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Antimicrobial properties of lignin-decorated thin multi-walled carbon nanotubes in poly(vinyl alcohol) nanocomposites

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ABSTRACT

Lignin-decorated thin multi-walled carbon nanotubes (t-MWNTs) were prepared to obtain mechanically strong poly(vinyl alcohol) (PVA) nanofibers (NFs) with high antimicrobial properties. The t-MWNTs were well-dispersed in the aqueous lignin solution owing to their good interaction with lignin molecules, resulting in decoration of the lignin molecules on the surface of the t-MWNTs. The lignin-decorated t-MWNT/PVA NF webs were prepared by electrospinning lignin/t-MWNT/PVA solutions containing 1 wt% t-MWNTs. They displayed enhanced mechanical properties in terms of breaking stress and modulus, compared to lignin/PVA nanofibers. Superior antimicrobial activity was also exhibited by the lignin/t-MWNTs/PVA composites compared to lignin/PVA composites. The mechanical properties of the lignin/t-MWNT/PVA NFs could be preserved even after the heat treatment of PVA, which is a necessary process for medical applications such as wound healing on the skin's dermal layer.

1. Introduction

Lignin has received much attention in various applications such as biosynthesis, antimicrobial activity, and as a resource for carbon fibers. The physical and biomedical properties of lignin are due to inherent functionalities resulting from its phenolic structure, i.e., an aromatic three-dimensional structure consisting of three types of phenylpropanoid monomers: coumaryl-, coniferyl-, and sinapyl alcohol [1–3]. Lignin is also the second most abundant natural polymer in the biosphere, next to cellulose, and generally exists in the cell walls of terrestrial plants [4]. Different sources from the biosphere affect its structure and properties [5,6]. Therefore, it is important to select a type of lignin depending on applications.

Antimicrobial and antioxidant nanofiber webs using lignin have recently been developed for biological applications such as wound dressing [7–9]. As the nanofiber webs have many small pores among very thin nanofibers, they can protect the human body against external environmental factors while allowing the diffusion of water vapor that is generated by the human body [10]. Recently, several researchers have reported the formation of lignin nanofibers with inherent mechanical, antimicrobial, and antioxidant properties by electrospinning lignin solutions, demonstrating the potential of lignin to serve as a resource for functional materials [11–13].

However, the poor mechanical properties of lignin-based nanofibers still limit their practical applications. Therefore, improving the mechanical properties of lignin-based nanofibers is essential. Carbon nanotubes (CNTs) may be effectively used as an ideal nanofiller in the lignin matrix to increase the nanofiber mechanical properties because CNTs have excellent mechanical, electrical, and thermal properties [14–18]. However, the poor dispersion of CNTs in the polymer matrix may also lower the mechanical properties of polymer/CNT composites. Both covalent and non-covalent functionalization methods are used to enhance the CNT dispersion in the polymer matrix; however, non-covalent CNT functionalization is more suitable as the functionalization should not result in a reduction in the antimicrobial properties of the CNT/polymer composites.

This study investigates the mechanical and antimicrobial properties of lignin/poly(vinyl alcohol) (PVA) composites including lignin-

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decorated thin-walled carbon nanotubes (t-MWNTs). Heat treated NFs were also obtained by electrospinning of a t-MWNT/lignin/PVA solution, and their mechanical and thermal properties were analyzed.

2. Materials and methods

2.1. Materials

Lignin containing sulfur impurities (4%), with a pH of 10.5, and an average molecular weight of approximately 10,000 g/mol was obtained from Sigma Aldrich, Korea. PVA (> 99% hydrolyzed, M_w = 89,000–98,000) was purchased from Sigma Aldrich, Korea. The lignin and PVA were used as received. Brain heart infusion (BHI) broth and phosphate buffered saline (PBS) were purchased from Fluka Analytical (Switzerland) and Sigma Aldrich (Korea), respectively, for the antimicrobial tests, and were used without further purification. t-MWNTs were synthesized via a chemical vapor deposition (CVD) method as described in our previous report [19], with an average diameter and length of 7–10 nm and 100–300 μm, respectively.

2.2. Preparation of lignin-decorated t-MWNT dispersion solutions

Aqueous lignin solutions with varying lignin quantities ranging from 15 to 2,000 mg in 100 ml of water were prepared to determine the appropriate t-MWNT dispersion condition. Fixed amounts of t-MWNTs were then added to each solution, yielding a final concentration of 10 mg of t-MWNTs in 100 ml of water. This resulted in lignin-to-t-MWNT ratios of 1.5, 40, and 200. Solutions containing t-MWNTs with various lignin concentrations were initially dispersed using a bath-type sonicator (JAC-3010, KODO Technical Research Co. Ltd., Korea) at 100 W and 4 °C for 5 h and then dispersed again using a probe-type sonicator (Vibra-cell 130, Sonics, USA) at 26 W and 4 °C for 3 h. The t-MWNT dispersions were visualized using a field-emission scanning electron microscope (FE-SEM, Nova NanoSEM 450, FEI, USA) and the stabilities of the CNT dispersions were examined using a UV–Vis spectrometer (V-670, Jasco, Japan).

