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Investigating two electrospinning mass transfer mechanisms

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Whipping and splitting—favored by separate processing conditions—result in different fiber diameters and diameter distributions, and can be identified by the measured current during processing.

In electrospinning processes, a polymer solution is drawn through a capillary and accelerated—as a jet of fluid—by an electric field toward a grounded collector.[1] During this flight, as the solvent evaporates and the polymer jet stretches, viscoelastic forces keep the solution together and form a continuous filament at the collector. The solvents that are most often used for electrospinning processes, however, are environmentally unfriendly halogenated compounds. There is thus a desire for greener alternatives to these materials.

With proper control of the solution and processing conditions in electrospinning, nanoscale fibers for a variety of polymers can be produced to support several applications (e.g., scaffolds for tissue engineering, and sensor devices). In many cases, specific and consistent polymer morphologies and fiber diameters are important to the eventual application. This means that a great deal of control over the processing conditions is required. Such conditions include solution parameters (inherent properties that are highly dependent on the nature and concentration of the polymer/solvent mixture) and processing parameters (e.g., applied voltage, tip-to-collector distance, and flow rate).[2,3] Slight modifications to any of these parameters can lead to appreciable variations in the final material that is produced.

In our recent work, we have focused on electrospinning of polycaprolactone (PCL) nanofibers,[4,5] which are of particular interest because of their biodegradability and applicability in the biomedical industry. For our electrospinning, we use a solvent mixture of tetrahydrofuran and methanol in an effort to replace halogenated solvents with these greener alternatives. We have also optimized our electrospinning process for the production of smaller fibers, with a narrower fiber diameter distribution. We achieved this optimization by varying parameters such as the the polymer concentration (5–35%), applied voltage (5–18kV), the tip-to-collector distance (5–20cm), and the solution flow rate (0.2–1.5ml/h).

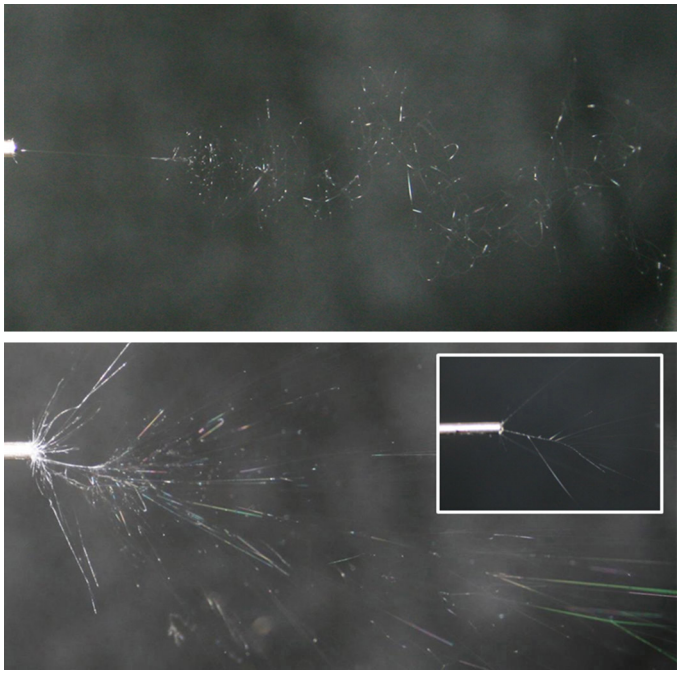

Figure 1. *Images of the (top) whipping and (bottom) splitting mass transfer mechanisms occurring during electrospinning of a polycaprolactone (PCL) solution. The top picture was taken under processing conditions of 8kV, tip-to-collector distance of 10cm, with a 20% PCL concentration at a flow rate of 1ml/h. The bottom picture was obtained under the same conditions, but with an applied voltage of 18kV. The picture shown in the inset was taken under conditions of 10kV at 10cm, for a 25% PCL solution at a flow rate of 1ml/h.*[4]

We have visually observed two distinctive mass transfer mechanisms by which the PCL solution can be transported to the collector to form fibers. These two mechanisms have previously been referred to as 'splitting'[1] and 'whipping.'[6] The whipping mechanism—illustrated at the top of Figure 1—generates a much longer path length than the

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splitting mechanism, and it involves considerable elongation of the main jet (which bends in a spiral shape and thins until it reaches the collector). In contrast, during splitting—shown at the bottom of Figure 1—the jet splays and branches into smaller jets that follow a more direct path to the collector. In the course of our experiments, we found that splitting occurred more often than whipping when we used higher processing voltages (i.e., 15–18kV) or for solutions with a higher PCL concentration (25–35%, as shown in the inset of Figure 1).

