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〈Research Paper〉

Effect of Inorganic Nanomaterials on the Morphology and Thermal Properties of PVA Nanocomposite Nanowebs

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Abstract— Poly(vinyl alcohol) (PVA), PVA/Montmorillonite (MMT), PVA/Silver (Ag), and PVA/MMT/Ag nanocomposite nanowebs were prepared by electrospinning technique in aqueous solution. In order to investigate the effect of inorganic materials on the morphology and thermal properties of PVA based nanocomposite nanowebs, experiments were performed with 5 wt.% of MMT and Ag. Field emission type scanning electron microscopy, transmission electron microscopy (TEM), reflection type X-ray diffraction (XRD), and thermal gravimetric analyzer were utilized to characterize nanocomposite nanowebs. TEM and XRD results show MMT and Ag were well dispersed in PVA nanowebs. Those inorganic nanoparticles enhanced thermal property of the nanocomposite nanowebs.

Keywords: *electrospinning, nanocomposite nanoweb, poly(vinyl alcohol), silver nanoparticles, montmorillonite*

1. Introduction

Polymer nanocomposites are a class of materials that have properties that offer significant commercial potential. It was commonly defined as the combination of a polymer matrix resin and inclusions that have at least one dimension (i.e. length, width, or thickness) in the nanometer size range. There are many types of nanocomposites that have received significant research and development including polymer/inorganic particle, polymer/polymer, metal/ceramic, and inorganic based nanocomposites.

These polymer nanocomposites have attracted great interest due to inorganic materials filled polymer composites often exhibit remarkable improvement in material properties with only a low percentage of inorganic materials. High degrees of stiffness, strength, conductivity and thermal resistance, etc. are realized with far less high density inorganic material, they are much lighter compared to conventional polymer composites. During the past 10 years, a lot of works were conducted on the elaboration of nanocomposite systems by embedding of inorganic particles into polymeric matrices[1-5].

Montmorillonite (MMT) is one of common things in those inorganic materials. It has been attracting great attention due to its remarkable improvement in mechanical, thermal, flame-retardant, and barrier properties of polymeric composites with small amounts (1-10 wt.%) of MMT fillers added[6]. These property improvements are attributed to the nanometric thickness and high aspect ratio of the individual clay platelets, as well as to the nanocomposite morphology with the platelets being exfoliated and well-dispersed. It is regularly used for packaging and medical applications. Feng et. al. and Kwon et. al. have been demonstrated successfully MMT as useful for biomedical application[7,8].

Silver nanoparticles are widely used as a photosensitive components, catalysts and chemical analysis. Additionally, due to its comparatively high safety, many researchers have successfully developed antibacterial and disinfectant agents with silver composite using various polymers. Microorganisms with resistance to the antimicrobial

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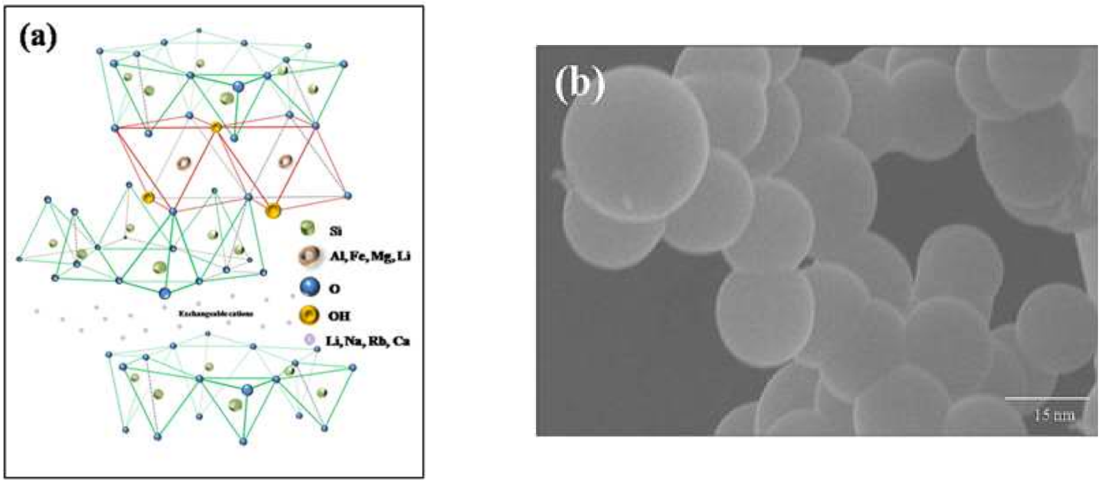

