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Carbon fibers modified with carbon nanotubes

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Abstract Carbon nanotubes were used to modify a polyacrylonitrile (PAN) polymer solution before the manufacture of the carbon fiber precursor. The modified PAN fibers were spun from a dimethylformamide solution containing a small amount of single-walled carbon nanotubes. The fibers were characterized by thermogravimetry and optical and scanning electron microscopy. Structure, morphology, and selected properties of the composite polymeric fibers and the fibers after carbonization are characterized. The mechanical properties of the fibers are examined. It is found that nanotubes in the PAN solution have a strong tendency to form agglomerates that inhibit suitable macromolecular chain orientation of the carbon fiber precursor. Fibers manufactured from such a solution have similar mechanical properties to those from a pure PAN precursor, and after carbonization the resultant carbon fibers are very weak. A comparison of pure carbon fibers and those containing nanotubes reveals slight differences in their structural ordering.

Introduction

Polyacrylonitrile (PAN)-based polymers belong to the most popular polymer precursors for carbon fibers applied in composite technologies, as well as for manufacturing porous and activated carbons for different purposes, including catalysis, electrochemistry, separation processes, energy storage devices, electrode materials etc. [1–4].

Recently, various polymeric matrices were investigated by being mixed with a small amount of constituents in the form of nanoparticles. Among nanofillers, the most popular are organofilicized layered silicates able to create nanoplatelets while dispersed in polymer matrix [5]. Another type of nanofillers is carbon nanotubes (CNTs) [6–9]. Owing to their specific properties, they are being considered as a modifying component for different matrices of composites [10–15]. Their exceptional mechanical properties, electrical and thermal conductivity, and superior length to diameter ratio make them very attractive for composite reinforcement [6, 16]. Effectiveness of reinforcement of polymers by CNTs may be realized by obtaining uniform dispersion of nanotubes in the matrix and also achieving interfacial adhesion between the nanotubes and the matrix. Adhesion can be realized by the creation of functional groups on the surface of nanotubes like carboxyl, acryl, and hydroxyl groups [17–19]. The use of nanoparticles, however, is often accompanied by the problem of their proper dispersion in polymeric solution. Owing to their high specific surface energy, they have a tendency to form agglomerates, which constitute defect sites in the composites and limit the reinforcement efficiency of the polymer matrices containing CNTs [6, 20, 21]. Mechanical properties enhancement was also analyzed in terms of nanotube orientation in PAN matrix. It was found that PAN macromolecular orientation increased with an increase of CNTs orientation in the polymer, and their presence in the polymer resulted in the higher crystallite size of the polymer. The limited property improvement in polymer/CNT composites was caused by the presence of

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chaotically-oriented CNTs [1]. Alignment of CNTs in the polymer matrix was the most important factor influencing the mechanical and functional properties of polymer/CNT composites [17].

The purpose of this investigation was to determine the effect of CNTs introduced into PAN fibers on carbonization process of such a precursor. A preliminary stabilized PAN fiber precursor was heated to different levels of carbonization temperature (from 1,000 to 1,850 °C). The structure, microstructure, and mechanical properties of the fibers after various stages of preparation were studied.

Experimental

Polyacrylonitrile fibers were spun in tow from a solution in dimethylformamide (DMF) containing single-wall CNTs in the form of nanohorns. Carbon 'nanohorns' belong to the family of CNTs, and are directly related to the group of single-wall CNTs [22]. Carbon nanohorns are defined as 'short, single-layered nanotubes with one end closed in a cone-shaped cap'. In many publications, they are called SWCNT and have the same graphitic carbon atom structure as normal CNTs. The SWCNTs used in this study were made by the arc discharge process (provided by NanoCraft, Inc. of Renton, USA). They had diameters in the range of 2–3 nm and were 30–50 nm long with a 19° closed-end called a carbon nanohorn. They were grown in the presence of iron as catalyst. The determined concentration of Fe catalyst by atomic absorption spectrometry using the electrothermal technique (spectrometer Model 3110, Perkin-Elmer Co.) was about 1.8 wt%.

