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Electrical conductivity of a single electrospun fiber of poly(methyl methacrylate) and multiwalled carbon nanotube nanocomposite

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Electrospinning produces polymeric fibers with diameters in the range of 10 μm–10 nm by accelerating a charged polymer jet under a high electric field. We report the preparation of conducting nanocomposite fibers of poly(methyl methacrylate) (PMMA) and multiwalled carbon nanotubes (MWCNTs) by electrospinning. The fibers obtained are long and well aligned. The carbon nanotubes are found to be oriented along the fiber axis. The room temperature dc electrical conductivity of a single fiber with MWCNT (0.05% w/w) shows about a ten orders of magnitude improvement from the pure PMMA. The conductivity increases with MWCNT concentration. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2193462]

Since the discovery of carbon nanotubes (CNTs) by Iijima, they have attracted the attention of researchers because of their unique structure and extraordinary physical properties.[1–3] CNTs offer the potential for exciting applications such as ultrastrong wires, nanoelectronic devices, field electron emitters, nanoprobes, nanocomposite materials, and more. Due to their high-aspect ratio, small diameter, light weight, high mechanical strength, good electrical and thermal conductivities, and good thermal and air stability, CNTs are recognized as the ultimate carbon fibers for high performance, multifunctional composites. However in many cases, processing difficulties have hampered the practical realization of their excellent properties. Bulk production of CNTs often results in a dense entangled network of nanotube bundles. Thus, separation of CNT bundles, their dispersion, and their alignment are elementary crucial steps in several useful applications.

It is difficult to obtain very long CNTs for useful applications. However long aligned polymer fibers could be obtained by several fairly simple schemes. In order to obtain conducting nanowires of sufficient length, one way, perhaps, would be to incorporate CNTs inside the polymer matrix and form the fibers. Controlled preparation of such long aligned nanofibers are useful in several applications as interconnects in nanoelectronics and in the design of sensors. Further, polymer composites with CNTs also improve the mechanical properties. However, one of the problems associated with the preparation of such conducting nanocomposite wires is the task of dispersing the nanotubes in the host polymer matrix due to chemical incompatibility between the polymer and the CNTs. In addition, the existence of van der Waal's forces between CNTs makes uniform dispersion difficult. Several attempts have been made to uniformly disperse CNTs for the preparation of the polymer composites such as using functionalized CNTs, *in situ* polymerization, and dispersion of CNTs and polymers in organic solvents through sonification, etc.[4–6]

Commonly used techniques for the fabrication of CNT composite materials rely on solution casting, melt spinning, and wet spinning. Recently, CNT-filled composite fibers have been produced by an electrospinning technique.[7–12] Electrospinning is a technique for producing polymer fibers in the range of 10 μm–10 nm by accelerating a charged polymer solution using a high electric field.[13–16] These fibers, due to their light weight and large surface area-to-volume ratio, have potential applications in several fields, such as "smart clothing" for military, filters, sensors, nanocomposites, nanoelectronic devices, wound dressing, etc. The electrospinning process can be divided into two stages, viz., jet elongation and bending instability. During the bending instability the fibers spiral violently and finally get collected on the collecting plate. Due to this reason the fibers obtained in this process are randomly oriented in the form of nonwoven mats or webs. For several applications, fairly well aligned fibers are essential. There are a few reports on the attempts to align these electrospun fibers.[17–21]

Electrospinning provides a very simple method of obtaining polymer-CNT nanocomposite fibers. It is observed that the CNTs align themselves uniaxially along the fiber axis. However, in such earlier attempts, increasing the mechanical properties was the main focus. In this letter we report the fabrication of nanocomposite fibers of multiwalled carbon nanotube (MWCNT) filled poly(methyl methacrylate) (PMMA) using an electrospinning process. The MWCNTs are found to be homogeneously dispersed and aligned inside the polymer matrix. Single fiber electrical conductivity of these fibers is measured and it is observed that the room temperature electrical conductivity of these fibers is significantly improved by the presence of MWCNTs.

PMMA (average M_v 996 000) obtained from Sigma-Aldrich and MWCNTs of ~95% purity obtained from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, China, were used without further purification. The CNTs were dispersed in chloroform using an ultrasonic bath

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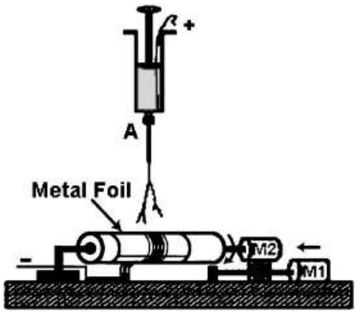

FIG. 1. A schematic diagram of the electrospinning setup. A polymer solution is taken inside a plastic syringe (A) with a fine copper wire inserted. This is connected to the high voltage power supply (+). Metal foil wrapped over a drum acts as the collector. A fine metal brush (−) was used to ground the metal foil. Motor M2 is a dc motor used to rotate the drum and M1 is a stepper motor used to move the drum along its axis to increase the area of fiber collected.

