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Antibacterial Properties of PLA Nonwoven Medical Dressings Coated with Nanostructured Silver

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Abstract: In this paper, magnetron sputtering was applied to deposit nano-structured silver films on the surfaces of polylactic acid (PLA) nonwovens, which were used in medical dressings. The influence of the coating thickness of the nano-structured sliver films on the antibacterial property of the nonwovens was studied. The antibacterial properties of the medical dressings were measured by shake flask test. The surface morphology of nano-structured silver films and the grain sizes of silver agglomerates were analyzed by atomic force microscope (AFM). Energy dispersive X-ray (EDX) was employed to analyze the surface elemental compositions. The study revealed that the antibacterial properties were improved as the film thickness increased. AFM images of the coated samples indicated that as the sputtering time prolonged, the film thickness was increased, the film became compacter, and the specific area of the film was also increased. Thus, the release rate of silver ions increased, leading to the improved antibacterial property. It was found that the reduction percentage of both tested bacteria-*Staphylococcus aureus* and *Escherichia coli* reached 100 % as the coating thickness exceeded 1 nm.

Keywords: Magnetron sputtering, PLA, Medical dressing, Nano-structured silver, Antibacterial property, Film thickness

Introduction

The antibacterial property of nano-structured silver is much better than that of ordinary silver due to its dimension effect, surface effect, and quantum tunneling effect [1]. At present, various techniques have been used to prepare nano-structured silver antibacterial materials in the textile industry, such as fiber modification, surface coating, and impregnation. Magnetron sputtering technique has been used to obtain the functional textile materials [2-6], but the antibacterial properties of textiles realized by sputtering were rarely reported.

In this study, magnetron sputtering was employed to deposit nano-structured silver films on the surfaces of polylactic acid (PLA) nonwovens to obtain antibacterial properties, which were used in antibacterial medical dressings. Shake flask test was used to investigate the antibacterial performance of all coated samples. Atomic force microscope (AFM) and energy dispersive X-ray (EDX) were applied to analyze the physical and chemical features of the coated materials.

Experimental

Materials Preparation

PLA nonwovens (Guoqiao Nonwoven Co. Ltd., Jiangxi, China) with an area mass of 35 g/m^2 were used. The samples were first immersed into acetone solution and rinsed in an ultrasonic bath for 30 min to remove the organic solvent and dust on the materials. Then the samples were washed with de-ionized water twice and dried at the temperature of 30~35 ºC in an oven. The dried samples were cut into 3 cm by 8 cm for sputter coating.

Sputter Coatings

The deposition of the silver films was performed using magnetron sputter coating system with a RF sputter source supplied by Shenyang Juzhi Co., Ltd. A 50 mm circular silver target with 99.99 % purity was used in argon plasma. The flat PLA sheet sample was mounted on the substrate holder with a distance of 170 mm from the target. Prior to the deposition process, the sputter chamber was evacuated to a base pressure of 5×10^{-4} Pa. During the sputtering, the substrate holder was rotating at a speed of 100 rpm to facilitate the uniform distribution of silver particles on the substrate, and the coating thickness was measured using a in-situ film thickness monitor (FTM-V) fixed in the sputtering chamber. In this study, the gas flow (15 cm^3/min), power (40 W), and pressure (2 Pa) were kept constant, while the coating thickness was set to be 0.5 nm, 1 nm, 2 nm, and 3 nm.

Antibacterial Test

The antibacterial effect was investigated using the shake flask test in accordance with GB15979-2002 Hygienic standard for disposable sanitary products [7]. The test bacteria were *Staphylococcus aureus* and *Escherichia coli*. In addition to the coated samples, an uncoated corresponding material was also tested for comparison. After incubation at 37±1 ºC for 36 h, bacteria were counted.

The antibacterial properties of the substrates coated with the silver film were evaluated by calculating the reduction percentage of bacteria by the following formula:

$$X_s = \frac{A-B}{A} \qquad (1)$$

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where X_s is the reduction percentage of bacteria, %, A is the number of bacteria colonies on the agar plate recovered from bacterial solution at 0 contact time, B is the number of bacteria colonies on the agar plate recovered from the specimen after shaking for 1 h. If the number of the bacteria after shaking was larger than the number at 0 contact time, X_s=0.

