



# High strength poly(vinyl alcohol)/poly(acrylic acid) cross-linked nanofibrous hybrid composites incorporating nano hybrid POSS



Eun-Sook Lee<sup>a</sup>, Danyun Lei<sup>b</sup>, Kesavan Devarayan<sup>b</sup>, Byoung-Suhk Kim<sup>a,b,\*</sup>

<sup>a</sup> Department of Organic Materials & Fiber Engineering, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju-si, Jeollabuk-do 561-756, Republic of Korea

<sup>b</sup> Department of BIN Fusion Technology, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju-si, Jeollabuk-do 561-756, Republic of Korea

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## ABSTRACT

A novel system for enhancing the mechanical properties of PVA/PAA cross-linked nanofibrous hybrid composites incorporating POSS was developed in this study. An electrospinning and followed by simple heat-treatment strategy was used to prepare nanofibrous PVA/PAA composite hydrogels. The mechanical properties have been dramatically improved by a heat-treatment as well as an incorporated nano hybrid POSS. The PVA/PAA composite nanofibers exhibited 2.3 times higher tensile strength and 4.4 times higher Young's modulus after heat-treatment, suggesting that the elasticity of these nanofibers was reinforced by the formation of chemically cross-linked networks. Moreover, compared to the heat-treated PVA/PAA nanofibers without POSS, the PVA/PAA/POSS hybrid nanofibers (POSS content ~0.6 wt.%) showed 3.3 times improvement in Young's modulus and 2.0 times increase in tensile strength after heat-treatment at 160 °C for 30 min. This suggests that the elasticity of these nanofibers were dramatically reinforced by the incorporated POSS nanoparticles as well as chemically cross-linked networks via an ester bond formation between —OH groups of PVA and —COOH groups in PAA.

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## 1. Introduction

Poly(vinyl alcohol) (PVA) is of particular interest due to excellent properties such as strength, water solubility, gas permeability, and thermal characteristics. These properties of PVA have led to its utilities in a variety of industries, including chemical engineering, pharmaceuticals, textiles, medical devices, and food additives [1–3]. However, in order to be useful in medical and pharmaceutical applications, the stability of PVA should be controlled in aqueous media by cross-linking either chemically or physically [4]. For instance, PVA membranes have been chemically cross-linked with difunctional glutaraldehyde (GA) in the presence of sulfuric acid, acetic acid, or methanol [5]. Other methods of chemical cross-linking of PVA, which include the use of electron beam or gamma irradiation, have also been investigated [6].

Electrospinning is a versatile and straightforward technique for production of fibers having diameters ranging from submicro- to nano-meter with higher surface area per unit mass and a very small pore size [7–10], which makes electrospun nanofibers as preferable material for many potential applications such as sensor materials,

tissue scaffolds, wound dressing, filtration, and separator in Li-ion battery [11–15]. However, because electrospun fiber membranes have very poor mechanical properties due to the random orientation within the fibers and broad distribution of fiber diameter, their applications are still limited and are great challenge until now. The electrospinning of the PVA solution has been extensively studied for the preparation of ultrafine separation filters, biodegradable mats and inorganic fibers. We have previously reported the enhanced water resistance of electrospun PVA/poly(acrylic acid) (PAA) composite fibers through heat treatment [16] and amphiphilic electrospun PVA hybrid fibers incorporating polyhedral oligosilsesquioxane (POSS) macromers as pendent groups [21], respectively. We found that the incorporation of the hydrophobic POSS hybrid nanoparticles onto the hydrophilic PVA chains resulted in an altered solubility and enhanced water resistance with an increasing POSS content. In general, hybrid POSS nanomaterials have attracted particular scientific and technological interests because of their excellent mechanical and thermal properties and its tunable chemical reactivity of one corner functional group (for instance, R' = alcohol, amines, carboxylic acids, epoxides, halides, nitriles, norbornenyls, olefins, silanols, thiols, etc.) [17,18]. POSS-containing materials are a new class of nanostructured hybrid materials, which are the hybridization of an organic polymer and inorganic material on a nanosize scale, as an interesting building block for the construction of organic–inorganic hybrid structures

\* Corresponding author at: Department of Organic Materials & Fiber Engineering, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju-si, Jeollabuk-do 561-756, Republic of Korea. Tel.: +82 63 270 2352; fax: +82 63 270 2348.

