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N-(Hydroxymethyl) Acrylamide as a Multifunctional Finish to Cotton and a Tether for Grafting Methacrylamide for Biocidal Coatings

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ABSTRACT: *N*-(hydroxymethyl) acrylamide (NMA) was immobilized on cotton surfaces through etherification, and then methacrylamide (MA) was grafted onto the treated surface. The coatings were characterized by ATR-IR spectroscopy and were rendered biocidal upon exposure to dilute household bleach. The treated fabrics were challenged with Gram-negative and Gram-positive bacteria; both NMA and NMA/MA-treated fabrics inactivated about 8 logs of *Escherichia coli* O157:H7 and *Staphylococcus aureus* within only 5 min of contact time. The coatings were also quite stable toward ultraviolet (UVA) light exposure and repeated laundering. Moreover, a substantial improvement in wrinkle recovery angle was obtained for the NMA/MA-treated fabrics. The new acyclic acrylamide *N*-halamine coating should be less expensive to produce and use than previous cyclic *N*-halamine coatings developed in these laboratories. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4405–4410, 2013

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INTRODUCTION

Because microorganisms can survive on textile materials for long periods of time, the risk of their transmission among visitors, patients, and healthcare workers is very high in healthcare environments. There are approximately 2 million people affected by one type of healthcare-associated infection each year in the United States resulting in an annual death rate of 90,000 and $4.5–$5.7 billion of healthcare cost.[1,2] Therefore, antimicrobial treatment of medical textiles such as bed sheets, pillows, uniforms, gowns, and socks is essential to reduce the risk of transmitting pathogenic microorganisms. In that sense, different types of antimicrobial agents such as quaternary ammonium salts,[3–6] light activated compounds,[7] heavy metals,[8] and *N*-halamines[9–13] have been used to prevent contamination of surfaces. Among these antimicrobials, *N*-halamines are attracting attention due to their long-term stabilities and effectiveness against a broad range of microorganisms with inactivation in a relatively short period of time. *N*-halamines inactivate microorganisms by transferring oxidative halogen to the cell membranes of pathogens resulting in oxidation of proteins.[14] These biocides are rechargeable; the oxidative halogen can be restored through a simple halogenation reaction using household bleach. To date, numerous *N*-halamine precursors have been bound to various surfaces via tethering groups such as siloxane[15–17] and epoxide,[18,19] grafting,[20,21] or electrostatic attractions.[22]

N-(hydroxymethyl) acrylamide (NMA) is a bifunctional monomer having an *N*-methylol and a vinyl group, so that it can be covalently attached onto cotton through an etherification reaction taking place between the cellulosic hydroxyl and the methylol groups, and then it can be homopolymerized or copolymerized via free radical polymerization. Therefore, NMA has been commercially used in the textile industry primarily to impart permanent press functionality to cellulosic materials.[23–25] Even though it has an amide functionality readily available for halogenation, there has not been reported a study suggesting NMA as an *N*-halamine precursor, possibly because it has an α-hydrogen adjacent to the amide group which could allow a dehydrohalogenation reaction, resulting in loss of biocidal activity and rechargeability (Figure 1).[26] In a previous study, it was shown that stable antimicrobial coatings on cotton fabric could be prepared by coating the copolymer of 3-chloro-2-hydroxypropyl-methacrylate and glycidyl methacrylate and subsequently

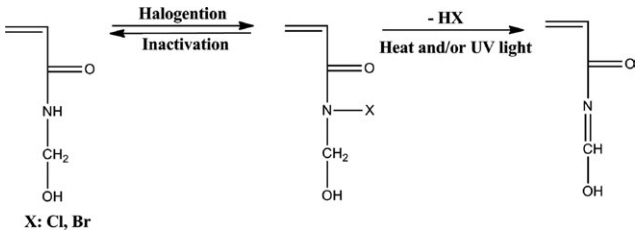

Figure 1. Rechargeability and α-dehydrohalogenation of NMA.

treating the surface with the potassium salt of 5,5-dimethylhydantoin.[18] Although the coating exhibited very effective antimicrobial activity and stability, the two-step coating process would be expensive to implement in an industrial process. Generally, it has been observed that cyclic *N*-halamines have significantly higher stabilities than do acyclic ones.[9] However, in this study, acyclic NMA was used as an *N*-halamine precursor and a tether to graft methacrylamide (MA) onto cotton fabric, so that an inexpensive means of obtaining multifunctional cotton fabric hopefully having biocidal and durable press functionalities might be provided. The syntheses of the NMA and NMA/MA coating materials should be less expensive in terms of starting material costs and less tedious in that preliminary syntheses steps for the coating materials are unnecessary than was the case for the various cyclic *N*-halamine materials developed earlier in these laboratories. Wrinkle recovery angle, washing and ultraviolet (UVA) light stabilities, and the biocidal efficacies of the NMA and NMA/MA-coated swatches were evaluated. To the best of our knowledge, this is the first study reporting antimicrobial NMA as an *N*-halamine compound.

