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Antibacterial properties of padded PP/PE nonwovens incorporating nano-sized silver colloids

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This paper deals with the effects that nano-sized silver colloids have on the antibacterial properties of PE/PP nonwovens against three kinds of bacteria: *Staphylococcus aureus*, *Klebsiella pneumoniae*, and *Escherichia coli*. These silver colloids comprise silver nanoparticles that are a non-toxic and non-tolerant disinfectant. PE/PP nonwovens are used as back sheets or coverstocks of baby diapers, adult diapers, sanitary napkins, and wipes. These materials are readily contaminated by bacteria present in moisture and dirt and can cause disease. We finished the nonwovens using a normal dipping–pad–dry method. From SEM images, we determined that the silver nanoparticles were generally dispersed well on the surface of the nonwoven fibers. We used the AATCC-100 test method to study the antibacterial properties of the treated fabrics. Bacteria were disinfected completely to below a count of 10 cells after 10 min when using the samples treated with 10 ppm of silver colloids. The ethanol-based silver/sulfur composite colloid (SNSE) has the best antibacterial efficacy when compared with the other nano-sized silver colloids. The silver particles having the smallest sizes gave the higher dispersibilities and the strongest antibacterial efficacies.

1. Introduction

In recent years, antibacterial agents that have been used industrially have included quaternary ammonium salts, metal salt solutions, and antibiotics. Unfortunately, some of these agents are toxic or poorly effective, which makes them not suitable for applications in health foods, filters, and textiles, and for the exclusion of pollution. In contrast, silver is a non-toxic, non-tolerant disinfectant that can reduce many bacterial infections significantly. As a natural renewable resource that has a number of unique properties, silver now attracts an increasing amount of scientific and industrial interest from fields as diverse as chemistry, medicine, biotechnology, food science, and textile science [1–3].

Silver nanoparticles have the properties of a high surface area, very small size (<10 nm), and high dispersion. Several studies have been undertaken to explain the antibacterial properties of Ag^+ ions toward bacteria. Polymeric or fibrous nano-composites of polymers and silver nanoparticles have been reported to have special properties [4, 5]. It is believed that the mechanism of the antibacterial effect of silver ions involves shrinkage of the cytoplasm membrane or its detachment from the cell wall. As a result, DNA molecules become condensed and lose their ability to replicate upon the infiltration of Ag ions. The silver ions also interact with the thiol groups of proteins, which induces the inactivation of bacterial proteins [6].

PE/PP nonwovens have excellent softness, regularity, and light weight. Demand for these materials continues to increase because they are very absorbent, breathable, and inexpensive. PE/PP nonwovens were used in coverstocks, medical disposables, sanitary products, and diapers, but they are readily contaminated by the bacteria present in moisture and dirt, which may cause disease. Moreover, these materials are often carriers of infectious disease agents.

In this study, we prepared PE/PP nonwovens using various kinds of nano-sized silver colloids and compared their antibacterial efficacy. Our studies involved counting the number of living microorganisms on the nonwovens at an initial time and 24 h after their treatment, observing bacteria on the nano-sized silver colloids as a function of the elapsed time, measuring the dispersibility of the silver nanoparticles in the solution (TEM), and observing of nano-sized silver colloids on the surface of the nonwoven (SEM). Moreover, we used UV-Vis spectrometry to investigate

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the properties of the various nano-sized silver colloids.

2. Experimental

2.1. Materials

The nano-sized silver colloids were supplied by NP-Tech Co., Ltd., Korea. Silver colloids were prepared by reduction of $AgNO_3$ solution using hydrazine solution in both the presence and absence of a surfactant. The Ag nanoparticles formed according to the following reaction:

$$N_2H_4 + 4Ag^+ + 4OH^- \rightarrow 4Ag^0 + 4H_2O + N_2$$

We applied three different types of nano-sized silver colloids: nano-sized silver particles dispersed in water (NSW), an ethanol-dispersed solution of the nano-sized silver particles (NSE), and nano-sized silver/sulfur composite particles dispersed in ethanol (SNSE) to prevent aggregation of the particles. The fabric samples of PE/PP spun-bond nonwovens were provided by Korea Vilene Co., Ltd., Korea; the density was 2.1 mg/cm^2 and the thickness was 0.17 mm.

