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Electrospinning of Polylactide Fibers Containing Silver Nanoparticles

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Abstract: Biodegradable polylactide (PLA) nanofibers containing silver nanoparticles were prepared by electrospinning. Solutions of PLA in dichloromethane/*N*,*N*-dimethylacetamide (DMAc) with different amounts of silver nitrate ($AgNO_3$) were used to spin nanofibers. DMAc was used as a reducing agent for Ag^+ ions in the PLA solution. In the dilute solution system, the intrinsic viscosity and Huggins constant of the PLA/Ag solutions decreased at $AgNO_3$ concentrations < 6 wt% whereas they increased at 9 wt% $AgNO_3$. On the other hand, dichloromethane/DMAc was found to be a good solvent with a similar solvating power to the Huggins constant results. The solution properties of the viscosity and electrical conductivity of the spinning solutions are strongly affected by the addition of $AgNO_3$. The mean diameters of the PLA/Ag nanofibers containing 0, 3, 6 and 9 wt% of $AgNO_3$ were 400.9±0.1, 352.6±0.3, 313.1±0.2 and 482.8±0.2 nm, respectively. The silver nanoparticles contributed to the formation of thinner PLA/Ag nanofibers. When the PLA nanofibers contained 6 wt% $AgNO_3$, silver nanoparticles with an average size of 4.9 nm were distributed homogeneously in the PLA nanaofibers.

Keywords: electrospinning, polylactide, silver nanoparicles.

Introduction

Electrospinning is a simple and very efficient method to fabricate nanofibers with diameters in the range from 50 to 500 nm and the process produces fibers from a polymer solution that is charged to high voltage.[1-6] These fibers, which have smaller pores, higher porosity, and higher surface area than regular fibers, have a variety of applications, such as tissue scaffolds, protective clothing, filtration systems, sanitary goods, and sensor assemblies.[7,8] Recently, the incorporation of metal nanoparticles into polymer nanofibers has enabled them to be used in novel applications such as sensor assemblies, biomedical materials, and nanoelectronic devices.[8-12]

Among the various aliphatic degradable polyesters, polylactide (PLA) has been considered as one of the most interesting and promising biodegradable materials.[13] In addition, it is suitable for easily producing thin and uniform electrospun nanofibers without beads and can be dissolved in various solvents such as methylene chloride and dimethylformamide.[14,15] Therefore, PLA has been used in various applications including packing and the biomedical field because of its biodegradability, biocompatibility, and ability to be dissolved in common solvents for processing.

Silver nanoparticles have attracted great interest because of their potential in various applications.[16-18] Extensive research into the reduction of silver nitrate ($AgNO_3$) by means such as UV irradiation, hydrogen, hydrazinium hydroxide, heat treatment, and chemical treatment has been undertaken.[19-25] Jing *et al*.[6] and Youk *et al*.[23,24] prepared nanofibers with silver nanoparticles using dimethylformamide as the reducing agent. *N*,*N*-Dimethylacetamide (DMAc) was used as a reducing agent for the Ag^+ ions in PLA solutions with ultrasonic treatment.[24] The presence of silver nanoparticles improves antibacterial activity significantly reduce the number of bacteria. Further, polymer nanofibers with silver nanoparticles can be prepared using polymers with a strong interaction with silver nanoparticles.[23]

The objective of this research was to fabricate PLA nanofibers with different amounts of silver nanoparticles by electrospinning the solution of PLA in dichloromethane/DMAc with different amounts of $AgNO_3$. We also investigated the effects of silver nanoparticles on the electrospinning and physical properties of PLA solution by characterizing viscosity, surface tension, electrical conductivity, morphology, and antibacterial activity.

Experimental

Materials. PLA (M_w=100,000) was dissolved in a mixed solvent of dichloromethane and DMAc (8/2 w/w) to prepare a 10 wt% solution with the desired amount of $AgNO_3$ (the weight percent of $AgNO_3$ was 3, 6, and 9 wt%, respectively, with respect to PLA used). PLA and $AgNO_3$ were dissolved

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in the mixed solvent using ultrasonic treatment for 10 min and stirred for 48 h at 25 °C to obtain homogeneous solutions.