E-mail address: [kbsuhk@jbnu.ac.kr](mailto:kbsuhk@jbnu.ac.kr) (B.-S. Kim).

[19,20]. Nowadays, more attention was attracted on the solution properties and nanoassemblies of POSS-based polymeric materials [21–23].

As far as POSS-based nanocomposites are concerned, several examples of electrospun polymer systems, containing POSS directly attached to macromolecule backbone or physical blending of POSS with polymer matrix, have been reported so far. Kim et al. studied the water resistance of the nanofiber web, obtained by electrospinning, based on the hybrid system PVA/POSS, made by incorporating POSS onto hydrophilic PVA backbone [21]. Wu et al. reported on the preparation of nanostructured fibrous hydrogel scaffolds of POSS–poly(ethylene glycol) hybrid thermoplastic polyurethanes incorporating Ag for antimicrobial applications [24]. Soares et al. reported a novel globular protein electrospun fiber mat with the addition of POSS, which may extend their use to biotechnology, drug delivery systems, textiles or advanced functional systems [25]. Coleman et al. reported the functionalized carbon nanofibers (CNF) with POSS for use as sensors [26]. Lin et al. reported POSS–polymethylmethacrylate (PMMA) nanofibers that can form a highly superhydrophobic membrane with a water contact angle  $> 160^\circ$  [27]. Nevertheless, very few systematic studies have been made on the mechanical properties of the nanofibers incorporating POSS. For instance, Xu et al. prepared the carbon fiber/POSS/carbon nanotube hybrid reinforcement in order to improve the interfacial properties between carbon fibers and an epoxy matrix, and reported that mechanical properties test results indicated the interlaminar shear strength (ILSS) and impact toughness were enhanced [28]. Marsano et al. reported that the presence of POSS improved the mechanical properties of electrospun poly(vinylidene fluoride) (PVDF) film [29].

In this study, we report the preparation and the mechanical properties of novel PVA/PAA cross-linked composite nanofibers incorporating POSS prepared by electrospinning and simple heat-treatment. To the best of our knowledge, for the first time, the mechanical properties of electrospun PVA/PAA cross-linked nanofibrous composites incorporating POSS were evaluated. The

obtained PVA/PAA/POSS cross-linked hybrid nanofibers were characterized by FT-IR spectroscopy, XRD, SEM, and tensile test. The heat-treated PVA/PAA/POSS hybrid nanofibers exhibited a dramatic increase in water resistance as well as enhanced mechanical properties depending on POSS contents. It was expected that chemically cross-linked ester bond between PVA and PAA as well as physically cross-linked nanohybrid POSS aggregations could significantly contribute to the mechanical strength required as a scaffold for tissue engineering.

