Radical Graft Polymerization of an Allyl Monomer onto Hydrophilic Polymers and Their Antibacterial Nanofibrous Membranes

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ABSTRACT: Hydrophilic poly (vinyl alcohol-*co*-ethylene) (PVA-*co*-PE) copolymers with 27 mol %, 32 mol % and 44 mol % ethylene were functionalized by melt radical graft copolymerization with 2,4-diamino-6-diallylamino-1,3,5-triazine (NDAM) using reactive extrusion. This functionalization imparts antibacterial properties. The covalent attachments of the NDAM as side chains onto the PVA-*co*-PE polymer backbones were confirmed. The effects of initiator concentrations and ethylene contents in PVA-*co*-PE polymers on grafting of NDAM were studied. The chain scissions of PVA-*co*-PE polymers during reactive extrusion were investigated by monitoring changes in the melt torque and FTIR spectra. The NDAM grafted PVA-*co*-PE polymers were successfully fabricated into hydrophilic nanofibers and nanofibrous membranes with sufficient surface exposure of the grafted NDAM. The hydrophilicity of the PVA-*co*-PE polymers and the large specific surface area offered by the nanofiber membranes significantly facilitated the chlorine activation process, enhanced the active chlorine contents of the grafted PVA-*co*-PE nanofiber membranes, and therefore led to their superior antibacterial properties.

KEYWORDS: radical graft polymerization, hydrophilic polymers, antibacterial nanofibrous membranes
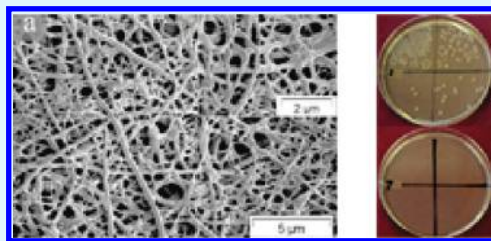
1. INTRODUCTION

The public health and safety concerns of emerging respiratory diseases such as influenza and severe acute respiratory syndrome (SARS), drug-resistant microorganisms in hospitals and public communities, as well as water-borne pathogens, have stimulated considerable research activities on development of antimicrobial polymers and medical products.[1,2] Many efforts in the past decades have been made to impart antibacterial properties to polymers by adding organic or inorganic biocides, copolymerizing monomers containing antimicrobial moieties, or grafting antimicrobial agents onto polymer chains.[1,3−10]

Polyolefin materials are widely used in medical devices, protective clothing, filtration media, food packaging, and hygienic products, where antimicrobial functions are highly desired. Because of the outstanding chemical stability, surface chemical modifications of polyolefin materials are relatively difficult to conduct. Surface coating of antimicrobial agents onto surfaces or blending them into polymers is the common practice to achieve certain functions, however, with limited durability and applications. In addition, once the antimicrobial agents are completely consumed, the antimicrobial property cannot be recharged any more.[11−13] To solve above problems, cyclic N-halamines showing superior and refreshable antimicrobial properties against a broad spectrum of pathogenic microorganisms were selected.[1,10] A melt free-radical graft polymerization of cyclic N-halamine precursors onto olefin polymer backbones using reactive extrusion was developed by our group.[2,14,15] Chlorination of the resulting polymers in dilute bleach converted the halamine

precursor structures to antimicrobial moieties. Hydrophobic polypropylene (PP) and polyethylene (PE) grafted with the N-halamine precursors were processed into fibers. It was found that the antimicrobial performance of extruded N-halamines grafted PP and PE fibers had strong dependence on the hydrophilic—hydrophobic natures and sizes of the polymer fibers.[2,14,15]

