Antimicrobial Polyethylene Terephthalate (PET) Treated with an Aromatic *N*-Halamine Precursor, *m*-Aramid

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Received 15 September 2008; accepted 23 June 2009
DOI 10.1002/app.31016
Published online 17 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A commercial *m*-aramid as *N*-halamine precursor has been coated onto polyethylene terephthalate (PET) fabric surface by pad-dry-curing process. The process is accomplished by padding the scoured PET fabric through the homogeneous *m*-aramid solution, drying at 150°C for 3 min, and curing at 230°C for 3 min. The PET surface coated with *m*-aramid was characterized using fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). FTIR exhibits new bands in the 1645 and 1524 cm^{-1} regions as characteristic of *m*-aramid bands, which indicate the PET fabric coated with *m*-aramid. XPS results show a distinguishable peak at binding energy 398.7 eV, which confirms the nitrogen atom of *m*-aramid on the PET surface. In addition, SEM image shows a layer of coating onto the PET surfaces, which demonstrates the presence of *m*-aramid coating on the surface of the PET. After exposure to dilute sodium hypochlorite solution, exhibition of antimicrobial activity on the coated PET is attributed to the conversion of *N*-halamine moieties from the *N*-halamine precursor. The chlorinated PET showed high antimicrobial activity against Gram-negative and Gram-positive bacteria. The chlorinated PET coated with 10% *m*-aramid exhibited about 6 log reductions of *S. aureus* and *E. coli* O157:H7 at a contact time of 10 and 30 min, respectively. Furthermore, the antimicrobial activity was durable and rechargeable after 25 wash cycles. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3835–3840, 2009

Key words: polyesters; biomaterials; coatings

INTRODUCTION

For the last few decades, *N*-halamine compounds have received considerable interest as biocides although the research efforts for *N*-halamine antimicrobials have been devoted to water disinfection.[1–3] Recently, applications of *N*-halamine antimicrobials to polymers and fibers have extensively studied.[4–12] *N*-Halamines refer to compounds that contain one or more nitrogen-halogen covalent bonds. It is known that *N*-halamine structures containing adjacent α-hydrogen of a nitrogen-halogen bond are less effective in the preparation of stable *N*-halamine. This is due to the fact that adjacent α-hydrogen of a nitrogen-halogen bond causes dehydrohalogenation. *N*-halamine compounds containing nitrogen with no adjacent α-hydrogen are preferred as *N*-halamine precursors.[4,6] In fact, synthesized *N*-halamine precursors have been studied for imparting antimicrobial properties to polymeric materials including cellulose, polyethylene terephthalate (PET), and nylon.[4,7–12] However, barely any research has been done to investigate the antimicrobial activity of commercially available *N*-halamine precursors, i.e., aromatic polyamides which contain an amide groups between two aromatic rings. Poly(*m*-phenyleneisophthalamide), *m*-aramid known as Nomex and poly(*p*-phenyleneterephthalamide), *p*-aramid known as Kevlar (Fig. 1) in the industry are high-performance aromatic polyamides which have wide variety of applications in daily life. More recently, they have been proposed as *N*-halamine precursors because no adjacent α-hydrogen of a nitrogen-halogen bond makes impossible the elimination of halogen after chlorination.[4,13] Moreover, Nomex can be chlorinated without any significant decomposition while Kevlar decomposes under the same chlorination conditions.[13,14]

A considerable amount of work has been made on finishing textiles with antimicrobial compounds since a wide range of textile products are good media for growth of microorganism.[15] In addition, consumers are increasingly aware of the hygienic life style and there is a necessary and expectation for a wide range of textile products treated with antimicrobial properties. Polyester fibers are used

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Contract grant sponsor: Yeungnam University.

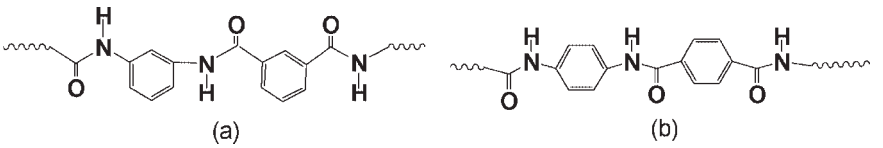

Figure 1 Chemical structures of (a) *m*-aramid (Nomex) and (b) *p*-aramid (Kevlar).