EXPERIMENTAL

Materials and Instrumentation

All chemicals were purchased from Aldrich Chemical (Milwaukee, WI) or Fisher Scientific (Fair Lawn, NJ) and used without further purification. A bleached (100%) cotton (Style 400 Cotton Print Cloth) was purchased from Testfabrics (West Pittston, PA). Clorox brand household bleach (Clorox, Inc., Oakland, CA) was used for chlorination. Bacterial cultures of *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* (O157:H7 ATCC 43895) were purchased from the American Type Culture Collection (Rockville, MD). Trypticase soy agar from Difco Laboratories (Detroit, MI) was used as a culture medium. ATR-IR data were obtained with 64 scans at 4 cm^{-1} resolution using a Nicolet 6700 FT-IR. UVA light stabilities were evaluated with an Accelerated Weathering Tester (The Q-panel Company, Cleveland, OH).

Coating onto Cotton Surface

The monomers in various concentrations were immobilized onto cotton fabric through a two-step coating procedure. First, NMA was covalently bound to the surface via etherification. For this step, a specified amount of NMA was dissolved in water together with 1 wt % of magnesium chloride, and the mixture was stirred for 15 min to produce a uniform solution. The cotton swatches were immersed in this solution and then uniformly padded through a laboratory wringer (Birch Brothers Southern, Waxhaw, NC). This process was repeated three times to ensure a uniform coating on the surface. The swatches were dried at 90°C for 5 min followed by curing at 175°C for 3 min. To remove noncovalently bonded compounds, the samples were washed with a 0.5 wt % detergent solution for 15 min, rinsed with tap water, and then dried at 45°C for 1 h.

In the second step, MA was grafted onto the treated surface through copolymerization with NMA via free radical polymerization and/or grafting on the cotton surface. In this step, 5 wt % of MA and 1 wt % of potassium persulfate were dissolved in water and stirred for 15 min at room temperature. The NMA-coated cotton swatches were soaked in this solution and uniformly coated using the laboratory wringer. Then water was removed from the swatches by drying at 60°C for 10 min, and curing was performed at 120°C for 5 min. The swatches were washed vigorously with a 0.5% detergent solution for 15 min and rinsed with water several times to remove any unbound chemicals.

Chlorination and Analytical Titration

The treated cotton swatches were chlorinated by soaking in a 10% aqueous solution of NaOCl (household bleach) at pH 7 (adjusted with 6*N* HCl) at ambient temperature for 1 h. Then the swatches were washed with distilled water and dried at 45°C for 1 h to remove occluded chlorine from the surface. The amount of loaded chlorine on the swatches was determined by an analytical titration procedure. The Cl^+ (%) on the cotton swatches was calculated according to eq. (1).

$$Cl^+\% = \left(\frac{35.45 \times N \times V}{2 \times W}\right) \times 100 \quad (1)$$

In this equation, Cl^+% is the weight percent of oxidative chlorine on the samples, *N* and *V* are the normality (equiv/L) and volume (L) of the titrant sodium thiosulfate, respectively, and *W* is the weight of the cotton sample (g).

Stability Testing

Washing tests were performed using AATCC Test Method 61-1996 to evaluate the stability and rechargeability of the coatings. In this procedure, the treated cotton swatches were washed for the equivalent of 5, 10, 25, and 50 machine washing cycles using a laboratory model Lauder-Ometer. The remaining chlorine loadings after each of the washing cycles (X column) and the restored chlorine loadings after each of the cycles both for chlorinated (Y column) and unchlorinated swatches (Z column) were measured using the analytical titration method described above.

The UVA light stability of bound chlorine and the coatings were evaluated by placing the chlorinated and unchlorinated swatches in a UV (Type A, 315–400 nm) chamber, Accelerated Weathering Tester (The Q-panel Company). The swatches were exposed to UVA light for times up to 96 h. The remaining and the restored chlorine loadings were measured after the specified UVA light exposure times.

