Fabrication and Electrical Characterization of Electrospun Polyacrylonitrile-Derived Carbon Nanofibers

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ABSTRACT: Carbon nanofibers were produced from a polyacrylonitrile/N,N-dimethylformamide precursor solution by an electrospinning process and later pyrolysis at temperatures ranging from 500 to 1100°C in an N_2 atmosphere for about 1 h. The morphological structure of the nanofibers was studied with scanning electron microscopy. Scanning electron microscopy images of carbonized polyacrylonitrile nanofibers without a gold coating showed that the carbonized polyacrylonitrile nanofibers possessed electrical properties. The thermal behavior of the nanofibers was studied with thermogravimetric analysis. An indirect four-point-probe method was used for the measurement of the conductivity of nanofiber mats. The conductivity increased sharply with the pyrolysis temperature. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 255–259, 2007

Key words: electrospinning; carbon nanofibers; electrical conductivity

INTRODUCTION

Carbon nanofibers, like other one-dimensional nanostructures such as nanowires, nanotubes, and molecular wires, have been receiving increasing attention because of their high length-to-diameter ratio. This is due to their potential applications in nanocomposites,[1] templates for nanotubes,[2] filters,[3] rechargeable batteries,[4] supercapacitors,[5] bottom–up assembly in nanoelectronics and photonics,[6] and so forth. Carbon nanofibers can be produced by a traditional vapor growth method[7] or by a plasma-enhanced chemical vapor deposition method, which were developed at the beginning of this century.[8] However, both methods involve a complicated process and have a high cost. Carbon nanofibers can also be produced by the stabilization, carbonization, and activation of electrospun precursors.

The nanosize diameter promises a high specific surface area and durable physical properties in compression.[9] Reneker et al.[3] produced carbon nanofibers with diameters in the range of 100 nm to a few micrometers from electrospun polyacrylonitrile (PAN) and mesophase pitch precursor fibers. Wang and coworkers[10,11] produced carbon nanofibers by carbonizing electrospun PAN nanofibers and studied their structure and conductivity.

In this study, PAN nanofibers as precursors of carbon nanofibers with diameters in the range of 130–280 nm were obtained through electrospinning. The morphologies and structures of the as-spun nanofibers were studied because they could provide basic knowledge about the formation of carbon nanofibers through the stabilization and carbonization of electrospun PAN nanofibers.

EXPERIMENTAL

Materials and apparatus

A power supplier with positive polarities (with a voltage range of 1–50 kV and a maximum amperage of 2 mA) was purchased from Hitek Power Co. (Littlehampton, West Sussex, UK). A microsyringe pump from Stoelting Co. (Wood Dale, IL) was used to control the throughput of the polymer solution. Pieces of aluminum foil (40×60 cm^2) were used as fiber collectors. Plastic syringes fitted with metal needles were used as electrospinning nozzles. An electrode from the power supplier was used to charge the polymer solution into the syringe via a metal needle.

