Antimicrobial Coatings Based on Hydantoin-Containing Polymer Networks for Textiles

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ABSTRACT: An advanced method with an initiator pretreatment was developed for the coating of nylon/cotton fabrics with the hydantoin-containing monomer 3-allyl-5,5-dimethylhydantoin and two water-soluble crosslinkers *N,N′*-methylene bisacrylamide and poly(ethylene glycol) 200 diacrylate. The formulations were applied to textiles by either batch coating or dip coating. In the dip-coating process, the influence of individual parameters on the fabric modification was investigated and evaluated. After treatment with chlorine, the hydantoin structure was transformed into antimicrobial active *N*-halamines. The modified fabrics exhibited potent antibacterial properties against *Staphylococcus aureus* and *Escherichia coli*. Our method, based on an initiator pretreatment and water-soluble crosslinkers, outperformed current technologies in the degree of fabric modification. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1646–1651, 2011

Key words: coatings; crosslinking; halogenated; modification

INTRODUCTION

Textiles have long been recognized as a medium to support the growth of microorganisms, a phenomenon associated with a range of unwanted effects, not only on the textile itself but also on the wearer. These effects include the generation of unpleasant odors, stains, and discoloration of the fabric; a reduction in fabric mechanical strength; and an increased likelihood of contamination.[1] For these reasons, the growth of microbes on textiles needs to be minimized during their use and storage.

One solution that has been explored for durable antimicrobial finishing is to make the finishes regenerable through the use of chlorine-containing *N*-halamine compounds. *N*-Halamine compounds are broad-spectrum disinfectants that have been used in water treatment.[2] The regenerable approach is based on the recharging of *N*-halamines with chlorine in a bleaching solution during the laundering of the fabrics. This concept was first proposed and demonstrated for the treatment of cotton by Sun and Xu in 1998.[3] Different heterocyclic *N*-halamine compounds have since been covalently attached to nylon[4] and polyester fibers[5] and grafted onto cellulosic fabrics[6–9] and synthetic fabrics.[10,11] Recently, a reactive extrusion process was explored to incorporate *N*-halamine precursor structures into polypropylene[12] and low-density polyethylene.[13] Moreover, a hydantoin derivative was grafted onto aromatic polyamide membranes to improve their chlorine resistance and antibiofouling properties.[14]

In most cases, the hydantoin-containing monomer, 3-allyl-5,5-dimethylhydantoin (ADMH) has been polymerized in the presence of other monomers or crosslinkers, such as triallyl-1,3,5-triazinetrion (TATAT). Although antimicrobial activity has been imparted to the textiles, the use of TATAT for commercial applications, which require a continuous process, has been a concern because of TATAT's low water solubility.[11] In our study, a nylon/cotton fabric was coated with ADMH and two water-soluble crosslinkers, *N,N′*-methylene bisacrylamide (MBAA) and poly(ethylene glycol) 200 diacrylate (PEGDA). Different coating procedures were evaluated to achieve a continuous process, which is preferred in the chemical modification of fabrics.

Our study also addressed the low concentration of radical species on nylon/cotton substrates. Because the low concentration can be an impediment to film formation, a method was developed to ensure a high concentration of radicals on the surface of the fabric. Figure 1 illustrates the novel strategy for the preparation of antimicrobial coatings on fabric substrates with initiator pretreatment.

In conjunction with the crosslinker type and initiator pretreatment, the influence of different coating methods (batch coating and dip coating) on the degree of fabric modification was studied. For dip coating, which better describes the situation in continuous processes, the influence of individual

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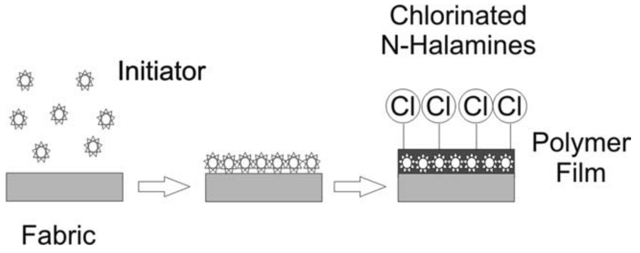

Figure 1 Schematic illustration of the strategy for preparing the antimicrobial coatings.