The preparation of all kinds of the precursor fibers and their subsequent oxidation and carbonization were realized under the same technological processing parameters.

The nanoconstituents were immersed in DMF solution and sonicated at room temperature for 1 h with a bath sonicator prior to being introduced into the polymer. PAN polymer was separately dissolved in DMF, and PAN/DMF solution was added to the SWCNTs/DMF suspension and homogenized while being stirred. After solidification, the fibers were dry-jet wet spun on a laboratory spinning machine using a 500 hole spinneret of 0.08 mm diameter. The fibers were stretched in two stages: in a plasticiting bath at 70 °C and under superheated steam at 135 °C, respectively. After the solvent had been rinsed out, the fibers were dried between 80 and 120 °C.

Three kinds of the PAN fibers were prepared.

(a) Control PAN polymer fibers (22% PAN spinning solution dissolved in DMF solution, total stretching of the fibers during the bath was about 1,000%);
(b) SWCNT/PAN composite fibers (1% by wt. CNTs in 22% PAN spinning solution dissolved in DMF solution), denoted as PAN-N—before sonication;
(c) SWCNT/PAN composite fibers (1% by wt. CNTs in 22% PAN spinning solution dissolved in DMF solution), denoted as PAN-S—after sonication.

Before carbonization, pure and modified (containing CNTs) PAN fibers were stabilized in an oxidizing atmosphere by a multistage process in the temperature range 150–280 °C. The oxidized fibers were carbonized at 1,000 and 1,350 °C in an argon atmosphere. One part of the composite fibers was heated up to 1,850 °C in order to determine its structural changes caused by the presence of CNTs. Morphology, structure, microstructure, and selected properties of the fibers were analyzed. The fibers were characterized by SEM (Nova NanoSEM 200, FEI) under magnification of ×2000. Microstructural parameters of carbon fibers were determined from X-ray diffraction (Philips system, $\lambda = 1.54$ Å) using the Scherrer equation. The mechanical properties of the fibers after various stages of preparation were measured using Zwick testing machine model 1435. Tensile mechanical test was made on a single filament, at 25 mm gauge length. CNTs content (in wt%) in PAN fibers was determined in relation to the weight of the polymer. Mercury porosimetry measurements were made to determine the pores sizes in PAN-based fibers precursors.

The total volume of the pores and the pore size distribution of pure PAN fibers and the fibers containing CNTs were measured with Hg porosimeter (Carlo–Erba).

Simultaneous Thermal Analysis type SDT 2960 thermogravimetric analyzer (TA Instruments Co.) was used to determine the differences in both types of PAN-based fibers and PAN-S fibers containing SWCNTs. The samples (3 mg) were placed in a platinum crucible and heated in air at the rate of 10 °C/min to 1,000 °C.

Relative changes of the electrical resistance were determined from room temperature to the temperature of liquid helium (300–4.2 K). Resistance was measured for pure and modified carbon fibers by the four-probe method with a Picowatt RV-Elektronikka OY AVS-47 resistance bridge equipped with helium-flow cryostat.

Results and discussion

Precursor and carbon fiber morphology

Dispersion of CNTs in the precursor materials may influence the fiber precursor morphology. Microscopic analysis of the fibers before and after dispersion process of CNTs in polymer solution provides information on their morphology. SEM microphotographs illustrate typical surfaces of pure

