Final Progress Report

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List of Abbreviations

ACHT: 2- amino-4-chloro-6-hydroxy-s-triazine
E. coli: *Escherichia coli*
S. aureus: *Staphylococcus aureus*
MAA: methacrylamide
B. subtilis: *Bacillus subtilis*
CES: chloroethyl ethyl sulfide
PEG-DIA: poly (ethylene glycol) diacrylate
PMAA: polymethacrylamide

Abstract

Protective clothing is one of the most important personal protective equipment for emergency responders, who are facing increased occupational threats in their high risk jobs. However, currently used protective clothing has significant shortfalls, including the lack of multiple-purpose protective clothing, the unsatisfactory protective performance, and the tradeoff between protection and comfort. Some of these problems cannot be solved using current principles and technologies. Innovative approaches are needed to develop wearable multipurpose protective clothing to enhance the safety and health of emergency responders.

The long term goal of this project is to develop novel wearable thermal, biological, and chemical protective clothing materials with enhanced comfort performance for emergency responders. To reach this goal, currently used thermal protective fabrics were chosen as the base material, and a coating technology was employed to coat reusable and rechargeable polymeric oxidizers onto the base fabrics through breathable flame-retardant coatings.

The specific aims of the proposed research are to: (1) screen reusable and rechargeable polymeric oxidizers that can effectively decontaminate surrogates of biological and chemical warfare agents; (2) establish the optimal formulations and technologies to coat the selected polymeric oxidizers onto thermal protective fabrics through breathable flame-retardant coatings containing chemical absorbents; (3) evaluate the thermal protective, biological protective and chemical protective functions, the mechanical properties, as well as the comfort performance of the new fabrics; and (4) provide preliminary data for the determination of the cost-effectiveness of the new approach.

In our studies, we first evaluated chloromelamines, N-halamines, nitroxyl radicals, photosensitizers and chromate salts as reusable oxidizers. We found that chloromelamines and amide-based N-halamines could effectively inactivate gram-negative bacteria, gram-positive bacteria, fungi, and viruses in less than 5 min, and spores in less than 3 h. Both of them could also oxidize different chemicals including CES. Other oxidizers showed little effect on spores. Therefore, we decided to use chloromelamines and amide-based N-halamines as the oxidizers for the next step.

Upon the successful completion of the first step, we studied how to incorporate the oxidizers into different fabrics. For chloromelamines, we synthesized a novel compound, ACHT, which could be directly covalently bound onto fabrics materials. The treated fabrics inactivated multi-drug resistant *E. coli* and *S. aureus* in less than 1 min. For amide-based N-halamines, we successfully grafted MAA onto different fabric materials including Nomex and Kevlar. To select coating formulations, we evaluated 5 commercially available textile coatings, and we have successfully formulated the coating formulations which bound tightly to Nomex and Kevlar, and the coatings were durable for 50 washes. We found that the treated textiles inactivated 1,000,000 spores/mL of *B. subtilis* spores in less than 2 h. The spore-killing functions were stable for more than 12 months, and most importantly, once it was lost, it could be easily recharged by washing in the presence of chlorine bleach. The recharge process could be repeated for more than 20 times. We also found that the treated fabrics decomposed 85% of CES in 30 min, and that the fire-resistant performances of the Nomex and Kevlar fabrics were not affected. Nevertheless, after treatment,

although the tearing strength was increased to around 2 times higher, the abrasion resistance decreased because the fabrics become more rigid than before.

These results successfully demonstrated the concept that wearable multi-purpose protective clothing can be developed to provide thermal, biological, and chemical protective activities simultaneously. These findings will serve as an important base for the continuation and expansion of the project to utilize the new technology in real applications to significantly enhance the occupational safety and health of emergency responders. Based on these results, an R01 application, Multi-Protective Clothing For Emergency Responders will be submitted to NIOSH to continue and expend the studies to achieve this long-term goal.

Highlights/Significant Findings

Chloromelamines and amide-based N-halamines could effectively inactivate gram-negative bacteria, gram-positive bacteria, fungi, and viruses in less than 5 min, and spores in less than 2 h. Both of them could also oxidize different chemicals including chloroethyl ethyl sulfide.

Choromelamines and amide-based N-halamines could be coated onto Nomex and Kevlar. The coated fabrics inactivated 1,000,000 spores/mL of *B. subtilis* spores in less than 2 h. The spore-killing functions were stable for more than 12 months, and most importantly, once it was lost, it could be easily recharged by washing in the presence of chlorine bleach. The recharge process could be repeated for more than 20 times. The treated fabrics decomposed 85% of CES in 30 min. The fire-resistant performance, tearing strength and comfort performance of the coated fabrics were not negatively affected.

