Dry-Jet Wet-Spun PAN/MWCNT Composite Fibers with Homogeneous Structure and Circular Cross-Section

Jian Zhang, Youwei Zhang, Degang Zhang, Jiongxin Zhao

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Chemical Fibers Research Institute, Donghua University, Shanghai 201620, People's Republic of China

ABSTRACT: To produce polyacrylonirtile (PAN) fiber precursor with desired cross-section shape, microstructure and mechanical properties, several measurements including adopting DMSO/water (95/5, v/v) mixture as the solvent of the spinning dope, ethanol/DMSO (60/40, v/v) mixture at 10°C as the coagulation medium, and modified multi-walled carbon nanotube (MWCNT) as the reinforcing nanofiller, as well as extra-drawing the as-spun fiber in air, were taken in the preparation of PAN fibers via dry-jet wet spinning. The morphology, structure, and properties, thermal behavior of the resultant fibers were studied. The results show that gel fibers with homogeneous dense structure and circular cross-section were obtained. High orientation of PAN molecules in fiber was achieved by additional drawing the as-spun fiber in air. After the introduction of a very small amount of modified MWCNT, the tensile strength and modulus of the fiber enhance substantially: there is a 19% increase in strength and a 62% increase in modulus at a MWCNT content of 1.0 wt %. Also, the heat release rate decreases during the oxidative stabilization. The uniform microstructure, circular cross-section, high orientation of PAN molecules, high tensile strength and modulus, as well as the gentle oxidative cyclization behavior, make the PAN/MWCNT composite fiber an attractive precursor candidate for carbon fiber. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: E58–E66, 2012

Key words: nanocomposites; fibers; microstructure; polyacrylonitrile; carbon nanotube

INTRODUCTION

PAN fiber becomes currently the predominant precursor for carbon fiber because of its simple processing, low manufacturing cost, and excellent mechanical properties. The performance of carbon fiber is sensitive to the structure and properties of PAN precursor fiber, which play an important role in the oxidative stabilization and carbonization treatments.[1,2] PAN precursor fibers are generally produced with wet-spinning or dry-jet wet-spinning method.[3–7] In dry-jet wet-spinning, the spinning dope is extruded through an air-gap before entering into a coagulation bath. The air-gap allows the extruded dope to cool somewhat before entering into the coagulation bath and also to relax the high stresses developed inside the spinnerette assembly. Thus, a higher spinning speed can be adopted and fibers with better properties can be obtained via dry-jet wet-spinning when compared with wet-spinning.

In both wet-spinning and dry-jet wet-spinning, the gelation (i.e., sol-gel transition) of the dope in the coagulation bath, is the key process to control the microstructure and mechanical properties of the resultant fibers. Because of the dual diffusions of the solvent and nonsolvent, the composition of the spinning dope will change continuously, which subsequently causes the sol-gel conversion via phase separation. However, the phase-separation-induced gelation usually results in fibers with undesirable skin-core structure, if the coagulation conditions are not optimized.[8]

The uniform fiber formation and high orientation of polymer molecules are crucial to fabricate high-performance PAN fibers.[9–12] Thermal-induced gelation can realize the uniform fiber formation and result in fiber with homogeneous microstructure. Ultra-drawing can induce the high orientation of polymer chains in the fiber. For the production of PAN precursor fiber, on one hand, researchers begin to study the thermal-induced gelation behavior of conventional molecular weight PAN ($M_\eta = 7.8 \times 10^4$ g/mol) concentrated solution in dimethyl sulfoxide (DMSO)[13,14] and explore the possibility of fiber formation via thermal-induced gelation. On the other hand, the normally adopted two-step draw process

(i.e., draw in hot water and boiling water) can only lead to a total draw ratio of 4–7. Extra draw at higher temperature such as stream draw and draw in glycerol bath (160°C)[15] is required to achieve a higher total draw ratio.

Carbon nanotubes (CNTs) have exceptional mechanical, electrical, thermal, and optical properties.[16,17] Besides the high strength and Young's modulus, they also show considerable flexibility and deformability. Thus, CNTs are applied as a high-performance reinforcing nano-material to lots of polymer matrix, such as polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyethylene (PE), PAN, and so on.[18–21]

A number of studies have been devoted to CNT-reinforced PAN fibers. For example, Kumar and co-workers[22] prepared single-walled carbon nanotube (SWCNT)/PAN composite fibers with a SWCNT content of 0, 5, and 10 wt %. When compared with the control PAN fibers, the composite fibers containing 10 wt % SWCNT were reported to exhibit a 100% increase in tensile modulus at room temperature and an order of magnitude increase in storage modulus at 150°C. They[23] also found that the breaking strength, modulus and strain of failure of the oxidized PAN fibers were improved by the addition of SWCNT. Also, Chae et al.[24] prepared various composite fibers via dry-jet wet spinning from the solution of PAN in dimethyl acetamide (DMAc) containing SWCNT, MWCNT (multi-walled carbon nanotube), double-walled carbon nanotube, or vapor grown carbon nanofibers, and compared the reinforcement efficiency of various CNTs in PAN fiber. It was found that an increase in the length of carbon nanotubes benefits to increase the tensile strength, elongation to break, and work of rupture of the composite fibers.

To obtain high-performance PAN-based carbon fibers, one must first prepare PAN fiber precursor with high quality, i.e., PAN fibers with circular cross-section, homogeneous dense structure, high tenacity, and high orientation. In a early paper,[25] we reported that using ethanol with a weaker coagulation ability to replace the commonly used water as the nonsolvent of the coagulation medium, the demixing of the spinning dope via nucleation and growth mechanism was favored during the coagulation process, resulting in homogeneous dense PAN fibers with low porosity.