The graft polymerization of cyclic N-halamine onto hydrophilic polymers, therefore, is worth further investigation. Poly (vinyl alcohol-*co*-ethylene) (PVA-*co*-PE), a hydrophilic thermoplastic copolymer of ethylene and vinyl alcohol with high resistance to chemicals such as organic solvents, would be an ideal candidate for the study. In addition, the grafted PVA-*co*-PE polymers with antimicrobial properties may find applications for protective clothing and water filtration media when they are processed into film or fiber forms. Moreover, nanofibers can offer greater specific surface areas when they are developed into nanofibrous membranes. The increased surface area of polymer nanofibrous membranes can enhance the exposure of the active sites for antimicrobial functionalization on the fibers, leading to improved antimicrobial properties.[16−24] A high throughput process was recently developed to produce nanoscale thermoplastic fibers and this process can be used to produce the antimicrobial PVA-*co*-PE nanofibrous membranes.[25,26]
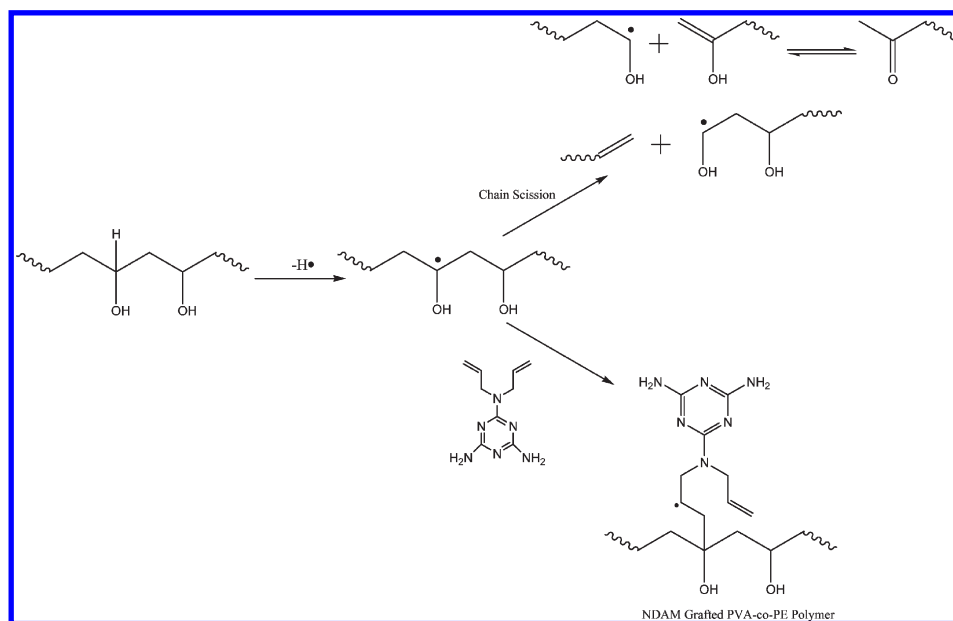
In this article, an N-halamine precursor, 2,4-diamino-6-diallylamino-1,3,5-triazine (NDAM) was successfully grafted onto

Scheme 1. Proposed Major Reactions of PVA-*co*-PE with NDAM in Reactive Extrusion Process

hydrophilic PVA-*co*-PE polymers with ethylene contents of 27, 32, and 44 mol % using a melt reactive extrusion process. The NDAM-grafted PVA-*co*-PE polymers were then fabricated into nanofibers and then nanofibrous membranes. The morphology and surface chemical structures of NDAM-grafted PVA-*co*-PE nanofibrous membranes were characterized. The chlorination of NDAM-grafted PVA-*co*-PE nanofibrous membranes in dilute bleach converted the NDAM precursor into biocidal halamine derivatives. The antimicrobial properties of chlorinated nanofibrous membranes were investigated against *Escherichia coli* (*E. coli*).

2. EXPERIMENTAL SECTION

Materials. Poly (vinyl alcohol-*co*-ethylene) (PVA-*co*-PE, ethylene contents 27, 32, and 44 mol %), and dicumyl peroxide (DCP) were purchased from Sigma-Aldrich (Milwaukee, WI). 2,4-Diamino-6-diallylamino-1,3,5-triazine (NDAM) was used as an N-halamine precursor, and was obtained from TCI (Portland, OR). Cellulose acetate butyrate (CAB; butyryl content 35−39%) was purchased from the Eastman Chemical (Kingsport, TN).

Preparation of NDAM-Grafted PVA-*co*-PE Polymers. The functionalization of PVA-*co*-PE polymers was performed with a Leistritz corotating twin-screw (18 mm) extruder (Model MIC 18/GL 30D, Nurnberg, Germany) at a feed rate of 12 g/min. Barrel temperature profiles were 120, 150, 185, 195, 205, and 210 °C. The extrudates were pelletized. The initiator concentration of DCP was 4, 8, and 12 mpm (moles per million grams of PVA-*co*-PE polymers). The concentration of NDAM was fixed at 450 mpm. To remove the unreacted monomer and homopolymers, the NDAM grafted PVA-*co*-PE pellets were dissolved in a hot solvent mixture of ethanol and water. Acetone was then added to the solution and the NDAM grafted PVA-*co*-PE precipitated in powder form. The precipitated PVA-*co*-PE powders grafted with NDAM were rinsed with acetone several times and dried until constant weight.