Electrospinning Process. PLA/Ag solutions were placed in a syringe and the syringe pump was used so that a stable drop of solution was suspended at the tip of a needle. The PLA/Ag solutions were fed through the needle tip using a syringe pump at a flow rate of 2 mL/h. The applied voltage was varied from 10 to 30 kV. The syringe used in this experiment had a capillary tip diameter of 21 gauge and contained an attached copper wire that was used as the positive electrode. A collector covered by an aluminum foil was used and the tip-to-collector distance (TCD) was set to 17 cm. A grounded take-up machine was positioned opposite the tip of the needle. Nanofibers were deposited on the aluminum foil and collected in the form of a web. All electrospun nanofibers were dried *in vacuo* for 24 h to remove residual solvent.

Characterization. UV-vis spectroscopy was obtained on an UV-visible spectroscopy system (Agilent 8453). Intrinsic ([η]) and specific viscosity of PLA solution in dichloromethane/DMAc containing different amounts of silver nanoparticles was measured by ubbelohode viscometer (Schott Co.) at 25 °C over the concentration range of 0.1 and 0.8 g/dL. Surface tension of the polymer solutions was determined using tensiometer (K100, Kruss Co.). All polymer dispersions of 20 mL were poured into a glass beaker that had been extensively rinsed with ethanol and deionized water to remove any surface-activity materials. The polymer solutions were equilibrated to 25 °C, and were measured 10 times per 100 sec. The surface tension (N/m) was calculated from the measured normal forces by the meniscus on the platinum plate. The results exhibit averages of five measurements using duplicate samples. The electrical conductivity of polymer solutions was determined by using conductivity meter (Orion 3 star, Thermal Co.). The polymer solutions were adjusted to 25 °C, and were measured 3 times per 60 sec. The morphology of electrospun PLA with silver nanoparticle web was examined with a field emission scanning electron microscopy (FE-SEM; JSM-6330F). The surfaces were coated with platinum under vacuum. The average diameter of the electrospun nanofibers was determined by image analysis (Image pro® Plus, Version 6; Media Cybernetics, Inc.). Silver nanoparticle distribution on the surface was investigated by energy dispersive spectroscopy (EDS). The morphologies of the electrospun PLA fibers containing silver nanoparticles collected and reduced on carbon-coated copper grids were observed on a high resolution transmission electron microscopy (HR-TEM; JEM 2000). The degree of crystallization of the PET fabrics was examined with a wide-angle X-ray diffractometer (WAXD; Rigaku Denki Co.) with nickel-filtered CuKα radiation at 40 kV and 100 mA. The scanning experiment was carried out at the equator over a 2θ range from 5° to 80° at a scan speed of 5°/min.

Antibacterial Test. The antibacterial activities of electrospun PLA nanofibers with and without $AgNO_3$ were tested by the film contact method (FC-TM-20-2003) which measures how many bacteria disappeared at the surface of the film.[26] The following microorganisms were used: Gram-positive *Staphylococcus aureus* (*S. aureus*) (ATCC 25923) and Gram-negative *Escherichia coli* (*E. coli*) (ATCC 25922). The samples were prepared by cutting the electrospun web to the required surface area (25.0±0.2 cm^2) and were incubated for 24 h at 37 °C and RH 90±5%. Then the number of bacteria colonies (CFU) was determined. The antibacterial efficacy (ABE) was calculated according to eq. (1):

$$\text{ABE}(\%) = \frac{(A-B)}{A} \times 100 \quad (1)$$

where A is the average number of bacteria on the untreated test piece after 24 h and B is the average number of bacteria on the antimicrobial test piece after 24 h.

Results and Discussion

The Physical Properties of PLA/Ag Solutions in Mixed Solvent. PLA solutions containing different amounts of silver nanoparticles were fabricated to study the effects of solution properties such as the viscosity, surface tension, electrical conductivity, and polymer concentration on the electrospinning of nanofibers. PLA solutions (containing $AgNO_3$ ranging from 0 to 9 wt% in mixed solvent) were prepared by electrospinning of the solution into ultrafine PLA fibers. In this study, DMAc was used as a reducing agent for the Ag^+ ions in the PLA solution with ultrasonic treatment. Figure 1 shows the change in the UV-vis absorption spectra of the 10 wt% PLA solutions as a function of $AgNO_3$ content after reflux at 25 °C for 48 h. The intensity of the UV absorption spectra of the refluxing solution containing silver nanoparticles at 425 nm increases with increasing $AgNO_3$ content, implying that the generation of silver nanoparticles becomes faster with increasing $AgNO_3$ content.[23] However, the position of the maximum absorption does not shift to a longer