In this study, we try the preparation of high-performance PAN fiber precursor via dry-jet-wet spinning by taking several measurements. The study on the thermal-induced gelation of PAN/DMSO concentrated solution by Tan et al.[14] showed that introduction of nonsolvent water and lowering down the temperature could accelerate the gelation. Therefore, use of DMSO/water (95/5, v/v) mixture as the sol-

vent of the spinning dope as well as the low coagulation temperature (10°C) were firstly adopted here to facilitate the thermal-induced gelation of the spinning dope. Secondly, ethanol/ DMSO (60/40, v/v) mixture was used as the coagulation medium to realize the homogeneous de-mixing of the spinning dope during the coagulation. These measurements are expected to realize the uniform fiber formation. Thirdly, reinforcing nanofiller MWCNT was introduced to further improve the mechanical properties of the fiber. Finally, besides the normal two-step draw process, extra-drawing of as-spun fibers in air was adopted to realize the high orientation of MWCNT and PAN molecules. The morphology, structure, properties, and thermal behavior of the resultant composite fibers and pure PAN fiber were studied.

EXPERIMENTAL

Materials

PAN terpolymer (Acrylonitrile : Methyl acrylate : Itaconic acid = 95.6 : 3.4 : 1.0) with a viscosity-average molecular weight of 7.8×10^4 g/mol, was purchased from Shanghai Petrochemical PAN Co. Ltd. Pristine MWCNT with diameter $\sim$ 10 nm and length $\sim$ 10 µm was purchased from Shenzhen Nanotech Port Co. Ltd. Analytically pure DMSO and ethanol were purchased from Shanghai Boer Chemical Reagent Co. Ltd. Concentrated nitric acid (HNO_3) and sulfuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used in all the experiments.

Modification of MWCNT

One hundred and forty microliter of concentrated HNO_3/H_2SO_4 mixture (1/3, v/v) was slowly added into a flask containing 1 g pristine MWCNT. Then the mixture was subjected to simultaneous sonication and mechanical stirring in a water bath for 4 h. After that, a certain amount of NaOH solution was added very slowly under stirring to adjust pH value of the mixture to be neutral. During the whole treatment process, the temperature of the water bath was maintained at 25°C via circulation. The mixture was purified by repeat centrifugal sedimentation and ultrasonic dispersion in deionized water. Finally, modified MWCNT was obtained after drying under vacuum at 40°C.

Preparation of PAN spinning dope

Modified MWCNTs were first dispersed in water at a concentration of 2 mg/mL via 1 h of simultaneous sonication and stirring at room temperature, to

obtain optically homogeneous dispersion. A certain amount of PAN terpolymer powder was then added. The mixture was further subjected to 15 min of shear-homogenization at 20,000 rpm using a high shear dispersing emulsifier (FA25, Fluko). After that, the mixture was poured into a surface dish and dried at 40°C. The dried PAN/MWCNT mixture was ground to fine powder. To prepare spinning dope, a certain amount of PAN/MWCNT mixture powder and DMSO/water (95/5, v/v) mixture were successively added into a glass bottle, followed with 2 h of swelling at 50°C and 6 h of dissolving at 80°C under stirring. After that, the solution was deaerated at 80°C overnight in a drying oven.

Preparation of PAN/MWCNT composite fibers by dry-jet wet spinning

The fibers were dry-jet wet-spun with a self-built experimental spinning apparatus. The dope with a PAN concentration of 22% and a certain amount of modified MWCNT passed through a spinneret of six holes (diameter of 0.15 mm), entered successively into a 10 mm air gap and a coagulation bath containing ethanol/DMSO (60/40, v/v) mixture at 10°C. After drawn in air, the as-spun fibers were taken up and kept immersed overnight in the ethanol/DMSO (80/20, v/v) mixture at room temperature. The remnant DMSO in the gel fibers was removed by ultrasonic extraction in ethanol. The fibers were further successively drawn in hot water (65°C) and boiling water, and finally heat-set at 120°C for 15 min. The total draw ratio was as high as 32. Three PAN fibers containing 0 wt %, 0.5 wt %, 1.0 wt % of modified MWCNT, which are denoted as M0, M0.5, and M1.0 in the article, respectively, were prepared.

A control PAN fiber was prepared via dry-jet wet spinning using a PAN/DMSO solution with a PAN concentration of 22% as the spinning dope and a water/DMSO (60/40, v/v) mixture at 50°C as the coagulation medium.

Characterization

Chemical composition of modified MWCNT and various fibers were analyzed by FTIR using a NEXUS-670 spectrometer (Nicolet) in the range of 400–4000 cm^{-1}. The microstructure of the gel fibers was examined with a scanning electron microscope (S-3000N). After the ethanol extraction, the gel fiber samples were fractured in liquid nitrogen, followed by drying overnight in a vacuum oven at room temperature. The samples were coated with gold in a sputtering device before observation. Single filament tensile properties were determined using a XQ-1 tensile testing machine at a crosshead speed of 10 mm/min with a gauge length of 20 mm. For each sample,

at least 10 filaments were tested. Dynamic mechanical tests of single filament were conducted on a dynamic thermal mechanical analyzer (DMA Q800, TA Instruments) at 10 Hz at a heating rate of 10°C/min at 25 mm gauge length. DSC analysis of the fibers was performed on a differential scanning calorimeter (Diamond DSC, PerkinElmer) over a temperature range of 50–350°C at a heating rate of 10°C/min in air. Wide angle X-ray diffraction (WAXD) patterns were obtained on scissored multifilament bundles or modified MWCNT powder using a D/max-2500PC X-ray diffractometer (Rigaku, Japan) with nickel-filtered Cu Kα radiation. The diffraction patterns were analyzed using AreaMax V.1.00 and MDI Jade 6.1. The crystallinity was determined using the integrated scans and the areas of the deconvoluted peaks. The PAN crystal size was also determined from the diffraction peak at 2θ∼ 16.5° using Scherrer equation ($K = 0.89$). From the azimuthal scans of the diffraction peak at 2θ∼ 16.5° on multifilament bundles, PAN molecular orientation was determined.[22,26]

