Preparation and characterization of P(AN-co-VA-co-DEMA) fibers coated with multiwalled carbon nanotubes by electrostatic interactions

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ABSTRACT: P(AN-co-VA-co-DEMA) terpolymers were synthesized by aqueous precipitation copolymerization of acrylonitrile (AN), vinyl acetate (VA), and 2-dimethylamino ethyl methacrylate (DEMA) with an $Na_2S_2O_5$–$NaClO_3$ redox initiating system and fibers from these terpolymers were thus prepared by a wet spinning method. Functionalized multiwalled carbon nanotube (F-MWNT) networks were created on the surface of P(AN-co-VA-co-DEMA) fibers by a simple dipping method. The morphology and interfacial interactions of the obtained F-MWNTs-coated fibers were characterized by scanning electron microscope, Raman spectroscopy, and Fourier transform infrared spectroscopy. The results showed that F-MWNTs were assembled on the fibers and the density of F-MWNTs can be controlled by adjusting the F-MWNTs content in the dipping solution. The assembly process was driven by electrostatic interactions between the negative charges on the nanotube sidewalls and the positive charges of the fibers. The F-MWNTs-coated fibers had a good conductivity. The volume resistivity of the fibers coated with 1.18 wt % F-MWNTs reached 0.27 $\Omega \cdot cm$, while the original mechanical properties were preserved. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42545.

INTRODUCTION

Carbon nanotubes (CNTs) exhibit excellent mechanical, thermal, and electronic properties and hence have received much attention in recent years for wide potential applications such as field emitters, sensors, conducting materials, and nanoelectronics.[1–3] CNTs/polymer composite fibers in which the nanotube architecture is established with a host polymer matrix are one of the most intriguing applications of CNTs. The large aspect ratio, mechanical, and electronic characteristics of CNTs make them ideal candidate as fillers in lightweight polymer composite fibers designed for structural or functional applications.[4–6] There have been many studies on fabrication of various CNTs/polymer composite fibers.[7–11] Among these fibers, polyacrylonitrile (PAN) fibers are of particular interest since they are commercially important and widely used in apparel, home furnishings, and industrial fabrics.[12,13]

At present, with the development of smart fabrics, conductive PAN fibers have become attractive. Incorporation of CNTs to PAN matrix can endow PAN fibers with better electrical properties.[14,15] However, how to effectively create CNTs networks in PAN matrix to form electrical pathway poses a major challenge. The most common method is to first disperse CNTs in the PAN spinning dopes with intense stirring and high-speed shearing,

and then to prepare the CNTs/PAN fibers by wet-spinning or electrospinning methods.[16,17] In these cases, the high viscosity of the spinning dopes would result in poor dispersion of CNTs and difficulty in spinning process.[18–20] The in-situ polymerization technique has been developed to achieve better dispersion of the CNTs in PAN matrix.[21–24] Monomers' solution with low viscosity can assure a good dispersion of CNTs in the initial stage and then the CNTs/PAN fibers with better electrical properties can be obtained after polymerization and spinning processes.[21] However, the polymerization process is complicated and difficult for large-scale production. In addition, it is less effective in constructing conductive CNT-to-CNT junction networks because most CNTs are covered by polymer chains in the matrix.[25]

Assembling CNTs on polymer surface is an effective method for fabrication of functional materials.[26,27] This method has several benefits: first, the process is simple; second, the CNTs on the fiber surface are more easy to form conductive networks without initial binding of polymer chains; and at last, the original properties of the target fibers could be preserved. However, the assembly of CNTs on PAN fibers has not much been explored. The lack of functional groups in PAN chains for anchoring or immobilizing CNTs become the key issue.
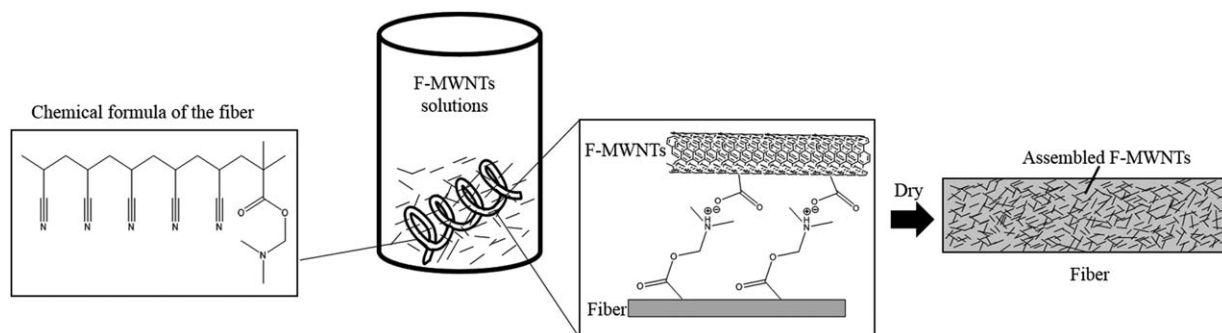
Figure 1. Schematic illustration of the assembly process of F-MWNTs on P(AN-co-VA-co-DEMA) fibers.