Translation of Findings

Since the 9.11 terrorist attack, the world in which emergency responders work has changed dramatically. Nowadays, emergency responders must be prepared for large-scale and long-term incidents involving a wide range of unanticipated and potentially combined hazards. Protective clothing is among the most important personal protective equipment for emergency responders. However, lessons learned from recent terrorist attacks suggest that currently used protective clothing has significant shortcomings, which include a lack of multiple-purpose protection, unsatisfactory protective performance, and an undesirable tradeoff between protection and comfort.

The results of the current project demonstrate that it is feasible to combine thermal, biological and chemical protective functions into one clothing system to provide multiple protections. These added protections are expected to significantly enhance the safety and health of emergency responders in dealing with future high-risk incidents involving multiple threats (e.g., bioterrorism/chemical terrorism incidents, fire accidents in biological and chemical containment facilities, military actions involving both biological and chemical warfare agents, etc.). With further improvements of the clothing design and more detailed tests of the new systems (which have been outlined in a separated R01 application, Multi-Protective Clothing For Emergency Responders; application number: 1R01OH009272-01A1; this application is currently pending), there is great potential for the new systems to be used in real applications in the near future to improve the safety and health of emergency responders.

Outcomes/Relevance/Impact

Treatments that can actually inactivate biological agents and decompose chemical agents have been developed to treat thermal protective clothing materials. These results demonstrated a new concept in the development of protective clothing: protective clothing can not only act as physical barriers of multiple hazards, but also inactivate them upon contact. This concept offers new insights and new opportunities in protective clothing design, which will significantly enhance the safety and health of emergency responders.

Scientific Report

Background

Emergency responders (firefighters, police, emergency medical workers, construction workers, etc.) have high levels of occupational risk in their "routine" jobs and even higher levels of threat in terrorism incidents. During the 9.11 attack at the World Trade Center, 450 emergency responders perished while responding to the attacks – about one-sixth of the total number of victims. Hundreds more were seriously injured. Since then, emergency responders have had to prepare to deal with new, multiple, and often unknown occupational hazards. The importance of protective clothing for emergency responders cannot be overemphasized; this is the last safeguard protecting the human body from exposure to hazardous agents. However, lessons learned from recent terrorist attacks suggest that currently used protective clothing has significant shortfalls.

For one thing, protective clothing is not designed for multiple hazards. The hazards encountered in terrorism incidents may include fire, heat, explosion, respiratory irritants, chemically hazardous materials, biologically hazardous materials, infectious agents from dead bodies, radioactive contaminants, etc. However, most protective clothing is designed for one hazard, not multiple hazards. For example, thermal protective clothing cannot protect emergency responders from biological and infectious disease hazards, and bio-protective clothing cannot protect the wearer from burns.

Further, in many cases, even the protection against a single hazard is inadequate. For instance, currently used chemical and biological protective clothing can largely prevent the penetration of chemical or biological agents, but the clothing cannot destroy these agents. Thus the clothing materials may serve not only as carriers of chemical and biological agents but also as excellent media for the growth and transmission of biological agents. As a result, clothing surfaces could become important sources of cross-contamination. Furthermore, in the case of a leakage or "strike through" of chemical or biological agents (which is not uncommon in real uses), the barrier function would be totally lost and the emergency responders would face great danger.

Finally, most protective clothing is not wearable enough to "allow extended wear during demanding physical labor". The design of protective clothing for emergency responders has been largely based on the concept that clothing materials are physical barriers to prevent the penetration of hazardous materials. To ensure the barrier functions, most protective clothing is heavy, thick, and/or air/moisture impermeable. Unfortunately, because of this design, protective clothing generates too much heat stress and inhibits the activities of users. Consequently, in terrorist attacks, some emergency responders have actually chosen not to wear their protective clothing because the clothing impeded their ability to accomplish their missions.

Clearly there is a need for the development of multiple-purpose protective clothing that is safe enough, practical enough, and wearable enough to protect emergency responders in their high risk "routine jobs" and in multiple-threat terrorism incidents.

Specific aims

The specific aims of the proposed research are to:

(1) screen reusable and rechargeable polymeric oxidizers that can effectively decontaminate surrogates of biological and chemical warfare agents;

(2) establish the optimal formulations and technologies to coat the selected polymeric oxidizers onto thermal protective fabrics using breathable flame-retardant coatings containing chemical-absorbents;

(3) evaluate the thermal protective, biological protective and chemical protective functions, mechanical properties, and comfort performance of the new fabrics; and

(4) collect preliminary data to determine the cost of the new approach.

Procedures and Methodology

The development of new protective clothing largely depends on the improvement of fabric materials. Therefore, in this project we developed novel wearable thermal, biological, and chemical protective clothing fabrics with enhanced comfort for emergency responders.

