



Characterization of Poly(butylene Terephthalate) Electrospun Nanofibres Containing Titanium Oxide

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ABSTRACT

Titanium oxide/poly(butylene terephthalate) (TiO₂/PBT) composite nanofibres were prepared by electrospinning technique. The electrospun PBT and TiO₂/PBT nanofibres were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction analysis (XRD), Instron, and thermogravimetric analysis (TGA). The diameter of PBT and the composite nanofibres were in the range of 500-100±50 nm. The beads formation was observed when the amount of PBT was less than 10 wt % in the polymeric solution. The TiO₂ (with size below 50 nm) nanoparticles were dispersed in the polymeric solution via sonication. The dispersion and embedment of TiO₂ nanoparticles within the nanofibres were confirmed by TEM. The XRD result indicated that TiO₂ nanoparticles were well loaded into PBT electrospun nanofibres mat and it was also observed that the composite nanofibres contain both forms (anatase and rutile) of TiO₂. The mechanical properties such as specific tensile strengths and modulus of the PBT/TiO₂ composite nanofibres were higher than those of pure PBT electrospun nanofibres. However, the elongation-at-break value of composite nanofibres was lower than that of the pure PBT nanofibres, which implies that the incorporation of TiO₂ nanoparticles made nanofibres stronger but less flexible.

Key Words:

poly(butylene terephthalate);
composite;
nanofibres;
electrospinning;
mechanical properties.

INTRODUCTION

The nanoscaled materials have wide range of technological applications in various fields, like chemical or biosensing, biomedicine, nanoelectronics, composites, filtration, biomaterials, due to their large surface area [1-6]. Several methods have been developed to fabricate nanofibres, such as template [7,8], self-assembly [9,10], phase separation [11], melt-blown [12] and electrospinning [13]. Currently, electrospinning is the most promising technique for

making polymeric and inorganic nanofibres within a broad range of diameters, from submicrometer to nanometers according to the selection of the processing parameters.

In an electrospinning process, a high electric field is generated between a polymer solution, which is held in a syringe with a metallic nozzle, and a metallic collector. The droplets of the polymer solution from the nozzle tip are converted into Taylor cones by an electric

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field [14]. When the voltage reaches a critical value, the electrostatic force draws the droplet into liquid jet and ultrafine fibres are produced on the collector after the evaporation of the solvents.

In most cases, the as-spun fibres deposit randomly on the collector forming a non-woven nanofibre mat. The advantage of electrospinning is that the polymers can be electrospun in both solution and in a melt state. The fibre diameter and bead formation might be controlled by adjusting various parameters such as voltage, flow rate of polymeric solution, distance from needle tip to collector, diameter of needle, concentration of the polymer solution, humidity and temperature during electrospinning.

The electrospun non-woven mats show a number of remarkable characteristics such as high porosity, large surface area per unit mass, 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 [15], electrically conductive nanofibre [16], drug delivery systems [17], fine filtration [18], catalyst and enzyme carrier, energy storage [19], metal ion recovery [20] and protective clothing [21].

Various polymeric materials such as polyacrylonitrile [22], nylon-6 [23], polyurethane [24], chitosan/polylactide blend [25] and poly(ethylene terephthalate) [26] etc, were fabricated via electrospinning process. Although, the nanofibres have wide range of applications in various fields, but their mechanical properties are comparatively low. The mechanical properties of nanofibres mat may be improved by the incorporation of reinforcing materials such as carbon nanotubes (CNTs), nanoclays, etc. The nanofibres of numerous polymeric composites like CNT/polycaprolactone [27], CNT/nylon [28], polyamide-6/organic-modified Fe-montmorillonite [29], polyvinyl alcohol/zinc acetate composite [30], etc. have been prepared by electrospinning, which show enhanced mechanical properties compared to their pure polymer nanofibres.

In the present study, TiO₂/PBT nanofibres were prepared via electrospinning technique. The study was primarily focused on the detailed morphological examination, and then to the enhancement of

mechanical properties and thermal stability of PBT nanofibres by incorporation of TiO₂ into the PBT nanofibres. In our study the titanium dioxide was selected due to its wide range of applications related to environmental cleaning (strong oxidizing power and non-toxicity) and protection, photocatalysis, gas sensing, and fabrication of solar cells and batteries [31-33].

