Concurrent Collection and Post-Drawing of Individual Electrospun Polymer Nanofibers to Enhance Macromolecular Alignment and Mechanical Properties

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ABSTRACT

The study reports a nanomanufacturing method that facilitates post-drawing of electrospun polymer nanofibers. Post-drawing is critical in conventional microfiber processing to enhance mechanical strength, but has been difficult to implement with nanofibers. Here, a parallel automated track collector was designed to permit continuous processing of thousands of individual nanofibers per minute under highly controllable drawing conditions. Post-drawing systematically induced macromolecular alignment and altered the chemical bond composition of polycaprolactone nanofibers with increasing draw ratio. The strength and stiffness of fibers with a draw ratio of 4 were enhanced by 7 and 15 times respectively and their mechanical properties exceeded previously reported values for conventional and nanoscale polycaprolactone structures.

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1. Introduction

Motivation to engineer stronger fiber materials reaches a wide variety of applications including aerospace, biomedical, and construction amongst others [1, 2]. Theoretical expectations predict that fiber diameter reduction will result in enhanced mechanical properties. This is generally true in practice for conventional wet and melt spun microfibers [3, 4]. For example, the tensile strength of polymer derived carbon fibers was increased by almost 4x by reducing the fiber diameter from 12 to 6 μm [5]. The relationship is also observed for electrospun nanofibers where fiber strength increases exponentially as diameter decreases below $\sim 500\text{ nm}$ [6-8]. However, regardless of diameter, electrospun nanofibers are considerably weaker than their much larger microfiber counterparts. For example, electrospun polyamide (PA) nanofibers were 3-12x weaker than melt spun/post-drawn PA fibers with some electrospun fibers being even weaker than bulk polyamide [9]. It can be hypothesized that the relative weakness of electrospun nanofibers compared to conventional fibers is due to vastly different manufacturing and processing conditions. Conventional polymer fibers are formed by extruding a polymer solution or melt through an orifice, followed by post-drawing processes that elongate the fiber to several times its original length to impart macromolecular alignment and mechanical strength. Environmental conditions and processing parameters can be tightly controlled and fibers are post-drawn in a solid or semi-solid (via temperature or residual solvent) state to limit spontaneous polymer chain relaxation back to a disordered organization. Electrospinning utilizes an electrostatic force to extrude a polymer solution through a needle tip. The thin jet of polymer solution ejected from the needle tip undergoes rapid elongations that subject the jet to a draw ratio up to 10^5 and strain rates up to 10^5 s^{-1} as it travels to a grounded target [10, 11]. However, despite these massive elongations, the resulting solid nanofibers have poor molecular organization. It has been proposed that fast polymer chain relaxation in electrospinning solutions, estimated from 0.1-0.01 s, undo initial jet induced organization during the later stages of electrospinning or at the collector in the continued presence of solvent [10, 12, 13]. Thus, an important difference between traditional and electrospinning

fabrication methods is the lack of an effective solid/semi-solid post-drawing step in electrospinning. This critical process is utilized to increase the strengths of wet and melt spun microfibers by 5-15x [4, 14-16]. The addition of a secondary post-drawing step at the collector stage is a logical approach to enhance the macromolecular alignment and mechanical properties of electrospun nanofibers. Ideally this step should occur after sufficient solvent evaporation has rendered the fibers to a semi-solid state that leaves fibers pliable, but slows polymer chain relaxation. This approach has been evident to those experienced in the field, however, technical difficulties associated with electrospinning has made post-drawing individual electrospun nanofibers impractical [9]. Here these technical impediments are overcome by an automated track collection and processing system with the capabilities to concurrently collect and draw thousands of individual aligned nanofibers per minute.

