taylor cone, resulting in the formation of undesirable beads.³⁰ An increase in solution conductivity can considerably decrease the fiber diameter, and the availability of ionic salts can also create smaller diameter fibers.³⁰ This increased charge density suppresses the Rayleigh instability experienced by the polymer jet, increasing the bending instability experienced by the electrospun fiber. The subsequent change in fiber morphology observed between DMSO and DMF cosolvent systems suggests a strong correlation between the aforementioned solvent properties and morphology.¹⁸,⁴⁹

**PBS Grade.** The major difference between the two grades of BioPBS is the reported melt flow index (MFI), 5 g/10 min and 22 g/10 min, for film and injection grade, respectively.⁵⁰ Bremner et al.⁵¹ established a relationship between MFI and the molecular weight distribution (MWD) using both viscosity average molecular weight (Mᵥ) and weight average molecular weight M₆. The most practical MWD to measure is Mᵥ by solution rheology and obtains a good correlation coefficient (R² = 0.93) by a linear least squares fit with the natural log of

![Figure 4. (a) Complex viscosity. (b) Interfacial surface tension between the solution and water. (c) Conductivity of BioPBS solutions prepared for electrospinning. Conductivity of neat CHCl₃ from ref 43. All data taken at 23 °C.](image-url)
MFI.\textsuperscript{51} It is important to note that if a solvent is used in the rheological analysis, then $\bar{M}_f$ will be a function of both the properties of the solvent and the polymer’s inherent molecular weight.\textsuperscript{53} Systems involving highly branched polymers or non-Newtonian polymer solutions are more complicated and require full rheological characterization of the polymer.\textsuperscript{53} The lower MFI of film grade BioPBS could be an indicator of a higher MWD, which explains the improved electrospinnability of the film grade BioPBS compared to the injection grade observed in Figure 3. Research suggests that the molecular weight of the polymer plays a significant role in its ability to be electrospun into defect-free fibers.\textsuperscript{4,27,41,52,53} This is due to its significant effect on solution properties such as viscosity, conductivity, and surface tension.\textsuperscript{54} Koski et al.\textsuperscript{53} varied the molecular weight of poly(vinyl alcohol) PVA from 9000 to 50 000 g/mol and observed a drastic change in the fiber morphology. PVA with lower molecular weights (9000–10 000 g/mol) produced beaded fibers, whereas PVA with molecular weights between 13 000 and 23 000 g/mol produced defect-free fibers. Further increases in molecular weight (from 31 000 to 50 000 g/mol) resulted in flattened fibers. If the difference in MFI of the BioPBS is inversely proportional to the molecular weight of the BioPBS as Bremner et al.\textsuperscript{51} reported, then the improved electrospinnability of film grade BioPBS relative to the injection grade can be attributed to an increase in the molecular weight between film and injection grade BioPBS.

\textbf{BioPBS Concentration and Solution Viscosity.} The same trend seen in the MFI of the film and injection grade BioPBS was observed in the solution’s complex viscosities, shown in Figure 4a. Regardless of the solvent used film grade BioPBS have higher complex viscosities compared to injection grade BioPBS. Further, an increase in the BioPBS concentration resulted in an increase in the viscosity of that solution because of an increase in polymer chain entanglements and molecular cohesion.\textsuperscript{41} Film grade BioPBS solutions were prepared in DMSO cosolvent systems with BioPBS concentrations of 5, 10, and 15\% (w/v), labeled FO-5, FO-10, and FO-15 respectively. A polymer solution has to have an optimal concentration, too high a concentration can prevent the polymer motion and too low the concentration will inhibit the appropriate polymer entanglements required to create fibers.\textsuperscript{46,41,48,49} Polymer concentration is one of the most crucial variables in the electrospinning process, a minimum concentration is necessary to produce fibers, whereas a higher concentration is necessary to produce bead-free fibers, as lower concentration solutions are prone to the formatio of unwanted droplets throughout the fiber because of the unbalanced effects of viscosity and the Coulombic stretching force.\textsuperscript{54} This morphology is observed in FO-5 (Figure 5a) and to a lesser degree in FO-10, as shown in Figure 5b. In FO-5, the viscosity is significantly lower than the FO-10 or FO-15 solutions; thus the Coulombic stretching force is far greater than the solution’s viscosity and causes the jet to break up into spherical droplets (roundness = $0.70 \pm 0.17$) held by surface tension.\textsuperscript{55} In FO-10, the solution has sufficient viscosity to maintain the fibrous form. However, the Coulombic stretching force is still prominent compared with respect to solution properties such as surface tension and viscosity. The Rayleigh instability is still prominent compared to the bending instability, which resulted in elongated beads (roundness = $0.55 \pm 0.15$). Bead-free fibers were observed in FO-15 solutions, as shown in Figure 5c. This is likely due to the further increase in viscosity and limited increase in surface tension, as illustrated in Figure 4a,b, respectively. The larger increase in viscosity relative to surface tension suppressed the Rayleigh instability in favor of the bending instability, which resulted in increased elongation forces, resulting in defect-free fibers.\textsuperscript{18,47} The concentration of the solution to be spun was found to have the greatest effect on fiber properties. When the solution concentration is low, there is not enough molecular cohesion to stabilize the jet required to produce the fibers; hence destabilization of the jet occurs, resulting in the production of fine spherical particles.\textsuperscript{55} The charged droplets naturally resist agglomeration and coagulation because of the electrostatic repulsion, resulting in particles with very small diameters, smaller than a conventional mechanical atomizer.\textsuperscript{56} When the molecular cohesion in the solution is high enough, a stable jet can be produced from the Taylor cone, resulting in the production of a continuous fiber,\textsuperscript{41} as observed in Figure 5c. Viscosity is dependent on the polymer being used, as different polymer solutions have different viscoelastic properties. However, regardless of the type of polymer used, a minimum viscosity is essential to produce smooth and bead-free nanofibers. To electrospin neat, defect-free fibers, the polymer concentration must be at least twice the entanglement concentration (EC). The EC is a boundary between an unentangled and entangled solution. In an unentangled solution, the polymer chains overlap but do not entangle,
whereas in an entangled solution, polymer chains overlap and entangle, constraining each other’s movement. \(^\text{37}\) The EC of BioPBS in DMSO/CHCl\(_3\) cosolvent solutions was found to be approximately 7.5 (% w/v). The frequency of beads amongst the fibers was calculated for BioPBS solutions ranging from 5 to 15 (% w/v) concentration, where the beaded morphology was present up until 15 (% w/v). The number of beads per 100 \(\mu\)m\(^2\) decreased with increasing BioPBS concentration, as shown in Figure 6b. At significantly lower viscosities, surface tension is the primary effect on the fiber morphology, and below a critical concentration, \(^\text{38}\) electrospayed drops form instead of electrospun fibers, as shown in Figure 5a. Too high of a viscosity, and the polymer will not form fibers at all, as jet formation is difficult at high viscosities. \(^\text{41}\)

