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The Effect of Viscosity and Filler on Electrospun Fiber Morphology

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ABSTRACT

Electrospinning is a simple technique to create nanometer-scale polymer fibers by application of a large static voltage to a viscous polymer solution, or spin-dope. At polymer concentrations higher than the critical concentration, above which polymer entanglement can occur, it was found polymer fibers could be electrospun, provided the spin-dope solution was sufficiently viscous. The requisite viscosity could be obtained by increased polymer concentration or by inclusion of insoluble filler, titanium dioxide in this case. Electrospun fibers of polyethylene oxide (PEO) were successfully fabricated that consisted of as little as 25 wt.% polymer. The remainder of the fiber weight consisted of titanium dioxide (TiO_2) particles that could not be electrospun alone. We demonstrate that it is possible to create a high-surface area structure of a material that cannot be electrospun by the inclusion of a small amount of polymer.

Key Words: Electrospinning; Spin-dope viscosity; Nanofibers; Inorganic nanoparticle fillers; Polymer matrix.

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INTRODUCTION

Electrospinning is a simple technique to produce extremely fine polymer fibers. Fibers are typically less than half a micron in diameter and can be as small as 30 nm in diameter.[1] Fibers are collected as a non-woven membrane, which has a very large surface area due to the small dimensions of the fibers. Much contemporary research in electrospinning is aimed at exploiting this large interfacial area, including sensors,[2] and biological scaffolds.[3] Many applications, however, require a large surface area of materials that cannot be electrospun alone. Catalysts, electrolytes, and semiconductor particles could all be used advantageously in an electrospun membrane, due to the large surface area. However, they will not form an electrospun fiber alone and any polymer used to carry them into the fiber will detract from the desired effect. For example, O'Reagan and Grätzel[4] have reported dye-sensitized photovoltaic cells that greatly benefit from a large interfacial area between a chromophore and a nanoporous titanium dioxide (TiO_2) layer. Small particles of TiO_2 will not, by themselves, electrospin into a fibrous structure. Yet particles of TiO_2 can be included in an electrospun fiber,[5] but cell performance suffers because the polymer used to make the fiber hinders electrical connectivity of the particles.

While a complete model of the electrospinning process has yet to be developed, it can be understood as a balance of surface tension of the solution, viscosity of the solution, and charge behavior in the solution. Hohman, et al.[6] have presented a model of the charge behavior. Renneker, et al.[7] have presented a similar model of the process that takes some other processing variables into account. It is widely accepted that the minimum concentration for a solution to be electrospun is above the critical concentration, i.e., the minimum concentration for entanglements to occur.

In this paper, we demonstrate that the effect of viscosity on fiber morphology is independent of polymer concentration, above a minimum concentration. Thus, above the critical polymer concentration, the viscosity effect on fiber morphology was the same whether the viscosity was derived from added polymer or from the addition of some other material.

EXPERIMENTAL

Spin-dope solutions were made of poly(ethylene oxide) (PEO) dissolved in a solvent consisting of ethanol and deionized water in a 7 : 2 ratio by weight. The PEO used had an average molecular weight of 300,000 Daltons. Certain spin-dope solutions contained TiO_2 nanoparticles obtained from Degussa (Titandioxid P25) that were used as received. All other chemicals were obtained from Aldrich and were used as received.

The electrospinning apparatus consisted of a DC power source (Gamma High Voltage Research, Inc. Model HV ES 30P/100), where the charged electrode wire was immersed in a polymer solution contained in a glass pipette. A second ground wire from the power source was attached to a conducting target where the fibers were collected. Scanning electron microscope (SEM) images were obtained by sputter coating the samples with gold and using an AMRAY 1400 SEM. Viscosity of the spin-dope solutions was measured with a Brookfield viscometer. Static and dynamic light scattering measurements of the hydrodynamic radius and interaction volume were conducted. Surface tension measurements were carried out using a KSV Sigma 70 automatic tensiometer and a Wilhelmy plate. Each solution measured was sampled ten times to give a mean and standard deviation of surface tension. All measurements were carried out at ambient temperature of about 25°C.