In this article, in order to introduce —N(CH$_3$)$_2$ pendant group to PAN, P(AN-co-VA-co-DEMA) terpolymers were synthesized by aqueous precipitation copolymerization of acrylonitrile (AN), vinyl acetate (VA), and 2-dimethylamino ethyl methacrylate (DEMA). The fibers from these terpolymers were thus prepared by a wet spinning method. The functionalized multiwalled carbon nanotubes (F-MWNTs) networks were then created on the surface of P(AN-co-VA-co-DEMA) fibers by dipping the fibers in the aqueous F-MWNT solution. The morphology and interfacial interactions of the obtained F-MWNTs-coated fibers were characterized and the electrical and mechanical properties were also investigated. These fibers showed much lower electrical percolation threshold (EPT) value and volume resistivity than that prepared by the solution mixing and in-situ polymerization methods.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was purchased from China Petroleum & Chemical Corporation (Shanghai, China), and was distilled before use. Sodium hydroxide, nitric acid, vinyl acetate (VA), sodium pyrosulfite (Na$_2$S$_2$O$_5$), sodium chlorate (NaClO$_3$), sodium thiocyanate (NaSCN), and 2-mercaptoethanol were of analytical grade and purchased from Sinopharm Chemical Reagent (Shanghai, China). 2-dimethylamino ethyl methacrylate (DEMA) was purchased from Xinyu Chemical Co., Ltd. (Jiangsu, China). MWNTs were produced by a chemical vapor deposition method described in our previous work.[28,29] The original MWNTs were acid-treated in a mixture of concentrated H$_2$SO$_4$ and HNO$_3$ (3 : 1, v/v) by ultrasonication for 12 h, followed by washing, filtrating, and drying.

Synthesis of the P(AN-co-VA-co-DEMA) Terpolymers

P(AN-co-VA-co-DEMA) terpolymers were synthesized by aqueous precipitation copolymerization. A typical process of the copolymerization was as follows. AN (129.5 g), VA (16.5 g), DEMA (3.75 g), 2-mercaptoethanol (0.144 g), NaClO$_3$ (0.9 g), and Na$_2$S$_2$O$_5$ (2.7 g) were dissolved in deionized water (850 mL). The polymerization was conducted under nitrogen at 300 rpm and 60°C for 1 h. Then the reaction was terminated by 5 wt % NaOH aqueous solution. The final white latex was washed and filtered several times. The obtained polymers were dried at 60°C in vacuum for 24 h.

Preparation of P(AN-co-VA-co-DEMA) Fibers

P(AN-co-VA-co-DEMA) spinning dopes with 13 wt % concentration were prepared by dissolving the polymer in 51.3 wt % NaSCN solvents at 60°C under stirring. The P(AN-co-VA-co-DEMA) fibers were then produced on a wet-spinning machine with three baths[29]. NaSCN/water ratios for bath I, II, and III were 11 : 89, 2 : 98, and 0 : 100, respectively. Bath I and II were maintained at ~5 and 60°C, respectively, while bath III was maintained at ~99°C. No fiber drawing took place in baths I and II, while fibers were drawn in bath III and allowed to relax in subsequent drying, carried out on a hot plate at 120°C. For structure and properties comparisons, all fibers were drawn to a draw ratio of 6.0. A 200-hole spinneret of 80 μm diameter was used in the spinning process. The temperature of the spinning dopes was maintained at 60°C and the take-up roller speed was 10 m/min to avoid jet stretch.