Fig. 1. (a) Schematic representation of MMT and (b) FE-SEM image of Ag nanoparticles.

activity of Ag are exceedingly rare. Such silver has a size of nano-level, the total surface area of the silver become larger in identity volume and antibacterial efficiency is increased[9-11].

In this study, we prepared poly(vinyl alcohol) (PVA), PVA/MMT, PVA/Ag, and PVA/MMT/Ag nanocomposite nanowebs by electrospinning technique in aqueous solution to investigate effect of MMT and Ag on morphology and thermal properties of PVA based nanocomposite nanoweb. Nanocomposite nanowebs were investigated using a series of characterization methods, including field emission type scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), reflection type X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The result indicates that the thermal properties of PVA based nanocomposite nanowebs are better than pure PVA nanowebs. It is therefore expected that the electrospun PVA based nanocomposite nanowebs can exhibit a better performance than PVA nanofiber mats for various applications.

2. Experimental

2.1 Materials

PVA with P_n (number-average degree of polymerization)= 1700 [fully hydrolyzed, degree of saponification (DS)= 99.9%] was obtained from DC Chemical Co., Seoul, Korea and MMT was purchased from Kunimine Industries Co., Japan. Aqueous Ag nanoparticle dispersion (AGS-WP001, 10,000 ppm) with diameters ca. 15-30 nm was got from Miji Tech., Korea. Doubly distilled water was used as a solvent to prepare all solutions. Fig. 1 is schematic representation of MMT and FE-SEM image of Ag nanoparticles.

2.2 Electrospinning Nanocomposite Nanowebs

To prepare electrospinning solution, 5 wt.% of MMT powder was dispersed in distilled water under magnetic stirring for 1h at room temperature. After the MMT was dispersed, PVA (7.5 wt.%) was added to the solution. The solution was heated in a water bath at 80 $^{\circ}$C under magnetic stirring for 2h followed by cooling to room temperature. PVA/Ag and PVA/MMT/Ag solutions were prepared by mixing with PVA solution and aqueous Ag nanoparticle dispersion. During electrospinning, a high voltage power (CHUNGPA EMT Co., Korea) was applied to the electrospinning solution contained in a syringe via an alligator clip attached to the syringe needle. The applied voltage was adjusted at 15 kV. The solution was delivered to the blunt needle tip via syringe pump to control the solution flow rate. Fibers were collected on an electrically grounded aluminum foil placed at 15 cm vertical distance to the needle tip. The above spinning conditions were found being the best

