Plasma assisted attachment of functionalized carbon nanotubes on poly(ethylene terephthalate) fabric to improve the electrical conductivity

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Abstract: In this article, we report a durable coating of polyester fabric with carbon nanotubes. Four fabric samples were prepared using different treatments to obtain the fabric with the lowest electrical resistance. Plasma treatment was performed to prepare the fabric surface for depositing amino functionalized carbon nanotubes (NH_2-MWCNT). Thermal properties, surface morphology and chemistry of the samples were investigated. Also color strength and electrical resistance of the fabric samples were determined. The results showed that the attachment of NH_2-MWCNT onto polyester fabric was affected by fabric surface morphology. The XPS results confirmed the presence of more oxygen-containing species on the PET fabric surface after plasma treatment and NH_2-MWCNT coating. The melting temperature and degree of crystallinity of the coated-PET fabric were higher than those of the pristine PET fabric. An improvement in the tensile strength of the PET fabric was also obtained after the plasma treatment and CNT coating. Electrical resistance of NH_2-MWCNT coated polyester fabric reduced substantially for pretreated fabric with plasma which was subsequently coated with NH_2-MWCNT in the presence of acrylic acid.

Keywords: coating, conductive textiles, carbon nanotubes, functionalization, plasma processing.

Poprawa przewodności elektrycznej tkaniny z poli(tereftalanu etylenu) przez wspomagane obróbką plazmową nanoszenie funkcjonalizowanych nanorurek węglowych

Streszczenie: W ramach pracy badano różne metody nanoszenia na powierzchnię tkaniny z poli(tereftalanu etylenu) (PET) trwałej powłoki z nanorurek węglowych w celu uzyskania materiałów o najmniejszej oporności elektrycznej. Przygotowano cztery próbki tkaniny PET, z których trzy poddano obróbce plazmowej. Następnie wszystkie próbki moczono w dyspersji funkcjonalizowanych aminą nanorurek węglowych (NH_2-MWCNT) działając ultradźwiękami w ciągu 5 min. W przypadku dwóch tkanin, które moczono w dyspersji różniącej się stężeniem NH_2-MWCNT po 5 min dodawano kwas akrylowy i utrzymywano działanie ultradźwięków przez kolejne 5 min. Wszystkie cztery próbki tkanin oraz próbkę referencyjną, z wyjściowej tkaniny PET poddano badaniom właściwości termicznych, morfologii powierzchni i składu chemicznego. Określono również intensywność ich barwy i oporność elektryczną. Stwierdzono, że ilość NH_2-MWCNT naniesionego na tkaninę PET zależy od morfologii jej powierzchni. Wyniki rentgenowskiej spektroskopii fotoelektronowej (XPS) wykazały, że na powierzchni tkaniny PET powlekanej NH_2-MWCNT po wstępnej obróbce plazmowej znalazła się większa ilość cząsteczek zawierających tlen, niż na tkaninie bez takiej obróbki. Temperatura topnienia (T_m) i stopień krystaliczności (X_C) w przypadku powlekanych tkanin PET były wyższe niż w wyjściowej tkaninie PET. Obróbka plazmowa zwiększyła także wytrzymałość na rozciąganie powlekanych tkanin. Stwierdzono, że oporność elektryczna była najniższa w przypadku tkanin powlekanych NH_2-MWCNT po wstępnej obróbce plazmowej i w obecności kwasu akrylowego.

Słowa kluczowe: powlekanie, tkaniny przewodzące, nanorurki węglowe, funkcjonalizacja, obróbka plazmowa.

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Electrically conducting polymer composites have received much attention recently compared to conventional metal-based electromagnetic interference (EMI) shielding materials because of their light weight, resistance to corrosion, flexibility and processing advantages [1]. The demand for electrically conductive textiles has been increasing greatly in recent years. Electro-conductive textiles have many potential applications including sensors, static charge dissipation, filters, EMI shielding and data transfer in clothing, military applications like camouflage and stealth technology and special purpose clothing acting as protection from dust and germ free purposes [2—3].