Preparation of F-MWNTs-Coated P(AN-co-VA-co-DEMA) Fibers

The procedure of preparing F-MWNTs-coated P(AN-co-VA-co-DEMA) fibers is shown in Figure 1. F-MWNTs were added to the deionized water, and the mixture was ultrasonicated for 120 min to obtain a homogenous dipping solution. The F-MWNTs-coated P(AN-co-VA-co-DEMA) fibers were then obtained by five cycles of dipping and drying. For a typical coating cycle, the fibers were immersed in this dipping solution for 10 min at room temperature followed by 20 min drying in air. In order to study the effect of solution concentration on the density of F-MWNTs coated on fiber surface, seven samples were prepared by immersing fibers in the solutions with various F-MWNTs contents (Table I).

Characterization

The FTIR spectra were recorded on a Nicolet 6700 FTIR spectrophotometer (USA). The ^{1}H-NMR spectra were recorded on a Bruker av400 NMR spectrophotometer (Germany), and DMSO-d6 was used as solvent. The Raman spectra were performed using an InVia-Reflex spectrophotometer (Britain) equipped with a laser with the excitation wavelength of 632.8 nm. SEM images were recorded on a Quanta-250 (Czech) and a Hitachi S-4800 (Japan) instruments. The element nitrogen was measured by a Vario el3 Elemental Analyzer (Italy) and used to calculate the contents of F-MWNTs on the fibers.

Volume resistivity of F-MWNTs-coated P(AN-co-VA-co-DEMA) fibers were measured with a VC 9808 electrometer (Shenzhen, China) at 25°C and 50% RH according to ASTM D4496 and

Table I. Results of Element Analysis and F-MWNTs Percentage on the Fiber Surface after Dipping Process

Sample	F-MWNTs contents in dipping solutions (wt %)	F-MWNTs percentage on the fiber surface (wt %)
1	0	0
2	0.001	0.04
3	0.005	0.25
4	0.01	0.51
5	0.05	0.59
6	0.1	0.76
7	0.2	1.18

D257 in the American Society for Testing and Materials,[30] and volume resistivity (ρ_v) was calculated as

$$\rho_V = \frac{n\pi d^2 R_V}{4l}$$

Where d and l are the diameter and length of the fibers, respectively, n is the number of the measured fibers, and R_V is the measured resistance. The reported values represent mean of 10 samples, where standard deviation relative to a mean value was less than 10%. The mechanical properties of the fibers were measured by a XQ-1 tensile-testing machine (Shanghai, China) at a speed of 5 mm/min with a testing length of 20 mm and initial load of 0.1 cN.

RESULTS AND DISCUSSION

Characterization of MWNTs and Fibers

Figure 2 shows the FTIR spectra of original MWNTs and functionalized MWNTs (F-MWNTs). In Figure 2(a), the peaks at 3446 cm^{-1} was attributed to the stretching of OH, while the peaks at 2856 and 2925 cm^{-1} were due to the stretching of CH_2. In Figure 2(b), a new peak at 1726 cm^{-1} assigned to the stretching vibration of C=O appeared, which indicated that the carboxylic groups must be introduced on the MWNTs after the acid treatment. In order to introduce —$N(CH_3)_2$ functional
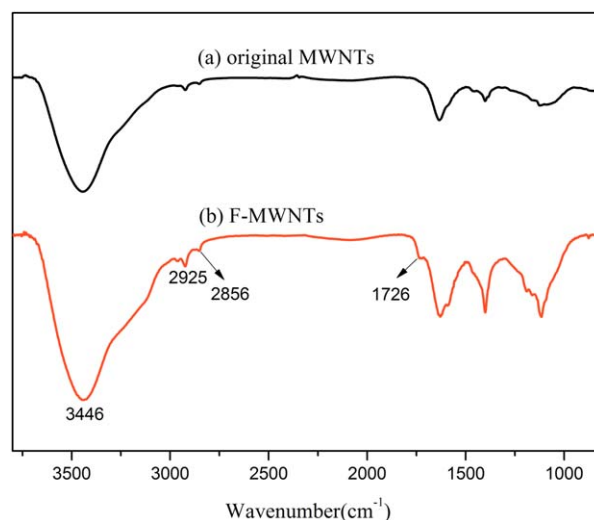