**Physical and Mechanical Properties. Porosity.** As previously mentioned, porosity is a crucial parameter for many biomedical applications and can be easily controlled by adjusting the type and concentration of the polymer, \(^\text{26}\) solvent system, \(^\text{26}\) or humidity. \(^\text{27, 59}\) The volatility of CHCl\(_3\) creates pores as the solvent evaporates. \(^\text{26}\) Areas with relatively a higher solvent content evaporate more rapidly compared to the more homogeneous regions, resulting in voids or pores forming along the fiber in these areas. \(^\text{26, 27}\) Megelski et al. \(^\text{26}\) investigated the effects of solvent volatility on the porosity of the resulting fiber: they varied the ratio of relatively volatile tetrahydrofuran (THF) with DMF, a less volatile solvent. As the ratio of THF/DMF changed from 10:0 to 0:10, the fiber morphology subsequently changed from highly porous in pure THF, to less porous structures in 3:1 THF/DMF, to completely nonporous fibers in pure DMF. \(^\text{26}\) Humidity was found to have a similar effect on fiber porosity as solvent volatility: as the relative humidity increased from 20 to 50%, the fiber morphology changed from smooth nonporous fibers to highly porous fibers, respectively. \(^\text{26}\) In a humid environment, moisture can condense on the relatively cold surface of a fiber, water vapor interacts with the solvent, and as they both evaporate, a pore is formed. \(^\text{26}\) Porosity is also dependent on the polymer chosen to electrospin. Wagner et al. \(^\text{39}\) showed that with increasing fractions of poly(\(L\)-lactic acid) (PLLA) in a PLLA:PHBV blend, that fiber porosity increased while the bead formation decreased.

**Table 3. Pore Size, Shape, and Porosity of Electrospun Fibrous Nonwoven Mats, Produced from Various BioPBS Grades and Concentrations**

| grade-solvent | pore diameter (nm) | pore size (\(\mu\)m\(^2\)) | roundness (%) | porosity (%) |
|---------------|-------------------|---------------------------|---------------|-------------|
| IO            | 226 ± 136         | 0.12 ± 0.12               | 63 ± 16       | 20.44 ± 1.08 |
| FO-5          | 655 ± 412         | 0.16 ± 0.15               | 49 ± 19       | 30.74 ± 2.55 |
| FO-10         | 599 ± 211         | 0.12 ± 0.07               | 43 ± 13       | 35.97 ± 2.60 |
| FO-12.5       | 481 ± 218         | 0.08 ± 0.07               | 43 ± 16       | 41.84 ± 2.18 |

**Figure 6. (a) Tensile strength and Young’s modulus against BioPBS concentration of nonwoven electrospun mats done using DMA: sample dimensions 15 \(\times\) 5 \(\times\) 0.15 mm (length \(\times\) width \(\times\) thickness) isothermal stress–strain displacement ramp test conducted at 23°C using a 1 mm/min ramp rate. (b) Fiber porosity (SEM image analysis 25000\(\times\) magnification) and frequency of beads among fibers (SEM image analysis, 25000\(\times\) magnification) against BioPBS concentration.**
concentration results in prominent changes in morphology, such as frequency of defects, fiber diameter, and fiber porosity. These nano- and microsized morphological changes affect the mechanical properties of the macrostructure, the nonwoven fibrous mat. Tensile properties of the BioPBS nonwoven mat such as tensile strength and Young’s modulus were found to increase with increasing concentrations. As BioPBS concentration increased, the frequency of beads along the fibers decreased (Figure 6b). The reduction of these defects resulted in an increase in tensile properties (Figure 6a). Beaded electrospun fibers can find applications in air filtration, where uniform diameters, narrow diameter distributions, and strength are less crucial, as increased bead size and frequency contribute to low pressure drops and increased filtration efficiency.