Currently used thermal protective fabrics (Nomex® and Kevlar®) were used as the base material, and a coating technology was employed to introduce biological and chemical protective functions. Coating is a simple, practical, and cost-effective approach to achieve multiple functions in one treatment, and it is currently widely used to introduce new functions into textile materials. Using this technology, reusable and rechargeable polymeric oxidizers were coated onto the base fabrics through breathable flame-retardant coatings. By carefully controlling the coating technologies, the original thermal protective functions of the base fabrics were retained. In addition, the polymeric oxidizers could effectively decontaminate chemical/biological and infectious agents on contact, making the fabrics much safer during wearing. Extensive uses may consume most of the oxidizers and reduce the biological/chemical protective function. However, the oxidizers can be easily regenerated by a recharge reaction, and the original protective activity can be readily resumed. The new fabrics developed were made air/moisture permeable by using breathable flame-retardant coatings to enhance the comfort performance.

Results and Discussion

To date, we have made exciting progress in achieving the specific aims. The major results are described below.

(1) To screen reusable and rechargeable polymeric oxidizers that can effectively decontaminate surrogates of biological and chemical warfare agents:

In this study, we have evaluated chloromelamines, N-halamines, nitroxyl radicals, photosensitizers and chromate salts. The chemicals were listed below in Table 1.

Table 1. Polymeric oxidizers (PO) used in the screening process

Code	Chemical name	Category	Sources
PO-1	Poly[2,4-bis(chloroamino)-6-vinyl-1,3,5-triazine]	Chloromelamine	Synthesized in the investigator's lab
PO-2	Poly[1-chloro-3-(4'-vinyl benzyl)-5,5-dimethylhydantoin]	N-halamine	Synthesized in the investigator's lab
PO-3	Poly[[6-[1,1,3,3-tetramethylbutyl)amino-striazine-2,4-diyl-[(2,2,6,6-tetramethyl-4-piperidyl)imino]-hexamethylene-[-[(2,2,6,6-tetramethyl-4-piperidyl)imino], N-oxides	Nitroxyl radical	Cytec Industries, Inc. (West Paterson, NJ)
PO-4	Protoporphyrin IX	Photosensitizer that generates singlet oxygen and free radicals	Sigma-Aldrich
PO-5	Polyvinylpyridinium chromates	Chromate salt	Sigma-Aldrich

We found that chloromelamines and amide-based N-halamines could effectively inactivate gram-negative bacteria, gram-positive bacteria, fungi, and viruses in less than 5 min, and spores in less than 2 hr. Both of them could also oxidize different chemicals including chloroethyl ethyl sulfide. Other oxidizers showed little effect on spores. Therefore, we decided to use chloromelamines and amide-based N-halamines as the oxidizers for the next step.

(2) To establish the optimal formulations and technologies to coat the selected polymeric oxidizers onto thermal protective fabrics using breathable flame-retardant coatings containing chemical-absorbents:

Upon the successful completion of the first step, we studied how to incorporate the oxidizers into different fabrics. For chloromelamines, we synthesized a novel compound, ACHT, which could be directly covalently bound onto fabrics materials. The treated fabrics inactivated multi-drug resistant E. coli and S. aureus in less than 1 min. For amide-based N-halamines, we successfully grafted MAA onto different fabric materials including Nomex and Kevlar.

The MAA treatment was studied in details. The fabrics were prepared through a 2-step approach: coating crosslinked PMAA onto Kevlar fabrics through the *in-situ* copolymerization/crosslinking of MAA with PEG-DIA, and chlorination of the coated fabrics to transform part of the amide groups of the coated PMAA into acyclic N-halamines to provide biological protective functions. In the coating process, MAA, PEG-DIA, and the initiator (sodium persulfate, $Na_2S_2O_8$) dispersed in a fire-retardant coating emulsions were padded onto the surfaces of Kevlar fabrics. The padded fabrics were cured at 110 °C for 20 min. During curing, the initiator generated free radicals, which initiated the copolymerization of MAA and PEG-DIA on the fabric surfaces. MAA formed PMAA polymer chains, and PEG-DIA acted as a crosslinker, crosslinkng the PMAA chains and generating an insoluble three-dimensional network that attached to Kevlar surfaces. After coating, the fabrics were treated with diluted chlorine bleach containing 1200 ppm of active chlorine to transform part of the coated PMAA moieties into acyclic N-halamines. The whole process is schematically shown in Figure 1.