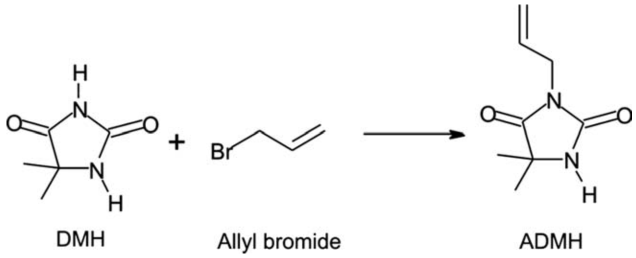

Figure 2 Synthesis of ADMH.[15]

parameters on the fabric modification was investigated and evaluated. Furthermore, the antimicrobial activity of the coated fabrics against Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* was tested.

EXPERIMENTAL

Materials

A 50/50 nylon/cotton blend ripstop woven fabric was used as a substrate throughout the study. The construction was 62 warp/in. and 48 weft/in. The monomer ADMH (Fig. 2) was synthesized from 5,5-dimethyl hydantoin (DMH; Sigma Aldrich) and allyl bromide (Acros Organics, Fair Lawn, NJ).[15] The initiator potassium persulfate (PPS; Sigma Aldrich), the nonionic wetting agent Triton X-100 (1% aqueous solution, SPI Supplies), and the crosslinkers MBAA (Sigma Aldrich, St. Louis, MO) and PEGDA (Polysciences, Warrington, PA) were used without further purification.

Instruments

Fourier transform infrared (FTIR)–attenuated total reflection (ATR) spectra were taken on a Bruker Tensor 27/Hyperion 1000 system (Bruker Optics, Billerica, MA) with a Ge ATR objective to characterize the compositions of the coatings. The instrumental parameters for obtaining ATR spectra were as follows: spectral region = 600–4000 cm^{-1}, number of scans = 64 scans/sample, and resolution = 4 cm^{-1}. For the chlorine concentration, scanning electron microscopy/energy-dispersive spectrometry (EDS) spectra were recorded on a Hitachi S-3400N scanning electron microscope with an X-ray tube (Hitachi High Technologies America, Pleasanton, CA). The operating voltage for the EDS analysis was 10–20 kV. The takeoff angle was 35°, and the elapsed lifetime was 50. All samples were tested for the presence of the same elements: C, O, Na, Al, Si, P, Cl, Ca, and Zn. The thickness of the coatings was measured by a Minitest 600 coating thickness gauge (Elektrophysik, Arlington Heights, IL) operating on the magnetic inductive principle. For each sample, 10 values were measured, and the average value was determined.

Antimicrobial coating

Both sides of a fabric sample (2 × 3 $in.^2$) were scratched with a wire scratch brush and washed with 100 mL of deionized (DI) water at 45°C for 30 min to remove impurities. After it was dried at 60°C, the weight of the sample (W_1) was determined. For the initiator pretreatment, the sample was placed in a solution of 0.85 g of PPS and 0.26 g of Triton X in 20 mL of DI water overnight.

To prepare the coating formulation, the monomer ADMH was first dissolved in 20–40 mL of DI water. A small amount of Triton X was then added, followed by the crosslinker MBAA or PEGDA (Table I). After the addition of PPS, the formulation was purged with nitrogen for 5 min.