Vautard et al. used three different techniques to induce surface defects on PAN-based carbon fibers; concluding that the frequency of defects predominately determined the fiber’s strength. An increase in the frequency of defects results in a decrease in the fiber strength. In this study, beaded fibers acted as defects within the nonwoven fibrous mat. A decrease in the frequency of beads resulted in an increase in tensile properties. It is also well known that an increase in porosity is linearly associated with a decrease in the Young’s modulus of that material. However, it was found that the presence of bead defects predominately affected the mechanical properties, irrespective of porosity. The tensile values reported in this study are within the range of those reported for the skin (1−20 MPa) or cardiac tissue (0.3−0.8 MPa) but are far too weak for structural tissues such as bones, tendons, or ligaments (50−100 MPa). It is recommended that further tensile testing should be conducted at 37 °C in simulated bodily fluid to get a better understanding of how these fibers would perform within a human body.

Figure 7. (a) 15% BioPBS concentration creates porous hierarchical electrospun fibers. (b) 5% BioPBS concentration creates electro-sprayed droplets connected by nanofibers (SEM images at 5000×, 10000×, and 25000×).

Figure 8. SEM images (magnification of 2000×) and corresponding histograms of BioPBS fiber morphology electrospun at (a–c) 20 cm electrode gap: (a) 15 kV 1.5 mL/h, (b) 22.5 kV 3.0 mL/h, (c) 30 kV 4.5 mL/h; 15 kV 1.5 mL/h (d) 20 cm, (e) 25 cm, (f) 30 cm.
Process Parameters. **Voltage.** The effect voltage has on morphology is still controversial among researchers.\(^{34}\) With increasing voltage, researchers have observed smaller fibers,\(^{26,29,30}\) larger fibers,\(^{6,67}\) or observed negligible effects on morphology.\(^{48}\) The rationale for how an increase in voltage results in smaller diameter is as follows: an increased voltage exposes the polymer jet to a greater electric field. This increases the elongation forces applied to the polymer because of higher Coulombic charges on the surface of the polymer.\(^{69}\) Mo et al.\(^{65}\) found that increasing the voltage from 9 to 15 kV resulted in a small decrease in fiber diameter, from roughly 0.75 to 0.5 μm. The polymer concentration was found to have a much greater effect on fiber diameter, a small change in concentration (7–9 w/v %) resulted in an increase in the fiber diameter from 0.8 to 1.5 μm, respectively.\(^{66}\) Lee et al.\(^{29}\) observed a similarly small reduction in fiber diameter, where the fiber diameter decreased from approximately 325 to 260 nm when the voltage was increased from 10 to 25 kV.

Conversely, a higher applied voltage could result in larger fibers because a higher build-up of charge at the needle causes the polymer jet to accelerate faster, resulting in more solution being ejected from the needle.\(^{60}\) Greater amounts of the polymer in the electrospinning jet results in a larger beaded fiber.\(^{34,67}\) Zhao et al.\(^{67}\) showed that a smaller voltage reduces the acceleration of the jet due to a weaker electric field, thereby increasing the amount of time the fiber is exposed to the electric field before reaching the collector, resulting in a thinner fiber. This suggests that a voltage approaching the minimum critical voltage could be effective at producing thin fibers. Furthermore, increasing the voltage, and hence the electric field, creates a larger charge being formed at the tip that can create droplets or beads.\(^{34}\) Bead formation could be due to the increased instability of the jets as the Taylor cone disappears.\(^{37}\)

Voltage was found to have a smaller effect on fiber morphology when compared to other variables such as concentration, choice of solvents,\(^{35,46}\) and distance to the collector.\(^{35,68}\) The results shown in Figure 8a–c suggest that with increasing voltage, both fiber diameter and fiber distribution increase. Smaller diameter fibers and distributions are observed in electrospun fibers at 15 kV, while at 22.5 and 30 kV, larger diameter fibers and distributions are observed. Such large distributions observed in both 22.5 and 30 kV suggest that a voltage close to the critical voltage should be used to produce smaller fibers with a narrower distribution. These results are in accordance with the results presented by Demir et al.\(^{66}\) and Zhao et al.\(^{67}\) and strengthens the rationale that increasing the applied voltage will increase the diameter of the resultant fibers.\(^{66,67}\)