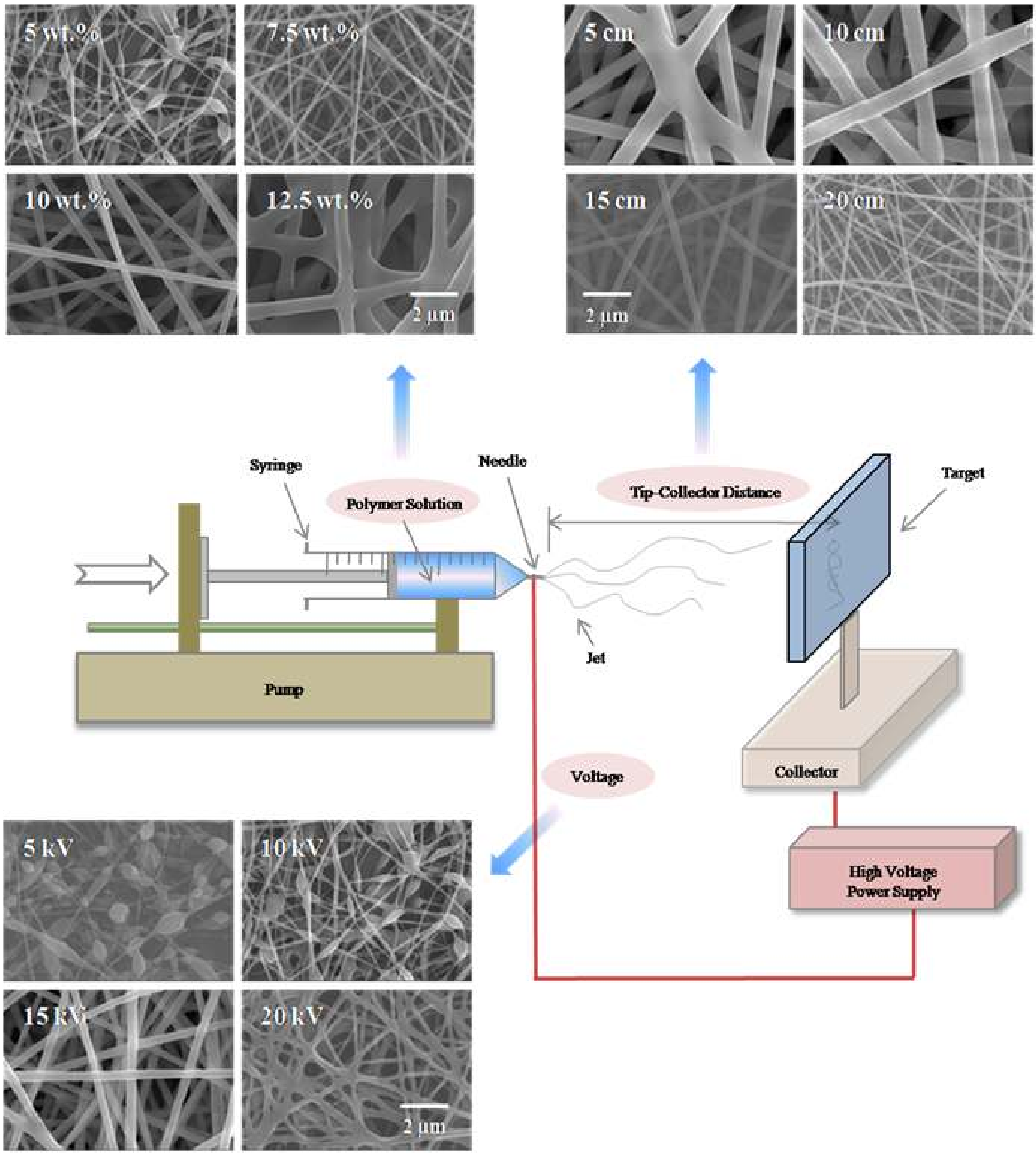

Fig. 2. Schematic representation of the electrospinning process and FE-SEM images of pure PVA nanowebs.

condition for PVA nanowebs in our previous report (Fig. 2)[12].

2.3 Characterizations

The morphology and properties characterization of PVA based nanocomposite nanowebs were observed with a FE-SEM (JEOL, model JSM-6380) after gold coating and a reflection type XRD (Philips model X'Pert APD) with the Cu Kα radiation with wavelength of 0.154 nm. The scanning rate was 2°/min ranging 1.5 to 50° (2θ). TEM analysis was conducted on an H-7600 model machine (HITACHI, LTD) with accelerating voltage of 100 kV. The thermal behavior of nanocomposite nanowebs were studied with TGA techniques (model Q-50) from TA instruments, USA, at the rate of 10 °C/min from room temperature to 600 °C under the nitrogen gas atmosphere.