Titania has two common crystalline forms (rutile and anatase) with the same titanium oxide chemical formula. The rutile TiO₂ has a tetragonal crystalline structure, while the anatase TiO₂ has an octahedral crystalline structure [34]. While the choice of PBT (a crystalline polymer closely related to the other thermoplastic polyesters) is due to its resistance against solvents, it also shrinks very little during formation, maintains its mechanical strength and heat-resistance. It is used as an insulator in the electrical and electronics industries. To our knowledge, TiO₂ has not been reported before for morphological study as well as the enhancement of mechanical and thermal stability of PBT electrospun nanofibres.

EXPERIMENTAL

Materials

Trifluoroacetic acid (TFA) and TiO₂ were purchased from Tokyo Chemical Industry© and Ducksan Chemicals, respectively. The PBT was kindly supplied by Korean Co Toray Saehan.

Electrospinning of PBT

The solutions of PBT were prepared by dissolving 4, 7, and 10 wt% of sample in TFA separately via magnetic stirrer. A known amount of TiO₂ was dispersed in the PBT solution by sonication (1 h) at room temperature.

The prepared PBT solution was added to a 10-mL glass syringe with a needle tip (0.5 mm diameter). The feeding rate of the polymer solutions was 0.2 mL/h, electrospinning voltage (20 kV) was applied to the needle and the distance between the needle tip and collector was 20 cm. The electrospinning of PBT was performed at 50°C in order to evaporate solvent quickly. The same experimental

conditions were applied for the preparation of TiO_2/PBT composites nanofibres.

Instrumentation

The micrographs of the gold-coated electrospun PBT and TiO_2/PBT nanofibres were analyzed using a JEOL JSM-5910 scanning electron microscope (SEM). The samples for transmission electron microscopy (TEM) were prepared by the direct deposition of the electrospun nanofibres onto the copper grid. The samples were analyzed by using Hitachi M-7600 TEM and the accelerated voltage was 100 kV. The tensile properties were measured using an Instron (Model M 4465). 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 because the pores in the cross-section of the nanofibre mat do not give true stress if the cross-section area is used for calculating the nominal stress. They were calculated by dividing the force by weight per length. The TGA thermograms of the PBT and TiO_2/PBT composites were obtained in a nitrogen atmosphere, at a heating rate of $20^\circ\text{C}/\text{min}$, in the range $25\text{-}1000^\circ\text{C}$ using a Diamond TG/DTA (Perkin Elmer).

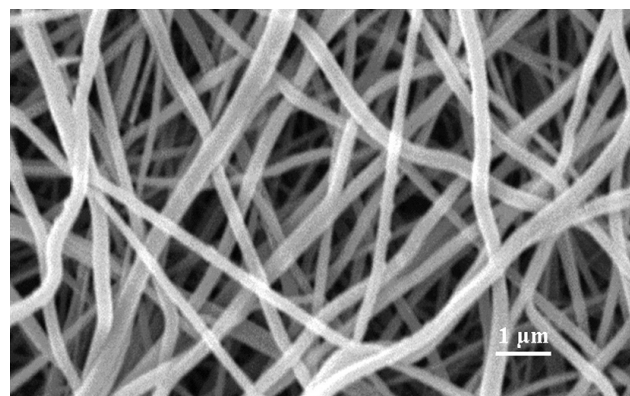
RESULTS AND DISCUSSION

Morphology of Nanofibres

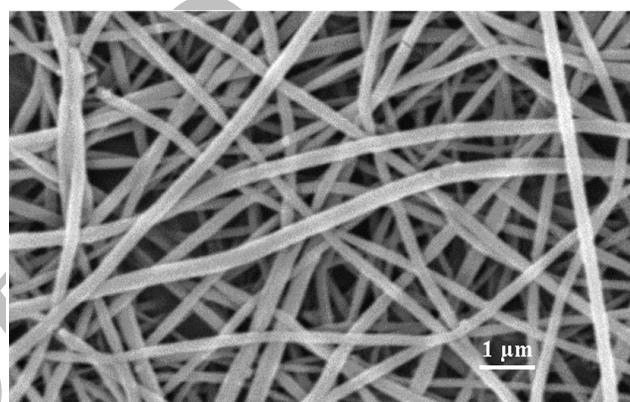
The morphology of the resulting non-woven nanofibres was characterized by SEM at an accelerating voltage of 20 kV. Figure 1 shows the SEM micrographs of electrospun PBT and TiO_2/PBT nanofibres, respectively which were randomly distributed on the collector. The average diameters of the PBT and TiO_2/PBT nanofibres were in the range of $500\text{-}100\pm 50$ nm (Figure 1a).

