Morphology, structure, and properties of metal oxide/polymer nanocomposite electrospun mats

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ABSTRACT: Adding nanoparticles into polymer solutions before electrospinning creates unique hierarchical morphologies dispersed throughout small diameter nanoparticle-polymeric fibers. Effects of polymer composition, nanoparticle (NP) type, loading, and electrospinning voltage conditions were studied. As examples, indium, iron, and titanium oxide engineered nanoparticles (NPs) were dispersed into polyvinylpyrrolidone or polystyrene and electrospun. NP loadings below 5 wt % did not affect critical voltage required for Taylor cone formation, whereas higher NP loadings require higher critical voltages. Polymeric fiber thickness and macroscopic morphology is not impacted by up to 5 wt % NP loadings, and NP dispersion throughout the fibers were similar to their dispersion in initial polymer suspension. NP loadings above 5 wt % increased viscosity, which decrease subsequent fiber diameter. Experiments in water containing inorganic and organic pollutants in water demonstrate that the polymer is largely nonporous. This work enables design of multifunctional nanomaterial-polymer composite fibers for wide-ranging applications such as water and air treatment.


KEYWORDS: electrospinning; fibers; nanocrystals; nanoparticles; nanowires

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INTRODUCTION

Electrospun polymer fibers with diameters in the submicron to nanometer range have unique characteristics that led to increasing interest in their applications as reinforcements for composite materials, air or water filtration, soft tissue prostheses, wound dressing, cosmetics, protective clothing, and sensors.1,2 Electrospinning uses an electrically charged jet of polymer solution to produce polymer filaments by applying a high voltage potential between 10–40 kV and a grounded collector. The surface tension on the fluid droplet at the syringe tip is overcome by the strength of the electric field and a charged jet of fluid stretches from the syringe tip and deposits onto the grounded collector, forming a mat of fibers with diameters in the micrometer and nanometer scales. Nanoparticle (NP) addition into polymers produces nanocomposites known to improve mechanical strength, resistance to wear, and thermal stability.3 Additionally, NP-polymer electrospun fiber composites also enhance the fiber performance due to the multifunctionality of NPs as biocides, sorbents, and photocatalysts. As NP-polymer composites are being synthesized, limited information across multiple NP types exists regarding impacts of NPs on polymer spinning behavior.

Synergistic effects of physical parameters dictate the structure and morphology of electrospun fibers.4 The electrospinning process is a balance of parameters including, but not limited to, conditions such as relative humidity, polymer weight, distance between capillary tip and collector plate, feed rate of solution, and solution composition.5–7 For example, adjusting the relative humidity in the environment affects the number, diameter, shape, and distribution of pores on the surface of electrospun fibers.5 Electrostatically, there is a balance between the induced charge on the polymer surface and the surface tension of that polymer. Surface tension is overcome by applying voltage. Viscosity dictates whether the polymer jet will break into droplets or travel as a continuous stream to the collector plate. High viscosity liquids will become jets, while low viscosity liquids will break up.4 By altering physical parameters and manipulating electrostatic forces, the fibers produced by electrospinning can have a variety of morphologies suited to different purposes. For example, fiber diameter may be manipulated via solution viscosity and applied voltage. Depending on the final use of electrospun fiber mats (i.e., nonwoven textiles), controlling fiber diameter can be controlled. In this work, fiber diameter is shown to vary as an effect of NP addition. The addition of NP
into solution adds another dimension to the process and its product. There are few examples in the literature of the effect of NP addition to polymer solutions prior to spinning and few investigations of the effect of NP on electrospinning process parameters.\textsuperscript{8,9} The effect of NP content on the formation of a Taylor cone in polymer solutions for electrospinning presents a gap in the literature that is important for future investigations of electrospun fibers using NPs for functionalization.