RESULTS AND DISCUSSION

Modification of MWCNT

Because of the exceptional mechanical properties as well as flexibility and deformability, CNTs are particularly attractive as reinforcing nanofillers in polymers. For the fabrication of high- performance polymer/CNT nanocomposites, critical challenge lies in achieving uniform dispersion of CNT in the polymer matrix and strong interfacial bonding between CNT and polymer matrix.[27,28] For well dispersion of CNTs in organic or polymer systems, covalent functionalization of the CNT[29,30] or noncovalent physical π-π stacking interactions[31,32] are needed to form strong interfacial bonding between nanotubes and the polymer matrix. Here, the MWCNT was treated with concentrated aqueous acids to introduce acidic groups onto the surface of carbon nanotubes.[33] To increase the ionization of acidic groups and thus facilitate the dispersion of the MWCNTs in water, the acid-oxidized MWCNT sample was further neutralized with NaOH.

The FTIR spectra of pristine MWCNT, modified MWCNT and various fibers are shown in Figure 1. As compared with pristine MWCNT, on the spectrum of modified MWCNT, the peak around 3428 cm^{-1}, which corresponds to the stretching vibration of hydroxyl groups, becomes larger. Meanwhile, there appear new peaks at 1711 cm^{-1}, 1187 cm^{-1} and 1116 cm^{-1}, corresponding to the stretching vibrations of carbonyl groups and C—O bonds, respectively.[34–36] These changes indicate the presence of carboxyl groups on the surface of modified
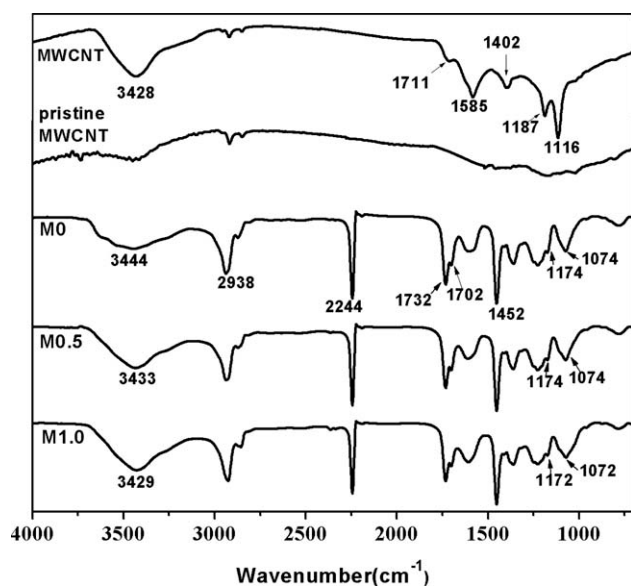
Figure 1 FTIR spectra of pristine MWCNT, modified MWCNT, and various PAN fibers with different content of modified MWCNT.

MWCNT. Furthermore, there also appear obvious asymmetric and symmetric stretching vibrations of COO$^-$ groups at 1585 cm^{-1} and 1402 cm^{-1} on the FTIR spectrum of modified MWCNT,[34] suggesting the introduced carboxyl groups are partially dissociated. The repulsion interactions between the negatively charged carboxylic ions are expected to prevent the conglomeration between the MWCNT and thus enhance the dispersion stability of MWCNT in water. Thus, well-dispersed MWCNT aqueous dispersion can be prepared at the help of sonication and stirring. Measurements (please see details in Experimental section) were also taken to ensure the uniform dispersion of MWCNT in the spinning dope.

As shown in Figure 1, the characteristic absorption bands of pure PAN fiber (M0) were observed at 2244 cm^{-1} (v(C≡N)), 1452 cm^{-1} (δ(CH$_2$)), 2938 cm^{-1} (v(CH)), 3444 cm^{-1} (v(OH)), 1732 cm^{-1} [v(C=O), from ester groups of methyl acrylate (MA) unit], 1702 cm^{-1} [v(C=O), from the associated carboxyl groups of itaconic acid (IA) unit], 1174 cm^{-1} [v(C—O), from ester groups of MA unit] and 1074 cm^{-1} [v(C—O), from carboxyl groups of IA unit]. All these peaks were found in FTIR spectra of the composite fibers. However, when compared with the pure PAN fiber, the stretching vibrations of —OH (3429 cm^{-1}), C—O from ester groups (1173 cm^{-1}), and C—O from carboxyl groups (1072 cm^{-1}) for the composite fibers shift to lower wavenumbers; meanwhile, the area ratio of v(OH) to v(C≡N) ($A_{v(OH)/v(C≡N)}$) increases with the increasing amount of MWCNT: the $A_{v(OH)/v(C≡N)}$ for M0, M0.5, and M1.0 are 3.5, 4.7, and 6.3, respectively. All these

changes indicate the presence of hydrogen bonding interactions between the modified MWCNT and PAN. The interactions are expected to enhance the interfacial adhesion between them, and result in PAN/MWCNT composite fibers with improved mechanical properties.

