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Multifunctional and Durable Nanofiber-Fabric-Layered Composite for Protective Application

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ABSTRACT: A multifunctional and durable nanofiber-fabric-layered composite (NFLC) material was prepared by depositing electrospun Ag/PAN hybrid nanofibers onto a Nylon/cotton 50: 50 fabric substrate. The NFLCs showed excellent aerosol barrier efficiency and good air/moisture permeability. In addition, they showed excellent antibacterial efficiency by completely inhibiting the growth of both Gram-negative *E. coli* and Gram-positive *S. aureus*. The interfacial adhesion between the nanofiber layer and fabric substrate was significantly improved by atmospheric plasma pretreatment of the substrate. The resultant NFLCs showed excellent resistance to peeling, twisting, and flexing forces. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 1219–1226, 2013

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INTRODUCTION

Electrospun nanofibers, featuring ultralarge specific surface areas and high porosities, have been considered as ideal material candidates in a wide range of applications including filtration,[1] tissue engineering,[2] homogeneous catalysis,[3] biomedical,[4] and electronic devices.[5] Recently, the integration of nanofiber materials into chemical and biological protective systems has attracted much research interest.[6,7] Given their unique structure and properties, nanofiber mats have been shown to effectively prevent the penetration of chemical and biological agents in the form of aerosols.[8,9] Unlike traditional protective materials, nanofiber mats do not sacrifice air and moisture permeability while providing ideal barrier efficiency.[10,11]

One main problem that limits the application of nanofibers is their durability. Most nanofiber mats are relatively weak,[12,13] and in the majority of cases, woven or nonwoven fabrics are used as supporting substrates for nanofiber mats to form nanofiber-fabric-layered composites (NFLCs), which combine the advantages of both nanofibers and regular fabrics. The biggest challenge here is to ensure good adhesion between the nanofiber layer and substrate fabric.[14,15] Conventional laminating methods, such as gluing and thermal pressing, are not suitable for the preparation of layered composites with electrospun nanofibers, because these methods will destroy the microstructure of nanofiber mats and eliminate their unique properties.[16,17] Atmospheric plasma treatment appears to be a promising method to improve the interfacial adhesion in NFLCs. As a facile, effective, environmental-friendly surface-modification method, atmospheric plasma treatment requires no wet chemistry and is operated under room temperature.[18,19] During the atmospheric plasma treatment, highly active species, such as electrons, ions, and radicals, are generated on the fabric surface and are available to enhance bonding with other materials at the interface.[20,21]

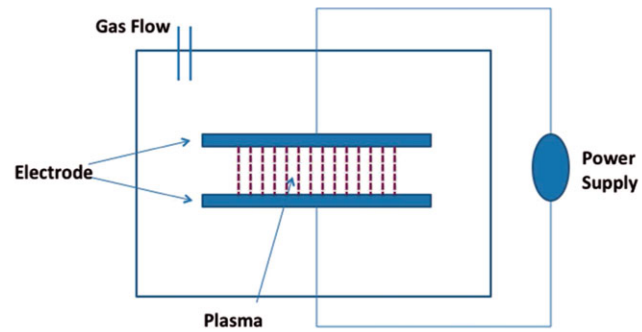

Figure 1. Schematic of the atmospheric plasma device NCAPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To make useful NFLCs for protective application, it is also important to incorporate functional organic/inorganic additives, such as absorbents, catalysts, and biocides, into nanofibers to handle various hazardous environments.[22–25] In previous studies, functional additives were directly added into the polymer solutions to be electrospun into nanofibers; however, the homogeneous dispersion of additives in the nanofiber matrix remains a key challenge.[26–28] Recently, the authors reported the preparation of PAN nanofibers embedded with silver nanoparticles by in situ reduction of Ag precursor in pre-electrospinning solution via atmospheric plasma treatment.[29] The Ag/PAN hybrid nanofibers have shown uniform Ag nanoparticle dispersion and excellent antimicrobial activity. In this study, the Ag/PAN hybrid nanofibers were deposited onto Nylon/cotton 50: 50 fabric to form a novel multifunctional NFLC material with both high-aerosol penetration resistance and excellent antimicrobial efficiency. Effect of atmospheric plasma pretreatment on the durability of resulting NFLCs was also investigated.

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN, M_w = 1,500,000), *N,N*-dimethylformamide (DMF), and silver nitrate ($AgNO_3$) were purchased from Sigma-Aldrich Co. (St. Louis, MO). All these reagents were used without further purification. Nylon 6,6/cotton (50/50) woven fabric (mass per unit area: 240 g/m^2) was acquired from Milliken & Company, USA.

Atmospheric Plasma Treatment

The atmospheric plasma treatment was carried out in the NC Atmospheric Plasma System, which is a capacitively coupled dielectric barrier discharge, as shown in Figure 1. The device has an active exposure area of 60 $\times$ 60 cm^2 between two copper electrodes. The plasma was operated by a 4.8 kW audio frequency power supply at 1–10 kHz.[30,31] In case of solution treatment, 10 mL of $AgNO_3$/PAN solution was added to a petri dish with a liquid depth of ~5 mm and treated as reported in a previous publication.[32] In case of fabric treatment, a sparse web was used to suspend the fabric to achieve full treatment on both sides of fabric.

