Effect of differently functionalized carbon nanotubes on the properties of composite nanofibres

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Effect of differently functionalized (carboxyl, amine and hydroxyl functionalized) multi-walled carbon nanotubes (MWCNTs) on the structure and properties of composite polyacrylonitrile nanofibres produced by electrospinning has been studied. Fourier transform infrared spectroscopy has been used to confirm the successful functionalization of carbon nanotubes while mechanical testing, electrical conductivity, scanning electron microscopy, differential scanning calorimetry and X-ray diffraction analysis have been used to characterize the composite polyacrylonitrile nanofibre webs. The addition of MWCNTs, either pristine or functionalized, results in slight increases in the diameter of nanofibres. The tensile strength, crystallinity, thermal properties are all found to be affected by the functional groups of the carbon nanotubes, while the conductivities of the nanowebs seem to be insensitive to the different functional groups of the carbon nanotubes.

Keywords: Carbon nanotubes, Composite, Electrospinning, Nanofibre, Polyacrylonitrile

1 Introduction

Carbon nanotubes (CNTs) are ideal reinforcing materials for polymers due to their excellent mechanical, electrical and thermal conductivity properties[1-4] and hence have been increasingly incorporated into polymers with the main challenge of achieving a good dispersion. Due to the strong intrinsic van der Waals forces, CNTs can aggregate and entangle together. The dispersibility of CNTs in various polymers is improved significantly by functionalization. The functional groups are also useful for the formation of further chemical links with other compounds[5,6].

As it is well known, polyacrylonitrile (PAN) is a notable polymer with its good stability and mechanical properties. It can be used in a variety of applications including textiles, automotive industry, medical sector as implant materials and drug delivery materials and plant coverings and for filtration applications[7]. Significant amount of research work has been reported on the incorporation of different types of CNTs into polymeric materials to form new types of composites that possess high mechanical, electrical and thermal conductivity properties. Good dispersion and good interfacial adhesion between the polymer matrix and the CNTs are essential to improve the mechanical and other properties of polymer/CNT nanocomposites[8]. Thus, there are various studies performed for the functionalization of CNTs[5-7,9]. There are many studies in literature about composite polymers containing carbon nanotubes[1,8,10-18] —either with carboxyl or amine functional groups. However, there are no studies performed in detail with the aim of comparing the effect of carbon nanotubes with different functional groups such as hydroxyl, amine and carboxyl on composite nanofibre webs, although it is very important to determine the most suitable functional group in order to have a better dispersion of carbon nanotubes, better adhesion between carbon nanotubes and polymer and to get the maximum benefit from the carbon nanotubes. All these may have an impact on tensile properties, crystallinity, thermal properties, etc. Besides, it is possible to find commercial composite products of hydroxyl-functionalized carbon nanotubes (CNT-OH), but it is difficult to find any studies related with the polymer composites containing CNT-OH[8].

Thus, in this study, comparative analysis has been performed between the pure PAN nanofibre web and the PAN composite nanofibre webs produced with pristine carbon nanotubes (p-MWCNT), carboxyl-

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functionalized carbon nanotubes (MWCNT-COOH), hydroxyl-functionalized carbon nanotubes (MWCNT-OH) and amine-functionalized carbon nanotubes (MWCNT-NH$_2$) using comprehensive characterization techniques such as electrical conductivity measurement, mechanical testing, Fourier transform ınfrared spectroscopy (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

2 Materials and Methods

2.1 Materials

PAN with a molecular weight of 150,000 g/mol was purchased from Sigma Aldrich. Multi-walled carbon nanotubes (MWCNTs) (diameter 60-100 nm, length 5-15 µm) were purchased from NTP China. Concentrated (98%) sulphuric acid (H$_2$SO$_4$), concentrated (65%) nitric acid (HNO$_3$), sodium nitrite (NaNO$_2$), thionyl chloride (SOCl$_2$) and ethylene glycol were purchased from Merck. Isophorone diamine, tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and sodium hydroxide (NaOH) were also used. All the chemicals were used as received without further purification.