Preparation of Nanofiber and Nanofibrous Membranes. The NDAM grafted PVA-*co*-PE nanofibers were prepared according to a previously published procedure.[25] Typically, mixtures of cellulose acetate butyrate (CAB)/NDAM-grafted PVA-*co*-PE powders with a blend ratio of 80/20 were gravimetrically fed into a Leistritz corotating twin-screw (18 mm) extruder (Model MIC 18/GL 30D, Nurnberg, Germany) at a feed rate of 12 g/min. Barrel temperature profiles were 150, 175, 190, 220, 235, and 240 °C. The blends were extruded and hot-drawn by a take-up device with a draw ratio of 25 (the area of cross section of the die to that of the extrudates) and cooled to room temperature. The NDAM grafted PVA-*co*-PE nanofibers in form of continuous yarns were prepared by the extraction of CAB/NDAM grafted PVA-*co*-PE composite fibers for 24 h with acetone to remove the CAB matrix. The technique of preparing PVA-*co*-PE nanofibrous membranes was reported elsewhere.[26] The typical procedure was that PVA-*co*-PE nanofibers were dispersed in an aqueous solution with a high speed shear mixer to form a stable suspension. The suspension was then coated on the surfaces of PP nonwoven substrates with a casting knife to form nanofibrous membranes.

Characterization. A torque rheometer (ATR Plasti-Corder, C. W. Brabender, USA) was used to monitor the melt flow behavior during reactive melt mixing. PVA-*co*-PE containing 27 mol % ethylene content, 4 mpm initiator DCP and 450 mpm NDAM were melt blended at 210 °C at a screw speed of 100 rpm for 5 min under nitrogen. The change in torque values of the sample was recorded. The same procedures were repeated for PVA-*co*-PE containing 32 mol % and 44 mol % ethylene.

The chemical structures of NDAM grafted PVA-*co*-PE polymers and nanofibrous membranes were characterized by Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) and FTIR spectrophotometer (Thermo, USA).

Nitrogen contents in the polymers were determined by analyzing ^{15}N of the purified products with an Europa Scientific Integra, continuous flow isotope ratio mass spectrometer (IRMS) integrated with online combustion.

The morphologies of fabricated NDAM grafted PVA-*co*-PE nanofibrous membranes were examined using a FEI XL-30 SFEG Scanning Electron Microscope (SEM).

Chlorination of NDAM-Grafted PVA-*co*-PE Nanofibrous Membranes. To transform the grafted precursor structures to N-halamine derivatives, the NDAM grafted PVA-*co*-PE nanofibrous membranes were immersed in dilute chlorine bleach (ca. 1500 ppm available chlorine) for 60 min at room temperature. The membranes were then
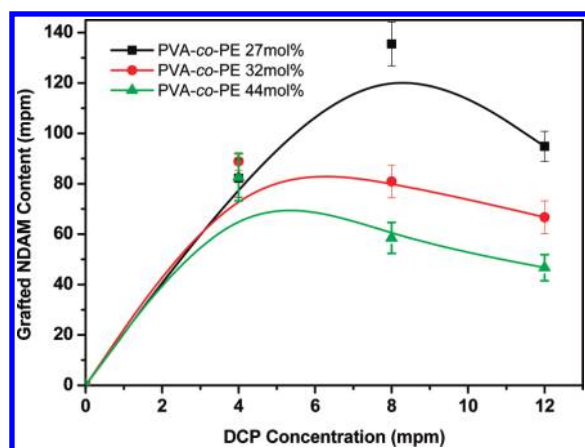
Figure 1. Influence of DCP initiator concentration and ethylene content of PVA-*co*-PE on grafting content of NDAM, [NDAM] = 450 mpm (moles per million grams of PVA-*co*-PE polymer).

washed thoroughly with excess amounts of distilled water until the starch/sodium iodine testing solution remained colorless. The available active chlorine contents of the NDAM grafted PVA-*co*-PE nanofibrous membranes were quantified according to a previously reported iodometric titration method.[15]

