

A HOT-STRETCHED NANOFIBER SHEET OF POLYACRYLONITRILE/MULTI-WALLED CARBON NANOTUBE COMPOSITES

Yanxin Liu, Zhongjie Du, Xiaoping Yang, The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, P. R. China
Jigui Lu, Seungkon Ryu, Department of Chemical Engineering, Chungnam National University, Daejeon 305-764, Korea

Abstract

A hot-stretched nanofiber sheet of polyacrylonitrile (PAN)/multi-walled carbon nanotube (MWCNT) composites was prepared by electrospinning of suspension, which was composed of PAN terpolymer and MWCNT, and by stretching the sheet at elevated temperature along the rotating direction of the fiber collector to improve mechanical properties of carbon composites. MWCNT was acid-modified to increase hydroxyl groups on the surface and covalent grafted with PAN bound carboxylic acid before mixing to PAN. TEM observation was carried out to confirm the existence of MWCNT in the nanofiber sheet. SEM observations have shown a strong adhesion of MWCNT to PAN in the stretched sheet. Electrospun fiber diameters of PAN and PAN/MWCNT were ranged 100-400 nm and 100-300 nm, respectively. When the sheet was hot-stretched, the average diameter decreased to one-half of the PAN/MWCNT nanofiber, the tensile strength and the modulus of the sheet increased as much as 251% and 118%, respectively in comparison with those of PAN nanofiber sheet. This was attributed to the well orientation of the MWNT along the fiber axis and compact stack of the nanofiber in the sheet. Moreover, the elongation of the sheet was reduced from 15.5% to 7.7% showing a heat stable composite material.

Introduction

Recently, multi-walled carbon nanotubes (MWCNTs) have been considered promising materials for the reinforcement of electrospun polymer nanofibers due to their excellent mechanical properties. However, the smooth surface of MWCNTs provides poor interfacial adhesion to the polymer matrix in the composite nanofibers. To improve the interfacial adhesion, surface modification of nanotubes is needed. Acid oxidization and covalent grafting of MWCNTs with matrix polymer are useful methods to enhance the interfacial adhesion of MWCNTs to the matrix. In a previous study, we demonstrated that oxidization of MWCNTs with concentrated $H_2SO_4-HNO_3$ (1:1, v/v) developed a large number of hydroxyl groups on the surface of MWCNTs. Here, MWCNTs were modified by grafting polyacrylonitrile copolymer chains onto the nanotube surface to improve their dispersion and interfacial adhesion to the polyacrylonitrile matrix. Polyacrylonitrile copolymer (PAN) (Mw=100,000 g/mol, UK Courtaulds Co.) composed of 93.0 wt% acrylonitrile, 5.3 wt% methyl acrylate and 1.7 wt% itaconic acid was used for functionalization of the MWCNTs. The hydroxyl groups present on the acid-oxidized MWCNTs reacted with the PAN-bound carboxylic acid in the presence of N, N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). Transmission electron microscopy and scanning electron microscopy (TEM, SEM) observations confirmed the functionalization.

Methods and procedures

PAN terpolymer was used for the graft-functionalization of MWNTs. 200 mg of PAN in 10 ml N, N'-dimethylformamide (DMF) was mixed to 50 ml DMF suspension containing 40.0 mg of acid-modified MWNTs, 50.0mg of DCC and 25.0 mg of DMAP. The resulting suspension was ultrasonically vibrated for 30 min and then stirred for 48 hours at 60°C under the nitrogen atmosphere. After vacuum filtration of the suspension, the extract was washed several times with DMF and homogenized again in DMF with ultrasonic vibrator for 30 min and then maintained it without stirring for 24 hours. Repeating this operation 8 times, the final product was dried under vacuum for 8 hours at 50°C.

A suspension for electrospinning was prepared by the ultrasonic mixing of 0.04 g PAN-functionalized MWCNTs, 2.0 g of PAN and 20.0 ml of DMF for 4 hours. Electrospinning was carried out at 23 °C using a 14 kV applied voltage with a distance of 140 mm between the spinneret and the fiber collector. The electrospun nanofibers were collected as a sheet on a 16 cm diameter drum rotating at a rate of 10.0 m/s, and the sheet was hot-stretched along the fiber direction using a 0.74 N tensile force under an air atmosphere at 140 °C for 5.0 minutes with a stretch ratio of 1.2.

Results and discussion

Figure 1 show TEM images of (a) acid-oxidized MWCNTs and (b) PAN-functionalized MWCNTs, and SEM images of (c) acid-oxidized MWCNTs and (d) PAN-functionalized MWCNTs. From TEM images, the acid-oxidized MWCNTs exhibited a semi-transparent appearance with sharp contrast to the background, while the edge of the PAN-functionalized MWCNTs became blurred. Also, the surface of PAN-functionalized MWCNTs looked smeared due to the swelling of the grafted polymer, in contrast to the smooth surface of acid-oxidized MWNTs. The SEM image of PAN-functionalized MWCNTs showed that the surface of the MWCNTs was surrounded by other materials. These results demonstrated PAN was linked to the surfaces of the MWCNTs.

