



Multiwalled-carbon Nanotubes/Poly (butylene terephthalate) Nanofibres: Morphological, Mechanical and Thermal Properties

Khalid Saeed^{1*} and Soo-Young Park²

(1) Department of Chemistry, University of Malakand, Chakdara Dir (Lower)
Khyber Pukhtoonkhwa, Pakistan

(2) Department of Polymer Science, Kyungpook National University
Buk-gu, Daegu 702-701, South Korea

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ABSTRACT

Poly(butylene terephthalate) (PBT) nanofibres containing functionalized multiwalled-carbon nanotubes (F-MWNTs) were prepared by electrospinning technique. The F-MWNTs were prepared by the introduction of aromatic amine ($\text{COC}_6\text{H}_4\text{-NH}_2$) groups onto their side wall via Friedel-Crafts acylation. The diameter of neat PBT nanofibres was below 500 nm and had smooth surface. The scanning electron microscopy (SEM) also showed that F-MWNTs/PBT composite nanofibres mat had similar morphology with that of pure PBT and without beads. The surface of the composite nanofibres was also smooth even by adding high quantity of F-MWNTs. The F-MWNTs were embedded within nanofibres and well oriented along the nanofibre axis, as confirmed by transmission electron microscopy (TEM). The mechanical properties (specific tensile strength and moduli) of the PBT nanofibres were significantly enhanced by the incorporation of F-MWNTs. It was also observed that the melt-crystallization temperature (T_c) of PBT nanofibres shifted to a higher temperature (about 10°C) by the incorporation of F-MWNTs which might be due to the nucleating effect of the nanotubes.

INTRODUCTION

Conventional polymeric fibres which are synthesized by wet, dry, melt and gel spinning methods have diameter range down to the micrometer scale. Electrospinning known as electrostatic spinning technique produces nanoscale fibres from both natural and synthetic sources with diameters ranging from few nanometers to several microns [1]. During this process, an electrical potential is applied between a droplet of a polymer melt, or solution, held at the end of a capillary tube and a

metallic collector. When the applied electric forces overcome the surface tension of the droplet, a charged jet of polymer solution is ejected from the needle tip and deposited on the metallic collector, which results in a thin mat of nanofibres by evaporation of the solvent.

In the previous research works, nanofibres from different polymeric materials such as polyurethane [2], polyaniline/polyethylene oxide blends [3], polymethyl methacrylate [4] and polycaprolactone/

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(*) To whom correspondence to be addressed.
E-mail: khalidkhalil2002@yahoo.com

hydroxyapatite-chitosan/polyvinyl alcohol [5] had been reported. The electrospinning technique is also used for the preparation of nanofibres from various reinforced materials/polymer composites, such as MWNTs/polyacrylonitrile, CNTs/(poly(ethylene terephthalate), MWNTs/poly(methyl methacrylate), poly(vinyl alcohol)/hydrotalcite, and poly(vinyl alcohol)/ oxidized starch fibres [6-10].

The nanofibre mats during electrospinning show excellent characteristics, e.g., high porosity, large surface area, high gas permeability, and small inter-fibrous pore size. These properties qualify non-woven mats for a number of applications such as, scaffolds in tissue engineering [11] and wound healing [12], antibacterial agents [13] electrically conductive nanofibre [14], drug delivery systems [15], nanofibrous membranes for fine filtration [16], protective clothing [17] and adsorbents [18].

Carbon nanotubes (CNTs) have received much attention due to their remarkable properties such as unique mechanical, optical, electrical, and thermal properties and high chemical stability since their discovery by Iijima in 1991 [19]. These remarkable properties of CNTs make them useful materials for a wide range of applications in various fields of science, such as heterogeneous catalyst supports [20-22], actuators [23], field emission devices [24], nanotube-based composites [25], hydrogen storage [26] chemical sensors [27] and nanoelectronic devices [28]. The diameters of CNTs have ranges between a nanometer to tens of nanometers with lengths up to centimeters [29]. CNTs behave either as metallic or semiconductors, depending upon their dimensions, electronic structure, and topological defects present on their surfaces [30,31]. Various techniques such as Fe-SEM, TEM, TGA, and Raman spectroscopy are used for the characterization of CNTs. It is also reported that the incorporation of even small quantities of CNTs into the polymeric materials significantly improves their mechanical, optical, electrical, and thermal properties [25].

