

Multiwalled Carbon Nanotube/Polyacrylonitrile Composite Fibers Prepared by *In Situ* Polymerization

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ABSTRACT: Multi-walled carbon nanotubes (CNTs) were mixed with polyacrylonitrile (PAN) by *in situ* polymerization or by mechanically mixing. The mixtures were then wet-spun into fibers, respectively. The effects of mixing method on the interfacial bonding between the components in the fibers and the properties of the fiber were investigated by Raman spectroscopy, TEM, SEM, and tensile strength testing. By *in situ* polymerization mixing, a thin layer of PAN molecules is observed to cover the surface of the CNT, which increases the diameter of CNT evidently. Results of Raman spectroscopy indicate that the layer of PAN molecules are strongly attached onto the surface of CNT through grafting poly-

merization, leading to strong chemical bonding between CNTs and PAN matrix in the obtained fibers. In contrast, no obvious chemical interactions are observed between them in the fibers prepared by mechanically mixing. In both cases, the CNTs have significantly strengthened the PAN fibers. However, the fibers prepared from *in situ* polymerization mixing are much stronger because of the interfacial bonding effect between the PAN molecules and CNTs. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1385–1389, 2011

Key words: multiwalled carbon nanotube; polyacrylonitrile; *in situ* polymerization; composite fiber

INTRODUCTION

Carbon nanotubes (CNTs) have attracted increasing attention since their discovery by Iijima in 1991¹ due to their excellent intrinsic properties such as high tensile strength, elastic modulus, and electric conductivity. CNTs have been used as additives for various polymers to improve their mechanical properties, electrical properties, and so on.^{2–4} Among these polymers, polyacrylonitrile (PAN) is particularly noticeable because of its widespread applications as carbon fiber precursor.^{5–12} Kumar et al.⁸ reported that a PAN fiber containing 10% single-walled CNTs (SWCNTs) exhibited one-fold and 10-fold increase in tensile strength at room temperature and at 150°C, respectively, and the composite fiber also showed 40°C improvement in the glass transition temperature. Andrews et al.¹³ reported that a PAN fiber

with 5% multiwalled CNTs (MWCNTs) content increased its tensile strength by 31%, the Young's modulus by 36% and the fracture energy by 83%. For oxidation-stabilized PAN fiber with 10% SWCNTs, the tensile strength, Young's modulus and fracture strain increase by 100%, 160 and 115%, respectively.¹⁴ For PAN-based carbon fiber including 1% SWCNTs, the tensile strength and Young's modulus are improved by 64 and 49%, respectively.¹⁵ In most works, CNTs were introduced into PAN matrix by mechanically mixing. The high viscosity of PAN solution would result in very difficult dispersion of CNTs. Zheng et al.¹⁶ and Hong et al.¹⁷ have prepared CNT/PAN mixture by *in situ* polymerization. They find that CNTs are better dispersed in this mixture than in the mechanically mixed CNT/PAN systems. Their results also indicate that there are some chemical interactions between CNTs and PAN.^{16–18} However, the details of the interactions between the components and the effects of the CNTs addition on fiber properties are still lacking.

In this work, CNT/PAN mixtures to produce PAN fibers were prepared by ways of mechanically mixing and *in situ* polymerization, respectively. The microstructures and mechanical properties of the obtained fibers were investigated to compare the strengthen effects of CNTs for the two mixing methods.