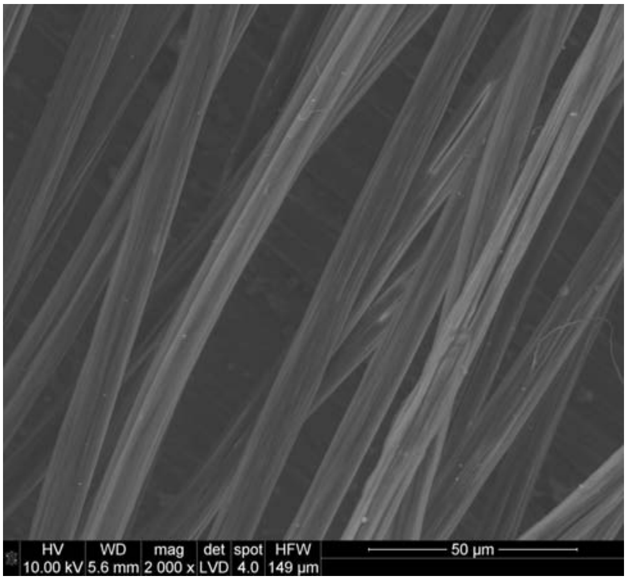

Fig. 1 SEM microphotograph of pure PAN fibers

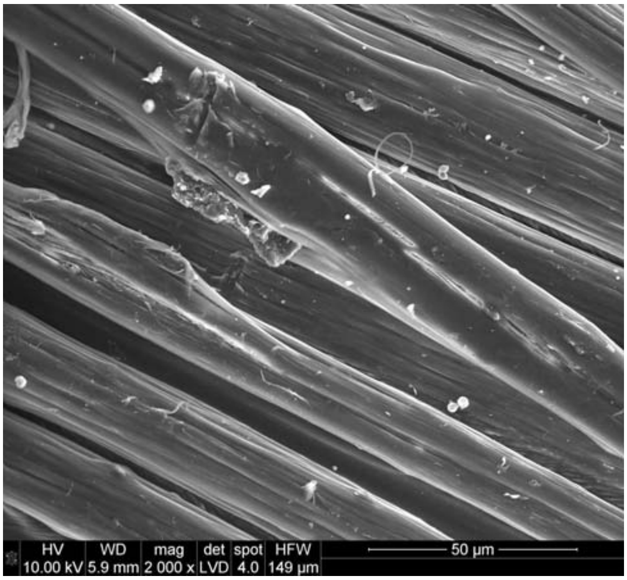

Fig. 2 SEM microphotograph of PAN fibers containing carbon nanotubes—PAN-N (the fiber surface shows a size of CNT clusters, without sonification)

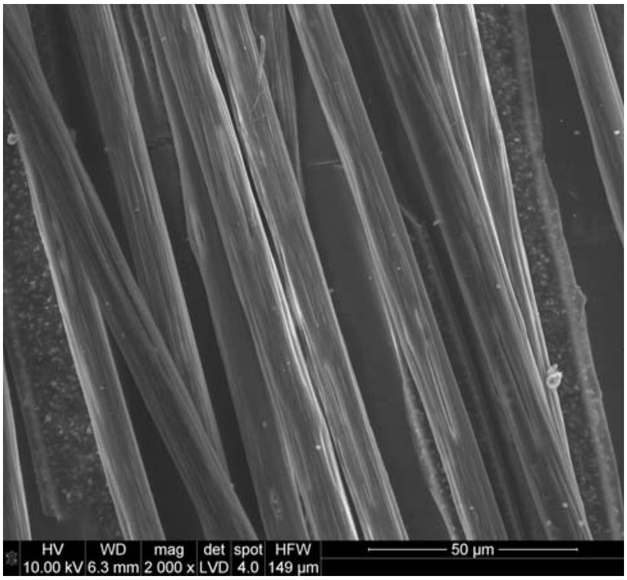

Fig. 3 SEM microphotograph of PAN fibers containing carbon nanotubes—PAN-S (after sonification)

