STRUCTURE AND PROPERTIES OF PAN BASED CARBON FIBERS MODIFIED WITH CARBON NANOTUBES

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Abstract

Carbon nanotubes have unique combination of mechanical, electrical and physico- chemical properties, what makes them attractive for potential various application in technical and medical areas. One of the major problem with the use of unmodified carbon nanotubes surface is its hydrophobic nature leading to agglomeration and creation of high size particles. In this study (MWNT) carbon nanotubes were introduced into (PAN) polyacrylonitryle solution in order to prepare PAN fibers precursor for carbon fibers. The precursor fibers were spun from solution containing multi wall carbon nanotubes and such fibers were subsequently subjected to further heat treatment. Morphology and selected physical and mechanical properties of composite polymeric fibers and the fibers after heat treatment up to 1500^{o}C were characterized..

Keywords: Carbon fibers, Carbon nanotubes, Carbon composites

Introduction

Polyacrylonitrile-based polymers belong to the most popular precursors of carbon fibers for composite technologies. Recently, various polymeric matrices were investigated by mixing them with small amount of constituents in the form of nanoparticles. Such nanocomposites exhibit to have some of their physical and mechanical properties superior to those of conventional composites reinforced with microcomponents. Carbon nanotubes constitute one of the possible nanocomponent to modify polymeric matrix of composite. Their properties including mechanical and electrical make them interesting component of composite. However, the use of nanoparticles is often accompanied by the problem of their dispersion in polymeric solution. Because of strong interaction between the nanoparticles, they have strong tendency to created agglomerates.
This work presents preliminary results related to the problem of preparation of PAN precursor with carbon nanotubes and its further treatment to obtain carbon fibers. The purpose of this investigation was to determine the effect of carbon nanotubes introduced into PAN solution in DMF followed by spinning process of PAN fibers on carbonization process of such a precursor. The structure, microstructure, mechanical and electrical properties of the fibers after carbonisation process were studied.

Material and methods

Spinning solution were prepared from polyacrylonitrile (PAN), Mavilon, from Hungarian firm Zoltek. Multiwall carbon nanotubes, used in this study, were made by electric arc process purchased from NanoCraft, Inc. of Renton (USA). Fiber precursors were spun from the solution in DMF containing multiwall nanotubes (MWNT). The diameters of nanotubes were about 5-20 nm and 300 to 2000 nm long.
Fibers were spun from the polymer solution by the wet-spinning process. A spinneret with 240 orifices of a diameter 80μm was used. The drawing process was performed in two stages: in a plasticising bath at a temperature of 70^{o}C and under superheated steam at 135^{o}C-140^{o}C, respectively.
Three kinds of PAN fibers have been prepared:

a) PAN - control PAN polymer fibers (22% PAN spinning solution dissolved in DMF solution, total drawing of the fibers during the bath was about 100 %);

b) NANO3 - MWNT/PAN composite fibers (3% by wt. carbon nanotubes in 22% PAN spinning solution dissolved in DMF solution);

c) NANO5 - MWNT/PAN composites fibers (5% by wt. carbon nanotubes in 22% PAN spinning solution dissolved in DMF solution,);

All fibers were oxidized at 240^{o}C for 8 h followed by carbonization at 1000^{o}C for 3h. Mechanical properties of the fibers were determined using Zwick machine. Microstructure of the fibers was examined with the scanning electron microscope (Jeol model JSM 5400). Structural parameters of carbon fibers were determined from X-ray diffraction.The electrical resistivity was measured from liquid nitrogen to 120^{o}C.

Results

X-ray diffraction analysis revealed a distinct difference in crystallites size (L_c) of carbon fibers containing carbon nanotubes in comparison to the pure carbon fibers, while both types of fibers show similar interplanar distances (d_{002}). The parameters were determined for the fibers carbonized at 1500°C, and Table 1 gathers the determined values. The fibers containing small amount of carbon nanotubes have greater crystallites.

Table 1. Structural and microstructural parameters of carbon fibers

Temperature, ^{0}C	Control		Modified	
	d_{002}, Å	L_c, Å	d_{002}, Å	L_c, Å
1500	3,43	35,32	3,43	42,41

Mechanical properties of carbon fibers prepared from pure PAN precursor and PAN modified with nanoparticles are shown in Figure 1,2.

It may be seen from these diagrams that mechanical properties of carbon fibers are relatively low and lower in comparison to carbon fiber precursor. The lowest values of mechanical parameters were obtained for NANO5 (Rm=0,3±0,1GPa) fibers characterized by higher concentration of nanofibers. On the other hand, 3% nanotubes added to PAN polymer does not change significantly carbon fiber strength (Rm=0,36±0,12GPa) as compared to the control PAN fibers (Rm=0,38±0,08GPa).