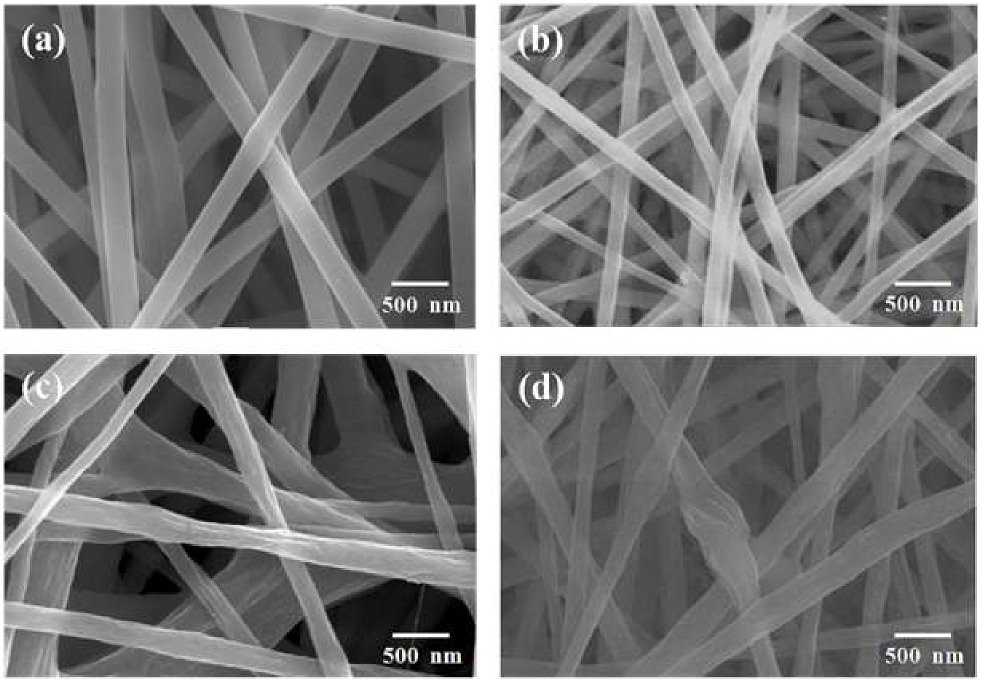

Fig. 3. FE-SEM images of (a) pure PVA, (b) PVA/Ag, (c) PVA/MMT, (d) PVA/MMT/Ag nanocomposite nanowebs (MMT 5 wt.%, Ag 5 wt.%).