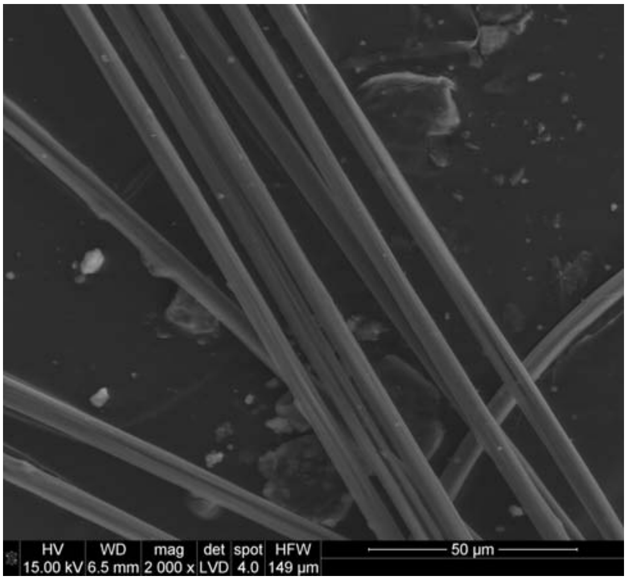

Fig. 4 SEM microphotograph of carbon fibers containing carbon nanotubes (after PAN solution sonification)

PAN fibers (Fig. 1), PAN fibers containing nanotubes, and resulting carbon fibers (Figs. 2, 3, 4). As one would expect the fibers containing nanotubes, which were spun and drawn from the solution without preliminary sonication show large defects (Fig. 2). Such defects are not observed for the pure PAN fibers (Fig. 1) and nanocomposite fibers obtained after optimization of the dispersion process (Figs. 3, 4).

The nanotubes were found in the form of clusters on the surface and within the inner part of the fibers. The presence of CNT clusters is likely to affect the thermal stresses in the matrix [23, 24]. When carbonized the thermal stresses induced by heating may exceed in a localized site the intrinsic strength of the fiber matrix/clusters boundary. The voids were formed as a result of detaching the agglomerated CNTs from the near surface region of carbon fibers during HT. The values of diameters of PAN fibers with SWCNT (PAN-N, PAN-S) are listed in Table 1. Mean diameter of PAN fibers containing nanotubes without preliminary sonication is relatively high (18.5 µm). The diameters of pure PAN precursor and PAN fibers with nanotubes after sonication are almost the same and distinctly lower than those obtained without preliminary sonication. The presence of

Table 1 Mechanical properties of pure PAN fibers and composite carbon fibers

Material	Tensile strength (GPa)	Young's modulus (GPa)	Elongation at break (%)	Diameter (μm)
Before carbonization				
PAN	0.55 ± 0.06	9.4 ± 1.2	12.7 ± 1.7	9.8 ± 0.4
PAN-N	0.50 ± 0.08	9.9 ± 2.1	14.3 ± 1.4	18.5 ± 1.9
PAN-S	0.61 ± 0.05	9.2 ± 1.4	12.6 ± 0.7	9.9 ± 0.3
After carbonization at 1,000 °C				
PAN	1.34 ± 0.33	145.8 ± 25.2	0.83 ± 0.22	5.2 ± 0.4
PAN-N	0.55 ± 0.23	122.6 ± 11.7	0.50 ± 0.17	11.3 ± 1.0
PAN-S	1.12 ± 0.32	169.3 ± 36.1	0.62 ± 0.09	5.2 ± 0.6
After carbonization at 1,350 °C				
PAN	1.00 ± 0.17	200 ± 17.6	0.44 ± 0.11	5.1 ± 0.2
PAN-S	1.00 ± 0.14	218 ± 17.5	0.43 ± 0.08	4.9 ± 0.2

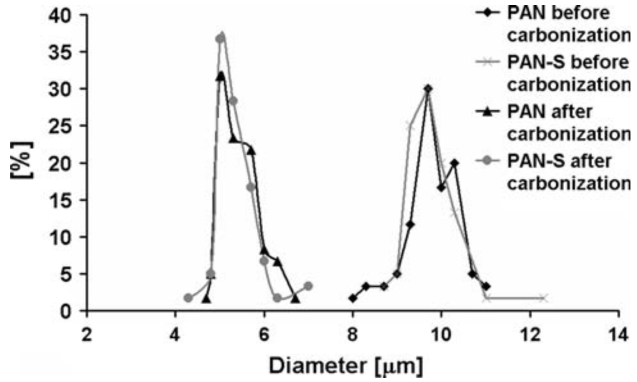

Fig. 5 Diameter distribution of PAN fibers and carbon fibers obtained at 1,000 °C