Then, with different methods, the coating formulation was applied to the fabric sample. In the case of batch coating, the wet sample was transferred from the initiator solution to the coating formulation and heated at approximately 90°C for a defined period of time. For dip coating, the wet sample was immersed in the coating formulation for 15 min and

TABLE I
Coating of the 50/50 Nylon/Cotton Fabric with Antibacterial Polymers

Crosslinker/coating method	W_1 (g)	ADMH (g)	Crosslinker (g)	PPS (g)	Water (mL)	Triton X (g)	T (°C)	Time (min)	W_2 (g)
MBAA batch	1.52	5.76	1.00	0.03	40	0.27	88	120	1.63
MBAA dip	1.53	2.79	0.50	0.05	20	0.15	130	4 × 15	1.72
PEGDA batch	1.55	5.67	1.20	0.15	40	0.28	90	5	1.79
PEGDA dip	1.49	5.63	1.22	0.03	40	0.28	90–130	3 × 15	1.78

W_1 = weight of the sample before coating; W_2 = weight of the sample with polymer coating; T = temperature.

then cured in an oven at 130°C (MBAA dip) or at 90–130°C (PEGDA dip) for the next 15 min. The procedure for dip coating was repeated several times. After the coating process, in both cases, the sample was washed with 100 mL of DI water at 45°C for 30 min. Finally, the fabric was dried at 60°C overnight, and the weight of the sample with polymer coating (W_2) was determined.

The degree of fabric modification was calculated from eq. (1):

$$\text{Degree of modification}(\%) = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

To transform the hydantoin structure present in the coating into an antimicrobial active form, fabric samples were bleached with sodium hypochlorite (13% chlorine). Specifically, grafted samples were treated with 50 mL of a 10 wt % NaOCl solution at 45°C for 30 min. After chlorination, the samples were washed with 100 mL of DI water containing soap for 30 min at 45°C and dried at 60°C overnight.

Antibacterial activity assessment

The antibacterial properties of the bleached samples were tested against *S. aureus*, a Gram-positive bacterium commonly found on the human body, and against *E. coli*, a Gram-negative bacterium. The tests were conducted in replicates according to AATCC test method 147.

The average width of the zone of inhibition was calculated with the following equation:

$$W = \frac{(T - D)}{2} \qquad (2)$$

where W is the width of the clear zone of inhibition (mm), T is the total diameter of the sample and clear zone (mm), and D is the diameter of the sample (mm).

RESULTS AND DISCUSSION

Because of the stability of allyl radicals, the homopolymerization of ADMH rarely occurs in radical processes.[16,17] In our study, the conversion of ADMH in solution without any crosslinker was evaluated to be 7%, whereas no polymer remained on the fabric surface. The coating of ADMH on the nylon/cotton 50/50 fabric was successful only when crosslinkers were added. These results indicate that without crosslinkers, the polymer was formed on the fabric; however, it was removed during washing.

Pretreatment of the fabric with the initiator was required to increase the concentration of free radicals on the fabric surface. However, a small amount of the initiator PPS was also added to the coating formulation to limit the desorption of PPS from the fabric during the coating process. First, the efficiency of dip coating versus batch coating was determined for both crosslinking agents (MBAA and PEGDA). Next, the composition of the coating formulation was systematically changed to determine the influence of individual parameters and the optimal coating conditions.

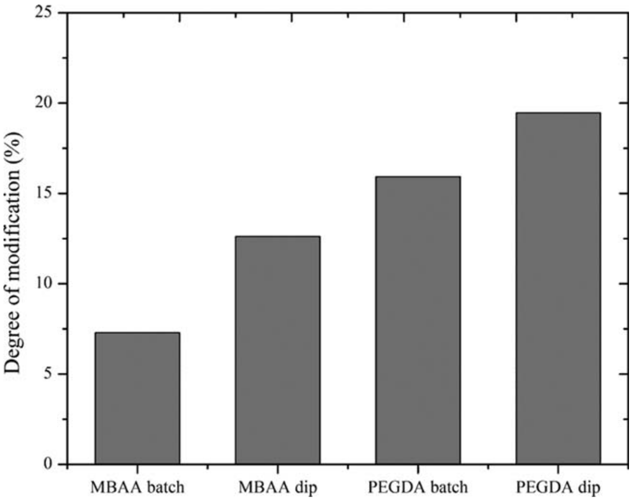

Figure 3 Influence of the crosslinker type and coating method on the fabric modification.

