A comparative parameter study: controlling fiber diameter and diameter distribution in centrifugal spinning of photocurable monomers

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Abstract

In this study, key factors for controlling the average fiber diameter and diameter distribution of fibers made via simultaneous centrifugal spinning and UV initiated polymerization are elucidated. Through systematic investigation, it was found that average fiber diameter has a strong dependence on monomer delivery rate through the orifice, which can be intuitively linked to both the orifice diameter and monomer mixture viscosity. On the other hand, the breadth of the fiber diameter distribution can be controlled by the spin speed of the rotating spinneret. Carefully tuning these process parameters allows near independent control of fiber diameter and its distribution, which could provide access to a widely tailorable range of fiber diameters and diameter distributions appropriate for different applications. Finally, under optimized process conditions, crosslinked fibers with average diameters of approximately 1.5 μm can be produced, which are one to two orders of magnitude smaller than photocured fibers fabricated in previous reports and comparable with the smallest melt blown nonwoven fibers produced commercially. Coupled with the advantages of cross-linked fibers made by in-situ photopolymerization, the capability to produce small fibers with tailored

diameter distributions by centrifugal spinning could further establish this technology as a competitive alternative to existing approaches.

1. Introduction

Nonwoven fibrous mats are composed of randomly oriented fibers connected by physical entanglements as opposed to stitching or weaving. Much research effort has focused on fine polymeric nonwoven fibers, given their significant potential in a wide range of applications, including filtration and separations [1, 2], tissue engineering scaffolds [3, 4], wound dressings [5], and smart textiles [6, 7].

Most nonwovens composed of fibers with micron or submicron diameters are fabricated by electrospinning [8], melt blowing [9, 10] or hybrids of the two methods such as melt electrospinning [11], gas-assisted electrospinning [12], free surface electrospinning [13, 14], and blow spinning [15]. Recently, a new spinning method called centrifugal spinning has been developed as a potentially high throughput and low energy consumption route to nonwoven synthetic fibers. Centrifugal spinning has been used in both melt and solution state production of a variety of polymeric [16, 17], inorganic [18], and composite [19] fibers. In this process, a polymer melt or polymer-solvent solution is delivered through orifices on a rotating spinneret. When the centrifugal force and hydrostatic pressure overcome the surface tension of the pendant drop formed at the spinning orifice outlet, the droplet is stretched into a thin fluid jet and further attenuated by the frictional force of air. As the temperature of the polymer melt decreases below the crystallization temperature, or the solvent of the polymer-solvent solution evaporates sufficiently, the fluid jet solidifies to form fibers that are deposited onto the collector near the spinneret.

A special attribute of this process is that the centrifugal force determines both the feed material delivery rate through the orifices and the amount of drawing force to which the fiber jets are subjected. This is contrary to other fiber spinning methods, where the material delivery rate, often controlled by a syringe/piston pump or an extruder, and the fiber drawing force, governed by either the hot air flow rate in melt blowing or the applied voltage field in electrospinning, can be independently manipulated.

Several studies have focused on the physics governing fiber initiation and attenuation in centrifugal spinning. Notably, Mellado et al. established a semi-empirical scaling framework for fiber radius as a function of viscosity, angular speed, distance to the collector, and radius of the orifice [20]. Ren et al identified and analyzed key dimensionless groups such as Weissenberg number, Capillary number, and Ohnesorge number, that determine fiber morphology and diameter using a variety of polymer-solvent solutions [21]. Taghavi and Larson proposed a theoretical model that allows for determination of fiber velocity and diameter by balancing centrifugal, inertial, and viscous forces [22]. Others have provided insight on the jet initiation stage and fiber flight trajectory using high speed photography [23, 24].

Although a versatile profile of polymeric nonwoven fibers has been fabricated from all the aforementioned methods, processing high performance polymers into fibers still remains challenging, because these materials typically possess excellent chemical resistance to most common solvents and only form polymer melts at excessively high temperatures where oxidation and degradation of the polymer during processing are a concern. In cases where high performance polymers can be dissolved into a solvent, solution state fiber spinning typically uses polymer-solvent solutions containing large amounts of solvent, and as a result concerns of

