Fabrication and characterization of centrifugally spun poly(acrylic acid) nanofibers

David De la Garza,1 Francisco De Santiago,1 Luis Materon,2 Mircea Chipara,3 Mataz Alcoutlabi ©1
1Department of Mechanical Engineering, University of Texas, Rio Grande Valley, Edinburg, Texas 78539
2Department of Biology, University of Texas, Rio Grande Valley, Edinburg, Texas 78539
3Department of Physics and Astronomy, University of Texas, Rio Grande Valley, Edinburg, Texas 78539
Correspondence to: M. Chipara (E-mail: mircea.chipara@utrgv.edu) and M. Alcoutlabi (E-mail: mataz.alcoutlabi@utrgv.edu)

ABSTRACT: The production of poly(acrylic acid) (PAA) nanofibers by the centrifugal spinning of PAA solutions in water is reported. The effect of the spinneret rotational speed and concentration of PAA solutions on the diameter of nanofibers and on their quality (assessed by the absence of beads) is discussed. The main physical properties of PAA such as glass-transition temperature (Tg) are studied in detail and compared to the feature of the as-received homopolymer. It is shown that the glass-transition temperature of the bulk polymer and the nanofibers has made them incredibly useful in many applications. Several methods have been used to fabricate polymer nanofibers such as electrospinning, melt blowing, centrifugal spinning (CF), coextrusion with a unique exit cutting die, liquid shear spinning, and touch and brush spinning. Electrospinning is the most used method to produce polymer fibers due to its ability to produce fibers with diameter ranging from micrometers to nanometers. However, slow fiber production (~0.3 g h⁻¹) and the application of an electric field are drawbacks to this method. An alternative to electrospinning is CFs. Forcespinning (FS), which is the trademark of CFs, was developed by Sarkar, Lozano, et al. at the University of Texas–Pan American and allows the more rapid production of fibers in the nanorange and microrange by centrifugal forces. This method permits the use of a larger number of polymers and composites solutions with higher concentrations to be utilized with a reduced production cost due to the use of less solvent, fast fiber production rate (1 g min⁻¹) because there is no need to apply an electric field to stretch the fibers. Many polymer nanofibers such as: poly(ethylene oxide), polypropylene, polyvinylpyrrolidone, poly-l-lactic acid, polycrylonitrile (PAN) and PAN nanocomposites, poly(e-caprolactone), cellulose acetate, and poly(ethylene terephthalate) have been successfully produced by CFs for use in different applications such as energy storage, filtration, and tissue scaffolding. Polymer nanofibers have also been used for antimicrobial applications. In recent work, composite nanofibers of chitosan and silver nanoparticles were successfully produced by CFs and their antimicrobial properties were reported.

In this work, poly(acrylic acid) (PAA) is herein first reported as produced by CF. PAA is a weak anionic polyelectrolyte with a hygroscopic nature and has been widely used for a variety of applications. PAA is typically mixed with other polymers in aqueous solutions and has previously been electrospun to form fibrous hydrogels due to the polymer’s ability to swell in response to environmental stimuli and its changes in pH. The adsorption capability of PAA allows for its use in water treatment as a metal ion scavenger and its use in disposable diapers. PAA has also been used in lithium-ion batteries as a binder for better battery performance and a recent study has been reported on the use
of composites containing PAA for humidity sensing due to the sensitivity of PAA to humidity.\textsuperscript{29} The antimicrobial properties of PAA together with other polymers and composites have been studied as well.\textsuperscript{30–32} One of these particular studies conducted by Gratzl et al. show that PAA containing diblock copolymers exhibit antimicrobial properties displaying better results with increasing acrylic acid content.\textsuperscript{30} In this work, PAA nanofibers are prepared by CF for use in antimicrobial applications. The morphology and thermal characterization of the PAA fibers and their bulk material counterpart are studied using different experimental techniques such as scanning electron microscope (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and Raman spectroscopy.

**EXPERIMENTAL**

**Materials.** The materials used are PAA polymer ($M_w = 450,000$) purchased from Sigma-Aldrich (USA) and deionized (DI) water.