Antibacterial Assessment. The antibacterial properties of the chlorinated NDAM grafted PVA-*co*-PE nanofibrous membranes were examined against *Escherichia coli* (*E. coli*) (K-12, a Gram-negative bacterium), according to a modified AATCC test method 100−1999. The concentration of the starting culture was 3×10^5 CFU/ml, which was measured by the UV−vis spectrophotometer at the wavelength of 600 nm. Unmodified PVA-*co*-PE nanofibrous membranes were used as a control. Two swatches of the control or the NDAM grafted PVA-*co*-PE nanofibrous membranes were placed in a sterilized container. One milliliter of *E. coli* suspension was dropped onto the surfaces of the nanofiber membranes. After a contact time of 30 s or 10 min, the inoculated controls or the NDAM-grafted PVA-*co*-PE nanofibrous membranes were placed into 100 mL of distilled water. The mixture was vigorously shaken for 1 min. Then 100 μL of microbial suspension was removed from the container and diluted to 10, 1×10^2, and 1×10^3 times in sequence. Finally, 100 μL of the microbial suspension and the three diluted solutions were placed onto four zones of a nutrient agar plate and incubated at 37 °C for 18 h. The reduction of bacteria was calculated according to the following equation:

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

where A and B are viable cells (colony forming unit mL^{-1}) on the agar plates corresponding to the control and NDAM grafted PVA-*co*-PE nanofibrous membranes, respectively.

3. RESULTS AND DISCUSSION

Melt Radical Grafting of NDAM onto PVA-*co*-PE Polymers. During melt graft polymerization, the peroxide initiator, DCP, generates two alkoxy radicals upon heating to its decomposition temperature. The alkoxy radicals abstracted hydrogen atoms from the backbone of PVA-*co*-PE polymer, leading to the formation of the macromolecular radicals of PVA-*co*-PE. The macromolecular radicals could initialize the grafting polymerization of the functional monomer of NDAM onto the backbones to form desired modified polymers or could undergo polymer chain session to produce lower molecular weight polymers, as shown in
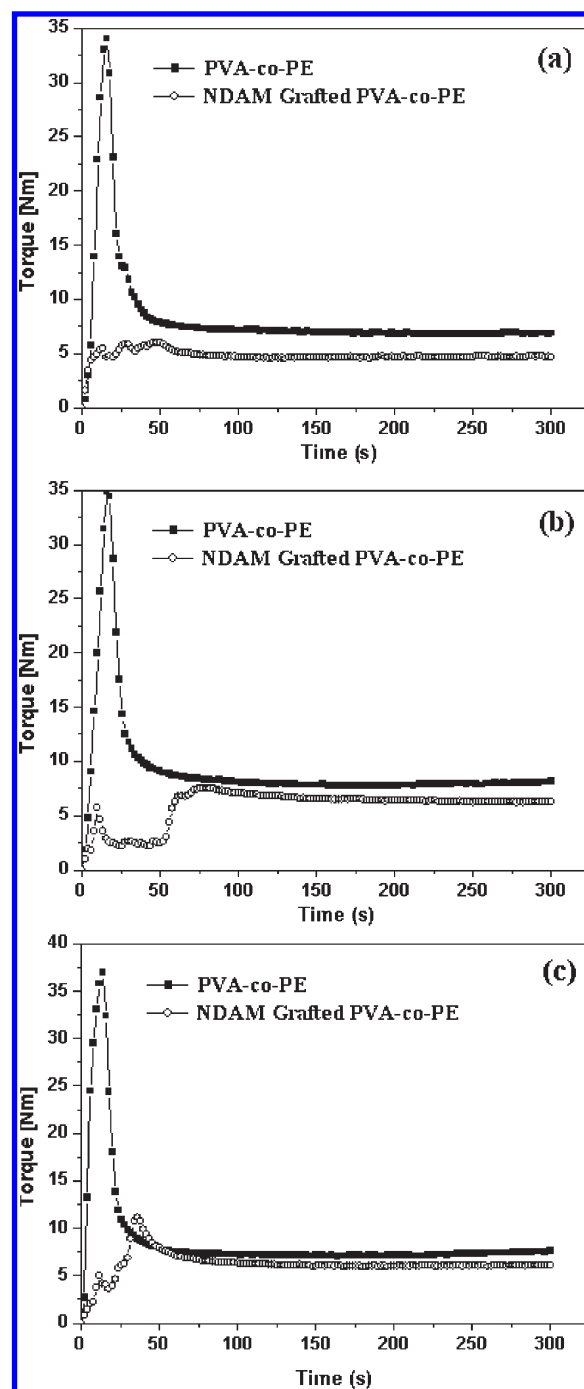

Figure 2. Torque evolution of PVA-*co*-PE polymers during the NDAM graft polymerization process: (a) ethylene 27 mol %, (b) ethylene 32 mol %, and (c) ethylene 44 mol %.

