

# Far-infrared Radiation Properties of Poly(vinyl alcohol) Nanofibrous Membranes Containing Germanium and Silicon Dioxide

J. Chung and S. Lee

Yonsei University, Seoul, Korea, SL158@yonsei.ac.kr

## ABSTRACT

Far-infrared radiation effect and antibacterial properties were introduced in PVA nanofibrous membrane using germanium (Ge) and silicon dioxide (SiO<sub>2</sub>). Composite fibers containing Ge and SiO<sub>2</sub> were fabricated at various concentrations of Ge and/or SiO<sub>2</sub> using electrospinning and layered on polypropylene nonwoven. Far-infrared emissivity and emissive power of Ge/SiO<sub>2</sub>/PVA nanocomposite fibers were examined in the range of 5-20 $\mu$ m of wavelength at 37°C. Antibacterial properties were assessed quantitatively by measuring the bacterial reductions of *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Escherichia Coli*. Layered fabric systems with electrospun PVA nanofibrous membranes containing Ge and SiO<sub>2</sub> nanoparticles showed significant increases in far-infrared emissivity and emissive power. The system exhibited a 99.9% bacterial reduction against both *Staphylococcus aureus* and *Escherichia Coli*, and showed a 34.8% reduction in *Klebsiella pneumoniae*.

**Keywords:** nanocomposite fiber, germanium, silicon dioxide, far-infrared radiation property, antibacterial property

## 1 INTRODUCTION

Polymer nanocomposites have been received much attention due to their potential applications in diverse fields. A number of characteristics and performances can be obtained with the addition of a functional material. Recently, germanium and ceramic powders have been applied to textile structures to exhibit far-infrared radiation effect [1,2]. It has been reported that infrared rays having a long wavelength such as far-infrared rays enhance blood circulation and metabolism and promote recovery of fatigue of muscles [3,4]. Electrospinning is a convenient fiber-forming process that can produce polymer fibers with diameters in the nanometer to micron range. The large surface areas of nanofibrous structure can maximize the functionalities as compared with those of conventional fibers with typical diameters of several microns. Furthermore, nanofibrous structures have numerous pores with pore dimensions that are small enough to prevent bacteria from entering but large enough for moisture vapor to diffuse through; thus they have been proposed for biomedical applications such as wound dressing, skin masks for therapeutical or medical treatments. Poly(vinyl alcohol) (PVA) is a non-toxic, water-soluble, and

biodegradable synthetic polymer. It has excellent chemical resistance, physical properties, and good fiber forming properties [5]. For these reasons, PVA has been electrospun into ultrafine fibers and applied to many applications, including drug delivery, wound dressing, biodegradable mats and many more [6]. In this study, nanocomposite fibers containing germanium and silicon dioxide nanoparticles were fabricated by electrospinning to impart far-infrared radiation effect. Far-infrared radiation properties of Ge/SiO<sub>2</sub>/PVA nanocomposite fiber webs with various concentrations of Ge and SiO<sub>2</sub> were assessed. In addition, antimicrobial activity of Ge/SiO<sub>2</sub>/PVA nanocomposite fibers was examined.

## 2 EXPERIMENTAL

Poly(vinyl alcohol) (>99% hydrolyzed, Mw=89,000-98,000, Sigma Aldrich Co., USA) was used as a polymer system, and distilled water was used as a solvent. Water-based nanosized colloidal germanium with a mean particle size under 50 nm at 5,000 ppm was supplied by Nanopoly Co. (Korea). Water-based nanosized colloidal SiO<sub>2</sub> with a mean particle size under 70 nm at 200,000 ppm was also supplied by Nanopoly Co. (Korea).

Solutions of eleven weight percent of PVA with various weight percent Ge and SiO<sub>2</sub> nanoparticles were prepared. Electrospinning was performed in a vertical electrospinning setup under a variety of conditions to find an optimum spinning condition. To form a layered fabric system, a 100% polypropylene, light-weight, highly porous spunbonded nonwoven was used as a substrate.

Morphology of electrospun nanocomposite fibers was examined using a field emission scanning electron microscope (FE-SEM) and a transmission electron microscope (TEM). Electrospun PVA nanocomposite fiber webs were heat-treated to stabilize PVA structures against dissolution in water.

Fourier Transform Infrared Spectrophotometer (FT-IR) was used to measure emissivity and emissive power of Ge/SiO<sub>2</sub>/PVA nanocomposite fibers. Far-infrared emissive power was determined in the range 5-20 $\mu$ m of wavelength at 37°C. Emissivity was measured from the relative value assuming that the emissivity of the black body is 1. Antibacterial properties of the layered fabric systems were evaluated quantitatively according to ASTM E 2149-01 by measuring the bacterial reductions of *Staphylococcus aureus* (ATCC 6538, Gram-positive bacterium), *Klebsiella pneumoniae* (ATCC 4532, Gram-negative bacterium), and *Escherichia Coli* (ATCC 25922).

