THE PREPARATION & CHARACTERIZATION OF ULTRATHIN FIBER NANOCOMPOSITES BY ELECTROSPINNING

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Abstract - Silver nanowires, derivatized C_{60} and nanocrystalline γ-Fe_2O_3 were successfully incorporated into ultra-thin fiber nanocomposites made of poly (vinyl pyrrolidone) (PVP), poly (vinyl alcohol) (PVA) and polystyrene (PS) via electrospinning. Optimum conditions were identified for various solvent, polymer concentration, nozzle-collector distance and applied voltage conditions to produce monofilament fibers of uniform diameter, consistent morphology and no bead formation. Characterizations of the new materials include SEM, EDS, thermal and ICP elemental analyses and magnetic data. The silver wires align coaxially with the long axis of the electrospun fibers minimizing bends in the fiber while the derivatized buckminsterfullerene, $C_{95}H_{66}O_4$, successfully incorporates into the fiber structure with a change in fiber surface morphology as seen previously in carbon nanotube composites. Processing of the magnetic fibers in the presence of a magnetic field gradient leads to the formation of the first known field responsive magnetic nanoribbons with uniform thickness.

Introduction. In recent years, nanoscience has clearly demonstrated its potential to impact traditional polymer processing and, in some cases, is already driving the production of commercial materials for specific applications[1]. One technique of particular importance is that of electrospinning, which allows for the preparation of polymer fibers with ultra-thin diameters, ranging roughly from nanometers to microns[2]. For example, many different polymers have been used to make very long, high surface area ultra-thin fibers with diameters ranging from 40-2000 nm[3].

To date, however, little work has been done in incorporating nanostructured materials into fibers made by electrospinning. Recently, superparamagnetic polymeric nanofibers were made electrospinning polymers containing colloidal suspensions of magnetite nanoparticles.[4] Here, the magnetic particles align in columns parallel to the long axis of the fiber.

In order to prepare property-specific ultra-thin fibers for targeted applications, we used the electrospinning technique to synthesize three new fiber nanocomposite materials that incorporate (1) magnetic nanoparticles, (2) derivatized C_{60} and (3) silver nanowires. Pure C_{60} appears to be the most impact resistant molecule known. When it or some of its derivatives are properly added to a polymer, it is expected to increase the impact resistance of the polymer. The potential value of ultra-thin fibers containing silver nanowires is in specific applications in the electronics industry and health care. Silver is both a conductor and antimicrobial agent.

Experimental. The electrospinning apparatus used is shown in Fig.1. The power supply was a Spellman high voltage power supply model CZE1000R. Fibers were collected on polished aluminum ground planes. PVP (MW 360,000), PVA 99% hydrolyzed (MW 85,000-124,000) and C_{60} (99% purity) were obtained from Sigma Aldrich and were used as received. Extrusion grade PS (MW 222,000) was purchased from BASF Mexicana and used as received. Solvents used were reagent grade. An aqueous ferrofluid, prepared earlier[5], was used as the source of magnetic particles, which consisted of nanocrystalline γ-Fe_2O_3 with an average particle diameter of 8 nm. The ferrofluid contained 5% by wt. Fe (as γ-Fe_2O_3). Silver nanowires were prepared by M. C. E. Servin by polyol reduction and had an average diameter of 200 nm. SEM/EDS analyses were performed on Ni coated samples on a Topcon SM-510.

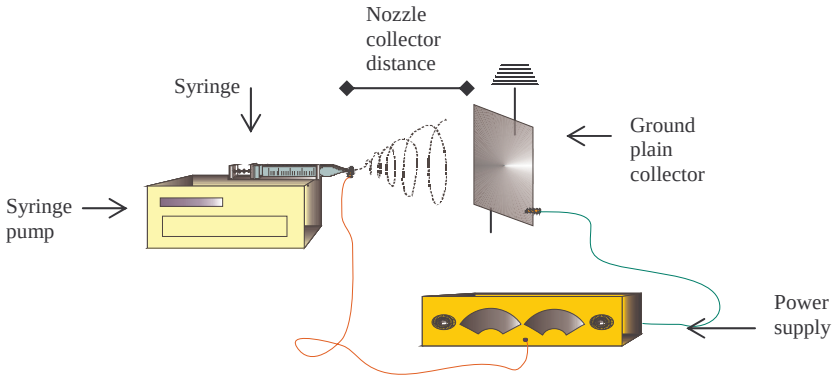


Fig. 1. Electrospinning process apparatus.

