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# Effects of pH on electrospun PVA/acid-treated MWNT composite nanofibers

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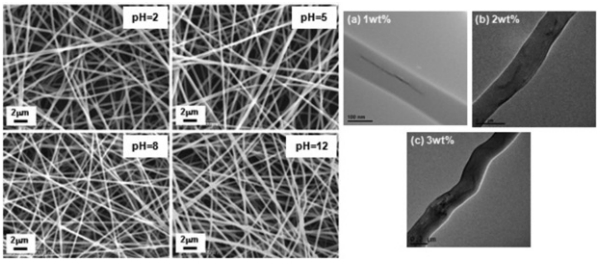
## HIGHLIGHTS

- Poly (vinyl alcohol)/multi-walled carbon nanotubes composite nanofibers.
- pH effects on the morphologies, microstructures and mechanical properties.
- Controlling the molecular interactions between PVA and acid-treated MWNTs.
- It is important for understanding the mechanism of enhanced mechanical properties.

## GRAPHICAL ABSTRACT

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## ABSTRACT

In this work, we studied the effects of multi-walled carbon nanotubes (MWNTs) concentration and pH on the morphologies, microstructures and mechanical properties of the resultant poly (vinyl alcohol) (PVA)/MWNT composite nanofibers prepared by electrospinning technique. The PVA solution dissolved in distilled water was blended with various acid-treated MWNTs concentrations ranging from 1.0 to 3.0 wt%, and then electrospun to produce PVA/acid-treated MWNT composite nanofibers. The PVA/acid-treated MWNT nanofibers were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), wide-angle X-ray diffraction (WAXD), and tensile testing. SEM analysis demonstrated that the PVA/MWNT nanofibers with acid-treated MWNTs of 1.0 wt% gave rather smaller diameter and narrower distribution, suggesting well-distribution of the MWNTs onto the PVA nanofiber matrix, as also confirmed by TEM analysis. In addition, it was observed that the PVA/acid-treated MWNT (MWNT concentration ~1.0 wt%) nanofibers at higher pH gave lower diameter than those at lower pH, due to a decreased molecular interaction between PVA and acid-treated CNTs, and thereby results in a decreased viscosity and their diameters. Moreover, the resultant nanofibers at lower pH have better mechanical properties than those at higher pH.



## 1. Introduction

Carbon nanotubes (CNTs) have attracted great attention as ideal fillers for reinforcement because of their unique physical and mechanical properties since the discovery by Ijima [1–4]. However, poor solubility and processability of the CNTs have hindered chemical manipulations and their further uses in applications [5–7]. Thus, both chemical functionalization and noncovalent wrapping methods have been studied. As functionalization of the CNTs is growing popular in nanotechnology, many new green techniques have been employed [8]. Among the functionalization techniques, there are either acid or basic treatments, but the former is a better functionalization treatment, because after the acid-treatments, there are small changes in the physical and chemical properties of the CNTs compared to the as-grown materials. Moreover, several techniques revealed the presence of oxygen-containing functional groups, such

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as —COOH or $-SO_3H$ groups, on the surface of the CNTs treated with a $HNO_3/H_2SO_4$ mixture [9]. Up to date, PVA/CNT composite materials have been widely studied [11–14] since the hydroxyl groups of the PVA and the carboxyl groups of the modified CNTs can form strong interaction via hydrogen bonding. Dalton et al. [11] produced the super-tough carbon-nanotube fibers which possess high tensile strength of 1.8 GPa and high Young's modulus of 80 GPa with the single-walled carbon nanotube (SWNT) and PVA by using a type of coagulation-based carbon-nanotubes spinning method to prepare these fibers. Lachman et al. [10] also studied the Raman response of carbon nanotube/PVA fibers under strain and found that the carboxylic groups played a major role in the stress-transfer mechanism, as they improved the transfer of stress from the matrix to the CNTs. Eitan et al. [15] modified the multi-walled carbon nanotubes (MWNT) by means of epoxide-based functional groups, as the MWNTs were first carboxylated along their walls, and followed by further reactions to attach diglycidyl ether of bisphenol-A-based epoxide resin, so in the case of an epoxy-based bulk polymer it is possible to obtain a covalent bond between the nanotube and the polymer matrix. Although a lot of works have been done to learn the interfacial interactions between the carbon nanotubes and the polymer chains and the load-transfer efficiency from the polymer to the carbon nanotubes, few people studied how pH value of the polymer/acid-treated MWNT solution affects the connections between the MWNT and polymer matrix. In this paper, we report the influence of pH on the morphologies and mechanical properties of the resultant electrospun PVA/acid-treated MWNT composite nanofibers.