low process throughput, environmental issues of solvent recovery and process safety are often introduced. On the other hand, melt state processing requires significant energy input [25] which can be a complicating cost factor with fluctuating/increasing energy costs. To attempt to address these issues, our group recently developed an alternative approach that combines electrospinning and photopolymerization of non-volatile monomers in a single step to form nonwoven fibers [26]. In this approach, a liquid mixture containing monomers and photoinitiator is delivered through an orifice and solidified in flight via UV initiated thiol-ene photopolymerization to form solid fibers containing a crosslinked molecular network. The process is controlled by a number of interrelated parameters including polymerization kinetics, solution elasticity, and fiber flight time, all of which can contribute to fiber formation and morphology [27]. Owing to the covalent crosslinks in the fiber product, the fibers possess excellent solvent stability, thermal stability (i.e., up to 450 °C in some cases) that is determined by the thermal stability of covalent bonds not material thermal transitions, and tunable physical and mechanical properties that can be tailored with monomer composition and architecture [26, 28, 29]. In some circumstances unreacted thiol and ene functional groups remain on the fiber surface and interior, which can be post modified by a variety of small molecules or secondary polymers [30-32]. The post functionalization further diversifies the properties and potential applications of crosslinked thiol-ene fibers. Thiol-ene fibers prepared this way are therefore ideal candidates to be used in high temperature and harsh environments, such as technical textiles, hot chemical/gas filtration, catalysis, composite materials, etc. This simultaneous photopolymerization and spinning concept is generalizable and has been

implemented in electrospinning, centrifugal spinning, and hydrodynamic shaping [26, 28-30, 32].

Most previous reactive fiber spinning studies have focused on identifying process conditions for fabricating defect free fibers or developing fundamental understanding of the physics and mechanics of the reactive fiber formation process. Unfortunately, little attention has been focused on how one might control the diameter distribution of fibers. The average fiber diameter and diameter distribution are important parameters for nonwovens because the size of the fiber primarily determines the specific surface area and pore size of the final nonwoven mat, properties that ultimately dictate suitability for end use applications. For example, numerous studies have found that fiber diameter has profound impact on cell proliferation and controlled drug release in scaffolds [3, 33, 34], and filtration properties of nonwoven membranes [35].

There have been a number of studies on tuning the diameter distributions of fibers made by polymer-solvent solution [17, 19, 20] and melt state [16] centrifugal spinning. Most of these studies concluded that the dominant parameters for controlling fiber diameter include polymer-solvent solution concentration, orifice diameter, spin speed, and processing temperature (melt state). It is expected that there will be intrinsic differences between reactive and polymer-solvent solution/melt centrifugal spinning processes. First, the photopolymerizable feedstock used in the present reactive processing study contains mostly monomers with trace amounts of polymer to tailor the rheology; the total polymer concentration is too low to be in the semi-dilute entangled regime typically required for forming defect free fibers by solution spinning [8, 36, 37]. As a result, the viscoelastic properties

and the delivery and drawing of the monomer solutions are very different from those of polymer-solvent solutions and melts. Second, the solidification mechanism in reactive centrifugal spinning is through photopolymerization, whereas in solution state spinning solidification it is driven by solvent evaporation and in melt state spinning it is sufficient cooling to induce crystallization or vitrification. It is apparent that the parameters influencing these mechanisms are different. For these reasons, it is difficult to predict how fiber size distribution can be manipulated in reactive centrifugal spinning simply based on previous solution or melt studies.

Therefore, the primary objective of this paper is to investigate how the average fiber diameter and diameter distribution can be controlled by varying process and material parameters such as monomer feed viscoelasticity, orifice size and spin speed. This will not only demonstrate the tunability of the process, but will also shed light on the underlying physics of fiber thinning in reactive centrifugal spinning. Another area of focus will be to establish the lower limit in average fiber diameter that is attainable using this method. Smaller fibers close to and below one micron provide large surface area to volume ratios, and are light weight. The ability to produce small fibers is particularly attractive for a number of applications and this capability could further establish simultaneous centrifugal spinning and photopolymerization technology as a competitive alternative to existing approaches.

2. Experimental

2.1 Materials

Dipentaerythritol pentaacrylate (5A), pentaerythritol tetrakis (3-mercaptopropionate) (4T), polyethylene oxide (PEO) with a viscosity average molecular weight (MW) of 10^6 g/mol,

anhydrous ethyl acetate, and formic acid (>88 wt%, reagent grade) were purchased from Sigma Aldrich. A commercial photoinitiator, Irgacure 2100, was kindly provided by BASF. Polyamide 6 (PA6, Aegis H95ZI) was purchased from Honeywell Co. All chemicals were used as received.

2.2 Photocurable monomer mix preparation

The photocurable monomer feed consists of ene functional monomer, thiol functional monomer with a trace amount of PEO, photoinitiator and ethyl acetate. Previously, it had been demonstrated that the elasticity of the monomer mixture, imparted by the addition of high MW PEO, plays an important role in controlling fiber formation and morphology in the in-situ centrifugal spinning and photopolymerization process. It was determined that a minimum of 100 ppm high MW PEO was necessary to suppress surface tension driven instabilities and form uniform fibers, provided photocuring kinetics and solidification were sufficiently fast [27]. In this study, dilute mixtures of high MW PEO in thiol monomer were prepared by dissolving appropriate amounts of PEO in 4T monomer at 70 °C for 18 hours. Unless otherwise specified, the stock concentration of PEO is 0.1 wt% in 4T, which is equivalent to 180 – 210 ppm in the final photocurable monomer feed depending on the final proportion of all components.