## 2. Experimental

### 2.1. Materials

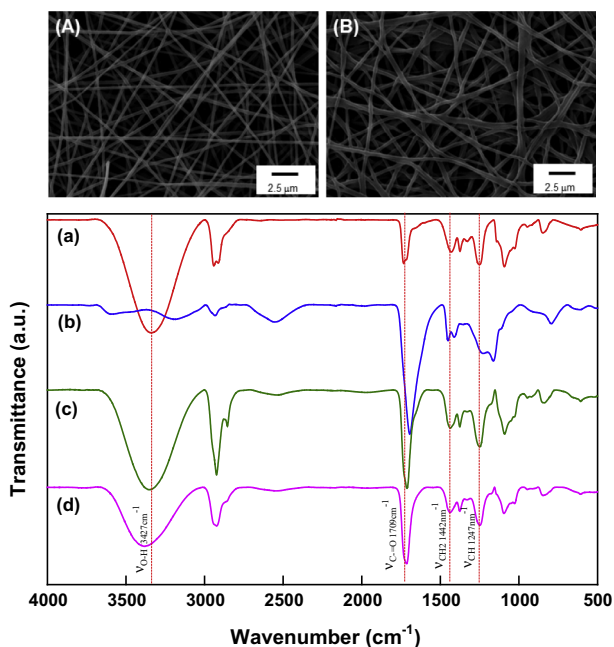
Poly(vinyl alcohol) (PVA) with the degree of hydrolysis (DH) = 88% and the degree of polymerization (DP) = 1,700 was kindly provided by Kuraray Co., Ltd., Japan. Poly(acrylic acid) (PAA) with a molecular weight of  $250 \text{ g mol}^{-1}$  was purchased from Wako Pure Chemical Industries, Ltd., Japan. Octa Maleamic Acid polyhedral oligosilsesquioxane (OMA-POSS,  $M_w = 1592 \text{ g mol}^{-1}$ ) were purchased from Hybrid Plastics, Inc. Dimethylformamide (DMF,  $>99.5\%$ ) was purchased from Wako Pure Chemical Industries, Ltd., Japan. All chemicals were of analytical grade and were used as received. Distilled water was used as the solvent.

### 2.2. Preparation of PVA/PAA Hybrid cross-linked nanofibers incorporating POSS

The solution for electrospinning was prepared by dissolving PVA in pure water to achieve a polymer concentration of  $\sim 10 \text{ wt.}\%$ . In order to improve the solubility of PVA polymer, the PVA solution was heated to about  $80^\circ \text{C}$  so as to disrupt the strong intra- and inter-chain bonding that may exist in PVA polymers. The concentrations of both PVA and PAA solutions (PVA/PAA = 50/50, w/w) were controlled to be  $\sim 10 \text{ wt.}\%$ , respectively. The POSS content in the PVA/PAA/POSS blend solutions was controlled to be 0.6–1.1 wt.%. The POSS solution of about 8 wt.% dissolved in DMF was used as a stock solution. Prior to electrospinning, the blend solutions of PVA/PAA with different POSS contents were sonicated for 1 h and further stirred for 2 days. Then the blend solutions were electrospun to produce the PVA/PAA/POSS hybrid nanofibers. The electrospinning experiments were performed at room temperature similar to our previous reports [7–10,16]. All solutions were electrospun onto a rotating metallic collector under the identical condition. Afterwards, the PVA/PAA/POSS hybrid nanofiber membranes were heat-treated in an oven at  $160^\circ \text{C}$  for 0.5 h to produce a chemically cross-linked hydrogels through an ester formation between the  $-\text{OH}$  groups in PVA and the  $-\text{COOH}$  groups in PAA.

### 2.3. Characterization

The morphologies of the resultant composite nanofiber mats were observed by using scanning electron microscopy (SEM, JSM-5900, Hitachi, Japan). In order to measure the fiber diameter, more than 50 times for each sample were measured and averaged to get the averaged fiber diameter. The changes in the functional groups of the PVA/PAA/POSS cross-linked composite nanofibers before and after heat-treatment were evaluated using Fourier transform infrared spectroscopy (FT-IR, Varian 1000 FT-IR Scimitar series, PIKE Technologies, USA). The wide-angle X-ray intensity curves of the PVA/PAA/POSS cross-linked hybrid nanofibers with different POSS content were measured with graphite-monochromatized  $\text{Cu K}\alpha$  radiation generated at 30 kV and 150 mA in a Rigaku D/MAX 2500 diffractometer at a scanning



**Fig. 1.** The typical SEM images (top) of H-PVA/PAA (heat-treated sample) (A) and HSD-PVA/PAA (heat-treated, swollen in water, and then dried) (B), composites nanofibers, and FT-IR spectra (bottom) of the pure PVA (a), pure PAA (b), as-spun PVA/PAA (c) and heat-treated PVA/PAA (d) composite nanofibers. Heat-treatment was carried out at  $160^\circ \text{C}$  for 30 min.

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