Interest exists in coupling the benefits of metal oxide nanoparticles with the process of electrospinning, affording several applications of economically produced, micrometer and nanometer-scale fibers.\textsuperscript{10} For example, adding antimicrobial silver NP to a mat of electrospun fibers grafted onto a membrane could help prevent bacterial membrane fouling.\textsuperscript{11} Electrospinning polymeric fibers for water treatment applications requires use of nonwater soluble polymers, and hence dissolution in nonaqueous solvents is required. Titanium dioxide (TiO\textsubscript{2}) is an inexpensive and effective photocatalyst and chemical sensor in environmental remediation, photovoltaics, and optics, and applications for electrospun fibers made with TiO\textsubscript{2} are beginning to be explored.\textsuperscript{12–15} Research on interactions of individual metal oxide nanoparticles with polymers during electrospinning have begun. For example, varying weight percentages of TiO\textsubscript{2} in a polyaniline solution affected nanocomposite fiber diameter, while operating parameters such as TiO\textsubscript{2} loading content, humidity, and temperature affected the physical properties, such as strength and brittleness, of electrospun polyacrylonitrile (PAN)-TiO\textsubscript{2} fibers.\textsuperscript{8,9} Less has been reported about the systematic influence of NP addition to polymer solutions on electrospinning parameters (e.g., solution viscosity) and resulting critical voltage or implications for fiber morphology.

This study investigated hybridizing electrospun fibers with NP and evaluated how the NP addition influenced polymer properties, electrospinning conditions, and electrospun fiber morphology. Specifically, we quantified the differences in critical voltage needed to produce an unstable and stable Taylor cone by loading two polymer solutions with different NP weight percentages. Voltage was slowly increased until a stable Taylor cone was observed. Nanoparticle-polymer composite solution viscosity was tested using rheometry. Metal oxide nanoparticles (TiO\textsubscript{2}, indium oxide (In\textsubscript{2}O\textsubscript{3}), hematite (Fe\textsubscript{2}O\textsubscript{3}) and electrospun polymeric fibers where characterized using transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX). TiO\textsubscript{2} was chosen because of its widespread use as a photocatalyst and arsenic absorbent, while In\textsubscript{2}O\textsubscript{3} was chosen due to its use in semiconductor industries plus its visual color observation ability and high sensitivity of morphology using scanning electron microscopy (SEM) in order to observe NP distribution in the fibers. Fe\textsubscript{2}O\textsubscript{3} was chosen because it is a good adsorbent of inorganic pollutants (such as arsenic) in drinking water. The results are intended to aid in optimization of electrospinning nanocomposites by showing how adding different NP mass fractions can affect viscosity, voltage, surface morphology, and diameter of fibers.

**EXPERIMENTAL**

**Materials**

Two polymers (Polyvinylpyrrolidone [PVP] K90 (MW 360,000 g/mol, Fluka Analytical) and Polystyrene (PS, MW 350,000 g/mol, Aldrich Chemistry) were used for electrospinning. These polymers were chosen based on their high molecular weights suitable for electrospinning. N,N-dimethylformamide (DMF, Sigma-Aldrich) was used as the organic solvent to dissolve both of the polymers.

Nanoparticles used for loading include indium oxide nanopowder from U.S. Research Nanomaterials, Inc. (Houston, TX) and Degussa AG Aerosol P25 TiO\textsubscript{2} (Frankfurt am Main, Germany). Fe\textsubscript{2}O\textsubscript{3} NPs were synthesized by modifying a previously published method.\textsuperscript{16} Briefly, anhydrous ferric acid (Sigma-Aldrich) was prepared over heat in a 4 mM HCl solution and 0.25 M FeCl\textsubscript{3} stock. The solution was then placed in a laboratory oven (HP 5890 series II) at 100 °C and incubated for 10 h. The Fe\textsubscript{2}O\textsubscript{3} NPs were centrifuged and washed five times with nanopure water. After rinsing, the Fe\textsubscript{2}O\textsubscript{3} NPs were stored at 4 °C.

In\textsubscript{2}O\textsubscript{3}-polymer composite, TiO\textsubscript{2}-polymer composite, and Fe\textsubscript{2}O\textsubscript{3}-polymer composite solutions were prepared by dispersing various NP concentrations (0, 0.05, 0.5, and 5 wt %) in DMF by 1 h of bath sonication (Branson 2510, Branson Ultrasonic, Danbury, CT). NP weight percentage loadings (0.05–5 wt %) into the polymers were chosen to span multiple orders of magnitude. Polymer (20 wt % of either PS or PVP) was added to the solution and gently stirred for 24 h at 40 °C.