Morphology of the composite fibers

SEM was used to observe the cross-section morphology of the gel fibers; the results are presented in Figure 2. The cross-section of pure PAN fiber is circular [Fig. 2(a)]. Also, the fiber is homogenous and dense with no visible skin-core structure [Fig. 2(b)]. This result is similar to that of PAN gel fiber obtained via wet-spinning in coagulation bath of ethanol/DMSO (60/40, v/v) mixture at room temperature,[25] expect that the microstructure of fiber M0 looks denser. Composite fibers M0.5 and M1.0 also have circular cross-section and homogenous microstructure. The packing density of the fibers seems to decrease somewhat with the increasing content of MWCNT. This suggests that the introduction of a small amount of modified MWCNT have minor effects on the cross-section shape and microstructure of the fibers. Furthermore, a control PAN fiber was prepared via dry-jet wet spinning using a PAN/DMSO solution with a PAN concentration of 22% as the spinning dope and a water/DMSO (60/40, v/v) mixture at 50°C as the coagulation medium. From Figure 2(g,h), one can see that the cross-section shape of the control PAN fiber is elliptical. Also, the control PAN fiber displays a distinct core-shell structure: a dense thin skin layer with no visible pores and a thick core layer with loose network structure and high porosity. The above results confirm that the measurements we adopted, which include using DMSO/water (95/5, v/v) mixture as the solvent of the spinning dope, and adopting ethanol/DMSO (60/40, v/v) mixture at low temperature as the coagulation medium, do benefit to the uniform fiber formation, resulting in fibers with homogeneous dense microstructure.

The cross-sections of the solution-spun fibers are usually not circular.[37,38] Dong et al. prepared PAN fiber under similar spinning conditions as we adopted here except that water was used as the nonsolvent of the coagulating medium. They obtained fiber with nephroid-shaped cross-section.[38] The difference in the fiber cross-section can be attributed to the different interactions between the nonsolvent and PAN. In Dong's case, due to stronger hydrogen bonding interactions between water and DMSO at lower temperature (10°C), the diffusion of DMSO out of the filament becomes quicker. Consequently, the DMSO coming out of the filament is much more than the water entering into the filament during the
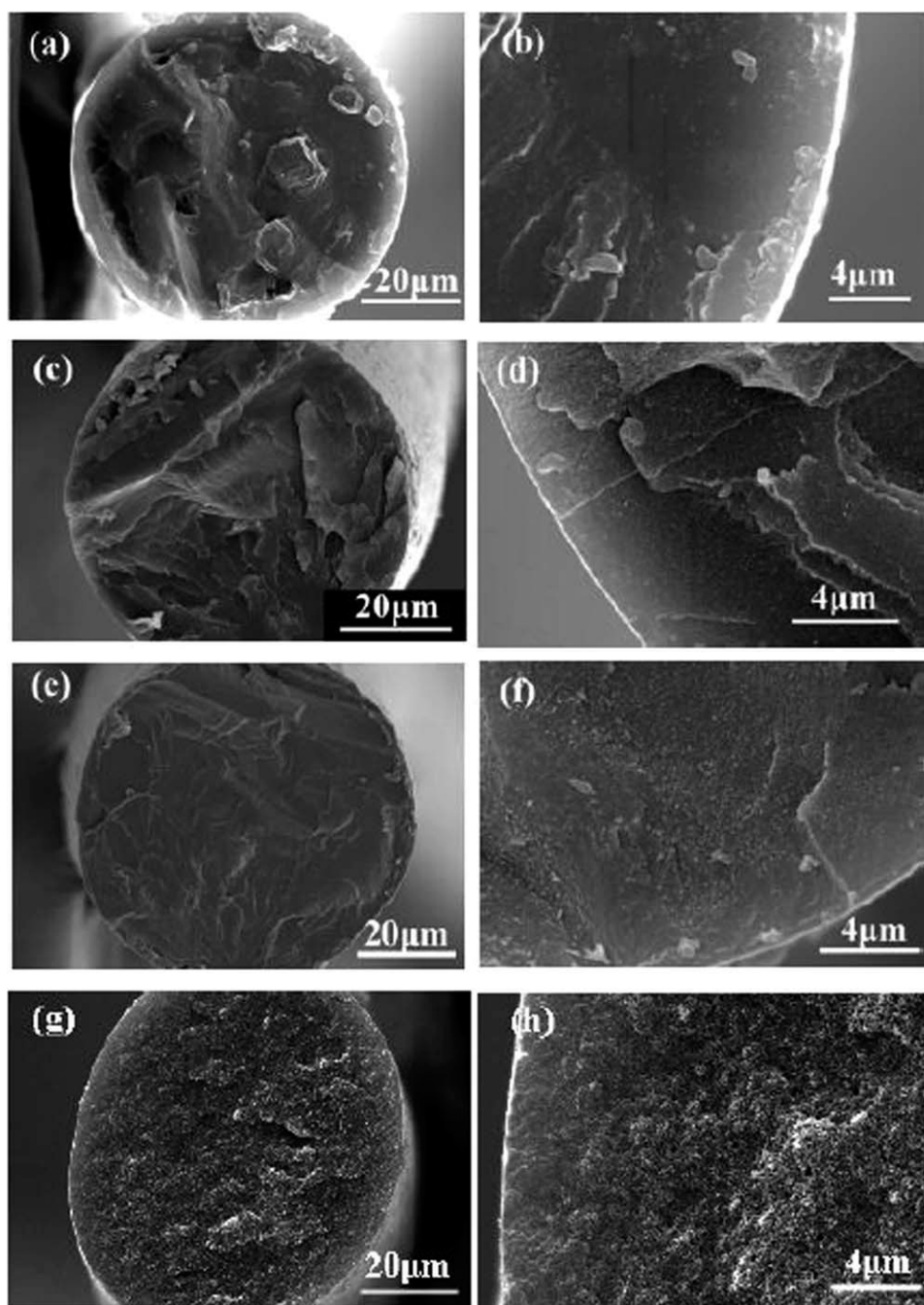
Figure 2 SEM micrographs of various as-spun PAN fibers containing different MWCNT contents (a, b: M0; c, d: M0.5; e, f: M1.0; g, h: control PAN fiber).

