Studies on the Synthesis of Electrospun PAN-Ag Composite Nanofibers for Antibacterial Application

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ABSTRACT: We have successfully synthesized polyacrylonitrile (PAN) nanofibers impregnated with Ag nanoparticles by electrospinning method at room temperature. Briefly, the PAN-Ag composite nanofibers were prepared by electrospinning PAN (10% *w/v*) in dimethyl formamide (DMF) solvent containing silver nitrate ($AgNO_3$) in the amounts of 8% by weight of PAN. The silver ions were reduced into silver particles in three different methods i.e., by refluxing the solution before electrospinning, treating with sodium borohydride ($NaBH_4$), as reducing agent, and heating the prepared composite nanofibers at 160°C. The prepared PAN nanofibers functionalized with Ag nanoparticles were characterized by field emission scanning electron microscopy (FESEM), SEM elemental detection X-ray analysis (SEM-EDAX), transmission electron microscopy (TEM), and ultraviolet-visible spectroscopy (UV-VIS) analytical techniques. UV-VIS spectra analysis showed distinct absorption band at 410 nm, suggesting the formation of Ag nanoparticles. TEM micrographs confirmed homogeneous dispersion of Ag nanoparticles on the surface of PAN nanofibers, and particle diameter was found to be 5–15 nm. It was found that all the three electrospun PAN-Ag composite nanofibers showed strong antibacterial activity toward both gram positive and gram negative bacteria. However, the antibacterial activity of PAN-Ag composite nanofibers membrane prepared by refluxed method was most prominent against *S. aureus* bacteria. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1178–1185, 2012

Key words: electrospinning; composite nanofibers; nanoparticles; antibacterial study

INTRODUCTION

Polymer/inorganic composite nanofiber materials containing metal nanoparticles have attracted a great deal of attention because of their unique optical, electrical, and catalytic properties. The properties of these nanocomposites are strongly dependent on the size, content, dispersivity, and structure of the metal nanoparticles that are incorporated within the polymer matrix.[1] The size and shape-dependent properties of nanocomposites fibers provide a challenge to synthetic chemists for obtaining highly functional advanced materials. Since past several years nanosized metallic particles, especially silver nanoparticles impregnated with polymer matrix have been synthesized successfully by various research groups using various synthetic techniques.[2–4] The polymers can acts as a stabilizer in such system, and its role is to prevent the further growth and aggregation of silver nanoparticles. Silver is particularly attractive among metal nanoparticles because of its significance widespread applications in biology,[5] antimicrobial properties,[6] optical properties, and oxidative catalysis.[7] There are many research literature reported on the synthesis of silver nanoparticles from Ag^+ ions. Few of them are chemical reduction using aqueous solution of sodium borohydride ($NaBH_4$), hydrazinium hydroxide (N_2H_4OH), dimethyl formamide (DMF), photoreduction by UV irradiation, and simple heat treatment. DMF is essentially used as a solvent and is also able to reduce Ag ions to the metallic silver even at room temperature and in the absence of any external reducing agent.[8–10] Recently Lee et al.,[11] have reported an antibacterial activity of silver nanoparticles prepared by chemical reduction of $AgNO_3$ in water with $NaBH_4$ in the presence of SDS as a stabilizer. The prepared silver nanoparticles were spherical in shape having diameters in the range of 10–20 nm and showed good antibacterial activity against *S. aureus* and *E. coli* bacteria. The fundamental mechanism by which silver kills bacteria is by disruption of metabolic processes. Since ancient times, the silver ion has been known to be effective reagent for killing of a broad range of microorganisms.[12,13] Similarly, Lanje et al., has reported on the preparation and antibacterial studies of silver nanoparticle using a simple and low cost chemical route by reducing silver nitrate with glucose in presence of protective

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agent polyvinylpyrrolidone (PVP).[14] The average particle size of prepared silver nanoparticles were about 15 nm, and antimicrobial properties were tested against *S.aureus, E.coli*, and *P.aeruginosa* microorganisms. Different types of polymers such as cellulose acetate, PVA, PAN, PVP, PVC, polyurethane etc, have been used as a stabilizers as well as polymer matrix for *in situ* formation of polymer-silver composite nanofibers.[15,16] Polyacrylonitrile (PAN) is an important engineering polymer material that has been widely used to produce a variety of synthetic fibers[17,18] having a unique thermal property (i.e., melting point = 317°C and glass transition temperature = 85°C) and good solvent resistance. Therefore, PAN-Ag nanocomposites are expected to provide a possibility to produce functional fibers with antielectrostatic, fungicidal, and ultraviolet-resisting effects.[19,20]