Although CNTs have found multiple applications, their dispersibility in solvents/polymer materials are still problematic. Because they take shapes of bundles/ropes due to interfibrous van der Waals forces in combination with their high surface area and high aspect ratio. To overcome this problem, various

approaches such as chemical functionalization [32], wrapping [33], surfactants [23], adsorption of amines [34] and radio frequency glow discharge plasma modification [35] are used.

In the present study, F-MWNTs/PBT composite nanofibres were fabricated by electrospinning technique. In this study aromatic amine-modified MWNTs were used as reinforcing materials. Trifluoroacetic acid was used as a solvent for easy solubility of PBT. The study was focused on morphological examination of PBT and F-MWNTs/PBT composite nanofibres to help enhancing the mechanical properties, thermal stability and the crystallization behaviour of PBT nanofibres by incorporation of F-MWNTs into them.

EXPERIMENTAL

Materials

Trifluoroacetic acid (TFA) and PBT was kindly supplied by Tokyo Chemical Industry[®] Co. (Japan) and Toray Saehan Co. (South Korea), respectively. The MWNTs were supplied by Iljin Nanotec[®] (South Korea) and manufactured by thermal chemical vapour deposition.

Functionalization of MWNTs

The MWNTs were functionalized by Friedel-Crafts acylation as discussed elsewhere [32]. The P-MWNTs, *p*-amino benzoic acid, and PPA were mechanically stirred at 130°C for 3 h in nitrogen atmosphere. The P₂O₅ was then added into the reaction flask and reaction was run for additional 12 h at 130°C. The reaction mixture was then cooled, diluted with water and the precipitate was collected and washed with ammonium hydroxide. The F-MWNTs were Soxhlet-extracted with distilled water for 72 h in order to remove the unreacted reagents. The F-MWNTs were then dried under a reduced pressure for 3 days at 100°C.

Electrospinning of PBT

A 10 wt% solution was prepared by dissolving PBT and F-MWNTs/PBT in TFA [36]. The composite solution was sonicated for 1 h in order to accelerate homogeneous dispersion of the F-MWNTs. The

prepared solution was added to a 10 mL glass syringe using a needle tip with a 0.5 mm diameter. The flow rate was 0.2 mL/h which was controlled by a syringe pump. Electrospinning voltage and distance between the needle tip and the collector were 15 kV and 12 cm, respectively.

Instrumentation

SEM Micrographs of the gold-coated PBT and composites nanofibres were analyzed using a Hitachi S-570 (Japan). The samples for transmission electron microscopy (TEM) were prepared by directly depositing the nanofibres onto the copper grids. The samples were analyzed using a Hitachi M-7600 (Japan) with an accelerated voltage of 100 kV.

The crystallization behaviour of the PBT and F-MWNTs/PBT nanofibres was determined at a heating rate of 10°C/min, using a Perkin Elmer differential scanning calorimeter (DSC) (USA). Thermogravimetric analysis (TGA) data were obtained under nitrogen atmosphere at a heating rate

of 20°C/min between 25°C and 900°C using a TA4000/Auto DSC 2910 system (USA).

The mechanical properties of the composite nanofibre mats were measured by Instron (Model M 4465, UK). The tests were carried out at room temperature with 30 mm gauge length and a 10 mm/min crosshead speed. The specific tensile strength and modulus were calculated by dividing the force by weight per length, because the pores in the cross section of the nanofibre mat do not give the true stress when the cross-sectional area is used for calculating the nominal stress.