Influence of the crosslinker type and coating method

The results of coating the polymer with water-soluble crosslinkers are shown in Figure 3. In the experiments with MBAA as a crosslinking agent, the volumes of the formulation for batch and dip coating were different (Table I). However, the same monomer and crosslinker concentration was chosen in both experiments, and therefore, the results of fabric modification could be compared. The weight of the samples increased by 7 and 12% after batch and dip coating, respectively. Batch and dip coating with PEGDA led to high degrees of modification of 16 and 20%, respectively.

Figure 4(a) shows the FTIR–ATR spectrum of the untreated fabric. The bands at 1650 and 1770 cm^{-1} in the spectrum of the modified fabric [Fig. 4(b)] were attributed to the imide and amide structures, respectively, of ADMH. These typical bands were observed on other fabrics modified with ADMH, as reported elsewhere.[10] Hence, both crosslinkers could be used to deposit a polymer film derived from ADMH on the fabric surface. Because higher degrees of fabric modification were achieved in dip mode, this process was used to optimize the coating formulation.

The polymer film crosslinked with MBAA showed a higher chlorine content after chlorination (16 %) than the film crosslinked with PEGDA (1%, data not

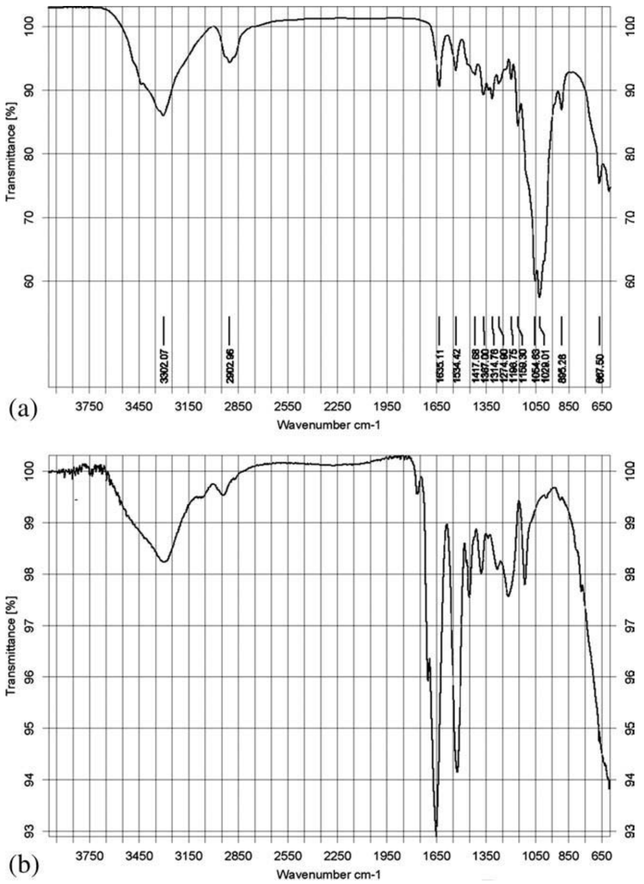

Figure 4 FTIR–ATR spectra in the region 600–4000 cm^{-1} of the (a) untreated fabric and (b) ADMH/MBAA-grafted fabric as specified in the Experimental section (Table I, MBAA batch).

presented here). The immense difference in the chlorine content relevant for antimicrobial properties might have been due to the chlorination of the amide structure of MBAA in addition to ADMH. The chlorination of polyacrylamide grafted onto cotton has been described and investigated.[18,19] Because of the poor chlorine content of the ADMH/PEGDA sample, the influence of the molar ratio and the total monomer concentration was determined with the ADMH/MBAA formulation. The following experiments were carried out under the same conditions as described in the Experimental section (Table I, MBAA dip).