Figure 2. FTIR spectra of original MWNTs and F-MWNTs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

group to PAN, P(AN-co-VA-co-DEMA) terpolymers were synthesized. Figure 3 shows the ^{1}H-NMR and FTIR spectra of P(AN-co-VA-co-DEMA) fibers. In Figure 3(a), the ^{1}H-NMR peak at 4.3 ppm assigned to the —OCH_2 in the DEMA groups[31] was observed, which indicates that the DEMA was successfully introduced in the chain of PAN. The percentage of DEMA in the copolymer, calculated from ^{1}H NMR data, was about 0.14 mmol/g. In Figure 3(b), the characteristic adsorption peaks of P(AN-co-VA-co-DEMA) fibers were as following: stretching of C≡N at 2240 cm^{-1}, stretching of C=O at 1738 cm^{-1}, bending of CH_2 at 1454 cm^{-1}, C—N stretching of —$N(CH_3)_2$ groups at 1125 cm^{-1}. The FTIR spectra confirmed that —$N(CH_3)_2$ functional group was introduced in the polymer chain.

Fiber Morphologies

The surface morphologies of P(AN-co-VA-co-DEMA) fibers coated with the F-MWNTs are presented in Figure 4. It was found that F-MWNTs were uniformly coated on the fiber surface. The percentages of coated F-MWNTs on the fibers were
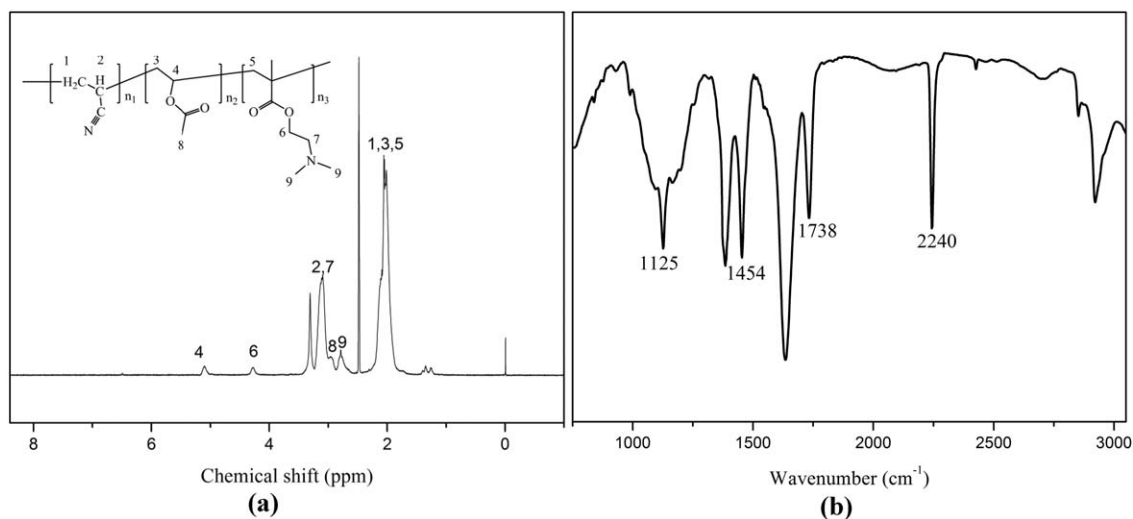