Preparation of Ag/PAN Solution

PAN was first dissolved in DMF at a concentration of 8 wt %, followed by the addition of 1.25 wt % Ag precursor ($AgNO_3$). The complex was stirred at room temperature in dark for 12 h to form a uniform transparent solution. The solution was then treated with helium atmospheric plasma for 5 min to obtain Ag/PAN solution.[29]

Nanofiber Deposition

The deposition of Ag/PAN nanofibers on the substrate fabric was obtained using the electrospinning setup shown in Figure 2. The fabric was cut into appropriate size (pretreated with plasma if needed), attached to an aluminum sheet, and fastened onto the grounded rotating drum. The Ag/PAN solution was collected in a 10-mL plastic syringe equipped with a 24-gauge needle tip. The syringe was then attached onto a syringe pump, with the needle tip pointing toward the rotating drum at a distance of 15 cm. The pump feed rate was maintained at 2 mL/h. During electrospinning, the needle tip was charged at 20 kV by a high-voltage generator. The rotating speed of the drum collector was maintained at 20 rpm, driven by a step motor.

Morphology Characterization

The nanoscale morphologies of Ag/PAN nanofibers and their depositions on substrate fabrics were examined using JEOL

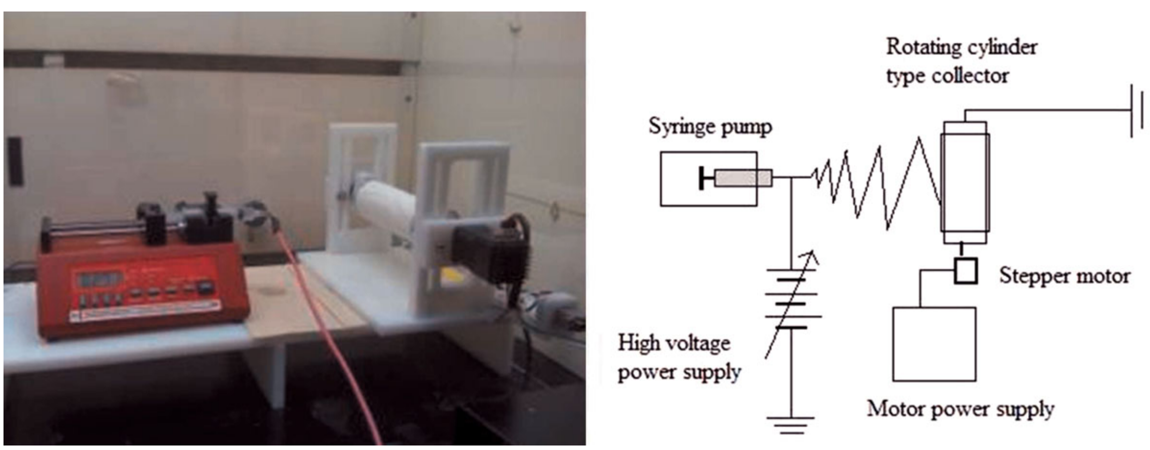

Figure 2. Photograph and schematic diagram of the electrospinning setup. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. Optical image of an Ag/PAN nanofiber-deposited Nylon/cotton 50: 50 fabric.

JSM-6400F field emission scanning electron microscopy at an accelerated voltage of 5 kV.

Aerosol Barrier Performance

The aerosol barrier performance of the nanofiber-deposited fabrics was evaluated using a TSI 3160 advanced filtration tester. The testing was performed with standard 300 nm NaCl particles. The face velocity used was 5.332 cm/s, and air flow rate was 32 L/min. Two condensation particle counters were used to simultaneously count the upstream and downstream particles. Both the aerosol barrier efficiencies and pressure resistances were calculated. For comparison, the aerosol barrier performance of Nylon/cotton fabric was also evaluated.

Moisture Vapor Transmission Rate

The moisture vapor transmission rates (MVTRs) of nanofiber-deposited fabrics were measured using the ASTM E96-80 standard and calculated in units of gram per square meter—24 h. For comparison, the MVTR of the Nylon/cotton fabric was also measured.

Antibacterial Activity

The antibacterial activity of nanofiber-deposited fabrics was tested by following Standard AATCC Test Method 147-2004 *Antibacterial Activity Assessment of Textile Materials: Parallel Streak Method*. Bacterial cultures were obtained from the USDA/ARS Food Fermentation Culture Collection (USDA/ARS Food Science Research Unit, Raleigh, NC) *Escherichia coli* (B179, Gram-negative) was propagated on Luria–Bertani agar or broth (BD Company; Sparks, MD), and *Staphylococcus aureus* (B31, Gram-positive) was propagated on TSB agar or broth (BD Company; Sparks, MD). To prepare cells for antimicrobial fiber assays, 5-mL LB broth or TSB broth (*E. coli* and *S. aureus*, respectively) was inoculated from individual colonies on an agar plate and then incubated for 18 h at 37°C on a shaker platform at 200 rpm (Eppendorf Thermomixer; Hamburg, Germany). Following incubation, cells were harvested by centrifugation (5000 $\times$ *g*, 10 min, 4°C, Sorvall RB-5C centrifuge) and resuspended in physiological saline (0.85% NaCl) to form a suspension with $\sim 10^8$ colony-forming units per milliliter (CFU/mL). Using a 4-mm inoculating loop, five parallel streaks of cell suspension were spread across an LB agar plate without reinoculating the loop between streaks. An aseptically cut, rectangular fabric (25×50 mm^2) specimen was gently pressed transversely face-down across the streak area on the agar plate. Duplicate plates for each treatment were incubated at 37°C for 24 h. Plates were evaluated visually for clearing and interruption of growth along streaks.