Electrospining method was thought to be a simple and user friendly fiber fabrication technique. It uses the electrostatic force to spin fibers from a polymeric solution. Electrospun fibers, however, are often collected in the form of randomly oriented, nonwoven fabrics.[21,22] In the recent years electrospinning has been widely used to produce various polymer nanofibers mats functionalized with inorganic nanoparticles. Bai et al.[23] have synthesized AgCl/PAN composite nanofibers by electrospinning method. The average diameter of the fibers and the number as well as the size of the AgCl particles varies with the change in mole ratio of silver ions to PAN polymer. Most recently Dong et al.,[24] have reported on the preparation of uniform Ag nanoparticle-embedded PVA and PVP nanofibers by electrospinning method. The Ag nanoparticles formed on the polymer matrix were in the range of 5–18 nm. Furthermore, the antibacterial study indicates that these Ag nanoparticle-embedded PVP nanofibers can effectively inhibit the propagation and biological activity of yeast cells. Rujitanaroj et al., have recently reported on preparation, characterization, and antibacterial activity of electrospun PAN fibrous membranes containing silver nanoparticle. Fiber size was found to be in the range of 180–230 nm and silver nanoparticles were in the size range of 5.3–7.8 nm. The authors reported that the antibacterial activity of the membrane against *S.aureus* and *E.coli* bacteria increases with increase in concentration of $AgNO_3$ and UV irradiation time.[25]

In this present study, we have prepared PAN nanofibers containing $AgNO_3$ by using electrospinning method. The reduction of silver ion into silver metallic nanoparticles could be performed by three different techniques such as chemical reduction using $NaBH_4$, heat treatment, and refluxed the PAN/DMF solutions containing $AgNO_3$ at 80°C for 2 h prior to electrospinning. The PAN nanofibers membrane functionalized with Ag nanoparticles (i.e., PAN-Ag nanocomposites) obtained was used to study for antibacterial properties against gram negative *E. coli* and gram positive *S. aureus* and *B. subtilis* bacteria.

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN) polymer (av. mol.wt. = 150,000) were purchased from Sigma-Aldrich Co, USA. *N*,*N*-dimethylformamide (DMF) and silver nitrate ($AgNO_3$, 99%) were obtained from Merck, India. Ethanol was purchased from Merck, Germany. Beef extract was purchased from Rankem, India. Peptone and NaCl were obtained Loba Chimie Ltd. India. Agar was purchased from Himedia Lab Ltd. Mumbai, India. *Escherichia coli* (NCIM 5051), *Bacillus subtilis* (NCIM 2699), and *Staphylococcus aureus* (NCIM 2654) bacterial stain were obtained from NCIM, Pune, India. Neat and clean glass beaker, conical flasks, funnel (Borosil), and disposable petri-dishes were used to carry out the experiments. Double distilled water was used through out the experiments. All the chemicals were used without further purifications.

Fabrication of PAN nanofiber containing silver nanoparticle

Polyacrylonitrile (PAN) polymer solution (12 wt %) was prepared by dissolving required amount of PAN polymer in DMF solvent. The mixture was stirred using a magnetic stirrer for 2–3 h at room temperature to form a clear solution. Then 8 wt % (w. r. t PAN polymer) of $AgNO_3$ was added to PAN/DMF transparent solution and was stirred for another 1 h. The above solution was then divided into two parts. One part of the solution was used directly for electrospinning and was loaded into a 3-mL plastic syringe fitted with a metallic needle. The PAN solution containing silver ion was pushed to the needle tip using the syringe pump and the feed rate was kept at 0.5 mL/h. Then a positive voltage of 12 kV was applied to the needle tip using high voltage power supply (Glassman Japan) and the negative voltage was connected to the grounded collector covered with aluminum foil which served as counter electrode. The tip to collector distance was maintained 15 cm. All the experiments were conducted at room temperature with a relative humidity (50%–55%) condition. Then the as spun PAN nanofibers containing silver ion could be reduced to metallic silver either by heat treatment or by chemical reduction process. A part of as spun PAN/$AgNO_3$ composite membrane was sintered at 160°C for 2 h and the other part of the composite membrane was immersed in the 0.1*M* $NaBH_4$ aqueous solution for 30 min at room temperature. Then the membrane was washed with distilled water and

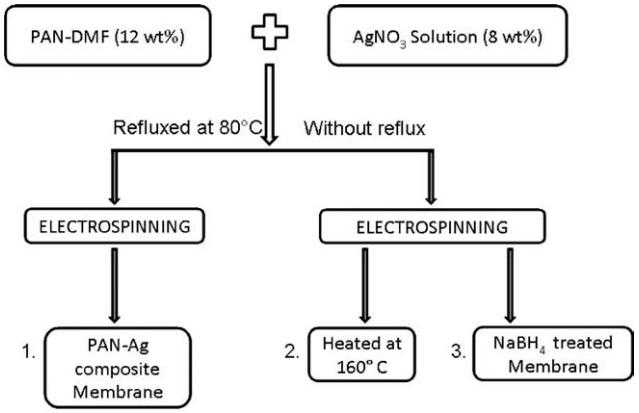

Figure 1 Flow chat of the synthesis of PAN-Ag composite nanofibers via electrospinning methods.

dried in an oven at 60°C for 2 h to obtain the PAN nanofibers containing Ag nanoparticles.

The other part of the PAN/DMF polymer solution was refluxed at 80°C using water bath for 2 h with constant stirring and then used this solution for electrospinning. The previous electrospinning parameters/condition was also maintained same in this case. The PAN nanofibers mats containing Ag nanoparticles in the form of membrane sheet was obtained from the collector and was studied for antibacterial study. Figure 1 shows the flow chart of the preparation of PAN nanofibers functionalized with Ag nanoparticles using electrospinning method.