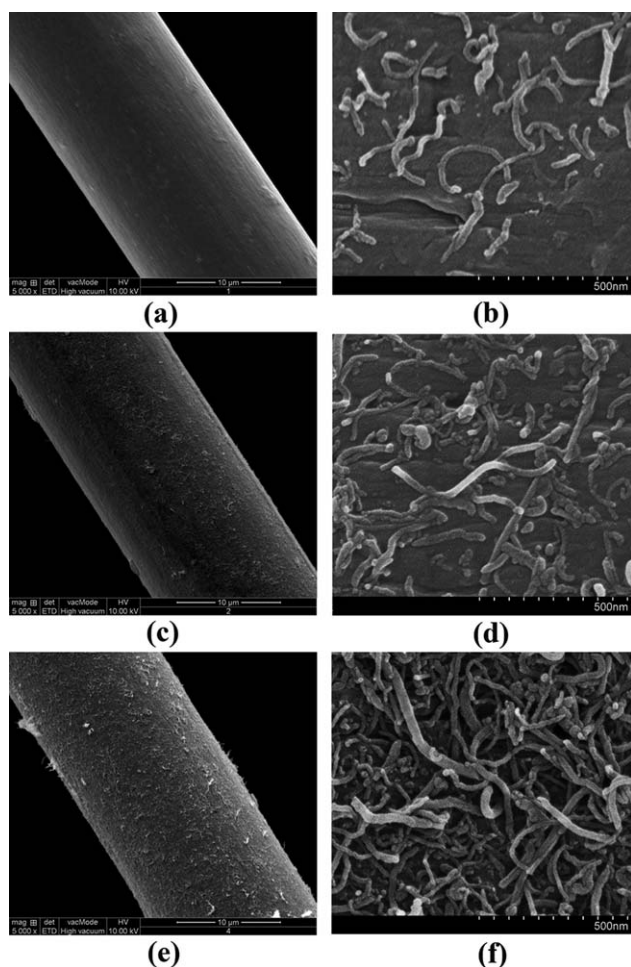**Figure 3.** (a) ^{1}H-NMR and (b) FTIR spectra of P(AN-co-VA-co-DEMA) fibers.

Figure 4. SEM images of F-MWNTs-coated P(AN-co-VA-co-DEMA) fibers: (a, b) sample 2; (c, d) sample 3; and (e, f) sample 5.

tra of F-MWNTs and P(AN-co-VA-co-DEMA) fibers coated with F-MWNTs is shown in Figure 5. In Figure 5(a), two strong peaks at 1326 (D-band) and 1582 cm^{-1} (G-band) were observed, which were attributed to disorder-induced features and the in-plane vibration of C—C bonds, respectively. When the fiber was coated with F-MWNTs, the intensity of these two peaks reduced [Figure 5(b–d)]. However, the up-shifts of D-band for F-MWNTs-coated sample were observed (the inset in Figure 5). These shifts resulted from the change of the chemical environment surrounding the carbon atoms in MWNTs.[22] This change could be attributed to the electrostatic interactions between the negative charges (carboxylic groups) on the nano-tube sidewalls and the positive charges (amino groups) of the fibers. Figure 6 shows the FTIR spectra of P(AN-co-VA-co-DEMA) fibers and F-MWNTs-coated samples. The intensities of the peaks in FTIR spectra were normalized by dividing by the intensities of the CH$_2$ bending deformation vibration at 1454 cm^{-1}. The normalized FTIR intensities of C—N band (I_{C-N}) at 1125 cm^{-1} are shown in Table II. When the fibers were coated with 0.25 wt % (sample 3) and 0.59 wt % F-MWNTs (sample 5), the I_{C-N} decreased from 0.95 for P(AN-co-VA-co-DEMA) fibers to 0.84 and 0.46, respectively. It was obvious that F-MWNTs had a great influence on the character-istic FTIR adsorption of —N(CH$_3$)$_2$ groups. These results

calculated by element analysis (Table I). The results indicated that the percentage of coated F-MWNTs can be controlled by the F-MWNTs content in the dipping solutions. When the F-MWNTs content in the dipping solution increased from 0.001 to 0.2 wt %, the percentage of coated F-MWNTs on the fiber surface increased from 0.04 to 1.18 wt %. For sample 2, there were only a few F-MWNTs coated on the fibers [Figure 4(a,b)] and the density of coated F-MWNTs was very low. For sample 3, the density increased and the F-MWNTs networks could be established [Figure 4(c,d)]. When the percentage of coated F-MWNTs increased further (sample 5, the percentage was 0.59 wt %), the F-MWNTs entangled together and the density was very high [Figure 4(e,f)]. This implied that high conductivity of the fibers could be obtained even at very low percentages of F-MWNTs coated. In this case, no binder was used and the F-MWNTs were self-assembled on the fiber surface during the dipping process. When P(AN-VA) fibers (a copolymer of AN and VA) were used as the substrate materials for comparison and treated with the same process, F-MWNTs were hardly found on the fiber surface, which suggested a strong interaction between the P(AN-co-VA-co-DEMA) fibers and F-MWNTs.