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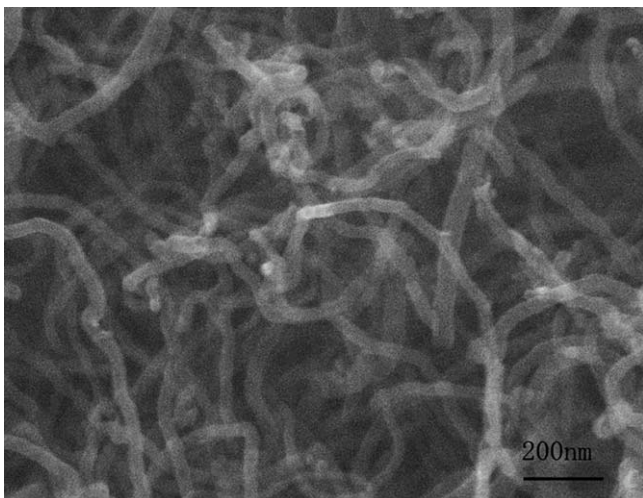


Figure 1 SEM image of the as-received multiwalled carbon nanotubes.

EXPERIMENT

Materials

MWCNTs were obtained from Shenzhen Nano Port Limited Corp. (Figure 1). The specifications are as follows: purity ≥ 95 wt %, ash ≤ 0.2 wt %, diameter 10–20 nm, length 5–15 μm , and specific surface area 40–300 m^2/g . The MWCNTs were used as received for mechanically mixing, while they were oxidized following the reported method¹⁹ prior to *in situ* polymerization. Acrylonitrile (AN, $>99\%$) was distilled twice to remove the stabilizing agent and to improve its purity. The initiator, 2,2-azobisisobutyronitrile (AIBN, 98%), was purified by re-crystallization. Methyl acrylate (MA, $>99\%$), itaconic acid (IA) and *N,N*-dimethylformamide (DMF, $>99\%$) were used as received. All of the chemical reagents were bought from Shanghai Chemical Reagent Co., Ltd., Shanghai, China.

Preparation of CNT/PAN mixture, PAN, and fibers

For the *in situ* polymerization, a certain amount of oxidized CNTs, 30g monomers mixture (AN : MA : IA = 96 : 3 : 1, by mass), 0.45 g initiator AIBN and 70 g solvent (DMF : H₂O = 30 : 70, by mass) were charged into a 250 mL three-necked flask equipped

with a mechanical stirrer, a nitrogen gas inlet, and an Allihn condenser. The mixture was ultrasonically agitated (40 kHz) for 20 min. The monomers were then initiated to polymerize by raising the temperature to 63°C. The entire reaction was carried out with the flask immersed in the ultrasonic bath (40 kHz). Black sediment was formed after 2.5 h reaction. The obtained slurry was then filtrated, washed with deionized water, and then dried at 50°C in vacuum oven to obtain the products. Two *in situ* polymerized precursors with the CNTs concentration of 3 wt % and 5 wt % were prepared to be coded as S3-I and S5-I, respectively. For comparison, the PAN used in the mechanically mixing was also synthesized under the same condition mentioned above but without addition of CNTs. The viscosity-averaged molecular weight of the pure PAN was 142,800 g/mol measured by Ubbelohde solution viscometer. While the molecular weight of PAN in *in situ* polymerized CNT/PAN composite was about 136,200 g/mol for S3-I, and 128,600 g/mol for S5-I, respectively.

The precursors were dissolved in DMF to obtain 25% spinning solutions. They were then wet-spun using a small scale spinning system (Shanxi Coal Chemistry Institute, China) as shown in Figure 2. The spinneret was single hole ($\phi 250 \mu\text{m}$). The speed of the take-up roller was 10 m/min. The final drawing ratio was 10. For the preparation of mechanically homogenized CNT/PAN mixture, 0.6 g of the as-received CNTs were added into 100 mL DMF and then ultrasonically dispersed (40 kHz) for 4 h. After that, PAN was slowly added in the above CNTs/DMF mixture to have a 20% concentration. The resultant mixture was stirred for additional 4 h. The suspension was then concentrated to produce 25% solid content. This fluid was also wet-spun into fibers under the same conditions mentioned above. The fibers prepared in this work are summarized in Table I.