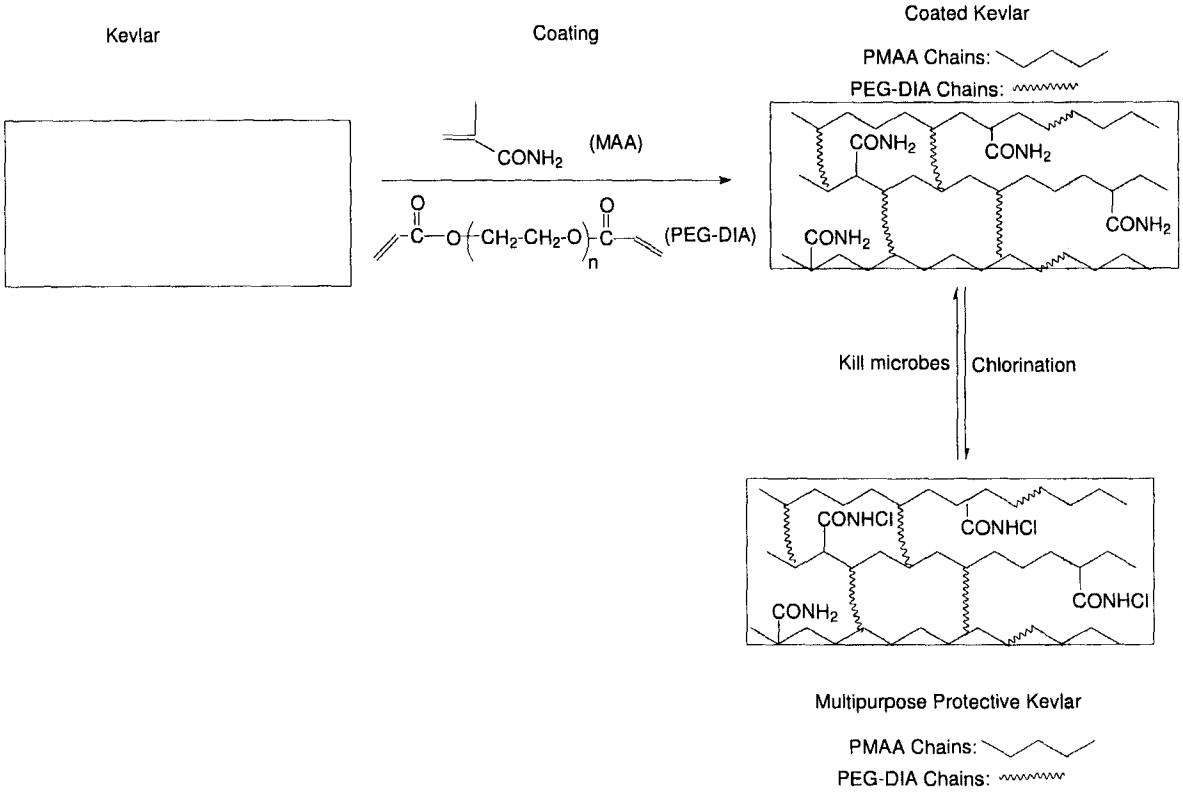

FIGURE 1. Simplified preparation process of the multipurpose protective fabrics, using coating onto Kevlar as an example

The influences of processing conditions on the coating reactions were investigated. Since it was the active chlorines on the coated fabrics that provided biological and chemical protective functions, the active chlorine content on the coated fabric was used as an indication of the effectiveness of the coating reactions.

As an example, Figure 2 presented the effects of varying initiator concentration on the coating reactions. Keeping other conditions constant, the active chlorine content on the coated fabrics increased and then decreased after an optimum initiator value of 3%. As the concentration of $Na_2S_2O_8$ increases, more initial free radicals were formed to initiate the copolymerization/crosslinking of MAA with PEG-DIA, thereby increasing the amount of coated PMAA and thus the active chlorine content. However, when the concentration of $Na_2S_2O_8$ was higher than the optimum value, further increase in initiator concentration might generate too much free radical, which would terminate the growing PMAA chains, leading to lower PMMA molecular weight, less available amide groups for chlorination, and thus, lower active chlorine content.