Wrinkle Recovery Angle Measurement

Wrinkle recovery angles (WRA) of the treated cotton fabrics were measured using AATCC test method 66-1998, Option 2. In this procedure, swatches having the dimensions of 40 mm × 15 mm were folded, and a 500 ± 5 g weight was applied for 5 min. Then the weight was removed, and the sum of the

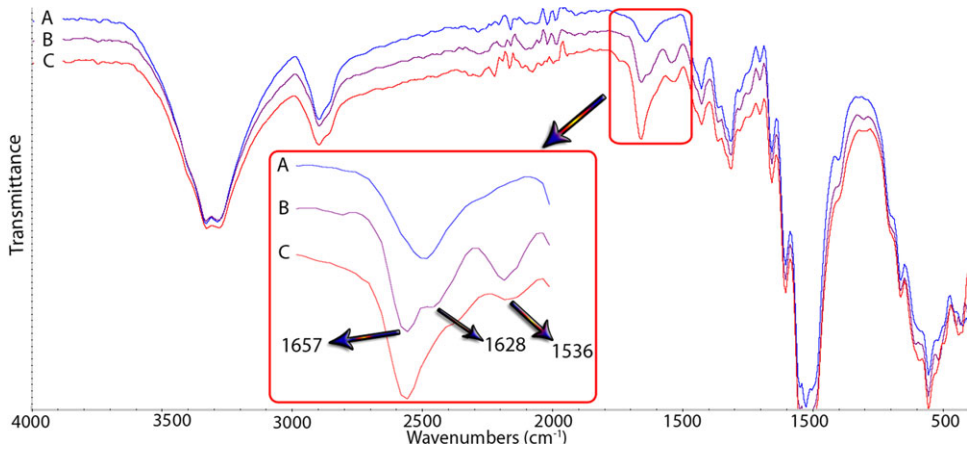

Figure 2. AT-IR characterization of the coatings; A: Pristine cotton, B: NMA-treated cotton, C: NMA/MA-treated cotton [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

recovery angle in warp (lengthwise yarns) and weft (widthwise yarns) direction is reported as WRA.

Biocidal Efficacy Testing

Squares of chlorinated and unchlorinated cotton samples (2.54 cm) were challenged with a Gram-positive bacterium, *S. aureus* (ATCC 6538), and a Gram-negative bacterium, *E. coli* O157:H7 (ATCC 43895), using a modified AATCC "sandwich" Test Method 100-1999. A known concentration of bacterial suspension (25 μL) was placed on the center of a swatch, and a second identical swatch was sandwiched over it. A sterile weight was placed on top to ensure sufficient contact with the bacteria. After contact times of 5, 30, and 60 min, the samples were quenched with 5.0 mL of sterile 0.02*N* sodium thiosulfate solution to remove oxidative chlorine. Serial dilutions of the quenched samples were made and plated on Trypticase agar. The plates were incubated at 37°C for 24 h and then counted to determine the number of viable bacteria.

RESULTS AND DISCUSSION

Characterization of the Coatings

The coatings on the cotton fabric were characterized by ATR-IR spectroscopy. Magnesium chloride in the presence of water catalyzed the reaction between the hydroxyl group of NMA and the hydroxyl groups of cellulose in the presence of heat.[24] As can be seen in Figure 2, there are three additional bands at 1657 cm^{-1}, 1628 cm^{-1}, and 1536 cm^{-1} appearing when NMA was coated onto the cotton surface. These bands correspond to the carbonyl vibrational stretching band modes of the amide group (amide I), double bond vibrational stretching band modes, and out-of-phase combination of the NH in-plane vibrational bending and the CN vibrational stretching bands (amide II), respectively.[27,28] After grafting MA onto the surface, the double bond vibrational stretching band modes disappeared, indicating that the polymerization had occurred. The vibrational band for the carbonyl group of MA could not be distinguished due to overlapping with the carbonyl stretching bands of NMA.

The coatings were further characterized by measuring the oxidative chlorine amount on the cotton fabrics treated with various NMA concentrations. A linear increase in chlorine loading with respect to increasing amount of grafted NMA (measured by weight gain) was observed, which further supports the immobilization of NMA through etherification (Figure 3).

The uniformity of the coatings was confirmed by titration of the chlorine loadings on multiple swatches taken from various positions on the fabric and by examination of SEM micrographs of the swatches.