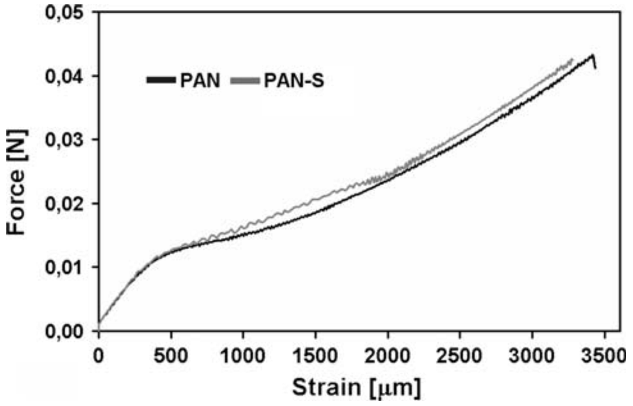

Fig. 6 Mechanical characteristics of PAN fibers in tensile test

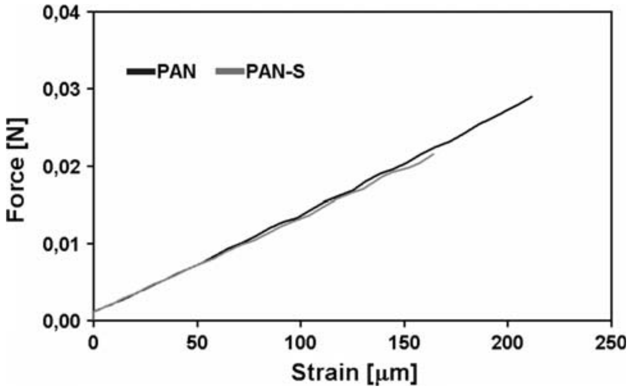

Fig. 7 Mechanical characteristics of PAN-based carbon fibers obtained at 1,000 °C

such a small number of non-uniformly distributed nanoconstituents in polymer matrix produces additional porosity inside the polymer precursor during the spinning process. Such a mechanism has also been confirmed for the PAN fibers containing ceramic nanoparticles [25]. The agglomerates within the polymer made macromolecular chain reorientation difficult during spinning and drawing of the fibers. On the contrary, the precursor fibers with nanotubes spun from the solution after sonication demonstrate the same diameters distribution like that for pure precursor fibers (Fig. 5).

Mechanical properties of fibers

The results of the mechanical tests of the fibers after various stages of processing are displayed in Table 1 and in Figs. 6 and 7. Although the fibers differ in the method of manufacturing (pure fibers, sonicated, and non-sonicated nanotubes containing precursor solution) their resultant mechanical characteristics are comparable. The presence of large-size defects in the fibers (PAN-N) matrix caused by the agglomerated carbon particles has no significant influence on the strength of the precursor. Although the diameters of these fibers are twice as high as those of pure and PAN-S fibers, their mechanical properties are nearly the same. The agglomerates of micrometric sizes (Fig. 2) can act as the particulate reinforcement of the polymer matrix. A slight positive effect of the agglomerated nanotubes on Young's modulus of these precursor fibers is, however, noticeable, although their quantity is very low. Figures 6 and 7 demonstrate typical examples of the dependencies between the strains and the tensile forces of single-filament PAN, PAN-S fibers, and the resultant fibers after carbonization. The strains to failure and the levels of the rupture stresses for pure polymer fibers and composite fibers are comparable. These data therefore suggest that well-dispersed CNTs are located between the polymer chains and cause weak interaction between strong polar nitrile groups and/or hydrogen bonds. In the case of the carbonized fibers, the breaking force is higher for the fibers without nanotubes. Table 2 shows the variation of the cumulative volume occupied by mercury and the pores sizes in the fibers precursors. Total volume of pores in pure PAN fibers is 0.461 cm^3/g, whereas in PAN containing agglomerated nanotubes the total porosity increases to 0.633 cm^3/g. There are two maxima in the pore size distribution in the obtained fibers. Such a bimodal distribution occurs in all analyzed fibers. Following distinctly higher fraction of large size pores (150–750 nm) presented in PAN-N fibers, their tensile strength is smaller. As a consequence, the presence of this pores fraction has also influence on resulting mechanical properties of carbon fibers.