Durability Against Peeling, Twisting, and Flexing Forces

The durability of nanofiber-deposited fabrics was evaluated by peel test (modified ASTM 2261: *Standard Test Method for Tearing Strength of Fabrics by the Tongue Procedure using an Instron® Tensile Tester*) and Gelbo Flex test (modified ASTM F392-93: *Standard Test Method for Flex Durability of Flexible Barrier Materials*). Before both testing, the nanofiber-deposited fabric samples were conditioned at standard temperature of 20°C ± 1°C and relative humidity of 65% ± 2% for at least 8 h.

The peeling test was performed on an Instron Tensile Tester. The nanofiber mat was held by the movable grip of the Tensile Tester and the fabric substrate held by the stationary grip, respectively. A 50-g load cell was used to detect the maximum load required to peel the nanofiber mat off the fabric surface at a constant rate of 50 mm/min, using a 0.5 in. gauge length. The adhesion strength was estimated in terms of gram force, and the average value of at least 10 test specimens was reported.

The Gelbo Flex test was performed on a Gelbo Flex Tester (IDM Instruments®). Nanofiber-deposited fabric samples were attached to the two circular clamping disks via hose clamps, and the samples were twisted and flexed for 1000 cycles.

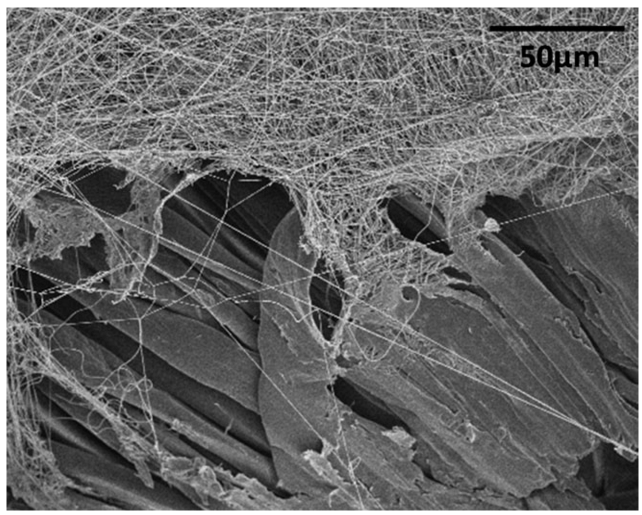

Figure 4. SEM images of Ag/PAN nanofiber-deposited Nylon/cotton 50: 50 fabric. Portions of deposited nanofibers were peeled off to show the Nylon/cotton fabric substrate.

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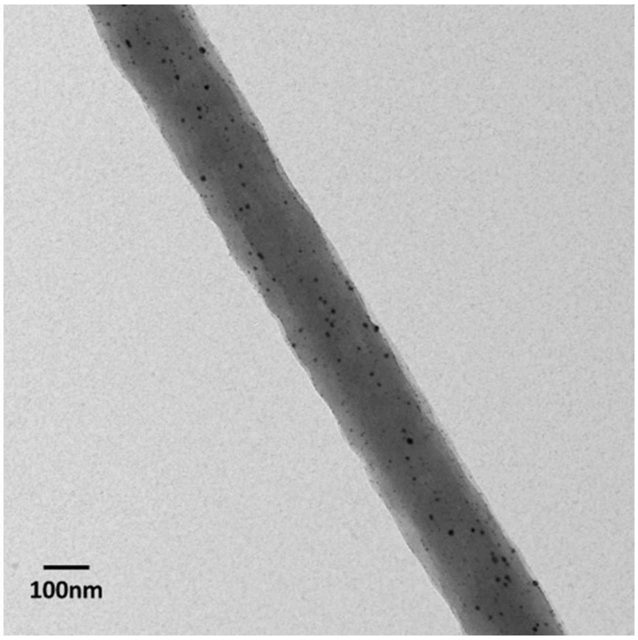

Figure 5. TEM image of an Ag/PAN nanofiber-Ag precursor concentration: 1.25 wt %.

A qualitative assessment of adhesion was determined by visual observation of the electrospun nanofiber/fabric substrate interface.