2.2. Experiments

The concentration of colloidal silver solutions was varied – 5, 10, or 20 ppm – by diluting each nano-sized silver colloid solution with distilled water. The real content of the silver in the nonwovens was 3.03, 6.06, or 12.12 ppm because the wet pick-up ratio of the nonwoven was 165%.

$$\text{wet pick-up ratio}(\%) = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100$$

The nonwovens were padded with each concentration of the colloid solutions at the pressure of 3.0 kgf/cm^2 by using an auto fade mangle. The samples were immediately dried at 120°C for 3 min.

2.3. Measurements

The morphologies and sizes of the particles formed in the various solutions were investigated by transmission electron microscopy (TEM) using a JEOL 2000FX operated at 200 kV and employing magnification of up to 200000. The specimen on the grid was shadowed with platinum to increase the contrast of the image. We used UV-visible spectroscopy (UNICAM 8700 spectrophotometer, UK) to determine the optical properties of the various nano-sized silver colloids.

We used the AATCC-100 test method (antibacterial activity assessment of textile materials) to study the antibacterial properties of the fabrics finished with the nano-sized silver colloids. The nonwovens were placed on a germ-containing agar plate and were inoculated with Gram-positive (*Staphylococcus aureus*, ATCC 6538) and Gram-negative (*Klebsiella pneumoniae*, ATCC 4352) bacteria. Specimens corresponding to untreated controls of the same material were placed in intimate contact with the nutrient agar, which previously had been streaked with an inoculum of the test bacterium. After incubation for 24 h, we evaluated the antibacterial properties of both the untreated fabric and the treated nonwovens.

$$\text{Percent reduction of bacteria}(\%) = \frac{A - B}{A} \times 100$$

A: The number of bacteria on the untreated fabric after 24 h;

B: The number of bacteria on the antibacterial-treated fabric after 24 h.

Next, we investigated the antibacterial properties of the diluted nano-sized silver colloidal solutions against *S. aureus* and *Escherichia coli (E. coli*, ATCC 25922). The test bacteria were cultivated directly in the nano-sized silver colloid solutions. We observed the percentage of the reduction of bacteria at each elapsed time (5, 15, and 30 min). The solutions were shaken at 35±1°C for 5, 15, and 30 min, and then we determined the bacterial cell growth inhibition rate by using the pour agar plate method (150 rpm/min).

This method was the antibacterial efficacy test-shake flask method (FC-TM-19-2001 Test Method), which was improved by the FITI Testing & Research Institute, Korea.

The dispersibility and affinity of the silver nanoparticles on the surface of the nonwovens were estimated by using scanning electron microscopy (SEM). The SEM micrographs were recorded using a JSM-6330F microscope (Jeol, Tokyo, Japan). We used a sputter coater to precoat conductive platinum onto the surface before measuring the microstructures at 1, 3, and 5 kV.

3. Results and discussion

3.1. Properties of nano-sized silver colloids

Fig. 1 presents TEM images of the nano-sized silver colloid. The silver nanoparticles had spherical shapes. The mean Ag particle size in the water-based colloid was 8.11 nm, and that of the ethanol-based colloids was ca. 3 nm. The ethanol-based silver colloids were dispersed evenly without aggregation, because ethanol is a more ionic solvent than is distilled water. The OH groups of ethanol stabilize the Ag ions and prevent aggregation of the particles.