2.2 Methods

2.2.1 Synthesis of MWNT-COOH

Gao *et al.*[19] method was used to carboxyl-functionalize the carbon nanotubes. MWCNT-COOH were prepared by oxidation of p-MWCNTs in a concentrated H$_2$SO$_4$/HNO$_3$ (3:1 by volume) mixture. Into a flask equipped with a condenser, p-MWCNTs (3 g), HNO$_3$ (65%, 25 mL), and H$_2$SO$_4$ (98%, 75 mL) were added with vigorous stirring. Before the reaction, flask was immersed in an ultrasonic bath (40 kHz) for 10 min. Then mixture was stirred for 100 min under reflux; the oil bath temperature was increased gradually from 90 °C to 133 °C. Aqueous NaOH was used to collect and treat the evolved brown gas. After cooling to room temperature, the reaction mixture was diluted with deionized water and then vacuum-filtered through a filter paper (Whatman 0.45 µm PTFE filter). The solid was dispersed in water and filtered again. Then distilled water was used to wash the filter cake several times. The dispersion, filtering, and washing steps were repeated until the *p*H of the filtrate reached 7 (at least four cycles were required). The filtered solid was dried under vacuum for 24 h at 60 °C, giving 1.8 g of MWCNT-COOH.

2.2.2 Synthesis of MWNT-OH

Gao *et al.*[19] method was used to hydroxyl-functionalize the carbon nanotubes. The as-prepared MWNT-COOH (0.2 g) was reacted with excess neat thionyl chloride (SOCl$_2$) (50 mL, 0.685 mol) for 24 h under reflux (the temperature of oil bath was 65-70 °C). After the reaction, the mixture was washed with THF (tetrahydrofuran) and filtered. In this section, acyl chloride-functionalized MWCNTs was obtained (MWCNT-COCl). The as-produced MWCNT-COCl was immediately reacted without further purification with glycol (50 mL, 0.9 mol) for 48 h at 120 °C. MWCNT-OH (0.05 g) was obtained by repeated filtration and washing with the distilled water.

2.2.3 Synthesis of MWNT-NH$_2$

Zhao *et al.*[5] method was used to amine-functionalize the carbon nanotubes. MWCNT-COOH (200 mg) was mixed with NaNO$_2$ (580 mg) and isophorone diamine (0.5 mL). Concentrated H$_2$SO$_4$ (0.36 mL) and 10 mL DMF was added. Then the mixture was stirred and heated for 1 h at 60 °C. The mixture was cooled to room temperature, then DMF was added and the mixture was filtered with a PTFE membrane (0.45 µm pore size). The solid was sonicated in DMF and filtered again, and the process was repeated till the DMF became colorless after sonication. The sample was then dried at 60 °C overnight under vacuum. 0.014 g MWCNT-NH$_2$ was obtained. The low yield of the amine-functionalization process was due to the repeated washing and filtration processes applied.

2.2.4 Preparation of PAN/MWCNT Composite Nanofibres

Required amount of either pristine or functionalized MWCNTs were added to the required amount of DMF and dispersed by ultrasonic tip for 10 min followed by the application of ultrasonic bath for 45 min. PAN (7 wt%) was added to the stable suspension of MWCNTs in DMF. The ratio of CNT to PAN was kept 1 w%. After PAN addition, solution was stirred at 60 °C and 400 rpm for 1.5 h by magnetic stirring. Then the solution was fed into electrospinning system (Fig 1) in order to produce nanofibre web.

In the electrospinning system, the composite polymer solution was loaded into a syringe and then purged to the needle tip by the syringe pump. A positive voltage from high-voltage power supply was applied to the needle tip and the rotating drum collector covered by aluminium foil was grounded.
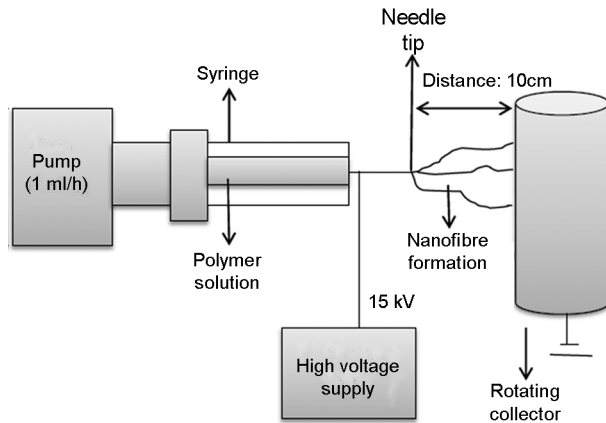
Fig. 1 — Schematic diagram of electrospinning system