RESULTS AND DISCUSSION

Nanofiber Deposition

Figure 3 shows optical images of an Ag/PAN nanofiber-deposited fabric. The nanofibers could be visually observed to cover the fabric substrate as a uniform and compact layer. As reported in the author's previous work,[29] the Ag/PAN nanofibers show yellow color instead of white (color of pure PAN nanofibers) due to the incorporation of Ag nanoparticles. Figure 4 presents SEM images of Ag/PAN nanofibers deposited on the Nylon/cotton fabric (nanofiber area density: 1.87 g/m^2). To enable visualization of the fabric substrate, portions of nanofiber layers have been peeled off. It is seen that the nanofiber layers were uniformly deposited, and they have high porosity with nanoscaled pore size, which can efficiently prevent aerosols of chemical and biological agents from penetrating through. Figure 5 shows a TEM image of a Ag/PAN nanofiber electrospun from 1.25 wt % silver precursor solution. It could be seen that the Ag nanoparticles (black dots) are dispersed in the fiber matrix uniformly. The area densities of nanofibers deposited on the fabric substrate with different deposition durations are listed in Table I.

Table I. Nanofiber Area Densities of Ag/PAN Nanofiber Coatings Prepared Using Different Deposition Durations

Deposition time (min)	Nanofiber area density (g/m^2)
15	0.93
30	1.87
45	2.8

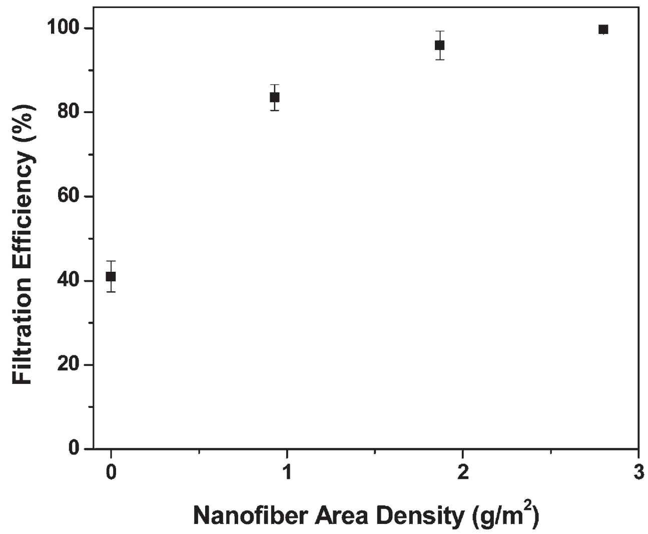

Figure 6. Aerosol barrier efficiency of Ag/PAN nanofiber-deposited Nylon/cotton 50: 50 fabrics prepared using different nanofiber area density. Ag precursor concentration: 1.25 wt %.

Aerosol Barrier Efficiency

Figure 6 shows the aerosol barrier efficiencies of Ag/PAN nanofiber-deposited Nylon/cotton fabrics with different nanofiber area density. Without nanofiber deposition, the fabric material has a barrier efficiency of only around 40%. A significant increase in barrier efficiency (over 80%) is observed in the Ag/PAN nanofiber-deposited Nylon/cotton fabric prepared with 15-min nanofiber deposition. Higher barrier efficiencies can be obtained by increasing the nanofiber area density. An average barrier efficiency of 99.96% is reached when the nanofiber area density is 45 min. In this case, the area density of nanofibers is 2.8 g/m^2, that is, about 1% of the substrate fabric (240 g/m^2).

The pressure resistances of Ag/PAN nanofiber-deposited Nylon/cotton fabrics were also tested, and the results are shown in Figure 7. It is seen that with the nanofiber area density increasing up to 2.8 g/m^2, the pressure resistance of nanofiber-deposited fabrics increases from 56.6 (at zero nanofiber area density) to 79.1 mm H_2O pressure, that is, a 40% resistance increase. However, at the same time, the barrier efficiency increases by 150% from 40% to 99.7% (Figure 6).

MVTR is another very important parameter for many applications, especially protective clothing. In general, the moisture vapor transmission behavior of fabrics is directly related to the comfort properties. The MVTR values of Ag/PAN nanofiber-deposited Nylon/cotton fabrics with different nanofiber area densities are shown in Figure 8. The results indicate that the deposition of electrospun fiber mats on woven fabrics does not alter the moisture vapor transmission through the fabric structure due to the high porosity of the electrospun nanofiber layer. Therefore, it can be concluded that depositing Ag/PAN nanofibers onto Nylon/cotton fabric can provide excellent aerosol

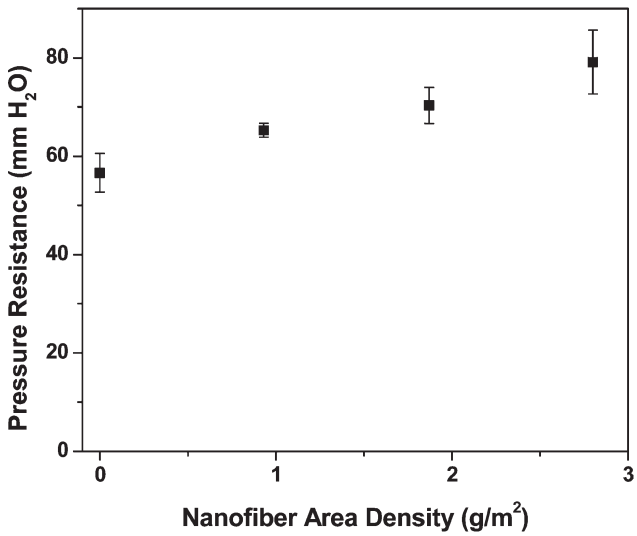

Figure 7. Pressure resistance of Ag/PAN nanofiber-deposited Nylon/cotton 50: 50 fabrics prepared using different nanofiber area density. Ag precursor concentration: 1.25 wt %.