considerably in the textile industry. They provide various favorable properties including relatively strong strength, low moisture regain, good heat and dimensional stability, and relatively lower production cost. However, the limited reaction sites of polyester, i.e., PET, could be one obstacle to applying PET on diverse functional applications such as antimicrobial finishing. Accordingly, the improvement of the antimicrobial properties of PET fibers may be important for a wide range of applications such as medical applications. Recently, medical textile is one of the most rapidly expanding fields in the technical textiles which are the fastest growing and prospective future of textile industries worldwide.[16]

In this study, one of the commercial uses of fiber-forming polymer, *m*-aramid, was coated on the surface of the PET in order to render antimicrobial. This study will demonstrate an alternative way of creating the *N*-halamine biocidal functionality on PET without synthesis of *N*-halamine precursors. The *m*-aramid coated onto PET fabric was characterized using fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy, x-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Antibacterial efficacy, durability and rechargeability after repeated laundering of coated *m*-aramid onto the PET fabrics were also investigated.

EXPERIMENTAL

Materials

Calcium chloride ($CaCl_2$) and dimethylacetamide (DMAc) were purchased from either Aldrich Chemical Co. or Fisher Scientific Co. They were used as supplied without further purification. The *m*-aramid was a Dupont fiber product. Polyester fabric (100%) was purchased from Korea Apparel Testing and Research Institute.

Preparation of PET fabric coated with *m*-aramid

A homogeneous solution of *m*-aramid was prepared by adding 3, 15, and 30 g of *m*-aramid fibers into 300 mL of dimethylacetamide (DMAc) including 3, 12, and 21 g of calcium chloride, respectively, while stirring at 120°C for 3 h. The homogeneous *m*-aramid solution was applied to scoured PET fabric using pad-dry-curing process. The process is accomplished by padding the scoured PET fabric through the homogeneous *m*-aramid solution to a wet pickup of about 100%, drying at 150°C for 3 min, and curing at 230°C for 3 min. The cured PET fabrics were boiled in 0.5% AATCC detergent solution for 5 min before washing with distilled water and air dried. For each sample, two replicates were performed.

Characterization of PET fabric coated with *m*-aramid

Fourier transform Infrared-attenuated total reflection spectroscopy

The FTIR spectra were obtained using a Spectrum GX (Bruker Co., Germany) equipped with ATR cell. The spectra between 700 to 4000 cm^{-1} with a resolution of 2 cm^{-1} were recorded.

X-ray photoelectron spectroscopy

XPS spectra were carried with a ULVAC-PHI Quantera SXM. Monochromate Al was used as an X-ray source. Beam size, beam power, electron source and pass energy were 100 μm, 100 W, 18 kV and 26 eV, respectively.

Scanning electron microscopy

SEM was conducted with a Hitachi S-570 at 15 kV accelerating voltage. Samples were coated with gold under argon purge before examination.

Chlorination and titration

A commercial 6% sodium hypochlorite solution was diluted to 3300 ppm of the commercial strength with distilled water. The diluted solution was applied to chlorinate the PET fabrics. The PET fabrics were soaked in the solution (pH buffered to 7) at ambient temperature for 60 min and rinsed with a large excess of distilled water. Then, the samples were dried at 45°C for 2 h to remove any unbounded chlorine. An iodometric/thiosulfate titration procedure was employed to analyze the oxidative chlorine content. The $[Cl^+]$% in the sample was calculated with the following equation:

$$[Cl^+]\% = (V \times N \times 35.45)/(W \times 2 \times 10)$$

where $[Cl^+]$% is the wt % of oxidative chlorine on the sample, V is equal to the volume of the titrant

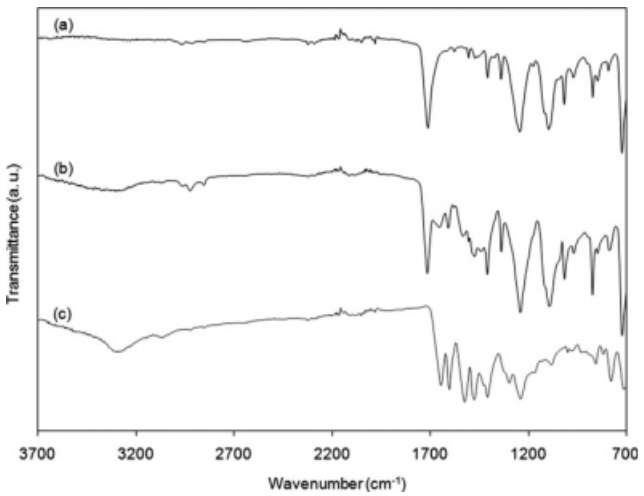

Figure 2 FTIR-ATR spectra of (a) untreated PET (b) PET treated with *m*-aramid (10%), and (c) *m*-aramid fiber.