RESULTS AND DISCUSSION

Morphological Characterization of PBT and Composite Nanofibres

Figure 1 shows the SEM images of the pure PBT and F-MWNTs/PBT nanofibres which were electrospun from 10 wt% solutions. The nanofibres of both PBT

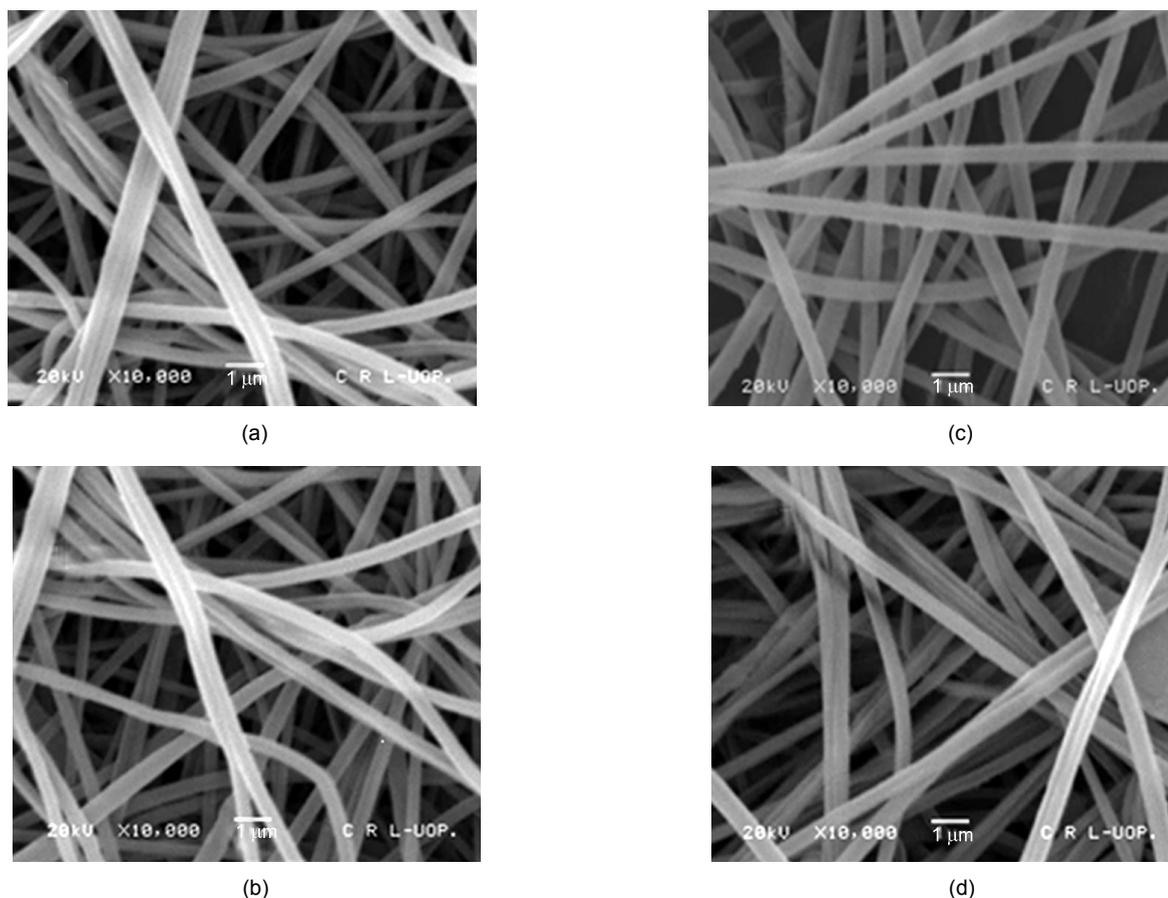


Figure 1. SEM Micrographs of F-MWNTs/PBT composite nanofibres: (a) 0, (b) 1, (c) 3 and (d) 7 wt% of F-MWNTs.

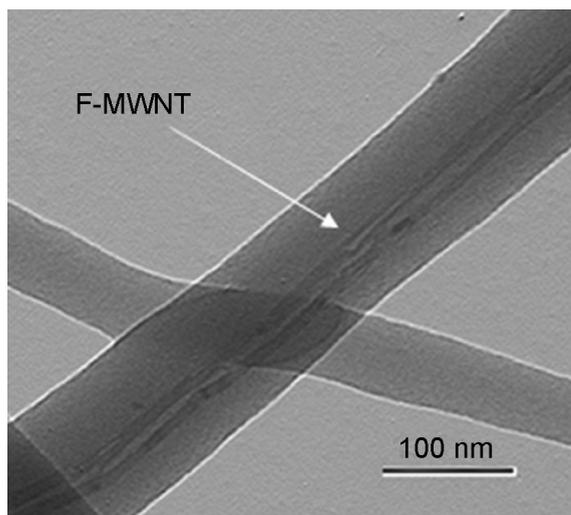


Figure 2. TEM Image of F-MWNTs/PBT composite nanofibres.