Washing Stability

The stability and durability toward machine washings of the coated swatches are summarized in Table I. Three types of experiments were performed: the X column represents the Cl^+ loadings of prechlorinated samples after each washing cycle, the Y column represents the Cl^+ loadings of prechlorinated and then rechlorinated samples after a given number of washing cycles, and the Z column represents the Cl^+ loadings of unchlorinated washed samples which were chlorinated after a given number of washing cycles. In general, NMA padded samples showed long-term stability toward repeated laundering. Even though a substantial amount of chlorine was lost after five machine washings, there was still enough chlorine for an

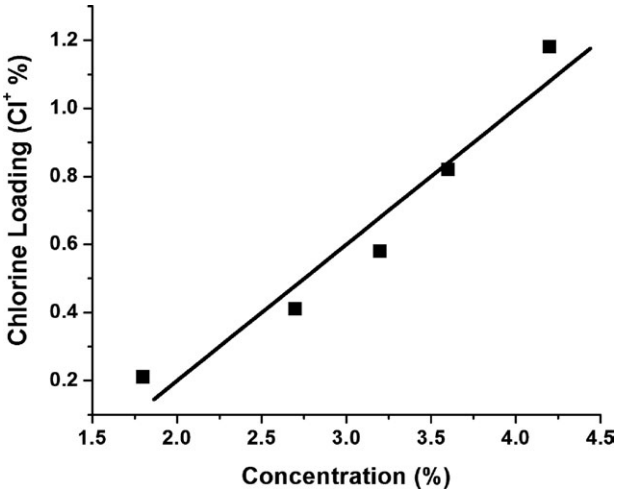

Figure 3. Effect of NMA concentration on chlorine loading.

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Table I. Washing Stabilities of the Coatings

	NMA treated (5 wt %)			NMA/MA treated (5/5 wt %)		
Washing cycles	X[a]	Y[b]	Z[c]	X[a]	Y[b]	Z[c]
0	0.76	0.76		0.40	0.40	
5	0.32	0.61	0.73	0.16	0.53	0.40
10	0.21	0.60	0.70	0.11	0.52	0.39
25	0.16	0.56	0.68	0.08	0.49	0.36
50	0.09	0.50	0.65	0.05	0.44	0.33

[a]X: chlorinated before washing, [b]Y: chlorinated before washing and rechlorinated after washing, [c]Z: unchlorinated before washing, but chlorinated after washing.

effective biocidal activity even after 50 machine washing cycles. A previous study had reported that 0.04% Cl^+ is sufficient to inactive microorganisms,[19] and the chlorine loading, independent of the nature of the *N*-halamine used, generally determines antimicrobial efficacy. When X column samples were rechlorinated (Table I-Y column), most of the chlorine could be restored which indicates that the loss in X columns was due mostly to N—Cl bond dissociation. Similarly with the NMA-coated swatches, a gradual decrease in chlorine loading with respect to increasing washing cycles was observed for the NMA/MA-treated fabrics (Table I-X column). Interestingly, after five machine washings, the loadings were higher than the initial chlorine loading for the Y column of NMA/MA-grafted swatches. A possible explanation for this unexpected result might be that when MA was grafted, a crosslinked film that was difficult to be penetrated was formed. The mechanical effect of the washings abrade this film which leads to NMA sites being more accessible to bleach, resulting in increased chlorine loading. It is interesting to note that the washing stability results for the NMA/MA-treated fabrics herein compare very favorably with those obtained for the more expensive cyclic *N*-halamine epoxide copolymer studied earlier (18% loss of coating [Z column] for NMA/MA versus 0% for the cyclic *N*-halamine after 50 washing cycles).[18]

UVA Light Stability

The stability of the coatings toward UVA light exposure is presented in Table II. When the chlorinated NMA-treated samples were exposed to UVA light, around 70% of the oxidative chlorine was lost within 24 h. However, when they were rechlorinated, the majority of this lost chlorine could be restored. The same swatch was further exposed to UVA light with rechlorination at 24 h intervals. At the end of 96 h of UVA light exposure, upon rechlorination, around 15% of the initial chlorine loading could be restored revealing that there was a decomposition taking place in the structure. The exact mechanism of this decomposition is not known at this time; however, it is speculated that the dehydrohalogenation reaction could be the reason for the observed decomposition (Figure 1). Conversely, when MA was grafted onto cotton, the chlorine loss by UVA exposure was less than the fabrics treated only with NMA. When these swatches were rechlorinated, much higher chlorine loadings