Magnetic fibers were prepared in two PVP solutions: ethanol/DMF (50/50 wt) and water/DMF (50/50 wt) in concentrations of 4 to 25% by weight. Ferrofluid was added to each solution and stirred for 12 hr. Electrospinning parameters were 12 cm for the nozzle to collector distance with a voltage drop of 10 kV, and 17 cm at 15 kV; flow rate of the viscous solutions was 3 ml/hr. During the electrospinning process, an 8 kG permanent magnet was placed behind the aluminum foil ground plane to access the effect of the magnetic field gradient on the fiber morphology. For the fullerene-loaded fiber synthesis, C_{60} was derivatized by a 1,3 dipolar cycloaddition of a long-chain malonic diester to form the compound illustrated in Fig. 2. The compound was characterized by NMR, IR and elemental analyses. It has the empirical formula $C_{95}H_{66}O_4$ and is here abbreviated as PTB for 'pig tail' buckminsterfullerene. PS and PTB DMF solutions were prepared; these were mixed and vigorously stirred for 12 hours. Electrospinning parameters were 10 and 15 cm with voltages of 10, 15 and 20 kV; flow rate was 3 ml/hr. Silver wire composite fiber syntheses were carried out in a PVP ethanol and a PVP ethanol/DMF mixture (50/50 wt). Suspensions of Ag wires in ethanol were added to each solution; the mixtures were vigorously stirred for 8 hours. Electrospinning parameters were 10 kV at 12 cm and 15 kV at 17 cm; flow rate was 3 ml/hr.

Fig. 2. 'Pig tail' derivative of C_{60}: $C_{95}H_{66}O_4$ (PTB).

Results and discussion. Ultra-thin fibers of polystyrene, PVP and PVA that contain nanocrystalline γ-Fe_2O_3, derivatized C_{60} and silver nanowires were prepared by electrospinning. A discussion of each system follows.

Magnetic polymer fibers. Numerous preparations of magnetic fibers[6] were carried out varying the solvent(s), constituent concentration and electrospinning parameters. SEM data shows that the best magnetic fibers were obtained using 10% PVP in 50/50 DMF/water with 20% ferrofluid and a nozzle to collector distance of 17 cm at 15 kV. SEM images of the magnetic fibers at 1K and 10K magnification are shown in Figs. 3a and 3b, respectively. The fibers exist as uniformly thick monofilaments and range in diameter from 90 to 190 nm with an average of 140 nm.

SEM data for numerous samples of the magnetic fibers suggest that a higher polymer concentration increased the fiber diameter, while a higher ferrofluid concentration (lower polymer concentration) decreased the fiber diameter.[7] The increase in fiber diameter with higher polymer concentration is understandable in terms of the balance between the viscoelastic forces active during polymer flow and the electrostatic forces that cause the so-called bending instability.[8]

a) b)