Fig. 2 presents UV-Vis spectra of the nano-sized silver colloids. NSE (the ethanol-based nano-sized silver colloid) exhibited the value of λ_{max} at the lowest wavelength (401.7 nm) because the Ag particle size in the ethanol-based colloid was the smallest. The low wavelength and narrow peak width reflect the small particle size distribution. This result agrees well with the findings from the TEM images of the nano-sized silver colloids (Fig. 1). The absorbance of NSW gave the highest yield, but that of SNSE was the lowest. We estimated that the difference in color affected the absorbance. Experimentally, we observed that the nonwovens treated with NSW (the water-based nano-sized silver colloid) had the deepest color at the same concentration. Interestingly, the color of the colloid was almost invisible in

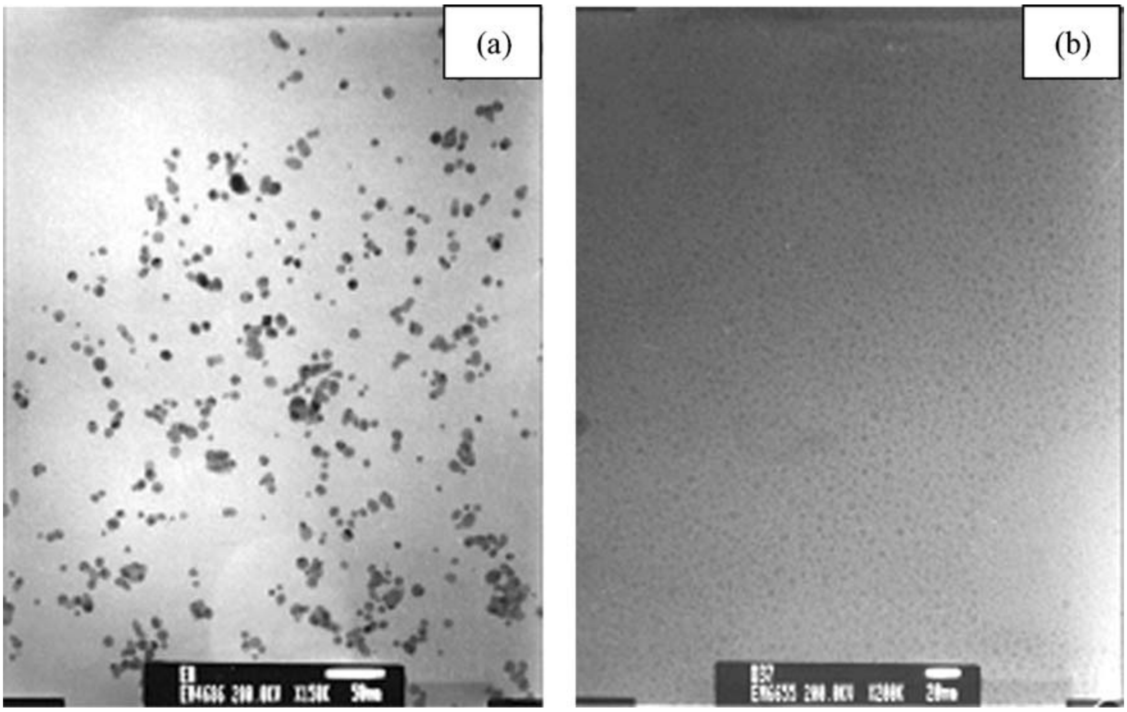

Figure 1 HR-TEM images of silver nanoparticle (×200 K): (a) water-based silver nanoparticles; (b) ethanol-based silver nanoparticles.

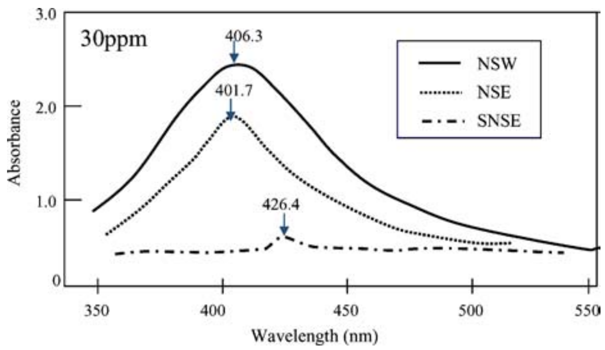

Figure 2 UV-Vis spectra of nano-sized silver colloids (30 ppm) in the presence of the base solutions.

