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# Short electrospun composite nanofibers: Effects of nanoparticle concentration and surface charge on fiber length

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ABSTRACT

Short composite nanofibers were fabricated by electrospinning polymer/$TiO_2$ nanoparticle solutions of 13 wt. % cellulose acetate as a polymer under a voltage of 5.5 kV and at a flow rate of 0.1 μL/min, and the nanoparticles could be added in concentrations as high as 50 wt. %. The length of the short composite nanofibers was significantly decreased from 112 to 70 μm by the addition of at least a 5 wt. % concentration of nanoparticles, and it gradually continued to decrease as the nanoparticle concentration was increased. The length of the short composite nanofibers with a low concentration of nanoparticles was affected by the surface charge of the nanoparticles, and negatively charged nanoparticles readily dispersed to the negatively charged polymers in solution, which resulted in an elongation of the fabricated short composite nanofibers.



## 1. Introduction

Research into composite fibers has recently intensified in various industrial fields. The presence of nanoparticles has resulted in an enhancement of the mechanical, photocatalytic, electrical, thermal, and optical properties of the fibers [1–16]. Nano-sized composite fibers can utilize the characteristic features of nanoparticles such as tunable electronic band gaps and a high surface area. Yu et al. have reported that the photoluminescent property of cadmium sulfate quantum-dots with a particle-size-dependent electronic band gap could be enhanced by embedding the cadmium quantum-dots into polyethylene oxide fiber [8]. This kind of material is expected to be applicable to the preparation of electroluminescent devices and nano-optoelectronic devices [8]. The photocatalytic efficiency of $TiO_2$ in the nanofiber morphology is highly superior to that of the $TiO_2$ film or nanoparticles [17,18]. The enhancement of photocatalytic efficiency is due to the high surface areas and high porosity of the $TiO_2$ nanofibers. The short fibers have several advantages compared to continuous fiber [19–21]. Anil et al. have reported using the short nanofibers as a drug carrier with a diameter and length of 4 nm and 50–400 nm, respectively, that could deliver the drugs to a tumor site within a much shorter period of time compared with that of a spherical nanoparticle [19]. Fu et al. report that the special regular short nanofiber microstructure has had a great impact on photocatalytic performance and removal efficiency, and that it greatly increases the permeability of visible light, expands the reaction zone, and promotes photocatalytic efficiency [20]. Jiang et al. report that the short electrospun polyimide fiber dispersed in a polymer matrix enhances the mechanical properties of a polymer matrix with the addition of only 2 wt. % of short fiber, whereas the amount of continuously long polyimide fiber required to even approximate the mechanical strength was much higher as 38 wt. % [21]. Therefore, the studies of both effects of nanoparticles and processing parameters on the fabrication of short composite fibers are relevant in order to find the optimum performance of short composite fibers that could contribute to further research such as drug carriers, material templates for hollow or porous structures of metal oxide, membranes, and high tensile and modulus materials.

The method that is commonly used to fabricate short fibers is called the vapor-grown technique. With this technique, a controllable length of short fibers can be achieved by altering the catalyst size, temperature processing, and catalyst activity [22,23]. This technique is feasible for industrial applications, however, several drawbacks persist, such as an extended chemical route and post-processing, which are necessary in order to enhance the physical properties of the carbon fibers. A novel method to fabricate short fibers is called the pressurized gyration process, which combines centrifugal spinning and solution blowing [24]. With this process, the diameter and length of obtained fibers are 60–1000 nm and

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200–800 mm, respectively. This method offers mass production capabilities, but the length of the nanofibers is too long for use as a filler. These problems have motivated many researchers to find more effective methods for the fabrication of short fibers or short composite fibers.

Electrospinning is a simple and reliable method for the fabrication of fibers with diameters in the nano to micro scale. A polymer solution is electrified by high voltage to form a cone jet, which stretches to fabricate the nanofibers. Composite nanofiber can be produced with this technique by utilizing a suspension of polymer/nanoparticles as a precursor [25–27]. The nanofibers prepared via the electrospinning method are generally continuous, and secondary processes must be applied in order to fabricate short nanofibers. Ali et al. used mechanical crushing as a secondary process in order to fabricate $TiO_2$ short nanofibers from the continuous electrospun fibers of polyvinylpirrolidone/$TiO_2$ [28]. In our previous studies, short electrospun polymer nanofibers could be fabricated in a one-step process. In these methods, the short nanofibers could be fabricated by cutting the continuous fibers using an electric spark [29], and by regulating the concentration of the polymer, the flow rate, and the working voltage [30]. One-step process methods of electrospinning can be applied to the fabrication of short composite nanofibers by replacing the polymer solution with a polymer/nanoparticle solution.

For the present study, the polymer/nanoparticle solutions consisted of cellulose acetate, $TiO_2$ nanoparticles, and organic solvents that were electrospun to fabricate short composite nanofibers. The goal of this work was to investigate the effect of the concentrations and the surface charges of the nanoparticles on the length of fabricated short composite nanofibers that could contribute to the development of drug delivery systems, material template fabrication, and fibril filler for composite materials. The morphologies of the fabricated short composite nanofibers and the conditions of the electrospun jets of the polymer/nanoparticle solutions were observed to elucidate the mechanism of fabrication for short composite nanofibers.