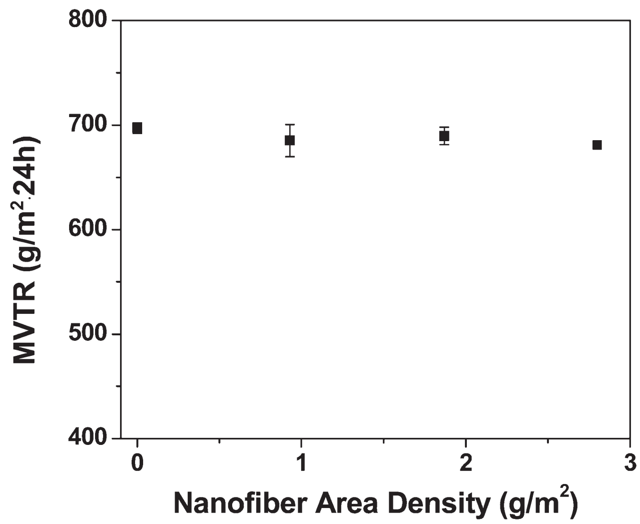

Figure 8. MVTR of Ag/PAN nanofiber-deposited Nylon/cotton 50: 50 fabrics prepared using different nanofiber area density. Ag precursor concentration: 1.25 wt %.

barrier efficiency without significantly sacrificing the air permeability and moisture vapor transmission.

Antimicrobial Activity

The antimicrobial properties of individual silver nanoparticle-containing nanofibers and the effect of silver precursor concentrations have already been studied quantitatively in our previous study.[29] The Ag/PAN nanofibers showed over six in log reduction on both *E. coli* and *S. aureus* cultures. In this work, the protective efficiency of Ag/PAN nanofiber-deposited Nylon/cotton fabrics against biological attack was evaluated by the Parallel Streak method (AATCC-147-2004). *E. coli* and *S. aureus* were used as representative Gram-negative and Gram-positive microorganisms, respectively. The bacteria culture was inoculated onto the agar plates with five streak lines. The nanofiber-deposited fabric specimens were pressed slightly onto the plates, with the nanofiber layers facing the streaks. The plates were then incubated for 24 h, and the antimicrobial activity was evaluated by the bacteria growth. As shown in Figures 9 and 10, for both *E. coli* and *S. aureus*, the bacteria grew underneath and surrounding the Nylon/cotton fabric, indicating that the substrate fabric had no antimicrobial activity. However, for the Ag/PAN nanofiber-deposited Nylon/cotton fabric, no bacterial growth can be seen underneath the specimen, which means that the composite materials are able to kill both *E. coli* and *S. aureus* while in contact with them. In addition, a clear zone of inhibition can be observed on both sides of the specimen in the case of *E. coli*, indicating additional effect against *E. coli* by the Ag^+ diffusion to external environment. It can be concluded that Ag/PAN nanofiber-deposited Nylon/cotton fabrics can efficiently kill both Gram-negative and Gram-positive microorganisms at direct contact and inhibit their growth in the vicinity of the materials.

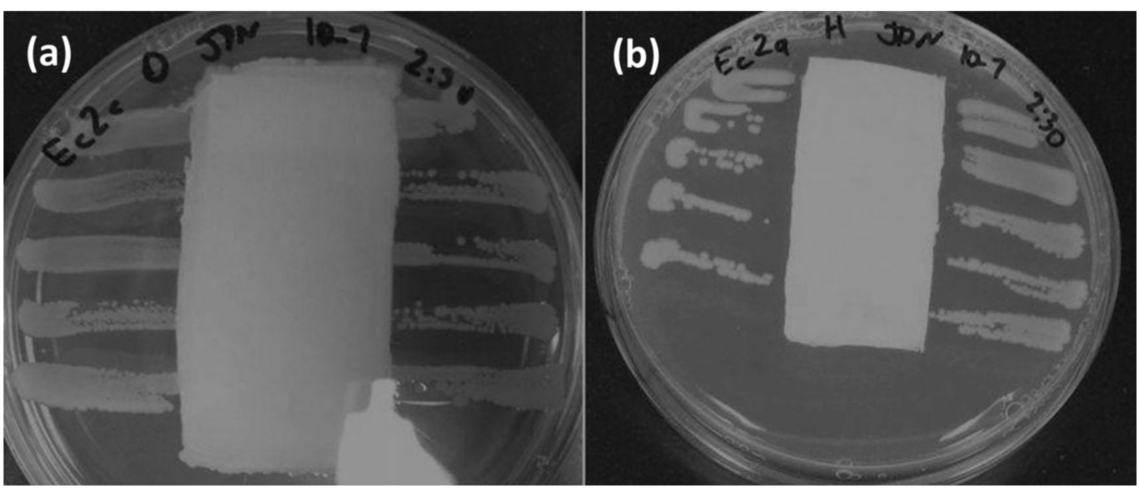

Figure 9. AATCC 147 Gram-negative (*E. coli*) testing plates of (a) Nylon/cotton fabric; (b) Ag/PAN nanofiber-deposited Nylon/cotton fabric (Ag precursor concentration: 1.25 wt %; nanofiber area density: 1.87 g/m^2).