Several methods have been used to produce electrically conductive fibers, yarns or fabrics including wet spinning, melt spinning or coating of fibers with electrically conductive materials such as metal powders, graphite, carbon black, carbon nanotubes or intrinsically conductive polymers like polyaniline, thiophene and polypyrrole. Among these manufacturing processes, coating techniques have gained more attention due to simplicity of the process and ease of handling. The textiles produced not only gain controllable electrical properties, but also maintain the physical properties of textiles such as mechanical strength and flexibility intact [2, 4, 5].

Carbon nanotubes (CNTs) have recently been applied as the electronic element to make wearable electronic textiles owing to their light weight, high surface area besides superior mechanical and electrical properties [6—8]. CNTs have been proved to be an ideal reinforcement in macroscopic composites to improve electrical, mechanical, and physical properties of materials [2].

Poly(ethylene terephthalate) (PET) fiber is elastic, tough and resistant to abrasion; implying PET clothes can last for a long time. In this aspect, it seems that PET fiber may be an ideal candidate for the manufacturing of electronic textiles. Unfortunately, little information is available at this time on manufacturing of durable CNT coated PET textiles [9—11] and this is the impetus of this study.

PET fiber is highly crystalline and hydrophobic in nature and presents an inherent low reactivity toward chemicals [11, 12] and this restricts the absorption of CNTs on its surface. Several physicochemical and chemical processes have been investigated and adopted for the surface modification of these fibers. These processes include co-spinning, non-covalent physical coating, plasma discharge, alkaline treatment for partial surface hydrolysis, partial aminolysis of surface ester groups, glycolysis, and graft polymerization [11]. Certain improvements in surface and adsorption properties can be imparted to PET fibers using plasma treatment and grafting of monomers like acrylic acid [12—15].

In this study oxygen plasma treatment and acrylic acid grafting was employed as means to attach amino functionalized CNTs onto the surface of PET fabric. The attachment of CNTs was confirmed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), color measurement, and scanning electron microscopy (SEM) analysis. The electrical conductivity of the CNT coated samples was analyzed and showed great improvement compared to untreated samples.

EXPERIMENTAL PART

Materials

Poly(ethylene terephthalate) (PET) fabric (130 g/m^2, 150 Den filaments in warp and weft, plain weave) was obtained from Hijab textile Co. (Shahrekord, Iran). Amino functionalized carbon nanotubes (NH$_2$-MWCNT) (purity >95 %, -NH$_2$ content: 0.45 wt %, diameter <8—15 nm, length 50 μm) were supplied from Neutrino Company (Iran). Triton X100 (surfactant) and acrylic acid was purchased from Merck.

Samples preparation

In order to obtain a uniform coating of NH$_2$-MWCNTs onto PET fabrics, it is necessary to prepare a well-dispersed colloidal solution. NH$_2$-MWCNT was dispersed in water, containing 1 g/dm^3 of Triton X100, by ultrasonication at the power of 40 W for 1 h. For samples which need to be treated with acrylic acid, 10 vol % of acrylic acid was added after the initial ultrasonication and the process was continued for another 5 min. Samples were soaked in the prepared dispersion for 1 min in the presence of ultrasounds. Then the samples were dried and plasma treatment was done for samples treated with acrylic acid in the previous step.

Plasma treatment of the samples (before and after soaking in NH$_2$-MWCNT dispersion, if needed) was done in a low pressure plasma equipment (Model: Junior Plasma, Europlasma, Belgium) working with oxygen gas flow rate of 20 sccm (standard cubic centimeter per minute) at the pressure of 13 Pa and power of 150 W for 120 s.

Methods of testing

To compare the amount of NH$_2$-MWCNTs adhered on the surface of the samples color measurement was done on the treated samples. The reflectance of treated samples were measured on a Color-eye 7000A spectrophotometer using illuminant D65 and 10° standard observer. Color strength (*K/S*) of dyed samples was calculated using Kubelka-Munk equation:

$$K / S = (1 - R)^2 / 2R \qquad (1)$$

where: *R* — observed reflectance, *K* — absorption coefficient, *S* — light scattering coefficient.

