Effect of Amine-Functionalized Carbon Nanotubes on the Properties of CNT-PAN Composite Nanofibers

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Abstract—PAN nanofibers reinforced with amine functionalized carbon nanotubes. The effect of amine functionalization and the effect of concentration of CNT on the conductivity and mechanical and morphological properties of composite nanofibers were examined. 1%CNT-NH_2 loaded PAN/CNT nanofiber showed the best mechanical properties. Conductivity increased with the incorporation of carbon nanotubes. While an increase of concentration of CNT increases the diameter of nanofiber, the use of functionalized CNT results to decrease of diameter of nanofiber.

Keywords—Amine functionalized carbon nanotube, electrospinning, nanofiber, polyacrylonitrile.

I. INTRODUCTION

AS reported by Iijima in 1990, carbon nanotubes (CNTs) are ideal materials for reinforcing polymer materials because of their high structural, mechanical, chemical, thermal and electrical performance [1], [2]. Dispersion of filler in polymer matrix and the interaction between the nano filler and polymer matrix affect the final properties of nano polymer composite [3], [4]. The chemical functionalization of CNT provides improvement adhesion between nanotubes and the polymer matrix leading to an effective stress transfer at the polymer-filler interface [5]. Functionalization of CNT improves the compability of CNT and the solubility [6]. However ın the case of composites made with functionalized carbon nanotubes, thanks to attached groups on the surface of CNTs, providing better interfacial bonding which leads to higher tensile strength of composites [7]. Amine functionalized carbon nanotubes/polymer composites has been a major interest lately. Due to strong π-π interaction between functionalized carbon nanotubes surface and nitrile group of PAN matrix, better adhesion is formed and it improves the thermal and mechanical properties [4].

In this study, the effect of NH_2 functional group of CNT and the different CNT loading on properties of Polyacrylonitril-Carbon nanotubes composite nanofiber has been studied. The morphology, thermal and mechanical, electrical conductivity properties of composite nanofibers which are produced by electrospinning technique have been analyzed.

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II. EXPERIMENTAL

A. Materials

PAN possessed a molecular weight of 150.000 g/mol was purchased from Sigma Aldrich. MWCNTs (NTP, from China) as pristine MWCNT (diameter 60-100 nm, length 5-15 μm).

Sodium nitrite ($NaNO_2$) was purchased from Merck. Isophorone diamine, Tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) and NaOH were also used.

B. Instrumentation

The FT-IR spectra of pristine and functionalized MWCNTs were recorded using Nicolet IS10 FT-IR spectrometer. A minimum of 16 scans were averaged with a signal resolution of 4 cm^{-1} within the 400–4000 cm^{-1} range and KBr pellet method was used to prepare samples.

The morphology and structure of the functionalized CNTs and CNT/PAN nanofibers were investigated by SEM Carl Zeiss EVO MA10. The SEM tests were applied at 5 kV voltage. Microtest LCR Meter 6370 (0,01 mΩ-100 MΩ) with two probe-four wire was used for measuring the electrical conductivity. Average has been taken from seven and more samples.

Tensile tester was used for the evaluation of mechanical properties. Average has been taken from seven and more samples. The crosshead speed was 20 mm/min and the gauge length was 15 mm. The length of nanofibers was 5 cm and the width was 5 mm. The nanofiber thicknesses were measured with digital micrometer.

C. Functionalization of Carbon Nanotubes

Zhao et al.'s amino functionalization method was used to functionalize carbon nanotubes [8]. 200 mg MWCNTs-COOH (functionalized from pristine carbon nanotube) were mixed with 580 mg $NaNO_2$ and 0,5 ml ısophoronediamine. 0,36 ml concentrated H_2SO_4 and 10 ml DMF was added into. The mixture, then stirred in the magnetic stirrer and heated for 1 h at 60°C. Then the mixture was cooled to room temperature and DMF was added to wash the solution. The mixture was filtered with a PTFE membrane (0.45 μm pore size). The solid was washed with DMF and filtered again, and this process was repeated until the DMF was colorless after filtration. This process removed any unreacted substance from the product. The sample was then dried at 60°C for overnight under vacuum to obtain MWCNT-NH_2 (amine functionalized multiwall carbon nanotube, f-CNT).