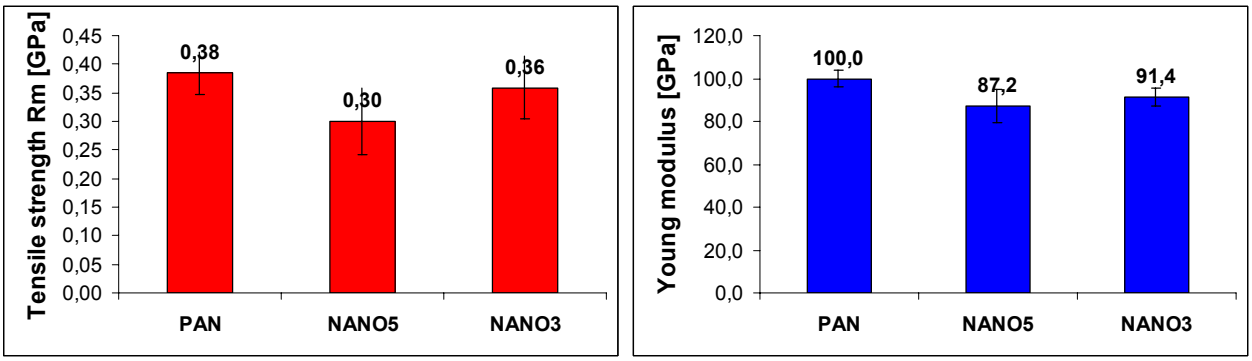

Figure 1,2. Mechanical properties of PAN-based and nanotubes – containing PAN-based carbon fibers after carbonization process at 1000°C.

SEM analysis shows that high – size defects are found in the fibers as a result of agglomeration of nanoparticles, (Figure 3, 4). The agglomerates and high size pores became a source of stresses concentration reducing the mechanical properties of carbon fibers. Large- sized voids on the surface of carbon fibers were created during HT as a results of partial detaching the nanotubes.

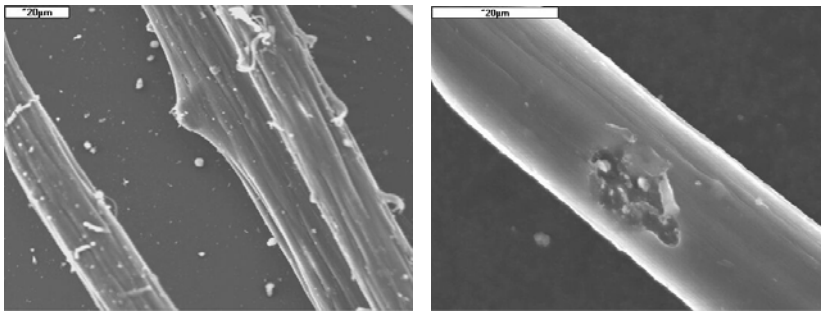

Figure 3,4. SEM microphotograph of carbon fibers containing carbon nanotubes.

Figure 5 compares the temperature dependences of the electrical resistances of carbon fibers obtained from pure PAN precursor and PAN modified with nanoparticles after carbonization at 1000°C. Resistivity mesurements showed that this property decreases with temperature from 7,8 μΩ*cm at -185°C , to 3,3 μΩ*cm at 120°C, respectively, for NANO5 sample. The presence of nanoadditives in carbon fibers decreases their resistance in comparison with pristine carbon fibers. The

differences in electrical properties between the carbon fibers studied are higher at low temperature, while at higher temperature range become lower.

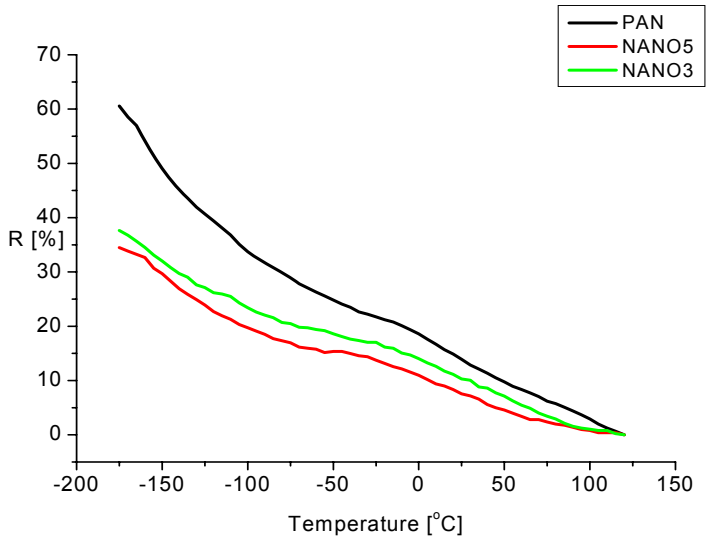

Figure 5. Relative resistance changes versus temperature for pure and modified carbon fibers.

Conclusion

The preliminary study indicates weak effect of CNT's on mechanical properties of the PAN precursors fibers. It may suggest that interaction between the polymer and nanocarbon phase is very low. Nanotubes were observed to have large tendency to create agglomerates. Simple sonification did not improve homogeneous dispersion of PAN solution before spinning process. Weak dispersion of carbon nanotubes and their non-uniform concentration in carbon fibers seem to be the major reason of reduction in the mechanical properties of the fibers after carbonization.
Further study will concentrate on preparation of homogeneously dispersed nanotubes in PAN solution and on determination of optimum nanotubes concentration to obtain suitable PAN precursor for carbon fibers of improved mechanical properties.

Acknowledgement

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