2. Results and Discussion

2.1 Automated track device

In this article we describe the automated track post drawing method and investigate the response of electrospun polycaprolactone (PCL) nanofibers to post-drawing at the collector stage before complete solvent evaporation. Key elements of this technology include (1) individual fiber drawing, (2) tight control over post-drawing processing parameters, (3) drawing immediately upon deposition during solvent evaporation and (4) simultaneous processing of thousands of nanofibers. The parallel plate collector design is used as the base method to collect ordered aligned individual nanofiber units (**Figure 1A**). The electric field created by the parallel plate collector causes nanofibers to suspend orthogonally across the gap between the plates, with one end adhered to each [17]. When the static plates are replaced with parallel automated tracks it allows the collector to overcome charge repulsion and non-continuous production limitations associated with the static parallel plates [18] (**Figure 1B-C**). The automated track method pulls charged fibers away from the collection area at steady state so that fiber accumulation does not continuously change the local electric field or inhibit subsequent nanofiber

Figure 1: (A) The electric field (field strength vectors in red, adapted from Li et al. [17], generated by a parallel plate collector induces electrospun nanofibers to align orthogonal to the direction of the plates and extend across the air gap between them. (B) Substitution of static parallel plates with automated tracks facilitates continuous collection of aligned individual fibers that are pulled down away from the collection area as they are deposited. (C) Post-drawing processing of thousands of individual fibers per minute was enabled by changing the angle of the tracks so that each fiber is elongated as it travels down away from the deposition area.

deposition. Here, post-drawing is seamlessly integrated into the parallel automated collecting system by repositioning the geometry of the tracks so that the distance between them increases as they travel away from the initial deposition area (**Figure 1C**). This allows fibers to be post-drawn in a semi-solid state as solvent evaporates, allowing chain rearrangement to occur more easily. A static frame was placed inside the device to remove the aligned post-drawn nanofibers from the automated tracks. As the fibers travel down the tracks and past the static frame they are sheared off of the tracks and adhere to the collection rack, where they remain in tension to impede chain relaxation in the samples (**Figure 2A**). post-draw, and transfer new nanofibers from the electrospinning jet to the rack. In this embodiment, the total elongation of the post-drawn nanofibers is the ratio of the distance between the tracks at initial deposition to the final distance between that tracks at fiber transfer to the collecting rack. An automated track device (**Figure 2B**) was built with adjustable rod locations so that the

position of the top and

Figure 2: (A) As fibers travel down the tracks they are deposited on a collecting rack placed inside of the device. Shear forces generated as the track moves past the rack cause individual fibers to break at their ends and transfer from the automated tracks to the static collecting rack. Processing conditions of final collected nanofibers are determined by the fixed positions of the tracks and the collecting rack as well as the velocity, V , of the tracks. Draw ratio (DR) and draw rate can be independently controlled by modifying these parameters with an adjustable device pictured in (B). A collective mesh of thousands of individually post-drawn aligned nanofibers is shown on the (C) rack after removal from the device. (D) Control samples (MDR) were collected on the rack without drawing $\theta=90^\circ$ and then manually post-drawn within a collective mesh.

bottom of the tracks could be modified. The draw ratio (DR, final fiber length divided by initial fiber length: $DR=L_{\text{final}}/L_{\text{initial}}$) and rate of draw can be independently controlled by adjusting track geometry, track speed, and the depth of the collecting rack (**Figure 2A**). To the investigators' knowledge, this is

the first approach capable of post-drawing individual electrospun nanofibers within a practical manufacturing system. Previous attempts to post-draw electrospun nanofibers have been performed at the (1) collector stage by stretching collective fiber entanglements into yarns [19, 20] or (2) after collection when random or aligned nanofiber mats were manually removed from a collector and subsequently drawn [21, 22]. The disadvantage of post-drawing collective fiber mats and yarns is that individual fibers cannot be elongated uniformly due to bonding and friction at fiber-fiber junctions [23-26]. Thus, nanofiber mats/yarns may fail at much lower elongations than possible for individual fibers. In our experiments, individual PCL nanofibers could be post-drawn to elongations nearly three times that of fibers within collective meshes. Further, total mat/yarn elongation is not an accurate reflection of individual fiber elongation because it is difficult to quantify fiber re-orientation within the mat and impossible to identify single fibers over the span of a sample. Automated track post-drawing presents the opportunity to draw individual polymer nanofibers from a known initial length to a known final length at a selected uniform rate. **With this system, the fibers are drawn immediately upon collection before complete solvent evaporation so that they can be elongated in a semi-solid state that is ideal for enhancing macromolecular alignment and mechanical properties.** Since thousands of individual fibers can be post-drawn simultaneously and then reassembled into a thick mat, it is also possible to characterize the effect of individual nanofiber post-drawing using macro characterization methods, such as X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), and conventional tensile testing.