This experiment consisted of three parts. In part one, the spin-dope solutions contained only PEO in various concentrations. In part two, spin-dope solutions contained both PEO and TiO_2 in various ratios always totaling 10 wt.%. Spin-dope solutions in part three contained 3 wt.% PEO and increasing amounts of added TiO_2. Table 1 shows the formulations of the spin-dope solutions used in each part of the experiment and the fiber morphology data collected.

Fiber characteristics were measured using the Scion Image software and the SEM images. In order to assess how well the spin-dope solutions performed (spinnability), several parameters were examined from each image taken at 5000×. Spinnability parameters measured were fiber diameter, bead diameter, and bead density calculated by dividing the number of beads by the number of fibers visible in an arbitrarily selected region of the membrane, 17.6 by 17.6 microns.

RESULTS AND DISCUSSION

Surface Tension

The surface tension of the pure water ethanol mixture used as the solvent was measured to be 24.98 mN/m with a standard deviation of 0.192 for 10 measurements. In order to determine the effect of added PEO to the surface tension, two additional solutions were prepared: a 2 wt.% solution of PEO and a 3 wt.% solution of PEO, both in the same ethanol/water solvent. The surface tension measured for the 2 wt.% solution of PEO was 24.89 mN/m with a standard deviation of 0.208 for 10 samples. The surface tension measured for the 3 wt.% solution was 24.76 mN/m with a standard deviation of 0.165 for 10 samples.

These values are quite comparable to literature values for pure ethanol (22.6 mN/m) and pure water (72.0 mN/m).[8] Since the measured surface tension values were within one

Table 1. Spin dope components and measured factors.

PEO (wt.%)	TiO_2 (wt.%)	Viscosity (cp)	Mean beads per fiber	Mean fiber diameter (nm)	Std dev (fiber diameter)	Mean bead diameter (nm)
3	0	3	0.45	96.53	39.08	649.74
5	0	16	0.00	246.39	89.23	none
7	0	66	0.00	516.12	231.41	none
10	0	130	0.00	397.93	39.08	none
2	8	8	0.64	105.18	48.40	369.47
3	7	10	1.10	131.44	70.95	437.44
5	5	47	0.47	285.70	161.54	785.71
7	3	84	0.33	323.53	172.56	675.20
3	0	3	0.45	96.53	39.08	649.74
3	7	10	1.10	131.44	70.95	437.44
3	8	29	1.98	162.05	63.99	570.06
3	9	36	1.96	176.67	89.75	634.18

or two standard deviations of each other it was concluded that the polymer, PEO, was not surface active and did not affect the surface tension on the spin-dope solutions.

Light Scattering

Dynamic light scattering experiments yielded an effective diameter of 26.8 nm for the PEO dissolved in the water–ethanol solvent used in electrospinning. In good agreement, static light scattering experiments showed a radius of gyration of 14.9 nm for the same system. Both these values correspond to a critical concentration of about 2.8 wt.%.

Scanning Electron Microscope

Figure 1 shows images of electrospun solutions containing 2 wt.% polymer, PEO. In the left image, no TiO_2 was added while 8 wt.% was added to the spin dope used in the image on the right. The image from the polymer TiO_2 mixture shows a highly porous structure that could be very fine fibers while the other image shows no fibers at all. The results of spin dope solutions of 3 wt.% polymer are shown in Fig. 2, again with no TiO_2 on the left and 7 wt.% TiO_2 added on the right. The critical concentration was expected to be just below 3 wt.%, yet no fibers are apparent in the image from the polymer-only solution, while fibers are clearly discernable in the right-hand image containing added TiO_2.

Images of fibers based on spin dopes of 4 wt.% polymer are shown in Fig. 3 and fibers based on spin dopes of 5 wt.% polymer are shown in Fig. 4. In both cases, the addition of TiO_2 particles results in a larger fiber diameter and a greater occurrence of beads than observed from a spin dope of the same polymer concentration without added particles. A larger fiber diameter is normally indicative of an increase in viscosity.[9] However, a higher bead density generally indicates a system with a viscosity too low to offset the