### 3 RESULTS AND DISCUSSION

Germanium and silicon dioxide nanoparticles were incorporated into PVA fibers by the inclusion of the nanoparticles in the electrospinning dope. Nanocomposite fibers with diameters ranging from 200 to 300 nm were obtained using electrospinning. The fibers were electrospun with a 30-gauge needle at a feed rate of 0.2 mL/hr, a voltage of 15-17 kV and a collecting distance of 13 cm. Nanoscale Ge and SiO<sub>2</sub> particles were observed inside the nanocomposite fiber as well as on the surface of the fiber.

Nanofibrous membranes containing Ge and SiO<sub>2</sub> were heat-treated at 210°C for 30 min. To confirm that the heat treatment stabilized the PVA nanocomposite fibers against dissolution in water, both heat-treated and untreated nanofiber webs were immersed in water at 18°C for 1 hr, and then the morphology of the membranes was examined using a FE-SEM. An untreated PVA nanofibrous membrane lost its fibrous structure after exposure to an aqueous environment, whereas the fibrous structure of the heat-treated Ge/SiO<sub>2</sub>/PVA nanocomposite fibers was maintained after immersion in water.

Layered fabric systems with electrospun nanocomposite fiber webs were developed at various concentrations of Ge and/or SiO<sub>2</sub> to impart far-infrared radiation effect. An electrospun PVA nanofibrous membrane without nanoparticles showed a far-infrared emissivity of 0.881 and an emissive power of  $3.40 \times 10^2$  W/m<sup>2</sup>. An emissivity and emissive power of the nanofibers electrospun from 11 wt% PVA solutions containing 0.5 wt% Ge were 0.887 and  $3.42 \times 10^2$  W/m<sup>2</sup>. Nanocomposite fibers electrospun from 11 wt% PVA solutions containing 1 wt% SiO<sub>2</sub> showed a far-infrared emissivity of 0.890 and an emissive power of  $3.43 \times 10^2$  W/m<sup>2</sup>. Multi-component composite fibers containing both Ge and SiO<sub>2</sub> were also developed. Nanocomposite fibers electrospun from 11 wt% PVA solutions containing 0.5 wt% Ge and 1 wt% SiO<sub>2</sub> showed a far-infrared emissivity of 0.891 and an emissive power of  $3.44 \times 10^2$  W/m<sup>2</sup>.

We also examined antimicrobial properties of Ge/SiO<sub>2</sub>/PVA nanocomposite fibers electrospun from 11 wt% PVA solutions containing 0.5 wt% Ge and 1 wt% SiO<sub>2</sub>. The antimicrobial properties were evaluated quantitatively, and three microorganisms were used for assessment: *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Escherichia Coli*. Layered fabric systems with the electrospun Ge/SiO<sub>2</sub>/PVA nanocomposite fiber webs exhibited a 99.9% bacterial reduction against both *Staphylococcus aureus* and *Escherichia Coli*. On the other hand, the same system showed a 34.8% reduction in *Klebsiella pneumoniae*. The lower reduction of Gram-negative *Klebsiella pneumoniae* than Gram-positive *Staphylococcus aureus* and *Escherichia Coli* might be due to that Gram-negative bacteria have more complex cell wall structures than Gram-positive bacteria [7]. The additional outer membrane of Gram-negative bacteria may protect

these organisms, resulting in lower reduction of Gram-negative *Klebsiella pneumoniae*.

### 4 CONCLUSIONS

Layered fabric systems with nanofibrous membranes containing Ge and SiO<sub>2</sub> were developed at various concentrations of Ge and/or SiO<sub>2</sub> to impart far-infrared radiation effect and antibacterial property via electrospinning. Multi-component composite fibers electrospun from 11 wt% PVA solutions containing 0.5 wt% Ge and 1 wt% SiO<sub>2</sub> exhibited a far-infrared emissivity of 0.891 and an emissive power of  $3.44 \times 10^2$  W/m<sup>2</sup>. The same system exhibited a 99.9% bacterial reduction against both *Staphylococcus aureus* and *Escherichia Coli*. The results showed that far-infrared radiation effect and antibacterial properties were successfully imparted to PVA nanofibers by electrospinning mixtures of polymers and functional nanoparticles. The results indicate that PVA nanofibrous membranes containing Ge and SiO<sub>2</sub> have high potential for medical and healthcare applications.

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