Characterization

Surface morphology of electrospun PAN-Ag composite nanofibers were characterized by using Carl-Zeiss FESEM (Carl-Zeiss Supra 55) equipped with Oxford INCA energy dispersive X-ray analyzer system and was operated at 10 KV. Energy dispersive X-ray analysis (EDAX) in SEM was also carried out for the elemental composition analysis of the samples. A Philips TEM (CM-200) was used to observe the Ag nanoparticles on the PAN nanofibers and the size of electrospun composite nanofibers. The composite fibers were collected on a carbon coated Cu grid (300 mesh) and was dried under vacuum for few hours before taking the imaging at 200 KV. IR transmittance spectra in the range of 600–4000 cm^{-1} were measured at room temperature using a Fourier-transform IR spectrometer (Thermo Nicolet, AVATAR 360-FT IR). Absorption spectrum was recorded using a Shimadzu UV-VIS Spectrophotometer (UV-2045).

Antimicrobial tests

The antimicrobial activity of PAN-Ag electrospun nanofibers membrane was analyzed by zone inhibition test for which the bactericidal experiment was carried out with gram negative bacteria *Escheria coli* and gram positive bacteria *Bacillus subtilis* and *Staphylococcus aureus.* From stock culture obtained from NCIM, PUNE, the microbes were inoculated in 200 mL nutrient media composed of peptone (10 g/L), NaCl (5 g/L), and beef extract (10 g/L) with the pH maintained at 7–7.5 in three separate flasks and were incubated for whole night at 37°C. Throughout this study, the same nutrient media was used for all strains, unless otherwise specified.

For zone inhibition test, next day, the nutrient agar was prepared with the above-mentioned constituents along with solidifying agent agar (20% *w/v*) followed by sterilization and then pouring into the sterilized disposable petri dishes. The petri plates were kept for solidification. Then from each (flask) bacterial suspension 100 μL volumes were removed and spread uniformly over the agar plates. Small circular pieces of (fixed weight) PAN-Ag composite ultra-fine fiber membranes (test samples) prepared by three different reduction methods were gently placed over the solidified agar gel in different petri dishes. Since there was high chance of discoloration of the membrane disc after zone inhibition test, the petri dishes bearing different groups of sample were properly marked for their identification. Then the petri plates were kept for incubation at 37°C for whole night. Next day the clear zones surrounding the disc were measured with the help of scale, which depicts the zone of inhibition for that particular bacterium.

RESULTS AND DISCUSSION

The entire synthetic procedure of PAN-Ag composite nanofibers using electrospinning mediated synthesis is illustrated in Figure 1. The Ag^+ ions present in PAN/Ag^+ as-spun composite nanofiber membrane can be reduced to Ag metallic nanoparticles by three different ways i.e., $NaBH_4$ treated, refluxed with DMF, and heat treatment. The mechanism involving the reduction of Ag^+ ions to silver particles in these cases are represented as below.

$$Ag^+ + BH_4^- \rightarrow Ag^0 + \frac{1}{2} + H_2 + \frac{1}{2}B_2H_6 \quad (NaBH_4 \text{ as reducing agent})$$

$$HCONMe_2 + 2\,Ag^+ + H_2O \rightarrow 2\,Ag^0 + Me_2NCOOH + H^+ \{\text{DMF as reducing agent}\}$$

$$Me_2NCOOH \rightarrow Me_2NH + CO_2 \uparrow$$

$$2AgNO_3 \xrightarrow{\Delta} 2Ag^0 + O_2 \uparrow + 2NO_2 \uparrow \quad (\text{heat treatment})$$

DMF has been used as a solvent for electrospinning PAN polymer and besides it can also act as a self reducing agent for reduction of Ag^+ ions.[10,25]

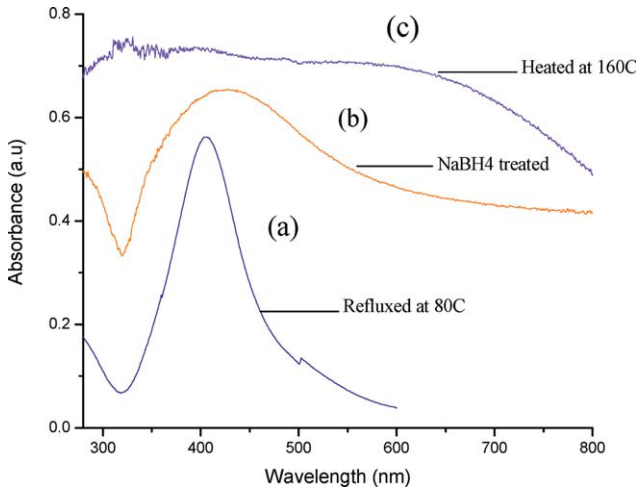

Figure 2 UV-Vis spectra of PAN-Ag nanocomposites prepared by (a) refluxed method, (b) $NaBH_4$ reduction method, and (c) heat treatment method. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