2.2 Post-drawing polycaprolactone nanofibers

The effects of post-drawing on polycaprolactone (PCL) nanofibers was evaluated by electrospinning fibers onto the collecting device set to an initial 40 mm gap (L in **Figure 2A**). Track angle (θ in **Figure 2A**) was adjusted from 90-60° so that fibers were elongated to draw ratios of 1, 2, 3, or 4 (DR1, DR2, DR3, DR4) before being transferred to the rack situated 11 cm below the top of the device. Track speed

was set to 8 mm/s for all samples, which resulted in a 0, 2.8, 5.6, and 7.7 mm/s, linear elongation rate

Figure 3: (Top) Scanning electron microscope (SEM) images show polycaprolactone nanofiber morphology for aligned samples individually post-drawn with the automated track device to a draw ratio of 1 (undrawn), 2, 3, or 4; control samples post-drawn within a collective mesh to draw ratio 2; and control samples collected on a flat plate. White arrows point to fiber necking. (Bottom left) Average values of initial and final post-drawn fiber length, fiber diameter and total number of fiber per samples are shown with standard deviation for $n=8$ replicates per group. (Bottom right) Samples were mounted on a plastic frame for subsequent tensile testing.

for DR1, DR2, DR3, and DR4 samples respectively. The average fiber diameter and fiber density of collected samples (**Figure 3**) were determined from scanning electron microscope (SEM) images. Undrawn nanofibers (DR1) had a diameter of 857 nm and the observed diameter reduction associated with post-drawing (DR2=603 nm, DR3=481 nm, DR4=383 nm) was close to that predicted by a conservation of volume model ($L_1 \cdot \pi r_1^2 = L_2 \cdot \pi r_2^2$, DR2=605 nm, DR3=494 nm, DR4=429 nm). The relative diameter distribution of nanofibers remained similar for all draw ratios (standard deviation range from 8.6-13.7% of average). Some undrawn samples were manually post-drawn at 2.5 mm/s within a collective mesh (**Figure 2D**) 72 hours after fabrication (to allow for residual solvent evaporation) as a control (MDR). Unlike samples drawn as individual fibers, these failed at a maximum draw ratio of 2.25 and exhibited sporadic necking (**Figure 3**) at a draw ratio of 2. We hypothesize that

automated track drawing was able to achieve greater draw ratios before failure (up to 4.5) because individual fibers without fiber-fiber junctions were drawn uniformly over their entire span.

Furthermore, it is likely that residual solvent enhanced fiber extensibility because post-drawing occurred immediately after electrospinning.

2.3 Macromolecular characterization

The effect of automated track post-drawing on PCL nanofiber macromolecular structure and organization was characterized through Fourier transform infrared spectroscopy (FTIR) and wide angle X-ray diffraction (WAXD) analysis. Peak shifts were observed in the FTIR spectra of PCL nanofibers under different processing conditions. Observed shifts indicate systematic changes in macromolecular structure dependent on draw ratio (**Figure 4**). As draw ratio increased, a new peak, indicative of antisymmetric stretching of the CH₂ bond, began to emerge at the 2920 cm⁻¹ wavelength (**Figure 4B**). At wave length 1727 cm⁻¹ (**Figure 4C**) there is a peak shift as draw ratio increases. This shift indicates that there is stretching in the carbonyl bond (C=O) associated with drawing. When a draw ratio is introduced, the characteristic peak at 1190 cm⁻¹ experiences a systematic decrease in the strength of OC-O molecular stretching (**Figure 4D**). Comparing all three shifts to randomly aligned control samples collected on a flat plate shows that these trends begin in undrawn (DR1) samples and continue through increasing draw ratio. This indicates that parallel plate electrospinning is in itself a post-drawing process. Control samples that were drawn within collective meshes to a draw ratio of two (MDR2, **Figure 2D**) had FTIR spectra similar to the automated track processed samples (DR2, individual nanofiber drawing) at a draw ratio of two. This would indicate that the observed changes in bond activity are related to the absolute magnitude of the draw ratio and not the percentage draw ratio to failure, which occurred at 2.25 for collective mesh samples and 4.5 for automated track drawn fibers.