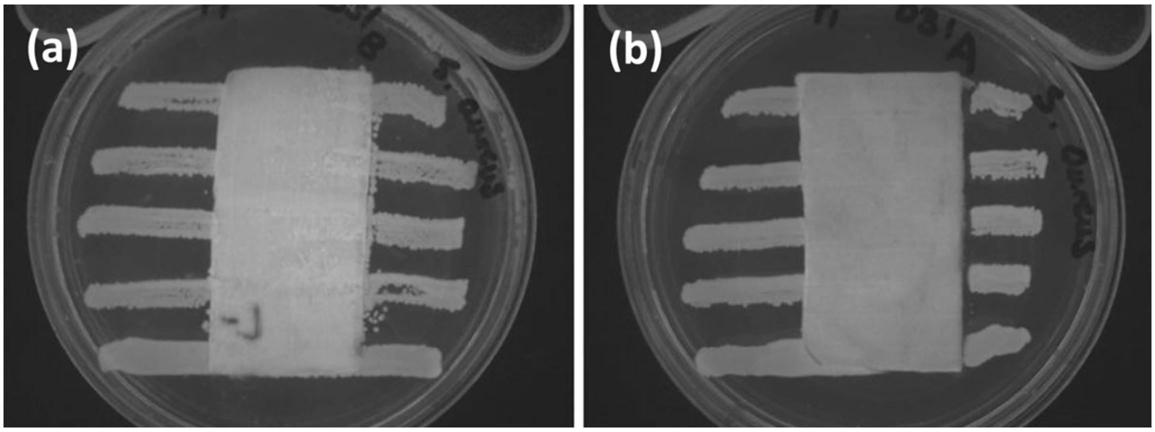

Figure 10. AATCC 147 Gram-positive (*S. aureus*) testing plates of (a) Nylon/cotton fabric; (b) Ag/PAN nanofiber-deposited Nylon/cotton fabric (Ag precursor concentration: 1.25 wt %; nanofiber area density: 1.87 g/m^2).

Table II. Peeling Test Results of Ag/PAN Nanofiber-Deposited Nylon/Cotton 50: 50 Fabrics[a]

	Substrate untreated	Substrate pretreated
Average force (gf)	5.77 ± 0.77	10.04 ± 0.45
Peak load (gf)	6.23 ± 0.72	11.78 ± 0.68

[a]Ag/PAN nanofibers were prepared with an Ag precursor concentration of 1.25 wt % and a nanofiber area density of 1.87 g/m^2.

Durability Against Peeling, Twisting, and Flexing Forces

Although Ag/PAN nanofiber-deposited Nylon/cotton fabrics can provide satisfactory protective performance, the interfacial adhesion between nanofibers and substrate must be improved before they can be used in practical applications. It has been reported that atmospheric plasma can provide active sites on polymer surfaces and enhance the interfacial adhesion.[20,21] In this work, to improve the adhesion and durability of Ag/PAN nanofiber-deposited Nylon/cotton fabrics, atmospheric plasma was used to treat the substrate fabric before nanofiber deposition.

Peeling tests were carried out on Ag/PAN nanofiber-deposited Nylon/cotton fabrics with and without substrate pretreatment. Table II shows the average forces needed to peel the nanofiber layers off from the substrate fabric along the fabric length and the maximum forces in this process. It is seen that with substrate pretreatment, both average force and peak load increase, which indicates the interfacial adhesion between the nanofiber layer, and the substrate has been improved.

The adhesion behavior was further investigated by observing the morphology of the substrate surface after the peeling test (Figure 11). As shown in Figure 11(a), without substrate pretreatment, very few nanofibers remain on the substrate fabric after peeling test, which means that the nanofiber layer was completely removed during the peeling process. However, with substrate pretreatment, a significant amount of nanofibers remain on the substrate fabric at the conclusion of the peeling test, as shown in Figure 11(b), indicating a strong interfacial adhesion between the nanofiber layer and the substrate.

Another durability assessment, Gelbo Flex testing, was performed to evaluate the ability of Ag/PAN nanofiber-deposited Nylon/cotton fabrics in retaining their shape and structure

