Effect of Dispersion of Carbon Nanotubes in Polyacrylonitrile Matrix on Mechanical and Thermal Behavior of Nanocomposites

A Fraczek, S Blazewicz
1AGH-University of Science and Technology, Faculty of Material Science and Ceramics, Department of Biomaterials, al. Mickiewicza 30, 30-059 Krakow, POLAND

E-mail: afraczek@op.pl

Abstract. The work deals with preparation of polyacrylonitrile (PAN)–based nanocomposites containing multi wall carbon nanotubes (MWCNTs). The effect of nanotubes addition to the PAN solution on selected properties of the obtained samples is discussed. The nanocomposites were characterized by scanning electron microscopy (SEM) and thermogravimetry. Agglomeration and dispersion of MWCNT in polymer solution were studied using Zetananosizer. The mechanical properties of the nanocomposites before and after optimization dispersion process were examined. It is found that improperly prepared PAN suspension containing nanotubes causes a significant reduction of the tensile strength of nanocomposite samples. The preparation procedure of the polymeric solution with carbon nanotubes and the sonication sequence have a significant impact on mechanical properties of the obtained samples. The thermogravimetry analysis of nanocomposite samples shows a raise of the temperature of maximum thermal degradation in the case of sample containing 1wt% of MWCNT.

1. Introduction
Polyacrylonitrile (PAN) is one of the most popular polymer used in producing a fibrous precursor for carbon fibers. PAN fibers are suitable for carbonization of high performance carbon fibers (compared to pitch, rayon) due to their high melting point and a great carbon yield (>50% of the original precursor mass) [1-3]. PAN-based carbon fibers have application in composite technology, electrochemistry, separation process, energy storage devices [4-6]. Moreover, polyacrylonitrile (PAN) has been widely used as separation membrane materials and porous membranes for lithium-ion polymer batteries [7,8]. Recently, the PAN polymer is also attempted to fabricate various compositions with nanoadditives such as nanosilica, nanomagnetite, nanohydroxyapatite and carbon nanotubes (CNTs). Carbon nanotubes are considered as potentially new class of reinforcement for polymer composites due to their mechanical properties. Carbon nanotubes are cylindrical tubes containing sp² hybridized carbon–carbon bonds along their length. Both single-walled carbon nanotubes and multi-walled carbon nanotubes may be viewed as single macromolecules and, because of their nanosize, are potentially defect-free structures [9,10]. Depending on the size, chirality and orientation carbon nanotubes exhibit unique mechanical, electrical and thermal properties. They show very high thermal stability up to 2800°C in vacuum, thermal conductivity about twice as high as diamond, and almost 1000 times

1 A. Fraczek, e-mail address: afraczek@op.pl
higher than copper [11-14]. Intense interest of researchers has been generated in utilizing these unique structures and outstanding properties for hydrogen storage, supercapacitors, biosensors, electromechanical actuators, and nanoprobes for high-resolution imaging etc [15]. Carbon nanotubes can be used as a reinforcement to improve mechanical properties, thermal stability and conductivity of nanocomposites, and also to prepare anisotropic nanocomposites [16-18]. In order to obtain full potential of CNTs as a reinforcement in composites they require to be well dispersed in polymer matrices, what can be achieved by using the sonication process [19,20]. The suitable interaction between carbon nanotubes and polymer matrix can be realized via chemical modification of the nanotubes surface [21].

The purpose of this investigation was to determine the effect of carbon nanotubes introduced into PAN-based composites. The influence of dispersion process of multi wall carbon nanotubes on mechanical properties and thermal stability of the obtained nanocomposites was studied.

2. Materials and methods

PAN-based composite containing MWCNTs has been prepared in the form of a thin film. The MWCNTs in this study were made by the arc discharge process (provided by NanoCraft, Inc. of Renton, USA). MWCNTs were 5 to 20nm in diameter and 300nm to 2000nm long. The structure of these nanotubes contains 99.5% carbon elements in the sp² form. The residual metal particles were not detected in this material.

Two preparation methods of MWCNTs/PAN solution were used:

I. Carbon nanotubes were immersed in the dimethylformamide (DMF) solution and sonicated at room temperature for 70 minutes using ultrasonic homogenizer - PALMER INSTRUMENTS, (Model: CP 130PB, 130W power, 20kHz) then PAN was added to the DMF/MWCNT solution and stirred until the polymer has been dissolved.

II. MWCNTs immersed in the PAN solution were directly sonicated at room temperature for 70min using ultrasounds. Such prepared suspensions were then poured on to Petri dish and left to evaporate the solvent at 40°C. The obtained composite samples were 60µm thick.