Figure 4: (A) A comparison of the full range FTIR spectra (3200cm^{-1} - 1000cm^{-1}) of polycaprolactone fiber samples subjected to different processing conditions. As draw ratio increases, a new peak emerges at 2920cm^{-1} , pictured in (B). The characteristic peak at 1727cm^{-1} (C) undergoes an incremental shift to the right with increasing draw ratio. In (D) the characteristic peaks 1165cm^{-1} and 1190cm^{-1} experience a systematic change where 1165cm^{-1} increases in intensity and 1190cm^{-1} decreases with increased draw ratio.

Wide angle X-ray diffraction analysis (WAXD) was performed at 15° intervals from 0 - 360° around samples in the plane of thin aligned fiber meshes (**Figure 5**). Undrawn (DR1), DR2, DR3, and DR4 samples were analyzed. An intensity differential was observed at the characteristic 21.7 degree peak. Peak height was maximum parallel to the direction of the nanofiber axis in all samples and weakest in the perpendicular configuration. DR4 samples had the most pronounced intensity

differential at this peak (83%) and DR1 had the smallest (15%), indicating draw induced texture. WAXD results indicate that the fibers experienced systematic enhancement of macromolecular alignment with increasing draw ratio.

Figure 5: Wide angle x-ray diffraction (WAXD) intensity was recorded at 15° intervals around aligned PCL nanofiber samples in the plane of the thin multi-fiber array. Samples with draw ratio (DR) from 1-4 all experienced an intensity differential at the 21.7° peak depending on the angle of the x-ray beam relative to the direction of the fiber axis. Peak differential, which was highest parallel to the fiber axis and lowest perpendicular to the fiber axis, increased with increasing draw ratio indicating post-drawing induced macromolecular orientation.

2.4 Mechanical Properties

Automated track post-drawing systematically increased the strength, stiffness, and toughness of electrospun PCL nanofibers with increasing draw ratio (**Figure 6**). Ultimate Tensile Strength (UTS) was enhanced with increasing draw ratio to an overall 7.4x from undrawn samples to DR4. Young's modulus was also enhanced systematically with increasing draw ratio to an overall 15.3x from undrawn samples to DR4. These increases are in the same order of magnitude as reported mechanical property enhancement associated with PCL microfibers post-drawn to draw ratios of 4-25 under various conditions (UTS increased by 5-15x [4, 16] & Young's modulus increased by

Figure 6: Tensile testing results for electrospun polycaprolactone (PCL) nanofibers individually post-drawn to a draw ratio (DR) of 1 (undrawn), 2, 3, and 4 are plotted with control PCL nanofibers post-drawn within a collective mesh to a ratio of 2 (MDR2) and samples collected on a flat plate as a random mesh (Rand). The stress strain curve of a representative sample of each DR1, DR2, DR3, DR4, MDR2, and Rand are plotted at top-left. Ultimate strength, Young's modulus, elongation at break, and toughness were calculated from stress strain curves for $n=8$ samples of each. All group to group comparisons with post hoc Mann-Whitney test have a p -value of $p<0.01$ except for those connected by lines.