**Distance between Electrodes.** Varying the distance between the electrodes, the electric field between the electrodes. Shortening the EG increases the electric field gradient and the jet’s acceleration, hence reducing the time available for evaporation. Lengthening the distance generally results in thinner fibers.\(^{54,70}\) SEM images and the corresponding histograms (Figure 8d–f) show a clear left shift toward smaller diameter fibers. Buchko et al.\(^{58}\) showed that when the EG was sufficiently small, an interconnected fibrous mesh formed on the collector because of the inability to remove the solvent in time. A larger EG, thus a longer period for the solvent to evaporate, allows the fiber to continue to elongate before solidifying. Conversely, too large a distance will create beaded fibers.4 Fiber diameter and jet current both decrease with increasing EG; this is because the flight time is increased, allowing more time for elongation, resulting in thinner fibers.\(^{39,67}\) The collector is commonly made from a conductive material and is grounded to form a stable electric field. Nonconducting materials result in a lower packing density.\(^{14}\) However, in some cases, like three-dimensional nanofibrous scaffolds, it is advantageous to allow the fibers to amass in a lower packing density, resulting in a more porous material.\(^{11}\) To this end, the EG of the electrospinning process must be optimized in terms of morphology with careful consideration given to the interaction effects between EG, flow rate, and the solvent used.

**CONCLUSIONS**

In this study, solution properties such as BioPBS concentration, type of the solvent system, and grade of BioPBS had a greater effect on the fiber morphology than process parameters, specifically the applied voltage and the distance between electrodes. The best cosolvent systems were found to be 10% DMSO/CHCl\(_3\) and 10% DMF/CHCl\(_3\). DMSO/CHCl\(_3\) cosolvent systems produced fibers with less bead defects compared to DMF/CHCl\(_3\), regardless of the BioPBS grade used. It was found that increasing BioPBS concentration yielded fibers with fewer bead defects, which at 15 (w/v) resulted in bead-free uniform fibers. Furthermore, increasing the BioPBS concentration was found to increase the porosity of the fibers while simultaneously reducing its pore size. Dynamic mechanical analysis showed that the reduction of bead defects resulted in a stronger nonwoven fibrous mat. It was determined that electrospun PBS fibrous nonwoven mats possess a high degree of porosity at the micro- and nanoscales, resulting in a hierarchical structure that has sufficient mechanical properties for applications in wound healing and soft tissue engineering. It is suggested that further investigation into biocompatibility, biodegradability, and mechanical properties under in vitro conditions be done in order to better predict the fiber’s performance in environments that more closely mimic those found within the human body.

**EXPERIMENTAL SECTION**

**Materials.** Two grades (film and injection) of BioPBS, product of PTT MCC BIOCHEM CO., Ltd., Thailand, were obtained from Competitive Green Technologies, Leamington, Canada. The film grade (PBS FZ91PM) had a MFI of 5 g/10 min (at 190 °C at 2.16 kg) and the injection grade (PBS FZ71PM) had a MFI of 22 g/10 min under the same conditions.\(^{30}\) Analytical grade chloroform, DMSO, and DMF were purchased from Sigma-Aldrich and used as received.

**Solution Preparation and Characterization.** Film grade BioPBS was dissolved in single solvent CHCl\(_3\) systems and cosolvent systems with DMSO and DMF, labeled FC, FO, and FF, respectively. Similarly, injection grade BioPBS was dissolved in the same solvent systems and labeled IC, IO, and IF, respectively. The BioPBS concentration was fixed at 15% (w/v) for initial solvent testing. The ratio of DMSO/CHCl\(_3\) and DMF/CHCl\(_3\) was varied from 10 to 50% (v/v). BioPBS was dissolved in all solvent systems at 50 °C under vigorous stirring. Single solvent systems were mixed for 2.5 h to ensure complete dissolution. Co-solvent systems required BioPBS to be first dissolved in CHCl\(_3\) for 2 h; then either DMSO or DMF was added dropwise and continually stirred for an additional 0.5 h. FO solutions were prepared with BioPBS concentrations of 5, 10, and 15% (w/v), labeled FO-5, FO-10, and FO-15, respectively. Solutions were cooled to room
temperature prior to characterization and electrospinning. The solution’s complex viscosity was measured using a MCR 302 rheometer (ANTON PARR, Austria) using a shear rate sweep from 100 to 0.01 s⁻¹ at 23 °C. Interfacial surface tension between the prepared solutions and water was measured using the Wilhelmy plate method in a KSV NIMA Langmuir–Blodgett trough (Biolin Scientific, Sweden). Solution conductivity was measured using an acumet AP85 pH/conductivity meter (Fisher Scientific); the conductivity meter was not sensitive enough to measure pure CHCl₃ (1.0 × 10⁻¹⁰ μS/cm). Because of the volatility of CHCl₃, the surface tension was measured with a capping layer of deionized water to prevent evaporation; hence the reported interfacial surface tension reflects the surface tension between the prepared solution and deionized water.