[sodium thiosulfate solution (mL)], N is equal to the normality of the titrant, and W is the weight of the sample (g). The constants, 35.45, are molecular weight of Cl and 2 is the change in oxidation state of Cl during titration, and 10 is to normalize the units in numerator and denominator to give % Cl.

Laundering test

AATCC Test Method 61-2001 was used to investigate the stability of oxidative chlorine on the PET fabrics coated with *m*-aramid after home laundering. A Launder-Ometer was fitted with stainless steel cylinders (3× 5 in.). The volume of 150 mL of water, 0.15% AATCC detergent, and 50 stainless steel balls were added to the cylinder and rotated for 45 min at 42 ± 0.5 rpm and 49°C. These testing conditions are the equivalent of five washing cycles in a home laundry. After detaching the cylinders, the samples within the cylinder were washed three times with 300 mL distilled water, then air dried at ambient temperature.

Antimicrobial test

PET control and chlorinated fabrics were challenged with *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* O157:H7 (ATCC 43,895) using a modified AATCC Test Method 100-1999. Bacterial suspensions (25 μL) made with pH 7 phosphate buffer were added to one inch square sample swatches. A second swatch was sandwiched over the first to ensure contact between the suspension and the fabric. After contact times of 10, 30, 60, and 120 min, the samples were quenched with 5.0 mL of sterile 0.02 *N* sodium thiosulfate solutions. The quenched samples were diluted using pH 7 phosphate buffer and plated on Typticase soy agar. The plates were incubated at 37°C for 24 h, and the number of bacteria was counted to determine the presence or absence of viable bacteria.

RESULTS AND DISCUSSION

Characterization of PET fabric coated with *m*-aramid

In this study, a commercially available fiber-forming polymer, *m*-aramid, was coated on the surface of PET fabric for rendering antimicrobial. The coated *m*-aramid onto the PET fabrics was characterized using FTIR-ATR, XPS, and SEM. The FTIR spectra of pure PET, coated *m*-aramid onto PET fabric, and *m*-aramid are presented in Figure 2. When the infrared spectra of pure PET and PET coated with *m*-aramid are compared, they appear similar, although careful inspection of these spectra reveals differences. The pure PET shows bands at about 1711, 1240, and 1092 cm^{-1} regions because of ester C═O stretching vibration band, C—O stretching band of ester, and C—O stretching band of glycol, respectively.[17] New bands appearing in the 1645 and 1524 cm^{-1} regions of the coated *m*-aramid onto PET are recognized as characteristic of *m*-aramid bands, which are the amide I band and the bending vibration of N—H, respectively.[13] Hence, the observation

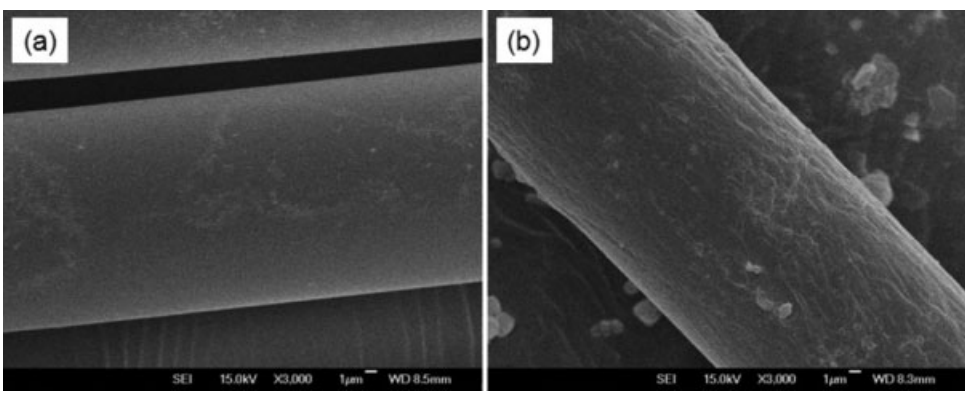

Figure 3 SEM traces of (a) untreated PET fabric, (b) PET treated with *m*-aramid (10%).