coagulation process, resulting in fibers with renal shape section. As the g_{13} of ethanol/PAN system is larger than that of water/PAN system,[25] much ethanol is expected to diffuse into the filament, thus the mass balance can be well kept and circular section fibers are obtained. Therefore, using ethanol/DMSO mixture as the coagulating agent, PAN fibers with homogeneous dense microstructure and circular cross-section, which is the ideal structure of PAN precursor for the production of high-performance carbon fibers,[2] can be prepared at a larger process-

ing window. This is very attractive for the practical production as it makes the structure regulation of the fibers easier.

No MWCNT was discerned in the SEM micrographs of fractured section of the composite fibers [Fig. 2(c–f)]. We used DMSO/water (95/5, v/v) mixture to etch the fiber surface and thus to disclose the MWCNT embedding in the PAN matrix. Figure 3 shows the SEM morphology of the etched surface of composite fiber M1.0. Single "cords" with some curliness were observed. Though their diameter (60–
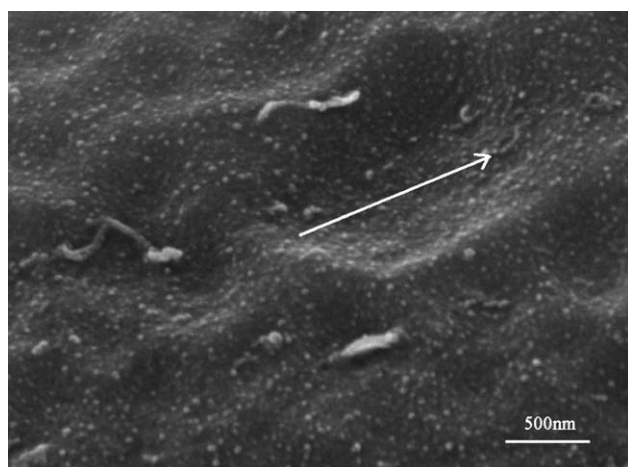
Figure 3 SEM micrograph of the surface of the composite fiber M1.0 after 1 min of sonication etching in DMSO/water (95/5, v/v) mixture (the arrow denotes the fiber axis direction).

Figure 4 WAXD patterns of modified MWCNT and various PAN fibers containing different amount of modified MWCNT.

200 nm) is much larger than that of disentangled single MWCNT, their shape bears a strong resemblance to that of disentangled single MWCNT. As there exist strong interactions including hydrogen bonding and π-π stacking interactions between MWCNT and PAN,[39,40] it is highly possible that the "cords" are composed of MWCNT core and PAN sheath (i.e., MWCNT wrapped with PAN) due to the short etching time. Furthermore, these "cords" are aligned somewhat parallel to the fiber axis (i.e., the drawing direction). This result suggests that MWCNTs are well-dispersed in the matrix of the composite fiber and they are orientated upon the action of jet stretching and air drawing.

Crystalline structure of the composite fibers

WAXD analysis was used to study the crystal structure and orientation of the composite fibers. Figure 4 shows the WAXD patterns of modified MWCNT and various PAN fibers containing different amount of modified MWCNT. In the XRD curves of the three fibers, a narrow strong peak and a broad weak peak appear at 16.5° and 29.5°, which correspond to the (200) and (020) planes of PAN crystallites, respectively.[40] For the modified MWCNT, there appears a narrow strong peak at 26.5°, which corresponds to the (002) diffraction of MWCNT. No distinct diffraction peak at 26.5° was observed in XRD patterns of fiber M0.5 and M1.0. This is possible due to the low content of MWCNT. The orientation of PAN molecules in the fibers was determined from the azimuthal scans of the diffraction peak at 2θ = 16.5°. The results are assembled in Table I.

The crystallinity of the fiber increases with the increasing content of MWCNT. Especially, the increase magnitude is larger at higher MWCNT con-
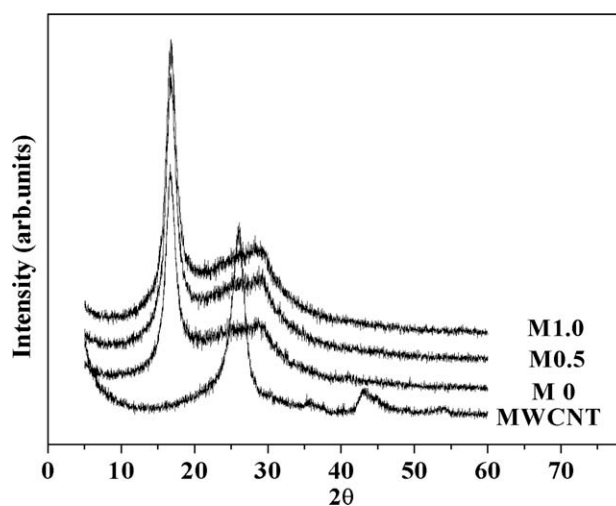
tent. The PAN crystal size obtained from the (200) diffraction peak in PAN/MWCNT composite fibers is larger than that in pure PAN fiber. The d-spacing of the (200) diffraction of PAN decreases with the increasing MWCNT content, indicating a closer packing of PAN molecules in the crystal.[15,41,42] The Herman's orientation factor of PAN molecules of pure PAN fiber is fairly high (0.86), which is much larger than that of dry-jet wet spun PAN using normal two-step drawing process,[24] and very close to that of gel-spun PAN fiber from PAN with a molecular weight of 2.5×10^5 g/moL with a total draw ratio of 51.[15] This result suggests that drawing the as-spun fiber in air (i.e., plasticizing drawing) can also achieve the efficient orientation of PAN molecules. Furthermore, after the introduction of MWCNT, the orientation of PAN crystal structure increases slightly, this result is consistent with the literature reports.[15,24] All the changes of the composite fibers as compared with the pure PAN fiber can be attributed to the well-dispersion of disentangled MWCNTs in the PAN matrix and their strong interactions. As the MWCNTs are more prone to be orientated upon drawing,[15,22,24,40] the PAN molecules