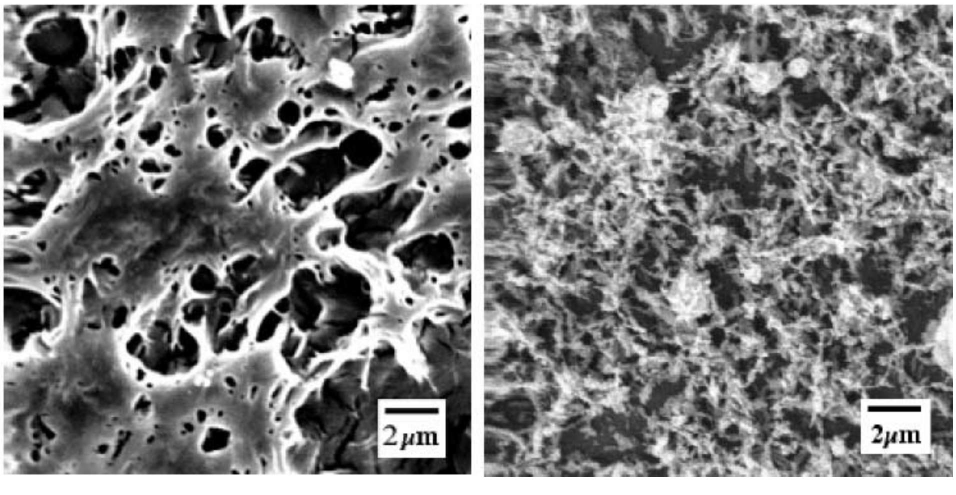

Figure 1. Scanning electron microscope images of 2 wt.% PEO alone (left) and with 8 wt.% TiO_2 (right).

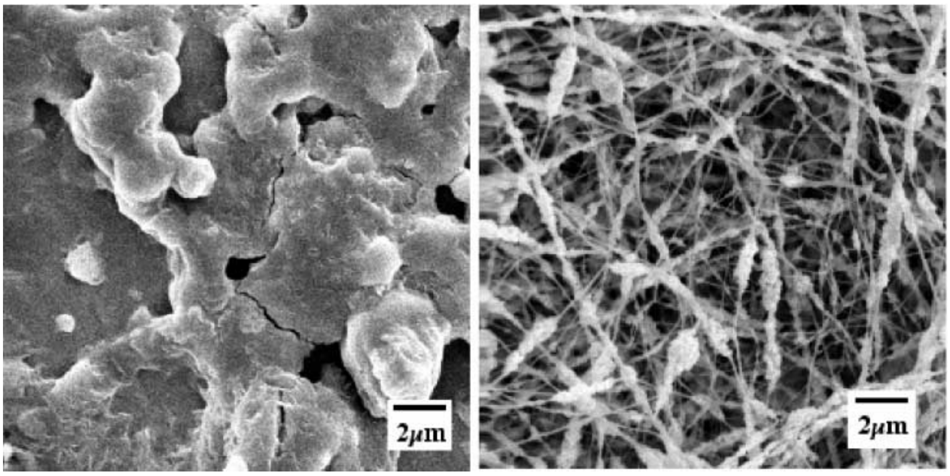

Figure 2. Scanning electron microscope images of 3 wt.% PEO alone (left) and with 7 wt.% TiO_2 (right).

surface tension. Since the addition of TiO_2 has induced these apparently contradictory effects, it is conceivable that the TiO_2 particles tend to aggregate causing beads, even though the particles increase the solution viscosity.

Fiber Characteristics and Viscosity

The mean fiber diameter for samples with and without TiO_2 particles is shown as a function of viscosity in Fig. 5. Data are shown for samples where the polymer and TiO_2