for 1 h. A required weight of PMMA was added to the CNT dispersion and stirred for 48 h using a magnetic stirrer. The resulting solution was used for electrospinning with a required weight percentage of PMMA and CNTs. To obtain an aligned fiber we used the modified experimental setup reported earlier (Fig. 1).[18] Electrospun fibers were collected on aluminum foil wrapped over a drum. The metal foil was electrically grounded by using a metallic brush that gently touched the foil. We have applied 5 kV of the electric potential difference between the electrodes, and the interelectrode distance was about 5 cm. The flow rate of the polymer solution was kept steady (0.6 mL/h) using a syringe pump fabricated in the lab. The morphology of the fibers was characterized by a scanning electron microscope (SEM) model JSM-840. Transmission electron microscopy (TEM) pictures were recorded using a JEOL 2000 FX11. For this the fibers were coated directly on the carbon coated copper grids without rotating the drum. The Raman spectra of the polymer-CNT composite fibers and pure MWCNTs were recorded by a Reinshaw Raman microscope at 633 nm wavelength. For the measurement of room temperature current-voltage (*I-V*) characteristics, one or two fibers were coated on a precleaned glass plate. Gold electrodes were coated on the fibers with a separation of approximately 500 μm by a mask evaporation method. The *I-V* characteristics of the fiber were measured using Keithley-238 source-measure unit.

Figure 2 shows SEM images of the composite fibers. Fibers several centimeters in length are obtained. The diameters of the fibers obtained are in the range of 6 μm–200 nm. The diameter is dependent on the interelectrode distance, electric field, concentration and flow rate.[15] The alignment achieved is in the direction of the rotation of the drum. This is in agreement with the results obtained by Fennesey *et al.*, who studied in detail such alignment with the change in rotation speed of the drum.[19] In the present case, alignment could be achieved when the rotation speed of the substrate was more than 1500 rpm. This corresponds to a linear velocity of about 3.0 m/s at the surface of the drum. For draw velocities less than this value, good alignment of fibers could not be achieved.

The dispersion and orientation of the CNTs are studied by TEM. Figures 3(a) and 3(b) show the bright field TEM images of the fiber. Since some portion of the polymer is removed by the electron beam, we are able to see the aligned CNTs clearly in that region [Fig. 3(b)]. This shows that the CNTs are also well dispersed inside the fiber. The diameter of the MWCNTs is in the range of 10–30 nm. Here we can observe that the long axes of the CNTs are aligned in the direction parallel to the fiber axis. Due to the sink flow and high extension of the electrospun jet, the CNTs are expected to be aligned in the direction of the fiber axis.[9] The pure PMMA fiber matrix is, in general, white in color, but with the addition of CNTs to the polymer matrix, the color becomes grayish. The presence of CNTs is also confirmed by the Raman spectroscopy. Figure 4 shows the Raman spectra of the MWCNT powder and the PMMA-CNT composite fiber. The *G* band ($1578\ \mathrm{cm}^{-1}$) as well as the *D* band ($1322\ \mathrm{cm}^{-1}$) is observed for all the compositions. The inten-

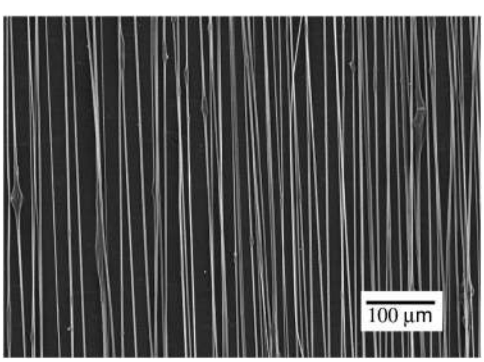

FIG. 2. SEM images of aligned fibers of MWCNT-PMMA obtained through electrospinning.

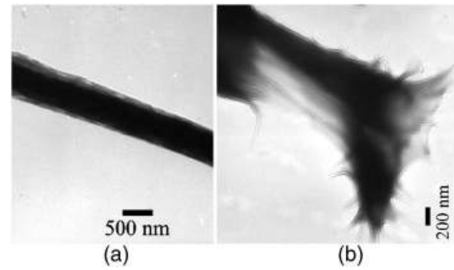

FIG. 3. (a) TEM images of one of the fibers under low resolution and (b) TEM image of a cut portion of the fiber where the aligned CNTs can be clearly seen because here, a part of the polymer has been removed by the intense electron beam during observation.