Table II. UVA Light Stabilities of the Coatings

	NMA treated (5 wt %)		NMA/MA treated (5/5 wt %)	
UVA light exposure time (h)	Chlorine remaining	Chlorine restored	Chlorine remaining	Chlorine restored
0	0.72		0.48	
12	0.35		0.29	
24	0.21	0.43	0.21	0.64
36	0.20		0.36	
48	0.13	0.37	0.32	0.70
60	0.16		0.32	
72	0.09	0.19	0.21	0.48
84	0.13		0.25	
96	0.10	0.19	0.19	0.41

than the initial value were obtained for the samples exposed to UVA light up to 72 h. As previously reported in an earlier study, crosslinking increases the halogen stability on a cotton surface.[29] Therefore, as observed in the washing results, a higher loading upon rechlorination could be due to formation of a crosslinked film on the surface upon grafting of MA leading to prevention of the bleach accessing inner sites. NMA is a small molecule and can undergo the etherification reaction with not only the outer surfaces of the cotton fibers but also the inner surfaces. Therefore, upon exposure to UVA light, the decomposition of the coating on the outer surface allowed bleach to reach the inner surface of cotton leading to chlorination of more N—H groups. Again, the UVA stabilities of the chlorinated acyclic *N*-halamine coating (NMA/MA) with a 60% loss of chlorine over 96 h of irradiation compared favorably with the cyclic *N*-halamine epoxide polymer (53% loss of chlorine)[18] over the same period of irradiation.

Wrinkle Recovery Measurement

The wrinkle recovery angle measurement results are shown in Table III. As can be seen, NMA treatment improved the wrinkle recovery angle of the swatches. However, this improvement was not enough to render the surface durable press even for the 10% NMA-treated fabrics. Conversely, when MA was grafted and polymerized on the surface, the wrinkle recovery angle increased tremendously, leading to a durable press functionality.

Table III. Wrinkle Recovery Angle Measurements

Sample	Wrinkle recovery angle ($W + F$)[a]	Chlorine loading (Cl^+%)
Pristine cotton	165	0
5% NMA-treated cotton	220	0.74
10% NMA-treated cotton	235	1.12
5% NMA/5% MA-treated cotton	285	0.45

[a]Total value for warp and filling wrinkle recovery angle.