Electrospinning of BioPBS Fibers. Electrospinning was conducted using a NANON-01A electrospinning setup (MECC CO., Ltd., Japan). Initial solvent testing was conducted using a solution of 15% (v/w) BioPBS concentration, 15 kV applied voltage, 1.5 mL/h flow rate, 20 cm EG, and 18 gauge blunt tipped needle, under ambient conditions (19–21 °C, 55–65% relative humidity). A custom-made adjustable, flat collector plate was used to achieve a greater EG. Polymer solutions were drawn into a 10 mL glass syringe, where 0.5 mL of each solution was electrospun to determine the fiber morphology. Two microliters of each solution was used to create a fibrous nonwoven sheet used for tensile testing. Electrospinning time varied depending on the cleaning frequency. To maintain a stable Taylor cone, the flow rate was raised proportionally with increasing applied voltage. Electrospun samples were dried at room temperature under a vacuum overnight before subsequent characterization.

Morphology and Structural Characterization. Morphology, specifically fiber diameter, diameter distribution, pore size, and porosity were observed using a Phenom ProX SEM (Phenom-World, The Netherlands) with a 10 kV acceleration voltage. Prior to imaging, samples were gold sputter-coated for s using a 108 manual sputter coater (TED PELLA, Inc). The presence of beads, fiber diameter, and diameter distribution was observed at 600× and 2000× magnification, respectively, while the pore size analysis was conducted at 25 000× magnification. Further analysis was conducted using DiameterJ, a plugin of ImageJ software (National Institutes of Health), where a minimum of two images were taken from random locations and used to calculate both fiber and pore size distributions. Traditional, statistical region merging and mixed segmentation were used to produce the most accurately segmented image.

Tensile strength and Young’s modulus of fibrous nonwoven mats were measured using Q800 DMA (TA Instruments). Rectangular, nonwoven fibrous mats with average dimensions of 15, 5.0.15 mm (length, width, thickness) were loaded into the DMA using tension film clamps. An isothermal stress strain, displacement ramp test was conducted at 23 °C, with a 0.001 N preload, 0.1% initial strain, and a 1 mm/min ramp rate.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: mohanthy@uoguelph.ca. Phone: +1-519-824-4120 ext. 56664. Fax: +1-519-763-8933 (A.K.M.).
*E-mail: mmisra@uoguelph.ca. Phone: +1-519-824-4120 ext. 58935, 519-824-4120 ext. 56766. Fax: +1-519-836-0227 (M.M.).

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This research is financially supported by the Natural Sciences and Engineering Research Council (NSERC), Canada Development Grants (Project # 400320), and the Ontario Ministry of Research, Innovation and Science (MRIS) Ontario Research Fund, Research Excellence Program Round-7 (ORF-RE07) (Project # 052644, 052665 and 052850).

REFERENCES
(1) Zong, X.; Kim, K.; Fang, D.; Ran, S.; Hsiao, B. S.; Chu, B. Structure and Process Relationship of Electrospun Bioabsorbable Nanofiber Membranes. Polymer 2002, 43, 4403–4412.
(2) Zini, E.; Scandola, M. Green Composites: An Overview. Polym. Compos. 2011, 32, 1905–1915.
(3) Smidt, M. Special: Industrial Biotech - A Sustainable Supply of Succinic Acid. Eur. Biotechnol. Newsl. 2011, 10, 70–71.
(4) Reneker, D. H.; Yarim, A. L. Electrospinning Jets and Polymer Nanofibers. Polymer 2008, 49, 2387–2425.
(5) Bhushani, J. A.; Anandharamakrishnan, C. Electrospinning and Electrospinning Techniques: Potential Food Based Applications. Trends Food Sci. Technol. 2014, 38, 21–33.
(6) Sun, B.; Long, Y. Z.; Zhang, H. D.; Li, M. M.; Duvail, J. L.; Jiang, X. Y.; Yin, H. L. Advances in Three-Dimensional Nanofibrous Macrostructures via Electrospinning. Prog. Polym. Sci. 2014, 39, 862–890.
(7) Martins, A.; Pinho, E. D.; Correlo, V. M.; Faria, S.; Marques, A. P.; Reis, R. L.; Neves, N. M. Biodegradable Nanofibers-Reinforced Microfibrous Composite Scaffolds for Bone Tissue Engineering. Tissue Eng., Part A 2010, 16, 3599–3609.
(8) Azad, A. K.; Serrsintham, N.; Chandrkachang, S.; Stevens, W. F. Chitosan Membrane as a Wound-Healing Dressing: Characterization and Clinical Application. J. Biomed. Mater. Res. B Appl. Biomater. 2004, 69, 216–222.
(9) Wang, L.; Zhang, L.; Yan, J.; Yin, Z.; Tang, C.; Guo, Y.; Li, D.; Wei, B.; Xu, Y.; Gu, Q. Electrospinning Vancomycin-Loaded Coating on Titanium Implants for the Prevention of Implant-Associated Infections. Int. J. Nanomed. 2014, 2014, 3027.
(10) Wendtorf, J. H.; Agarwal, S.; Greiner, A. Medicinal Applications for Electrospun Nanofibers. Electrospinning; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2012; pp 217–236.
(11) Currey, J. D. Biomechanics of Mineralized Skeletons; American Geophysical Union, 2013; pp 11–25.
(12) Zhang, Y.; Ouyang, H.; Lim, C. T.; Ramakrishna, S.; Huang, Z.-M. Electrospinning of Gelatin Fibers and gelatin/PCL Composite Fibrous Scaffolds. J. Biomed. Mater. Res. B Appl. Biomater. 2005, 72, 156–165.
(13) Lin, C.-C.; Fu, S.-J.; Lin, Y.-C.; Yang, I.-K.; Gu, Y. Chitosan-Coated Electrospun PLA Fibers for Rapid Mineralization of Calcium Phosphate. Int. J. Biol. Macromol. 2014, 68, 39–47.
(14) Munteanu, B. S.; Aytac, Z.; Prigoce, G. M.; Uyar, T.; Vasile, C. Polyactic Acid (PLA)/Silver-NP/VitaminE Bionanocomposite Electrospun Nanofibers with Antibacterial and Antioxidant Activity. J. Nanopart. Res. 2014, 16, 2643.
(15) Xu, J.; Zhang, J.; Gao, W.; Liang, H.; Wang, H.; Li, J. Preparation of chitosan/PLA Blend Micro/nanofibers by Electrospinning. Mater. Lett. 2009, 63, 658–660.
(16) Gu, S. Y.; Ren, J.; Vacceso, G. J. Process Optimization and Empirical Modeling for Electrospun Polyacrylonitrile (PAN) Nano-fiber Precursor of Carbon Nanofibers. Eur. Polym. J. 2005, 41, 2559–2568.