During the electrospinning process, beads were observed in nanofibres mat, which disappeared when the polymer concentration was increased to 10 wt% in polymer solution [35]. It was also observed that the diameter of the nanofibres increased with an increase in the concentration of the PBT solution in accordance with an increase in viscosity, as also reported in previously published research works [27,28].

After optimization of electrospinning process for



(a)



(b)

Figure 1. SEM micrographs of: (a) PBT and (b) TiO_2/PBT composite nanofibres.

PBT solutions in TFA, TiO_2/PBT composite solution was electrospun to nanofibres. Figure 1b shows the TiO_2/PBT nanofibres which have almost similar morphology and diameter with those of pure PBT nanofibres. The SEM micrograph (Figure 1b) also demonstrates that the TiO_2/PBT nanofibres have smooth surface.

In order to investigate the loading of TiO_2 within the electrospun nanofibres, TEM images of the electrospun TiO_2/PBT nanofibres were obtained, which had been directly deposited on copper grids (Figure 2). The dark spots in TEM images shows the presence of TiO_2 nanoparticles in the PBT nanofibre (Figure 2). These results indicate that TiO_2 particles were present in dispersed form. The low magnification image shows a cluster of TiO_2 nanoparticle in the nanofibre whereas high magnification inset image shows clearly that TiO_2 nanoparticles having sizes less than 50 nm and are

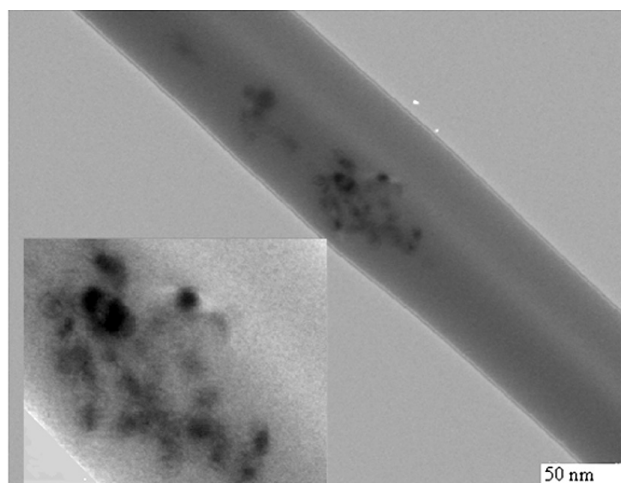


Figure 2. TEM images of the TiO₂/PBT composite nanofibres.

alienated from each other. In TiO₂/PBT nanofibres, TiO₂ were well embedding within the nanofibres.

XRD Analysis

The XRD pattern was further employed to analyze the TiO₂/PBT nanofibres, and the resulting pattern is shown in Figure 3. The TiO₂ particles had dominant peaks at 2θ of 25.7, 27.6, 42, 45.4 and 65.4 and 67.0 which are due to both crystalline forms (rutile and anatase) of TiO₂ [36-39]. The peaks clearly indicate that TiO₂ nanoparticles had been well loaded into PBT polymer mat without any structural modification to form organic-inorganic composite nanofibres

Mechanical Properties of TiO₂/PBT Nanofibres

Tensile tests were performed for both nanofibres mats in order to study the effect of TiO₂ on the PBT nanofibres. Table 1 shows the mechanical properties of pure PBT and TiO₂/PBT nanofibres. The specific tensile strengths of PBT and TiO₂/PBT nanofibres were 159 and 228 kgf.cm/g, respectively, and the specific moduli were 931 and 1385 kgf.cm/g,