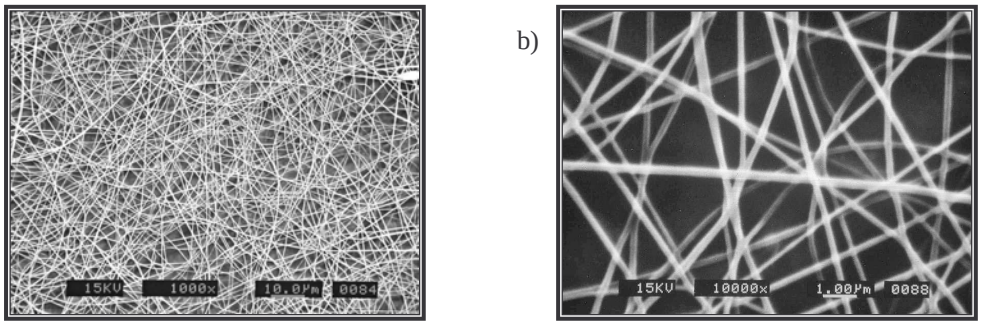
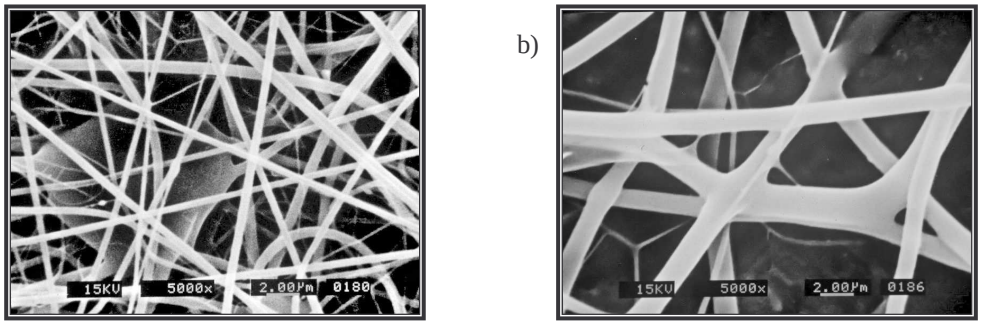


Fig. 3. SEM images of magnetic PVP fibers at (a) 1 K and (b) 10 K magnification (10% PVP in 50/50 DMF/water with 20% ferrofluid; 17 cm, 15 kV).

Figs. 3a and 3b also show the absence of beading commonly seen at the junction of electrospun fibers that occurs as a result of poor processing conditions.[9] Optimum fiber morphology and homogeneity result from the proper balance between jet charge density and viscosity[8]. Much thicker magnetic fibers were made by changing the solvent to DMF/ethanol (*vide infra*, also Fig. 4a).

To further explore the magnetic field effects on fiber morphology during processing, a permanent magnet was placed behind the aluminum foil ground plane proximal to the jet impact area. SEM images of fibers produced in the absence and presence of the field gradient are shown in Figs. 4a and 4b, respectively. In Fig 4a, the diameter of the fibers range from 300 to 350 nm, while under the same processing conditions, but in the presence of the field gradient, the apparent fiber diameters are much larger and range from 1.3 to 1.4 μm. Additionally, fibers produced in the presence of the field gradient show some branching (Fig. 4b) as opposed the monofilaments obtained in the absence of the field. A profound change in the fiber morphology occurs in the presence of the field gradient to produce flattened ribbons as may be seen in Fig. 4c. This morphology change may result from impaction of the fiber jet as it hits the collection plate. Clearly, the interaction of the charged magnetic jet with the field gradient is complex. The thicker fibers may result from a decreased bending instability caused by the magnetic field gradient.

a) b)



c) d)

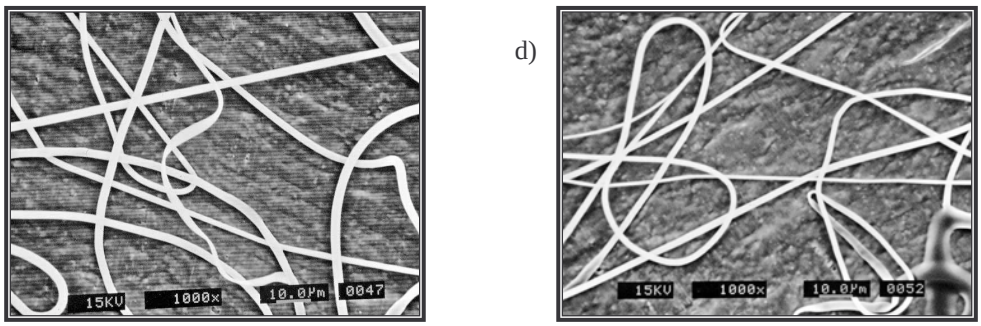


Fig. 4. SEM images of magnetic PVP fibers (a) and ribbons (b) through (d) at 5K and 10K magnification, respectively (12 % PVP in 50./50 DMF/water with 20% ferrofluid, 15 cm, 15 kV); (a) zero field preparation; (b) through (d) preparations in magnetic field.