ORCID
Amar K. Mohanty: 0000-0002-1079-2481
Manjusri Misra: 0000-0003-2179-7699

ACS Omega 2018, 3, 5547–5557
(17) Liu, S.-J.; Kau, Y.-C.; Chou, C.-Y.; Chen, J.-K.; Wu, R.-C.; Yeh, W.-L. Electrospun PLGA/collagen Nanofibrous Membrane as Early-Stage Wound Dressing. J. Membr. Sci. 2010, 355, 53–59.

(18) Klairutseamee, W.; Supahol, P.; Jangchud, I. Electrospinnability of Poly(butylene Succinate): Effects of Solvents and Organic Salt on the Fiber Size and Morphology. J. Appl. Polym. Sci. 2015, 132, 42716.

(19) Jeong, E. H.; Im, S. S.; Youk, J. H. Electrospinning and Structural Characterization of Ultrafine Poly(butylene Succinate) Fibers. Polymer 2005, 46, 9538–9543.

(20) Zhang, D.; Chang, J.; Zeng, Y. Fabrication of Fibrous Poly(butylene Succinate)/collastone/apate Composite Scaffolds by Electrospinning and Biomimetic Process. J. Mater. Sci. Mater. Med. 2008, 19, 443–449.

(21) Liu, Y.; He, J.-H.; Yu, J.-Y. Preparation and Morphology of Poly(butylene Succinate) Nanofibers via Electrospinning. Fibres Text. East. Eur. 2007, 15, 30–33.

(22) Tian, L.; Wang, P.; Zhao, Z.; Ji, J. Antimicrobial Activity of Electrospun Poly(butylene Succinate) Fiber Mats Containing PVP-Capped Silver Nanoparticles. Appl. Biochem. Biotechnol. 2013, 171, 1890–1899.

(23) Xu, J.; Guo, B.-H. Poly(butylene Succinate) and Its Copolymers: Research, Development and Industrialization. Biotechnol. J. 2010, 5, 1149–1163.

(24) Yoo, E. S.; Im, S. S. Melting Behavior of Poly(butylene Succinate) during Heating Scan by DSC. J. Polym. Sci., Part B: Polym. Phys. 1999, 37, 1357–1366.

(25) Gan, Z.; Abe, H.; Kurokawa, H.; Doi, Y. Solid-State Microstructures, Thermal Properties, and Crystallization of Biodegradable Poly(butylene Succinate) (PBS) and Its Copolymers. Biomacromolecules 2001, 2, 605–613.

(26) Megelks, S.; Stephens, J. S.; Chase, D. B.; Rabolt, J. F. Micro- and Nanostructured Surface Morphology on Electrospun Polymer Fibers. Macromolecules 2002, 35, 8456–8466.

(27) Casper, C. L.; Stephens, J. S.; Tassi, N. G.; Chase, D. B.; Rabolt, J. F. Controlling Surface Morphology of Electrospun Polyesters: Effect of Humidity and Molecular Weight in the Electrospinning Process. Macromolecules 2004, 37, 573–578.

(28) Wannatong, L.; Sirivat, A.; Supaphol, P. Effects of Solvents on Electrospun Polymeric Fibers: Preliminary Study on Polystyrene. Polym. Int. 2004, 53, 1851–1859.

(29) Lee, J. S.; Choi, K. H.; Ghim, H. D.; Kim, S. S.; Chun, D. H.; Kim, H. Y.; Lyoo, W. S. Role of Molecular Weight of Atactic Poly(vinyl Alcohol) (PVA) in the Structure and Properties of PVA Nanofabric Prepared by Electrospinning. J. Appl. Polym. Sci. 2004, 93, 1638–1646.