Scheme 1. Another potential side reaction during the process is homopolymerization of the monomer to form poly (2,4-diamino-6-diallylamino-1,3,5-triazine). Typically, the undesired polymer chain scission and homopolymerization of the monomer often occurred during the reactive extrusion process, leading to low molecular weight and mechanical properties of the grafted polymers, as well as low grafting yields of the monomer.[2,14] However, the chemical structures of polymer, monomer and initiator have significant influence on the grafting efficiency and the occurrence of chain scissions.[2,14] To minimize the
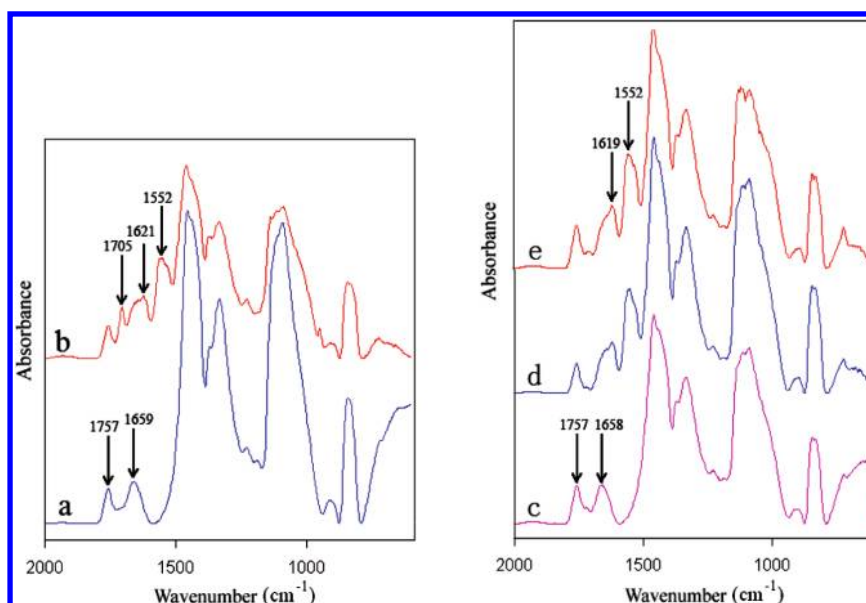
Figure 3. FTIR spectra of (a) virgin PVA-*co*-PE polymer containing 27 mol % ethylene, (b) NDAM-grafted PVA-*co*-PE polymer containing 27 mol % ethylene, (c) virgin PVA-*co*-PE polymer containing 32 mol % ethylene, (d) NDAM-grafted PVA-*co*-PE polymer containing 32 mol % ethylene, and (e) NDAM grafted PVA-*co*-PE polymer containing 44 mol % ethylene.

homopolymerization of the monomer, DCP was selected as the initiator because its alkoxide radicals will preferentially abstract hydrogen atoms from active C–H bonds instead of having radical addition reactions with the monomer.[27] The effects of the initiator concentrations and ethylene contents of PVA-*co*-PE on the grafting yields of the NDAM to the PVA-*co*-PE backbones were studied. Figure 1 shows the grafting contents of NDAM as a function of the initiator concentration for PVA-*co*-PE polymers containing 27, 32, and 44 mol % ethylene. For PVA-*co*-PE polymers containing 27, 32, and 44 mol % ethylene, the grafting contents of NDAM reached values of 82.2 ± 7.5 mpm, 88.9 ± 3.51 mpm and 82.6 ± 9.37 mpm, respectively, for an initiator concentration of 4 mpm. A further increase in DCP concentration from 4 mpm to 8 mpm and 12 mpm did not improve the grafting contents, but instead resulted in continuous drop of the NDAM grafting contents for two of the polymers. Interestingly, only for the PVA-*co*-PE with 27 mol % ethylene, the grafted NDAM increased as the initiator concentration was raised, and reached the maximum of 135.5 ± 8.75 mpm for an initiator concentration of 8 mpm, followed by a drop to 94.85 ± 5.99 mpm for 12 mpm DCP. The overall trend of grafted NDAM groups on the polymers is consistent with the increased alcohol contents or tertiary C–H bonds in the polymers. When the ethylene content is 27 mol %, the copolymer contains 73 mol % alcohol units, leading to the highest grafting yields. But when there is anm overwhelming amount of initiators in the system, side reactions could be promoted as well.