Derivatized buckminsterfullerene loaded nanofibers. Numerous preparations of PTB (Fig. 2) loaded fibers were carried out varying the solvent(s), constituent concentration and electrospinning parameters. [7] Upon addition of PTB to PS, we observe a dramatic reduction in fiber diameter as seen in the SEM images in Figs. 5a and 5b. In both cases, the fiber morphology is homogeneous with no beading. The fibers in both cases were prepared using 10% PS in DMF processed at 15 cm and 20kV; PTB was added at 1% and was completely dissolved in the DMF before processing.

a) b)

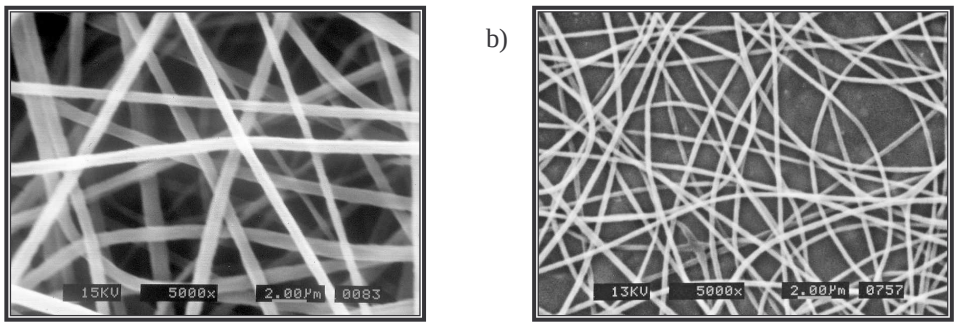
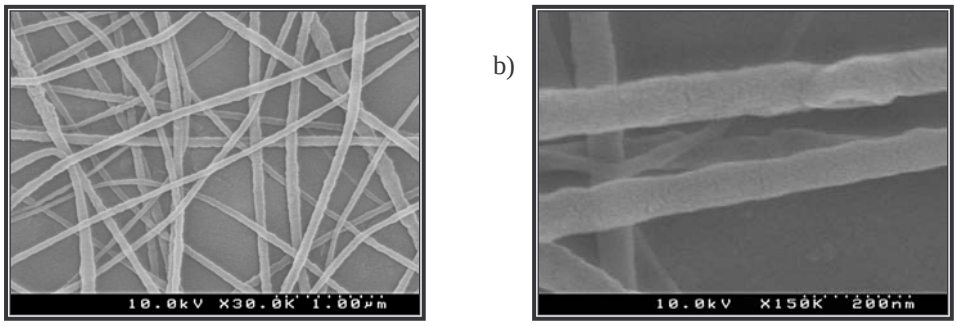


Fig. 5. Comparison between PS and PS/PTB polymer fibers at 5K magnification; (a) 10% PS; (b) 10% PS with 1% PTB; 15 cm , 20 kV for both preparations.