Fourier transform infrared measurements were carried out using a Nicolet 670 with the resolution of 4 cm^{-1}. An average of 40 scans was recorded in the ATR mode.

The surface morphology of pristine and NH$_2$-MWCNT coated samples was studied using a KY-KY-EM3200 digital

scanning electron microscope (KYKY Technology, China) after coating the samples with gold.

The chemical compositions of fabric samples were analyzed using X-ray photoelectron spectrometer (XPS), a dual-anode VG XR3E2 X-ray source system (Germany) employing an Al X-ray source operating at 15 kV. The pressure within the XPS chamber was less than 10^{-6} Pa. The spectra were normalized with respect to the C-C peak positioned at 285 eV.

Differential scanning calorimetry (DSC 2010, TA Instrument) was used to study the crystalline structure of the CNT coated PET fabric. The heating and cooling rates were 10 °C/min in the 20—300 °C temperature range. Crystallinity was calculated using the following equation:

$$X_C = \frac{\Delta H_f}{\Delta H_f^\circ} \cdot 100 \ \% \tag{2}$$

where: ΔH_f — measured melting enthalpy, ΔH_f° — melting enthalpy of 100 % crystalline polymer, which in the case of PET equals to 140.1 J/g.

Tensile properties (in warp direction) of the fabric samples were determined with a tensile tester machine (Elima Co., Iran) according to ISO 13934-1:2013.

The electrical conductivity of NH_2-MWCNT is higher than 100 S/cm. The high electrical conductivity of NH_2-MWCNT can facilitate the charge transfer in the fabric. Electrical resistance measurements were performed on all samples after conditioning in 25 °C and 65 % of relative humidity for 24 h. The resistance was measured five times on each side of the sample and the average values were taken. A four-probe set-up was used according to AATCC Test Method 76-2005. The two inner copper electrodes were connected to a high impedance voltmeter while the outer copper electrodes of 2 cm separation were connected to a current source and ammeter in series. The fabric sample (5 × 5 cm) was placed onto the copper electrodes with a load of 0.2 kg. The electrical surface resistivity of each sample was calculated using equation:

$$R_S = V / I \tag{3}$$

where: R_S — surface resistivity in Ω/sq, V — the potential difference, I — the current.

RESULTS AND DISCUSSION

To find the best process for coating of PET fabric with NH_2-MWCNT, four samples were treated with the following procedures:

— for sample 1, pristine PET was treated with 10 wt % NH_2-MWCNT dispersion in the presence of ultrasounds for 5 min;

— for sample 2, plasma treated PET sample was coated with 10 wt % NH_2-MWCNT dispersion in the presence of ultrasounds for 5 min;

— for sample 3, plasma treated PET sample was coated with 10 wt % of NH_2-MWCNT dispersion in the pre-
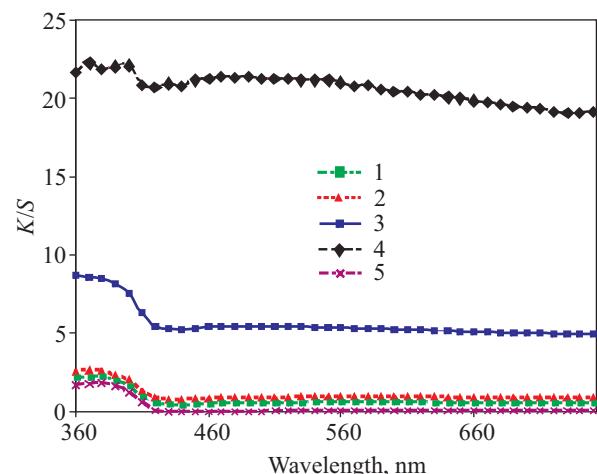
Fig. 1. Color strengths of investigated samples expressed by *K/S* ratio

sence of ultrasounds for 5 min and then acrylic acid was added and ultrasonication was continued for another 5 min;

— for sample 4, plasma treated PET sample was coated with 5 wt % NH_2-MWCNT dispersion in the presence of ultrasounds for 5 min and then acrylic acid, as in the case of sample 3, was added.