TABLE I
WAXD Results for PAN Fibers Containing Different Amounts of Modified MWCNT

Sample	M0	M0.5	M1.0
Crystallinity (%)	55.5	56.6	61.7
d-spacing (2θ = 16.5°, nm)	0.530	0.529	0.528
Crystal size (2θ = 16.5°, nm)	3.5	4.0	3.9
f_{PAN}[a]	0.86	0.88	0.90

[a] Herman's orientation factor of PAN molecules determined via azimuthal scans of the diffraction peak at 2θ = 16.5°.

Mechanical Properties of PAN Fibers Containing Different Amounts of Modified MWCNT

Sample	Linear density (dtex)	Bulk density (g/cm³)	Tensile strength		Breaking elongation		Tensile modulus	
			MPa	CV%	%	CV%	GPa	CV%
M0	1.45	1.18	761	5.68	13.7	6.84	7.02	12.5
M0.5	1.43	1.18	822	5.37	12.7	6.53	10.5	11.4
M1.0	1.38	1.19	906	5.62	12.6	6.82	11.4	12.2

bonded to MWCNTs are induced to be aligned along the draw direction. Thus their crystallization and orientation are facilitated.

Static and dynamic mechanical properties of the composite fibers

The tensile properties of the various fibers are listed in Table II. Both the strength and modulus of the composite fibers increase significantly, while the elongation to break decreases slightly with the increasing MWCNT content. At a MWCNT content of 1.0 wt %, there is a 19% increase in the tensile strength and a 62% increase in the tensile modulus, indicating that the fibers are enhanced substantially by introduction of a very small amount of MWCNT. Furthermore, after the introduction of MWCNT, the improvement in the modulus is much larger than that of the tensile strength. This result is inconsistent with that of Kumar and coworkers,[24] who reported that the PAN composite fiber containing 5 wt % of MWCNT exhibited a 69% increase in the tensile strength and a 38% increase in the modulus as compared with the control PAN fiber. That is, the improvement in the high strain properties (tensile strength) was larger than that of the low strain properties (modulus). They attributed the improvement in the high strain properties partially to the nanotube length; and the improvement in the low strain properties to PAN interactions with the nanotube. The difference may arise from the modification of MWCNT. Kumar and coworker used pristine MWCNT; while we used modified MWCNT. The long MWCNT may be broken into short ones via chemical modification.

The storage modulus and tan δ as a function of the temperature for various PAN fibers at a frequency of 10 Hz is shown in Figure 5. Storage modulus of the composite fiber M1.0 in the entire
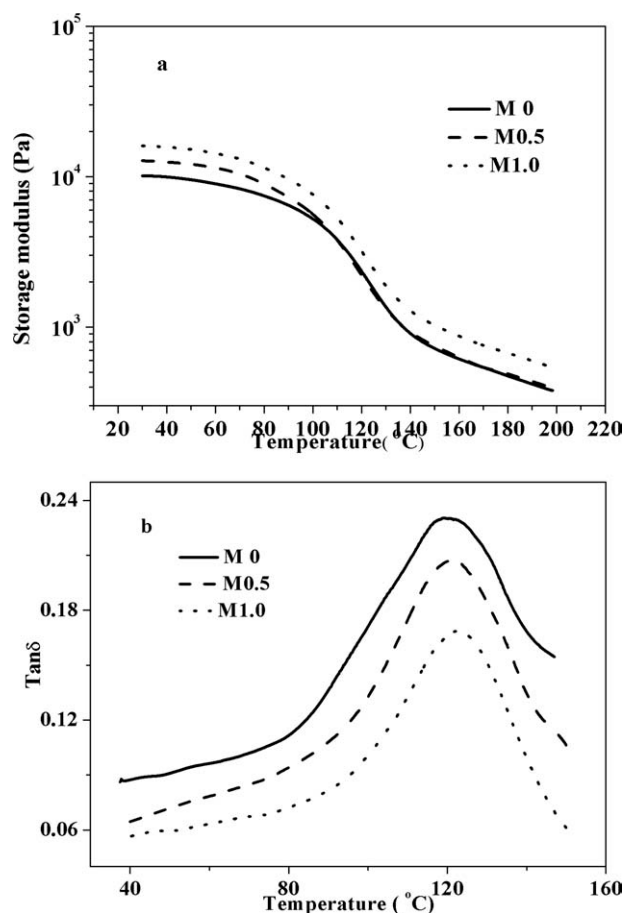