Significant differences in mechanical properties between the examined fibers are revealed after HT to 1,000 °C and to 1,350 °C. Because of the brittle character of carbon fibers, they are much more susceptible to the presence of small defects, so the influence of the agglomerated nanotubes in this matrix is much stronger than in the case of the precursor fibers. The brittle nature of carbon fibers is manifested in the significant decrease of strain to failure as the carbonization temperature increases. Generally, the obtained values of elongation at breaks (Table 1) are much lower in comparison to typical values of IM (intermediate modulus) carbon fibers. These values are rather closer to HM (high modulus) type carbon fibers. There is a difference in strength between pure carbon fibers and both types of carbonized composite fibers (PAN-N and PAN-S). A negative influence of CNTs, both as the dispersed form and as the aggregates on the carbon fibers' strength, is evident. In particular, the presence of nanotubes in the form of aggregates (PAN-N) inside carbon fibers caused a drastic fall in strength and the decrease of elongation at break of carbon fibers. Notwithstanding that all the polymer fibers precursors were drawn to a draw ratio of about 10 (total fiber stretching), the precursors with the agglomerated nanotubes showed high diameters and subsequent HT led to carbon fibers with 11 μm diameters. Such high values of diameters cannot be ascribed to the presence of agglomerates inside the fibers only. They are also caused by the porous nature of this precursor and resulting carbon fibers. On the contrary, Young's modulus of carbon fibers containing uniformly distributed nanotubes increases as a function of carbonization temperature and is higher than for pure carbon fibers.

Table 2 Porosimetric data of PAN fibers precursors

	Total pores volume (cm^3/g)	Fraction of small pores, 4–15 nm (%)	Fraction of large pores, 150–750 nm (%)
PAN	0.461	10.38	12.26
PAN-N	0.633	5.60	30.65
PAN-S	0.414	16.05	9.2

Structural changes

The crystallite parameters were determined for pure carbon fibers and fibers containing SWCNTs obtained at 1,850 °C. The diffractograms are shown in Fig. 8a, and the calculated values of interplanar distance and crystallite sizes are displayed in Table 3. The table also contains structural parameters for pure carbon fibers.

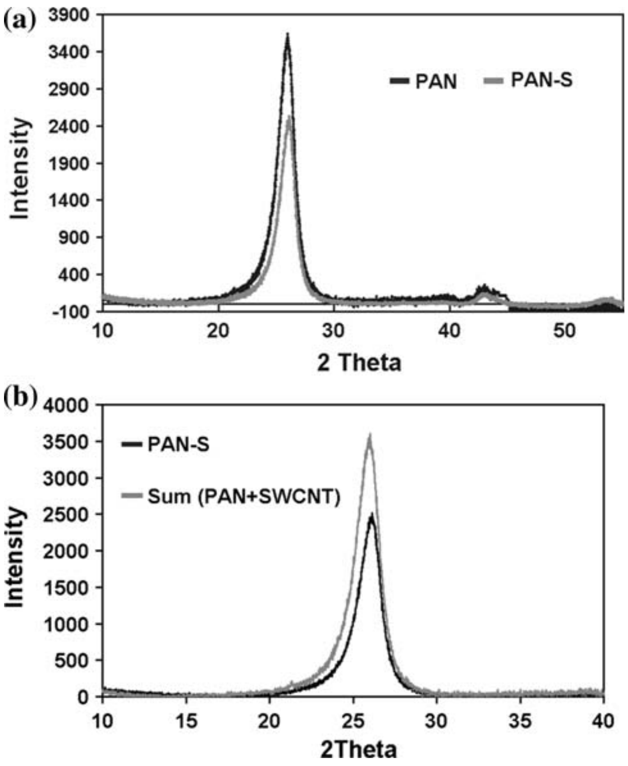

Fig. 8 **a** XRD patterns of pure and SWCNT-modified carbon fibers obtained at 1,850 °C; **b** diffraction pattern of SWCNT-modified carbon fibers obtained by mathematical addition of pure carbon components of the sum (PAN + SWCNT)