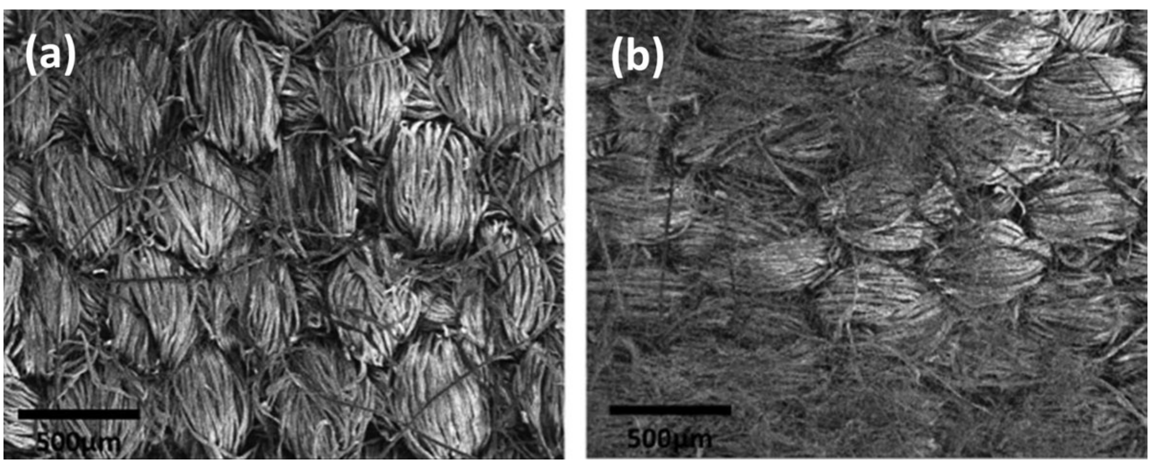

Figure 11. Substrate fabric surface (a) without pretreatment; (b) with pretreatment after peeling test.

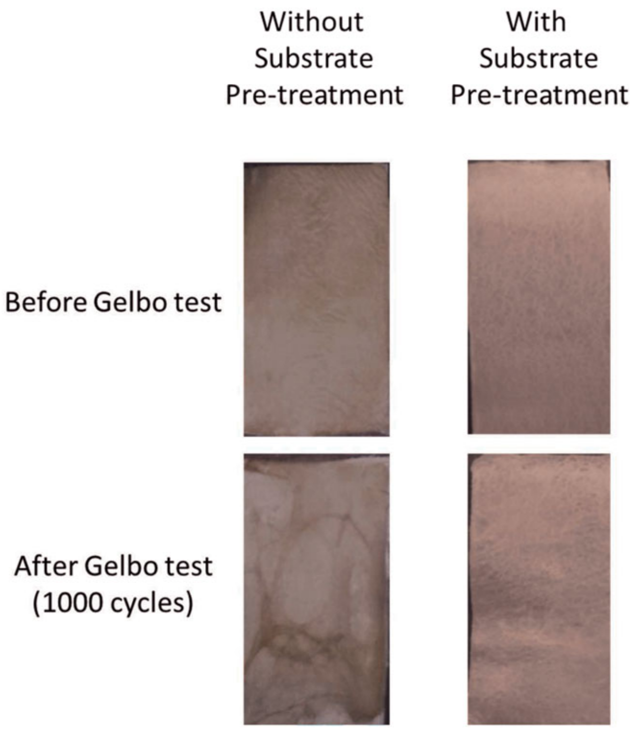

Figure 12. Gelbo Flex test results of Ag/PAN nanofiber-deposited Nylon/cotton fabrics. Nanofiber area density: 1.87 g/m^2.

under repetitive twisting and flexing strains. Figure 12 shows photographs of Ag/PAN nanofiber-deposited Nylon/cotton fabrics after 1000 cycles of Gelbo Flex test. It is observed that without substrate pretreatment, the nanofiber layer is almost completely removed after 1000 testing cycles. With substrate pretreatment, nanofibers prepared with different Ag precursor concentrations do not appear to be significantly damaged after 1000 testing cycles.

Results of peeling and Gelbo Flex tests demonstrate that the pretreatment of substrate fabric by atmospheric plasma can significantly improve the durability of nanofiber layers on the substrate fabrics. This improvement may be mainly attributed to the active species or enhanced roughness on the fabric surface created by the atmospheric plasma, which provides extra bonding between the nanofibers and the fabric surface.

CONCLUSIONS

Multifunctional and durable NFLC material with excellent durability was prepared by depositing Ag/PAN nanofibers onto Nylon/cotton 50 : 50 fabric. The resultant Ag/PAN nanofiber-deposited Nylon/cotton fabrics showed over 99.7% aerosol barrier efficiency by ~1% wt increase. The pressure resistance and MVTR of Ag/PAN nanofiber-deposited Nylon/cotton fabrics did not change significantly after the nanofiber deposition. In addition, Ag/PAN nanofiber-deposited Nylon/cotton fabrics showed good antimicrobial activities against Gram-negative *E. coli* and Gram-positive *S. aureus*. By pretreatment of substrate fabric via atmospheric plasma, the durability of Ag/PAN nanofiber-deposited Nylon/cotton fabrics was also improved significantly. With substrate pretreatment, the Ag/PAN nanofiber-deposited Nylon/cotton fabrics demonstrated the ability to withstand greater peeling, twisting, and flexing forces. Given the high-barrier efficiency, good antimicrobial activity, improved durability, and high-moisture vapor and air permeabilities, the Ag/PAN nanofiber-deposited Nylon/cotton fabric developed in this research is a promising material candidate for protective applications.