3.75- 11x [14, 15]). Undrawn fibers collected across parallel plates were 3.6x stronger and 3.2x stiffer than random electrospun meshes collected on flat plates. This increase could be attributed to electrostatically induced stretching of the fiber across the parallel plates, which could be considered to be a post-drawing process in itself and has been shown to induce macromolecular alignment [27, 28]. The maximum elongation at break of PCL nanofiber samples decreased with increasing draw ratio by an overall 3.4x from undrawn samples to DR4. However, DR4 nanofibers were still extensible to 42.5% ($\sigma=7.1$, $n=8$) and the toughness of nanofiber samples increased with increasing draw ratio by 2.8x from undrawn samples to DR4. Fibers drawn as a collective mesh (MDR2) broke at lower elongation than all samples post-drawn using automated tracks. MDR2 samples were less than half as extensible as automated track drawn DR2 samples with matched draw ratio and were even less extensible than DR4 samples that had been drawn 3x farther. The average UTS of DR4 post-drawn PCL electrospun nanofiber samples was 1.66GPa ($\sigma=0.61$, $n=8$), which exceeds reported values for post-drawn PCL microfibers (275-768MPa) [4, 16] and electrospun PCL nanofibers without post-drawing (3.5-600MPa) [7, 29, 30]. The average Young's modulus of DR4 post-drawn nanofibers was 5.89GPa ($\sigma=1.91$, $n=8$), which exceeds reported values for post-drawn microfibers (200-465MPa) [4, 14, 15] and electrospun PCL nanofibers without post-drawing (0.62-3.7GPa)[7, 30, 31]. Since post-drawing ratio is associated with a reduction in fiber diameter there is an inverse relationship where mechanical strength increased with decreasing fiber diameter (**Figure 7**). This trend has also been observed in other studies where fiber diameter was modulated by electrospinning parameters and not post-drawing [6-8]. However, with post-drawing associated fiber diameter reduction, the sharp exponential increase in mechanical properties occurs at a higher fiber diameter and results in overall stronger nanofibers [7]. This indicates that different mechanisms are involved in diameter reduction strengthening associated with automated track post-drawing and diameter reduction strengthening associated with inherent variations to the electrospinning process.

Figure 7: The ultimate strength of various PCL structures is plotted against fiber diameter or film/bar thickness (x-axis in log scale). For automated track, individually post-drawn electrospun nanofibers (AT Post-drawn Espun nanofiber) decreasing diameter is mediated by post-drawing from draw ratios (DR) of 1, 2, 3, and 4. The largest diameter point on that curve was collected as a random mesh. For other electrospun nanofibers (Espun nanofiber) decreasing diameter is mediated by changing solution concentration or preferential individual fiber selection from a diameter distributed sample. For films (Post-drawn film) decreasing thickness is mediated by bi-axial drawing. For melt and wet spun fibers (Post-drawn conventional fiber) diameter is decreased by post-drawing, but diameter can be made consistent for different draw ratios by adjusting the pre-drawn fiber diameter. Only one thickness of PCL bars (Bulk PCL) were reported.

2.5 Applications

The need and potential impact of mechanically enhanced electrospun polymer nanofibers reaches a wide variety of applications. One specific application that requires stronger PCL nanofibers is tissue engineering grafts for load bearing orthopedic applications. Directed long distance cellular growth is required for regeneration of aligned tissues such as nerve, muscle, tendon and ligament. Polymer nanofibers, with similar size scale to cells, are able to promote cell alignment and elongation along the nanofiber direction through physical guidance cues. Previous research has established the potential of PCL nanofibers in such applications. However, in load bearing applications, PCL nanofibers are much weaker than mechanically robust tissues like ligament [30, 35, 36]. For example, PCL nanofiber grafts for anterior cruciate ligament (ACL) replacement had a 7.4x lower failure strength and a 6.4x lower Young's modulus than the native tissue [37]. Previous attempts to enhance the mechanical strength by electrospinning high molecular weight PCL nanofibers raised the failure strength of grafts by 2.4x, but still only reached 33% of the ultimate tensile strength of ACL tissue [38]. The mechanical enhancement of PCL nanofibers demonstrated through post-draw processing (7.4x ultimate strength and 15.3x Young's modulus) would be sufficient to match native ACL mechanical properties for this application.