Table 3 Structural and microstructural parameters of carbon fibers obtained at 1,000 and 1,850 °C and obtained by mathematical composition of pure components of carbon fibers and the nanotubes, sum (PAN + SWCNT)

Temp (°C)	Sum		Modified		Pure fibers	
	d_{002} (nm)	L_c (nm)	d_{002} (nm)	L_c (nm)	d_{002} (nm)	L_c (nm)
1,000	–	–	0.3450	1.1	0.3520	1.6
1,850	0.3447	4.6	0.3413	4.3	0.3425	4.7

It is apparent from the diffraction patterns that the presence of nanotubes in composite carbon fibers slightly changes the intensity of (002) peak in comparison with pure fibers (Fig. 8a). To evaluate the real effect of nanotubes on the fibers' structure, the figure also compares the diffraction peaks of carbon fibers containing nanotubes and the diffraction pattern obtained by mathematical composition of pure components of carbon fibers and the nanotubes (Fig. 8b). By summation of the intensities of the pure carbon fibers and the nanotubes the resulting (002) peak differs from that obtained directly from composite carbon fibers. It may suggest that CNTs influence the crystallinity of the carbon fibers matrix.

As shown in the table, the fibers with nanotubes after heat treatment to 1,850 °C have better structural ordering expressed by the lowest interplanar distance. On the other hand, the presence of a small number of nanotubes in the carbon matrix noticeably inhibits the crystallite growth during carbonization.

Thermal analysis

The differential thermal analysis (DTA) and thermogravimetry (TG) measurements of pure and composite PAN fibers revealed some slight differences in the behavior of both samples. Such a measurement may also be considered as a thermal stability test of PAN-based fibers. Figure 9a displays two runs made in air; the presence of nanotubes causes 3 °C displacement of the beginning of oxidation process of composite fibers toward lower temperature (about 279 °C) compared with pure carbon fibers (282 °C). TG curves (Fig. 9b) indicate that during the oxidation to 300 °C the observed mass loss of the composite fiber is more than twice as low (7.2 wt%) as that of the pure fibers (15.6 wt%). It may suggest that the presence of well-dispersed nanotubes in PAN solution enhances crystallinity in PAN fibers (macromolecular chain ordering), resulting in their higher thermal stability during oxidation in air. At higher temperature range (above 500 °C) both runs of oxidation are comparable.