Influence of the molar ratio

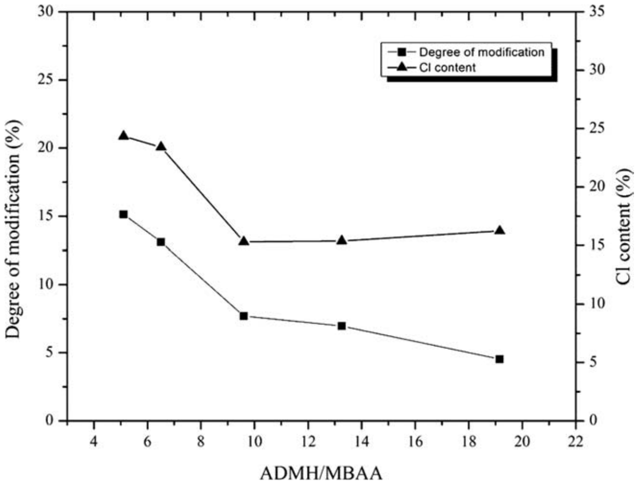

Figure 5 Influence of the ADMH/MBAA molar ratio in the formulation on the (■) fabric modification and (▲) chlorine content (total ADMH/MBAA concentration = 13.2 wt %, contact time = 4 × 15 min, curing time = 4 × 15 min, curing temperature = 130 °C).

As shown in Figure 5, the maximum degree of the fabric modification (15%) was obtained by dip coating when the ADMH/MBAA molar ratio was 5 : 1. Higher molar ratios decreased the fabric modification considerably. These results indicate that a fairly high amount of crosslinker was required to form a polymer network on the fabric surface, which ensured that ADMH could not be removed during the washing step. Molar ratios lower than 5 : 1 could not be realized because of the limited solubility of ADMH and MBAA in water. Similar molar ratio results were also reported for an ADMH/TATAT mixture deposited onto a poly(ethylene terephthalate) substrate.[10] The total monomer concentration used for the poly(ethylene terephthalate) modification was 0.625 wt %, which explained the lower modification yields of 6%.

The chlorine concentration of the modified cotton/nylon fabric samples was also a function of the ADMH/MBAA molar ratio. The chlorine concentration correlated to the degree of fabric modification. The thickness of the coatings as a function of the ADMH/MBAA molar ratio is shown in Figure 6.

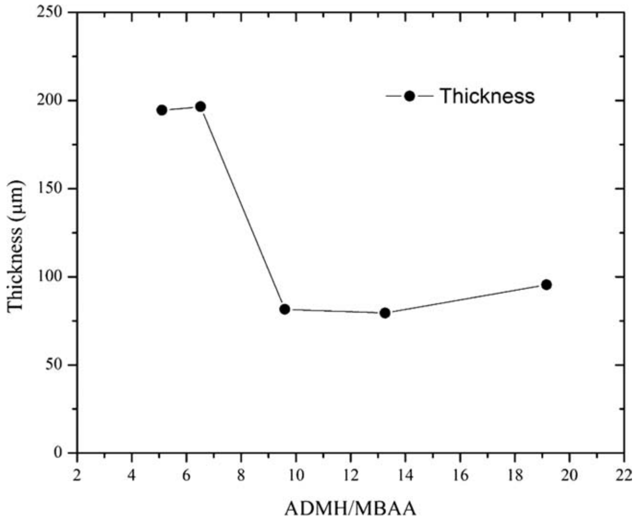

Figure 6 Influence of the ADMH/MBAA molar ratio in the formulation on the (●) coating thickness (total ADMH/MBAA concentration = 13.2 wt %, contact time = 4 × 15 min, curing time = 4 × 15 min, curing temperature = 130°C).