Raman and FTIR spectra were employed to understand the driving forces about this assembly process.[32,33] The Raman spec-
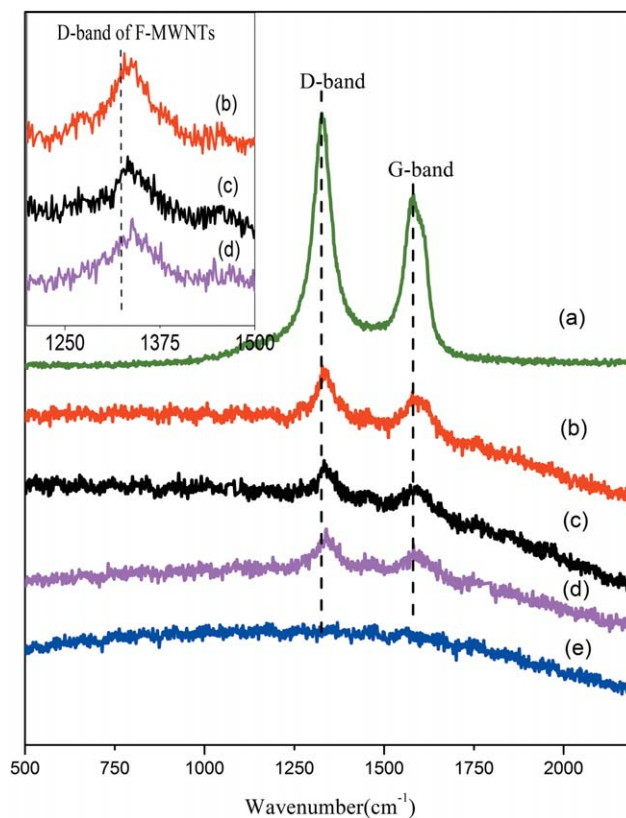

Figure 5. Raman spectra of (a) F-MWNTs, F-MWNTs-coated P(AN-co-VA-co-DEMA) fibers; (b) sample 7; (c) sample 5; (d) sample 3; and (e) P(AN-co-VA-co-DEMA) fibers. The inset is the normalized data of the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
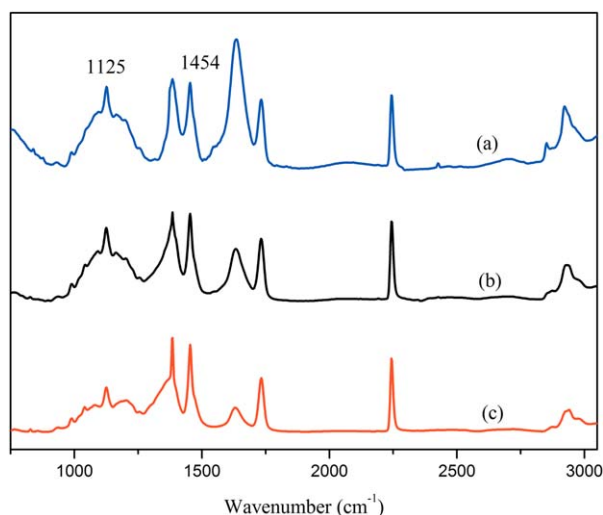
Figure 6. FTIR spectra of (a) P(AN-co-VA-co-DEMA) fibers and F-MWNTs-coated P(AN-co-VA-co-DEMA) fibers: (b) sample 3; (c) sample 5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

confirmed the existence of the electrostatic interaction between F-MWNTs and P(AN-co-VA-co-DEMA) fibers.

Electrical and Mechanical Properties of F-MWNTs-Coated Fibers

Figure 7 shows the effect of percentage of coated F-MWNTs on the volume resistivity of the fibers. The volume resistivity decreased with the increase of the percentage of coated F-MWNTs. At an F-MWNTs percentage of 0.25 wt % (sample 3), the volume resistivity was more than 3800 Ω·cm, which indicated that the F-MWNTs networks were not effectively established. At an F-MWNTs percentage of 0.59 wt % (sample 5), a significant reduction in resistivity at 1.72 Ω·cm was observed. This stepwise change in resistivity may result from the formation of interconnected F-MWNT networks [Figure 3(e,f)] and can be regarded as an electrical percolation threshold (EPT). Compared to the blending method,[18] F-MWNTs-coated P(AN-co-VA-co-DEMA) fibers showed much lower EPT value and volume resistivity. Compared to in-situ polymerization method,[24] the EPT value was very close, but the volume resistivity at EPT was about 6 orders of magnitude smaller. The excellent conductivity of our products could be attributed to the fact that the MWNT-to-MWNT junction networks were effectively created on the fiber surface and the F-MWNTs were not encapsulated by polymer chains. After the fibers (sample 5) were washed with deionized water for 5 times at room tempera-