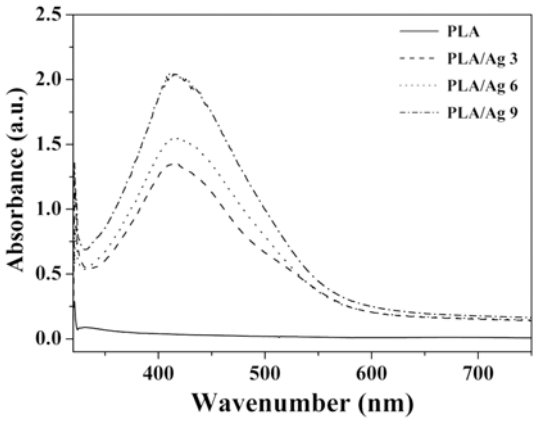

Figure 1. The change in UV-visible absorption of PLA solutions as a function of silver nanoparticle content.

wavelength. The result shows that the distribution of silver nanoparticles is not changed.

The viscosity of the polymer solution affects the spinnability of nanofibers in the electrospinning process. In dilute solution, the viscosity of polymer solutions in the solvent provides considerable information on the chemical nature of the polymers because it reflects the physicochemical state of individual polymer chains.[27,28] The parameters of critical concentration (C^*) and Huggins constant (K_H) of solutions in the dilute concentration regime are used, where C^* refers to the onset concentration to produce molecular entanglement, which is given by eq. (2):[29]

$$C^* = \frac{1}{[\eta]} \tag{2}$$

where $[\eta]$ is the intrinsic viscosity of the solution. K_H represents the degree of polymer–solvent interaction and is obtained by eq. (3):[30]

$$\frac{\eta_{sp}}{C} = [\eta] + K_H[\eta]^2 C \tag{3}$$

where η_{sp} is the specific viscosity and C is the solution concentration. It is known that the polymer chains maintain unperturbed dimensions and give a value of $K_H = 0.52$ in a θ solvent. In a good solvent, the polymer chains take extended conformations and give K_H values less than 0.52. However, the K_H value in a poor solvent lies between 0.8 and 1.3.[29] Figure 2 shows the plot of intrinsic (η_{rel}/C) and reduced (η_{red}) viscosity versus concentration (C) for PLA solutions and the resulting values of $[\eta]$, C^*, and K_H for PLA solutions containing $AgNO_3$ at various concentrations are summarized in Table I. The intrinsic viscosity increased up to 6 wt% $AgNO_3$, which may start to increase the chain dimension. On the other hand, it decreased at 9 wt% $AgNO_3$, implying that the presence of a lot of silver nanoparticles obstructs the increasing chain dimension in dilute solution. They have values of K_H lower than 0.52 in all samples regardless of the

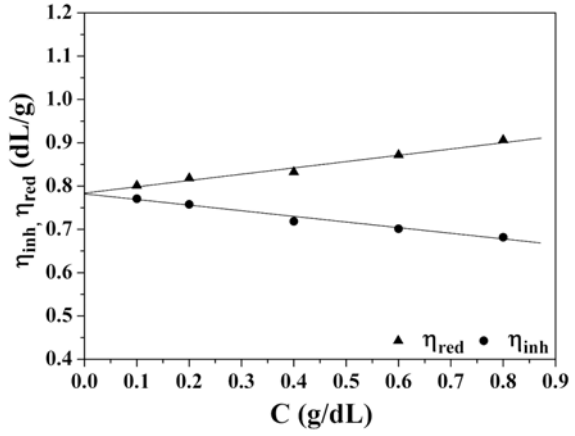

Figure 2. Intrinsic ($[\eta]$) and reduced viscosity (η_{red}) of dilute PLA solutions in mixed solvent at 25 °C.

Table I. Values of $[\eta]$, C^*, and K_H of PLA Solutions with Silver Nanoparticles in Mixed Solvent

	$[\eta]$	C^*	K_H
PLA	0.78	1.28	0.21
PLA/Ag 3	0.81	1.22	0.22
PLA/Ag 6	0.84	1.19	0.23
PLA/Ag 9	0.71	1.41	0.20

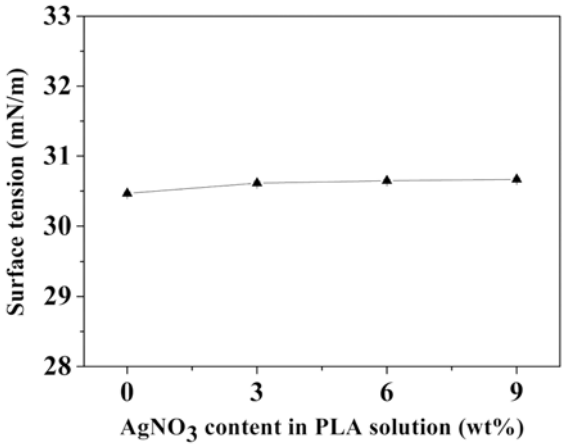

Figure 3. Surface tension of PLA solutions in mixed solvent as a function of silver nanoparticle content at 25 °C.