Because of high electric field, solution was drawn from needle tip onto the nonwoven mat wound on the aluminium foil and then collected in nanofibre web form. In electrospinning system, the feeding rate of the polymer solution was 1 mL/h, the applied voltage was 15 kV and the distance between the needle tip and collector was 10 cm.

2.3 Characterization

The FTIR spectra of pristine and functionalized MWCNTs were recorded using Nicolet IS10 FTIR spectrometer. A minimum of 16 scans were averaged with a signal resolution of 4 cm^{-1} within the 400-4,000 cm^{-1} range. Both KBr and ATR method were used to collect the IR.

The morphology and structure of the CNT/PAN nanofibres coated with gold were investigated by SEM Carl Zeiss EVO MA10. The SEM images were obtained using a voltage of 5 kV. The diameters of the nanofibres were measured on SEM photomicrographs and analysed using Image J Software. At least 50 measurements were taken and used in the calculation of the average nanofibre diameter.

DSC Q10 was used with nitrogen gas (flow rate of 50 mL/min) for thermal analysis in the range of 30-350˚C. Indium was used for the calibration of temperature and heat flow. Sample preparation was carried out in an air atmosphere.

Microtest LCR Meter 6370 (0.01 mΩ-100 MΩ) with two circular probe having four wire systems was used for the measurement of resistance of composite nanofibres. The integrated thickness meter was used to measure the thicknesses of the samples. Volume conductivity of the samples in S/cm was calculated following Eq. (1) as indicated in ASTM standards[20,21]. Volume resistance values were measured and the

conductivities of the composite nanofibres in S/cm were calculated by using following equation:

$$\gamma_v = t /(AxR_v) \qquad \qquad ... (1)$$

where R_v is the volume resistance (Ω); A, the area of the electrodes (cm^2); and t, the distance between electrodes (cm). At least 7 measurements were taken to obtain average value of electrical conductivity and thickness of nanofibre web.

Tensile tester was used for the evaluation of mechanical properties. Tensile strength, breaking elongation and modulus of the webs were obtained with a 100 N load cell at a crosshead speed of 20 mm/min. At least 7 measurements were performed to obtain average values of mechanical properties of nanofibre web. For mechanical testing, 50 mm × 5 mm test specimens were prepared and the gauge length was set as 15 mm.

Wide-angle X-ray diffraction traces were obtained using a Bruker® AXS D8 Advance X-ray diffractometer system using nickel filtered CuK$_\alpha$ radiation (λ 0.15406 nm), and voltage and current settings of 40 kV and 40 mA respectively. Counting was carried out at 10 steps per degree. The observed equatorial X-ray scattering data were collected in reflection mode in the 5-40º 2θ range. X-ray data-curve fitting developed by Hindeleh *et al.*[22] has been applied. Apparent X-ray crystallinity was based on the ratio of the integrated intensity under the resolved peaks to the integrated intensity of the total scatter under the experimental trace[23].

3 Results and Discussion

3.1 FTIR Study

FTIR spectroscopy was used to monitor the presence of surface functional groups at each step in the chemical functionalization. To characterize the surface modification of MWCNT-COOH, carbon nanotubes were dispersed in THF. Figure 2 shows the comparison of FTIR spectra of p-MWCNTs, MWCNT-COOH and MWCNT-OH.

