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Synthesizing Magnetic Nanocomposite Fibers for Undergraduate Nanotechnology Laboratory

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Abstract

Flexible magnetic nanocomposite fibers were produced by an electrospinning method using a polymeric solution containing poly(acrylonitrile) and magnetite nanoparticles. The educational objective of this study was to demonstrate nanomanufacturing to undergraduate students in the College of Engineering at Wichita State University (WSU). Magnetic nanoparticles (~10 nm) were prepared using a chemical co-precipitation of ferric and ferrous chloride salts in the presence of an ammonium hydroxide solution. The effect of magnetic particle concentrations (e.g., 0%, 1%, 5%, 10%, 20%, and 30%) on nanocomposite fibers, distribution, and morphology were studied using scanning electron microscopy (SEM). This experimental study indicated that the average diameter of the magnetic nanocomposite fibers ranged from 400 nm to 1.0 μm . The magnetic responses were found to increase linearly with increasing percent loading of the magnetic nanoparticles.

Keywords: Poly(acrylonitrile), magnetite nanoparticles, electrospinning, and nanocomposite fibers.

1. INTRODUCTION

Electrospinning is a relatively easy and direct method of fabricating a non-woven mat of polymeric fibers compared to conventional methods such as melt spinning, wet spinning, and extrusion molding. It offers a distinct advantage of forming fibers in the micro- to nanometer range with a high surface area-to-volume ratio compared to conventional fibers [1,2]. Electrospinning utilizes a high electric field (or force) on the surface of a polymeric solution to overcome surface tension to produce a very slim charged jet. When the charge is applied, mutual charge repulsion induces longitudinal stresses. As the intensity of the electrostatic field is increased beyond certain limits, the hemispherical surface of the solution at the tip of the capillary elongates to form a unique structure called a Taylor cone [1-4]. The jet first extends in a straight path for some distance, called the jet length, and then instability occurs by bending the jet into a looping path that results in a series of spiral motions [5,6]. In order to minimize these instabilities, the jet undergoes a large amount of plastic stretching that consequently reduces the fiber diameter to a nanoscale. Finally, the solvent evaporates and nanofibers are collected on a collector screen placed at some distance from the capillary, as shown in Figure 1 [14,15].

Figure 1: Simplified schematic of the electrospinning process and resulting polymeric electrospun fibers. A polymeric solution in a syringe (A) is fed to a needle (B). A high-voltage supply (C) is connected to the needle to produce a fine jet of polymer solution (D). The electrospun fibers dry out in transit, resulting in fine fibers, which are collected on the ground mesh (E).

Generally, the diameter of electrospun nanofibers is in the range of 50 nm to 500 nm, and they can be as small as 10 nm by changing the system and process parameters [1-4]. Understanding and optimizing these parameters would result in nanoscale fiber fabrication with minimum bead formation. In this laboratory session, students who took the Introduction to Nanotechnology Laboratory course gained the basic mechanisms of nanofiber manufacturing by varying the following system and process parameters:

1. System Parameters

- Polymer and solvent types and structures
- Viscosity, conductivity/chargeability, and surface tension of polymers

2. Process Parameters

- Electric potential, flow rate, and polymer concentration
- Distance between capillary and collection screen
- Temperature, humidity, and air velocity
- Nanoparticle inclusions
- Target rotation

The electrospinning process is usually carried out at room temperature under normal conditions. However, if the temperature is slightly above room temperature, the evaporation rate will increase, which can help in reducing the fiber diameter. Increased humidity and airflow reduce fiber diameter to some extent. At high concentration or molecular weight, sufficient molecular chain entanglement in the polymer solution prevents the breakup of the electrically driven jet and allows the electrostatic field to elongate it. It has been experimentally determined that at higher viscosity, the spinning drop changed from hemispherical to conical shape, and the length of the jet improved. The spinning voltage needed to eject a jet from the tip of a capillary depends upon the solution's viscosity. If solution viscosity is too high, greater spinning voltage is

needed to overcome the surface tension and viscoelastic forces. High voltage reduces fiber diameter. Therefore, viscosity of the solution should be compromised between very low and very high values, depending on what is needed. The tip-to-target distance has a remarkable effect on electrospun fibers. As the distance increases, the jet will have more time to stretch plastically, during which time a greater amount of solvent evaporates, thus reducing the fiber diameter. The morphology of the fibers depends upon the flow rate of the solution and some of the other above parameters. When the flow rate exceeds the threshold value, beads and pores on the fibers can be observed. As the conductivity of the solution increases, the fiber diameter will decrease [1-8,14].