The final monomer ene to thiol functional group molar ratio was kept constant at 4 to 1 for all monomer mixes to provide sufficient curing kinetics and reduce the oxygen inhibition effect of acrylate polymerizations [26, 28]. The photoinitiator loading was kept constant at 5 wt% of the overall monomer feed. In addition, various amounts of ethyl acetate ranging from 0 - 18 wt% were added to adjust the final viscosities of the monomer feed. Although other reactive monomers with low viscosities such as 1, 6-hexanediol diacrylate can also be used, ethyl

acetate was preferred in this study because it could adjust viscosity without significantly affecting the photopolymerization kinetics or gel point.

The components were mixed in a scintillation vial using a vortex mixer (Thermolyne 37600) to make a homogeneous monomer feed mixture. The solution was then loaded into a syringe masked from room light, which was used to transfer the monomer mixture into the spinneret. The monomer mixture was prepared in a room that minimized stray UV light to prevent pre-exposure that could initiate photopolymerization prior to fiber spinning.

2.3 Nylon-formic acid solution preparation

As a comparison to reactive centrifugal spinning, various amounts of PA6 were added to formic acid to form solutions containing 71 to 83 wt% formic acid. Although polymer-solvent solutions are typically described in terms of the concentration of polymer, in this study, these solutions were labeled by the wt% of the solvent in order to allow easier comparison with the photocurable monomer feed mixtures. The solution was gently stirred at room temperature overnight to ensure complete dissolution. The solution was loaded to a syringe, which was used to transfer the solution into the spinneret.

2.4 Centrifugal spinning

The in-situ centrifugal spinning and photopolymerization of the monomer feed mixture was performed using a lab scale Forcespinning apparatus (FibeRio Cyclone L1000) equipped with a custom UV light source comprised of a power supply, an igniter, a lamp housing (Photon Technology International LPS-220, LPS-221, LPS-A1010), a Mercury short arc lamp (Osram HBO 103W/2), and a UV transparent reflective mirror (Edmund optics). A detailed description of the light source design was reported previously [27]. The pre-mixed monomer feed was transferred

to the spinneret by a masked syringe to prevent exposure to stray UV light. The spinneret holds about 2 mL of liquid and is cylindrical with two opposing orifices. Two Luer-lock blunt-tip needles 3.81 cm in length with different diameters (337 μm , 260 μm , 210 μm) were connected to both sides of the spinneret, leading to a rotational radius of 11.6 cm. It should also be mentioned that in Section 3.4, Luer-lock blunt-tip needles of 2.54 cm in length and 159 μm in diameter were employed to fabricate fibers with smaller diameters, because a needle length of 3.81 cm was not available for this diameter. All photopolymerized fibers were formed at a constant light intensity of 1160 mW/cm², measured by a radiometer (Coherent Field Max II) in the same plane as the orifice outlet, and a spin speed of 2500 rpm (unless otherwise specified in Section 3.2). For PA6-formic acid solution state centrifugal spinning, the spinning procedure was essentially identical to the aforementioned method, except no light source was used. The spin speed was held constant at 4500 rpm (unless otherwise specified in Section 3.2).

In both cases, single orifice flow rates were measured by precisely weighing the spinneret containing the desired feed before and after the spinning process. The spin times ranged between 30 to 180 seconds to ensure accurate measurements of the flow rates. The spin time was determined to be long enough to minimize the effects of cycle initiation and termination, but short enough to prevent the spinneret from being starved of feed during the spinning cycle. This is important because in centrifugal spinning, hydrostatic pressure of fluid inside the spinneret can influence the feed delivery rate through the orifice [17]. However, we observed that in our system, the feed delivery rate was independent of the initial fluid level inside the spinneret due to its geometry, which was in agreement with the analysis of Mellado

and coworkers [20]. A more detailed explanation is presented in Supporting Information Table S1.

2.5 *Material characterization*

Viscosities of feed materials were measured by a shear rheometer (TA instruments AR-2000 EX). Frequency sweeps were performed from 0.1 to 10 rad/s with 5% strain rate in the linear viscoelastic regime. Elasticities of the monomer mix solutions were measured by a capillary breakup extensional rheometer (CaBER, Thermo Haake CaBER 1) equipped with parallel plates 4 mm in diameter. The laser micrometer of CaBER recorded the filament diameter evolution over time at 1000 Hz. Five measurements were taken for each monomer mix solution. The time evolution of filament diameter was fit to an elastic fluid model to obtain the fluid relaxation time [38].