D. Preparation of Composite Nanofibers

1 and 3 wt% f-CNT/DMF solution was dispersed with ultrasonic homogenizer for 10 minutes and then processed with ultrasonic bath for 45 minutes. PAN (with 7 wt% PAN concentration) was dissolved in the stable suspension of MWCNT in DMF. After the addition of PAN, solution was stirred at 60°C by magnetic stirring. Then the solution was feeded into electrospinnig system in order to produce nanofiber web. On electrospinning system, the feeding rate of the polymer solutions was 1 mL/h with 15 kV electrospinning voltage and the distance between the needle tip and collector was 10 cm.

III. RESULTS AND DISCUSSION

A. Infrared Spectroscopy

FT-IR was used to monitor the surface functional groups at functionalized CNT. KBr pellets were used to characterize amine functionalized carbon nanotubes.

Peaks at 3400-3500 cm-1 can be attributed to –OH and N-H stretching [8]. Peak at 1632 cm^{-1} can be assigned to C-C stretching of carbon nanotube structure and C=O stretching of amide structure. Peaks at 1547 cm^{-1} and 1139 cm^{-1} are attributed to C-NH, C=N and C-C stretching respectively. N-C=O stretching at 621 cm^{-1} is obtained. Peaks show that amine functionalized CNT could be obtained from this process the amide structure [9].
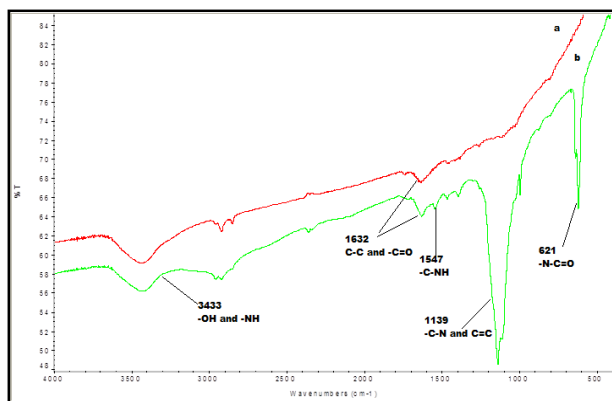

Fig. 1 FTIR spectra of a) pristine carbon nanotube b) amine functionalized carbon nanotube

B. The Morphology of Composite Nanofibers

The SEM images of PAN/CNT composite nanofibers can be seen in Fıg 2. The surface morphology of the the 1% CNT loaded nanofiber is smooth and straight. With the 3% CNT loading, some agglomerations occur. Also the bead formation was observed at 3% CNT loaded nanofiber due to less dispersion and agglomeration of CNTs at high concentration. Beads areas act as stress concentration points which affect the mechanical properties [10].
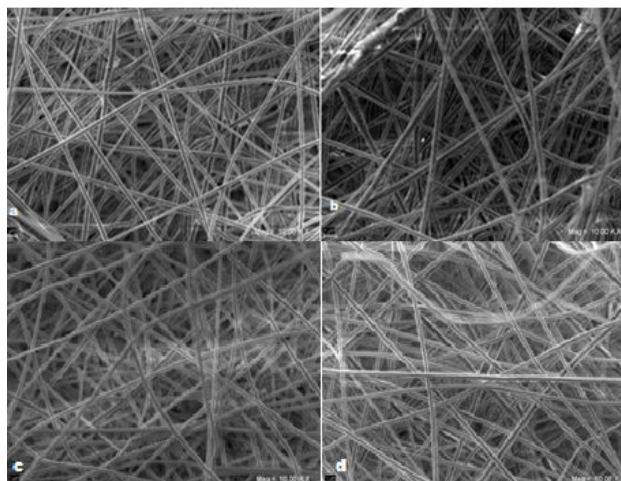