Table II. Normalized FTIR Intensity of C—N Band as Determined by FTIR

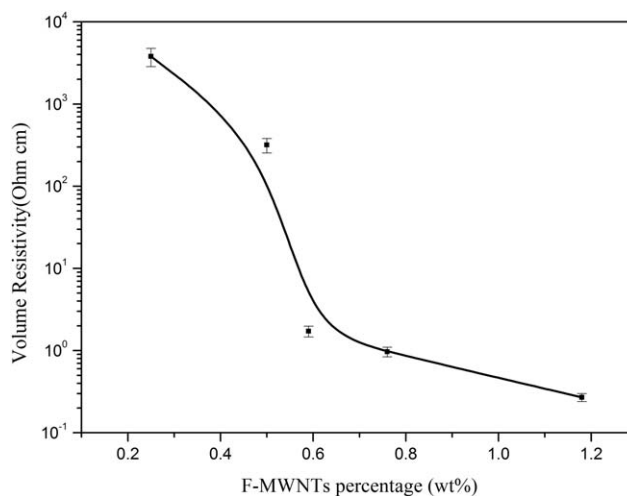| Sample	F-MWNTs percentage on the fiber surface (wt %)	I_{C-N}
1	0	0.95
3	0.25	0.84
5	0.59	0.46

Figure 7. Resistivity as a function of F-MWNTs percentage.

ture followed by drying, the volume resistivity increased about 7% to 1.84 Ω·cm, which indicated the good abrasion resistance of the CNT layer on fibers. The stress–strain curves of F-MWNTs-coated fibers were shown in Figure 8. When compared with the P(AN-co-VA-co-DEMA) fibers, the mechanical properties of F-MWNTs-coated fibers were almost preserved.

CONCLUSIONS

The creation of MWNT networks on PAN fibers can be easily achieved through electrostatic interactions using a simple assembly method. F-MWNTs were firmly attached on the fibers due to the interaction between amine groups and carboxylic groups. As the uniformly formed F-MWNT networks on the surface of fibers provided efficient conductive pathways, F-MWNTs-coated P(AN-co-VA-co-DEMA) fibers showed much lower EPT and volume resistivity than which prepared by the solution mixing and in-situ polymerization methods, meanwhile, the good mechanical properties of the obtained fibers were preserved. Therefore, the F-MWNTs-coated P(AN-co-VA-
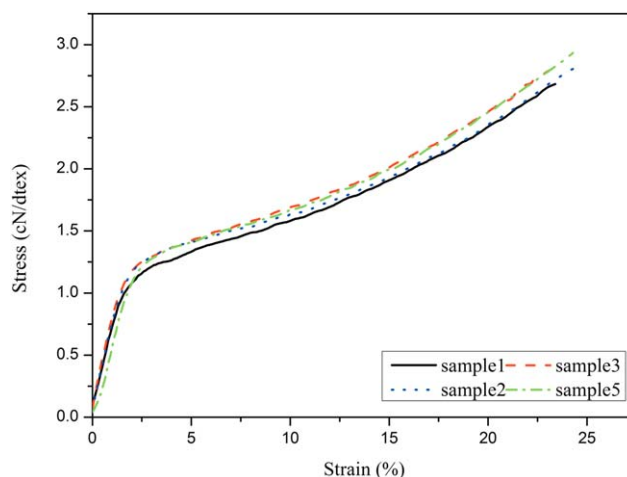

Figure 8. Strain–stress curve of F-MWNTs-coated P(AN-co-VA-co-DEMA) fibers compared with the original ones. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

co-DEMA) fibers with outstanding electrical conductivities can be widely used for electronic materials or other fields such as static and electromagnetic wave shielding materials, carbon fiber precursors, and other wearable fabrics. Future efforts should concentrate on preparation of these fibers with controllable conductivities for different applications.

ACKNOWLEDGMENTS

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