The density of the monomer mix was determined to be 1.15 g/cm^3 by measuring the weight of a known volume of the solution. The surface tension was determined to be 40.93 mN/m using an axisymmetric pendant droplet of the monomer mix with methods described previously [39]. To avoid curing of monomers in ambient light during measurement, photoinitiator was not added in the solutions used for these characterizations.

2.6 *Fiber diameter characterization*

Fiber morphologies were examined by scanning electron microscopy (SEM, Hitachi S-5500). ImageJ (National Institutes of Health) was used to measure the diameters of the fibers. For every fiber sample, 15 to 20 SEM images were taken and more than 150 counts of fibers were measured to provide a representative statistical analysis of fiber diameter. Fiber diameters were fit to log-normal distributions as previously described [9, 40].

3. Results and Discussion

3.1 *Effect of viscosity and orifice diameter on average fiber diameter*

In this section, a spin speed of 2500 rpm was employed because it provided both a sufficient centrifugal force for fiber formation and adequate fiber flight time for solidification by photopolymerization. This allows access to a relatively wide processing window for a range of monomer feed viscosities and orifice diameters.

Figure 1 displays a collage of SEM images, in which fibers were formed using different orifices (337 μm , 260 μm , or 210 μm) and monomer feed viscosities that was controlled by varying non-reactive EA diluent between 0 and 18 wt%. Fiber mats containing large filaments (i.e., roughly equal to or greater than 100 μm in diameter), uniform and well cured fibers, and fibers with fused junctions were obtained. The photographs of the entire fiber mats for all conditions are also provided in Figure S1 of the Supporting Information. This matrix of conditions demonstrates that the fiber morphology can be manipulated by controlling either the viscosity or the orifice size independently, or tailoring them in concert. In the upcoming section, the effects of the two individual parameters and the interactions between them in defining the final fiber morphology and diameter distribution will be the focus.

Figure 1. SEM images of fibers made from monomer feeds containing various amounts of EA (ranging from 3 wt% to 18 wt%) and different orifice diameters (337 μm , 260 μm , and 210 μm). Images with green frames indicate conditions that formed defect free fibers, while images with

red frames indicate conditions that formed fused fibers or unstretched fibers. The 100 μm scale bar applies to all images.

Figure 2. (a) Viscosities and (b) delivery rates of monomer feed mixtures containing various amounts of EA through two orifices of the spinneret.

The viscosities of the monomer feed mixtures containing different amounts of EA are shown in Figure 2(a), while the flow rates through the orifices at various spinning conditions (varying wt% EA and orifice diameter) are shown in Figure 2(b). It is expected that for any given monomer mixture, the flow rate is higher with increasing orifice diameter. It is also expected that the flow rate increases with increasing wt% EA (i.e., decreasing mixture viscosity) for any given orifice diameter. This can be rationalized by considering the viscous resistance to flow, which acts against the outwardly directed capillary force and centrifugal force as the monomer mixture travels along the narrow and long needle/capillary toward the orifice opening, is reduced for lower viscosities and larger orifices. It should also be noted that the effect of

viscosity on flow rate is more profound for larger orifices, indicated by the steeper slope of the flow rate curve as orifice diameter increases from 210 μm to 337 μm .

Figure 3. Data of Figure 2 plotted as monomer mix flow rate versus inverse of its viscosity. The red, green, and purple areas correspond to a flow rate that is too low, close to optimal, and too high, respectively, to form continuous and defect-free fibers at this particular spin speed. The solid symbols represent conditions where defect free fibers were made, and open symbols represent conditions where the resultant fibers contained defects or no fiber could be made. The SEM images and photograph shows typical fiber morphologies in each regime.

In Figure 3, data from Figure 2 are replotted as flow rate versus the inverse of viscosity. The flow rates are clearly linearly proportional to the inverse of viscosity. This behavior (i.e., liquid flow through a long and narrow tube) is analogous to pressure driven capillary flow, where a liquid is forced through a capillary of known diameter under a fixed pressure drop and its flow rate is measured. The viscosity of the fluid can be described and measured by the following:

$$\eta = \frac{\Delta P R^4}{8 Q L}$$

where η is the viscosity of the fluid, ΔP is the applied pressure drop, R and L are the radius and length of the capillary, and Q is the fluid flow rate through the capillary. In centrifugal spinning, the fluid flow through the needle capillary during the jet initiation stage is similar to that in pressure driven capillary flow, where the centrifugal force and the hydrodynamic pressure can be combined and considered as an effective pressure drop, ΔP . Although the above equation is designed to describe a Newtonian fluid in a capillary, the monomer mixtures in this case contain such low concentrations of polymer that they can essentially be considered near-Newtonian fluids for this analysis. Using this relationship, it is therefore expected that at the same spin speed and orifice diameter, the flow rate and the viscosity are inversely proportional to each other and this was the motivation for plotting Figure 3 in this manner.