For comparison, an untreated PET sample was used as a reference (sample 5).

K/S values as a function of wavelength for prepared samples are shown in Fig. 1. It can be seen that the samples prepared without acrylic acid did not show significant difference from the reference sample. It means that only ultrasound and plasma treatment alone or in conjunction can not lead to a high amount of adsorption of NH_2-MWCNT on PET fabric. Only the samples prepared
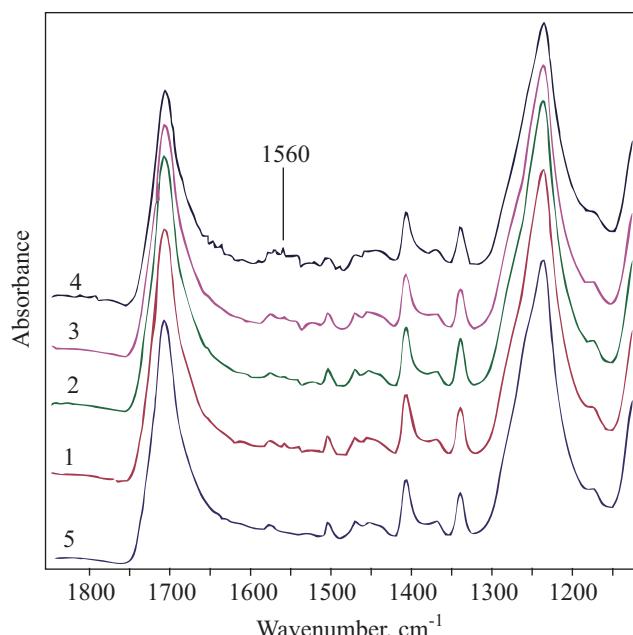
Fig. 2. ATR-FTIR spectra of prepared samples
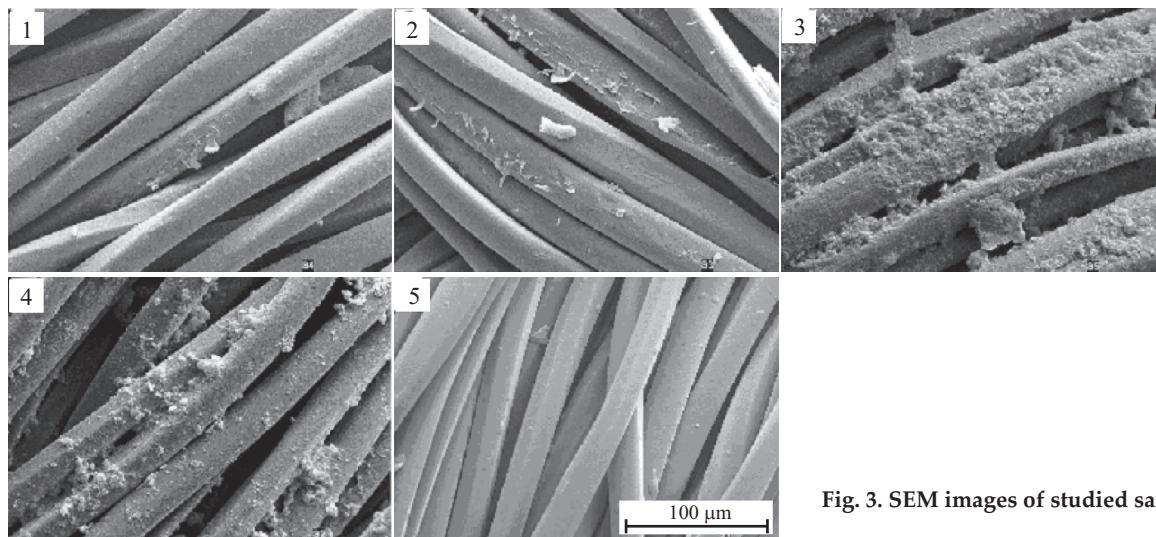
Fig. 3. SEM images of studied samples

in the presence of acrylic acid (samples 3 and 4) showed high K/S value. The amount of NH$_2$-MWCNTs deposited on the PET fabric increased with increasing amount of them in the soaking bath.