$AgNO_3$ content. The value of K_H increased up to 6 wt% $AgNO_3$, while it decreased at 9 wt% $AgNO_3$. This suggests that dichloromethane/DMAc is a good solvent and the solvating power increases up to 6 wt% $AgNO_3$, while it decreases at 9 wt% $AgNO_3$.

Surface tension and electrical conductivity are important parameters in electrospinning. To prepare nanofibers by electrospinning, suitable parameters are required. Figure 3 shows the effects of $AgNO_3$ concentration in PLA solutions on the surface tension. The surface tension does not change

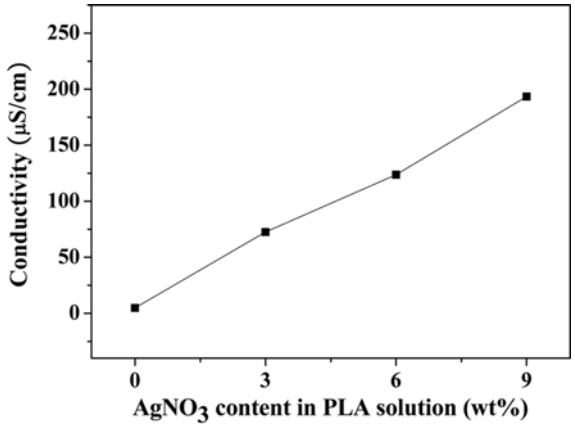

Figure 4. Electrical conductivity of PLA solutions in mixed solvent as a function of silver nanoparticle content at 25 °C.

with an increase in $AgNO_3$ concentration. The constancy of surface tension of PLA solutions with increasing $AgNO_3$ content may be attributed to stability in the interfacial composition of the polymer dispersion. The solutions did not change. This suggests that $AgNO_3$ is homogeneously distributed in all samples. Figure 4 shows the variation of electrical conductivity of PLA solutions with $AgNO_3$ content. The electrical conductivity of PLA/Ag solutions gradually increases from 4.9 to 193.4 μS/cm with increasing $AgNO_3$ content. The PLA solutions with silver nanoparticles have higher electrical conductivity than PLA solutions without silver nanoparticles. In other words, the electrical conductivity of spinning solution is enhanced after adding silver nanoparticles. The electrical conductivity of PLA solution is increased with adding silver because of the nano particles.

Morphology of PLA/Ag Nanofibers. Figure 5 shows FE-SEM images of PLA nanofibers showing the effects of $AgNO_3$ content. PLA/Ag blend solutions with silver nanoparticle concentrations ranging from 0 to 9 wt% were prepared with the concentration of the PLA solution fixed at 10 wt%. All samples could be produced without bead and as uniform nanofibers. The addition of a small number of silver nanoparticles in PLA solutions has little effect on the electrospun fiber morphology. The distribution of fiber diameters was calculated from FE-SEM images and analyzed using image analysis software in Figure 6. The diameters of the PLA/Ag nanofibers with 0, 3, 6, and 9 wt% of $AgNO_3$ were 400.9±0.1, 352.6±0.3, 313.1±0.2, and 482.8±0.2 nm, respectively. The silver nanoparticles have an effect on the formation

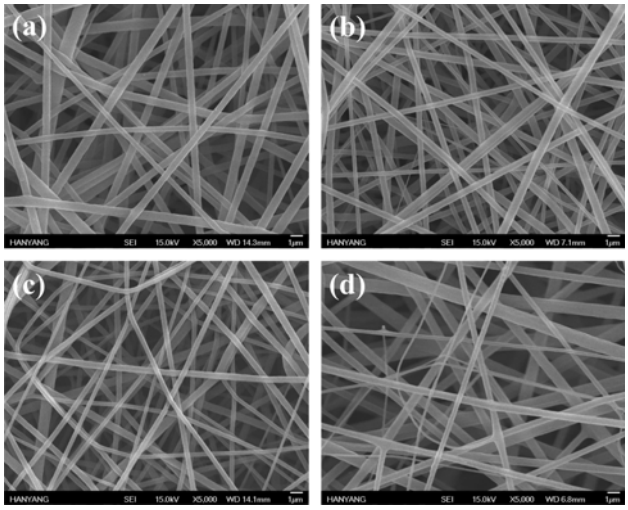

Figure 5. FE-SEM images of PLA electrospun nanofibers showing the effects of nanoparticle content: (a) 0 wt% $AgNO_3$, (b) 3 wt% $AgNO_3$, (c) 6 wt% $AgNO_3$, and (d) 9 wt% $AgNO_3$.