Surface Characterization

The surface morphology and grain size of nano-structured silver films before and after sputtering were scanned by the CSPM4000 AFM in contact mode which was provided by Guangzhou Benyuan Co. Ltd. The scanning frequency was 1 Hz.

EDX Analysis

The X-ray energy dispersive spectrometer offered by OXFORD (OXFORD INCA) was applied to analyze the elemental compositions and quantity of PLA nonwovens deposited with nano-structured silver films.

Results and Discussion

Effect of Film Thickness on Antibacterial Performance

The antibacterial performances of the PLA nonwovens coated with nano-structured silver films are shown in Table 1. The uncoated PLA nonwoven was not effective against *S. aureus* and *E. coli* since the percent reduction of both bacteria was 0. All silver coated samples, however, were very effective against both test bacteria with a reduction of over 86 % for *E. coli* and over 98 % for *S. aureus*, indicating excellent antibacterial property of nano-structured silver coatings. The results also showed that the coated samples were more effective against *S. aureus* than *E. coli* under the same sputtering condition, and the antibacterial performance was significantly improved as the coating thickness was increased. Considering price and biological toxicity of nano-structured silver, the coating thickness of 1 nm was preferable to assure the outstanding antibacterial property.

AFM Analysis

The AFM image of the uncoated PLA nonwoven is presented in Figure 1(a), which shows some particulate substances on its surface. They seemed to be dusts adsorbed on it. The AFM images of PLA surfaces sputtered with different thicknesses of silver films are given in Figures 1(b)~1(e).

AFM image in Figure 1(b) indicates that some silver nano-particles scattered on the PLA surface when the film thickness was about 0.5 nm, but these particles appeared not to cover up the original PLA surface completely. As the PLA nonwoven was coated with a silver film of 1 nm, the granular structure of silver nano-particles with variable sizes was clearly recognized, as illustrated in Figure 1(c). Image in Figure 1(d) reveals that the average grain diameter was much larger than that of 1 nm layer when the film thickness reached 2 nm. Image in Figure 1(e) displays the surface structure of the PLA fiber coated with a silver film of 3 nm. It can be seen that the surface of PLA fibers was covered with dense silver particles with clear granular structure.

The AFM images revealed that the nano-structured silver film consisted of particles with variable sizes. The particle sizes were dependent on the sputtering time, and the increased deposition time led to larger average diameter of silver particles and compacter film structure [8]. It is believed that the silver particles on PLA surface became denser, and the rate of collision between sputtered particles and the deposited silver particles significantly was increased as deposition time was prolonged, contributing to the formation of agglomeration. Therefore the grain sizes were increased as the sputtering time was extended.

In literatures [6-9], it was reported that the antibacterial effect of silver mainly depended on the activity and total amount of silver released from the coating. By comprehensive analysis of AFM images and anti-bacterial test results, it can be concluded that the coverage and compactness of silver film increased as deposition time was prolonged, leading to the increased release rate of silver ions. The improvement in the antibacterial properties of the nano-sized silver films on the PLA nonwovens was enhanced by the increased release rate of silver ions led by the accretion of the film compactness.

EDX Analysis

Figures 2(a)~2(e) show the EDX spectra of the samples with different coating thicknesses. It can be seen from the Figure 2(a) that the uncoated sample was composed primarily of oxygen and carbon elements. While after sputter coating, silver peak besides oxygen and carbon was detected as illustrated in Figures 2(b)~2(e). The EDX spectra confirm that nano-structured silver particles were deposited on the PLA nonwovens. Quantitative analysis of EDX in Figure 2 illuminates that the silver weight percentage per unit surface of samples gradually increased as the film thickness was increased, which provided evidence for the increased release rate of silver ions and the improved antibacterial properties.