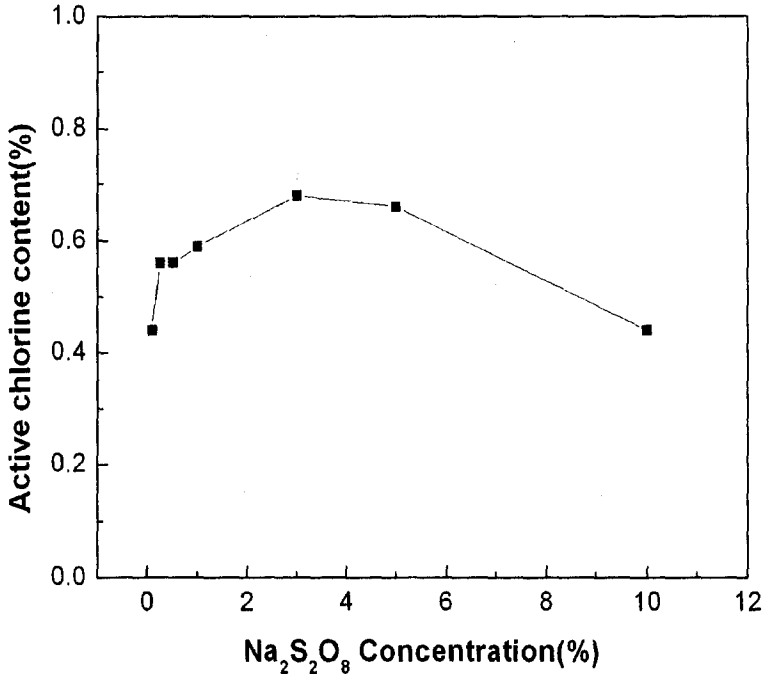

FIGURE 2. The effects of initiator concentration on the active chlorine content of chlorinated PMAA-coated Kevlar fabrics (MAA concentration: 10 wt%; PEG-DIA molar content in the monomer mixture: 5%; Temperature: 110°C; Time: 20 min)

Figure 3 showed the effects of PEG-DIA molar content in monomer mixtures on the coating reactions. Without the presence of PEG-DIA, no active chlorine could be detected on the resultant fabrics. This was a reasonable finding because if PEG-DIA was not included in the coating formula, MAA would polymerize into linear PMAA. However, PMAA was water soluble, which could be easily removed in the washing process. The addition of PEG-DIA led to the formation of insoluble three-dimensional PMAA/PEG-DIA coating networks on the fabrics, resulting in detectable active chlorines on Kevlar surfaces. As expected, in the range of 0-15% of PEG-DIA molar content in the monomer mixtures, increasing PEG-DIA content significantly increased active chlorine content on the coated fabrics. For instance, at a PEG-DIA content of 1%, the active chlorine content was 0.15%; when the former was increased to 2.5%, the latter was raised to 0.55%. After that, the increasing trend became less obvious, and at a PEG-DIA content of 14.3%, the active chlorine content slowly increased to 0.7%.

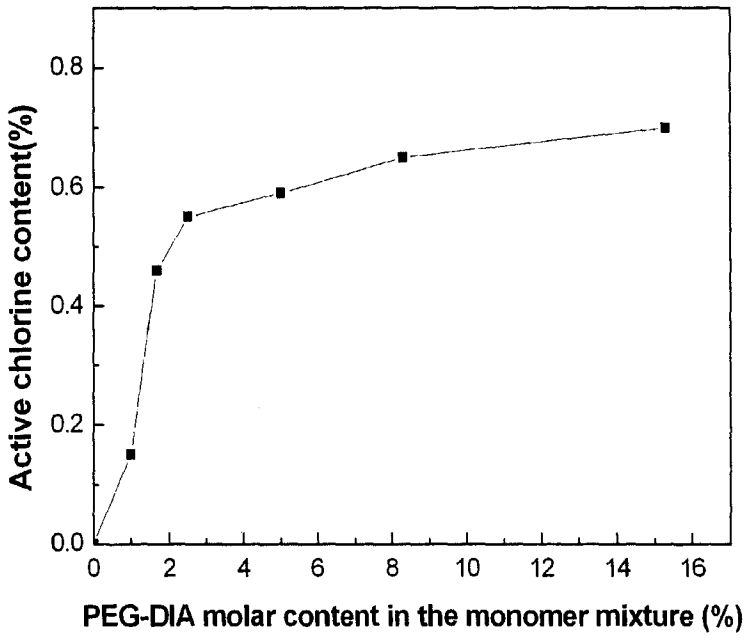

FIGURE 3. The effects of PEG-DIA molar content in the monomer mixture on the active chlorine content of chlorinated PMAA-coated Kevlar fabrics (MAA concentration: 10 wt%; $Na_2S_2O_8$ concentration: 0.5%; Temperature: 110°C; Time: 20 min)

The coating reactions were characterized with ATR-IR studies, as shown in Figure 4. In the spectrum of uncoated Kevlar (Figure 4, a), the peak centered at 3415 cm^{-1} was attributable to the stretching vibration of the N-H bond, and the band at 1650 cm^{-1} was caused by the C=O stretching vibration of the amide groups. In the spectrum of the chlorinated PMAA-coated Kevlar fabric (Figure 4, b), in addition to the 3415 and 1650 cm^{-1} bands, two new peaks at 2917 and 2847 cm^{-1} could be observed, which must be related to the C-H vibrations of the coated PMAA and PEG-DIA polymer chains. Moreover, in the difference spectrum (Figure 4, c, subtracting spectrum a from spectrum b), three new peaks at 1738, 1668, and 1591 cm^{-1} could be detected. The 1738 cm^{-1} peak was assigned to the C=O stretching vibration of the ester groups of the PEG-DIA moieties, and the 1668 and 1591 cm^{-1} bands were attributed to the amide I and amide II vibrations of the chlorinated amide groups of the coated PMAA polymer chains. These findings further suggested that PMAA/PEG-DIA networks were successfully coated onto the surface of Kevlar fabrics.