and F-MWNTs/PBT were randomly oriented along the axis. The diameters of the nanofibres were below 500 nm. The composite nanofibres (Figures 1b and 1c) had more or less similar morphology with those of PBT nanofibres. The surfaces of F-MWNTs/PBT composite nanofibres even having a high quantity of F-MWNTs (5 wt%) are smooth and without beads. This might be due to the better dispersion of the F-MWNTs in the F-MWNTs/PBT composite nanofibres.

The MWNTs/PBT electrospun nanofibres were also prepared by Matthew et al. [37] in which they used hexafluoroisopropanol as solvent, and reported that the nanofibres have diameter distribution within 200-4000 nm with more rough surfaces.

The TEM analyses were performed in order to determine the orientation and embedment of the F-MWNTs within the PBT nanofibres. Figure 2 shows the TEM image of the F-MWNTs/PBT nanofibres in which most of the nanotubes are well oriented along the axes of the nanofibres. The F-MWNTs are also well embedded within the fibres and the individual nanotubes (rather than aggregates or bundles) are well dispersed in the nanofibres. The TEM images also show that the surface of the F-MWNTs/PBT composite nanofibres is smooth.

Thermal Properties of PBT and Composite Nanofibres

Figure 3 shows the DSC thermograms of pure PBT

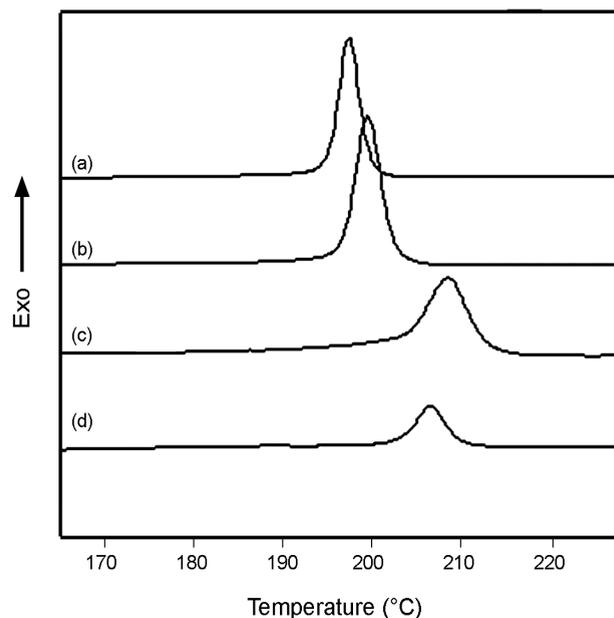


Figure 3. DSC Cooling curves of F-MWNTs/PBT composites nanofibres: (a) 0, (b) 1, (c) 3 and (d) 7 wt% of F-MWNTs.

and F-MWNTs/PBT nanofibres as functions of F-MWNTs content. Pure PBT nanofibres show a T_c peak (crystallization upon cooling from the melt state) at about 197°C. The T_c of F-MWNTs/PBT nanofibres has shifted to a higher temperature (about 200-208°C). The increase of T_c can be explained by