Compared to the spectra of pristine MWCNTs, a new peak around 1724 cm^{-1} is appeared in the spectrum of MWCNT-COOH and assigned to the carbonyl (-C=O) stretching of the carboxylic acid (-COOH) group. The peak at 3424 cm^{-1} is due to -OH stretching vibrations of the carboxylic acid group. The IR peak located at 1648 cm^{-1} with medium intensity is due to C=C stretching vibration indicating the graphitic structure of MWCNTs[5]. There appears a

new band in the spectrum of MWCNT-COOH at 1120 cm^{-1} due to C-O stretching vibration occurring in alcohols probably formed during the purification step[24]. The bands at 1034 cm^{-1} appearing as a shoulder and at 1184 cm^{-1} appearing as a stronger peak in the MWCNT-COOH spectrum are also due to the C-O vibration[5,25]. Additionally, there are strong peaks at 2927 and 2855 cm^{-1} due to asymmetrical and symmetrical methylene (CH$_2$) stretching vibrations[5]. These results suggest that carboxylic acid groups are successfully introduced onto the MWCNT surfaces. In the FTIR spectrum of MWCNT-OH (Fig 2c), the broadening of the peak at 3401 cm^{-1} shows the successful hydroxyl-functionalization of MWCNTs.

To characterize the MWCNT-NH$_2$, KBr pellets were prepared and used during the collection of FTIR spectrum. FTIR spectrum was recorded with a KBr pellet ranging from 4000 cm^{-1} to 400 cm^{-1} and is presented in Fig 3. In comparison with pristine MWCNTs, a few new peaks appeared in the spectra of MWCN-NH$_2$. The peaks in the 3500-3400 cm^{-1} region are attributed to -OH and -N-H stretching vibrations[5]. The peak at 1632 cm^{-1} is assigned to C=C stretching of carbon nanotube structure and C=O stretching of amide (-NH-C=O) structure. The peaks at 1547 cm^{-1} and 1139 cm^{-1} are attributed to C-NH, C=N and C-C stretching vibrations respectively. From the amide structure, N-C=O stretching at 621 cm^{-1} is obtained[26].

3.2 Analysis of Morphological Properties of Nanofibres

SEM images of pure PAN and composite nanofibres are presented in Fig. 4. All the nanowebs show uniform and bead-free structures.
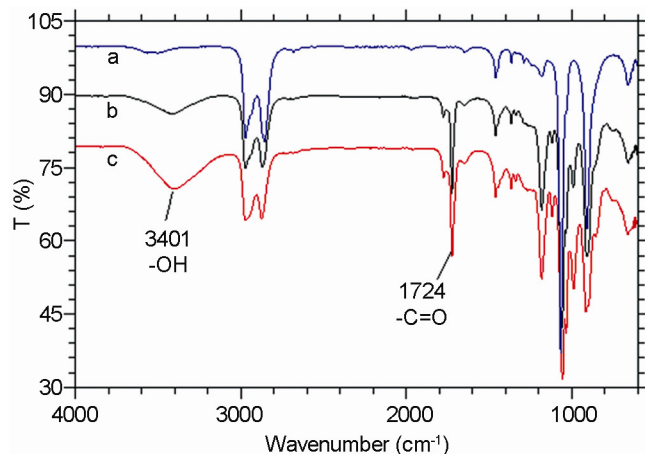
The diameters of PAN/MWCNT composite nanofibres obtained from SEM observations are pure PAN 312±35.26 nm, PAN/p-MWCNT 343±64.83 nm, PAN/MWCNT-COOH 325±61.25 nm, PAN/CNT-OH 340±47.94 nm, and PAN/CNT-NH$_2$ 328±65.93 nm.

Though not very clear, a tendency of increase in the average diameters of nanofibres is observed with the addition of MWCNTs which might have been due to the additional filler effect. The differences between the average nanofibre diameters may become more apparent for higher additive contents.

3.3 Analysis of Mechanical Properties

As can be seen from Table 1, all the CNTs with functional groups show higher strength than that of the pristine MWCNTs due to the better dispersibility of functionalized MWCNTs[8]. However, MWCNT-NH$_2$ results in a slightly higher strength and modulus than that of the p-MWCNTs in comparison to MWCNT-COOH and MWCNT-OH. This can be attributed to the better interfacial bonding and less agglomeration tendency of amine groups in PAN matrix due to the presence of nitrile groups in the PAN $(C_3H_3N)_n$ structure[1,24]. While PAN/MWCNT-NH$_2$ has slightly higher E-modulus than that of PAN/p-MWCNT; the other two PAN/MWCNT-COOH and PAN/MWCNT-OH show slightly lower E-modulus than that of PAN/p-MWCNT.