We have refluxed the PAN and $AgNO_3$ solution in DMF solvent to increase the reaction rate. The formation of a yellow-brown color solution after refluxing confirmed the reduction of Ag^+ ion to silver nanoparticles. Figure 2 shows the UV-Vis spectra of PAN-Ag nanocomposites prepared by three reduction methods. Figure 2(a) represents Ag functionalized PAN polymer prepared by refluxing PAN-$AgNO_3$ (8 wt %) solution in DMF solvent at 80°C. The surface plasmon absorption band of Ag nanoparticles with size ranges between 2 and 50 nm would be basically observed in the UV-Vis spectrum at a wavelength in the range of 400–450 nm.[10,11,15] We have observed an absorption maximum peak at 405 nm [Fig. 2(a)], which indicates the formation of Ag nanoparticles. We have electrospun this PAN solution containing Ag nanoparticles to obtain the silver nanoparticles embedded on and within PAN nanofibers membrane. Similarly to obtain silver nanoparticles impregnated PAN nanofibers membrane, the Ag^+ ions present in the electrospun PAN nanofiber membrane were reduced to silver nanoparticles using sodium borohydride [Fig. 2(b)] and heat treatment [Fig. 2(c)] technique. The surface plasmon absorption band between 400–450 nm in the UV-Vis spectra confirmed the formation of Ag nanoparticles. These silver nanoparticles functionalized PAN nanofibers membrane has been used for antimicrobial applications.

Figure 3 shows the SEM images of PAN-Ag composite membrane synthesized by sodium borohydride reduction method. It is observed from the images [Fig. 3(a,b)] that the obtained fibers are tubular in shape and have a smooth morphology. However, the

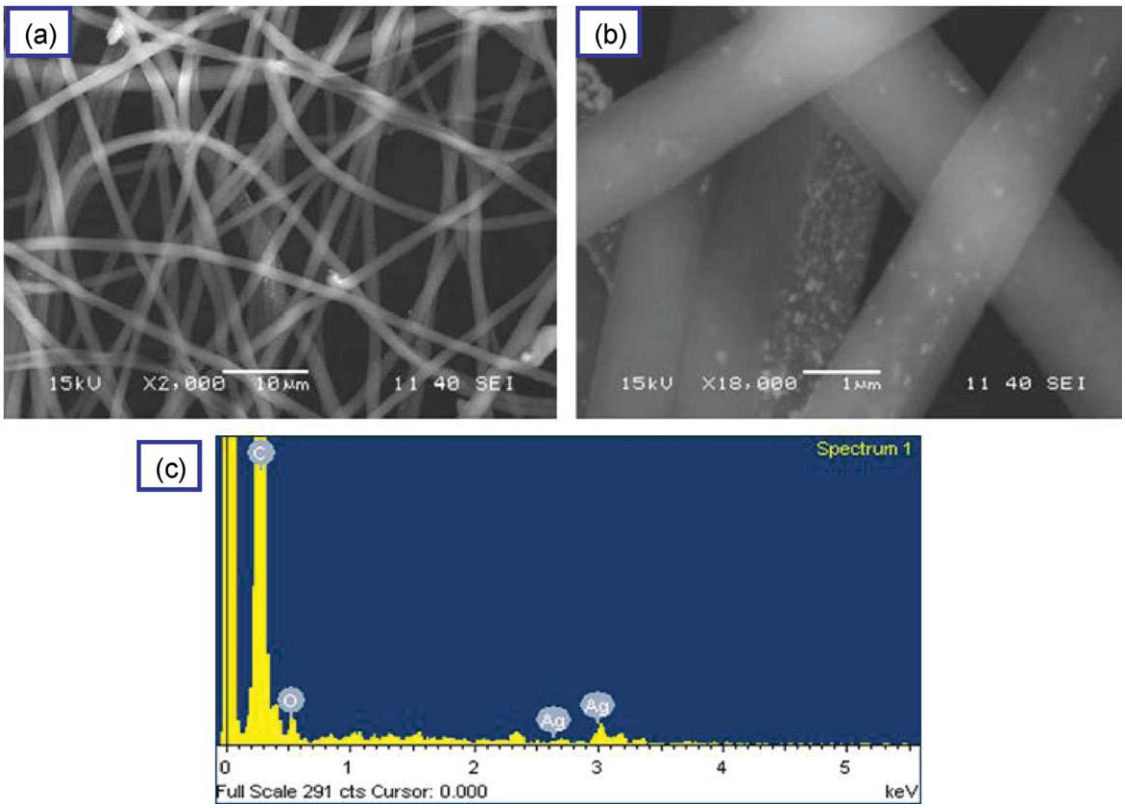

Figure 3 SEM images of PAN-Ag nanofibers prepared by $NaBH_4$ reduction method; (a) low magnification, (b) higher magnification images, and (c) EDAX spectrum. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