Figure 5 Storage modulus (a) and tanδ (b) vs. temperature plots of various PAN fibers containing different amounts of MWCNT.
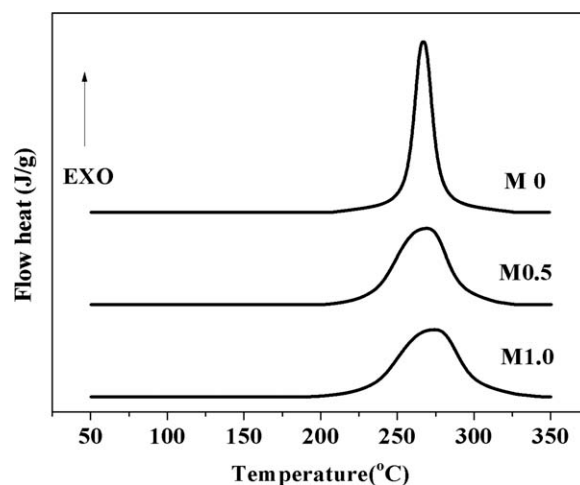

Figure 6 DSC plots of various PAN fibers containing different amounts of MWCNT in air at a heating rate of 10°C/min.

TABLE III
Analysis of DSC Exothermic Curves for PAN Fibers Containing Different Amounts of Modified MWCNT

Sample	Initiation temp.(°C)	Peak temp. (°C)	FWHM (°C)	Heat release (J/g)	Heat release rate (J/g·min)
M0	207	266	18	501	42
M0.5	200	269	38	532	41
M1.0	193	274	44	547	36

temperature range is substantially higher than that of the pure PAN fiber [Fig. 5(a)]. As the MWCNT content increases from 0% to 1.0%, the glass transition temperature (tanδ peak temperature) of the fiber increases from 119°C to 122°C; while the magnitude of the tanδ peak decreases from 0.23 to 0.17 [Fig. 5(b)]. This modulus increase, T_g increase as well as the tanδ decrease with the introduction of MWCNT was also observed in other PAN/CNT composite fibers.[15,22,24] The T_g increase reflects the restriction of MWCNT to the motion of PAN molecules. The modulus increase and tanδ decrease reflect the enhancement of elasticity by MWCNT. The significant changes in modulus, T_g and tanδ as well as the significant improvements in the tensile strength and modulus caused by the introduction of a very small amount of MWCNT (1.0 wt %), also suggest the well-dispersion of MWCNT in the PAN matrix and their strong interactions.

Thermal behavior of the composite fibers

To produce carbon fiber, PAN fiber precursor has to be successively subjected to oxidative stabilization and carbonization treatments. The aim of the oxidative stabilization treatment is to convert the linear PAN structure to ladder-shaped one, and endow the fiber with good stability at high temperatures during the carbonization treatment. Various reactions including cyclization, dehydrogenation, oxidization, and decomposition are occurred in the oxidative stabilization treatment, the thermal stability of the resulted fiber is mainly related to the degree of cyclization reaction. DSC analysis is frequently used to study the exothermic cyclization of PAN fiber. The exotherm peak of PAN homopolymer is sharp and narrow, which easily renders the uncontrollable heat release and results in "melting" down and coalescing of fibers in a tow. Acidic comonomers, such as methacrylic acid (MAA) and IA, initiate the nitrile cyclization during thermo-oxidative stabilization in ionic mechanism, and thus reduce the initiation temperature in PAN.[43,44]

Here, we used DSC to study the exothermic behavior of various fibers during the oxidative stabilization. The exotherm of pure PAN fiber shows a single peak initiating at about 207°C with a maximum peak at 266°C (Fig. 6, Table III). The full width at half-maximum (FWHM) of the exothermic peak is 18°C. The initiation temperature is close to that of IA-AN copolymer reported by Bajaj et al.[44] After the introduction of MWCNT, the exotherm peak broadens, the initiation temperature and heat release rate decrease, indicating that the introduction of MWCNT makes the reactions during the oxidative stabilization proceed in a gentle way. This change benefits to the control and improvement of the properties of oxidized fibers. The lower initiation temperature and broader exotherm of the PAN/MWCNT composite fibers as compared with the pure PAN fiber were also reported by other researchers.[43,44] These changes can be attributed to the carboxyl groups on the surface of MWCNT, which act as external initiator for nitrile cyclization in PAN.

CONCLUSIONS

The carboxyl groups were efficiently introduced onto the surfaces of the MWCNTs via chemical modification. Three PAN fibers containing 0 wt %, 0.5 wt %, and 1.0 wt % of modified MWCNTs with homogeneous dense microstructure and circular cross-section were prepared via dry-jet wet spinning of PAN solution in DMSO/water (95/5, v/v) mixture into a coagulation bath containing ethanol/DMSO (60/40, v/v) mixture at 10°C. By additional drawing the as-spun fiber in air, high-performance fiber with high orientation of PAN molecules was obtained. After the introduction of a very small amount of modified MWCNTs, the crystallinity, the crystal size and orientation, storage modulus, and T_g of the fiber increase. Also, the tensile strength and modulus of the fiber enhance substantially. Furthermore, the nitrile cyclization during the oxidative stabilization is initiated at a lower temperature and the heat release rate slows down. The fabrication of composite carbon fibers from these composite precursor fibers and their microstructure and mechanical properties will be reported elsewhere.