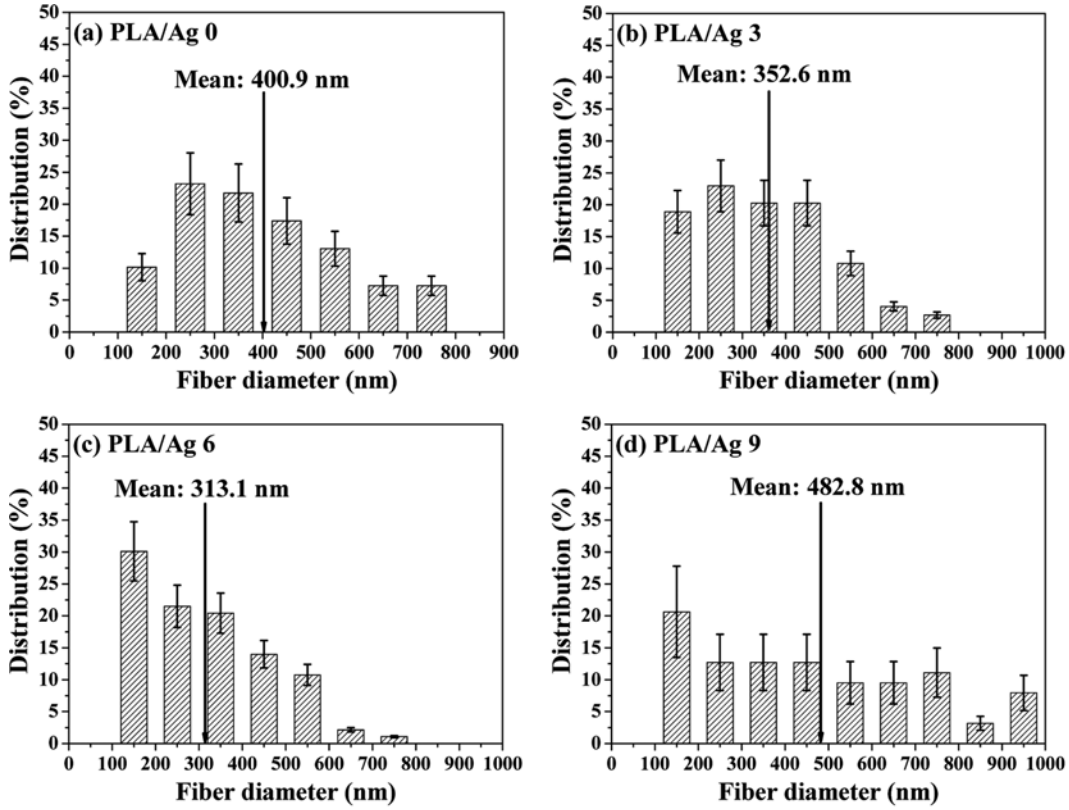

Figure 6. Diameter distribution of PLA electrospun nanofibers as a function of silver nanoparticle content: (a) 0 wt% $AgNO_3$, (b) 3 wt% $AgNO_3$, (c) 6 wt% $AgNO_3$, and (d) 9 wt% $AgNO_3$.

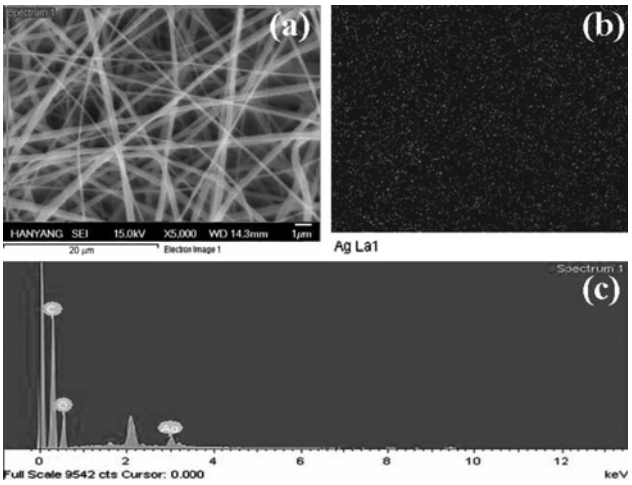

Figure 7. FE-SEM images of PLA/Ag electrospun nanofiber surface (a), silver elemental distribution by EDS (b), and EDS spectrum (c).