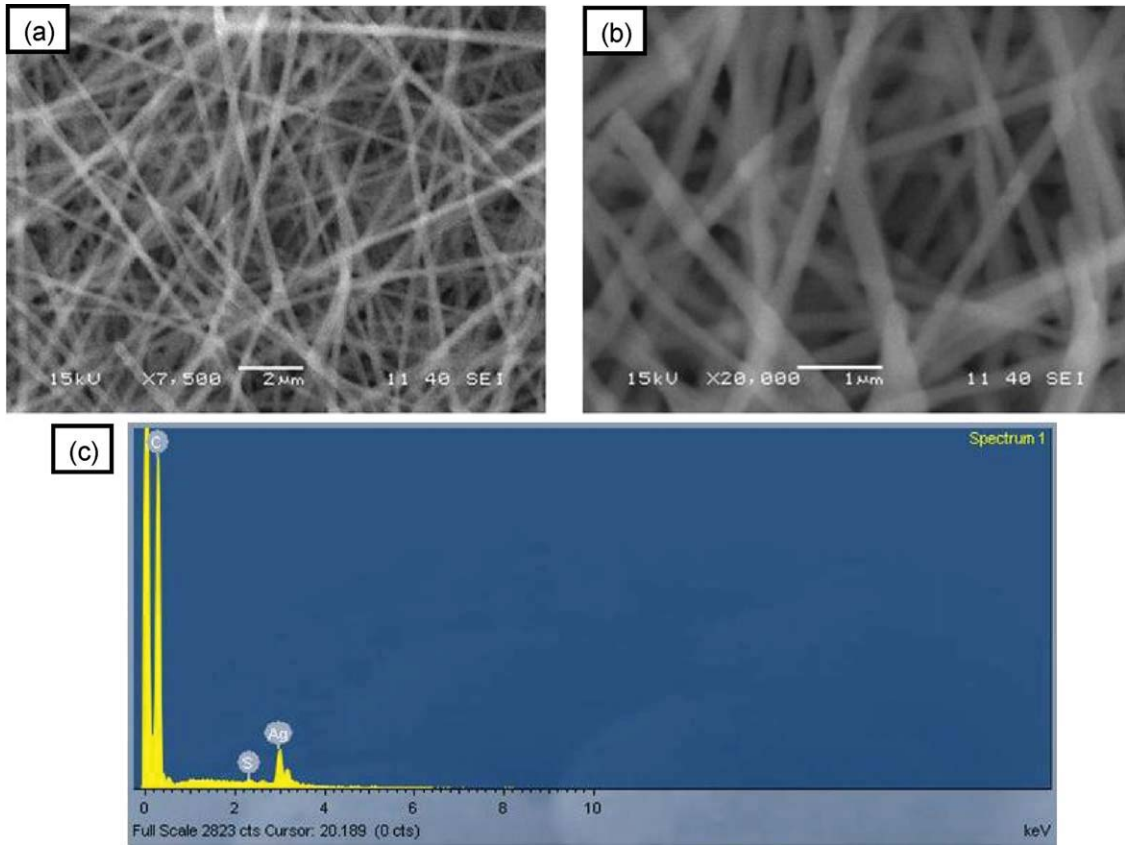

Figure 4 SEM micrographs of PAN-Ag composite nanofibers prepared by refluxed method; (a, b) different magnification and (c) EDAX spectrum. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

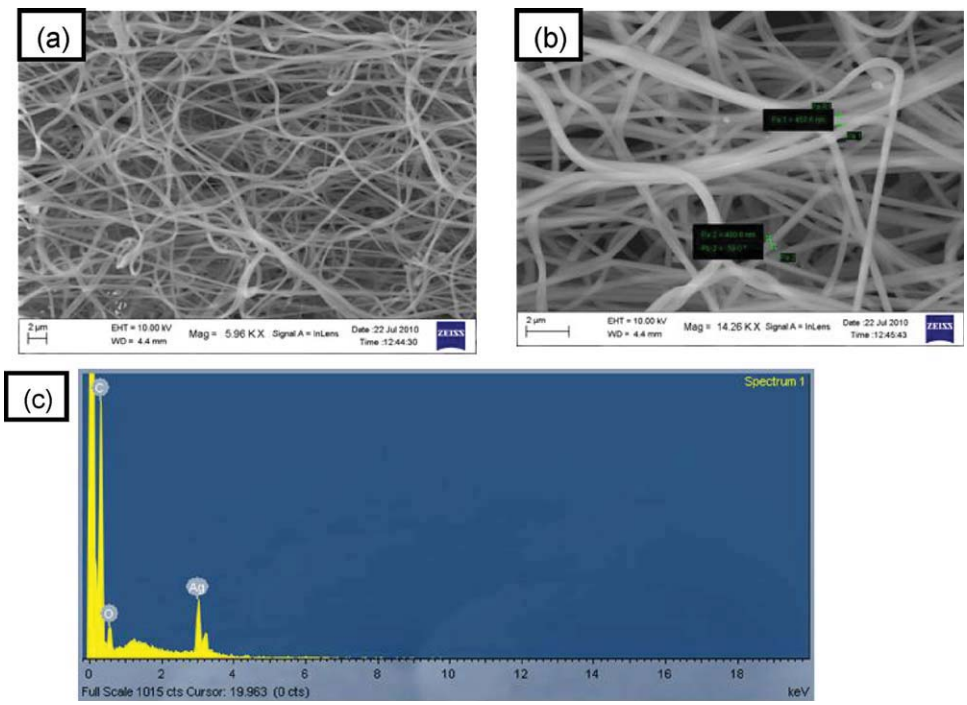

Figure 5 SEM Images of PAN-Ag composite nanofibers prepared by heat treatment method; (a, b) different magnification and (c) EDAX spectrum. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