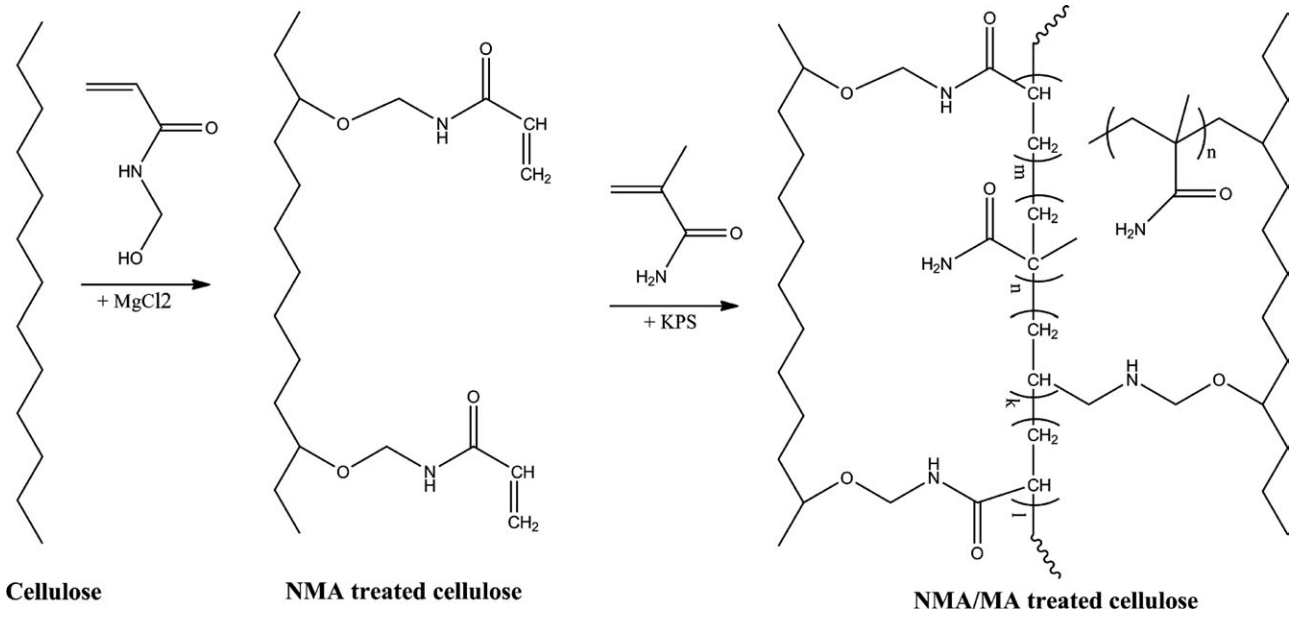

Figure 4. Intermolecular and intramolecular crosslinking of cotton through NMA/MA treatment.

This tremendous increment is due to formation of long polymer chains that are tethered to the cellulose at multiple points resulting in intermolecular and intramolecular crosslinking of cellulose (Figure 4).

Biocidal Efficacy Tests

The chlorinated and unchlorinated swatches were challenged with about 8 logs of *E. coli* O157:H7 and *S. aureus*, and the results are illustrated in Table IV. Both NMA-treated and MA-grafted samples showed excellent biocidal efficacies. Both types of samples exhibited complete inactivation of the Gram-negative and Gram-positive bacteria within 5 min of contact time. Conversely, the unchlorinated swatches, which served as controls, did not provide significant inactivation even after 60 min of contact time. The limited reductions that they exhibited were due to adhesion of bacteria to the surface, rather than to inactivation.[30] The same efficacy was noted for the cyclic *N*-halamine epoxide polymer coating in the earlier study.[18]

It should be noted that the starting chlorine loadings shown in the several tables vary somewhat. Even though the concentrations of the monomers were the same in the coating baths for the various experiments, slight variations in the fabric material and coating procedures used for the swatches in each experiment cause small chlorine loading differences.

CONCLUSIONS

In this study, NMA was used as an *N*-halamine precursor and a tether in grafting MA onto cotton fabric. The fabrics were rendered biocidal by exposure to dilute household bleach. Rechargeable and stable coatings against UV light and laundering were obtained with NMA/MA-treated fabrics. However, it was found that solely NMA-treated cotton fabric also provided sufficient washing and UVA light stabilities for industrial applications, even though it possessed an α-hydrogen adjacent to the amide group. When chlorinated, both NMA and NMA/MA-treated fabrics exhibited an excellent biocidal activity by providing about 8 logs reduction of *E. coli* O157:H7 and *S. aureus* within only 5 min of contact time. Moreover, NMA/MA-treated fabrics not only had antimicrobial but also had durable press functionality due to intercrosslinking and intracrosslinking of cellulose macromolecules.

This study reported for the first time that stable and rechargeable biocidal coatings on cotton fabric can be obtained with a simple pad-dry-cure treatment with NMA using water as a solvent. NMA could not only serve as an *N*-halamine precursor but also could be used to tether vinyl monomers through free radical polymerization, so that cotton fabric having multifunctionality could be obtained. Also, the acyclic *N*-halamine coating functioned almost as well as an earlier cyclic *N*-halamine epoxide coating as regards stabilities to washing and UVA

Table IV. Biocidal Efficacy Test Results

Sample	Contact time (min)	Bacterial reduction (log) *E. coli* O157:H7[a]	Bacterial reduction (log) *S. aureus*[b]
NMA (5 wt %)	60	0.01	1.26
NMA/MA (5/5 wt %)	60	0.12	1.31
NMA-Cl (5 wt %)	5	7.99	7.97
Cl^+% = 0.78	30	7.99	7.97
	60	7.99	7.97
NMA/MA-Cl	5	7.99	7.97
(5/5 wt %)	30	7.99	7.97
Cl^+% = 0.45	60	7.99	7.97

[a]Total bacteria concentration is 9.67×10^7 CFU (7.99 logs), [b]Total bacteria concentration is 9.33×10^7 CFU (7.97 logs).

irradiation and as well as regards antimicrobial efficacy. Thus, the less expensive coating process discussed herein would seem to be a more viable process for industrial use.