3.4 Electrical Conductivity of Composite Nanofibres

It has been reported that MWCNTs possess a high aspect ratio and p-bonds and that the electrons are normally transferred through the p-bonds of CNTs[11]. The results presented in Table 1 showed that the incorporation of 1w% MWCNT significantly improves

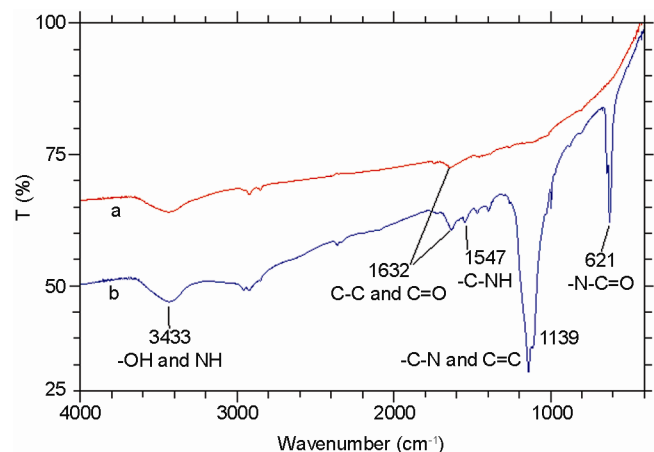Fig. 2 — FTIR spectra of (a) p-MWCNT; (b) MWCNT-COOH; and (c) MWCNT-OH

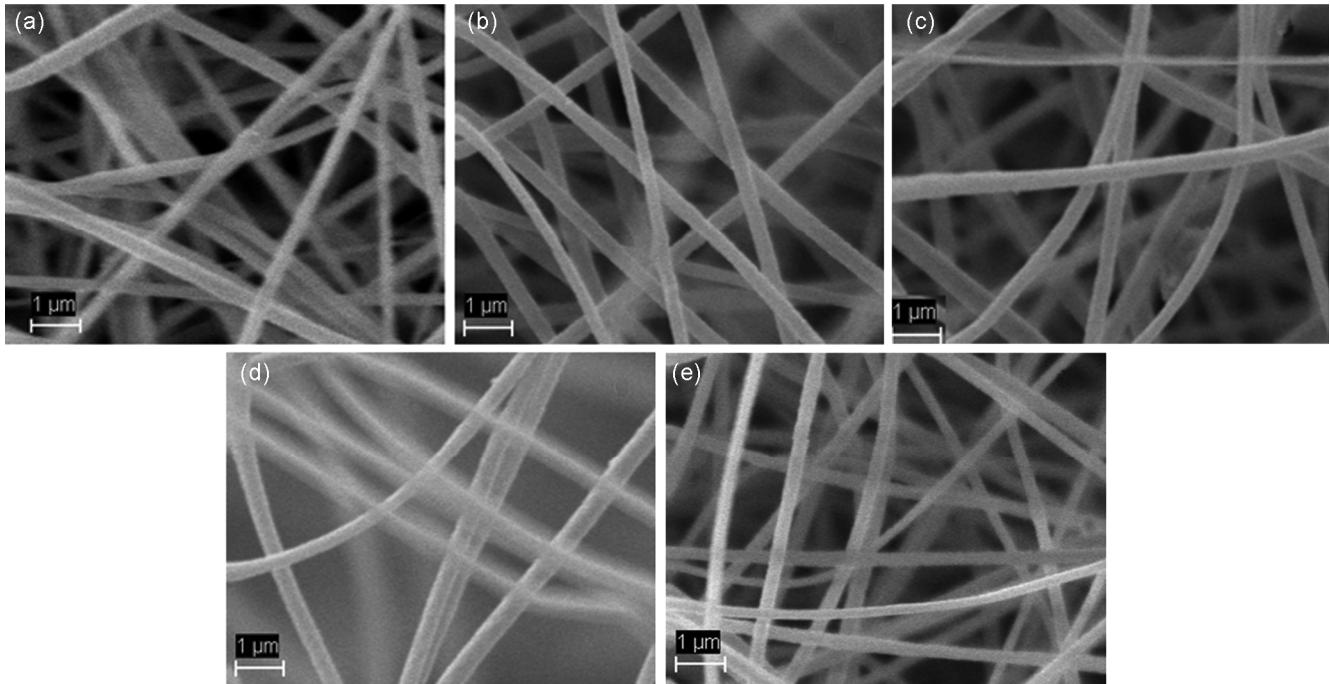Fig. 3 — FTIR spectra of (a) p-MWCNT; and (b) MWCNT-NH$_2$