All reagents were used without further purification. PAN with a weight-average molecular weight of 150,000 g/mol (Aldrich, St. Louis, MO) was dissolved in slightly heated N,N-dimethylformamide (DMF), which was purchased from Merck Co. (Whitehouse Station, NJ), to yield an 8 wt % solution. The polymer solution was electrospun from a
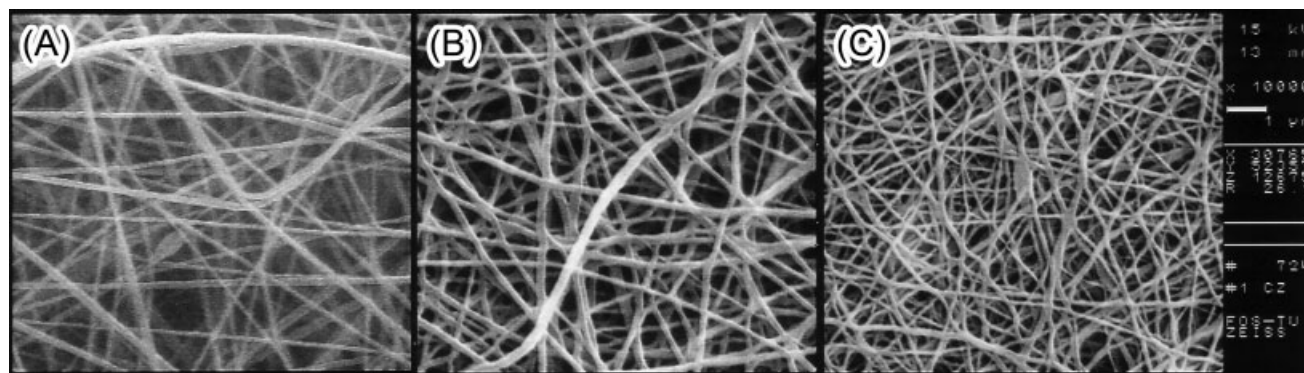
Figure 1 SEM micrographs of (A) PAN, (B) stabilized, and (C) carbonized nanofibers.

10-mL syringe mounted on a syringe pump providing a flow rate equal to 1.0 μL/h. In all cases, the PAN solution was electrospun from a syringe needle charged to 20 kV. The electrospinning distance was set at 10 cm.

For carbonization, the as-spun PAN fibers were placed in a tube furnace and stabilized in air for 30 min at 350°C, then carbonized for 1 h in nitrogen at 750°C, and finally heated at 1100°C in nitrogen for another hour; the ramp rate was 5°C/min between 350 and 1100°C.

Characterization

The diameter and morphology of the gold-sputtered electrospun nanofibers were determined and examined with scanning electron microscopy (SEM; DSM 960A, Zeiss, Oberkochen, Germany); the measurements of about 100 random fibers were carried out to determine the average fiber diameter and distribution. SEM also was used to examine the conductivity of PAN nanofibers. To get an idea about the electrical properties of the fibers, images were taken of fibers with and without gold sputtering. SEM micrographs were analyzed with SemAfore software version 4 from JEOL (Skandinaviska, Sollentuna, Sweden). The uniformity and average particle diameter were calculated with this software. The thermal properties of the electrospun fibers were analyzed by thermogravimetric analysis (model TGAQ50, TA Instruments, New Castle, DE) at a heating rate of 20°C/min. A four-point-probe device (CPS-06 contact probe, Alessi, Irvine, CA) was employed to measure the volume conductivity of the electrospun PAN and carbon nanofibers.

RESULTS AND DISCUSSION

Structural characterization of the nanofibers

Figure 1 shows SEM micrographs of electrospun, stabilized, and carbonized nanofibers at the same mag-

nification. Figure 1(A) shows that a collection of electrospun polymer fibers formed a dense mat. An analysis of this image with the software showed that the PAN nanofibers had an average diameter of 149 nm. After the stabilization and carbonization process, the mat retained its shape, and the average diameters shrank to 140 and 109 nm [Fig. 1(B,C)].

Figure 2 shows the diameter distributions of as-spun PAN, stabilized, and carbonized nanofibers. The diameter of the PAN nanofibers ranged from 75 to 350 nm. Most of the fibers varied between 100 and 175 nm. The statistical analysis of the recorded data gave an average diameter of 149 nm. The stabilized and carbonized PAN nanofibers had average diameters of 140 and 109 nm, respectively.

Evaluating the electrical properties of the nanofibers with SEM

SEM was used to examine two samples of PAN fibers for the evaluation of the electrical properties; one sample was coated with gold, and the other one was not exposed to the sputtering process. Figure 3(A) shows the PAN nanofibers without a gold coating. This dim image indicates that the PAN nanofibers had low electrical properties. Figure 3(B) shows the carbon nanofibers without a gold coating. A comparison of the SEM images of the PAN and carbonized PAN nanofibers without a gold coating showed that the carbonized PAN nanofibers possessed electrical properties.