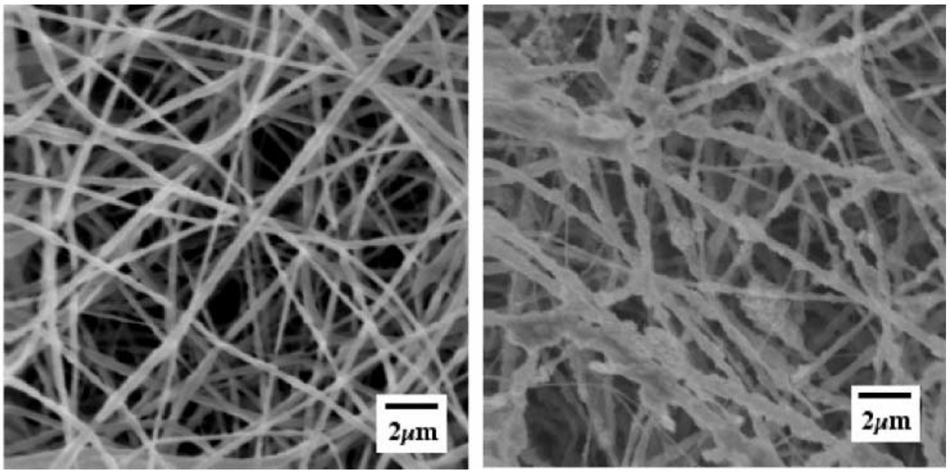

Figure 3. Scanning electron microscope images of 4 wt.% PEO alone (left) and with 6 wt.% TiO_2 (right).

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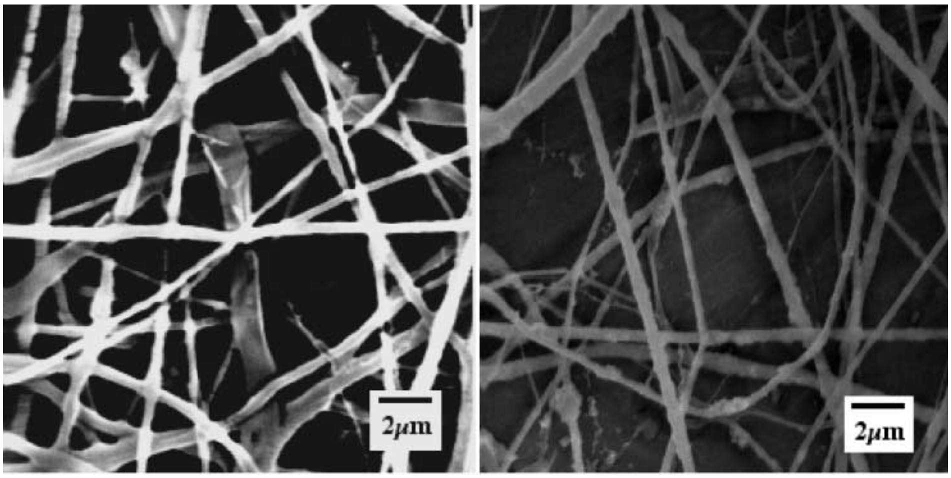

Figure 4. Scanning electron microscope images of 5 wt.% PEO alone (left) and with 5 wt.% TiO_2 (right).

contents were varied but were always equal to 10 wt.% and for samples containing 3 wt.% polymer and a varied amount of TiO_2 filler. In all cases, for any given viscosity, the fiber sizes were within about one standard deviation of each other. In general, higher spin-dope viscosity resulted in a larger mean fiber diameter.

Figure 6 shows the mean bead diameter as a function of spin-dope viscosity. While the standard deviations were significant, the general trend shows increasing bead diameter with increasing spin-dope viscosity. No beads were observed in the samples containing only PEO. Thus, it is conceivable that the observed beads were, at least partially, formed by

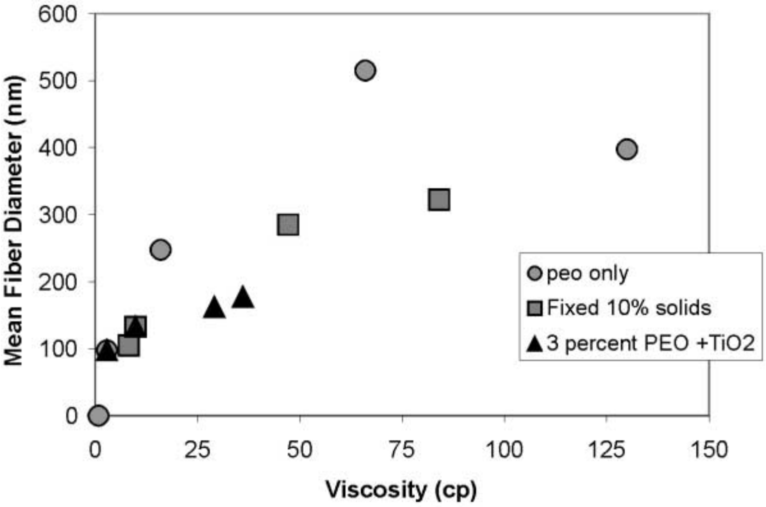

Figure 5. Mean fiber diameter as a function of viscosity.