Fig. 4 — SEM images of (a) pure PAN; (b) PAN/p-MWCNT; (c)PAN/MCNT-COOH; (d) PAN/MWCNT-OH; and (e) PAN/MWCNT-NH$_2$ nanofibres

Table 1 — Tensile properties and conductivities of pure PAN and composite nanofibres

Sample	Tensile strength MPa	Breaking elongation %	E-modulus MPa	Conductivity S/cm
Pure PAN	1.56±0.23	17.24±2.41	12.6±1.77	10^{-12}
PAN/p-MWCNT	2.18±0.29	12.63±1.72	19.5±6.72	$1.92*10^7$ $\pm0.59*10^{-7}$
PAN/MWCNT-COOH	2.25±0.37	17.28±2.44	14.5±6.37	$1.72*10^7$ $\pm0.33*10^{-7}$
PAN/CNT-OH	2.25±0.16	15.00±2.98	14.8±7.96	$2.09*10^7$ $\pm0.73*10^{-7}$
PAN/CNT-NH$_2$	2.41±0.73	14.32±3.34	22.8±6.76	$2.60*10^7$ $\pm0.76*10^{-7}$

the electrical conductivity of composite PAN nanofibre webs in comparison to insulator pure PAN nanoweb and the composite PAN nanofibres become antistatic materials. The electrical conductivity values are found to vary between 1.9×10^{-7} and 2.6×10^{-7} S/cm compared to insulator PAN having the conductivity of 10^{-12} S/cm (ref. 27). The results further show that the functionalization of carbon nanotubes with different functional groups has insignificant effect on conductivity.

3.5 Analysis of X-ray Diffraction Results

Crystallinity values of composite samples containing functionalized CNTs vary between 16.2% and 23.6 % (Table 2). While PAN/MWCNT-NH$_2$ shows similar crystallinity (22.7%) to that of PAN/p-MWCNT (22.6%), the others show lower crystallinity values than that of PAN/p-MWCNT and the lowest one belongs to PAN/MWCNT-COOH. It is a common experience in polymer science that the introduction of bulky side groups almost always disrupts the crystalline structure. The side groups (-OH, -COOH, -NH$_2$) attached to CNTs allow the formation of bonds with acrylonitrile (AN) units of PAN polymer chains, which, in turn, cause the whole PAN-CNT composite chains unable to pack efficiently, and consequently result in the reduction of the degree of order[28]. Since the concentration of pristine and functionalized MWCNTs was only 1 w%, the net effect on crystallinity is not expected to be too high. The lowest crystallinity is found to be 16.2% which is due to the bulky nature of -COOH functionalized MWCNTs, causing decrystallization via disruption of order.

3.6 Thermal Analysis

The thermal properties such as cyclization temperature (T_c) and enthalpy values of pure PAN and PAN/MWCNT composite nanofibres are examined by DSC technique operating at a heating rate of 20˚C/min under nitrogen atmosphere. Sample preparation is carried out in an air atmosphere.

In the absence of inert atmosphere, samples might have been exposed to minor oxidative reactions during the sample preparation, but such effect is likely to be minimum on the DSC thermograms since the DSC thermograms do not show an additional oxidation peak on the high temperature side. The cyclization temperatures and enthalpy values can be seen in Table 3.

Throughout the DSC scanning process (thermal treatment process) of PAN polymer, a series of chemical reactions occur which provide the conversion of double bonded carbon-carbon (C=C) and nitrile (−C≡N) to nitrilo (−C=N) groups; and these reactions primarily include cyclization, dehydrogenation and oxidation which generate ladder-like molecular structures and make PAN fibres heat-resistant and infusible. In the present study, since DSC thermograms are obtained under nitrogen atmosphere only, no oxidation reactions are expected to occur. The exothermic peak (ΔH) observed at 314.80 °C on the DSC thermogram of pure PAN nanofibre is attributed to the cyclization of nitrile (C≡N) groups[29-31].