ATR-FTIR spectra of investigated samples are presented in Fig. 2. The gradual increase (from sample 1 to 4) of the peak at 1560 cm^{-1}, attributed to amine groups, confirms the presence of higher amounts of NH$_2$-MWCNTs on the surface of samples 3 and 4.

SEM images shown in Fig. 3, confirm the higher amount of NH$_2$-MWCNTs on the surfaces of samples 3 and 4 and the polymerization of acrylic acid to poly-acrylic acid on the surface of these samples in the final plasma treatment stage is evident.

The surface of sample 5 is rough as expected and no difference can be seen on the surface of sample 1 compared to reference sample 5. It is due to very little adsorption of NH$_2$-MWCNTs on this sample. The surface of sample 2 is rough due to the etching effect of the pretreat-

ment of the sample with oxygen plasma. But this pretreatment did not lead to any remarkable adsorption of NH$_2$-MWCNTs on sample 2 compared to samples 1 and 5. The surfaces of samples 3 and 4 show higher amounts of NH$_2$-MWCNTs and grafted poly-acrylic acid. The sample treated with higher amount of NH$_2$-MWCNTs (sample 3) showed the higher amount of deposition of the nanoparticles.

XPS analysis was used to collect the elemental information of the fabric samples. XPS overall scans of the pristine PET fabric and sample 3 are shown in Fig. 4. As expected, PET fabric exhibited two intense and narrow signals at around 285 and 532 eV, corresponding to the carbon and oxygen, respectively [16, 17]. The XPS spectra show that a decrease in intensity of C 1s peak along with an increase in intensity of O 1s peak after the plasma treatment and NH$_2$-MWCNT coating. The O/C ratio significantly increased from 0.25 in the pristine PET fabric to 0.38 for the coated sample. These results indicate that the