NPs (Figure 1) were analyzed using transmission electron microscopy (TEM) and X-ray Diffraction (XRD). Five hundred particles of each material were counted by hand using ImageJ.\textsuperscript{17} TiO\textsubscript{2} NPs averaged 27 ± 7 nm in size, In\textsubscript{2}O\textsubscript{3} NP averaged 80 ± 17 nm, and

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**Figure 1.** TEM Images of (a) TiO\textsubscript{2}, (b) In\textsubscript{2}O\textsubscript{3}, and (c) Fe\textsubscript{2}O\textsubscript{3} nanoparticles utilized for fiber hybridization.
**Electrospinning**

An apparatus similar to previously published electrospinning systems was constructed. Briefly, electrospinning was performed using a high voltage power supply that provided up to 40 kV (Gamma High Voltage, Ormond Beach, FL), a syringe pump (New Era NE-300, Farmingdale, NY), a 10 mL plastic syringe, and a grounded aluminum foil coated collector that was placed 15 cm away from the syringe tip. The experimental procedure involved loading the solution into a plastic 10 mL syringe fitted with a stainless steel needle that was connected to the high voltage power supply. The NP-polymer composite solution was injected at 20 μL/h through a stainless steel, 22-gauge needle (Sigma-Aldrich stainless steel 304 syringe needle) with an alligator clip attached to charge the needle and the polymer solution as it exited the capillary tip. The entire system was enclosed to mitigate the effects of air currents on the system and for safety. Humidity was measured using a Xikar hygrometer and was maintained at 40% at 75 °F using a sponge saturated with deionized water inside the electrospinning enclosure. All experiments were run grouped by metal oxide on the same day in quick succession to maintain similar ambient experimental conditions.

**Analytical Methods**

Nanoparticles were characterized using a Philips CM200-FEG transmission electron microscope and a Siemens D5000 powder X-ray diffractometer. SEM images of fibers were obtained using a JEOL 2010F. Viscosity of polymer solutions was measured using a TA Instruments AR-G2 rheometer. Fiber diameters were measured using ImageJ software (National Institutes of Health, Washington, D.C.).

**RESULTS AND DISCUSSION**

**Effect of Nanoparticle Doping on Critical Voltages to Produce Taylor Cones**

Taylor cone formation is an important feature of the electrospinning process because it indicates that the voltage applied affects the surface tension of the solution, and because it is a precursor to a stable, continuous polymer jet. The charged jet is the distinguishing characteristic between electrospinning and electrospaying, where the end result of electrospaying is charged polymer droplets without fiber formation. The critical voltage occurs when the jet forms. Droplet shape at the tip varies with applied voltage. At lower voltages, the originating drop at the capillary tip is larger than the diameter of the capillary tip. As voltage increases, the jet originates first from the bottom of the drop, and then the drop diameter decreases with increasing voltage until the jet emerges from the solution within the syringe tip. Little is known about the dependence of these voltages on NP loadings in polymers.

Fe2O3 averaged 46 ± 3 nm. The XRD reflections of In2O3 NPs are characteristic of phase-pure nanocuboids. TiO2 was mostly anatase. Fe2O3 crystalline phase identification was confirmed by comparing XRD reflections with the pattern of the Joint Committee on Powder Diffraction Standards database (see supporting information S1–S3).

Figure 2 shows critical voltages for In2O3 and TiO2 NPs at different loadings in PS. Figure S4 in supporting information shows a companion plot using PVP. For both polymers, the critical voltage did not vary for NP loadings lower than 0.5 wt%. The critical voltage needed to produce a Taylor cone without NP in solution was 10 kV. The critical voltage needed to form a stable Taylor cone increased (p < 0.05, Student’s t test) by roughly 25% when adding up to 5 wt% TiO2 and In2O3 in PS or PVP. The increase in voltage needed to form a Taylor cone may be attributed to increasing viscosity caused by NP addition. Interestingly, there was not a statistical difference (p < 0.05) between 0.05 and 0.5 wt% NP to increase critical voltage or polymer solution viscosity. Similar variability has been seen for small weight percentages (0–10 wt% PS NPs) in linear PS chains; the mechanism is yet to be explained.