**Preparation of Polymer Solutions.** The PAA solutions of various concentrations (8–15 wt %) were obtained by dissolving the polymer in DI water. All solutions were homogenized by stirring for 24 h.

**CF Setup.** The CF method (Figure 1) uses centrifugal forces to extrude the polymer solution or melt through the needle-based spinneret to obtain nanofibers. The fiber jets were formed by high rotational speed of the spinneret. Two 30-gauge half-inch sterile needles (Fisher Scientific, USA) were inserted into the spinneret on each side and 2 mL of the precursor solution was injected into the spinneret orifice. The FS equipment was set to a spinning time of 3 min and spinneret rotational speeds varied from 4000 to 8000 rpm. Fiber samples were removed from the collectors with a microscopic glass slide for characterization tests and square fiber mats were produced for antimicrobial testing. The PAA solutions were prepared at room temperature for 24–48 h.

Figure 1. Schematic of the CFs method displaying the collectors, spinneret, and fiber web. [Color figure can be viewed at wileyonlinelibrary.com]

The temperature and humidity were controlled during the CF of PAA fibers. All samples were stored under vacuum at 80 °C for 24 h, in order to remove any residual water. The experiments were conducted at room temperature (22–25 °C) and a humidity between 60 and 70%.

**Characterization Analysis**

**Scanning Electron Microscopy.** The fiber morphology was examined with a Zeiss Sigma VP field emission SEM. A thin layer of gold was used to coat the samples for 30 s at 45 mA with a Desk II Denton Vacuum Sputter prior to imaging. Several SEM images were taken of each fibers sample at different regions to measure the fiber diameters and generate histograms to display the fiber diameter distribution. An average of 50–80 fibers from the SEM images were selected to measure fiber diameter with the AxioVision microscope software and a QI Macros software was used to generate the histograms.

**Raman Spectroscopy.** Raman measurements have been obtained by using Renishaw inVia Raman Microscope equipped with a laser diode, operating at 785 nm.

**Differential Scanning Calorimetry.** The thermal properties of the PAA bulk powder and nanofibers were acquired using TA Instruments, DSC Q100 (USA). To obtain thermograms for the PAA nanofibers, the DSC scans were conducted from 40 to 225 °C at heating and cooling rates of 1, 2, 5, 10, 15, 20, 25, 30, 40, 45, and 50 °C min\(^{-1}\). All tests were completed under a nitrogen atmosphere.

**Thermogravimetric Analysis.** The thermal degradation of the PAA nanofibers was investigated using TA Instruments TGA Q500 under a nitrogen atmosphere. All samples were heated up to 800 °C at a heating rate of 10 °C min\(^{-1}\).

**Antimicrobial Testing.** The antimicrobial testing was conducted via the Kirby–Bauer method using Escherichia coli and Staphylococcus aureus bacteria. The bacteria were grown onto a nutrient broth (1:10 ratio) and 100 μL of the bacterial suspension from the dilution was added to the surface of agar plates. An L-shaped glass rod was used to fully disperse the suspension on the plate. Half-inch circular fiber mats were placed on the surface of the agar plate and placed in an incubator at 37 °C for 24 h for further analysis.

**RESULTS AND DISCUSSION**

**Fiber Surface Characterization: SEM Analysis.** Figure 2(a) shows the SEM image for 12 wt % PAA nanofibers centrifugally spun at a spinneret rotational speed of 6000 rpm. Similar images were collected for all nanofiber samples ranging from 9 to 14 wt %. The rotational speed of the spinneret was varied from 4000 to 8000 rpm for all polymer solutions. Figures S1–S6 in the supplementary data sheet show the SEM images of PAA nanofibers spun at different concentrations (9–14 wt. %) and rotational speeds between 4000 and 8000 rpm. Sparse to no fiber formation resulted at 8 wt % and 15 wt % PAA solution concentrations as well as at a spinneret rotational speed below 4000 rpm and above 8000 rpm for all other solutions due to either an insufficient
ejection time of the polymer solution or limited fiber elongation and solvent evaporation. Variations in the spinneret rotational speeds played an important factor in the formation of beads and average fiber diameters. The average fiber diameter for nanofibers centrifugally spun at 6000 rpm and PAA concentration of 12 wt % was 1100 nm, while the PAA nanofibers spun at 8000 rpm with the same polymer concentration had an average fiber diameter of 900 nm [Figure 2(b)]. This is due to the stretching of the nanofibers while the solvent is evaporating as the spinning rate is increased. The 12 wt % PAA concentration was found to be optimal displaying the lowest amount of beaded fibers unlike the SEM image shown in Figure 2(c) for a 9 wt % PAA concentration where a significant amount of beads were formed after CF. As expected, lower polymer concentrations produced a smaller average fiber diameter as shown in Figure 3.21 The figure shows the average fiber diameter as a function of PAA concentration. The PAA nanofibers were centrifugally spun at a spinneret rotational speed of 6000 rpm. The average nanofiber diameters ranged from 800 to 1400 nm as the PAA concentration was increased while the spinneret speed was kept constant at 6000 rpm. The correlation coefficient for the linear fitting was $R^2 = 0.958$. 