Characterization

Raman spectroscopy (Dilor LabRaman I) was utilized for structural analysis of the materials with 632.8 nm He-Ne laser excitation. High-resolution transition electron microscopy (HRTEM, Philips TECNAI F30) and field-emission scanning electron

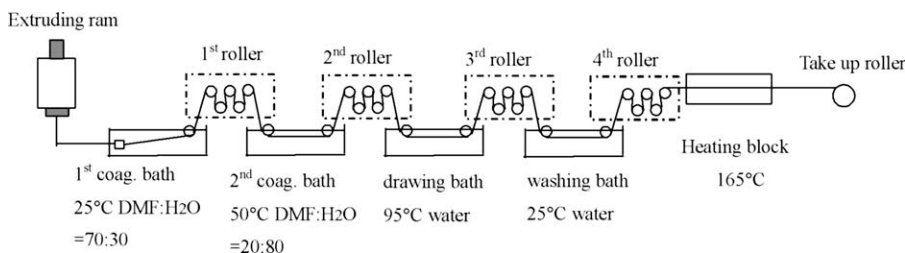


Figure 2 Schematic wet-spinning process to prepare PAN fibers.

TABLE I
Fibers Prepared in this Work

Fibers	<i>In situ</i> polymerization		Mechanical mixing	
	PAN (wt %)	CNT (wt %)	PAN (wt %)	CNT (wt %)
PAN	100	–	–	–
S3-I	97	3	–	–
S5-I	95	5	–	–
S3-M	–	–	97	3

microscopy (FESEM, LEO1530 at 20 kV) were used to study the CNT dispersion inside the fibers. Mechanical properties of the fibers were measured using a universal testing machine (SUN2500, Galdini Company, Italy) at a cross-head speed of 10 mm/min and the gauge length of 25 mm. Twenty-five fibers were randomly selected and tested for each fiber sample and the average value was used.

RESULTS AND DISCUSSION

Figure 3 shows the Raman spectra of CNTs, pure PAN, S3-I, S5-I, and S3-M. No absorbance from 1000 ~ 1800 cm^{-1} for pure PAN has been found, but the CNTs exhibit two strong peaks at 1322 cm^{-1} and 1581 cm^{-1} , respectively. The strong peak at 1581 cm^{-1} (G line) is assigned to the high-frequency E_{2g} first-order mode, which is the main feature of CNT. The sharp peak at 1322 cm^{-1} (D line) is attributed to disorder-induced features, which is due to the finite particle size effect or lattice distortion of graphite crystals in the CNTs.²⁰ Similar to the pure CNTs, two strong Raman scattering peaks have been

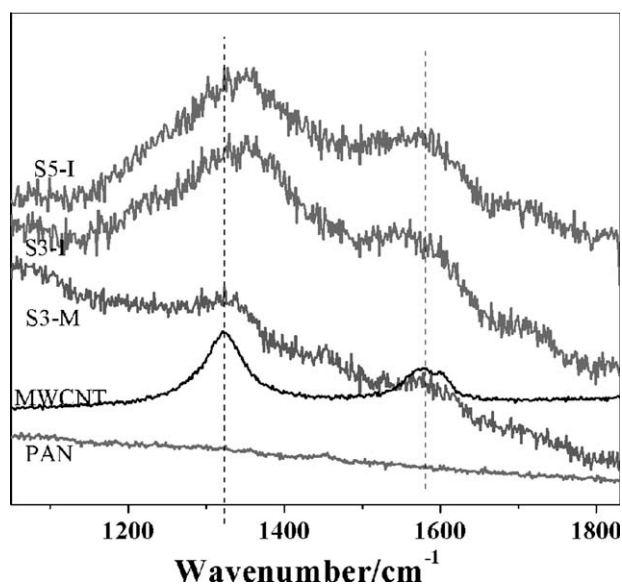


Figure 3 Raman spectra of PAN, CNT, and CNT/PAN fibers.