the nonwovens treated with SNSE below 30 ppm; this observation suggests that this sample may be a good antibacterial finishing agent that will not influence the intrinsic color of the fabric. Furthermore, the stability of the nanoparticles in the colloidal silver decreased proportionally with respect to time. After 7 days, we investigated a slight red-shift in the UV-Vis spectra of the NSW and NSE nano-sized silver colloids, which suggest an increase in the degree of nanoparticle aggregation. Although some aggregation occurred, the antibacterial properties remained as a result of the very small particle size. On the other hand, the UV-Vis spectrum of the SNSE sample did not display a shift in λ_{max} because of the higher stability of the Ag-S particles.

Fig. 3 displays the rate of bacterial reduction of the SNSE nano-sized silver colloid solution as a function of the elapsed time. In Fig. 3a, we observe that after 5 min in the 3-ppm nano-sized silver colloid, *S. aureus* bacteria decreased from 1.2×10^5 to 3.1×10^2 (1/500) and *E. coli* bacteria were disinfected to below 10 cells; after 15 min, the *S. aureus* bacteria were disinfected completely to below 10 cells. Fig. 3b indicates that both *S. aureus* and *E. coli* decreased to below 10 cells within 5 min in the 12-ppm nano-sized silver colloid. These findings suggest that the Ag-S particles display a dominant antibacterial efficacy.

3.2. Antibacterial activity of nonwovens

Table I lists the antibacterial properties of fabrics treated with the nano-sized silver colloids. At the initial stage, number of *S. aureus* cells was 1.3×10^5 in the untreated fabric. After 24 h, the number of bacterial cells was 7.3×10^7 (i.e., a 560-fold increase). All of the specimens exhibited excellent percentage reductions against *S. aureus*, but there is a clear effect of the silver nanoparticle's concentration. In contrast, PNSW did not display an antibacterial property against *K. pneumoniae*. These conflicting results arise from the nature of the bacteria: *S. aureus* is a Gram-positive bacterium and *K.pneumoniae* is a Gram-negative one. Generally, Gram-negative bacteria are stronger than Gram-positive bacteria. Ethanol provides a higher dispersion of the silver particles than did water. Moreover, the sizes of the silver nanoparticles in the ethanol base were smaller than they were in the water base. We infer from Fig. 1 that the size of the Ag particle and the degree of dispersion in the ethanol base would provide superior antibacterial properties, which we corroborated from the TEM images of the colloidal particles. For that reason, PNSE has higher antibacterial efficacy against Gram-negative bacteria than does PNSW. The antibacterial properties increase as the concentration of the nano-sized silver colloids increased. This finding is in good accord with the experimental results we determined for PNSE against *K.pneumoniae*: if the colloid concentration of PNSW is >30 ppm, we will obtain sufficient antibacterial properties.

Fig. 4 presents the effect that the silver nanoparticles have against *S. aureus* on the nonwoven fabric. In

TABLE I Bacterial reduction on nonwovens finished using nano-sized silver colloids

	Bacteria	*S. aureus*			*K. pneumoniae*		
Sample	Start	1.3×10^5	1.3×10^5	1.3×10^5	1.2×10^5	1.2×10^5	1.2×10^5
PNSW[a]	Concentration	0 ppm	10 ppm	20 ppm	0 ppm	10 ppm	20 ppm
	After 24 hr	7.3×10^7	9.9×10^5	<10	6.8×10^7	5.5×10^7	5.4×10^7
	% reduction of bacteria	–	98.6	**99.9**	–	18.5	19.4
PNSE[b]	Concentration	0 ppm	10 ppm	20 ppm	0 ppm	10 ppm	20 ppm
	After 24 hr	7.3×10^7	1.5×10^5	1.5×10^5	6.8×10^7	5.8×10^7	<10
	% reduction of bacteria	–	**99.8**	**99.8**	–	14.2	**99.9**
PSNSE[c]	Concentration	0 ppm	5 ppm	20 ppm	0 ppm	5 ppm	20 ppm
	After 24 hr	7.3×10^7	<10	<10	6.8×10^7	<10	<10
	% reduction of bacteria	–	**99.9**	**99.9**	–	**99.9**	**99.9**

[a]The water-based nano-sized silver colloid was padded on the sample.
[b]The ethanol-based nano-sized silver colloid was padded on the sample.
[c]The ethanol-based nano-silver/sulfur composite colloid was padded on the sample.