of thinner PLA nanofibers. The diameter of PLA/Ag nanofibers dramatically decreases up to 6 wt% $AgNO_3$, while it increased at 9 wt% $AgNO_3$, as shown in Figures 5 and 6. In particular, PLA nanofibers with 6 wt% $AgNO_3$ have the lowest fiber diameter among all of the samples and their size distribution is very narrow. Therefore, the average diameter of PLA/Ag nanofibers depends on the amount of $AgNO_3$. The surface of the PLA/Ag nanofiber is shown in Figure 7(a). The elemental silver distribution of the PLA/Ag nanofibers is shown in Figure 7(b). The mapping of the PLA/Ag nanofibers on silver indicates the surface dispersion ratio of elemental silver. The EDS spectrum of the nanofibers provides the PLA/Ag nanofiber composition including silver in Figure 7(c). Silver nanoparticles were evenly distributed in the PLA nanofibers.

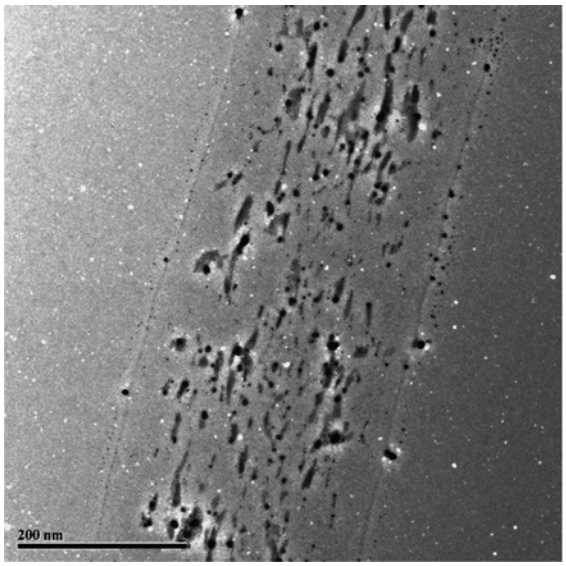

Figure 8. HR-TEM image of PLA electrospun nanofibers with 6 wt% $AgNO_3$.

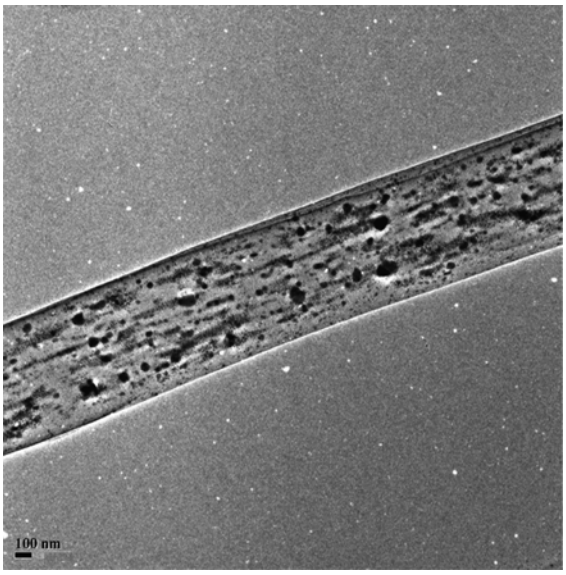

Figure 9. HR-TEM image of PLA electrospun nanofibers with 9 wt% $AgNO_3$.

Figure 8 shows a TEM image of PLA nanofibers containing 6 wt% $AgNO_3$. The silver nanoparticles are uniformly distributed with a very narrow size distribution in the PLA nanofibers with an average size of 4.9 nm and they have an almost spherical shape. This suggests that the silver nanoparticles are well stabilized by DMAc during the electrospinning process. Furthermore, when the PLA/Ag blend solution is homogeneous, phase separation does not occur during the electrospinning process and the silver nanoparticles are homogeneously distributed in the PLA nanofibers. Figure 9 shows a TEM image of the 10 wt% PLA nanofibers containing 9 wt% $AgNO_3$. The average size of silver nanoparticles in the PLA nanofibers is 8.8 nm. In addition,