The thinnest PTB/PS fibers were prepared using the same concentrations with spinning at 10 cm at 10 kV. These fibers are shown in Figs. 6a and 6b and have diameters in the range of 70 to 80 nm. A change in surface morphology of the fibers takes place with the addition of PTB to form rough-surfaced fibers. The surface roughness is similar to that observed in carbon nanotube composite fibers[10]. In the present case, the roughness is attributed to a head-to-surface, tail-to-polymer orientation of the PTB in the PS fiber. Fibers spun with twice the amount of PTB showed a significant increase in surface roughness (Fig. 6c).

a) b)



c)

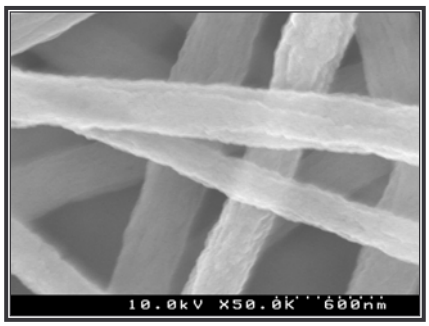


Fig. 6. SEM images of PS/PTB rough-surfaced fibers. (a) and (b) 10 % PS and 1% PTB in DMF; 10 cm, 10 kV. (c) 10% PS and 2% PTB in DMF;15 cm, 20 kV.

Silver wire composite fibers. Many preparations of silver wire-loaded fibers were carried out by varying the solvent(s), constituent concentration and electrospinning parameters[7]. As a consequence of the polyol reduction, the silver wires are coated with a very thin layer of PVP for stability before being mixed with the electrospinning solution. Fig. 7 shows SEM images of fibers prepared from 15 to 18% PVP in ethanol and in DMF/ethanol solvents, respectively, with 35% Ag. A large distribution of fiber diameters is seen that ranges from 250 to 650 nm (d_{avg} = 390 nm; Fig. 7a) and from 200 to 800 nm (d_{avg} = 430 nm; Fig. 7b). The fibers are monofilaments of uniform thickness as was observed for the magnetic and PTB fibers.

Two characteristics of the Ag fibers is the unusual straightness of the fibers as compared to that of most fibers prepared by electrospinning and the more than usual parallel alignment of the fibers upon collection. We attribute the straightness of the fibers to the presence of the silver wires, which in the native state, also exist as straight rods or wires. This assumption presupposes that the silver wires are internal to the polymer fiber, which is supported by EDS data showing a high concentration of C rather than Ag at the fiber surface.[11] TEM studies of the Ag fibers have been hampered by sensitivity to the electron beam. Presumably, the presence of the Ag wire affects the bending instability of the fiber in such a way as to prevent reduction of the fiber diameter.

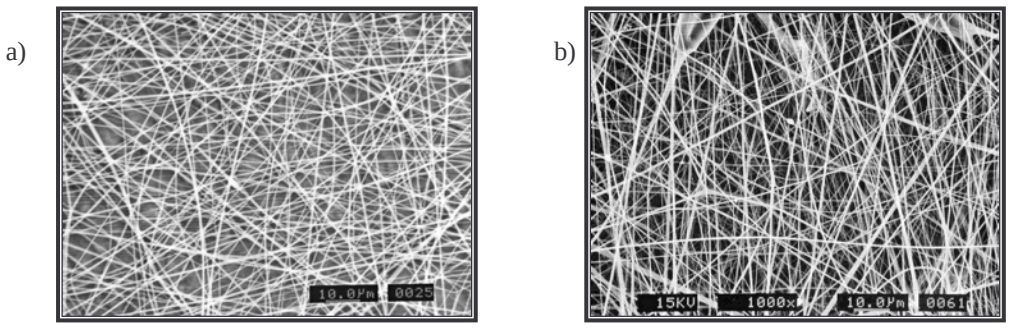


Fig. 7. SEM images of silver wire / PVP composite fibers. (a) 18% PVP, 35% Ag in DMF/ethanol; 17cm, 15kV. (b) 15% PVP, 35% Ag in ethanol; 17 cm, 15 kV.

To further test the proposed Ag-coated fiber structure, a sample of fibers was sonicated to induce fiber breakage. The results are shown for fibers before and after sonication in Figs. 8a and 8b, respectively. After sonication, several 90º kinks in the fibers are observed suggestive of internal silver wire breakage.