References

1. Ogawa, H.; Saito, K. Carbon 1995, 33, 783.
2. Zhang, W. X.; Liu, J.; Wu, G. Carbon 2003, 41, 2805.

3. Bajaj, P.; Screekumar, T. V.; Sen, K. J Appl Polym Sci 2002, 86, 773.

4. Bahrami, H. S.; Bajaj, P.; Sen, K. J Appl Polym Sci 2003, 89, 1825.

5. Bogun, M.; Mikolajczyk, T.; Kurzak, A.; Blazewicz, M.; Rajzer, I. Fibers Text East Eur 2006, 14, 13.

6. Dong, X. G.; Wang, C. G.; Chen, J. Polym Bull 2007, 58, 1005.

7. Zeng, X. M.; Chen, J. M.; Zhao, J. X.; Wu, C. X.; Pan, D.; Pan, N. J Appl Polym Sci 2009, 114, 3621.

8. Ge, H. Y.; Liu, H. S.; Chen, J.; Wang, C. G. J Appl Polym Sci 2008, 108, 947.

9. Qian, B. J.; Lin, W. P.; He, J. M.; Hu, P. P.; Wu, C. X. J Polym Eng 1996, 15, 327.

10. Gerasimov, V. I.; Chvalun, S. N.; Kazarin, L. A.; Goponenko, A. A.; Mashchenko, V. I.; Filyakin, A. M. Fiber Chem 2001, 33, 183.

11. Xu, Q.; Xu, L. H.; Cao, W. Y.; Wu, S. Z. Polym Adv Technol 2005, 16, 642.

12. Sawai, D.; Fujii, Y.; Kanamoto, T. Polymer, 2006, 47, 4445.

13. Ma, C. X.; Du, W. P.; Chen, H. F.; Liu, Z. L.; Qin, Z. Y.; Pan, D. J Polym Sci Part B: Polym Phys 2008, 46, 2637.

14. Tan, L. J.; Liu, S. P.; Pan, D. J Phys Chem B 2009, 113, 603.

15. Chae, H. G.; Minus, M. L.; Kumar, S. Polymer 2007, 47, 3494.

16. Iijima, S. Nature 1991, 354, 56.

17. Iijima, S.; Ichihashi, T. Nature 1993, 363, 603.

18. Sterzynski, T.; Tomaszewska, J.; Piszczek, K.; Skórczewska, K. Compos Sci Technol 2010, 70, 966.

19. Kim, J. Y.; Choi, H. J.; Kang, C. S.; Kim, S. H. Polym Compos 2010, 31, 858.

20. Kanagaraj, S.; Guedes, R. M.; Oliverira, M. S. A.; Simones, J. A. O. J Nanosci Nanotechno 2008, 8, 4008.

21. Mikolajczyk, T.; Szparaga, G.; Bogun, M.; Fracek, S.; Blazewicz, S. J Appl Polym Sci 2010, 115, 3628.

22. Sreekumar, T. V.; Liu, T.; Min, B. G.; Guo, H.; Kumar, S.; Hauge, R. H.; Smalley, R. E. Adv Mater 2004, 16, 58.

23. Min, B. G.; Sreekumar, T. V.; Uchida, T.; Kumar, S. Carbon 2005, 43, 599.

24. Chae, H. G.; Sreekumar, T. V.; Uchida, T.; Kumar, S. Polymer, 2005, 46, 10925.

25. Zhang, J.; Zhang, Y. W.; Zhao, J. X. Polym Bull 2011, 67, 1073.

26. Koganemaru, A.; Bin, Y.; Agari, Y.; Matsuo, M. Adv Funct Mater 2004, 14, 842.

27. Ajayan, P. M. Chem Rev 1999, 99, 1787.

28. Wang, C. C.; Guo, Z. X.; Fu, S. K.; Zhu, D. B. Prog Polym Sci 2004, 29, 1079.

29. Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. Science, 1998, 282, 95.

30. Saini, R. K.; Chiang, I. W.; Peng, H.; Smalley, R. E.; Billups, W. E.; Hauge, R. H.; Margrave, J. L. J Am Chem Soc 2003, 125, 3617.

31. Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. J Am Chem Soc 2001, 123, 3838.

32. Skakalova, V.; Kaiser, A. B.; Dettlaff-Weglikowska, U.; Hrncarikova, K.; Roth, S. J Phys Chem B 2005, 109, 7174.

33. Esumi, K.; Ishigami, A.; Nakajima, A.; Sawada, K.; Honda, H. Carbon 1996, 34, 279.

34. Ishizaki, C.; Marti, I. Carbon 1981, 19, 409.

35. Shaffer, M. S. P.; Fan, X.; Windle, A. H. Carbon 1998, 36, 1603.

36. Liu, L. Q.; Qin, Y. J.; Guo, Z. X.; Zhu, D. B. Carbon 2003, 41, 331.

37. Weisenberger, M. C.; Grulke, E. A.; Jacques, D.; Rantell, T.; Andrewsa, R. J Nanosci Nanotechnol 2003, 3, 535.

38. Dong, R. J.; Keuser, M.; Zeng, X. M.; Zhao, J. X.; Zhang, Y. W.; Wu, C. X.; Pan, D. J Polym Sci Part B: Polym Phys 2008, 46, 1997.

39. Vaisman, L.; Wachtel, E.; Wagner, H. D.; Marom, G. Polymer, 2007, 48, 6843.

40. Ge, J. J.; Hou, H. Q.; Li, Q.; Graham, M. J.; Greiner, A.; Reneker, D. H.; Harris, F. W.; Cheng, S. Z. D. J Am Chem Soc 2004, 126, 15754.

41. Bashir, Z. J Polym Sci Part B: Polym Phys 1994, 32, 1115.

42. Sawai, D.; Yamane, A.; Kameda, T.; Kanamoto, T.; Ito, M.; Yamazaki, H.; Hisatani, K. Macromolecules 1999, 32, 5622.

43. Sreekumar, T. V.; Chandra, L.; Srivastava, A.; Kumar, S. Carbon, 2007, 45, 1114.

44. Bajaj, P.; Sreekumar, T. V.; Sen, K. Polymer, 2001, 42, 1707.