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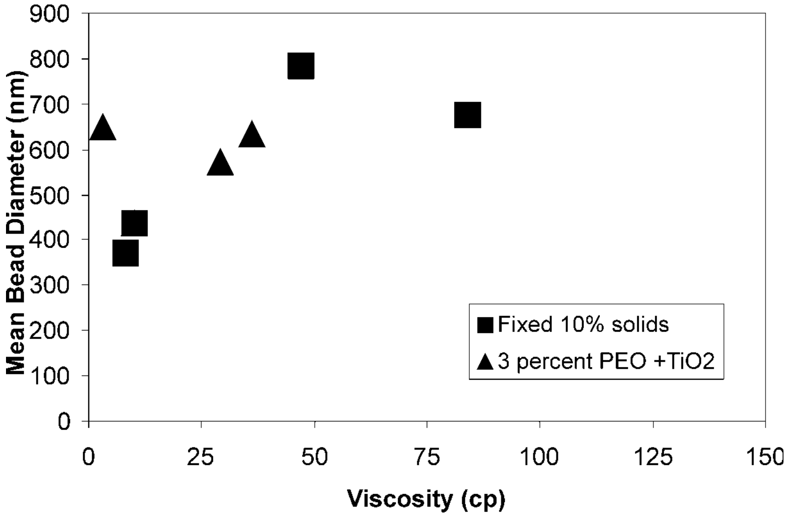

Figure 6. Mean bead diameter as a function of viscosity.

aggregation of the TiO_2 particles in the solution. The number of beads per observed fiber length, i.e. the bead density, is shown as a function of viscosity in Fig. 7. In the case where the polymer content was fixed at 3 wt.% and the spin-dope viscosity was increased by addition of TiO_2 (triangles), more beads occurred at higher viscosity. Alternatively, when the solid content of the spin-dope was held constant at 10 wt.% and the ratio of polymer to filler varied, the bead density generally decreased at higher viscosity. These higher viscosity samples had a higher polymer content, which gave rise to the increased viscosity.

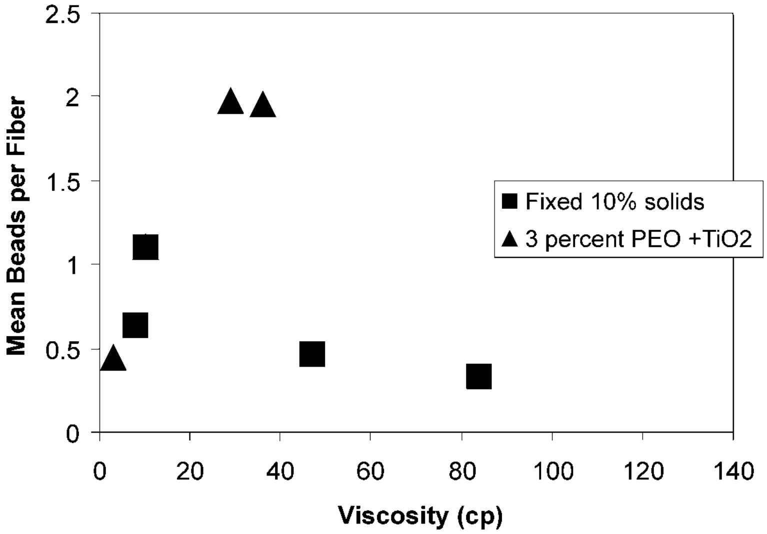

Figure 7. Mean bead density as a function of viscosity.

Both of these observations suggest that the aggregation of TiO_2 particles significantly contributed to bead formation.

CONCLUSION

The most promising advantage of electrospun membranes is the large surface area that can be achieved relatively simply. The prerequisite for electrospinning of entangled polymers in solution can be met with a minimum amount of polymer, as we have shown here; creating fibers of 75–80 wt.% TiO_2. Further increases may be possible with higher molecular weight matrix polymers. We have demonstrated that fiber morphology depends on spin-dope viscosity and that the desired viscosity can be obtained by addition of filler material other than the matrix polymer, even if the filler does not dissolve. This can open the field of electrospinning to other materials that would not otherwise be readily electrospun.

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