Electrical conductivity of the carbon nanofibers

Although the process of charge conduction in small-diameter polymers is not clearly understood, it has been suggested that unusual current conduction properties arise when the size of the wires is reduced below a certain critical thickness. Hence, it is expected that new polymeric wires and contacts may behave more favorably when they are confined
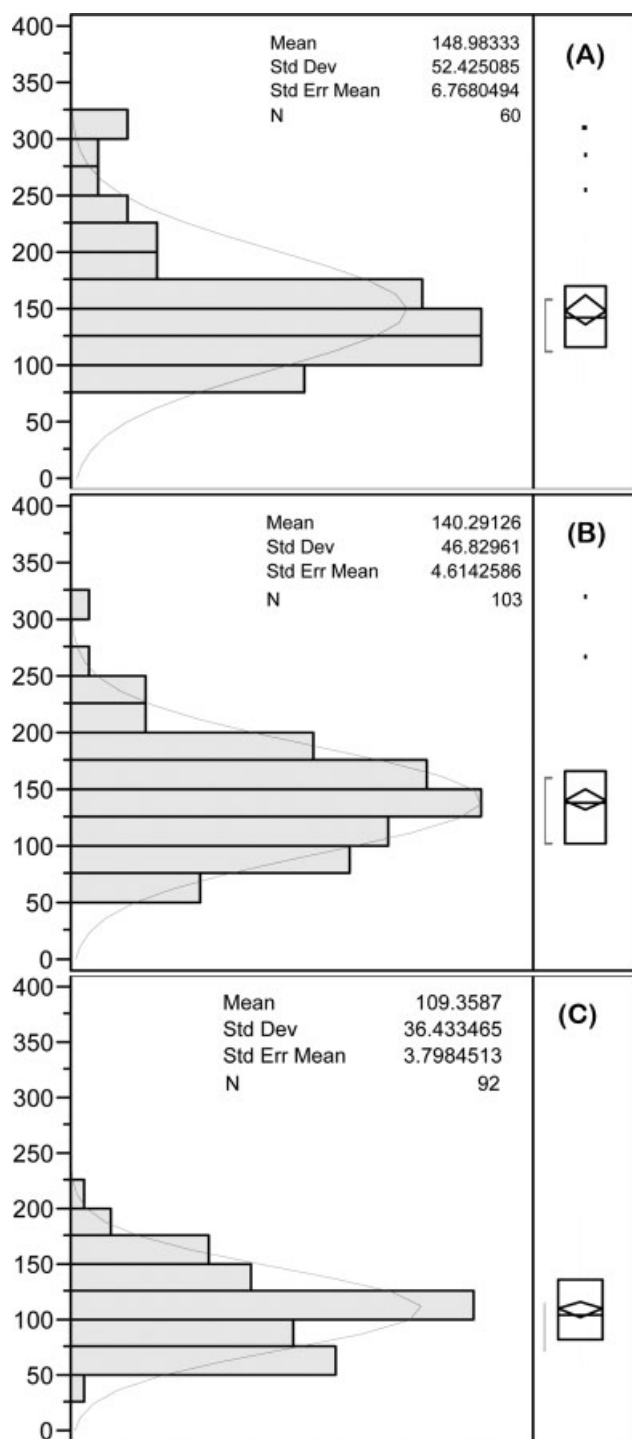
Figure 2 Diameter distributions of (A) PAN, (B) stabilized, and (C) carbonized nanofibers.

to operate in such reduced dimensional regimes (nanoscale).

Stabilized nanofibers and pyrolysis at 600°C did not generate a conductance high enough to be detected. At temperatures higher than 600°C, the conductivity increased sharply with an increasing pyrolysis temperature. Figure 4 shows the conduc-

tivity of nanofiber mats that were pyrolyzed at 600, 700, 900, and 1100°C for 1 h. The electrical conductivities of the carbonized webs were measured to be 150 and 600 S/cm at 900 and 1100°C, respectively.