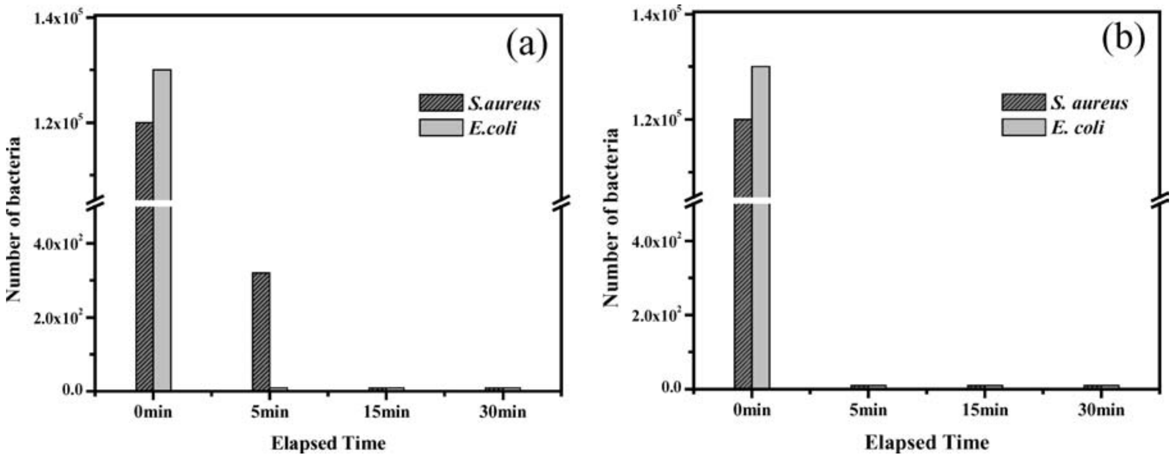

Figure 3 Reduction in the number of bacteria in the SNSE nano-sized silver colloids as a function of the elapsed time: (a) 3 ppm; (b) 12 ppm.

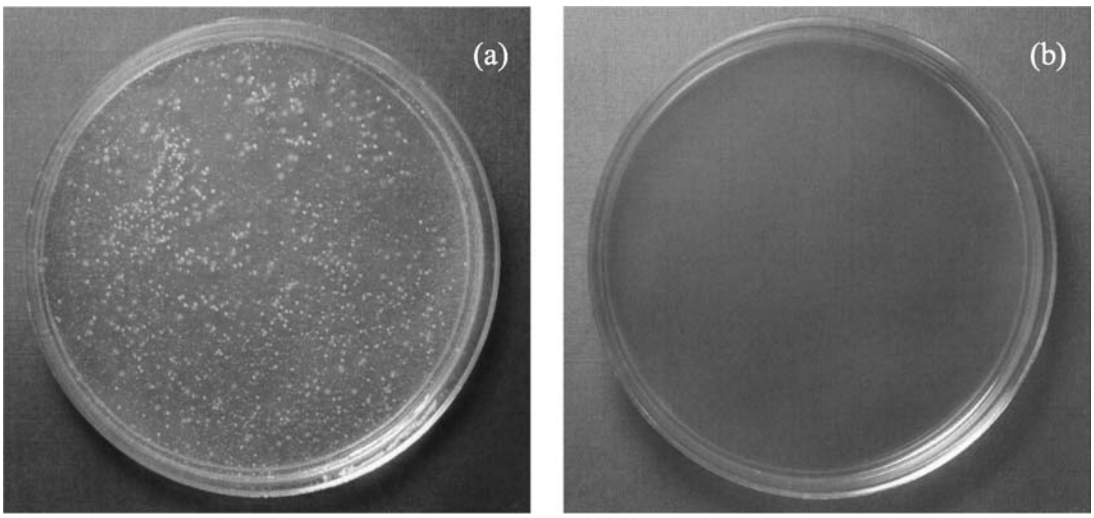

Figure 4 Photographic image of the incubation of *Staphylococcus aureus* on the nonwoven fabric after 24 h: (a) untreated; (b) treated with NSW (20 ppm).