The final fiber morphologies corresponding to the data in Figure 3 can be categorized into three regimes. In the first regime, shaded red in Figure 3 (also corresponds to the upper right corner in Figure 1), either no fiber was formed or the fiber mat contained significant amounts of large filaments around 100 μm in diameter or larger. Both scenarios are results of the monomer mixture being too viscous. In the first case, the centrifugal force was insufficient to overcome the capillary force and surface tension of the monomer mixture, and therefore very little monomer was delivered through the orifice. This can be confirmed by flow rates that were close to zero. In the latter scenario, the centrifugal force exceeded the surface tension and stretched the exiting monomer into filament jets, but failed to overcome the viscous and elastic stresses, which act to stabilize the filament and resist further jet thinning. As a result, the initial thick filament jet either remained attached to the spinneret orifice, indicated by the red circle

in the lower left photograph of the spinneret in Figure 3, or was disengaged from the spinneret (possibly facilitated by the action of centrifugal forces) and deposited in the fiber mat as shown in the upper left SEM micrograph in Figure 3. These phenomena have been reported in other spinning methods previously, and such spinning mixtures have been commonly referred to in the literature as ‘having poor spinnability’ due to an excessively high viscosity [41, 42].

In the second regime, shaded green region in Figure 3 (also corresponds to the center images in Figure 1), the fibers were relatively uniform in fiber diameter and well cured. The monomer mixture viscosity was well-matched with the selected orifice size to provide moderate material delivery rate through the orifice. The randomness of the fiber orientations in the mat shown in the SEM image also suggests that fibers may have undergone a sufficient amount of whipping during processing and lay down on the collector. It is also worth noting that the optimal flow rates for this photocurable system are up to 100 g/hour per orifice, which is one to two orders of magnitude higher than most solution state bench-scale electrospinning conditions reported in the literature [2, 8, 39, 42].

In the third regime, shaded blue region in Figure 3 (also corresponds to the left bottom corner images in Figure 1), the process becomes limited by the reaction kinetics; because fibers did not completely cure before being deposited onto the collector they formed fused fibers. It is anticipated that the low viscosity and high flow rates in this regime also produce high fiber flight velocities leading to insufficient total flight time for the fibers to cure. In addition, the fibers that were produced in this regime appeared to be much more aligned along the spinning direction. This is an indication that the monomer jets exit the orifice with a high linear velocity

along the orifice axis and are directly deposited onto the collector without whipping, unlike the more randomly oriented fibers in the green regime of Figure 3.

Figure 4. Average diameters of fibers made from monomer mixtures containing various amounts of EA and different orifice sizes as a function of inverse monomer mix viscosity. The blue, green, and orange tiles indicate the optimal viscosity range for orifice diameters of 337 μm, 260 μm, and 210 μm, respectively. The error bars represent the standard deviations of the fiber diameter distributions.

Figure 4 shows the average diameters and standard deviations of fiber diameters produced from monomer mixtures with different viscosities and from three different orifice sizes. Average fiber diameter clearly increases with increasing orifice diameter. This is expected because more monomer can be delivered through a larger orifice while holding centrifugal force (i.e., correlated to spin speed) constant. Under conditions where there is a similar extent

of drawing, the fibers with larger initial fiber diameters would also have larger final fiber diameters.

There is an optimal viscosity window for each orifice size, labeled by the blue, green, and orange bars for orifices with 337 μm , 260 μm , and 210 μm diameters, respectively. Further, the suitable monomer viscosity range is narrower for larger orifices, because the flow rates of liquids through larger orifices have a stronger dependence on viscosity, as demonstrated previously in Figure 3.

In addition, Figure 4 shows that holding orifice size constant but increasing the amount of EA diluent increases fiber diameter. This is contrary to the common knowledge of polymer-solvent solution state spinning, regardless of whether the process is electrospinning, centrifugal spinning, or blow spinning, where increasing the amount of solvent or decreasing polymer concentration typically generates fibers with smaller diameters [15, 19, 41, 43, 44]. As will be discussed shortly, this is most likely because a significant portion of fiber thinning during processing of a polymer-solvent solution (e.g., 70-95 wt% solvent) is due to solvent evaporation.

Figure 5. Master curve of average fiber diameter plotted against flow rate made from monomer mixtures containing various amounts of EA and using different orifices. All runs were conducted at 2500 rpm. The error bars represent the standard deviations of the fiber diameter distributions.

Even more interestingly, the average fiber diameters of the three spinning series with different orifice diameters in Figure 4 collapse into a single master curve when plotted against flow rate as shown in Figure 5. This shows that when the spin speed was kept constant, fiber diameter can be practically determined by the flow rate, regardless of solution viscosity or orifice size.