Solution viscosity can influence the voltage needed to successfully produce a polymer jet in electrospinning and also affect fiber diameter, droplet shape, and jet trajectory. Viscosity increased (p < 0.05, Student’s t test) with higher mass fraction of nanoparticles (Figure 3). Increasing solution viscosity requires increased voltage to produce a Taylor cone and a charged jet. According to the Einstein-Batchelor law for spherical particle suspensions, adding particles should increase the viscosity of their host polymer. However, this is not the case for all NP loadings. Polymer nanocomposites display a variety of unexpected behavior, most notably a reduction in viscosity. Reduced viscosity has been observed in PS solutions containing dispersed fullerene and magnetite NPs. This phenomenon has been attributed to a decrease in excluded volume due to a change in polymer conformation; the viscosity of polymer melts do not follow convention when NPs are introduced.

**Morphology of Nanoparticle-Polymer Fibers**

Changes in viscosity are known to affect morphology of electrospun fibers. For example, beading in polymer fibers refers to segments of polymer that are thicker than adjacent elongated fiber. Beading is usually round in nature, much like pearls on a necklace (Figure 5). Beads form in electrospun fibers due to the competition between capillary forces and electrical stress. Polymer molecular weight and solution concentration have been
tions with higher viscosity and surface tension, we believe a dent's
wt % and 0.5 wt % NPs. However, with the addition of 5 wt %
of PS. The PS fiber diameters double with the addition of 0.05
without any NPs, which is consistent with the higher viscosity
tion of 0.5 and 5 wt % NPs. For PS, fiber diameter was 0.8
0.05 wt % NPs, then decreasing by roughly half with the addi-
of 1.6
m
m
m
m, increasing by a few microns with the addition of
0.05 wt % NPs, then decreasing by roughly half with the addi-
tion of 0.5 and 5 wt % NPs. For PS, fiber diameter was 0.8 µm
without any NPs, which is consistent with the higher viscosity
of PS. The PS fiber diameters double with the addition of 0.05
wt % and 0.5 wt % NPs. However, with the addition of 5 wt %
NP, diameter decreased in size by roughly half (p < 0.05, Stu-
dent’s t test). Based upon what is known about spinning solu-
tions with higher viscosity and surface tension, we believe a
variation in fiber diameter of polymer solutions containing NPs
was caused by the increased voltage needed to form a charged
jet.1,5,19

Distribution of NPs in Electrospun Fibers

The distribution of NPs in fibers becomes important for certain
applications, for example, when NPs in fiber function as reac-
tive sites for sorbents.34 In order for nanocomposite electrospun
fibers to be useful, NPs must be readily accessible.32 Figures 4–6
show NP distributions in the fibers. The 5 wt % NP-polymer
solutions shown in Figure 4 are the best example of desirable
distribution of NPs obtained in this study. Nanoparticle aggre-
gates were counted manually inside 10 µm² areas using TEM
images like those found in Figure 4 (n = 500 aggregates). The
5 wt % In₂O₃ shows the most uniform distribution, with an
average of 6 ± 2 NP cluster/10 µm² area, versus 4 ± 1 cluster/
10 µm² area for 5 wt % TiO₂. EDX analysis confirmed indium
titanium presence in electrospun fibers observed utilizing
backscatter SEM imaging (Figure 5). Figure 5 also shows magni-
ified images of PVP fibers with 1 wt % In₂O₃ added, which
formed both polymer beads and aggregated In₂O₃ beads. NP
aggregations may occur due to polymer-nanoparticle interac-
tions, as well as electrostatic forces between the nanoparticles
themselves. NP distributions in polymers are not well under-
stood; this is due to a lack of theoretical studies, systematic
experimental results, and the challenges of processing nanocom-
posites.35 Existing literature reports suggest a lack in consensus
on a single quantitative method for the evaluation of the state
of dispersion of nanoparticles in solutions. Khare et al. pro-
posed a method for obtaining free space length (Lₜ).36 Lₜ is
described as the characteristic size of unreinforced polymer
domains within nanoparticle suspensions. By quantifying the
size of these unreinforced particle domains, dispersion states
can be distinguished between polymer suspensions. Lₜ is
reduced as a product of more uniform dispersion, decreasing
particle size, and increased nanoparticle loading.36 The Lₜ of a
5% TiO₂ suspension before and after spinning was found using
the TEM images shown in Figure 6 in accordance with the pre-
viously published method.36 The Lₜ of 5% TiO₂ in PS before
spinning was 161 ± 16 nm, while that of 5% TiO₂ in PS after
spinning was 155 ± 6 nm. Changes in the state of dispersion
of NPs can influence electrospinning performance; in this case, the
state of dispersion of the TiO₂ suspensions in polystyrene was
similar before and after spinning despite the method of data
interpretation.