The changes in the torque values during the reactive melt mixing process can be used to characterize molecular weights of PVA-*co*-PE due to the proportional relationship between polymer molecular weight and melt viscosity/torque value. Figure 2 shows the torque evolutions of PVA-*co*-PE polymers with the three different ethylene contents during the reactive mixing process. The concentrations of initiator and monomer were maintained at 4 mpm and 450 mpm, respectively, for the experiments. Compared with the torque values of virgin PVA-*co*-PE polymers, the NDAM grafted PVA-*co*-PE polymers all

demonstrated lower torque values during the melt mixing process. This indicated PVA-*co*-PE polymer chain scission occurred during the melt graft polymerization process, resulting in reduced molecular weights. The ratio of the final torque value of the NDAM grafted PVA-*co*-PE to that of the unmodified PVA-*co*-PE was measured to compare the chain scission extents of PVA-*co*-PE polymers. The ratios for PVA-*co*-PE containing 27, 32, and 44 mol % ethylene were 0.68, 0.78 and 0.80, respectively. The results suggested that the PVA-*co*-PE sample containing 44 mol % ethylene had the least chain scission, followed by samples containing 32 and 27 mol % ethylene. Because the chain scission should occur at the tertiary carbon radicals on the alcohol units, more alcohol content should have more possibility of the chain scission reactions.

The successful graft copolymerization of the NDAM monomer onto PVA-co-PE polymers was confirmed with FTIR analysis, as shown in Figure 3. All NDAM -grafted PVA-*co*-PE showed two new characteristic absorption bands of NDAM, centered around 1620 and 1552 cm^{-1} in the FTIR spectra. These bands are attributed to bending deformation of aminoazine and planar triazine ring stretching vibration, respectively. The vibration band at 1757 cm^{-1} was assigned to the unhydrolyzed ester carbonyl bond in the PVA-*co*-PE polymers, which was unchanged during the reaction. The appearance of the absorption band at 1658 cm^{-1} in the virgin PVA-*co*-PE spectra was assigned to the unsaturated –C=C bonds produced from the thermal dehydration of the vinyl alcohol components.[28] It should be noted that the band at 1658 cm^{-1} overlapped with the bending band of NDAM at 1620 cm^{-1} in the spectra of all NDAM-grafted PVA-*co*-PE. Moreover, in the spectrum of NDAM grafted PVA-*co*-PE containing 27 mol % ethylene, a new and sharp absorption band at 1705 cm^{-1} appeared, which could be attributed to unsaturated aldehydes and ketones formed because of chain session and dehydration reactions. However, there was no such absorption band observed in the spectra of the virgin PVA-*co*-PE with 27 mol % ethylene content, as well as the NDAM-grafted PVA-*co*-PE containing 32 and 44 mol % ethylene. The PVA-*co*-PE
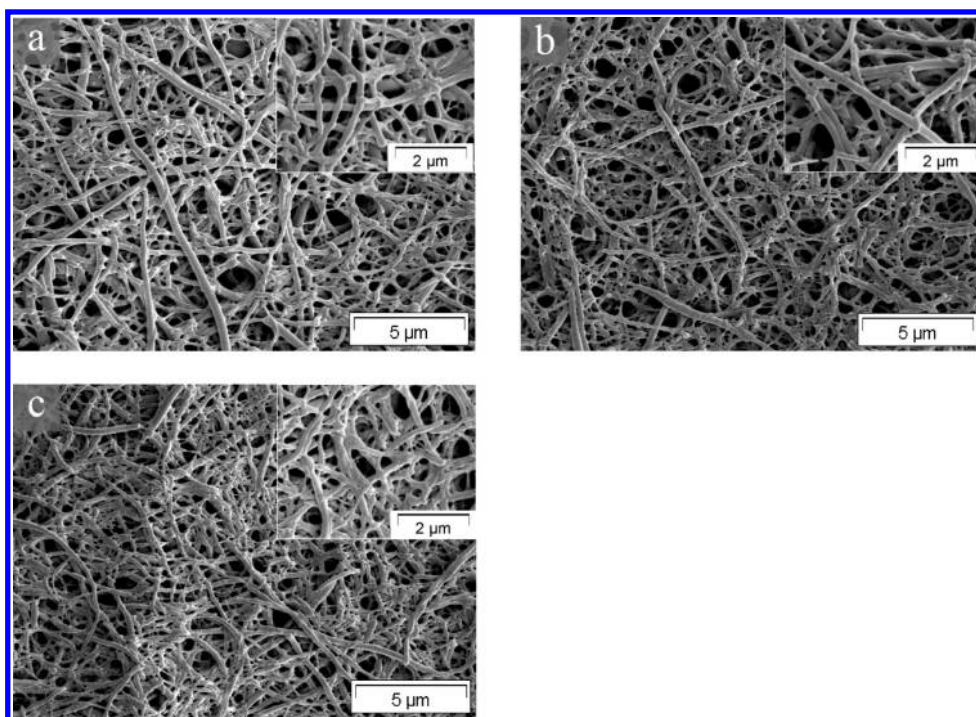
Figure 4. SEM images of NDAM grafted PVA-*co*-PE nanofiber membranes containing (a) 27, (b) 32, and (c) 44 mol % ethylene. [DCP] = 4 mpm and [NDAM] = 450 mpm (moles per million grams of PVA-*co*-PE polymer).