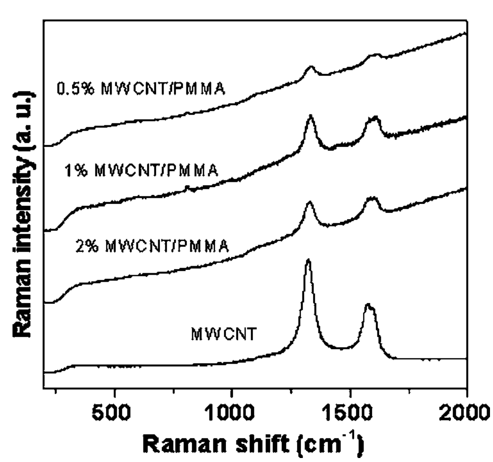

FIG. 4. Raman spectra of the fibers with different weight percentages of MWCNT content. The *G*-band peak broadened and shifted towards the higher frequency side with the decrease in the MWCNT content.

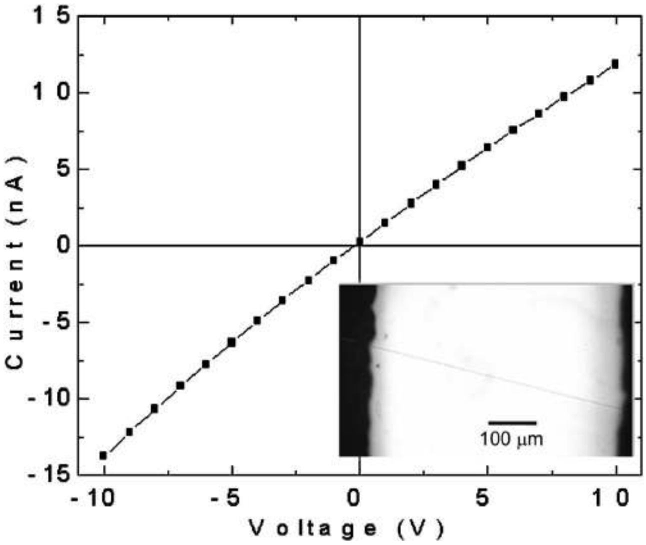

FIG. 5. The *I-V* characteristics of a single fiber. The resistance of the fiber from the slope of the line is about 780 MΩ. The inset shows the single fiber obtained between the gold electrodes.

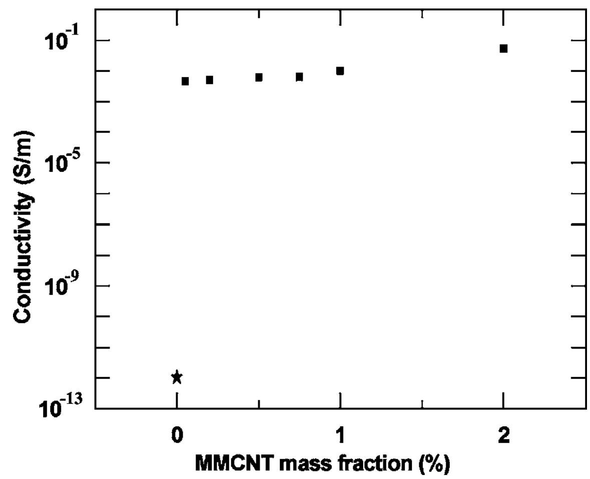

FIG. 6. Variation of the conductivity of the single composite fibers with a different mass fraction of MWCNT. The symbol (*) corresponds to the data used from literature (Ref. 23).

sity of the peaks is decreased with the increase in the PMMA weight percentage. There is a shift towards the higher wave numbers with the increase in the PMMA percentage. This shift in the peak of the *D* band has been calculated to range from 4 to 9 cm^{-1} as the concentration of the CNT is varied from 2% to 0.5%. It is similar to the results reported by Stephan *et al.*[22] This shift may be due to the change in the environment of the CNTs with the PMMA concentration. In the case of the *G* band, a broadening was also observed with the increase in the PMMA weight percentage.

The *I-V* characteristics of the single fiber show a linear ohmic behavior. A typical *I-V* characteristic for a single fiber with 2% (w/w) of the CNTs loading is shown in Fig. 5. The optical microscope image of the single fiber with the gold electrodes (separation of 500 μm) is shown in the inset of Fig. 5. The dc conductivity (σ) of the fiber is of the order of 10^{-2} S/m. It is observed that the σ increases by nearly ten orders of magnitude from pure PMMA (10^{-12} S/m from standard literature).[23] The conductivity of pure MWCNTs obtained from the manufacturer is 10^4 S/m. Further, from Fig. 6 we observe the conductivity of the fiber further increases by nearly one order of magnitude from 4.5×10^{-3} to 5.3×10^{-2} (S/m) as we vary the concentration of the MWCNTs from 0.05% to 2%. The composites show percolative behavior with the percolation limit well below the lowest (0.05% w/w) loading attempted here.

In summary, we have prepared long, continuous, and well aligned PMMA-MWCNT nanocomposite fibers over a large area by electropinning. The CNTs are aligned in the direction of the fiber axis. The composite fibers show a ten orders increase in the electrical conductivity with a very low percolation threshold.

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