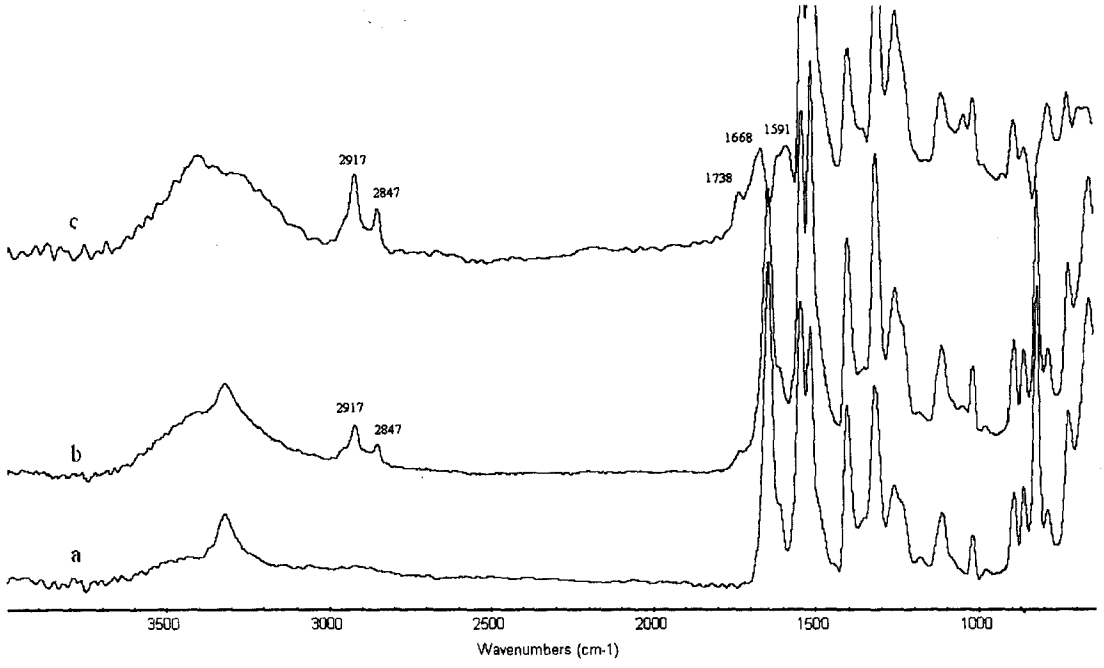

FIGURE 4. ATR-IR spectra of (a) uncoated Kevlar fabrics, (b) chlorinated PMAA-coated Kevlar fabrics, and (c) difference spectrum of spectrum b and spectrum a (subtracting spectrum a from spectrum b).

(3) To evaluate the thermal protective, biological protective and chemical protective functions, mechanical properties, and comfort performance of the new fabrics.:

The biological protective functions of the chlorinated MAA-coated Kevlar fabrics were challenged with gram-negative bacteria, gram-positive bacteria, fungi, viruses and spores. The minimum contact time for a total kill of each microbial species was presented in Table I. With 0.65% active chlorine content, the chlorinated PMAA coated Kevlar fabrics provided a total kill 10^8-10^9 CFU/mL of *E. coli*, *S. aureus*, and *C. tropicalis* in 5 min. In the antiviral tests, it took 20 min for the fabrics to offer a total kill of 10^6-10^7 PFU/mL of MS2 virus. *Bacillus subtilis* spores (surrogate of anthrax spores) are known to be highly resistant to disinfections; spore coat, cortex and inner protoplast have been identified as possible barriers against the attack of biocidal agents. However, with 1.0% active chlorine content, the chlorinated PMAA coated Kevlar fabrics provided a total kill of 10^4-10^5 cells /mL of the spore in 2 h. To the best of our knowledge, this is the first example of Kevlar fabrics (one of the most widely used fabric materials in fire/thermal protective clothing) that can inactivate not only gram-negative bacteria, gram-positive bacteria, and fungi, but also viruses and spores. These unique characteristics make the coated Kevlar fabrics attractive candidates for a wide range of multipurpose protective applications.