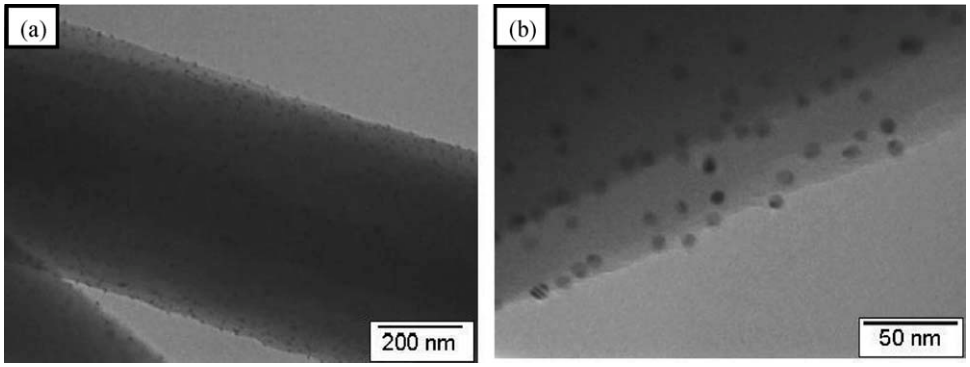

Figure 6 TEM micrographs of PAN-Ag composite nanofibers prepared by refluxed method; (a, b) different magnification images.

magnified SEM image [Fig. 3(b)] indicates the presence of some aggregated form of the Ag particles on and within the PAN fibers. The sizes of the fibers are found to be in the range of 500 nm to 1 μm. To evaluate the chemical composition of the samples, we have carried out the SEM EDAX analysis of the PAN-Ag composite fibers. Figure 3(c) shows the EDAX pattern of the PAN-Ag composite nanofibers prepared by borohydride reduction method. The elemental compositions of the composite fibers were found to be 78.31% of carbon, 12.44% of oxygen, and 8.25% of Ag, which confirm the formation of PAN-Ag composite fibers.

Figure 4 provides the SEM images of the PAN-Ag composite membrane synthesized by refluxing with DMF solvent. This image indicates that the fibers are cylindrical shape and have smooth morphology. In this case the fibers obtained are in the range of 200–500 nm in diameter, which is much smaller than that of borohydride reduction method. This might be because of the *in situ* formation of Ag nanoparticles and presence of $AgNO_3$ in PAN solution that the conductance of the system increases and hence smaller size fibers can be obtained.[16] As the Ag particles are below 50 nm we haven't observed any Ag nanoparticles in the magnified SEM images. From the chemical analysis EDAX data [Fig. 4(c)], we found that the wt % of carbon is 90.64 and of Ag is 9.04%, with little impurities of S (0.32%) that confirm the formation of PAN-Ag composites. Similarly, Figure 5 indicates the SEM images of the PAN-Ag composite membranes obtained by heating of the PAN/$AgNO_3$ composite membrane above 160°C. These images also suggest the formation of continuous ultrafine fibers having diameter in the range of 200–500 nm. The SEM-EDAX spectra [Fig. 5(c)] suggest the presence of C, Ag, and O atoms, indicating the formation of Ag/Ag_2O nanoparticles on the surface of PAN fibers.

Figure 6 represents the TEM images of the PAN-Ag composite nanofibers prepared by refluxing $AgNO_3$ in DMF/PAN solution at 80°C. It is observed that uniform, spherical Ag nanoparticles with a narrow size distribution having diameter in the range of 7–10 nm are formed on and within the fibers. However, the diameters of the PAN fibers are found to be 400 nm, which is consistent with the results obtained from SEM. Figure 7 shows the TEM micrographs of the PAN-Ag composite membrane prepared by $NaBH_4$ reduction method. In this case also spherical Ag nanoparticles are formed on and within the fiber surface, but they polydisperse in nature. The size of the Ag nanoparticles as measured from the TEM micrographs is found to be in the range of 5–20 nm.

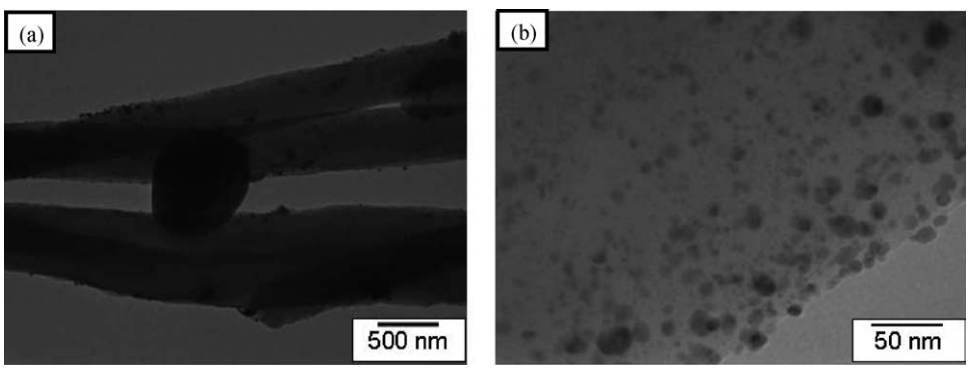

Figure 7 TEM micrographs of PAN-Ag composite nanofibers, prepared by $NaBH_4$ reduction; (a, b) different magnification images.