Figure 2. SEM images and fiber diameter distribution of (a) 12 wt % PAA concentration spun @ 6000 rpm, (b) 12 wt % PAA concentration spun @ 8000 rpm, and (c) 9 wt % PAA concentration spun at 4000 rpm. The SEM images were obtained at different magnifications: (A1, B1) 600x, (C1) 300x, (A2, B2) 7000x, and (C2) 15,000x. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 3. Average fiber diameter versus PAA concentration. The PAA fibers were force spun at a spinneret rotational speed of 6000 rpm. [Color figure can be viewed at wileyonlinelibrary.com]
Table I. Average Fiber Diameter of PAA Fibers Centrifugally Spun at Different Spinneret Rotational Speeds (4000, 6000, and 8000 rpm) and at Different PAA Concentrations Between 9 and 14 wt %

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average fiber diameter (nm)</th>
<th>Standard deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9%–4000 rpm</td>
<td>884.04</td>
<td>195.68</td>
</tr>
<tr>
<td>9%–6000 rpm</td>
<td>796.60</td>
<td>207.92</td>
</tr>
<tr>
<td>10%–4000 rpm</td>
<td>942.73</td>
<td>245.51</td>
</tr>
<tr>
<td>10%–6000 rpm</td>
<td>803.74</td>
<td>233.04</td>
</tr>
<tr>
<td>10%–8000 rpm</td>
<td>860.93</td>
<td>241.13</td>
</tr>
<tr>
<td>11%–4000 rpm</td>
<td>1004.46</td>
<td>238.49</td>
</tr>
<tr>
<td>11%–6000 rpm</td>
<td>996.44</td>
<td>253.88</td>
</tr>
<tr>
<td>11%–8000 rpm</td>
<td>1010.22</td>
<td>313.01</td>
</tr>
<tr>
<td>12%–4000 rpm</td>
<td>1197.38</td>
<td>354.79</td>
</tr>
<tr>
<td>12%–6000 rpm</td>
<td>1118.37</td>
<td>296.14</td>
</tr>
<tr>
<td>12%–8000 rpm</td>
<td>906.15</td>
<td>239.65</td>
</tr>
<tr>
<td>13%–4000 rpm</td>
<td>1214.29</td>
<td>370.76</td>
</tr>
<tr>
<td>13%–6000 rpm</td>
<td>1027.55</td>
<td>277.43</td>
</tr>
<tr>
<td>14%–4000 rpm</td>
<td>1410.38</td>
<td>429.61</td>
</tr>
<tr>
<td>14%–8000 rpm</td>
<td>1380.86</td>
<td>393.21</td>
</tr>
</tbody>
</table>

As illustrated in Table I, the average fiber diameter of PAA fibers for different concentrations varied with the rotational speed of the spinneret. There is a significant effect of the polymer concentration on the average fiber diameter at each spinneret speed. The fiber diameter increases with increasing concentration. In fact, both the rotational speed of the spinneret and polymer concentration are important parameters that affect the fiber morphology and formation during CF. Figures S1-S6 in the supplementary data sheets show all the SEM images of PAA fibers spun at different PAA concentrations (9–14 wt %) and rotational speeds between 4000 and 8000 rpm.