2.3. Preparation of lignin/t-MWNT/PVA spinning solution via electrospinning

For the electrospinning of the solution, PVA (2.22 g) aqueous solution (water 10 ml) with concentrations of 10 wt.% was prepared, and 2.22 g of lignin was added into PVA aqueous solution. The solution was heated to 80 °C and stirred for 6 h. For the solution containing t-MWNTs, lignin/t-MWNT dispersion and t-MWNT were prepared, as were lignin/PVA aqueous solutions simultaneously. The amount of t-MWNT was calculated to a final total polymer concentration of 1 wt.%. The mixed solution was kept under mechanical agitation at 80 °C overnight and was then cooled for an hour before the electrospinning process. Electrospinning was carried out in a vertical electrospinning machine (NCC-ESP100, NanoNC Co., Korea) on a substrate material of nonwoven polyester. The prepared solutions were loaded into a 10 ml syringe with a 21 G needle and were electrospun at a voltage of 25–30 kV, a feed rate of 7–10 μl/min, and at a tip-to-collector distance of 10 cm. The electrospun nanofibers were then vacuum-dried at 50 °C for 24 h.

2.4. Heat treatment of electrospun lignin/t-MWNT/PVA NFs

The curing of lignin/PVA and lignin/t-MWNT/PVA NFs was carried out in two steps. First, the nanofibers were treated with water vapor for 3 h at 80 °C in a steam oven. Subsequently, the NFs were heat-treated at 200 °C for 1 h in an oven.

2.5. Water uptake and retention tests of heat treated NF webs

The water uptake and retention of the crosslinked lignin/PVA and lignin/t-MWNT/PVA NFs were measured following the procedure described in British Pharmacopoeia (1993). The nanofiber samples were stored in a desiccator for 24 h before testing, and all tests were performed in triplicate. The dry NF webs were weighed (W_d) and then immersed in water. After 24 h, the NF webs were blotted with filter paper to eliminate excess water, and were then weighed (W_w) to estimate the water uptake ability. To measure the water retention, the wet NF webs were wrapped with filter paper, placed into centrifuge tubes, and centrifuged at 500 rpm for 3 min. The centrifuged NF webs were then weighed instantly () and the percentage water uptake (E_u) and water retention (E_R) were calculated using Eqs. (1) and (2).

$$E_U = [(W_w - W_d)/W_d] \times 100 \quad (1)$$

$$E_R = [(W'_w - W_d)/W_d] \times 100 \quad (2)$$

2.6. Characterization

The morphology of the nanofibers was observed using field-emission transmission electron microscopy (FE-TEM, Tecnai G2, FEI, USA) and field-emission scanning electron microscopy (Nova NanoSEM 450, FEI, USA) using Pt-coated samples. The distributions of the fiber diameters were also calculated from the SEM micro-images using ImageJ software (National Institute of Health, USA). Raman spectra of the t-MWNTs and lignin/t-MWNTs were performed using a Renishaw, inVia Raman microscope (514 laser lines, Renishaw Corporate, UK). Absorption spectra of the t-MWNTs and lignin/t-MWNTs, which were taken as 80% of the supernatant after the dispersion solutions were centrifuged through an ultracentrifuge system (15,000g, optima MAX-XP Ultracentrifuge, BECKMAN Coulter) for 1 h to remove any insoluble materials, were obtained through UV–VIS spectrophotometer (Shimadzu Solidspec-3700). Tensile tests were carried out using a universal testing machine (UTM, UTM 5567A, Instron, USA) in accordance with the ASTM D638 standard. Testing samples were prepared by cutting the electro-spun lignin/PVA and lignin/t-MWNT/PVA NF webs with a web area average density of 40 g/m^2 into a dog-bone type dumb-bell specimen. The samples were prepared in dog-bone form with dimensions of 25 (length) × 10 (width) × 10 (narrow portion length) × 3 (narrow portion width) × 0.10 (thickness) in mm. We have used the following measurement conditions: gauge length = 25 mm; crosshead speed = 10 mm/min; load cell = 100 N. At least 10 samples were tested and the average value was used. We also carried out differential scanning calorimeter (DSC) measurements (TA instrument 2010 DSC Du pont) for all samples in order to understand the effect of the reinforced tubes on the thermal stability of NF (heating rate = 10 °C/min). Thermogravimetric analysis (TGA, Q50, TA Instruments, USA) was used to analyze the thermal degradation of NFs; the sample amounting to 10 mg was heated from 40 °C to 900 °C at a rate of 10 °C /min under a N_2 atmosphere. The antimicrobial activity of the lignin/t-MWNT/PVA composites was measured using a serial dilution method [20] (see Supplementary Data). The minimum inhibitory concentration (MIC) and the minimum bactericidal concentration (MBC) for the lignin/PVA and lignin/t-MWNT/PVA composites containing 1 and 3 wt.% t-MWNTs were determined by comparing the lowest concentrations at which visible microbial growth and the growth of microorganisms were inhibited, respectively. Staphylococcus aureus was used as the reference strain in ASTM E2149-10 testing.

3. Results and discussion

Ideally, carbon nanotube fillers should be individually dispersed within a polymer matrix and maintain their aspect-ratio, namely a small diameter and a long length, in order to exploit the superior