Table 1. Antibacterial test results

Coating thickness (nm)	Percent reduction of bacteria	
	Escherichia coli.	*Staphylococcus aureus*
0	0.00	0.00
0.5	86.25	98.71
1	100.00	100.00
2	100.00	100.00
3	100.00	100.00

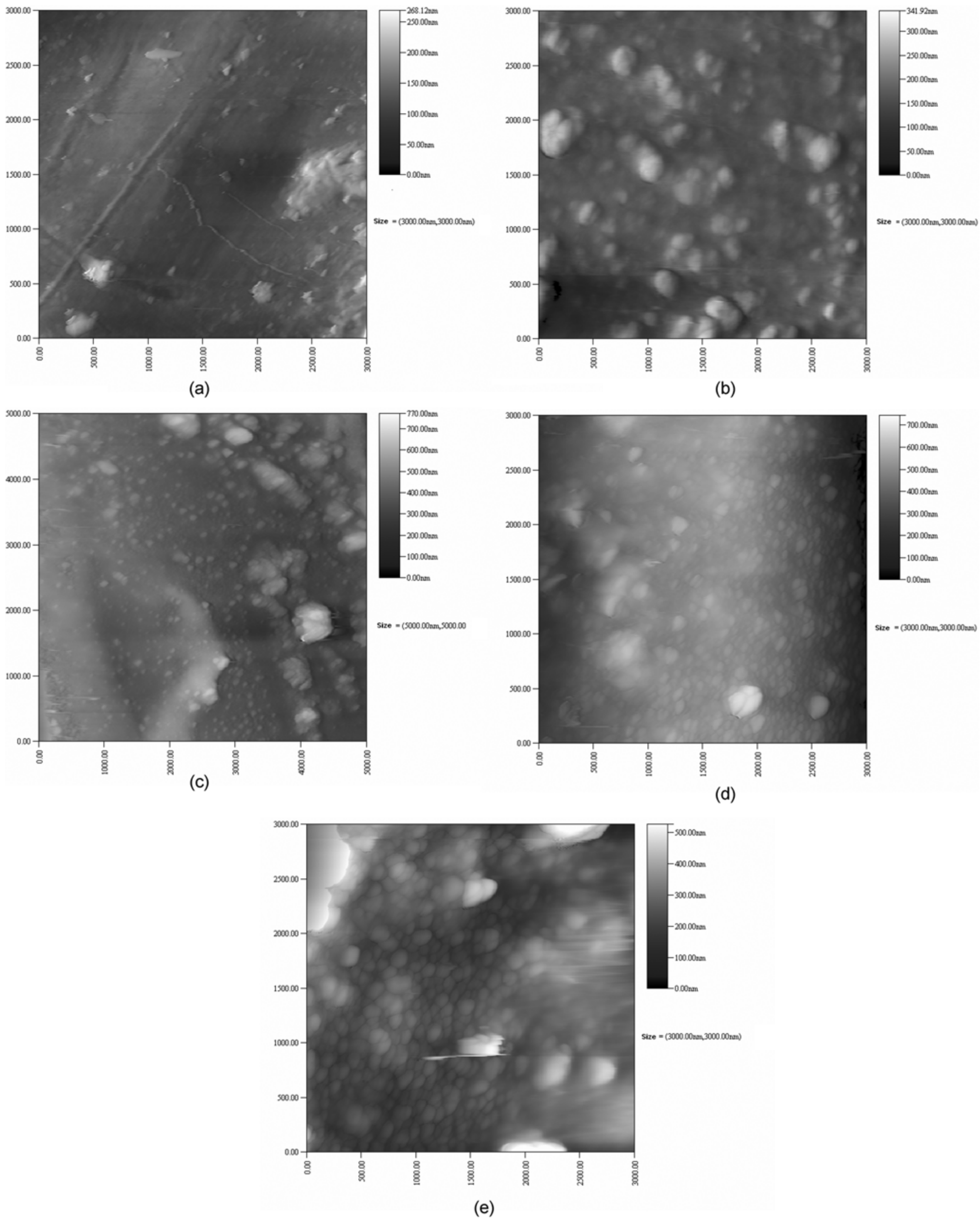

Figure 1. AFM images of PLA nonwovens uncoated and coated with silver films; (a) uncoated, (b) 0.5 nm coating, (c) 1 nm coating, (d) 2 nm coating, and (e) 3 nm coating.