observed for the samples S3-I and S5-I prepared from *in situ* polymerization. The strong and sharp peak at 1322 cm^{-1} for CNTs has shifted more than 30 cm^{-1} to 1352 cm^{-1} for sample S3-I and to 1360 cm^{-1} for sample S5-I, respectively. However, the S3-M prepared from mechanically mixing exhibits two weak Raman scattering peaks at about 1333 cm^{-1} and 1581 cm^{-1} , respectively. These results indicate that there might be some chemical interactions between the CNTs and PAN, leading to the variation of the chemical environment surrounding the carbon atoms in CNT, which results in the shift of the Raman peaks of CNTs. Moreover, greater shifts (30 cm^{-1}) of S3-I and of S5-I than that of S3-M (~ 10 cm^{-1}) indicate stronger interfacial interactions between the components in the materials prepared from *in situ* polymerization method. However, no obvious change in the absorption peak at 1581 cm^{-1} has been observed for samples S3-I and S5-I. The peak intensity increases with increasing CNT content, indicating that the main structure of the CNT does not change during the *in situ*

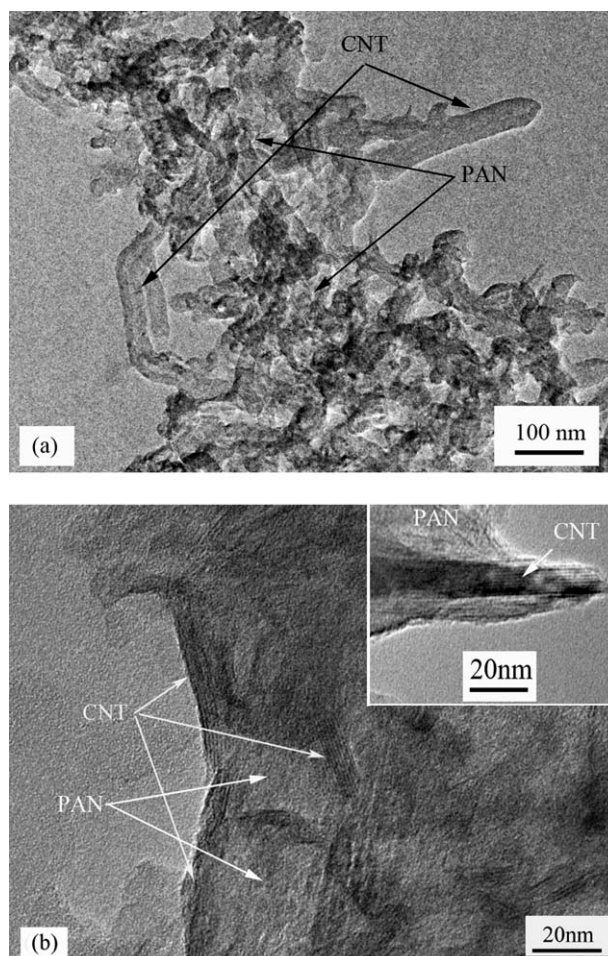


Figure 4 TEM images of the CNT/PAN mixture prepared from mechanically mixing (a) and from *in situ* polymerization (b).