Raman Spectroscopy. Figure 4 shows the Raman spectrum of PAA bulk and nanofibers obtained using a laser operating at 785 nm in the Raman shifts range 100–1000 cm$^{-1}$. Several lines were noticed and assigned as follows:

The line located at 508 cm$^{-1}$ corresponds to bending motions of cis C=O groups. As this line is not shifted toward lower Raman shifts, it is possible to conclude that the amount of water within these nanofibers is very low. Generally, the presence of water in PAA shifts some Raman lines, providing an efficient tool for the quantification of water content. The large band observed between 613 and 645 cm$^{-1}$ corresponds to the bending vibrations of trans C=O units. As this line is not shifted below 600 cm$^{-1}$, it is confirmed that water is not present in the nanofibers. The line at 840 cm$^{-1}$ corresponds to symmetric vibrations in C=O and $\tau$ vibrations in CH$_2$. The position of this line confirms the lack of water. The Raman spectrum of the PAA fiber structure from 1000 to 2000 cm$^{-1}$ is shown in Figure 5.

The line located at about 1100 cm$^{-1}$ represents $\rho$ motions of CH$_2$ units. The line at 1329 cm$^{-1}$ reflects asymmetric of C=C=O units. This line is almost absent in PAA gels and if water is present. The line noticed at 1458 cm$^{-1}$ is associated with the delta motions of CH$_2$ units and is also absent in PAA gels. The line noticed at 1669 cm$^{-1}$ corresponds to the vibration of C=O unit. The absence of any line around 1700 cm$^{-1}$ is an additional confirmation of the absence of water in the nanofibers. Figure 6 shows the Raman spectrum of the PAA fibers from 2600 to 3700 cm$^{-1}$. The pure water Raman peak was reported at 3453 cm$^{-1}$ and is not observed in the actual spectra.

The Raman investigations showed that the molecular motions in PAA are not affected by the one-dimensional character of nanofiber/microfiber and consequently, within the experimental errors, the Raman spectra of PAA powder and PAA nanofibers are identical. Based on the position of Raman lines, it is concluded that the amount of adsorbed water is low (typically below 10 wt %). Furthermore, the local dynamics of PAA nanofiber/microfiber affecting the molecular
polarizability was investigated in this work and is confirmed by previous studies. It is worthwhile to mention here that water has its own Raman lines. Therefore, water can be detected by Raman spectroscopy in two ways: directly, via the Raman vibrations of water, and indirectly via modifications triggered by the water presence in PAA.

The main problem with water detection by Raman spectroscopy is caused by the experimental configuration. The Raman spectrometer that was used to conduct the experiments discussed in this work operates in the reflection mode. Technically, this makes almost impossible to use the Raman spectrometer to measure a water droplet, as the reflected laser beam is very weak and hence, the noise masks the absorption lines (however, the spectrum is nicely recorded in the transmission configuration). Consequently, the analysis was focused on the shift of some Raman lines due to the water retention within the nanofibers, which is in agreement with results reported in the literature. This approach is not very sensitive to the presence of water and hence, relatively small amounts of water adsorbed by the polymer will not be reflected in the Raman spectrum but will be observed during TGA experiments. The estimated amount of water appears to be in the order of few weight percentages.

DSC Results. To investigate the structure and thermal properties of PAA nanofibers and bulk powder, DSC measurements have been performed at different scanning rates ranging from 1 to 50 °C min⁻¹. PAA is essentially an amorphous polymer and consequently, this study investigated the dynamics of the glass-transition temperature in bulk PAA and nanofibers of PAA.

The DSC spectra of the heating branch of bulk PAA is shown in Figure 7. It is noticed that for all heating rates, the DSC spectrum shows a sigmoidal dependence of heat flow versus temperature. The glass-transition temperature is typically defined in the middle of this dependence. However, this empirical definition is improved by defining the glass-transition temperature as the coordinate of the inflection point of the aforementioned sigmoidal dependence. Because the location of the inflection point cannot be accurately estimated, a mathematical transformation (derivative) will convert the inflection point into an extremum point, whose position is easier and more accurately estimated. Each recorded thermogram, shown in Figure 7, was numerically differentiated to obtain a graph that shows the dependence of the derivative of heat flow with respect to temperature (dH/dT). This dependence is shown in Figure 8. Similar data have been obtained for all samples at all heating rates.