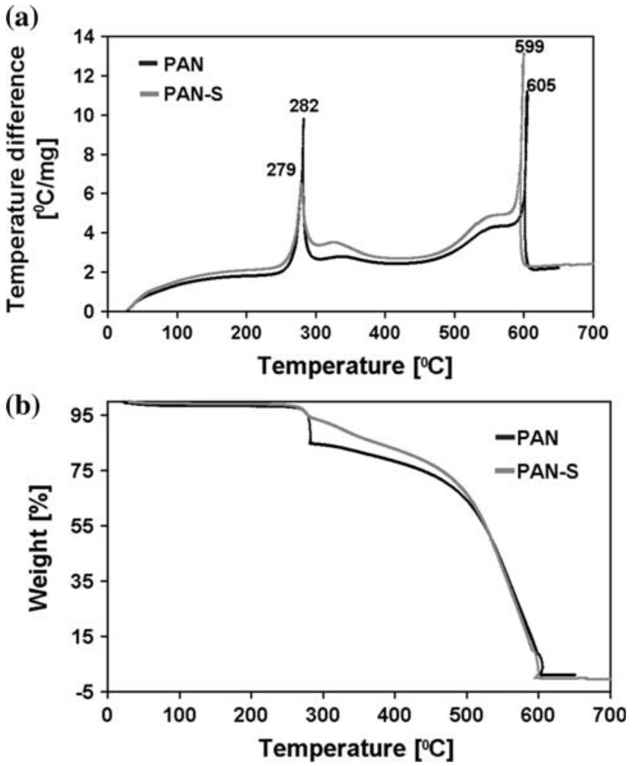

Fig. 9 **a** DTA analysis of pure PAN fibers and PAN fibers containing SWCNTs (PAN-S); **b** TG analysis of pure PAN fibers and PAN fibers containing SWCNTs (PAN-S)

Electrical properties

Results of four-probe electrical conductivity measurement are shown in Fig. 10. The fibers were carbonized at 1,000 °C. Neither run shows any distinct difference above 50–250 K. Fibers' conductivity, however, changes at low temperature. Carbon fibers containing nanotubes show a strong decrease of conductivity, which may be explained to weak localization of free carries with temperature decreasing. This effect in pure carbon fibers studied here is

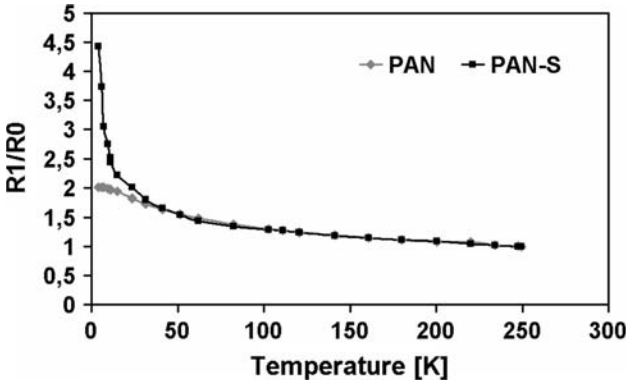

Fig. 10 Relative resistance changes versus temperature for pure carbon fibers and carbon fibers modified with SWCNTs

not observed. The difference of the observed relations may be explained by the fact that an interlayer spacing of pure carbon fibers obtained at 1,000 °C ($d_{002} = 0.352$ nm) is greater in comparison with SWCNT-modified carbon fibers (0.345 nm). Such a d_{002} value is characteristic for a turbostratic, disordered structure [26], while in composite fibers this type of the structure only dominates. Pure, low carbonized fiber has the structure, where the condition for weak disorder is not respected. The strongest 2D weak localization effect was observed for carbon fibers with d_{002} around 0.341–0.340 nm. When d_{002} increases, starting from 0.341 nm the 2D weak localization effect decreases and disappears above 0.345 nm [27]. Thus, this effect in pure carbon fibers studied here is not observed.

Conclusions

Polyacrylonitrile fiber precursors modified with CNTs were studied and compared with a pure precursor. Nanotubes introduced to polymer solution were observed to have a strong tendency to create agglomerates. Direct incorporation of CNTs without their optimal dispersion into PAN fibers during the following HT induced the creation of large voids on the surface of carbon fibers. The agglomerates in PAN spinning solution affected the rheological behavior and made it difficult to obtain the fibers of low diameters (below 15 μm) under the draw ratio of 10. After sonication in optimum conditions, homogeneous PAN solution can be obtained. The presence of well-dispersed nanotubes in polymer matrix promotes an increase of crystallinity in precursor fibers, improving its thermal stability in an oxidative atmosphere. A small quantity of nanotubes (1 wt%) in the PAN fibers has no significant influence on mechanical behavior of the composite fibers. The strength of carbon fibers containing CNTs is slightly lower than that of pure carbon fibers, while Young's modulus increases. The carbonization process is accompanied by significant reduction in strain to failure of the fibers. Slight effect of structural ordering has been observed for carbon fibers containing CNTs.

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