In such a way three kinds of samples, based on PAN solution containing multi wall carbon nanotubes, were prepared:

- PAN - control PAN polymer film (10% PAN solution dissolved in DMF solution);
- MWCNT-N - MWCNT/PAN composite film (0.5% by wt. carbon nanotubes in 10% PAN solution dissolved in DMF solution) – subjected to sonication process in PAN solution only;
- MWCNT-S - MWCNT/PAN composite film (0.5% by wt. carbon nanotubes in 10% PAN solution dissolved in DMF solution) – gradual sonication process in DMF and then in PAN solution;
- MWCNT-S1 - MWCNT/PAN composite film (1% by wt. carbon nanotubes in 10% PAN solution dissolved in DMF solution) - gradual sonication process in DMF and then in PAN solution;

The size distribution of carbon nanotubes in polymeric matrices, morphology, thermal stability and mechanical properties of nanocomposite samples were analyzed. The investigation of the particles size (agglomerates) was conducted in PAN polymer solutions by the method of DLS (Dynamic Light Scattering, Malvern Zetasizer Nano ZS) in the range from 0.6nm to 6µm, with the laser light source of the length of the wave λ = 520nm. The nanocomposite films were characterized by SEM (Nova NanoSEM 200, FEI) under magnification of 2 000x and 50 000x. The roughness of the composites surface was determined using profilometry technique (Hommel Tester T1000, Hommelwerke Co., Germany).

STA (Simultaneous Thermal Analysis) type SDT 2960 thermogravimetric analyzer (TA Instruments Co.) was used to determine the differences in both types of PAN-based samples and composite samples containing MWCNT (MWCNT-S and MWCNT-S1). The samples (3 mg) were placed in a platinum crucible and heated in air at 10°C/min to 1000°C.

The mechanical properties of the composites were measured using Zwick testing machine model 1435. Tensile mechanical test was made on the samples (5mm 40mm dimension).

3. Results and discussion

The agglomeration/dispersion of MWCNT in the PAN solution seem to be a crucial problem in preparation of suitable polymeric-based composites. In order to demonstrate the dispersion effect of
MWCNT, two different solutions were analyzed. The degree of dispersion of carbon nanotubes in the PAN suspensions sonicated by means of ultrasound for 70 minutes is shown in Figure 1.

![Size distribution of multi wall carbon nanotubes in 10%wt PAN solution for (MWCNT-N) and for (MWCNT-S)](image)

Figure 1. Size distribution of multi wall carbon nanotubes in 10%wt PAN solution for (MWCNT-N) and for (MWCNT-S)

The figure compares the agglomerates sizes and their distribution in polymer solutions, which were prepared in different way; mean value of the agglomerates dispersed and sonicated in pure DMF followed by PAN solution preparation is about 459 nm, while an introduction of nanotubes directly to PAN solution and sonication treatment causes creation of agglomerations of the size of 4145 nm. These two procedures of PAN solution containing MWCNTs reveal a strong influence of the sonication phase; gradual sonication of the suspension with nanotubes, first in DMF and then in 10% PAN solution leads to the distinctly more effective dispersion process of the nanotubes in the resulting PAN solution. As it results from our previous experiments the amount of carbon nanotubes does not have influence on its size distribution.

3.1. Roughness of nanocomposite surface

The presence of carbon nanotubes in the polymer matrices changes their surface topography (Table 1). The highest roughness was observed for nanocomposites containing large-size agglomerates. On the contrary, the lowest values of the surface roughness was obtained for pure PAN–based samples.

| Material  | PAN | MWCNT-N | MWCNT-S | MWCNT-S1 |
|-----------|-----|----------|----------|----------|
| Roughness Ra [µm] | 0.04±0.01 | 0.52±0.15 | 0.20±0.05 | 0.25±0.09 |