PA6-formic acid solutions with viscosities similar to the photocurable monomer mixtures were processed using centrifugal spinning to compare the factors affecting fiber diameter in the photocurable system to a conventional polymer-solvent solution system. The spin speed was

kept at 4500 rpm to provide sufficient centrifugal force for drawing the PA6-formic acid solutions while maintaining a reasonably wide processing window that resulted in defect free fibers. The viscosity, flow rates, and SE images of fiber samples were collected and are presented in Figure S2 and S3. Figure 6 shows the fiber diameter distributions of PA6 fibers processed from solutions with different viscosities using two different orifice diameters as a function of the flow rate.

Figure 6. Average fiber diameter produced from PA6-formic acid solutions (71-83 wt% formic acid, at increments of 3 wt%) plotted against flow rate. The error bars represent the standard deviations of the fiber diameter distributions.

Comparing Figure 5 and Figure 6, two contrasting trends can be observed for photocurable and solution state centrifugal spinning. First, as flow rate increases, the average fiber diameter increases for the photocurable system, but decreases for the PA6-formic acid system. Second, the fiber diameters of the photocured fibers depend solely on the flow rate through the orifices, whereas the average fiber diameters of fibers processed from 210 μm

diameter orifices were three to four times smaller than those from 337 μm diameter orifices at the same flow rate.

These trends can be mainly attributed to the fundamentally different fiber solidification mechanisms of the two systems. In the photocurable system, the solidification is mainly driven by photopolymerization. Although the monomer mixtures contain some solvent, the amount is small enough (<18 wt% as compared to 70-95 wt% used in typical solution state fiber processing) that the effect of solvent evaporation on fiber diameter reduction is minimal. This is evidenced by the residual amounts of EA in the final fiber product, measured by thermogravimetric analysis (TGA) as shown in Figure S4 in the Supporting Information. TGA results show that the amount of EA that evaporated during spinning for photocurable monomer mixture was at most 9 wt%, which is clearly insufficient to account for any significant reductions in fiber diameter. Therefore, as EA content increases, the increase in monomer mix flow rate strongly dominates any filament thinning due to solvent evaporation, leading to an overall increase in final fiber diameter. For this reason, the photocurable fiber process more closely resembles a melt state fiber process, where fiber diameters are strongly dependent on melt delivery rate and the ratio between material delivered through the orifice and fiber drawing force applied [9, 16, 45, 46].

Alternatively, in polymer-solvent solution state fiber spinning, fiber solidifies following sufficient solvent evaporation. Solutions containing more solvent take longer to evaporate to a point that results in solidification, thereby rendering more time for the fluid jets to be drawn. In addition, solutions containing more solvent may undergo additional thinning due to reduced viscous stresses even before solvent evaporation takes place [19]. In total, as solvent content

increases, the enhanced thinning of fibers due to solvent evaporation and lower viscosity overwhelms the incremental increase of solution delivery rate as shown in Figure S3(a), generating smaller fibers. Numerous reports concerning centrifugal spinning or electrospinning of a variety of polymer-solvent systems have commented on polymer concentration as the most important process parameter on impacting fiber formation and fiber diameter distribution [36, 41, 47-49].

3.2 *Effect of spin speed*

To investigate the impact of spin speed on fiber diameter and distribution, spin speed was varied from 1500 to 6500 rpm for photocurable monomer mixtures and from 2500 to 10500 rpm for PA6-formic acid solutions. The diluent content was 12 wt% EA and 80 wt% formic acid for the photocurable monomer mixture and the polymer-solvent solution, respectively. The orifice diameter was kept constant at 210 μm .

Figure 7 shows SEM images of photocured fibers processed at various spin speeds from the same monomer mixture. Below 1500 rpm, no fiber was formed, because the centrifugal force did not sufficiently exceed the surface tension and capillary force of the exiting liquid at the orifice outlet, and no monomer was delivered through the orifices as a result. From 1500 to 5500 rpm, fibers were produced without defects, indicating the centrifugal force at this spin speed is strong enough to consistently deliver solution through the orifices. This range of spin speeds also provides sufficient flight time for the fibers to cure completely [27]. At 6500 rpm and above, the fibers passed through the UV exposed region too rapidly and did not completely solidify before being deposited onto the collector, forming fused fiber junctions. For comparison, PA6 solution containing 80 wt% formic acid was processed at spin speeds ranging

from 2500 to 10500 rpm at increments of 2000 rpm. SEM images of the resulting samples revealed that fibers were free of defects in this operating window, and the images are presented in Figure S5.