Fig. 4a, we observe that many *S. aureus* bacteria are present on the untreated nonwovens; in Fig. 4b, there are significantly fewer. As indicated in Fig. 5, *K. pneumoniae*, a Gram-negative, stronger bacterium, was infected by the silver nanoparticles within 24 h. PSNSE has particularly high antibacterial properties against all of the bacteria we studied (number of bacteria: <10 cells); PSNSE displays this astonishing effect despite its very low concentration. SNSE was produced in an Ag-sulfur composition. Sulfur is a good disinfectant and a toxic agent, but the Ag-sulfur composite is non-toxic. The addition of sulfur enhances the antibacterial properties and the stability of the Ag ions. The average silver particle size of SNSE is larger than that

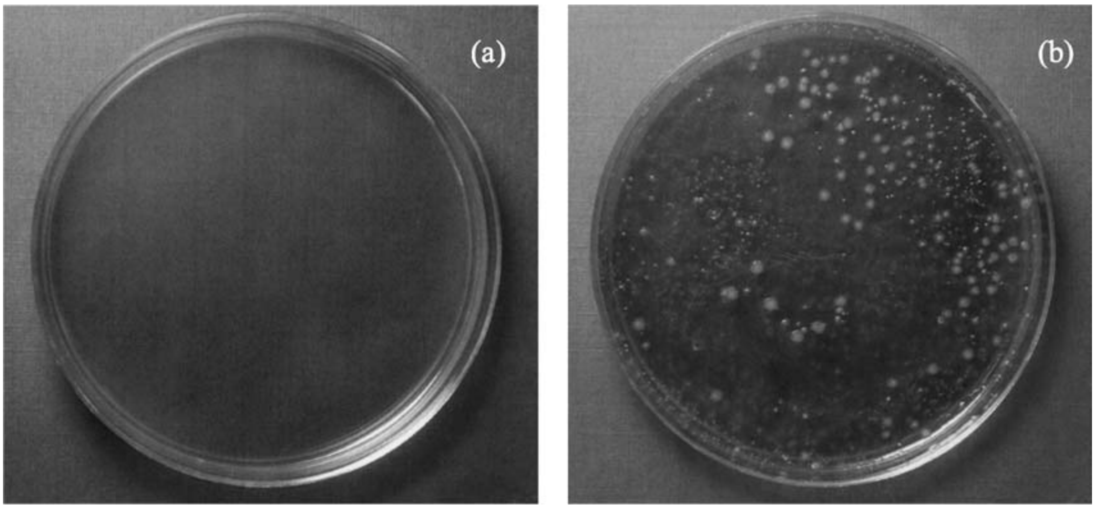

Figure 5 Photographic image of the incubation of *Klebsiella Pneumoniae* on the nonwoven fabric after 24 h: (a) untreated; (b) treated with NSE (20 ppm).