## 2. Experimental

### 2.1. Materials

Poly(vinyl alcohol) (PVA) (degree of polymerization ~1700 and degree of hydrolysis 88%) was kindly provided by Kuraray Co. Ltd., Japan and used without further purification. Multi-walled carbon nanotubes (MWNTs, diameter ~15–25 nm, [16]) grown by chemical vapor deposition (CVD) method were used as a nanofiller. To improve the miscibility of the MWNTs with PVA, pristine MWNTs were acid-treated using sulfuric and nitric acid solution ($H_2SO_4$:$HNO_3$ = 3:1) [9] under sonication for 3 h at about 50 °C, and then kept for 1 day. Afterwards, acid-treated MWNTs were thoroughly rinsed 4–5 times with access amounts of deionized water until pH became neutral, and subsequently was vacuum-dried. The resultant acid-treated MWNTs were dispersed in dimethylformamide (DMF) (Wako Pure Chemical Industries, Ltd.: >99.5%) under sonication for 3 h, and then used as a stock solution. The MWNT concentration in the PVA/MWNTs blend solutions was controlled to be 1.0–3.0 wt%. Before electrospinning, mixed solutions of PVA and MWNTs were sonicated for 3 h. and stirred for 24 h, and then electrospun to produce the PVA/MWNTs composite nanofibers with different MWNT contents. The PVA was dissolved in the distilled water with different pH values ranging from 2 to 12 and mixed with different amounts of MWNTs to produce the PVA/MWNTs composite solutions, and then used for electrospinning to produce the PVA/MWNTs composite nanofibers with different pHs. The concentration of aqueous PVA solution was ca. 12.0 wt%. The pH of the PVA/MWNTs blend solutions was measured by pH meter (inoLab Level 3, Germany) with an accuracy of ±0.5.

### 2.2. The electrospun PVA/MWNTs composite nanofibers

A high-voltage power supply (CPS-60 Ko22V1, Chunpa EMT Co., Republic of Korea) capable of generating voltage up to 80 kV, was used as a source of electric field. The aqueous PVA/MWNTs dispersion solutions with various pHs and MWNT contents were supplied through a plastic syringe attached to a capillary tip with inner diameter of 0.6 mm. The copper wire connected to a positive electrode (anode) was inserted into the polymer solution, and a negative electrode (cathode) was attached to a metallic collector [17–21]. The collecting roller was placed at distance of 15 cm from the capillary tip, and a voltage of 12 kV was applied to the copper wire, while the receiving collector was rotating.

### 2.3. Characterization

#### 2.3.1. Electron microscopy

Scanning electron microscopy (SEM, VE-8800, Keynece Co., Japan) was used to characterize the fiber morphology, average diameter and its distribution of the resultant PVA/MWNTs composite nanofibers. Transmission electron microscopy (TEM) (JEOL model 2010 FasTEM, accelerating voltage 200 kV) was used to investigate the morphologies of the pristine and the acid-treated MWNTs as well as the alignment of the MWNTs in the resulting PVA/MWNTs composite nanofibers.

#### 2.3.2. Raman spectroscopy

The Raman spectra were recorded with a Raman spectrometer (Hololab 5000, Kaiser Optical Systems Inc., USA), and argon laser at 532 nm, with a Kaiser holographic edge filter. Typically 50 mW of laser light was used at the sample with a ×50 long distance microscope objective. Integration time was around 40 s, and the spectral resolution was 1.2 $cm^{-1}$.

#### 2.3.3. Wide-angle X-ray diffraction (WAXD)

The WAXD experiments were performed at room temperature with nanofiber samples using a Rotaflex RTP300 (Rigaku Co., Japan) X-ray diffractometer operating at 50 kV and 200 mA. Nickel-filtered Cu $K_\alpha$ radiation was used for the measurements, along with an angular range of $5 < 2\theta < 50^\circ$.

#### 2.3.4. Mechanical properties

The mechanical behavior was determined by a universal testing machine (TENSILON RTC1250A, A&D Company, Ltd., Japan) under a crosshead speed 5.0 mm/min at room temperature. In according with ASTM D-638, samples were prepared in the form of a dumbbell-shape and, then, at least five specimens were tested for tensile behavior and the average values were reported. All specimens were dried in a vacuum oven at 25 °C for a day before use. Three parameters were determined from each stress–strain curves: Young's modulus, tensile strength, and elongation at break. Elastic modulus or Young's modulus is the initial slope of the stress–strain curve. Tensile strength is the stress at failure and the strain corresponding to the tensile strength is the failure strain.

## 3. Results and discussion

### 3.1. Effects of MWNT contents on PVA/MWNTs composite fibers

Fig. 1 shows SEM images (top) and the change in average fiber diameters (bottom) for the electrospun PVA/MWNT composite nanofibers with different concentrations of MWNTs at pH ≈7. It could be seen that the PVA/MWNTs nanofibers with 1.0 wt% MWNTs exhibited the smallest diameter and narrower diameter distribution, suggesting well-distribution of the MWNTs onto the PVA nanofibers. This may be attributed to the fact that the MWNTs have a good conductivity and therefore reduce an electrostatic potential to give smaller diameter during electrospinning. On the other hand, as the concentration of MWNTs increased to 2.0 and 3.0 wt%, the diameter and its distribution of the PVA/MWNTs nanofibers became bigger and broader, which