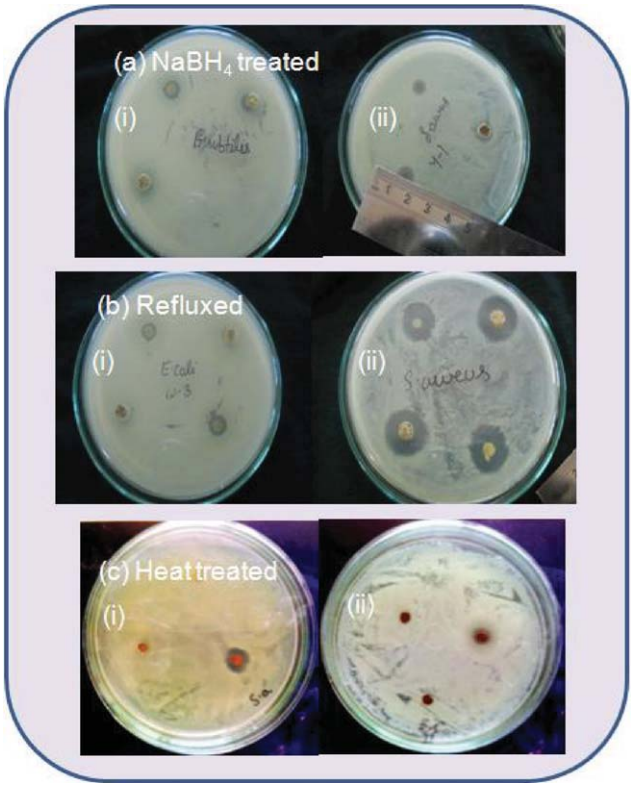

Figure 8 Photographs showing zone of inhibition of the PAN-Ag composite nanofibers membrane prepared by (a) $NaBH_4$ reduction method against (i) *B. subtilis* (ii) *S. aureus;* (b) refluxed method against (i) *E. coli* (ii) *S. aureus*, and (c).heat treatment method against (i) *S. aureus* and (ii) *B. subtilis* bacteria. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

Antibacterial activity

The antibacterial activity of PAN nanofibers membrane functionalized with the Ag nanoparticles was assessed against bacterial strain *S. aureus, E. coli, and B. subtilis*. The length of the inhibition zones of the composite fibers mats were analyzed and are shown in the Figure 8. It is reported that electrospun pure PAN nanofibers mats shows nonbacterial properties against *S. aureus* and *E coli* bacterial, and hence inhibition zone is absent in case of PAN fibers mats.[15] However, the Ag nanoparticles loaded polymer fibers show strong bactericidal properties.[15,25] We have used all three different types of PAN nanofibers mat functionalized with Ag nanoparticles (containing 8 wt % of $AgNO_3$ w. r. t. to PAN) for the antibacterial test against the above three mentioned bacterial strain. The length of inhibition zone against the three bacteria is reported in Table I. It is observed from the table that all the three different PAN-Ag composite nanofibers mats prepared by different reduction methods show good antibacterial properties. However, the length of inhibition zone is found to be highest against S. aureus bacteria for the PAN-Ag composite membrane that was prepared by refluxing Ag^+ ions in DMF solvent in the presence of PAN polymer prior to electrospinning. This data showed a very good antibacterial property. This result can be interpreted as in case of PAN-Ag composite fibers prepared by refluxed method where the silver ion present on the surface as well as inside PAN polymer solution get reduced *in situ* to Ag nanoparticles. The rate of formation of Ag particles is also increases because of refluxing in DMF solvents. However, DMF solvent can also acts as a reducing agent for Ag^+ ions to form Ag nanoparticles, but the rate of reduction is very slow and takes several days for complete reduction of silver ions into silver nanoparticles.[25] Since the Ag nanoparticles dispersed PAN matrix has been electrospun to form PAN-Ag nanocomposites in this refluxed method, there is a greater probability of formation of uniform Ag nanoparticles on and within the surface of the fibers. The nanoparticles formed were also smaller in size (i.e., 7–10 nm) as compared to other two reduction methods. As a result, these nanofiber mats show better antibacterial properties. However, for PAN-Ag composite membrane prepared by $NaBH_4$ and heat treatment method, the Ag nanoparticles formed were comparatively larger in size and perhaps more in numbers embedded inside the polymer matrix and hence less exposure to bacterial cell. Similarly in case of heat treatment nanofiber mat, there might be presence of mixture of Ag and Ag_2O nanoparticles on and inside the fiber surface. Although all the three PAN-Ag composite nanofibers membrane show good antibacterial properties, the composite fibers membrane prepared by refluxed method is best for killing the *S.aureus* microorganism.