Samples with functionalized CNTs generally show higher cyclization temperatures than PAN/p-MWCNT, except for the PAN/MWCNT-COOH. It is suggested that the cyclization of nitrile groups of PAN chains proceeds via two mechanisms as ionic and free radical reactions. The cyclization of nitrile groups of pure PAN initiated through a free radical mechanism is considered to take place as a result of inter- or intra- molecular jumping of free radicals which accept hydrogen atoms from nearby macromolecules and propagate along the chain direction. On the other hand, the ionic reaction of PAN chains is suggested to require an acid such as carboxylic acid or acrylic acid. The acid molecules make a nucleophilic attack on the carbon atom of nearby nitrile group and cause it to cyclize. As a result of different reaction rates and reaction mechanisms, DSC thermograms show the exothermic peaks located at different temperatures[32]. It seems that the cyclization of nitrile groups in pure PAN nanofibres can be initiated at a higher temperature through an only free radical mechanism.

Enthalpy values of composite nanofibres with functionalized CNTs are found to decrease compared to PAN/p-MWCNT and the lowest one belongs to PAN/MWCNT-NH$_2$. The functional groups are considered to be useful as external initiating agents for the nitrile cyclization of PAN. The decrease in enthalpy of composite nanofibres might have been due to easy formation of free radicals on the nitrile groups as a result of the decomposition of functional groups and the subsequent recombination between the intramolecular radicals[32].

4 Conclusion

4.1 A tendency of increase in the average diameters of nanofibres is observed with the addition of MWCNTs. There are not any pronounced differences between diameters of the nanofibres produced with the addition of differently functionalized carbon nanotubes, this may also be due to low amount of carbon nanotube which is necessary to get better mechanical properties

4.2 All MWCNTs with functional groups provide higher strength than p-MWCNTs. However, MWCNT-NH$_2$ provides slightly more strength and E-modulus than that of MWCNTs with other functional groups (-COOH and -OH).

4.3 Composite nanofibres containing MWCNT-NH$_2$ show similar crystallinity to that of nanofibres containing p-MWCNTs and has highest crystallinity value. Nanofibres which contained MWCNT-COOH and MWCNT-OH show lower crystallinity values than that of the nanofibres which contained p-MWCNT. The lowest crystallinity is observed for PAN/MWCNT-COOH.

Table 2— X-ray diffraction results of pure PAN and composite nanofibres.

Sample	Degree of order , % (PAN)	2θ, deg		
		PAN (100)	CNT (002)	PAN (110)
Pure PAN	22.6	16.70	29.20	-
PAN/p-MWCNT	23.6	17.2	26.5 (Broad)	29.2 (Broad)
PAN/MWCNT-COOH	16.2	17.0	26.5 (Broad)	29.2 (Broad)
PAN/CNT-OH	19.1	17.2	26.5	29.2
PAN/CNT-NH2	22.7	16.9	26.5	29.2

Table 3 — Cyclization temperatures and enthalpy values of pure PAN and composite nanofibres

Sample	T_c ,°C	ΔH, J/g
Pure PAN	314.8	483.8
PAN/p-MWCNT	317.4	296.3
PAN/MWCNT-COOH	313.1	270.9
PAN/CNT-OH	320.8	266.9
PAN/CNT-NH$_2$	321.0	221.9

4.4 Insulating PAN becomes semi conductive material with static electric discharge ability as a result of the addition of the pristine and functionalized CNTs (10^{-7} S/cm). Results show that the functionalization of carbon nanotubes with different functional groups has insignificant effect on conductivity.

4.5 The composite nanofibres containing functionalized MWCNTs show generally higher cyclization temperature than PAN/p-MWCNT samples except for PAN/MWCNT-COOH.

4.6 Enthalpy values of composite nanofibres with functionalized MWCNTs decrease in comparison to PAN/p-MWCNT nanofibre. The lowest value belongs to PAN/MWCNT-NH$_2$.

Acknowledgement

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