Because electrospun nanofibers have a large surface area per unit mass, these non-woven fibers can be used in various fields: filtration and separation of micron-, submicron-, and nanosize organic and inorganic particles; HF antenna fabrication; light-weight, colorful, and invisible fabric productions; and biomedical applications, such as wound dressing, tissue engineering scaffolds, and artificial blood vessels. Other promising areas of electrospun nanofibers include advanced nanocomposite fabrications to improve crack resistance and reduce aircraft interior noise [8-11].

Although significant progress has been made during the past decades for increasing the properties of nanofibers, the problem of flexible magnetic nanofiber fabrication has not been solved yet. This paper presents the fabrication of highly magnetic and flexible nanocomposite fibers using polyacrylonitrile (PAN) [13], dimethylformamide (DMF) [12], and magnetite nanoparticles (~10 nm) in the electrospinning process. In this demonstration, students learn, in detail, the sample preparation and nanomanufacturing of nanocomposite fibers by electrospinning.

2. EXPERIMENTAL

2.1 Materials

Unless otherwise specified, all chemicals used in these studies were purchased from Sigma-Aldrich and are all reagent grades. PAN with a molecular weight of 150,000 and DMF were directly used without further purifications or modifications [12,13].

Figure 2: Photographs showing magnetite nanoparticles in a weigh pan (left) and TEM image of those particles (~10 nm) (right).

Magnetic nanoparticles were prepared using 50 ml of 2 M HCl (36.5–38%) and 55 M ammonium hydroxide (NH₄OH) (28–30%) solutions in a 100 ml beaker. In separate beakers, 2.00 g of ferric chloride (FeCl₃·6H₂O) was dissolved in 40 ml of 2 M HCl, and 1.25 g of ferrous

chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 10 ml of 2 M HCl. The two solutions were then combined and stirred vigorously at 1,200 rpm. At room temperature, 55 ml of 5 M ammonium hydroxide was added dropwise in 5 minutes. The magnetite particles (~ 10 nm) were then collected using an Nd magnet and dried in an oven overnight. Figure 2 shows the photograph of the magnetite nanoparticles in a weigh pan (left) and transmission electron microscopy (TEM) image (right).

2.2 Methods

A number of weight percent magnetic nanoparticles (1%, 5%, 10%, 20%, and 30%) were dispersed in DMF (90%) and sonicated for 30 minutes. PAN (10% in DMF), in the form of powder, was then added to the dispersion while stirring at 40°C for 2 hours. A ready-to-spin dispersion/solution was placed in a plastic syringe that was connected to high DC voltage through a platinum wire. The syringe containing polymeric solution was connected to a capillary with an inside diameter of 0.5 mm. A syringe pump connected to the wide end of the syringe controlled the flow rate and speed. Electrospun fibers were collected on a grounded screen. The fibers were then dried in an oven at 60°C for 8 hours to minimize any residual solvent or moisture. A scanning electron microscope (SEM) was also used to determine the fiber diameter, orientation, and shape. Figure 3 shows a photograph of the electrospinning unit utilized in this study.

Figure 3: Electrospinning unit utilized in present study.

3. RESULTS AND DISCUSSION

In these experiments, only the magnetite concentrations were changed from 0% to 30%, while other processing parameters, such as mass flow rate (1 ml/hr), tip-to-target distance (15 cm), and applied voltage (20 kV) were kept constant in order to study the effects of magnetic nanoparticles on fiber diameter. Figure 4 shows the SEM images of nanocomposite fiber diameters and morphologies as a function of magnetite concentrations. It was determined that the loading of magnetic nanoparticles generally resulted in the increase of nanocomposite fiber diameters. For example, the average fiber diameter of 0% magnetic nanoparticles was about 400 nm, while that of 30% magnetic nanoparticles was about $1.08\ \mu\text{m}$. This may be due to the

increase in the solution viscosity by increasing the load. As the concentration of magnetic nanoparticles changed, the fiber morphology changed as well. In addition, SEM images show that some of the magnetic nanoparticles are all visible on or near the surface of the fibers. The equation ($d = 19.49 \eta^{0.43}$) shows the viscosity (η) effect on the diameter (d) of the electrospun fibers [14-16], where the fiber diameters increase with increasing solution viscosity. Table 1 gives the summary of superparamagnetic and flexible nanocomposite fiber fabrication conditions and their average diameters.