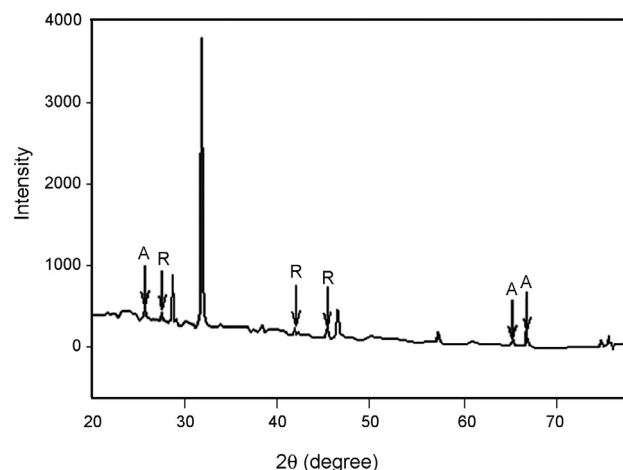


Figure 3. XRD pattern of TiO₂/PBT composite nanofibres.

respectively.

The specific tensile strengths and specific modulus of TiO₂/PBT nanofibres were improved as compared to those of pure PBT while the elongation-at-break of TiO₂/PBT was lower than that of pure PBT nanofibres. The enhancement of the specific tensile strengths and specific modulus of TiO₂/PBT nanofibres indicated that the composite nanofibres were tougher and more resistant to deformation [40].

The decrease in elongation-at-break of TiO₂/PBT implies that the incorporation of TiO₂ made nanofibres stronger but less flexible. The increase in tensile strength and modulus but lower elongation-at-break has been also reported by Jeon et al. where, they incorporated AgNO₃ into poly(ε-caprolactone)-based polyurethane nanofibres [41].

Thermal Properties of TiO₂/PBT Nanofibres

Figure 4 shows the TGA curves of the PBT and TiO₂/PBT nanofibres. The TG curve of pure PBT nanofibres presenting that initial mass of nanofibres remained constant up to 350°C, and then it started to drop sharply and reduced abruptly. The PBT nanofibres started weight loss at about 360°C and

Table 1. Mechanical properties of pure PBT and TiO₂/PBT composites nanofibres.

Samples	Specific tensile strength (kgf.cm/g)	Specific modulus (kgf.cm/g)	Elongation-at-break (%)
PBT	159.3 ± 41.9	931.1 ± 596.0	51.01 ± 8.3
TiO ₂ (5 wt%)/PBT	228.5 ± 20.7	1385.7 ± 274.2	46.2 ± 7.1

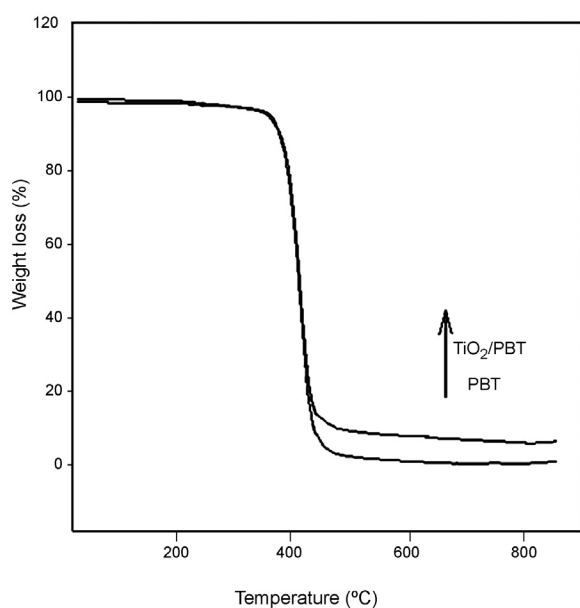


Figure 4. TGA thermograms of PBT and TiO_2/PBT composite nanofibres.

completely decomposed at about 450°C . The thermogram of the TiO_2/PBT shows that the composite nanofibres also decomposed at about 450°C . The residual amount which was contributed to TiO_2 particles in the composite nanofibres remained at higher temperatures.

CONCLUSION

In this work, we presented the preparation and characterization of PBT and TiO_2/PBT nanofibres with diameters in the range $500\text{-}100\pm 50$ nm. The surface of TiO_2/PBT nanofibres was smooth and showed almost similar morphology and diameter as the pure PBT nanofibres. It was also observed that TiO_2 particles were well embedded within the nanofibres. The mechanical properties of composite nanofibres were improved as compared to those of pure PBT nanofibres.

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