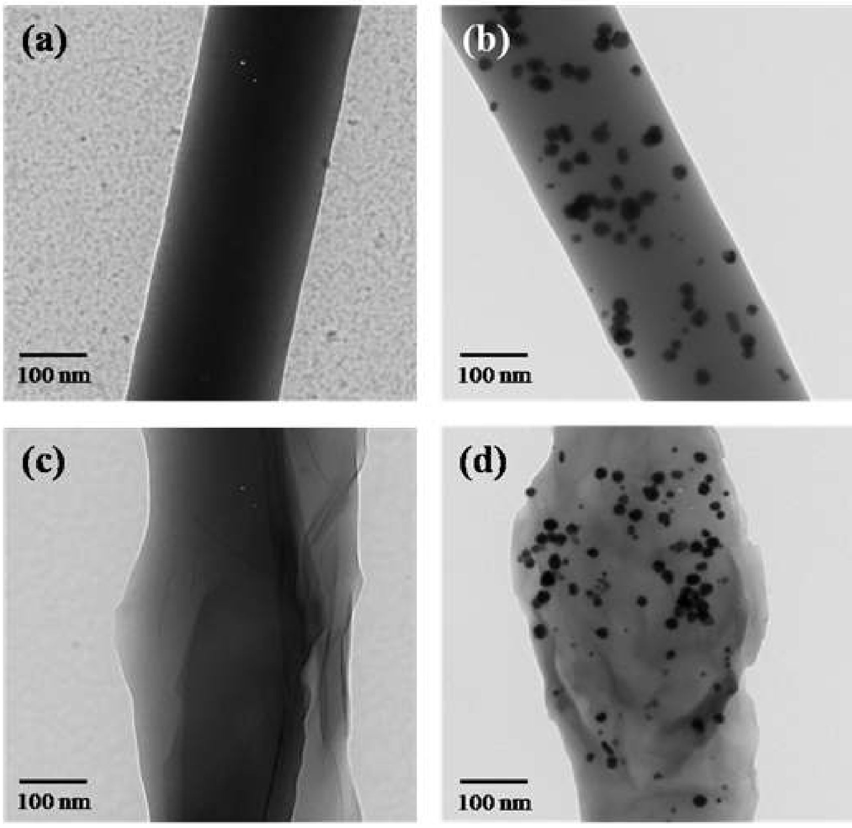

Fig. 4. TEM images of (a) pure PVA, (b) PVA/Ag, (c) PVA/MMT, (d) PVA/MMT/Ag nanocomposite nanowebs (MMT 5 wt.%, Ag 5 wt.%).

3. Results and Discussion

Fig. 3 and 4 demonstrate FE-SEM and TEM images of PVA, PVA/MMT, PVA/Ag and PVA/MMT/Ag nanocomposite nanowebs electrospun with 5 wt.% of MMT and 5 wt.% of Ag nanoparticles. Uniform PVA nanowebs with an average diameter of nanometer-scale (~ 250 nm) could be prepared from the 7.5 wt.% of PVA and Ag nanoparticle does not effect on morphology and diameter of PVA nanowebs. Otherwise, PVA/MMT and PVA/MMT/Ag nanocomposite nanowebs have rough surface. This is common phenomenon of polymer/MMT clay nanocomposites. MMT contents were important parameters which had effects on the morphology of electrospun PVA nanofibers. The diameter of nanofibers increases but fibers homogeneity decreases with MMT contents. TEM images (Fig. 4) present an actual image of clay platelets and Ag nanoparticles to permit identification of internal morphology of nanocomposites. It can be clearly observed that each silicate platelet forms a dark line in the nanofibers. The size of the dark line is about 2-10 nm thick which indicates good dispersion and exfoliation of MMT layers in the nanowebs. And it is perceived that the Ag nanoparticles are distributed uniformly in the nanowebs without aggregation.

The XRD pattern of PVA based nanocomposite nanowebs show diffraction peaks at 2θ of ca. 19.3°, 38.2°, and 44.6°, respectively (Fig. 5B). The pure PVA nanoweb shows a significant crystalline peak at about 19.3° (Fig. 5A), which is because of the occurrence of string inter- and intra molecular hydrogen bonding. In case of a clay-polymer composite, unexfoliated or intercalated MMT usually show a peak in the range 3~9° (2θ). In exfoliated nanocomposites, generally single silicate layers (1-3 nm thick) are homogeneously dispersed in the polymer matrix, and XRD patterns with no distinct diffraction peak in the range of 3~9° (2θ) could be observed. Except the diffraction peaks of PVA, all the other peaks are corresponding to the silver phase. These peaks are corresponding to the 111 and 200 planes of the silver nanocrystals with cubic symmetry[13]. These XRD results indicate that MMT