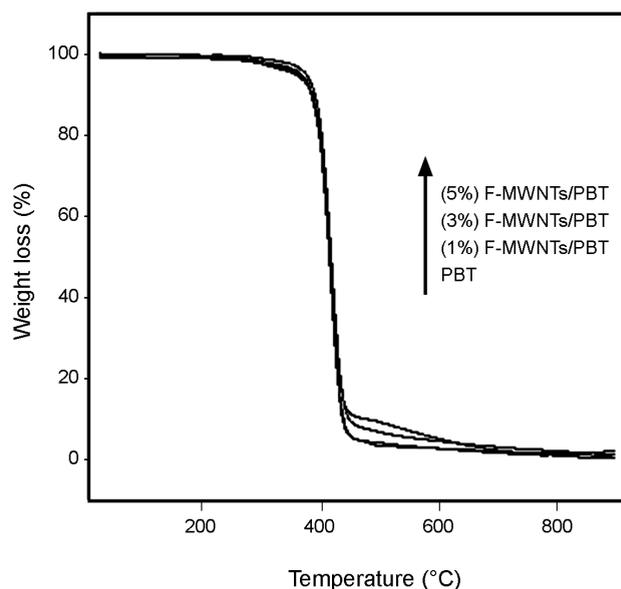


Figure 4. TGA Thermograms of F-MWNTs/PBT composites nanofibres.

Table 1. Mechanical properties of PBT and MWNTs/PBT composites nanofibres.

Samples	Specific tensile strength (kgf cm/g)	Specific modulus (kgf cm/g)	Elongation-at-break (%)
PBT	194.2 ± 55.8	2082.4 ± 791.7	38.6 ± 2.4
1 wt% F-MWNTs/PBT	199.2 ± 30.1	2203.6 ± 227.5	43.5 ± 9.5
3 wt% F-MWNTs/PBT	231.1 ± 74.8	2133.6 ± 390.9	38.4 ± 8.9
5 wt% F-MWNTs/PBT	230.9 ± 33.0	2712.5 ± 86.9	37.8 ± 7.4

the assumption that F-MWNTs act as efficient nucleating agents for the crystallization of PBT nanofibres and the crystallization rate is increased as compared to that of the neat PBT nanofibres.

Figure 4 shows the TGA thermograms of the PBT and F-MWNTs/PBT nanofibres. The TG thermograms of pure PBT and F-MWNTs/PBT nanofibres show that initially the mass of electrospun nanofibres remains constant (up to 350°C), and then it starts to drop sharply. The PBT nanofibres completely decompose at about 450°C. The thermograms of the F-MWNTs/PBT show that almost all decompositions of the composite nano-fibres occur at about 450°C. The residual amount contributing to F-MWNTs in composite nanofibres remains at higher temperatures.

Mechanical Properties of PBT and Composite Nanofibres

Table 1 shows the mechanical properties of pure PBT and F-MWNTs/PBT composite nanofibres. The specific tensile strengths of PBT and F-MWNTs (5 wt%)/PBT nanofibres are 194 and 230 kgf cm/g and the specific moduli are 2082 and 2712 kgf cm/g for the given order of materials. The specific tensile strengths and moduli of F-MWNTs/PBT composite nanofibres are enhanced as compared to those of PBT nanofibres.

The elongation-at-break of F-MWNTs/PBT was increased by the incorporation of a small quantity of F-MWNTs (1 wt%) and when its amount increased to 7 wt% there was a gradual decrease in elongation-at-break compared to that of pure PBT nanofibres. The improvement of the specific tensile strengths and specific modulus of composites nanofibres indicated that the composite nanofibres are tougher and more resistant to deformation [38]. The decrease in elongation-at-break of composite nanofibres (at high

quantity of F-MWNTs) implies that the incorporation of F-MWNTs made nanofibres stronger but less flexible. The increase in tensile strength and modulus and drop in elongation-at-break have been also reported by McCullen et al. [29] and Jeon et al. [39] where the latter group incorporated AgNO₃ into poly(ϵ -caprolactone)-based polyurethane nanofibres and the former incorporated MWNTs into poly(ethylene oxide).

CONCLUSION

This work demonstrates the fabrication, mechanical and thermal properties, and morphological studies of PBT and F-MWNTs/PBT nanofibres. The morphological studies show that the F-MWNTs are well embedded within the nanofibres and also both PBT and composites nanofibres have smooth surfaces. The mechanical properties of F-MWNTs/PBT nanofibres were higher than those of the pure PBT nanofibres. The DSC analyses show that the T_c of PBT nanofibres shifts towards higher temperature (about 10°C) by incorporation of F-MWNTs in them. This increase in T_c is due to the nucleation effect of the nanotubes.

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