Table I. Antibacterial, antifungal, antiviral and anti-spore efficacies of the chlorinated PMAA-coated kevlar fabrics

Microorganisms	Active chlorine content (%)	Minimum contact time for a total kill
*E. coli**	0.65	5 min
*S. aureus**	0.65	5 min
*C. tropicalis**	0.65	5 min
MS2 virus**	0.65	20 min
*Bacillus subtilis****	1.0	2 hr

* Bacterial or fungal concentration: 10^8-10^9 CFU/mL; ** Viral concentration: 10^6-10^7 PFU/mL; *** Spore concentration: 10^4-10^5 spores/mL

The bio-protective effect of the chlorinated PMAA-coated Kevlar fabrics were also confirmed by SEM studies. The chlorinated PMAA-coated Kevlar fabrics and uncoated Kevlar fabrics were first contacted with *E. coli*, *S. aureus,* and *C. tropicalis* suspensions, respectively, and then incubated in the corresponding broth solutions. At the end of incubation, the broth solutions containing uncoated Kevlar fabrics became very cloudy, indicating heavy microbial growth. In the broth solutions that contained chlorinated PMAA-coated Kevlar fabrics, however, the broth solutions remained very clear. Shown in Figure 5 were the scanning electron micrographs of the resultant fabrics. A large amount *E. coli*, *S. aureus,* or *C. tropicalis* adhered to the uncoated Kevlar (Figure 5, a-c), indicating that uncoated Kevlar did not have any capabilities to inactivate biological agents. This could cause serious cross-contamination and cross-infection concerns in real applications, particularly in incidents involving biological agents. On the coated samples (Figure 5, a'-c'), however, only domains containing the coatings could be detected on the fiber surfaces, and no adherent microorganisms could be observed, further suggesting the potent biological protective functions of the PMAA coated Kevlar fabric materials.

To determine the chemical protective functions, 1 μl of each CES was placed onto the surface of 1 gram of treated fabric. After a certain period of contact time (1 min–8 h), the fabric was placed into 10 ml methylene chloride to quench the reaction. After vigorous shaking, the composition of the solution was analyzed by GC-MS to determine whether the coated polymeric oxidizers can decontaminate the CW simulants. The sample procedures were also applied to the untreated original fabrics to serve as controls. After 30 min, around 85% of the original CES was decomposed on the coated fabric. The uncoated fabric, however, did not show any decomposing effect.

Durability and rechargeability are important features of the chlorinated PMAA coated fabrics. The coated fabrics have been stored at 21 °C and 65% RH for more than three months. During this period of time, the active chlorine content and the antibacterial, antifungal, antiviral, and anti-spore functions of the samples were essentially the same, suggesting excellent storage stability. Meanwhile, coated Kevlar fabrics containing 0.65% of active chlorine were also treated with 0.3% sodium thiosulfate to quench the active chlorine and then re-bleached with 1200 ppm of active chlorine solutions at room temperature for 1 h. After 50 cycles of the "quenching-bleaching" treatments, the chlorine contents and biological protective activities of the fabrics were still the same, indicating that the biological protective functions were fully rechargeable (see Figure 1 for mechanism).