(27% ethylene) contains a high vinyl alcohol (73 mol %) concentration. Its chain scission and dehydration reactions could be more significant, which might lead to the observation of unsaturated carbonyl structures in the polymer.

NDAM-Grafted PVA-*co*-PE Nanofibrous Membranes. To increase the surface exposure of grafted NDAM, the NDAM grafted PVA-*co*-PE polymers prepared with 4 mpm DCP and 450 mpm NDAM were fabricated into nanofibers and nanofibrous membranes. The morphologies of the NDAM grafted PVA-co-PE nanofibrous membranes containing 27, 32, and 44 mol % ethylene were characterized with SEM and are presented in Figure 4. NDAM grafted PVA-*co*-PE nanofibers demonstrated the well-defined nanofibrous, but randomly distributed morphologies in membranes. The nanofibers interconnected with each other and formed weblike structures, which make them superior in capturing and then eliminating the microorganisms.

The surface exposure of grafted NDAM on grafted PVA-*co*-PE nanofibrous membranes containing 27, 32, and 44 mol % ethylene were further analyzed with FTIR-ATR spectroscopy. The FTIR-ATR spectra were quite similar to those in Figure 3, with the existence of characteristic absorption bands of NDAM at 1623 and 1550 cm^{-1}.

Activation of NDAM-Grafted PVA-*co*-PE Nanofibrous Membranes. To achieve the desired antibacterial properties, the NDAM structures grafted into PVA-*co*-PE should be activated in dilute chlorine bleach solutions, which can convert −N−H in the precursor into biocidal N−Cl (halamine) structure. The halamine structures can be measured by analyzing active chlorine contents of the polymers, which also represent the antibacterial activities. A minimum amount of 200 ppm active chlorine could offer the polymer materials powerful antibacterial activities.[11] In addition, the antibacterial properties could be recharged with the same chlorination process for repeated uses.
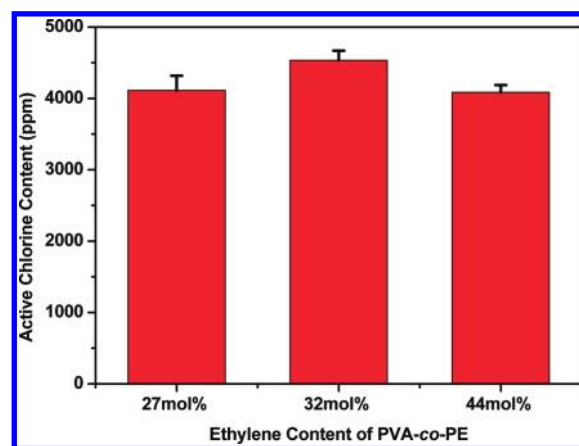

Figure 5. Active chlorine content of NDAM grafted PVA-*co*-PE nanofibers with 27, 32, and 44 mol % ethylene after chlorination. [DCP] = 4 mpm and [NDAM] = 450 mpm (moles per million grams of PVA-*co*-PE polymer).