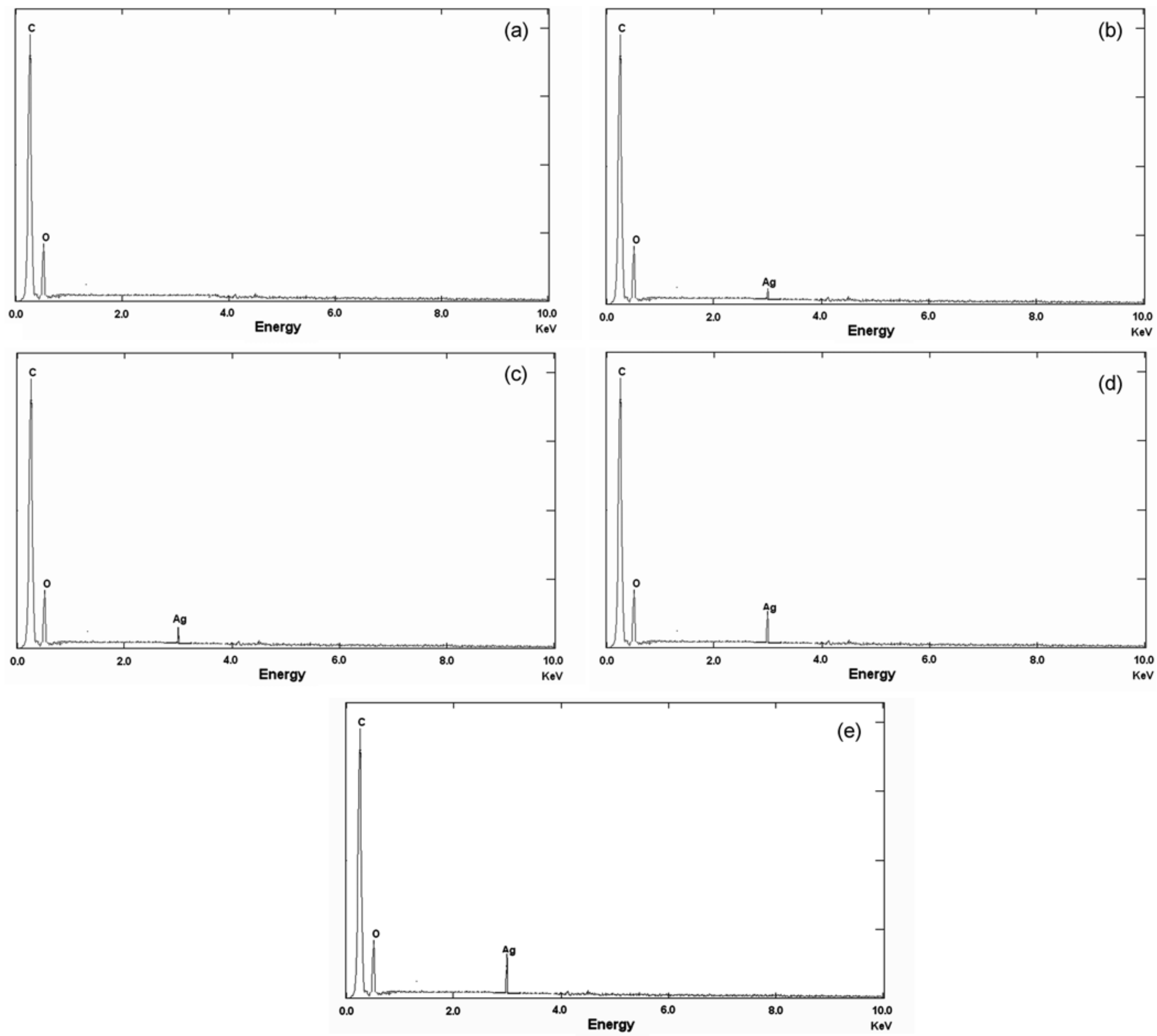

Figure 2. EDX spectra of silver films with different thicknesses; (a) uncoated, (b) 0.5 nm coating, (c) 1 nm coating, (d) 2 nm coating, and (e) 3 nm coating.

Conclusion

The antibacterial properties of PLA nonwoven medical dressings deposited with nanostructured silver films were investigated in this work. It was found that nano-structured silver showed excellent antibacterial property and the deposition thickness was the major factor affecting the antibacterial properties of the PLA nonwovens. The investigation also revealed that the percent reduction of both bacteria, *S. aureus* and *E. coli*, achieved 100 % when the coating thickness reached 1 nm. AFM and EDX observations indicated that the increased deposition time led to the increased coating thickness, contributed to the increase in release rate of silver ions from the coating and resulted in the improved antibacterial properties.

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