Figure 9 shows the heating rate as a function of temperature for three different samples (bulk PAA, nanofibers obtained at 6000 rpm, and nanofibers obtained at 8000 rpm) at different heating rates. Each of these three curves is characterized by a single glass transition. Differences have been noticed between bulk and spun nanofibers.
The glass-transition temperatures were obtained by nonisothermal DSC measurements, at various heating rates. The DSC experiment began with three heating–cooling cycles at a constant rate of (10 °C min⁻¹) between 25 and 250 °C, followed by 11 heating–cooling cycles at a heating rate between 1 and 50 °C min⁻¹.

Each cycle, the sample was annealed for 10 min at 250 °C followed by cooling to 25 °C to start a new cycle. The second and third thermograms were identical, supporting the full erasure of the residual stresses caused by the sample preparation and processing. To improve the accuracy in the estimation of the glass-transition temperature, each DSC thermogram representing the heat flow versus temperature (at a given constant heating rate) was differentiated and the extremum point at the peak of the heating rate at the glass-transition temperature, each DSC thermogram representing processing. To improve the accuracy in the estimation of the glass-transition temperature, each DSC thermogram representing the heat flow versus temperature (at a given constant heating rate) was differentiated and the extremum point at the peak of the heating rate at the glass-transition temperature was identified, with the relaxation parameter represented by Tg, the glass-transition temperature.

Therefore, the fractional free volume at the glass-transition temperature as the spinning rate was increased. This explains the dependence of the glass-transition temperature. Parameter B is decreasing as the spinning rate was increased, while A showed an increase as the spinning rate was increased. These results indicate that the fractional free volume at Tg (which is related to B) is decreasing as the spinning rate is increased. This suggests a local order due to the stretching of the nano-fiber during CF. Therefore, the fractional volume at Tg decreases as the spinning rate is increased. The increase in A suggests that the expansion coefficient decreases.

The shift of the glass temperature to higher temperatures may be a consequence of water desorption. The release of the adsorbed water and the formation of anhydride groups may also contribute to the shift of the glass-transition temperature.

It is worthwhile to mention here that the modified WLF equation [eq. (1)] allows for the estimation of the glass-transition temperature, Tg, and of the WLF constant, C1g. The other WLF constant,
as observed in relaxation/creep measurements.\textsuperscript{37–39} Studying the dynamics and thermodynamic of the glass transition in amorphous polymers and glass forming liquids is very complex and is beyond the scope of this work.

**TGA Results.** The thermogravimetric results of PAA microfibers are shown in Figure 10. The first derivative curve of the thermograms of PAA fibers is also shown in the figure. The TGA experiments were performed under an N\textsubscript{2} atmosphere. The temperature scans were conducted from 25 to 800 °C at a heating rate of 10 °C min\textsuperscript{-1}. The TGA curve shows a total mass loss of 90\% which can be divided into three steps. The first step (30–150 °C, mass loss of about 4\%) is attributed to the departure of physisorbed water and preliminary formation of anhydride groups. The second step at (~250 °C, mass loss of ~30\%) is caused by the dehydration of adjacent carboxylic group to form anhydrides. The last step demonstrates the full degradation of the sample only leaving carbonaceous residue and it can be observed that there is about a 10\% residual mass at 800 °C. TGA data confirmed that the amount of physisorbed water is below 10 wt %. Based on the derivative weight loss of the PAA fibers, the most mass loss of ~30 and 46\% occurs at 250 and 450 °C, respectively. Within experimental errors, we did not notice any substantial difference between TGA of nanofibers obtained at different spinning rates (between 4000 and 8000 rpm).