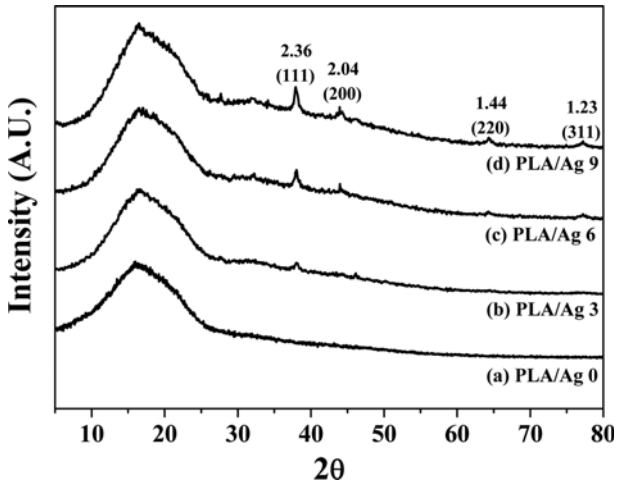

Figure 10. WAXD patterns of PLA electrospun nanofibers showing the effects of silver nanoparticle content: (a) 0 wt% $AgNO_3$, (b) 3 wt% $AgNO_3$, (c) 6 wt% $AgNO_3$, and (d) 9 wt% $AgNO_3$.

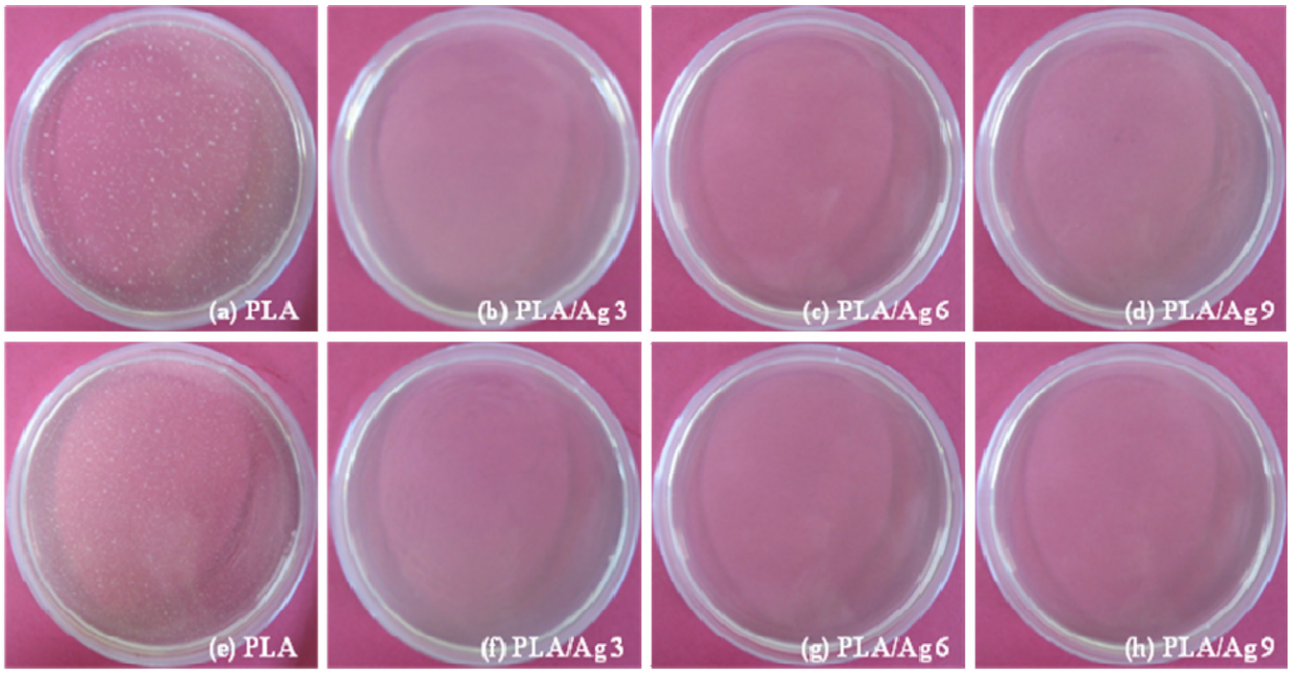

Figure 11. Antibacterial activity of PLA electrospun nanofibers against *S. aureus* at various silver nanoparticle content ((a) 0 wt% $AgNO_3$, (b) 3 wt% $AgNO_3$, (c) 6 wt% $AgNO_3$, and (d) 9 wt% $AgNO_3$) and *E. coli* ((e) 0 wt% $AgNO_3$, (f) 3 wt% $AgNO_3$, (g) 6 wt% $AgNO_3$, and (h) 9 wt% $AgNO_3$) after 24 h.

silver nanoparticles of PLA nanofibers with 9 wt% $AgNO_3$ are slightly larger than those with 6 wt% $AgNO_3$. This implies that at high $AgNO_3$ concentrations, aggregation of silver nanoparticles occurs during the electrospinning process and therefore PLA nanofibers become weaken.