The impact of both mass transfer mechanisms on the fiber diameter is illustrated in Figure 2. We obtained these scanning electron microscope (SEM) images for fibers that were spun with an applied voltage of 8 or 18kV at 10cm, with a 20% PCL concentration and a flow rate of 1ml/h. Although we observe small diameters for both sets of fibers, much larger diameters are seen when splitting has occurred (i.e., for the 18kV spinning) than when whipping took place (i.e., for the 8kV spinning). We attribute the larger diameters that result from the splitting mechanism to the much shorter path lengths, and thus shorter flight times for stretching and thinning. Our measurements have also revealed that there is a much broader diameter distribution for fibers that were obtained from the splitting mechanism than from whipping. The fiber diameter distribution for three different voltage conditions is shown in Figure 3. We find the narrowest distribution at 8V (when only the whipping mechanism is active). Our results also indicate that the diameter distributions increase as the voltage increases and the splitting mechanism becomes more dominant, i.e., splitting occurs at 80 and 99% of the processing time at 15 and 18kV conditions, respectively.

When we measured the current during our electrospinning process, we identified two different regions. We found that whipping produced a measured current of about 10–60nA, whereas splitting generated a much higher current of 500–1200nA. We attribute this higher current during splitting to multiplication of the surface area because of jet

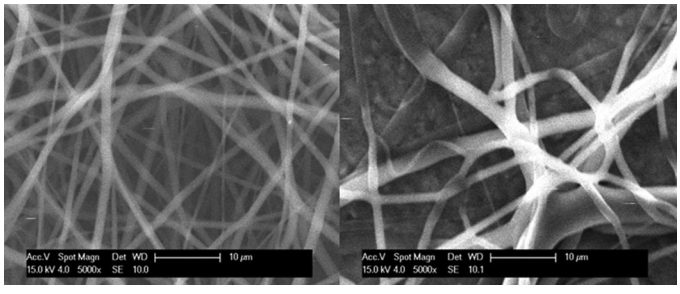

Figure 2. *Scanning electron microscope images of fibers spun under different processing conditions. Left: Applied voltage of 8kV, tip-to-collector distance of 10cm, with a 20% PCL solution at a flow rate of 1ml/h. Right: The same conditions, but with an applied voltage of 18kV.*

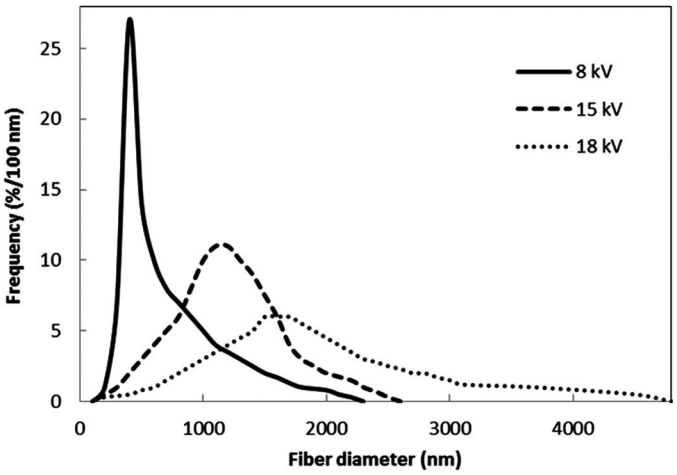

Figure 3. *Fiber diameter distribution for electrospun fibers at 8, 15, and 18kV. Fibers were processed from a 20% PCL solution at a flow rate of 1 ml/h and with a tip-to-collector distance of 10cm.*[4]

branching. This therefore leads to an increase in the number of possible conductive paths. Our results present a potential way to monitor the electrospinning process, i.e., the desired smaller fibers and smaller diameter distributions are generated by whipping and portrayed by lower observed processing current.

In our electrospinning study, we have shown how two distinctive mass transfer mechanisms—known as whipping and splitting—affect the diameter and diameter distribution of spun fibers. Whipping results in smaller fiber diameters and narrower fiber diameter distributions, whereas splitting produces a broad range of fiber diameters. As such, electrospinning processing parameters should be set carefully to achieve the correct fiber diameters and diameter distributions. We have also found that the measured current during processing is indicative of the transfer mechanism. Smaller, steady currents are characteristic of whipping, and higher, fluctuating currents are produced by splitting. In our future work we will expand these studies to focus on different additives. In this way we will be able to gain a greater understanding of the underlying physical properties that govern the electrospinning process so that better control and optimization of the final products can be scaled up to industrial levels.

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