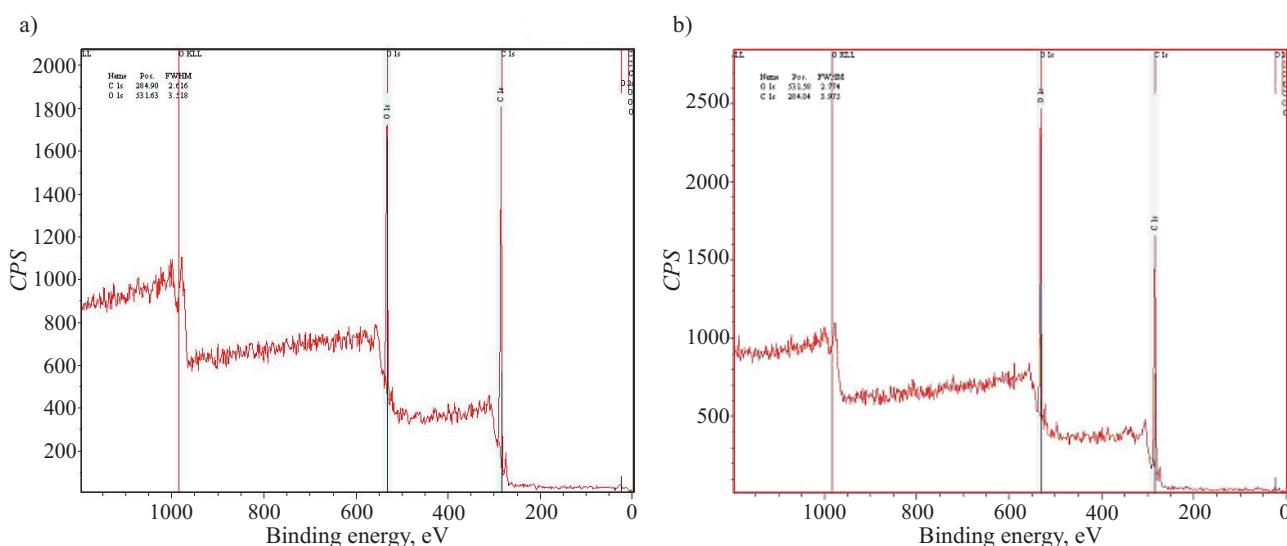
Fig. 4. Overall XPS scan survey of: a) the pristine PET fabric (sample 5), b) NH$_2$-MWCNT coated fabric (sample 3)
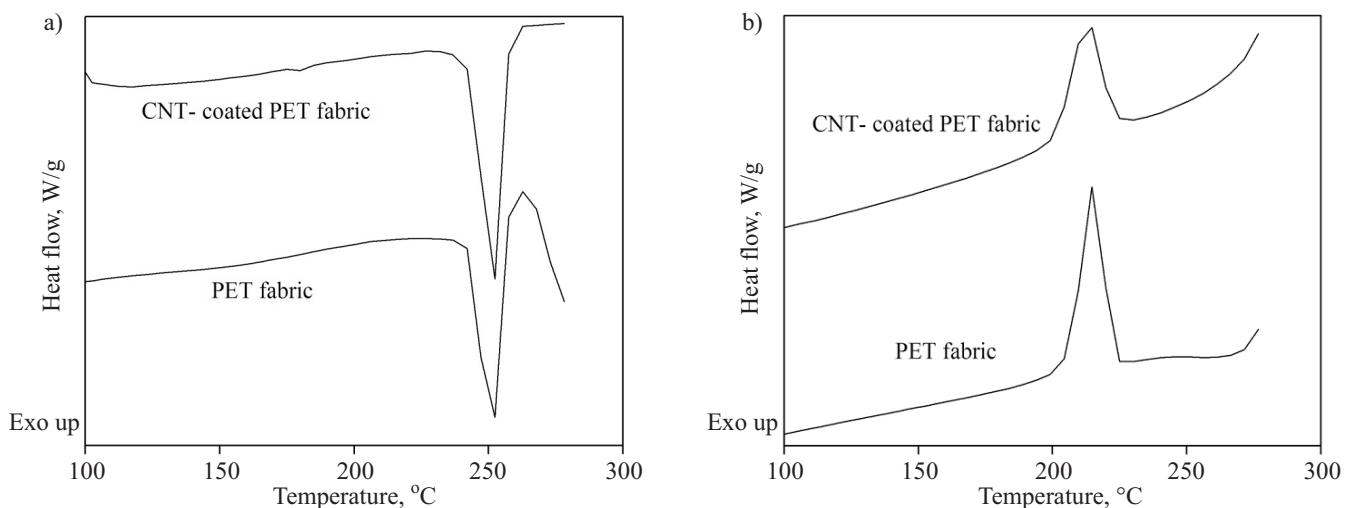
Fig. 5. DSC thermograms for PET fabric (sample 5) and NH$_2$-MWCNT coated PET fabric (sample 3): a) heating cycle, b) cooling cycle

oxygen-containing species were formed onto the PET surface due to the plasma treatment and coating with NH$_2$-MWCNTs.

DSC was performed on the pristine PET fabric and sample 3 to investigate the effect of plasma treatment and NH$_2$-MWCNT coating on the crystalline structure of PET fabric. The DSC curves of pristine PET fabric and sample 3 are illustrated in Fig. 5. The DSC results are also summarized in Table 1. As it is shown in Table 1, the coating of NH$_2$-MWCNT enhanced the crystallinity (X_C) of PET fabric because of the nucleating effect of CNTs. Moreover, the melting temperature (T_m) of NH$_2$-MWCNT coated sample is slightly higher than that of the pristine PET fabric. In addition, the NH$_2$-MWCNTs deposition also changed the cooling behavior and crystallization temperature (T_c) of the PET fabric. The results suggest that the crystallization begins sooner at a higher temperature in NH$_2$-MWCNT coated sample as compared with the pristine PET fabric. This heterogeneous nucleation of PET with CNTs is known and was reported by the others [18—20].