2.6 Scalability

Alteration of the electrospinning process can be divided into two classifications, spinneret modifications or collector modifications [39]. Spinneret modifications are generally employed when considering production rate limitations while collector modifications focus on the fiber orientation and mesh architecture. Various research conducted in the design of high throughput spinnerets, such as multiple spinnerets and nozzleless spinning, increased production rates up to several thousand times that of traditional electrospinning [40-43]. The automated track design would be considered a modification of the collector stage which allows control over fibrous mesh organization but also

improves production rates because it is a continuous process capable of overcoming charge buildup in deposited fibers. Furthermore, because this approach involves a change in design of the collecting point rather than the spinneret, it is compatible with most high throughput spinneret advances. For example, multiple automated track devices arranged in a collecting array could be directly combined with a high throughput nozzleless spinneret configuration.

3. Conclusions

In summary, the automated track approach facilitates integration of electrospun polymer nanofiber manufacturing with critical post-drawing steps fundamental to conventional fiber processing. The key elements of this technology include the ability to post-draw individual electrospun nanofibers under controlled draw conditions, simultaneous processing of thousands of fibers per minute, and the ability to draw semi-solid nanofibers immediately upon deposition/prior to complete solvent evaporation. This investigation, performed using PCL nanofibers as a model system, demonstrated the capability of automated track post-drawing to engineer polymer nanofibers with enhanced macromolecular orientation and mechanical properties. The simplicity of this collector based approach render it compatible with most polymers that can be electrospun across parallel plates and it is expected to be compatible with high yield multi-needle and nozzleless spinnerets for scalability.

4. Experimental Section

4.1 Automated track device

The automated track collector utilizes variable track angle to simultaneously elongate fibers as they are collected and overcome charge buildup from collected fibers. Acrylic was used to fabricate the walls, baseplate and environmental chamber to reduce interference from conductive surfaces. A Computer Numerical Control (CNC) mill was used to machine the walls and cut the channels which hold the track shafts. A Legend36ext Laser Cutter was used to fabricate the baseplate and environmental

chamber. A 12V Compact Round-Face DC Gearmotor was installed to turn the aluminum tracks. The aluminum tracks are made from latex (0.014 in. thick) with a layer of aluminum foil tape (0.007 in. thick). The tracks are grounded using two terminal blocks grounded to the voltage source. The terminals contact the moving tracks with wire brushes extending from both terminals.

4.2 Electrospinning

An 18 wt% PCL (mw 80,000 Sigma Aldrich) solution was prepared in a 3:1 mixture of dichloromethane (DCM, Sigma Aldrich) and dimethylformamide (DMF, Sigma Aldrich). Solutions were prepared in 20 mL glass vials. Each solution was allowed to mix overnight at room temperature (65F°). For all samples, electrospinning was performed at a voltage of 10kV with the needle positioned 17 cm from the tracks for a period of fifteen minutes. The syringe pump (New Era Pump Systems) was set to a rate of 0.8 mL/hour and extruded the polymer through a 21 gauge needle. Temperature was monitored and samples were only collected between 55-65F°. The device was contained in an acrylic box to act as an environment control. This design served to further insulate the electrospinning process from the surrounding environment, preventing interference from outside conductive points and air flow from the fume hood. A humidifier (ReptiFogger; ZooMed) and controller (HygroTherm; ZooMed) connected to the box allowed the relative humidity (RH%) to be regulated and kept to a range of 45-55% for all samples [44]. Eight samples at each draw ratio were collected (DR1, DR2, DR3, DR4).

Samples were also collected at DR1 and allowed to dry over 72 hr before being manually post stretched to a draw ratio of 2 (MDR2) by extending the width of the collecting rack at a rate of approximately 2.5 mm/s. The extended drying time ensured that sufficient time for solvent evaporation had passed and only completely dry fibers were tensile tested for all MDR2 samples. Randomly aligned fibers were collected in the same manner and under the same conditions by replacing the automated track collector with a flat, grounded collection aluminum target. After fabrication, both drawn and randomly aligned fiber samples were mounted on plastic frames. Each sample contained a 12x7 mm nanofiber square