(30) Moghe, A. K.; Hufenus, R.; Hudson, S. M.; Gupta, B. S. Effect of Addition of a Fugitive Salt on Electrospinnability of Poly(e-caprolactone). Polymer 2009, 50, 3311–3318.

(31) Rayleigh, L. Investigation of the Character of the Equilibrium of an Incompressible Heavy Fluid of Variable Density. Proc. London Math. Soc. 1882, 1–41, 170–177.

(32) Vautard, F.; Dentzer, J.; Nardin, M.; Schultz, J.; Defoort, B. Influence of Surface Defects on the Tensile Strength of Carbon Fibers. Appl. Surf. Sci. 2014, 322, 185–193.

(33) Wong, S.-C.; Baji, A.; Leng, S. Effect of Fiber Diameter on Tensile Properties of Electropun Poly(e-caprolactone). Polym. Sci., Part B: Polym. Phys. 2008, 49, 4713–4722.

(34) Rezvani, Z.; Venugopal, J. R.; Urbanska, A. M.; Mills, D. K.; Ramakrishna, S.; Mozafari, M. A Bird’s Eye View on the Use of Electrospun Nanofibrous Scaffolds for Bone Tissue Engineering: Current State-of-the-art, Emerging Directions and Future Trends. Nanomaterials 2016, 6, 12181–2200.

(35) Yang, Q.; Li, Z.; Hong, Y.; Zhao, Y.; Qiu, S.; Wang, C.; Wei, Y. Influence of Solvents on the Formation of Ultrathin Uniform Poly(vinyl Pyrrolidone) Nanofibers with Electrospinning. J. Polym. Sci., Part B: Polym. Phys. 2004, 42, 3721–3726.

(36) Li, Z.; Wang, C. Effects of Working Parameters on Electrospinning; Springer; 2013; pp 15–28.

(37) Angammana, C. J.; Jayaram, S. H. Fundamentals of Electrospinning and Processing Technologies. Part. Sci. Technol. 2016, 34, 72–82.

(38) Buchko, C. J.; Chen, L. C.; Shen, Y.; Martin, D. C. Processing and Microstructural Characterization of Porous Biocompatible Protein Polymer Thin Films. Polymer 1999, 40, 7397–7407.

(39) Mi, H.-Y.; Jing, X.; Tunug, L.-S. Fabrication of Porous Synthetic Polymer Scaffolds for Tissue Engineering. J. Cell. Plast. 2014, 51, 165–196.

(40) Rodoplu, D.; Mutlu, M. Effects of Electrospinning Setup and Process Parameters on Nanofiber Morphology Intended for the Modification of Quartz Crystal Microbalance Surfaces. J. Eng. Fiber Fabr. 2012, 7, 118–123.

(41) Haider, A.; Haider, S.; Kang, I.-K. A Comprehensive Review Summarizing the Effect of Electrospinning Parameters and Potential Applications of Nanofibers in Biomedical and Biotechnology. Arabian J. Chem. 2015, DOI: 10.1016/j.arabjc.2015.11.015.

(42) Hansen, C. M. Solubility Parameters—An Introduction. Hansen Solubility Parameters: A User’s Handbook, 2nd ed.; CRC Press: Boca Raton, FL, 2007.

(43) Comyn, J. Handbook of Organic Solvent Properties. Int. J. Adhes. Adhes. 1997, 17, 177.

(44) Tanaka, T.; Takahashi, M.; Kawaguchi, S.; Hashimoto, T.; Saitoh, H.; Koyua, T.; Taniguchi, M.; Lloyd, D. R. Formation of Microporous Membranes of poly(1,4-Butylene Succinate) via Non-solvent and Thermally Induced Phase Separation. Desalin. Water Treat. 2010, 17, 176–182.

(45) Ghosh, P. Interfacial Tension. NPTEL—Chem. Eng.—Interfacial Eng. 2009, 1–22.

(46) Casasola, R.; Thomas, N. L.; Trybala, A.; Georgiadou, S. Electrospun Poly Lactic Acid (PLA) Fibres: Effect of Different Solvent Systems on Fibre Morphology and Diameter. Polymer 2014, 55, 4728–4737.

(47) Maneek-in, J.; Nithitanakul, M.; Supaphol, P. Effects of Solvent Properties, Solvent System, Electrostatic Field Strength, and Inorganic Salt Addition on Electrospun Polystyrene Fibres. Iran. Polym. J. 2006, 15, 341–354.

(48) Shin, Y. M.; Hohman, M. M.; Brenner, M. P.; Rutledge, G. C. Experimental Characterization of Electrospinning: The Electrically Forced Jet and Instabilities. Polymer 2001, 42, 09955–09967.

(49) Wendorff, J. H.; Agarwal, S.; Greiner, A. Nanofiber Properties. Electrospinning; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2012; pp 69–104.

(50) PTT MCC Biochem Co. Ltd. APPLICATION BioPBSTM Compound—Injection Molding. http://www.pttmcc.com/new/contect.php?mid=W072 (accessed Nov 9, 2017).