Figure 4: SEM images showing nanocomposite fiber diameters and morphologies as a function of magnetite concentrations.

Table 1: Summary of nanocomposite fiber fabrication at various particle concentrations.

Conditions	Average Fibers Diameter (nm)
PAN/DMF (90:10) plus 0 wt % magnetic particles	400
PAN/DMF (90:10) plus 1 wt % magnetic particles	570
PAN/DMF (90:10) plus 5 wt % magnetic particles	950
PAN/DMF (90:10) plus 10 wt % magnetic particles	660
PAN/DMF (90:10) plus 20 wt % magnetic particles	750
PAN/DMF (90:10) plus 30 wt % magnetic particles	1080

4. EDUCATION IN NANOTECHNOLOGY

Nanotechnology is the fabrication, manipulation, and characterization of materials at the nanoscale (usually between 1 and 100 nm), which will significantly affect economic, educational, and social developments in all areas, such as engineering, science, defense, biomedical, biology, etc. It is one of the leading technologies for educational revolution in the new millennium. Nanotechnology education is being offered by many universities around the world for the integration of all engineering and science courses for our future generation [17-20].

Several nanotechnology programs and centers in the U.S., Japan, Europe, Australia, and many other countries have been undertaken by the government and by private sectors to intensify the teaching, research, and development in nanotechnology. It is reported that development in nanotechnology will change the traditional practices of design, analysis, simulation, and manufacturing for new engineering products. Therefore, it becomes a challenge for the academic community to educate undergraduate engineering and science students with all the necessary information and leadership in this emerging field [17].

The corresponding author has developed two new courses, namely Nanomaterials Fabrication and Characterization (MS and PhD levels) and Introduction to Nanotechnology (BS level) in the College of Engineering at Wichita State University (WSU). In the first nanotechnology course, nanoparticles, nanofibers, nanofilms, nanotubes, nanocomposites fabrication techniques, and their applications were taught in detail. There were 35 students in the spring 2007 class, most of whom were engineering students. Homework sets involved the evaluation of recently published nanotechnology papers. In the term project, the students prepared reports on applications of nanomaterials and devices, such as nanocomposite manufacturing for the aircraft industry, nanoelectromechanical systems, microelectromechanical systems, and nanotechnology applications for fuel and solar cells.

In the second nanotechnology course, which was offered in fall 2007, similar topics were covered at the introductory level. There was homework, term projects, exams, and laboratory sessions. A nanotechnology laboratory has been set up in the Department of Mechanical Engineering at WSU and is dedicated to perform a number of nanotechnology experiments for students. This laboratory has several pieces of new equipment, such as an atomic force microscope (AFM), corrosion testing units, electrospinning unit, UV lithography, dry and wet etching, plasma cleaner, AC/DC power units, UV-Vis spectroscopy, optical microscopes, zeta potential/nanosizer, fume hood, spin-coating unit, capacitance bridge, contact angle and surface tension measurement devices, and an electrostatic self-assembly (ESA) nanofilm coating unit. Plans are to have undergraduate students work on the electrospinning method in the nanotechnology laboratory. Students will produce nanofibers using the described electrospinning method and then characterize properties such as fiber size, porosity, mechanical strength, and

sound absorption utilizing the equipment available in the laboratory. This will provide them with hands-on experience in how nanomaterials can be produced and later in how their properties can be characterized.

5. CONCLUSION

We have demonstrated the synthesis of magnetic nanocomposite fibers using the electrospinning method. Magnetite nanoparticles in the range of 0% to 30% were dispersed with DMF, and then PAN was added to the dispersion. Electrospinning experiments were conducted on these samples at constant pump speed, DC voltage, solvent concentration, and ground-screen distance. The SEM analysis proved that the diameters of superparamagnetic nanocomposite fibers were in the range of 400 nm to 1.08 μm . This demonstration improved students' knowledge of how to design, analyze, and manufacture nanomaterials and devices using the electrospinning method.

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