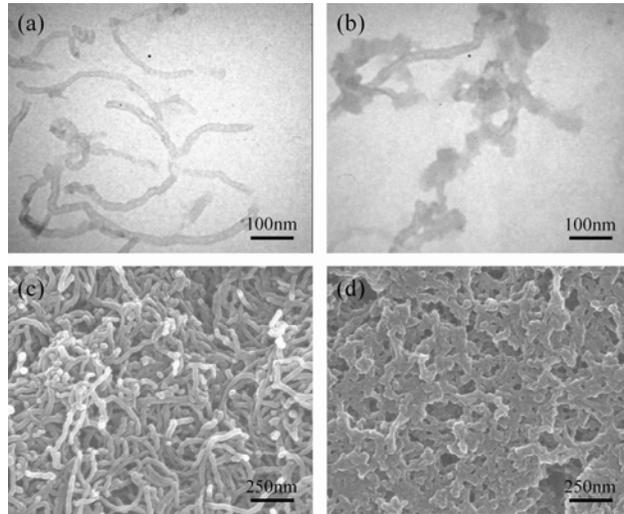


Figure 1. TEM images of (a) acid-oxidized MWCNTs, (b) PAN-functionalized MWCNTs, and SEM images of (c) acid-oxidized MWCNTs, and (d) PAN-functionalized MWCNTs.

Figure 2 shows SEM images of (a, b) a sheet of PAN nanofibers, (c, d) a sheet of PAN/MWCNT composite nanofibers, and (e, f) a hot-stretched sheet of PAN/MWCNT composite nanofibers. The rotating collector produced some alignment of the electrospun fibers in the sheet. In contrast to the non-stretched fibers, the hot-stretched fibers showed a remarkable alignment along the sheet. Fiber diameters were measured using Image J software and are listed in Table 1. The average diameter of the hot-stretched PAN/MWCNT composite fibers was in the range of 50-150 nm, which was one half of the non-stretched fibers. The fibers were well compacted in the hot-stretched sheet.

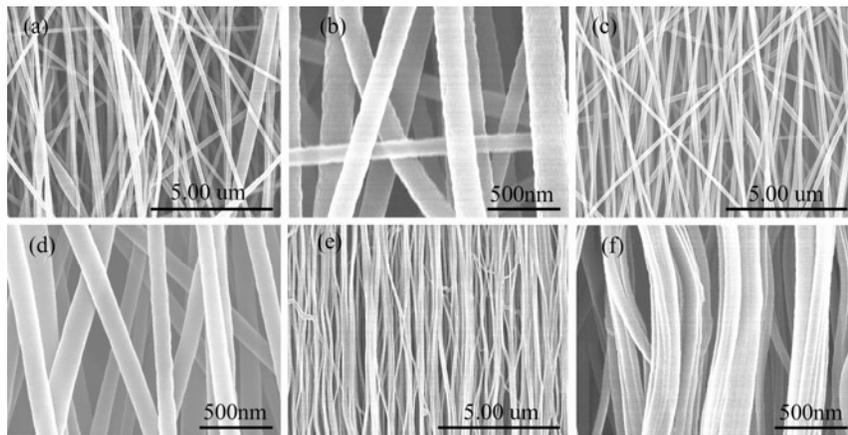


Figure 2. SEM images of (a, b) a sheet of pure PAN nanofibers, (c, d) a sheet of PAN/MWCNT composite nanofibers, and (e, f) a hot-stretched sheet of PAN/MWCNT composite nanofibers.

Figure 3(a) shows a TEM image of a non-stretched composite nanofiber. The average diameter of the fiber is in the range of 100-300 nm (Table 1), and MWCNTs with a diameter of 10-20 nm were well aligned along the fiber axis in the composite fiber. **Figure 3(b)** shows a fracture surface of non-stretched composite fiber obtained from the broken sheet after tensile testing. A nanotube was pulled out of the fiber, while the other end of the tube was still embedded in the fiber. The diameter of the stretched nanotube was larger than that of PAN-functionalized MWCNTs. It is believed that some polymer that was strongly attached to the MWCNTs was drawn together from the nanofiber host. This indicated strong interfacial adhesion between carbon nanotubes and the PAN matrix in the composite nanofiber. This interconnection originated from the PAN molecule chains grafted on the surface of MWCNTs which acted as a link between the nanotube and the PAN matrix.