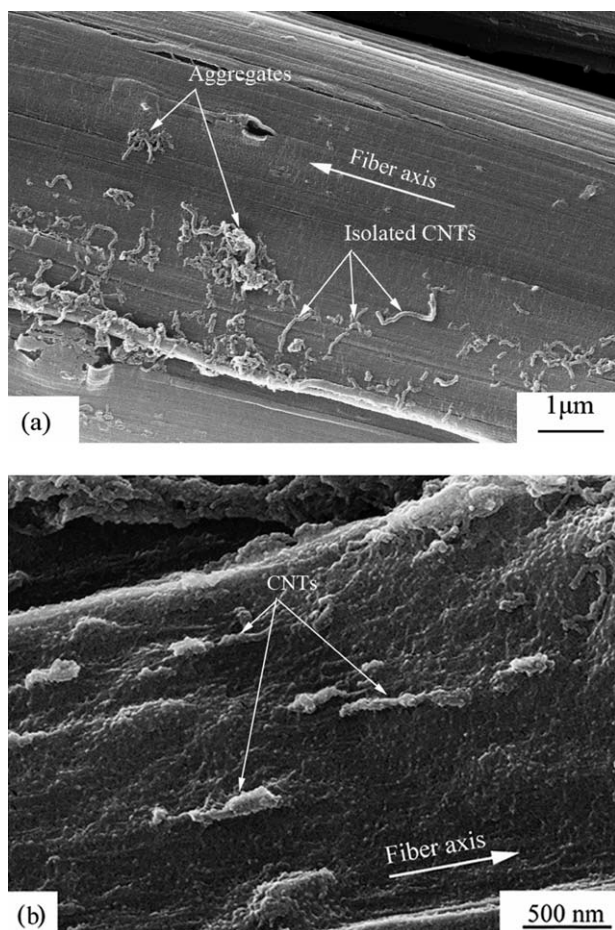


Figure 5 SEM images of the surfaces of the CNT/PAN fibers after solvent DMF extraction. The fibers were prepared from mechanically mixing (a) and from *in situ* polymerization (b).

polymerization, which is important to maintain the excellent properties of the CNT.

S3-M and S3-I were dissolved in DMF separately to dip-coat with a 300-mesh carbon coated Cu grid, respectively. After solvent evaporation, the samples were subjected to TEM observation, with the photographs shown in Figure 4. The CNTs in the S3-M are rather “clean,” and no obvious PAN layer can be found to attach onto them. However, the CNTs in the *in situ* polymerization sample (S3-I) are uniformly distributed in PAN matrix. In addition, the CNTs are covered completely by PAN molecules. The insert figure is a single CNT embedded in PAN matrix prepared by *in situ* polymerization. Combining the results of the Raman analysis, it is rational to draw that strong chemical interaction exists between the CNTs and PAN molecules in the fibers prepared from *in situ* polymerization. Because those PAN molecules at the interface were less soluble in DMF, it is thought that they were grafting polymerized onto CNTs.

To further examine the CNTs distribution, the fibers prepared from pure PAN, from *in situ* polymerization S3-I and S5-I, and from mechanically mixing S3-M were soaked in solvent DMF in an ultrasonic bath for 2 min. It is found that the pure PAN fibers were dissolved in the DMF completely, while the fibers containing CNTs retained fiber shape, which is similar to the results reported in literatures.^{8,21–22} The SEM images of the solvent-treated fibers are shown in Figure 5. For S3-M fibers, the CNTs are randomly dispersed and the alignment along the fiber axis is poor, which might result in the low intensity of Raman scattering mentioned above. The CNTs shown in the image are also very clean, which is consistent with the TEM observation. However, it can be seen that every carbon nanotube in the S3-I fibers is enveloped by a layer of PAN, increasing its diameter from original 10–20 nm to 42–125 nm. It can be found that the CNTs are also well aligned along the fiber axis. It is worth noting that the PAN layers surrounding the CNTs are more resistant to the solvent DMF. Even when an entire fiber loses its shape, the PAN layers on CNT interfaces still remain un-extracted. This implies that some PAN chains were grafted onto CNTs during the *in situ* polymerization, leading to the presence of PAN layer on the surfaces of CNTs even after DMF extraction. Those results are also consistent with the Raman analysis.