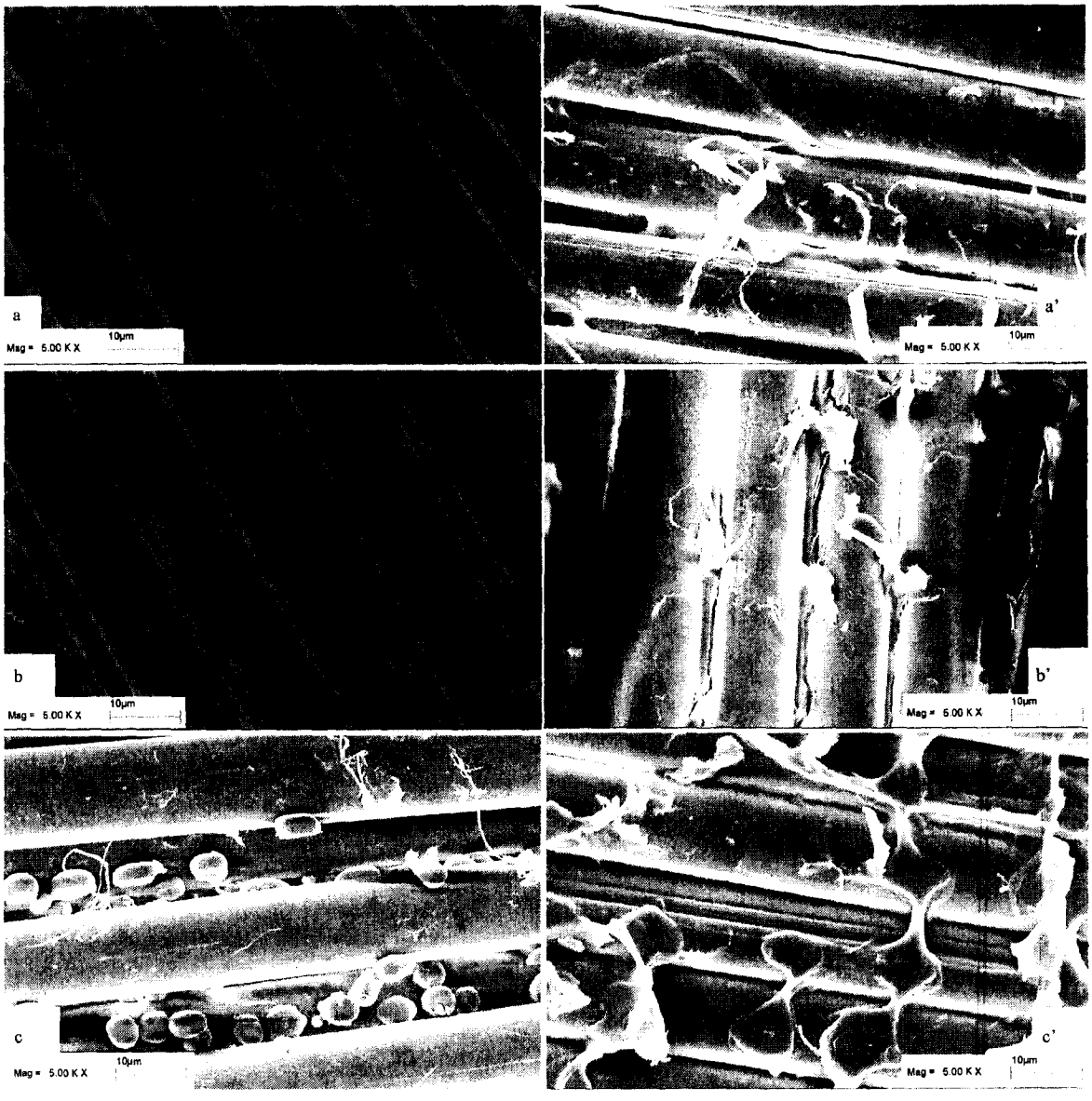

FIGURE 5. SEM results of the biological protective functions of the fabric samples: (a) uncoated Kevlar fabrics challenged with S. aureus, (a') chlorinated PMAA-coated Kevlar fabrics challenged with S. aureus, (b) uncoated Kevlar fabrics challenged with E. coli, (b') chlorinated PMAA-coated Kevlar fabrics challenged with E. coli, (c) uncoated Kevlar fabrics challenged with C. tropicalis, and (c') chlorinated PMAA-coated Kevlar fabrics challenged with C. tropicalis.

Another attractive feature of the chlorinated PMAA coated Kevlar fabric was that most of the original excellent physical properties of the fabric were successfully retained. The limiting oxygen index (LOI) of the fabrics were unchanged after the coating treatment, and both fabrics passed the vertical flame test following test procedures specified in California Fire Code Title 19,1237.1, suggesting that the coating treatment had no negative impact on the fire protective functions of the fabrics. The coating significantly increased the tearing strength (more than two folds of increase) because the coatings could bind the fibers together to share the tearing force. The moisture permeation rates of the coated and uncoated fabrics were essentially the same, indicating that the crosslinked PMAA based coatings had little negative impact on the comfort performance of the fabrics.

(4) To collect preliminary data to determine the cost of the new approach

If the thermal fabrics are coated with the PMAA technology, at reagents grade, the added cost of the chemicals for the thermal protective fabrics will be less than $0.5/yard, pointing to excellent cost-effectiveness of the new approach. For real applications, chemicals at industrial grade will be even less expensive, but the consummation of energy and water will need to be counted, and this will be determined if the new technology is to be used in large scale preparation.

Conclusions

Chloromelamines and amide-based N-halamines could effectively inactivate gram-negative bacteria, gram-positive bacteria, fungi, and viruses in less than 5 min, and spores in less than 2 hr. Both of them could also oxidize different chemicals including chloroethyl ethyl sulfide (CES).

Choromelamines and amide-based N-halamines could be coated onto Nomex and Kevlar. The coated fabrics inactivated 1,000,000 spores/mL of *B. subtilis* spores in less than 2 h. The spore-killing functions were stable for more than 12 weeks, and most importantly, once it was lost, it could be easily recharged by washing in the presence of chlorine bleach. The recharge process could be repeated for more than 50 times without affecting the biocidal functions. The treated fabrics decomposed 85% of CES in 30 min. The fire-resistant performances, strength, and comfort performance of the original fabrics were not negatively affected. The coating approach points to great cost-effectiveness.

Publications

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Yao J, Sun Y: [2008] Preparation and Characterization of Polymerizable Hindered Amine-Based Antimicrobial Fibrous Materials. Industrial & Engineering Chemistry Research, in press.

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