Figure 7. SEM images of photocured fibers made at various spin speeds ranging from 1500 to 6500 rpm. The monomer mix solution contained 64 wt% 5A, 19 wt% 4T, 12 wt% ethyl acetate, 5 wt% Irgacure 2100 and 190 ppm high MW PEO, and was processed from 210 μm diameter orifices. The 30 μm scale bar applies to all images in this figure.

Fiber diameter analysis was performed on all defect free fiber samples and the distributions were fit to a log normal function as previously described [9]. Sample log normal fits to photocured fiber diameter distributions are also provided in Figure S6 in the Supporting Information. For all fiber samples, the average and median of fiber diameters are nearly equal, indicating that the distribution of fibers produced by centrifugal spinning approximately follows a log-normal distribution. This is in good agreement with previous studies on solution or melt

state centrifugal spinning [9, 10, 16]. Flow rate measurements and parameters of log normal distribution fitting are presented in Table S2 (photocurable) and Table S3 (PA6-formic acid) in the Supporting Information.

Figure 8. Fit log-normal distribution functions for photocured fibers processed at different spin speeds.

Figure 9. Fit log-normal distribution functions for PA6-formic acid based fibers processed at different spin speeds.

Figure 8 and Figure 9 show the fit log-normal diameter distribution functions for photocurable and PA6-formic acid fibers, respectively, processed at various spin speeds. For both systems, although the material flow rate increases by over an order of magnitude over the range of spin speeds, the average fiber diameter increases consistently but still remains within one standard deviation. This can be understood as the result of two concurrent phenomena unique to centrifugal spinning. As spin speed increases, the centrifugal force delivers more material through the orifice, forming liquid jets with larger initial diameter which translates to a larger final diameter. On the other hand, the larger centrifugal force also enhances fiber thinning, leading to smaller final fiber diameter. The coupled but opposite effects of material delivery and fiber drawing by centrifugal force eventually lead to only subtle changes in average fiber diameter. Similar trends in diameter progression as a function of spin speed has been previously observed by other researchers in both solution state and melt state centrifugal spinning [16, 17, 19, 41, 50].

It is also worth noting that as spin speed increases, the width of fiber diameter distribution increases for photocured fibers, but decreases for PA6-formic acid based fibers consistent with other polymeric fibers produced by solution state centrifugal spinning [19, 41]. SEM images in Figure 7 clearly show that thick fibers appear more frequently at higher spin speeds for the photocurable system. One possible conjecture is that at higher spin speeds, the monomer jets are first exposed to UV light earlier in their flight path and have less time to undergo thinning before photoreactions begin. However, it is presently difficult to definitively conclude the exact cause of this contrasting trend in the breadth of the fiber diameter

distribution for these two systems. Unfortunately, there are not many existing studies to compare to because the majority report only the fiber morphology and average fiber diameter.

3.3 Effect of elasticity

Figure 10. (a) Average diameter and (b) coefficient of variation of photocured fibers made from monomer mixtures containing 100, 200, 400, and 600 ppm high MW PEO. (c) Relaxation times of the monomer mixtures containing 100, 200, and 600 ppm high MW PEO.

In our previous report, it was shown that monomer mixture elasticity is crucial for fiber formation. Monomer mix elasticity, imparted by the addition of high MW PEO, helps stabilize liquid jets against surface tension driven Rayleigh instabilities and prevents formation of undesired morphologies such as fibers with non-uniform diameters, beads-on-string and droplets [27]. Others have also shown similar effects of solution elasticity in the formation of electrospun or melt blown fibers [10, 51].

Despite its crucial role in fiber formation, we found that monomer elasticity has minimal influence on fiber diameter distribution. Four monomer mixtures with the exact same monomer, photoinitiator and diluent content, but containing 100, 200, 400, and 600 ppm of high MW PEO, were processed under the same conditions (spin speed = 2500 rpm, orifice

diameter = 260 μm , light intensity = 1160 mW/cm^2) by centrifugal spinning to form defect free fibers. Figure 10 (a) shows that average diameters of fibers processed from the four solutions are statistically the same. This result is unexpected, because given all other parameters as equal, the monomer jets with higher elasticity should possess higher resistance against self-thinning to form larger final fibers.

This trend can be explained by the relative timescales of polymerization kinetics and self-thinning of monomer jets. As previously reported, gel time, the time it takes for the monomers to form an infinite network, is the relevant characteristic timescale of the polymerization kinetics. For the 5A-4T system, at the specified light intensity in this study, the gel time is around 1 millisecond [27]. On the other hand, the fluid relaxation time, a timescale concerning elasticity, ranged between 30 to 100 milliseconds as shown in Figure 10 (c). The dash line indicates a power law fitting to the fluid relaxation times. The original CaBER data are presented in Figure S7 in the Supporting Information. The polymerization timescale is one to two orders of magnitude smaller than the elasticity timescale, suggesting that monomer jets have very limited time to undergo thinning before solidification. Therefore, the thinning behavior of monomer jets with different elasticities may not be drastically different during such a short timeframe.