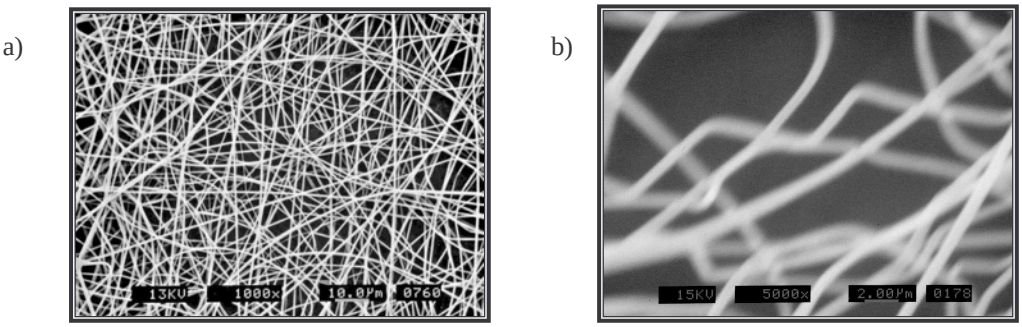


Fig. 8. SEM images of silver wire / PVA composite fibers; 15% PVA, 20% Ag in water; 15 cm, 20 kV. (a) Before sonication. (b) After sonication; note sharp bends in the fibers.

Summary and Conclusions. Nanocrystalline γ-Fe_2O_3, derivatized C_{60} and silver nanowires were successfully incorporated into ultra-thin fibers of PS, PVP and PVA using the electrospinning technique. In each case, the optimum conditions were identified to produce fibers of uniform diameter, consistent morphology and no bead formation by varying the solvent, polymer concentration, nozzle-collector distance and applied voltage. Incorporation of the nanostructured materials into the electrospun fibers in all three cases leads to new and/or unexpected fiber and surface morphology. These include magnetic field responsive nanoribbons, fullerene loaded polymer fibers and insulator coated conducting fibers. Further studies of these systems for industrial applications in smart textile materials, health care and electronics are underway. To our knowledge, this work is the first report on the use of the electrospinning technique for the production of ultra-thin polymer fibers at the national level in Mexico.

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References and Notes.

[1] Xerox Corp., for example, has developed the nanotechnology for the bottom-up and large-scale production of xerographic toner that will replace traditional melt blend processing and lead to customer cost savings (H. Mahabadi, Xerox Canadian Research Centre). Also, see Arizmendi, L.; MC Thesis, *Preparación de Membranas Fibrosas de Polímeros Fluorescentes por electrohilado y su Aplicación en Biosensores*, Centro de Investigacion en Quimica Aplicada, Saltillo, Coah., October, 2006.

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[6] Magnetization vs applied field and temperature data for the magnetic fibers shows superparamagnetic behavior identical to that of the starting ferrofluid (ref. 5) suggesting a homogeneous dispersion and non aggregated state for the nanocrystalline γ-Fe_2O_3.

[7] Martinez Ibañez, M.A.; MC Thesis, *Preparacion y Caracterizacion de nuevos compositos de nanofibras via Tecnologia de Electrohilado*, Centro de Investigacion en Quimica Aplicada, Saltillo, Coah., Septiembre, 2006

[8] During the electrospinning process, the polymer jet travels from the nozzle to ground plane to close the electrical circuit. During this process, the charged jet undergoes a whipping instability that stretches and bends it at very high speed due to electrostatic repulsions within the jet. The looping jet trajectory results in fiber diameter reduction and solvent evaporation At the same time, dynamic viscoelastic forces in the polymer work to prevent the charged jet from being stretched. See: Reneker, D.H.; Yarin, A.L.; Fong, H.; Koombhongse, S., *J Appl Phys* , **87**, (2000), 4531-4647.

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[11] Silver content of the fibers was verified by elemental analysis (ICP) and TGA; SEM imagery showed the presence of only one type of fiber, which was polymer-coated and the absence of uncoated or bare silver wires. Contactless electrical conductivity measurements of the Ag fibers are underway.