## 2. Experimental

### 2.1. Preparation of the polymer/nanoparticle solutions

The polymer/nanoparticle solutions consisted of cellulose acetate polymer powder with a number-average molecular weight of 30,000 (Sigma Aldrich, UK), $TiO_2$ nanoparticles with a diameter of 10–30 nm (TTO-51C (rutile type), Ishihara Sangyo Kaisha, Ltd., Japan), and organic solvents that consisted of acetone (>99.5%, Kanto Chemical, Japan) and *N*,*N*-dimethyl acetamide (DMAc) (>99.5%, Sigma Aldrich, UK) with a volume ratio of 2:1. The concentration of the polymer was set at 13 wt. % and the concentrations of $TiO_2$ nanoparticles in the polymer/nanoparticle solutions were varied from 0.5 to 17 wt. % for the fabrication of short composite nanofibers. The prepared polymer/nanoparticle solutions turned to short composite nanofibers with 4–56 wt. % nanoparticles after evaporation of the organic solvent. The suspension was prepared by pouring the $TiO_2$ nanoparticles into 15 mL of organic solvent, which was then subjected to an ultrasonic homogenizer in a closed bottle for 30 min. The polymer powder was added into the suspension of $TiO_2$ nanoparticles and organic solvent and then stirred and homogenized for 3 h. During the ultrasound-homogenization process, the weight of the suspension decreased as a portion of the organic solvent was evaporated. After dispersion, organic solvent was added to compensate for the weight loss of the suspension and to return the weight ratio of each component to the original amount. Polymer/nanoparticle solutions of various pHs were prepared using either aqueous sodium hydroxide or hydrochloric acid. The pH of the solution was measured using a digital pH meter (Cyberscan pH 110, EUTECH INSTRUSMENTS) with a glass electrode (EC620131, EUTECH INSTRUSMENTS). The viscosity of each solution was measured using a viscometer (TVE-22H cone plate type, Toki Sangyo Co., Ltd, Japan).

### 2.2. Electrospinning of the polymer/nanoparticle solutions

A conventional electrospinning setup was used to fabricate short composite nanofibers. The polymer/nanoparticle solutions were loaded into a 1000 cc syringe (TTL 2-432, Hamilton Company) with a stainless needle (OD: 0.46 mm, ID: 0.26 mm). A high-voltage power supply (HER-15P5-LV, Matsusada Precision Inc.) was connected to the stainless needle to electrify the polymer/nanoparticle solutions. The voltage was increased gradually to find the appropriate voltage for conducting electrospinning. The flow rates of polymer/nanoparticle solutions were controlled via a micro syringe pump (ESP64, EiCom Corporation). The voltage and the flow rates were set at 5.5 kV and 0.1 μL/min, respectively [30]. A 30 mm × 30 mm aluminum plate that was used to collect the electrospun nanofibers was connected to the ground, and a 3 mm × 3 mm silicon wafer was attached to observe the nanofibers. The distance between the needle tip and the aluminum plate was set at 90 mm. The ambient temperature and humidity were maintained at 20 °C and 60% using a temperature controller and an integrated humidifier (PAU-300S, Apiste Corporation), respectively.

### 2.3. Measurement of the zeta potential of $TiO_2$ nanoparticles

The zeta potential of the nanoparticles was measured at pH values ranging from 2 to 11 via a Nanozeta apparatus (Malvern Zetasizer, Nano ZS, UK). The $TiO_2$ nanoparticles were dispersed into 100 mL of deionized water with a concentration 0.05 wt. %. Then, 1 M of either aqueous sodium hydroxide or hydrochloride acid was dropped gradually into the solution to control the pH.

### 2.4. Observation of short composite nanofibers

The diameters and the lengths of fabricated short composite nanofibers were measured using the ruler function of image processing software during observation with a digital microscope at a resolution of 2.11 megapixels (VH-8000, Keyence Corporation). Two types of lenses, a low-range lens and a high-range zoom lens with a magnification ranging from 25 to 3,000× (VH-Z450, Keyence Corporation), were used for the observation. The distribution and the average lengths of the short composite fibers were determined for more than 200 fibers. The morphologies of the short composite nanofibers were observed using a scanning electron microscope (SEM) (JSM-6340F, JEOL Ltd.) with a maximum magnification factor of 650,000× and a resolution of 1.2 nm at an acceleration voltage of 20 kV.

The conditions of the electrospinning jets of various polymer/nanoparticle solutions were observed using a CCD camera with a resolution of 0.4 megapixels, twice-digital zoom, and 0.8 lux of minimum illumination (MTV-73x11HN, Mintron Enterprise Co., Ltd). A monocular optical lens with a diameter of 50 mm and a magnification factor of 8 (M0850, Specwell) was attached to the CCD camera. The images were taken at a speed of 30 fps and were recorded on a personal computer.