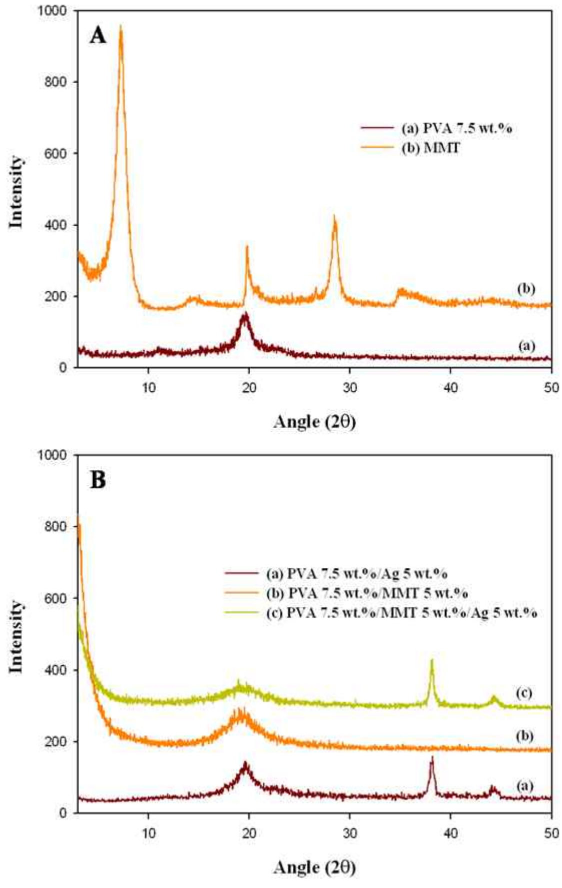

Fig. 5. XRD data of [A] (a) pure PVA (b) MMT clay and [B] (a) PVA/Ag, (b) PVA/MMT, (c) PVA/MMT/Ag nanocomposite nanowebs (MMT 5 wt.%, Ag 5 wt.%).

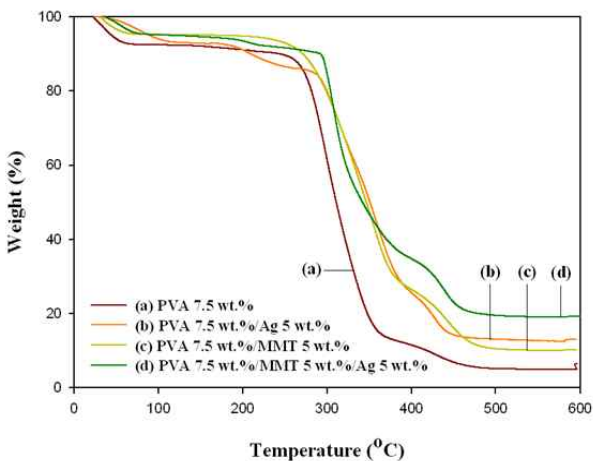

Fig. 6. TGA data of (a) pure PVA, (b) PVA/Ag, (c) PVA/MMT, (d) PVA/MMT/Ag nanocomposite nanowebs (MMT 5 wt.%, Ag 5 wt.%).

Table 1. Thermal behavior of nanowebs

Sample	T_{1st}[a] (°C)	T_{2st}[b] (°C)	Ash (%)
PVA 7.5 wt.%	58	260	4.8
PVA 7.5 wt.%/Ag 5 wt.%	59	255	12.2
PVA 7.5 wt.%/MMT 5 wt.%	103	284	10.4
PVA 7.5 wt.%/MMT 5 wt.%/Ag 5 wt.%	65	282	20.1

a : 1st decomposition temperature
b : 2nd decomposition temperature

and Ag particles are well exfoliated and dispersed in the PVA based nanocomposite nanowebs.

Thermal stability of electrospun PVA based nanocomposite nanowebs was measured using TGA in nitrogen atmosphere. Fig. 6 shows TGA thermograms of different decomposition temperature with 5 wt.% of MMT and Ag contents. The most below curve of the TGA data represent the pure PVA. There is typical three weight loss peaks were observed in the TGA curve for bulk PVA. The first peak at 50-70 °C was due to moisture vaporization, the second peak at 260-380 °C was due to the thermal degradation of PVA, and the third peak at 430-460 °C was due to the by product formation of PVA during the TGA thermal degradation process. Within up to 225 °C, there is an increased in thermal stability from the pure PVA nanowebs to PVA/MMT/Ag nanocomposite nanowebs.

The higher thermal stability might be attributed to contents of inorganic materials in the nanowebs.

4. Conclusion

PVA based nanocomposite nanowebs could be fabricated by the electrospinning method in aqueous solutions. Different with Ag nanoparticles, MMT content has important roles for the morphology of the electrospun nanofiber mats. The study shows that the introduction of MMT and Ag results in improvement of thermal stability of the PVA matrix. XRD patterns and TEM micrographs suggest the coexistence of exfoliated MMT layers and Ag nanoparticles in nanowebs. These results mean that the fabrication of nanocomposite with small amount of inorganic fillers can be useful way to control of materials properties.

Acknowledgements

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