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REFERENCES

1. Llata, E.; Gaynes, R. P.; Fridkin, S.; Weinstein, R. A. *Clin. Infect. Dis.* **2009**, *48*, 1434.
2. Burke, J. P. *N. Engl. J. Med.* **2003**, *348*, 651.
3. Thorsteinsson, T.; Masson, M.; Kristinsson, K. G.; Hjalmarsdottir, M. A.; Hilmarsson, H.; Loftsson, T. *J. Med. Chem.* **2003**, *46*, 4173.
4. Sauvet, G.; Dupond, S.; Kazmierski, K.; Chojnowski, J. *J. Appl. Polym. Sci.* **2000**, *75*, 1005.
5. Tiller, J. C.; Liao, C. J.; Lewis, K.; Klibanov, A. M. *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 5981.
6. Madkour, A. E.; Tew, G. N. *Polym. Int.* **2008**, *57*, 6.
7. Wilson, M. *Infect. Control Hosp. Epidemiol.* **2003**, *24*, 782.
8. Dubas, S. T.; Kumlangdudsana, P.; Potiyaraj, P. *Colloids Surf. A: Physicochem. Eng. Aspects* **2006**, *289*, 105.
9. Worley, S. D.; Williams, D. E. *Crit. Rev. Environ. Sci. Technol.* **1988**, *18*, 133.
10. Sun, X.; Cao, Z.; Porteous, N.; Sun, Y. *Acta Biomater.* **2011**, *8*, 1498.
11. Badrossamay, M. R.; Sun, G. *Polym. Eng. Sci.* **2009**, *49*, 359.
12. Zhao, N.; Zhanel, G. G.; Liu, S. *J. Appl. Polym. Sci.* **2011**, *120*, 611.
13. Grunzinger, S. J.; Kurt, P.; Brunson, K. M.; Wood, L.; Ohman, D. E.; Wynne, K. J. *Polymer* **2007**, *48*, 4653.
14. Denyer, S. P.; Stewart, G. *Int. Biodeter. Biodegr.* **1998**, *41*, 261.
15. Liang, J.; Owens, J. R.; Huang, T. S.; Worley, S. D. *J. Appl. Polym. Sci.* **2006**, *101*, 3448.
16. Worley, S. D.; Chen, Y.; Wang, J. W.; Wu, R.; Cho, U.; Broughton, R. M.; Kim, J.; Wei, C. I.; Williams, J. F.; Chen, J. *Surf. Coat. Int. Part B: Coat. Trans.* **2005**, *88*, 93.
17. Kocer, H. B.; Worley, S. D.; Broughton, R. M.; Huang, T. S. *React. Funct. Polym.* **2011**, *71*, 561.
18. Kocer, H. B.; Cerkez, I.; Worley, S. D.; Broughton, R. M.; Huang, T. S. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2845.
19. Liang, J.; Chen, Y.; Ren, X.; Wu, R.; Barnes, K.; Worley, S. D.; Broughton, R. M.; Cho, U.; Kocer, H.; Huang, T. S. *Ind. Eng. Chem. Res.* **2007**, *46*, 6425.
20. Sun, Y.; Sun, G. *J. Appl. Polym. Sci.* **2003**, *88*, 1032.
21. Sun, Y.; Sun, G. *J. Appl. Polym. Sci.* **2001**, *81*, 617.
22. Cerkez, I.; Kocer, H. B.; Worley, S. D.; Broughton, R. M.; Huang, T. S. *Langmuir* **2011**, *27*, 4091.
23. Shih, F. F.; Bertoniere, N. R.; Rowland, S. P. *Text. Res. J.* **1980**, *50*, 433.
24. Shin, Y.; Hollies, N. R. S.; Yeh, K. *Text. Res. J.* **1989**, *59*, 635.
25. Reinhardt, R. M.; Arthur, J. C. *Text. Res. J.* **1980**, *50*, 261.
26. Kaminski, J. J.; Bodor, N.; Higuchi, T. *J. Pharm. Sci.* **1976**, *65*, 553.
27. Gurdag, G.; Oz, G. M. *Polym. Adv. Technol.* **2009**, *20*, 216.
28. Barth, A.; Zscherp, C. *Quart. Rev. Biophys.* **2002**, *35*, 369.
29. Cerkez, I.; Kocer, H. B.; Worley, S. D.; Broughton, R. M.; Huang, T. S. *J. Appl. Polym. Sci.* **2012**, *124*, 4230.
30. Bazaka, K.; Jacob, M. V.; Crawford, R. J.; Ivanova, E. P. *Acta Biomater.* **2011**, *7*, 2015.