CONCLUSIONS

$PAN/AgNO_3$ composite nanofibers containing 8 wt % of $AgNO_3$ with respect to PAN have been prepared by electrospinning method. The reduction of Ag^+ ions on and inside the fiber surface leads to form PAN-Ag composite ultrafine fibers. We have performed three different methods such as refluxing

TABLE I
Antibacterial Activities of PAN-Ag Composite Fibers Prepared by Different Synthetic Strategies

		Zone of inhibition in mm		
Sl. No	Microorganisms	Reduction using $NaBH_4$	Heated at 160°C	Refluxed at 80°C
1	*Bacillus subtilis*	7.5	6	10
2	*Staphylococcus aureus*	9	10	20
3	*Escherichia coli*	Not recognisible	6	9

in DMF prior to electrospinning, using $NaBH_4$ as reducing agent, and on heating at higher temperature (160°C) to prepare PAN-Ag composite membrane. The obtained PAN-Ag composite nanofibers were characterized by UV-VIS, SEM, EDAX, and TEM analytical techniques. UV-VIS spectra confirmed the formation of Ag nanoparticles. SEM micrographs show that the fibers have a smooth morphology and having diameter in the range of 200–500 nm for refluxed and heat treated fibers. However, an increase in fiber diameter was observed for PAN-Ag composite membrane prepared by borohydride reduction method. The antibacterial activity of PAN-Ag composite nanofibers prepared by all three methods has been studied against three microorganisms such as *S. aureus, E coli, and S. Bacillus*. All the three PAN-Ag composite fibers membrane shows good antibacterial properties. However, the PAN-Ag composite nanofibers membrane prepared by refluxed method is most potential composite membrane for antibacterial properties against *S.aureus* bacteria. This result might be because of a formation of more percentage of Ag nanoparticles on the fibers surface and perhaps because of smaller particle size as compared to nanocomposite fibers prepared by heat treatment and borohydride reduction method.

References

1. Son, W. K.; Youk, J. H.; Park, W. H. Carbohydr Polym 2006, 65, 430.
2. Bai, J.; Li, Y.; Li, M.; Yang, Q. Appl Surf Sci 2008, 254, 4520.
3. Rujitanaroj, P.; Pimpha, N.; Supaphol, P. Polymer 2008, 49, 4723.
4. Francis, L.; Giunco, F.; Balakrishnan, A.; Marsano, E. Curr Appl Phys 2010, 10, 1005.
5. Chen, J.; Saeki, F.; Wiley, B. J.; Au, L.; Li, X .D.; Xia, Y. Nano Lett 2005, 5, 473.
6. Kim, J. S.; Kuk, E.; Yu, K. N.; Lee, H. J.; Jeong, D. H.; Cho, M. H. Nanomedicine 2007, 3, 95.
7. Shirashi, Y.; Toshima, N. Colloid Surf A 2000, 169, 59.
8. Navaladian, S.; Viswanathan, B.; Viswanath, R. P.; Varadarajan, T. K. Nanoscale Res Lett 2007, 2, 44.
9. Santos, I. P.; Rodriguez, C. S.; Liz-Marzan, L. M. J Colloid Interf Sci 2000, 221, 236.
10. Lee, H. K.; Jeong, E. H.; Baek, C. K.; Youk, J. H. Mater Lett 2005, 59, 2977.
11. Lee, S. M.; Song, K. C.; Lee, B.S. Korean J Chem Eng 2010, 27, 688.
12. Das, M. R.; Sarma, R. K.; Saikia, R.; Kale, V. S.; Shelke, M. V.; Sengupta, P. Colloid Surf B 2011, 83, 16.
13. Silver, S.; Phung, L. T. Annu Rev Microbiol 1996, 50, 753.
14. Lanje, A. S.; Sharma, S. J.; Pode, R. B. J Chem Pharm Res 2010, 2, 478.
15. Lala, N. L.; Ramaseshan, R.; Bojun, L.; Sundarajan, S.; Bharate, R. S.; Ying-Jun, L.; Ramakrishna, S. Biotechnology and Bioengineering 2007, 97, 1357.
16. Jin, W. J.; Jeon, H. J.; Kim, J. H.; Youk, J. H. Syntheic Metals 2007, 157, 454.
17. Lee, H. K.; Jeong, E. H.; Baek, C. K.; Youk, J. H. Mater Lett 2005, 59, 3046.
18. Lee, D. Y.; Cho, J.; Kim, Y.; Oh, Y. J Korean Sens Soc, 2008, 17, 281.
19. Feng, Q. L.; Cui, F. Z. J. W.; Kin, J. J Mater Sci Lett 1994, 64, 1159.
20. Sichani, G. N.; Morshed, M.; Amirnasr, M.; Abedi, D. J Appl Polym Sci 2010, 116, 1021.
21. Saquing, C. D.; Manasco, J. L.; Khan, S. A. Small, 2009, 5, 944.
22. Zhang, W. X.; Wang, Y. Z.; Sun, C. F. J Polym Res 2007, 14, 467.
23. Bai, J.; Yang, Q.; Chen, X. Nanotechnology 2007, 18, 305601.
24. Dong, G.; Xiao, X.; Qiu, J. Nanopart Res 2010, 12, 1319.
25. Rujitanaroj, P.; Pimpha, N.; Supaphol, P. J Appl Polym Sci. 2010, 116, 1967.