3.2. Mechanical properties

The results of the mechanical tests of PAN composite samples are summarized in Table 2. The presence of large-size defects in the composites (MWCNT-N) matrix caused by the agglomerated carbon particles resulted in a drastic fall in strength (almost 18%) and 54% decrease in Young’s modulus in comparison with the pure polymer. The mechanical properties of nanocomposites containing 0.5 %wt (MWCNT-S) and 1%wt (MWCNT-S1) nanotubes after an optimum dispersion process are considerably higher that those obtained for pure polymer samples and for the samples which were not sonicated (MWCNT-N). The samples of nanocomposites prepared from the suspension subjected to preliminary sonication in optimum condition show distinctly better mechanical properties as compared to those obtained from pure PAN samples (the tensile strength is 14% higher) and in comparison with sonicated in PAN solution (30% higher than MWCNT-N). It is
worth to note that the elongation to break the MWCNT-S1 sample is almost twice higher than that obtained for the pure PAN sample. Young’s modulus also increases for the nanocomposite samples in comparison with the pure polymer material. The most effective improvement of the mechanical properties was noted for the samples containing 1% wt of carbon nanotubes (MWCNT-S1). The polymer samples obtained by preliminary introduction of nanotubes in DMF have better mechanical properties. It may suggest that in these composite samples the carbon nanotubes are located between the polymer chains and probably have an influence on supramolecular structure of polyacrylonitrile during solidification.

### Table 2. Mechanical properties of pure PAN samples and composite samples.

| Material  | Tensile strength Rm [MPa] | Young’s modulus E [GPa] | Elongation to break ε [%] |
|-----------|--------------------------|------------------------|-------------------------|
| Before optimization process | | | |
| PAN       | 61,5±7,0                 | 2,6±0,4                | 5,9±0,5                 |
| MWCNT-N   | 50,7±5,1                 | 1,2±0,1                | 6,0±1,3                 |
| After optimization process | | | |
| MWCNT-S   | 72,0±3,3                 | 2,8±0,3                | 5,8±0,8                 |
| MWCNT-S1  | 80,4±7,7                 | 3,2±0,4                | 8,9±0,8                 |

In order to verify the possible orientation of CNTs in the polymer matrix, the fracture surface of the samples after breaking tensile test was observed using SEM (Figures 2 A,B). The microphotographs revealed that most of the carbon nanotubes demonstrate almost unidirectional orientation within the polymer matrix. The diameters of as–received MWCNTs are ranged from 5 to 20nm, whereas the observed carbon nanotubes over the cross-section area of the composites in the microphotograph (Fig.2B) are significantly thicker. It may be explained by the presence of a polymeric layer covering the nanotubes. The distinguished direction of the nanotubes orientation corresponds to the direction of a tensile force loading the samples. Thus, nanotubes are oriented parallel to the breaking force. It is the well known case that such nanoadditives in the form of nanotubes cannot act as classical fibrous reinforcement element (like in unidirectional fiber reinforced composite). To explain the possible role of carbon nanotubes in the improvement of the mechanical properties it can be assumed that these elements create a form of “cross-linking bridges” between the polymer chains.

3.3. Thermal analysis

Figures 4 A and B present the thermal degradation behavior of MWCNT/PAN nanocomposites with two different concentrations of MWCNTs. The DTA curves clearly show that the presence of MWCNTs inside the polymer matrix causes 3°C and 10°C displacement of the beginning of oxidation process of the composite samples towards lower temperature in comparison with pure PAN samples (312,7°C) (Figure 4A). TG curves (Figure 4B) indicate that during the oxidation at 200°C the observed
mass loss for the composite sample (MWCNT-S1) is almost twice lower (3.1 wt%) than for the samples made of pure PAN (5.1 wt%). It may suggest that the presence of well-dispersed nanotubes in the PAN solution enhances the crystallinity of PAN matrix, resulting in higher thermal stability of the composite samples during oxidation in air. DTA curves show that the degradation temperatures of MWCNT/PAN nanocomposites at maximum weight loss is 686.1°C and 708.9°C for the sample containing 0.5 wt% and 1 wt% of MWCNT, respectively. These values are higher than that for pure polymer sample (681.6°C). It is probable, that the amount of carbon nanotubes and their own thermal characteristics at maximum weight loss (778°C) have the decisive influence on the degradation temperature of the obtained nanocomposites. Hence, by adding a small amount of nanotubes into PAN polymer the temperature degradation is shifted towards higher values.

![Figure 4 A,B. Differential thermal analysis (DTA) (detail A) and thermogravimetry analysis (TG) (detail B) of pure PAN samples and composites samples: MWCNT-S and MWCNT-S1.](image)

4. Conclusion

MWCNs/PAN nanocomposites have been prepared and their selected properties analyzed. Preliminary sonication of MWCNTs in DMF solution followed by sonication of PAN suspension leads to effective dispersion of carbon nanotube in the PAN solution. Two samples differing in nanotubes amount (0.5 wt%, and 1 wt%) obtained in such a way represent good mechanical properties and distinctly higher that those measured for pure polymer samples. On the contrary, direct preparation of PAN solution with nanotubes and its subjecting to sonication results in aggregation of nanotubes within the solution, and the nanocomposite samples had poor mechanical properties. Data of thermal analysis
indicate that the presence of 1% wt of nanotubes in polymer matrix improves thermal stability of the obtained nanocomposite samples.