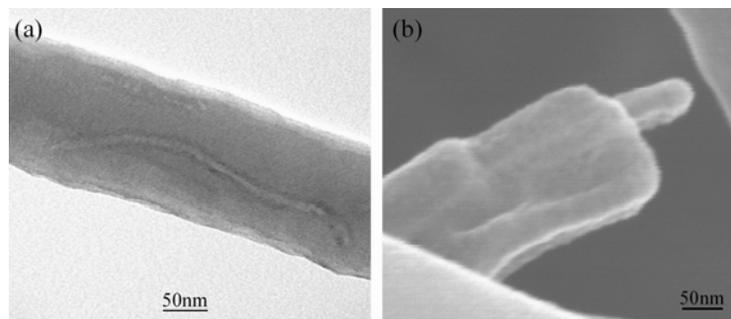


Figure 3. (a) TEM image of PAN/MWCNT composite nanofiber prepared by electrospinning and (b) SEM image of the fracture surface of PAN/MWCNT composite nanofibers.

Figure 4 shows a relationship between strain and tensile strength for various nanofiber sheets. Tensile testing of the nanofiber sheets was conducted along the fiber direction. The detailed mechanical properties are listed in Table 1. When PAN-functionalized MWCNTs (2.0 wt % of MWCNTs with respect to the PAN matrix) were incorporated into the composite nanofiber sheet, the tensile strength and modulus were increased by as much as 122.5 % and 6.7 % respectively, compared to those of a non-stretched sheet of these fibers, and increased by 251.5 % and 118.2 % respectively, compared to those of a sheet of pure PAN nanofibers. Moreover, the elongation of the hot-stretched sheet was reduced by 10.5 % and 50.0 % respectively, compared to those of non-stretched sheet and a pure PAN nanofiber sheet. This was attributed to the remarkable alignment of MWCNTs in the fibers, strong interfacial adhesion between nanotubes and the PAN matrix, and compact unidirectional stacking of nanofibers in the hot-stretched sheet of composite nanofibers.

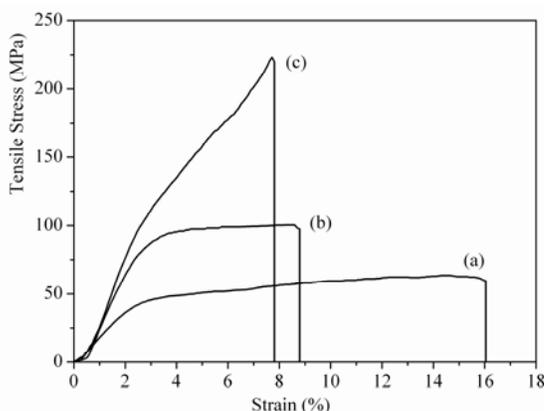


Figure 4. Stress-strain curves of (a) a sheet of pure PAN nanofibers, (b) a sheet of PAN/MWCNT composite nanofibers, and (c) a hot-stretched sheet of PAN/MWCNT composite nanofibers.

Table 1. Mechanical properties of various nanofiber sheets.

Nanofiber sheet	Diameter (nm)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PAN	100~400	63.5	2.2	15.4
PAN/MWCNT	100~300	100.3	4.5	8.6
Heat-stretched PAN/MWCNT	50~200	223.2	4.8	7.7

In summary, MWCNTs were modified by grafting PAN chains onto the nanotube surface to improve their dispersion and interfacial adhesion to a PAN matrix. Composite nanofibers were then prepared by electrospinning. A hot-stretched sheet of these nanofibers exhibited larger tensile strengths and moduli than non-stretched and pure PAN nanofiber sheets.

Acknowledgements

The authors thank the National Natural Science Foundation of China (No. 50503004 and 30471907) for their support.

References

- Ge, J. J. and Hou, H. 2004. Assembly of well-aligned multiwalled carbon nanotubes in confined polyacrylonitrile environments: electrospun composites nanofiber sheets. *Journal of the American Chemistry Society* 126(48):15754-15761.
- Hou, H. and Ge, J. J. 2005. Electrospun polyacrylonitrile nanofibers containing a high concentration of well-aligned multiwall carbon nanotubes. *Chemistry of Materials* 17(5):967-973.
- Kong, H. and Gao, C. 2004. Controlled functionalization of multiwalled carbon nanotubes by in situ atom transfer radical polymerization. *Journal of the American Chemistry Society* 126(2):412-413.
- Lin, Y. and Zhou, B. 2003. Polymeric carbon nanocomposites from carbon nanotubes functionalized with matrix polymer. *Macromolecules* 36(19):7199-7204.
- Liu, Y. and Du Z. 2006. Covalent functionalization of multiwalled carbon nanotubes with poly (acrylic acid). *Chinese Journal of Chemistry* 24(4):563-568.
- Sen, R. and Zhao, B. 2004. Preparation of single-walled carbon nanotube reinforced polystyrene and polyurethane nanofibers and membranes by electrospinning. *Nano Letter* 4(3):459-464.
- Zhang, W. D. and Shen, L. 2004. Carbon nanotubes reinforced nylon-6 composite prepared by simple melt-compounding. *Macromolecules* 37(2):256-259.