![Figure 10. TGA and derivative thermogravimetric curves of the PAA fibers. The TGA thermogram was conducted in nitrogen atmosphere. The samples were heated from 25 to 800 °C at a heating rate of 10 °C min\textsuperscript{-1}.](image)

**Figure 11. In vitro antimicrobial results of PAA nanofibers done on (a) S. aureus and (b) E. coli as well as the (c) estimated diameter of the inhibition zones. [Color figure can be viewed at wileyonlinelibrary.com]**
**Table II.** Estimated Diameter of the Inhibition Zones for the Antibacterial/Microbial Activity Results of PAA Nanofibers Against *S. aureus* and *E. coli*

<table>
<thead>
<tr>
<th>Fibers/bacteria system</th>
<th>Average diameter of the inhibition zone (in.)</th>
<th>Standard deviation</th>
</tr>
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<tbody>
<tr>
<td>PAA/<em>S. aureus</em></td>
<td>0.76</td>
<td>0.14</td>
</tr>
<tr>
<td>PAA/<em>E. coli</em></td>
<td>0.62</td>
<td>0.07</td>
</tr>
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</table>

**Antimicrobial Results.** The PAA fibers were tested for their antimicrobial activity. Figure 11(a,b) displays images taken of agar plates filled with both *E. coli* and *S. aureus* and the bacteria inhibition zone exhibited by the PAA nanofibers. Although the half-inch polymer nanofibers are not visible after 24 h, the clear inhibition zone exhibited by PAA is present in both the *S. aureus* and the *E. coli* agar plates. A strong antimicrobial activity in the *S. aureus* agar plate is demonstrated by a close connection of both half-inch fiber mats placed on the bacteria. However, the inhibition zone on the right section of the same plate could not be measured properly.

The PAA fibers placed on the surface of the agar plates filled with *E. coli* bacteria produced differences in antimicrobial activity. It can be noticed that inhibition is clear on the left of the plate but not on the right. Nonsterile conditions of nanofiber production and antimicrobial testing resulted in a visibly whiter portion on this particular plate which suggests that some sort of fungus grew on the pathogenic bacteria after testing. Measurements were conducted on clearer inhibition zones and Figure 11(c) shows that PAA generated a larger inhibition zone of about 0.76 in. in the Gram-negative bacteria (*S. aureus*) than in the Gram-positive bacteria (*E. coli*) with an inhibition zone of 0.62 in. The antimicrobial activity experiments against *E. coli* and *S. aureus* were performed using eight different samples made from PAA fibers (eight for *E. coli* and eight for *S. aureus*). The antimicrobial activity results shown in Figure 11 were based on the estimated average diameter of the inhibition zones of the eight PAA fiber samples. The standard deviations for the antimicrobial activity measurements of PAA fibers against *E. coli* and *S. aureus* are illustrated in Table II.

**CONCLUSIONS**

PAA nanofibers were fabricated for the first time by CF. The results showed an increase in nanofibers’ diameter with increasing polymer concentration. A 12 wt% PAA concentration in a DI water solution was found to be the optimal concentration displaying sparse to no beaded nanofibers for three different spinneret speeds. As expected, faster spinning rates caused by higher spinneret rotational speeds decreased the fiber diameter due to the stretching of the fibers when pushed out of the needles in the CF equipment. The average fiber diameter for the 12 wt% PAA in DI water spun at 6000 rpm was 1100 nm while the average fiber diameter for the same concentration spun at 8000 rpm was 900 nm.

Detailed analysis of the Raman spectra of PAA powder and PAA nanofibers revealed that the two spectra are almost identical suggesting that there are no significant differences in the molecular motions of PAA bulk and PAA nanofibers. Additionally, the lack of Raman line shifts indicates that water is not present in PAA nanofibers. However, orientational effects have been averaged out in these measurements performed on mats of PAA nanofibers. The lack of single PAA fibers prevented us from observing potential contributions due to the stretching of the polymer.

The DSC scans conducted on PAA nanofibers demonstrated that the polymer is amorphous and glass-transition temperatures increased with increasing heating rates according to the WLF dependence for both pristine (bulk) and centrifugally spun fibers on various spinning rates.

The PAA nanofibers were tested for their antimicrobial properties and presented large inhibition zones of both Gram-positive *E. coli* and Gram-negative *S. aureus* pathogenic bacteria. Half-inch PAA fiber mats exhibited strong antimicrobial results with about 0.62 and 0.76 in. inhibition zones on *S. aureus* and *E. coli* agar plates, respectively.

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**REFERENCES**

3. Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. *Compos. Sci. Technol.* 2003, 63(15), 2223.