Characterization of Silver Nanoparticles Formed on the PLA Web. Figure 10 shows the WAXD patterns of the PLA nanofibers, showing the influence of silver nanoparticle content. The WAXD patterns of PLA electrospun nanofibers exhibited only a broad diffraction peak at 2θ of about 16.4°, which is in good agreement with the value reported for PLA.[32] Peaks of PLA/Ag nanofibers were observed at $2\theta/\theta$=38.18°, 44.39°, 64.58°, and 77.54°, which correspond to diffraction from the (111), (200), (220), and (311) planes of metallic silver, respectively.[6] This suggests that the silver nanoparticles are embedded in the PLA electrospun nanofibers. This is in good agreement with the TEM results. In addition, their intensities are remarkably enhanced with increasing $AgNO_3$ content in the PLA solutions.

Antibacterial Activity of PLA/Ag Nanofibers. The antibacterial activity of silver nanoparticles in PLA nanofibers was examined against Gram-positive *S. aureus* and Gram-negative *E. coli* using the film contact method, as shown in Figure 11 and Table II. Figure 11 shows the result of the antibacterial test of PLA nanofibers containing different amounts of silver nanoparticles against *S. aureus* and *E. coli* for 24 h incubation. The antibacterial efficacies (ABE) for the samples are summarized in Table II. The ABE of PLA nanofibers against *S. aureus* and *E. coli* are 66.1% and 60.0%, respectively. However, when these bacteria are incubated on the PLA nanofibers with different concentrations of silver nanoparticles, bacterial colonies are not observed for PLA nanofibers with silver nanoparticles. This means that silver nanoparticles and silver ions inhibit the growth of the bacteria. The number of bacteria in samples containing silver nanoparticles is reduced by 99.9% after 24 h incubation, indicating that the silver nanoparticles exerted an influence on the antibacterial activity of the composite fibers and this activity is

Table II. Antibacterial Activity of PLA/Ag Nanofibers Against *S. aureus* and *E. coli*

Bacteria	Materials	Initial CFU[a]	CFU[a] After 24 h	ABE (%)[b]
S. aureus	PLA	1.0×10^5	7.8×10^6	66.1
	PLA/Ag 3	1.0×10^5	< 10	99.9
	PLA/Ag 6	1.0×10^5	< 10	99.9
	PLA/Ag 9	1.0×10^5	< 10	99.9
E. coli	PLA	1.5×10^5	1.2×10^7	60.0
	PLA/Ag 3	1.5×10^5	< 10	99.9
	PLA/Ag 6	1.5×10^5	< 10	99.9
	PLA/Ag 9	1.5×10^5	< 10	99.9

[a]Colony forming units. [b]Antibacterial efficacies - percent reduction of bacteria (%).

quite strong. Therefore, small amounts of $AgNO_3$ endow PLA nanofibers with very strong antibacterial activity.[31,32]

Conclusions

PLA nanofibers with silver nanoparticles were successfully prepared by electrospinning through the control of the solution properties such as solution viscosity, surface tension, and electrical conductivity. In addition, the silver nanoparticles proved to be uniformly distributed in the PLA nanofibers. The silver nanoparticles in the PLA solutions affected the electrospinnability. This investigation showed that silver nanoparticles in PLA solutions modify the dispersion properties of PLA solutions and morphological characteristics of PLA electrospun nanofibers, producing PLA nanofibers of smaller diameter without beads. When PLA/Ag nanofibers were electrospun with a 10 wt% PLA solution containing 6 wt% $AgNO_3$, silver nanoparticles were homogeneously distributed in the PLA nanofibers. In contrast, when PLA nanofibers with silver nanoparticles were electrospun from a 10 wt% solution containing 9 wt% $AgNO_3$, silver nanoparticles aggregated in the PLA nanofibers. In particular, 6 wt% silver nanoparticles in PLA nanofibers contributed more effectively to the narrow distribution of diameters of fabricated PLA/Ag nanofibers than other samples. Conclusively, PLA nanofibers with 6 wt% silver nanoparticles turned out to be the most suitable for the easy production of thin and uniform electrospun nanofibers.

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