Pyrolysis of the PAN nanofibers

The TGA curves of the PAN nanofibers (Fig. 5) show a dramatic weight loss between 300 and 450°C, which indicates the decomposition of PAN. About 40% of the weight was lost in this temperature range. For the stabilized PAN nanofibers, this weight-loss peak started from 300°C; when the temperature was increased to 450°C, about 20% of the weight was lost. Beyond 450°C, the weight decreased at a much slower rate, from 60 wt % at 450°C to 50 wt % at 800°C and to 45 wt % at 900°C. For the stabilized PAN nanofibers, these numbers were about 58 and 42 wt % at 800 and 900°C, respectively. The TGA curve for the carbonized nanofibers indicates that only about 5 wt % of the weight was lost at 900°C.

During the complicated pyrolysis process, PAN generally goes through stabilization between 200 and 400°C and carbonization at higher temperatures. Stabilization involves dehydrogenation, cyclization, and, if it occurs in the air, oxidation. The exothermic process is due to the uncontrolled thermal polymerization of the nitrile group with the release of the heat of polymerization. During carbonization, the fibers lose non-carbon elements, as well as partial carbon, in the form of volatile byproduct gases, such as HCN, NH, and H. Finally, a graphite-like structure is formed. The initial heating of stabilized PAN fibers causes the growth of graphite-like ribbons by a dehydrogenation mechanism. Denitrogenation, which occurs as the temperature is increased, is responsible for the growth in the area and the transformation of these ribbons into thin, sheetlike structures and, at higher temperatures, for the bonding of adjacent sheets. These sheets contain numerous vacancy imperfections and are folded to enclose pencil-shaped voids oriented in the general direction of the fiber axis. The lengths of each block or sheet are relatively short, with each succeeding block disoriented with respect to its neighbor.

The basic structural unit (BSU)[12] of carbon fibers consists of a stack of conductive turbostratic layers that can split, twist, fold, and join other BSUs to form microdomains that can also split, twist, fold, and join to form carbon fibers.[13] At low temperatures or immediately after stabilization, the oriented BSUs due to heteroatoms and the voids between them are isolated, and so the fibers are not conductive. Further increasing the temperature causes the disappearance of the heteroatoms and decreases the
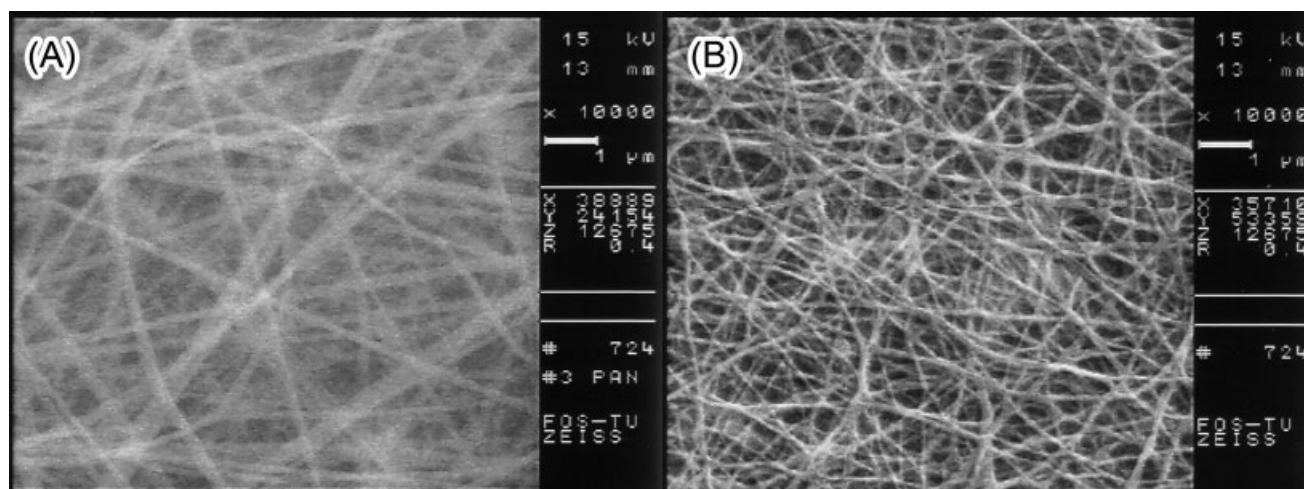
Figure 3   SEM images of (A) PAN and (B) carbon nanofibers without a gold coating.