Fig. 2 Sem images of a) 1% CNT loaded PAN/CNT nanofiber b) 3% CNT loaded PAN/CNT nanofiber c) 1% CNT-NH_2 loaded PAN/CNT nanofiber d) 3% CNT-NH_2 loaded PAN/CNT nanofiber

Diameters of composite nanofibers can be seen at Table I. 1% CNT loaded PAN/CNT nanofiber's diameter is 338 nm while 3% CNT loaded PAN/CNT nanofiber's diameter is 343 nm. An increase in the concentration of carbon nanotubes increases the viscosity. Increased viscosity enlarges the diameter of nanofibers. But with the functionalization of carbon nanotubes, diameters of nanofibers decrease compared to pristine carbon nanotubes/PAN nanofibers. It may be due to an increase of conductivity of the solution that leads to accelerating the jet [11].

TABLE I
DIAMETERS OF COMPOSITE NANOFIBERS

1% CNT loaded PAN/CNT nanofiber (nm)	1% CNT-NH_2 loaded PAN/CNT nanofiber (nm)	3% CNT loaded PAN/CNT nanofiber (nm)	3% CNT-NH_2 loaded PAN/CNT nanofiber (nm)
338	333	343	308

C. Mechanical Properties of Composite Nanofibers

In Table II, mechanical properties of pristine and functional carbon nanotube/PAN composite nanofibers can be seen. With the 3% loading of carbon nanotube, tensile strength decreases, this may be due to an increase of agglomeration and beads in the structure. Also amine functional group improves the mechanical properties thanks to amine group's better interfacial bonding in PAN matrix due to the presence of nitrile group in the PAN $(C_3H_3N)_n$ [12].

TABLE II
MECHANICAL PROPERTIES OF COMPOSITE NANOFIBERS

	Tensile Strength (N/mm^2)	Tensile Strain (%)	Modulus (N/mm^2)
1% CNT loaded PAN/CNT nanofiber	2,18	12,63	19,53
1%CNT-NH$_2$ loaded PAN/CNT nanofiber	2,41	14,32	22,83
3% CNT loaded PAN/CNT nanofiber	1,7	12,65	9,09
3% CNT-NH$_2$ loaded PAN/CNT nanofiber	2	16,23	9,52

D. Conductivity of Composite Nanofibers

Normally, PAN has insulating behavior in solutions and nanofibers. It is reinforced with nanofiller or other polymers to improve conductivity. As seen in Table III, 1 and 3 % CNT loaded PAN nanofiber demonstrate $2,6 \times 10^{-7}$ S/cm and $1,63 \times 10^{-7}$ S/cm respectively. But functional group on the surface of carbon nanotube did not show significant changes. Thanks to good dispersion, polymeric layer is formed around the CNTs and it ensulates them. Thus, due to inhibition of formation conductive network in the polymer, conductivity does not improve much [12].

TABLE III
CONDUCTIVITY OF COMPOSITE NANOFIBERS

	Conductivity (S/cm)
CNT/PAN nanofiber (%1)	$2,6 \times 10^{-7}$
CNT-NH$_2$/PAN nanofiber (%1)	$2,6 \times 10^{-7}$
CNT/PAN nanofiber (%3)	$1,63 \times 10^{-7}$
CNT-NH$_2$/PAN nanofiber (%3)	$1,56 \times 10^{-7}$

IV. CONCLUSION

Amine groups have been attached on the surface of carbon nanotubes successfully.

Polyacrylonitrile nanofibers reinforced with amine functionalized carbon nanotubes have been prepared by electrospinning.

Diameters of nanofibers increased with the increasing viscosity. 1 % carbon nanotubes loaded nanofibers showed the best mechanical properties. It indicates that some agglomerations occur at high amounts of carbon nanotubes and nanofiber's mechanical properties reduced.

Carbon nanotubes also improved the conductivity of ınsultor PAN nanofibers.

While an increase in the concentration of carbon nanotubes increases the diameter of nanofiber, functionalization of CNT results to decrease of diameter of nanofiber.

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