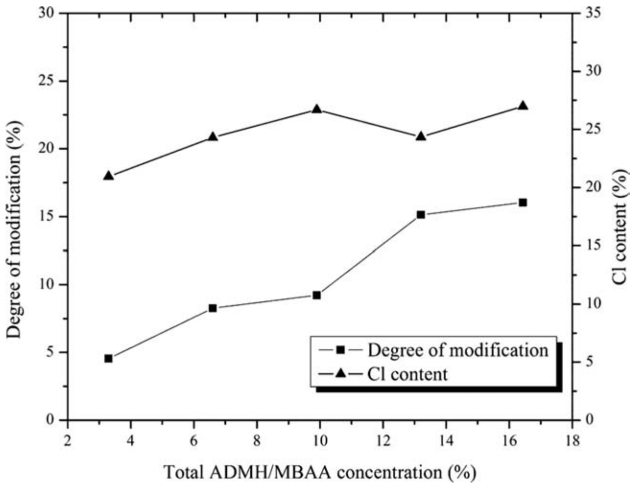

Figure 7 Influence of the total ADMH/MBAA concentration in the formulation on the (■) fabric modification and (▲) chlorine content (ADMH/MBAA molar ratio = 5 : 1, contact time = 4 × 15 min, curing time = 4 × 15 min, curing temperature = 130°C).

The coating thickness ranged from 75 to 200 μm. In general, scanning electron microscopy/EDS analysis investigates up to 10 μm of the sample surface. As this thickness is negligible compared to the coating thickness, this method was accurate for all ADMH/MBAA samples in this thickness range.

Influence of the total monomer concentration

The results achieved by the dip coating of the 50/50 nylon/cotton fabric at different total monomer concentrations are presented in Figure 7. Because the monomer concentration in the fabric was directly proportional to the monomer concentration in the solution, the degree of the fabric modification gradually increased when the total ADMH/MBAA concentration was increased from 3.3 to 16.4 wt %. The maximum fabric modification (16%) was, therefore, obtained for the highest ADMH/MBAA concentration (16.4 wt %). These findings were also confirmed by the results of the chlorine concentration.

The total ADMH/MBAA concentration could be used to control the coating thickness. The correlation of these parameters is given in Figure 8. The coating produced with a total ADMH/MBAA concentration of 3.3 wt % had a thickness of 104 μm. When a total ADMH/MBAA concentration of 16.4 wt % was used, the coating thickness was 185 μm.

Antibacterial properties

The antibacterial properties of samples crosslinked with PEGDA or MBAA were evaluated against *S. aureus* (Table II). Unlike the untreated fabric, bacterial colonies were not identified under the sample contact area; this left us to conclude that there was

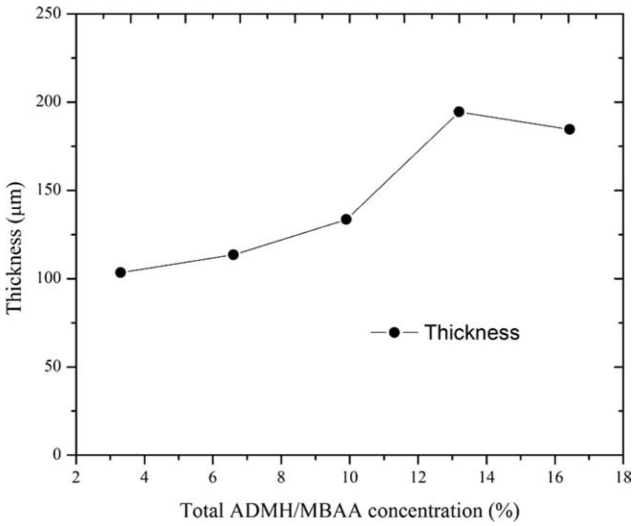

Figure 8 Influence of the ADMH/MBAA concentration in the formulation on the (●) coating thickness (ADMH/MBAA molar ratio = 5 : 1, contact time = 4 × 15 min, curing time = 4 × 15 min, curing temperature = 130°C).

antibacterial activity against the test organisms on the samples. The interpretation of measured zones of inhibition might have indicated coating leaching. The ADMH/MBAA sample was also tested against Gram-negative bacteria. In the test with *E. coli*, the material was an efficient antibacterial agent. Because this sample was synthesized with an improved procedure, a durable coating was produced, and hence, there was no zone of inhibition detected. Tests of coating durability after repeated washing cycles are in process. The ideal durability of coatings is ensured by the covalent bonding between the substrate and the polymer layer. The mechanism of radical graft polymerization of ADMH on cotton cellulose is based on cellulosic radicals that initiate the grafting polymerization of ADMH, as stated elsewhere.[20] This chemically grafted cotton was converted to biocide after chlorine treatment, and the coating was durable during the chlorination.