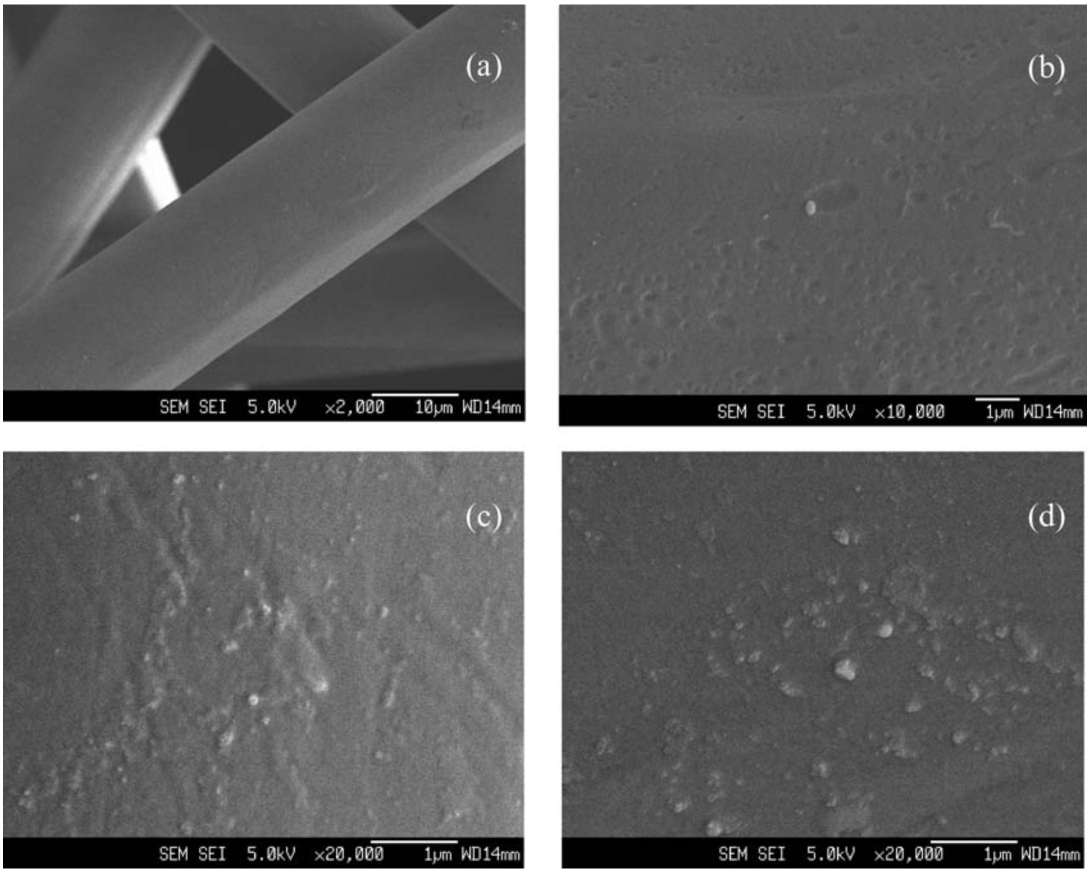

Figure 6 SEM images of the nonwovens finished with nano-sized silver colloids: (a) control; (b) PNSW (30 ppm); (c) PNSE (30 ppm); (d) PSNSE (30 ppm).

of NSE because of the structure of the Ag-S composites, yet they still have excellent antibacterial efficacy. We obtained SEM micrographs (Fig. 6) to observe the surfaces of the antibacterial-treated nonwovens. The silver nanoparticles were generally well-dispersed on these surfaces.

4. Conclusions

We have investigated the antibacterial properties of nano-sized silver colloids against bacteria when we padded solutions of various colloids onto PE/PP spunbond nonwovens. From TEM images, we determined that the average sizes of the silver particles were <10 nm for all three of the types of nano-sized silver colloids we studied. PE/PP nonwovens that we treated with the nano-sized silver colloids had good antibacterial properties. In particular, SNSE (the ethanol-based nano-sized silver/sulfur composite colloid) exhibited the highest antibacterial efficacy. SEM images indicated that the silver nanoparticles generally were well-dispersed on the surfaces of the nonwoven fibers. Because longer wavelengths for λ_{max} in the UV-Vis spectra indicate larger mean particle sizes, we observed that the wavelength red-shifted as the stability of the nano-sized silver colloids decreased. We used nano-sized silver colloid as antibacterial agents and obtained sufficiently good results; the antibacterial properties of these silver nanoparticles are clear even at low concentrations. We expect that they will display a high level of performance if they are applied to back sheets or coverstocks.

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