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REFERENCES

1. Gopal, R.; Kaur, S.; Ma, Z.; Chan, C.; Ramakrishna, S.; Matsuura, T. *J. Membr. Sci.* **2006,** *281*, 581.
2. Choi, J. S.; Lee, S. J.; Christ, G. J.; Atala, A.; Yoo, J. J. *Biomaterials* **2008,** *29*, 2899.
3. Stasiak, M.; Řben, C.; Rosenberger, N.; Schleth, F.; Studer, A.; Greiner, A.; Wendorff, J. H. *Polymer* **2007,** *48*, 5208.
4. Shi, Q.; Chen, X.; Lu, T.; Jing, X. *Biomaterials* **2008,** *29*, 1118.
5. Thavasi, V.; Singh, G.; Ramakrishna, S. *Energy Environ. Sci.* **2008,** *1*, 205.
6. Sundarrajan, S.; Chandrasekaran, A. R.; Ramakrishna, S. *J. Am. Ceram. Soc.* **2010,** *93*, 20.
7. Ramakrishna, S.; Fujihara, K.; Teo, W. E.; Yong, T.; Ma, Z.; Ramaseshan, R. *Mater. Today* **2006,** *9*, 40.
8. Lee, S.; Obendorf, S. K. *Text. Res. J.* **2007,** *77*, 696.
9. Gibson, P.; Schreuder-Gibson, H.; Rivin, D. *Colloids Surf. A: Physicochem. Eng. Aspects* **2001,** *187*, 469.
10. Vitchuli, N.; Shi, Q.; Nowak, J.; McCord, M.; Bourham, M.; Zhang, X. *J. Appl. Polym. Sci.* **2010,** *116*, 2181.
11. Sumin, L.; Kimura, D.; Lee, K. H.; Park, J. C.; Kim, I. S. *Text. Res. J.* **2010,** *80*, 99.
12. Teo, W. E.; Ramakrishna, S. *Compos. Sci. Technol.* **2009,** *69*, 1804.
13. Ding, B.; Kimura, E.; Sato, T.; Fujita, S.; Shiratori, S. *Polymer* **2004,** *45*, 1895.
14. Heikkil, P.; Sipil, A.; Peltola, M.; Harlin, A.; Taipale, A. *Text. Res. J.* **2007,** *77*, 864.
15. Zhou, F. L.; Gong, R. H.; Porat, I. *Surf. Coat. Technol.* **2010,** *204*, 3459.
16. Kanafchian, M.; Valizadeh, M.; Haghi, A. *Kor. J. Chem. Eng.* **2010,** *28*, 4.
17. Kim, B. S.; Kimura, N.; Kim, H. K.; Watanabe, K.; Kim, I. S. *J. Nanosci. Nanotechnol.* **2011,** *11*, 4929.
18. Denes, F. S.; Manolache, S. *Prog. Polym. Sci.* **2004,** *29*, 815.
19. Deichmann, T.; McCord, M. G.; Bourham, M. A.; Gries, T. *J. Appl. Polym. Sci.* **2011,** *121*, 1875.
20. Wang, Y.; Li, Y.; Sun, G.; Zhang, G.; Liu, H.; Du, J.; Yang, S.; Bai, J.; Yang, Q. *J. Appl. Polym. Sci.* **2007,** *105*, 3618.
21. Cheng, S.; Yuen, C.; Kan, C.; Cheuk, K.; Daoud, W.; Lam, P.; Tsoi, W. *Vacuum* **2010,** *84*, 1466.

22. Kim, K.; Lee, C.; Kim, I.; Kim, J. *Fibers Polym.* **2009,** *10*, 60.
23. Sundarrajan, S.; Venkatesan, A.; Ramakrishna, S. *Macromol. Rapid Commun.* **2009,** *30*, 1769.
24. Ramaseshan, R.; Ramakrishna, S. *J. Am. Ceram. Soc.* **2007,** *90*, 1836.
25. Ji, L.; Medford, A. J.; Zhang, X. *Polymer* **2009,** *50*, 605.
26. Dong, H.; Fey, E.; Gandelman, A.; Jones, W. E., Jr. *Chem. Mater.* **2006,** *18*, 2008.
27. Shi, Q.; Vitchuli, N.; Nowak, J.; Noar, J.; Caldwell, J. M.; Breidt, F.; Bourham, M.; McCord, M.; Zhang, X. J. *Mater. Chem.* **2011,** *21*, 10330.
28. Saquing, C. D.; Manasco, J. L.; Khan, S. A. *Small* **2009,** *5*, 944.
29. Shi, Q.; Vitchuli, N.; Nowak, J.; Caldwell, J. M.; Breidt, F.; Bourham, M.; Zhang, X.; McCord, M. *Eur. Polym. J.* **2011,** *47*, 1402.
30. Matthews, S. R.; McCord, M. G.; Bourham, M. A. *Plasma Process. Polym.* **2005,** *2*, 702.
31. Matthews, S. R.; Hwang, Y. J.; McCord, M. G.; Bourham, M. A. *J. Appl. Polym. Sci.* **2004,** *94*, 2383.
32. Shi, Q.; Vitchuli, N.; Nowak, J.; Lin, Z.; Guo, B.; McCord, M.; Bourham, M.; Zhang, X. *J. Polym. Sci. Part B: Polym. Phys.* **2011,** *49*, 115.