Table I. Effect of NP Loading and Polymer on Electrospun Fiber Diameter

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. NP</th>
<th>0.05 wt % NP</th>
<th>0.5 wt % NP</th>
<th>5 wt % NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>In₂O₃ in PVP</td>
<td>1.6 ± 0.25</td>
<td>1.93 ± 0.53</td>
<td>0.59 ± 0.15</td>
<td>0.81 ± 0.23</td>
</tr>
<tr>
<td>TiO₂ in PVP</td>
<td>1.6 ± 0.25</td>
<td>1.75 ± 0.41</td>
<td>0.68 ± 0.20</td>
<td>0.83 ± 0.35</td>
</tr>
<tr>
<td>In₂O₃ in PS</td>
<td>0.81 ± 0.20</td>
<td>1.9 ± 0.43</td>
<td>1.8 ± 0.52</td>
<td>0.82 ± 0.20</td>
</tr>
<tr>
<td>TiO₂ in PS</td>
<td>0.81 ± 0.20</td>
<td>1.45 ± 0.53</td>
<td>3.8 ± 1.8</td>
<td>0.72 ± 0.48</td>
</tr>
</tbody>
</table>

Average diameter of fiber to 1 SD. Measurements were made in triplicate. PVP solutions showed no effect with 0.05 wt % NP addition, and then a reduction in half of fiber diameter by addition of 0.5 and 5 wt % NP. PS with no NP addition had a lower fiber diameter, which is consistent with the higher viscosity of PS. Adding 0.05 wt % NP significantly increased fiber diameter, but was unchanged at highest NP loading of 5 wt %.
In addition to assessing the state of dispersion of 5% TiO$_2$ in PS, the particle size distributions of this suspension were evaluated. Particles were manually counted and measured using ImageJ ($n = 500$ particles). Figure 7 shows the particle sizes distributions for loose TiO$_2$ NPs, 5% TiO$_2$ in PS prior to spinning, and 5% TiO$_2$ in PS after spinning. The figure indicates that between the three phases of the experiment the NPs were in the 10–20 nm range in size and could not exert effects on nanoparticle dispersion or electrospinning performance by changing diameter. Coupled with the uniformity of state of dispersion throughout the experiment, these results indicate little to no influence on electrospinning performance by interactions.

Figure 4. SEM images of PS fibers with In$_2$O$_3$ and TiO$_2$. Fibers with no NP added are smooth and continuous. NP addition increases beading and branching. Backscatter mode shows that NPs are evenly distributed in fibers.
of nanoparticles with the polymer matrix or within the nanoparticle aggregates. The nanoparticles formed aggregates as soon as they were suspended, despite sonication, and maintained their state through the experiment.

Figure 8 shows SEM magnifications of Fe$_2$O$_3$ in PS. Fe$_2$O$_3$ NPs were added to PS solution for comparison against TiO$_2$ and In$_2$O$_3$. Electrospinning is based on the manipulation of charge. Nanoscale Fe$_2$O$_3$ is highly conductive, displays behavior unique to nanoparticles, and may behave differently in the electrospinning system. Similar with TiO$_2$ and In$_2$O$_3$, the Fe$_2$O$_3$ nanoparticles are
discernible at 0.5 wt % in the fiber, and are well distributed through the polymer filament.