The level of system order can be evaluated by the melting entropy (ΔS_m) using the following relationship:

$$\Delta S_m = \Delta H_m / T_m \qquad (4)$$

The higher ΔS_m value for NH$_2$-MWCNT coated PET fabric suggests that the transition of the system from a solid to molten state occurred with a higher change in the macromolecular arrangement, indicating that higher interaction and maximal macromolecular order in the solid state are present. In conclusion, the DSC results proved that the crystal structure of PET in the coated fabric was improved by the plasma treatment and CNT coating.

After the plasma treatment and coating with NH$_2$-MWCNT, tensile strength of the PET fabric increased from 460 ± 13 N to 507 ± 20 N, whereas the elongation decreased from 16 ± 1 to 12 ± 2 %. It seems that a good dispersion of NH$_2$-MWCNTs onto the PET fabric surface and an increase in crystallinity have an important role in achieving better tensile strength for the coated sample.

T a b l e 1. Thermal characteristics of pristine PET fabric (sample 5) and NH$_2$-MWCNT coated PET fabric (sample 3)

Number of sample	T_m °C	ΔH_m J/g	$T_{c,onset}$ °C	$\Delta T = T_m - T_c$ °C	X_C %	ΔS_m J·K^{-1}·g^{-1}
5	250.4	36.9	225	25.4	26.3	0.147
3	253.8	53.0	233	20.8	37.9	0.208

Usually lower degree of super cooling ($\Delta T = T_m - T_c$) reflects higher nucleation and crystallization rates. As shown in Table 1, the NH$_2$-MWCNT coated PET fabric has a lower degree of super cooling as compared to the pristine PET fabric. An efficient dispersion of NH$_2$-MWCNTs onto the PET fabric surface due to plasma treatment offers higher surface area for crystal nucleation. This could be explained by the increase in $\Delta T = T_m - T_c$ and T_c for sample 3.

T a b l e 2. Surface resistance of NH$_2$-MWCNT coated samples compared to pristine polyester fabric

Number of sample	1	2	3	4	3 (after washing)	5
Surface resistance, Ω/sq	7·10^{11}	2·10^{11}	3.2·10^3	4·10^5	3·10^3	8·10^{11}

Table 2 shows the surface resistance of NH$_2$-MWCNT coated samples compared to the pristine polyester fabric. The sample with the highest amount of NH$_2$-MWCNT deposition showed the lowest surface resistance. After the plasma treatment, surface roughness of fabrics increased and more NH$_2$-MWCNTs were attached onto the fibers surface. When using acrylic acid (samples 3 and 4), the highest amount of NH$_2$-MWCNTs was trapped and attached to the fibers surfaces. This gives rise to the deve-

lopment of electrically conductive networks in the PET fabrics and enhances their electrical conductance.

CONCLUSION

Four procedures were conducted to deposit NH$_2$-MWCNTs on PET samples and the best procedure was selected. Plasma treated fabric, subsequently coated with NH$_2$-MWCNTs in the presence of acrylic acid was chosen as the best sample for conducting static charge. ATR-FTIR analysis indicated the incorporation of amine functionalities on the fabric surface after coating with NH$_2$-MWCNTs. The rough surface of plasma treated sample is responsible for bigger deposition of NH$_2$-MWCNTs on the fabric surface and thereby the electrical resistance of NH$_2$-MWCNTs coated fabric decreased. The XPS spectra showed a decrease in intensity of C 1s peak along with an increase in intensity of O 1s peak after the plasma treatment and NH$_2$-MWCNT coating. DSC results proved that the plasma treatment and CNT coating affected the microstructure of the PET fabric significantly. Comparison of ΔS_m values demonstrated that macromolecular system organization is higher for the NH$_2$-MWCNT coated fabric. An improvement in the tensile strength and an increase in T_c of coated PET fabric with respect to the pristine PET were achieved due to good dispersion of CNTs onto the PET fabric surface.

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