The active chlorine contents of the chlorinated NDAM-grafted PVA-*co*-PE nanofibrous membranes were determined by the titration method.[2,15] Figure 5 displays the active chlorine contents of the NDAM grafted PVA-*co*-PE nanofiber membranes containing 27 mol %, 32 mol % and 44 mol % ethylene with 4 mpm DCP and 450mpm NDAM. The active chlorine contents for all three NDAM grafted PVA-*co*-PE nanofibers were above 4000 ppm, much higher than those previously reported for the NDAM grafted polyolefins.[2] The trend of active chlorine contents on the NDAM grafted PVA-*co*-PE nanofiber membranes was consistent with the measured grafting contents of NDAM on PVA-*co*-PE polymers at the initiator and monomer
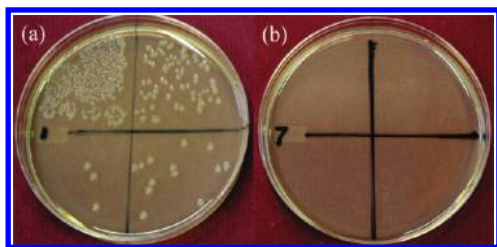
Figure 6. Antibacterial test of PVA-*co*-PE nanofiber membranes, (a) Virgin PVA-*co*-PE nanofiber membranes, (b) NDAM-grafted PVA-*co*-PE nanofiber membranes after chlorination. Ethylene content = 32 mol %, contact time = 10 min.

concentrations of 4 mpm and 450 mpm, respectively (Figure 1). It should be noted that the chlorination had very little influence on the tensile strength of polymer nanofibers because the N—Cl moiety transformation predominately occurred on fiber surfaces. The results clearly demonstrated that polymer hydrophilicity could be a major reason for achieving high active chlorination of the modified polymers. In addition, the decrease in the fiber diameters might also have increased the chlorination efficiency of NDAM in the modified polymers.

Furthermore, the chlorine storage stability is another concern. Our previous study reported the active chlorine content of about 500 ppm for NDAM grafted polypropylene ultrafine fibers decreased by 30% over a 30-day period in a conditioning room (21 °C, 65% RH).[2] It can be expected that the active chlorine higher than 4000 ppm offered by chlorinated NDAM grafted PVA-*co*-PE nanofibrous membranes in the current study can last much longer.

Antibacterial Activity Assessment. The antibacterial properties of NDAM grafted PVA-*co*-PE nanofibrous membranes against *Escherichia coli* (*E. coli*) were investigated based on a modified AATCC test method 100−1999. All chlorinated NDAM-grafted PVA-*co*-PE nanofibrous membranes exhibited excellent antibacterial properties against the tested bacterium. The bactericidal rate of 99.999% was obtained within both contact times of 30 s and 10 min. The antibacterial test of NDAM grafted PVA-*co*-PE nanofibrous membranes with 32 mol % ethylene within 10 min contact time are shown in Figure 6. No viable colony of the bacterium was found on the agar plate for the chlorinated NDAM grafted PVA-*co*-PE nanofibrous membrane, while proliferated colonies of *E. coli* were observed for the virgin PVA-*co*-PE nanofibrous membrane.

CONCLUSIONS

An N-halamine precursor of NDAM was successfully introduced onto the backbone of the PVA-*co*-PE polymers with 27, 32, and 44 mol % ethylene as side groups by melt radical graft copolymerization during reactive extrusion. The structures of polymers (contents of alcohol units) and the initiator concentration influenced the grafting efficiency of NDAM on the polymers. The highest grafting contents were obtained for the polymers with highest alcohol contents. The melt graft copolymerization initiated by the peroxide initiators caused obvious chain scissions of the PVA-*co*-PE polymers. The FTIR spectra confirmed the covalent attachment of the NDAM in the melt grafted PVA-*co*-PE polymer backbones. It was also found that the radical grafting process produced segments containing unsaturated aldehyde and ketone from chain scissions for PVA-*co*-PE polymers having 27 mol % ethylene. The NDAM grafted PVA-*co*-PE polymers were fabricated into well-defined and interconnected nanofibrous morphologies. The surface chemical structure analysis proved the effective exposure of grafted NDAM on surfaces of nanofibrous membrane. The chlorination of the NDAM grafted PVA-*co*-PE nanofibrous membranes resulted in high concentrations of active chlorine above 4000 ppm. The chlorinated PVA-*co*-PE nanofibrous membranes grafted with NDAM all exhibited excellent antibacterial properties against *E. coli* bacterium.

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