**Demonstration of Adsorption by a TiO$_2$-PS Composite Fiber**

A motivation for the experiments detailed in this paper was to effectively harness the potential benefits of suspending nanoparticles such as TiO$_2$ in a polymer scaffold in order to facilitate their use as active sites for remediation processes, such as adsorption. The aim was to make a hybrid NP-polymer fiber in a single step, without posttreatment (e.g., attachment of NP after spinning a polymer fiber, calcination of a nonpolymeric metal sol). Our control experiments with TiO$_2$ alone in water confirmed literature reports demonstrating its ability to remove As(V). Therefore, a single-point arsenate [As(V)] adsorption experiment was conducted using a hybrid NP-polymeric fiber created from a dispersion of 5 wt % TiO$_2$ in polystyrene and DMF. With the incorporation of TiO$_2$ in the fiber, sorption of As(V) was expected; however, upon experimentation, no As(V) sorbed onto the composite fiber. We hypothesized that while TiO$_2$ is well dispersed in the polymeric fiber, the fiber was smooth and all measurements indicated that it was nonporous. Separately, recent work (Hoogesteijn von Reitzenstein et al., in preparation) shows that dispersing graphene platelets in PS/DMF prior to electrospinning created fibers with surface porosity. These pores provide access points between the aqueous phase and the graphene embedded within the polymeric fibers.

Therefore, we spun a hybrid NP-polymeric fiber by dispersing both TiO$_2$ and graphene together in PS/DMF. The resulting fibers are porous (Figure 9), but did not adsorb As(V). To prove the porosity could allow sorption of pollutants by NPs within the polymeric fiber adsorption experiments using a nonpolar organic pollutant [phenanthrene (C$_{14}$H$_{10}$)] confirmed >50 times more adsorption on the hybrid fiber than a polymer-only (control) fiber (no NP). The phenanthrene sorption, on a mass removal basis (mg phenanthrene per g graphene) is equivalent between a dispersion of graphene in water (no fiber) and the hybrid NP-polymer fiber, thus proving the organic pollutant adsorbs only to the graphene and that the graphene NP surface is available within the pores of the fiber for phenanthrene. We suspect that the lack of As(V) sorption in the hybrid TiO$_2$/graphene-polymer fiber was not due to the lack of pore formation.
but rather that the polymer still encompassed the TiO$_2$ NP within the fiber. A way to create pores and allow connectivity between As(V) in water and TiO$_2$ could be to use new TiO$_2$-graphene nanoparticles. Multifunctional TiO$_2$-graphene composite nanomaterials have been synthesized with TiO$_2$ encapsulated within crumpled graphene sheets.$^{38,39}$ These types of materials may provide a one-step method to synthesize water-stable hybrid NP-polymeric fibers and nonwoven textiles capable of pollutant removal from water.

**CONCLUSIONS**

This study investigated the effect of NP addition on electrospun polymer fibers and how viscosity, critical voltage, and fiber morphology changed as a result. Viscosity and critical voltage increased with increasing weight percentage of nanoparticles in the polymer solution. Critical voltage needed to produce a Taylor cone was higher for PS than for PVP. Fiber morphology was not directly affected by NP addition; instead the increase in viscosity and higher surface tension as a result of the 5 wt % NP concentration caused a roughly 50% decrease in diameter. Taking higher critical voltages and viscosities into account when adding NPs to polymer solutions has implications for future electrospinning applications, specifically for applications where fiber diameter and surface morphology are important. While even distribution of NP was observed, it is important to sonicate electrospinning solutions containing NP to prevent agglomeration. The voltage changes needed to successfully spin higher weight percentages of NP-polymer composites can affect this technology’s the scale up process, including the power required to produce such fibers. Finally, NP weight percentage significantly affected the number of reactive sites available for NP functionality. Special attention needs to be paid to experimental parameters and solution composition in order to optimize fiber production. Overall, TiO$_2$ and In$_2$O$_3$ NPs can be successfully integrated into electrospin fibers with adjustments to voltage based on NP concentration in polymer solution. The potential for high surface area, low volume, functionalization capability, and ease of synthesis make electrospun fibers good candidates for water treatment applications such as nanofiltration and ion exchange. Further work should focus on functionalizing electrospun fibers with embedded NPs for water treatment purposes.

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