(51) Brenner, T.; Rudin, A.; Cook, D. G. Melt Flow Index Values and Molecular Weight Distributions of Commercial Thermoplastics. J. Appl. Polym. Sci. 1990, 41, 1617–1627.

(52) Pouraskhab, V.; Mohanty, A. K.; Misra, M. Electrosprinning of Aqueous Lignin/poly(ethylene Oxide) Complexes. J. Appl. Polym. Sci. 2015, 132, 41260.

(53) Koski, A.; Yim, K.; Shivkumar, S. Effect of Molecular Weight on Fibrous PVA Produced by Electrospinning. Mater. Lett. 2004, 58, 493–497.

(54) Wang, P.; Wang, Y.; Tong, L. Functionalized Polymer Nanofibers: A Versatile Platform for Manipulating Light at the Nanoscale. Light Sci. Appl. 2013, 2, No. e102.

(55) Ghorani, B.; Tucker, N. Fundamentals of Electrospinning as a Novel Delivery Vehicle for Bioactive Compounds in Food Nanotechnology. Food Hydrocoll. 2015, 51, 227–240.

(56) Jaworek, A. Micro- and Nanoparticle Production by Electrospaying. Powder Technol. 2007, 176, 18–35.

(57) McKee, M. G.; Wilkes, G. L.; Colby, R. H.; Long, T. E. Correlations of Solution Rheology with Electrospun Fiber Formation in Linear and Branched Polymers. Macromolecules 2004, 37, 1760–1767.
(58) Deitzel, J. M.; Kleinmeyer, J.; Harris, D.; Beck Tan, N. The Effect of Processing Variables on the Morphology of Electrospun Nanofibers and Textiles. *Polymer* 2001, 42, 261−272.
(59) Wagner, A.; Poursorkhabi, V.; Mohanty, A. K.; Misra, M. Analysis of Porous Electrospun Fibers from Poly( L-Lactic acid)/ Poly[(3-Hydroxybutyrate-Co-3-Hydroxyvalerate) Blends. *ACS Sustainable Chem. Eng.* 2014, 2, 1976−1982.
(60) Ramakrishna, S.; Fujihara, K.; Teo, W.-E.; Lim, T.-C.; Ma, Z. Electrospinning Process. An Introduction to Electrospinning and Nanofibers; World Scientific, 2005; pp 90−154.
(61) Wang, Z.; Zhao, C.; Pan, Z. Porous Bead-on-String Poly(lactic Acid) Fibrous Membranes for Air Filtration. *J. Colloid Interface Sci.* 2015, 441, 121−129.
(62) Niinomi, M.; Hattori, T.; Niwa, S. Material Characteristics and Biocompatibility of Low Rigidity Titanium Alloys for Biomedical Applications. In *Biomaterials in Orthopedics*; Yaszemski, M., Trantolo, D., Lewandrowski, K., Hasirci, V., Altobelli, D., Wise, D., Eds.; Marcel Dekker, INC.: Basel, 2004; pp 41−62.
(63) Holzapfel, G. A. Biomechanics of Soft Tissue. In *Handbook of Material Behavior*; Lemaitre, J., Ed.; Academic Press, 2000; pp 2−15.
(64) Tallawi, M.; Zebrowski, D. C.; Rai, R.; Roether, J. A.; Schubert, D. W.; El Fray, M.; Engel, F. B.; Aifantis, K. E.; Boccaccini, A. R. Poly(Glycerol Sebacate)/Poly(Butylene Succinate-Butylene Dilinoleate) Fibrous Scaffolds for Cardiac Tissue Engineering. *Tissue Eng., Part C* 2015, 21, 585–596.
(65) Mo, X. M.; Xu, C. Y.; Kotaki, M.; Ramakrishna, S. Electrospun P(LLA-CL) Nanofiber: A Biomimetic Extracellular Matrix for Smooth Muscle Cell and Endothelial Cell Proliferation. *Biomaterials* 2004, 25, 1883−1890.
(66) Demir, M. M.; Yilgor, I.; Yilgor, E.; Erman, B. Electrospinning of Polyurethane Fibers. *Polymer* 2002, 43, 3303−3309.
(67) Zhao, S.; Wu, X.; Wang, L.; Huang, Y. Electrospinning of Ethyl-Cyanoethyl Cellulose/tetrahydrofuran Solutions. *J. Appl. Polym. Sci.* 2004, 91, 242−246.
(68) Yördem, O. S.; Papila, M.; Menceloglu, Y. Z. Effects of Electrospinning Parameters on Polyacrylonitrile Nanofiber Diameter: An Investigation by Response Surface Methodology. *Mater. Des.* 2008, 29, 34−44.
(69) Zuo, W.; Zhu, M.; Yang, W.; Yu, H.; Chen, Y.; Zhang, Y. Experimental Study on Relationship between Jet Instability and Formation of Beaded Fibers during Electrospinning. *Polym. Eng. Sci.* 2005, 45, 704−709.
(70) Geng, X.; Kwon, O.; Jang, J. Electrospinning of Chitosan Dissolved in Concentrated Acetic Acid Solution. *Biomaterials* 2005, 26, 5427−5432.