The coefficient of variance presented in Figure 10 (b), which describes the normalized width of the log normal distribution, was calculated as previously reported [10]. There is only a 6% maximum difference in the coefficient of variation (CV) across the entire range of PEO content, with the minimum CV occurring at 400 ppm PEO. Such a small change in the CV may be simply attributed to the relatively small range of solution relaxation times in this study. For

example, Tan et al. reported a decrease in the CV of melt blown fibers from 60% to 10% when the fluid relaxation times of a polymer melt increased over five orders of magnitude [10]. Such a large range of elasticity is difficult to achieve in this system due to the limited solubility of PEO in 4T. Nonetheless, this analysis suggests that the optimal loading of PEO to achieve a narrow fiber distribution is around 400 ppm.

3.4 Smallest and largest fibers achieved

Figure 11. Smallest and largest fibers made by simultaneous photopolymerization and centrifugal spinning. The four different samples clearly indicate the tunability of the process with regards to both average diameter and width of the diameter distribution.

To demonstrate the tunability of this process, four representative samples with distinctive average fiber diameters and diameter distributions were fabricated by leveraging the results obtained from the previous sections and varying processing parameters such as the solution viscosity, orifice size, and spin speed. Figure 11 compares the diameter distribution fit functions

of the largest and smallest fibers. The process conditions and the fitting parameters are reported in Table 1, where μ and X_c are the measured and fit average of logarithmic diameter, σ and δ are the measured and fit standard deviation of logarithmic diameter, $\text{Med}[\log(d)]$ is the median of the fiber diameter distribution, and R^2 is the coefficient of determination. The SEM images of the corresponding fiber samples from Figure 11 are presented in Figure S8 in the Supporting Information.

Table 1. Process conditions and statistical analysis of the fiber diameter distributions for the smallest and largest thiol-ene fibers achieved in simultaneous photopolymerization and centrifugal spinning. Run numbers are correlated with Figure 11.

Run	wt% EA	Spin Speed (rpm)	Orifice Diameter (μm)	Orifice Length (inch)	d_{av} (μm)	μ	σ	Med [$\log(D)$]	x_c	δ	R^2
1	12	1500	159	1	1.55 ± 0.37	0.18	0.11	0.19	0.22	0.07	0.97
2	12	3500	159	1	1.71 ± 0.61	0.21	0.15	0.20	0.22	0.16	0.97
3	6	2500	337	1.5	15.81 ± 1.63	1.20	0.05	1.20	1.21	0.04	0.96
4	6	4000	337	1.5	12.22 ± 4.01	1.06	0.15	1.07	1.11	0.14	0.96

As shown in Figure 11 and Table 1, the average fiber diameter and the width of the diameter distribution can be manipulated essentially independently. The average fiber diameters in this demonstration span across an order of magnitude, highlighting the processability and tunability of this fabrication method. By optimizing process variables, we were able to obtain fibers with average diameters just above one micron, comparable with the smallest nonwoven fibers made commercially by melt blowing methods [9, 10, 52]. In addition, it is worth noting that the smallest orifices used in this study are 0.15 mm in diameter, which

are much larger than the orifices used in some studies that produce electrospun and melt blown submicron fibers [53, 54]. The use of exceedingly small orifices is often considered difficult in industrial settings because of orifice clogging by foreign materials such as dust particles (typically tens of microns in diameter).

4. Conclusions

In this study, we have investigated parameters affecting fiber quality and final fiber diameters in the simultaneous centrifugal spinning and thiol-ene photopolymerization process. It was found that monomer mix viscosity and orifice diameter have significant impact on monomer delivery rate through the orifice which ultimately affects the final fiber diameter. Spin speed influences the width of diameter distribution but not the average fiber diameter, which can be attributed to the coupled but opposite effects of the changes in centrifugal force on solution delivery and fiber drawing. Monomer mixture elasticity has minimal effect on fiber diameter and distribution despite its crucial role in fiber formation. In addition, we observed that the dominating factors in determining final fiber diameter are solution delivery rate for centrifugal spinning of photocurable monomer mixtures, but concentration of polymer for centrifugal spinning of polymer-solvent solutions. We believe such differences originate from the different mechanics in fiber solidification in the two fiber fabrication methods.

Using these parameters, the average fiber diameter and the width of the distribution can be widely and independently tuned. The smallest photocured fibers fabricated in this study were approximately 1.5 μm in diameter, which is comparable to typical melt blown fibers. We believe the ability to precisely control fiber diameter distribution and fabricate fibers in the

single-micron range demonstrates the potential of this technology as a scalable and tunable method for novel high performance fiber fabrication.

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