void space by joining sequentially oriented and touching graphite-like layers and aligning them more parallel to the fiber axis. The distorted sheets of BSUs associated with tilt and twist boundaries are
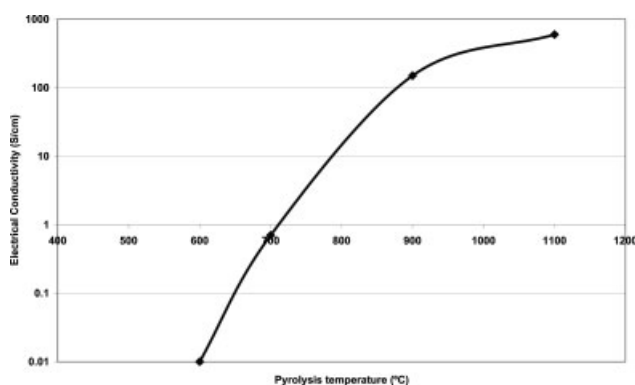

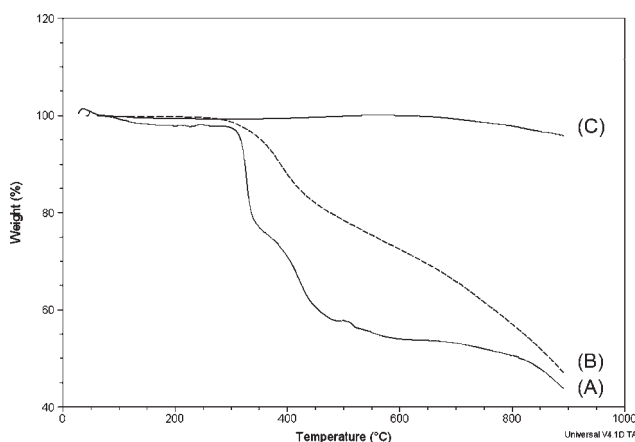**Figure 4**   Pyrolysis temperature versus the conductivity.

Figure 5   TGA thermograms of (A) PAN, (B) stabilized, and (C) carbonized nanofibers.

bonded to one another wherever the boundaries of adjacent sheets touch. The more compact the fiber is, the larger the number is of contact areas and the greater the chance is for adjacent sheets to bond. The lateral cohesion thus formed causes the strength of the fiber to increase. Specifically, the distortions within the polyaromatic graphene layers or sheets tend to be removed by the accumulation of any structural defects at their boundaries. This induces a progressive increase in the width and radius of the curvature of the aromatic layers that can be correlated with the stiffness, stacking order, and diameter of the graphitic layers. The longer, better oriented, and more graphitic microstructures exhibit higher values of the thermal and electrical conductivities.

CONCLUSIONS

PAN nanofibers with diameters in the range of 130–280 nm were obtained by the electrospinning of PAN/DMF solutions. Evaluating the electrical properties of the nanofibers with SEM indicated that the PAN nanofibers had low electrical properties, whereas the carbonized PAN nanofibers possessed electrical properties. The measurement of the electrical conductivity of nanofiber mats showed that increasing the pyrolysis temperature increased the conductivity of the nanofibers. All results indicated that the carbon nanofibers were composed of turbostratic layers of graphite oriented preferentially at some angle to the fiber axis. Increasing the pyrolysis temperature resulted in a reduction of the interlayer spacing, a decrease in the void space, growth in the thickness and area of the graphitic crystallites, and an increase in the preferred orientation of the microstructure. All these changes increased the electrical and thermal conductance.

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