(**Figure 3**). All tests were performed within two weeks of sample collection

4.3 Material characterization

PCL samples of DR1-4, MDR2 and random alignment were mounted on plastic slides (**Figure 3**) and characterized with a Bruker Tensor 27 FT-IR Fourier transform infrared spectroscopy (FTIR) spectrometer. OPUS Data Collection and Analysis Spectroscopy Software is used to analyze the FTIR spectra and characteristic peaks for each sample. The major characteristic peaks for PCL occur at 2949cm^{-1} and 2865cm^{-1} , indicating CH_2 vibrations and at 1727cm^{-1} indicating C=O vibrations. Peaks at 1165cm^{-1} and 1190cm^{-1} were also observed and analyzed. Full range FTIR wavelengths of each sample type were normalized and plotted.

Wide angle X-ray diffraction (WAXD) analysis of PCL fibers was performed by FullScaleNANO Inc. (www.fullscalenano.com, Tallahassee, FL) on fiber samples of DR1-4 mounted on aluminum frames. Data was collected using a Siemens D500 Bragg Brentano goniometer using unmonochromated $\text{CuK}\alpha$ (30mA at 40kV) with a graphite diffracted beam monochromator and scintillation detector. Samples were mounted on a phi-axis rotation stage and were aligned for attachment in the initial 0° rotation direction. Data was acquired using 0.05° steps with a $2.4^\circ/\text{min}$ scan rate. The data was collected at each phi-angle where the phi-angle varied from 0 to 360° in 15° intervals. At 0° and 180° positions the nanofibers are aligned parallel to the direction of the beam, at 90° and 270° positions the nanofibers are aligned perpendicular to the beam. Peak height was normalized in **Figure 5**.

4.4 Mechanical Testing

To determine ultimate tensile strength, fibers were tested in a SHIMPO tensile tester at a rate of 2 mm/min until failure. Samples are tested at low strain rates to reduce noise and obtain smooth stress-strain curves. The slow strain rate also eliminates the risk of causing brittle behavior induced by high

rates of strain [31]. Individual framed samples were loaded into the SHIMPO and the sides cut away before testing so that the nanofibers took on the entire load. Young's modulus was determined by finding the slope of the linear region of the stress-strain curve which occurred between 0-0.35 strain for most samples. To determine where the linear region ended, first a linear trendline was fit to the full plot to failure of each individual curve obtained for each sample. If the r^2 value for the trendline was <0.95 then the range of data used to generate a new trendline was incrementally decreased to improve the linear fit. The lower endpoint was fixed at zero and the upper endpoint was decreased from the strain at failure toward zero in 0.05 increments of strain. This process was repeated until the r^2 value for the trendline was >0.95 , indicating a 95% fit to the curve. The slope of the equation of the trendline was taken as the Young's Modulus for that particular sample. Toughness was calculated using the stress-strain curves for each sample prior to failure. Riemann sums were used to find the area under the curve for each sample. Averaging these values determined the average toughness per draw ratio

The cross-sectional area of samples was determined with SEM imaging. For each sample, five pictures were taken at 850x magnification to determine fiber density and five pictures were taken at 8500x magnification to determine individual fiber diameter. The ImageJ plug-in Cell Counter was used to quantify the number of fibers over a distance of 100 μm perpendicular to fiber alignment. Fiber diameter was determined with the measurement tool in ImageJ. An average of both values was taken for each sample to find average number of fibers per 100 μm perpendicular to fiber alignment and average fiber diameter per sample, seen in the table in **Figure 3**. Total number of fibers per sample was calculated as the average number of fibers per 100 μm multiplied by 120 for a 12 mm wide sample. The average fiber cross-sectional area was calculated as $0.25 \cdot \pi \cdot (\text{AvgDiameter})^2$. Total sample area was then calculated as total number of fibers multiplied by average individual fiber cross-sectional area. Stress was calculated as the moving average force exerted during testing divided by the calculated cross-sectional area of the individual sample tested. Strain was calculated as displacement + initial

sample length divided by the initial sample length of 7 mm.

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Graphical Abstract