CONCLUSIONS

An advanced method based on an initiator pretreatment was developed for the coating of nylon/cotton

TABLE II
Results of the Antibacterial Activity Assessment

Fabric sample	Test organism	Growth under the sample	Zone of inhibition (mm)
ADMH/PEGDA	*S. aureus*	No	3.45
ADMH/MBAA	*S. aureus*	No	5.75
ADMH/MBAA	*E. coli*	No	0
Untreated fabric	*S. aureus* and *E. coli*	Yes	0

fabrics with antimicrobial polymers based on the hydantoin-containing monomer ADMH. The water-soluble crosslinkers PEGDA and MBAA were used to achieve the substantial attachment of hydantoin-containing polymer networks to the fabric surface. For the dip-coating process, which led to higher degrees of fabric modification, optimum coating conditions were found with the ADMH/MBAA formulation. In addition, the method controlled the thickness of the ADMH/MBAA coating on the 50/50 nylon/cotton fabric.

The hydantoin structure was transferred into an antimicrobial active form by bleaching. The results of the chlorine concentration indicated that in addition to the hydantoin structure of ADMH, the amide structure of MBAA was also chlorinated. The samples coated with these hydantoin-containing polymer networks exhibited potent antibacterial properties against *S. aureus* and *E. coli*. Fabrics protected against biological agents have great potential for the production of military overgarments and other accessories. They could also be used to provide protection to healthcare professionals.

References

1. Gao, Y.; Cranston, R. Text Res J 2008, 78, 60.
2. Worley, S. D.; Williams, D. E. CRC Crit Rev Environ Control 1988, 18, 133.
3. Sun, G.; Xu, X. J. Text Chem Color 1998, 30, 26.
4. Lin, J.; Winkelmann, C.; Worley, S. D.; Broughton, R. M.; Williams, J. F. J Appl Polym Sci 2001, 81, 943.
5. Lin, J.; Winkelmann, C.; Worley, S. D.; Kim, J. H.; Wei, C. I.; Cho, U. C.; Broughton, R. M.; Santiago, J. I.; Williams, J. F. J Appl Polym Sci 2002, 85, 177.
6. Sun, Y.; Sun, G. J Appl Polym Sci 2002, 84, 1592.
7. Qian, L.; Sun, G. J Appl Polym Sci 2004, 91, 2588.
8. Luo, J.; Sun, Y. J Polym Sci Part A: Polym Chem 2006, 44, 3588.
9. Liu, S.; Sun, G. Ind Eng Chem Res 2006, 45, 6477.
10. Sun, Y.; Sun, G. J Appl Polym Sci 2001, 81, 1517.
11. Sun, Y.; Sun, G. J Appl Polym Sci 2003, 88, 1032.
12. Badrossamay, M. R.; Sun, G. J Biomed Mater Res Appl Biomater 2009, 89B, 93.
13. Badrossamay, M. R.; Sun, G. Macromolecules 2009, 42, 1948.
14. Wei, X.; Wang, Z.; Chen, J.; Wang, J.; Wang, S. J Membr Sci 2010, 346, 152.
15. Sun, Y.; Sun, G. J Appl Polym Sci 2001, 80, 2460.
16. Bartlett, P. D.; Tate, F. A. J Am Chem Soc 1953, 75, 91.
17. Schildknecht, C. E. Allyl Compounds and Their Polymers; Wiley: New York, 1973; p 30.
18. Sun, Y.; Sun, G. J Appl Polym Sci 2008, 108, 3480.
19. Hong, K. H.; Liu, N.; Sun, G. Eur Polym J 2009, 45, 2443.
20. Liu, S.; Sun, G. Carbohydr Polym 2008, 71, 614.