Acknowledgements
This work has been supported by the Polish Ministry of Science and Higher Education, project no 3763/T02/2006/31.

References
[1] Cato AD, Edie DD 2003 Flow behavior of mesophase pitch *Carbon* 41 1411-7
[2] Wangxi Z, Jie L, Gang W 2003 Evolution of structure and properties of PAN precursors during their conversion to carbon fibers *Carbon* 41(14) 2805-12
[3] Rahaman MSA, Ismail AF, Mustafa A 2007 A review of heat treatment on polyacrylonitrile fiber. *Polymer Degradation and Stability* 92 1421-1432
[4] Min BG, Sreekumar TV, Uchida T, Kumar S 2005 Oxidative stabilization of PAN/SWNT composite fiber *Carbon* 43 599–604
[5] Chae HG, Sreekumar TV, Uchida T, Kumar S 2005 A comparison of reinforcement efficiency of various types of carbon nanotubes in polyacrylonitrile fibers *Polymer* 46 10925-10935
[6] Lau KT, Hu D 2002 Effectiveness of using carbon nanotubes as nano-reinforcements for advanced composite structures *Carbon* 40 1597 — 1617
[7] Wan LS, Xu ZK, Huang XJ, Che AF, Wang ZG 2006 A novel process for the post-treatment of polyacrylonitrile-based membranes: Performance improvement and possible mechanism. *Journal of Membrane Science* 277 157–164
[8] Min HS, Ko JM, Kim DW 2003 Preparation and characterization of porous Polyacrylonitrile membranes for lithium-ion polymer batteries *Journal of Power Sources* 119-121 469-471
[9] Chae HG, Minus ML, Kumar S 2006 Oriented and exfoliated single wall carbon nanotubes in polyacrylonitrile. *Polymers* 47 3494-3504
[10] Barber AH, Cohen SR, Kenig S, Wagner HD 2004 Interfacial fracture energy measurements for multi-walled carbon nanotubes pulled from a polymer matrix. *Composites Science and Technology* 64 2283–2289
[11] Lau KT, Hui D 2002 Effectiveness of using carbon nanotubes as nano-reinforcements for advanced composites structures *Carbon* 40 1597-1617
[12] Kuan HC, Ma CCM, Chang WP, Yuen SM, Wu HH, Lee TM 2005 Synthesis, thermal, mechanical and rheological properties of multiwall carbon nanotubes/waterborne polyurethane nanocomposites *Composite Science and Technology* 65 1703-1710
[13] Thostenson ET, Ren Z, Chou TW 2001 Advances in the science and technology of carbon nanotubes and their composites: a review *Composites Science and Technology* 61 1899-912
[14] Haggenmueller R, Gommans HH, Rinzler AG, Fischer JE, Winey KI 2000 Aligned single-wall carbon nanotubes composites by melt processing methods *Chem Phys Lett* 330(3-4) 219-25
[15] Xiong J, Zheng Z, Qin X, Li M, Li H, Wang X 2006 The thermal and mechanical properties of polyurethane/multi-walled carbon nanotubes composite *Carbon* 44 270-2707
[16] Wei C, Srivastava D, Cho K 2002 Thermal expansion and diffusion coefficients of carbon nanotube-polymer composites *Nano Lett* 2 647–50
[17] Park C, Ounaies Z, Watson KA, Crooks RE, Smith JJ, Lowther SE, et al. 2002 Dispersion of single wall carbon nanotubes by in situ polymerization under sonication *Chem Phys Lett* 364 303–8
[18] Tsui F, Jin L, Zhou O 2000 Anisotropic magnetic susceptibility of multiwalled carbon nanotubes *Appl Phys Lett* 76 1452–4
[19] Sreekumar TV, Chandra L, Srivastava A, Kumar S 2007 Oxidative stabilization of polyacrylonitrile in the presence of functionalized carbon nanotubes *Carbon* 45 1105-1136
[20] Owens FJ 2005 Properties of composites of fluorininated single walled carbon nanotubes and polyacrylonitrile *Materials Letters* 59 3720-3723
[21] Xie XL, Mai YW, Zhou XP 2005 Dispersion and alignment of carbon nanotubes in polymer matrix: A review *Materials Science and Engineering R* 49 89–112