After the pure PAN fibers and CNT/PAN composite fibers were oxidation-stabilized in air at 220°C for 24 h, the fiber shrinkages were 44% for PAN, 26% for S3-M, and 19% for both S3-I and S5-I (Fig. 6), respectively. The fact that carbon nanotubes do not shrink leads to lower shrinkages of the fibers containing CNTs.²⁰ Furthermore, the thermal shrinkages for the fibers from *in situ* polymerization method are the lowest, which is possibly related to

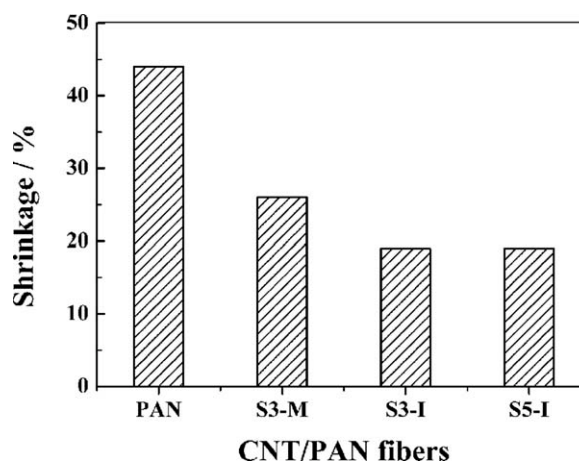


Figure 6 Thermal shrinkages of PAN and CNT/PAN fibers after oxidation-stabilization.

TABLE II
Mechanical Properties of CNT/PAN Fibers

Fiber	Diameter (μm)	Tensile strength (MPa)	Fracture strain (%)
PAN	51.3	217.2	11.5
S3- M	41.6	233.0	7.2
S3-I	56.0	275.4	12.1
S5- I	50.7	295.0	11.8

the good compatibility between PAN and CNTs.⁸ At the same time, the good CNT alignment in the *in situ* polymerized fibers may also be responsible for the low shrinkages, which can be seen in Figure 5. The reduced shrinkage of the *in situ* polymerized fibers is expected to produce final carbon fibers with high-modulus,⁸ because less PAN molecular chain relaxation may happen during oxidation-stabilization to result in better alignment of carbon fibrils in the final carbon fibers.

The tensile strengths of the different fibers are summarized in Table II. The tensile strengths for the fibers prepared from *in situ* polymerization are much higher than that of PAN fiber. When the fiber containing 3% CNTs (S3-I), the tensile strength increases by a factor of 26.8%, and it increases up to 38.5% with 5% CNT content (S5-I). It is found that the fracture strains for the *in situ* polymerized fibers are almost the same as that of the pure PAN fiber. However, the improvement in tensile strength for the fibers with a 3% CNT content prepared from mechanically mixing (S3-M) is only 7.3%, while the fracture strain decreases 37.4%. At the same time, the XRD analysis (the spectra are not shown) of the CNT indicate that the crystallization structure of the CNT has been changed after oxidation treatment. However, the crystallization structure variation of CNTs is thought not to be the main factor to influence the mechanical properties of the resulted composite fibers.²³ It is therefore concluded that, the poor dispersion and poor interfacial bonding are considered to be responsible for the low improvement in tensile strength and for the drop in fracture strain for the fibers prepared by mechanically mixing.²⁴ In contrast, the strong chemical bonding and much better dispersion and alignment of CNTs would be combined to strengthen the fibers prepared from the *in situ* polymerization method.

CONCLUSIONS

PAN fibers containing CNTs have been successfully prepared by mechanically mixing the two components and by *in situ* polymerization. The microstructures and mechanical properties of the obtained

fibers were investigated. Results from Raman spectrum analysis, SEM and TEM indicate that some PAN chains are grafted onto the CNTs when *in situ* polymerization. The PAN layer on CNT is helpful to interact with PAN molecules in the fiber matrix. The strong interfacial interaction between PAN matrix and CNTs leads to better distribution and alignment of CNTs when compared with the fibers prepared from mechanically mixing, resulting in greater improvement in tensile strength of PAN fibers prepared from the *in situ* polymerization manner. It is found that the fibers prepared from *in situ* polymerization possess very low thermal shrinkage. Therefore, the work suggests an alternative method to prepare carbon fibers with high-modulus.

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