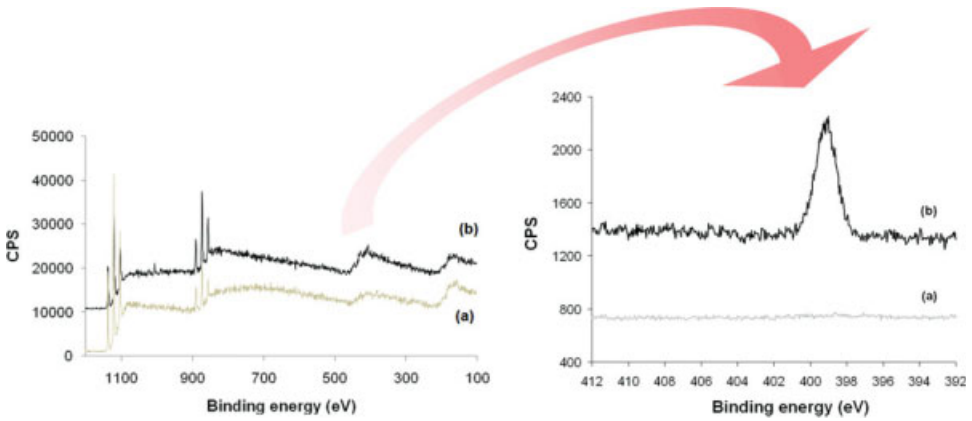

Figure 4 XPS spectra of (a) untreated PET and (b) PET treated with *m*-aramid (10%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of these new bands confirms that *m*-aramid is coated onto PET fabric surfaces.

It is reported that the morphology and homogeneity coating is significantly affected by the substrate surface.[18] The feature surface of coated PET fabric was observed by SEM. Figure 3 presents the surface morphologies of pure PET and PET fabrics coated with *m*-aramid. The PET fabric coated with 10% *m*-aramid show a noticeable difference as compared with pure PET fabric as shown in Figure 3. The SEM image of pure PET fabric before coating shows smooth surface. On the other hand, the PET treated with *m*-aramid had a layer of coating, which demonstrates the presence of *m*-aramid coating on the PET surfaces. Further confirmation of coating of *m*-armaid onto PET fabric was observed by XPS. The XPS spectra of pure PET fabric and the PET fabric coated with *m*-aramid are shown in Figure 4. The results of the PET fabric coated with *m*-aramid show a distinguishable peak at binding energy 398.7 eV, which indicates the existence of nitrogen atom of the PET surface coated with *m*-aramid. In terms of the quantitative elemental analysis, the nitrogen content on the PET surfaces coated with *m*-aramid was 8.0%.

Chlorination and titration

The cycle of disinfection by the chlorinated *m*-aramid on the surface of the PET and recharging with diluted chlorine bleach is shown in Figure 5. It demonstrates that the PET coated with *m*-aramid is antimicrobial after chlorination and capable of being regenerated once the initial chlorine charge is exhausted. The oxidative chlorine content of the PET fabrics coated with *m*-aramid at various concentration of *m*-aramid is shown in Figure 6. The results show that PET fabrics coated with 10% *m*-aramid obtain highest chlorine content as compared with those of 1% and 5% *m*-aramid. This may be due to the fact that higher concentration of *m*-aramid on the PET fabrics possibly has higher content of N—H bonds, indicating more capable of generating chlorine charge on the surface of the PET fabrics. Therefore, increasing the concentration of *m*-aramid on the surface of PET fabrics caused increase in the oxidative chlorine content on the PET surface.

Durability and rechargeability of the PET fabric coated with *m*-aramid

As shown in Figure 5, chlorination on the coated surface of the PET with *m*-aramid renders antimicrobials, but it is required to recharge the antimicrobial functions since the repeated inactivation of *N*-chloramine results in exhaustion of the initial chlorine charge. Accordingly, rechargeability is necessary for the chlorinated *N*-halamines on the surface of PET to retain the antimicrobial function after repeated uses. The results of the durability and recharging effectiveness of *m*-aramid coated PET fabrics are listed in Table I. After 25 wash cycles, prechlorinated samples retained 19% of the oxidative chlorine. On

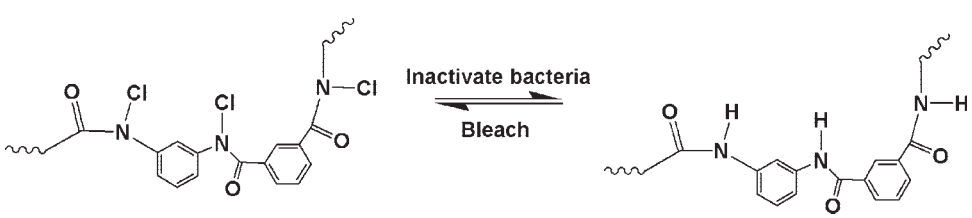

Figure 5 Scheme of the function of *m*-aramid disinfection.

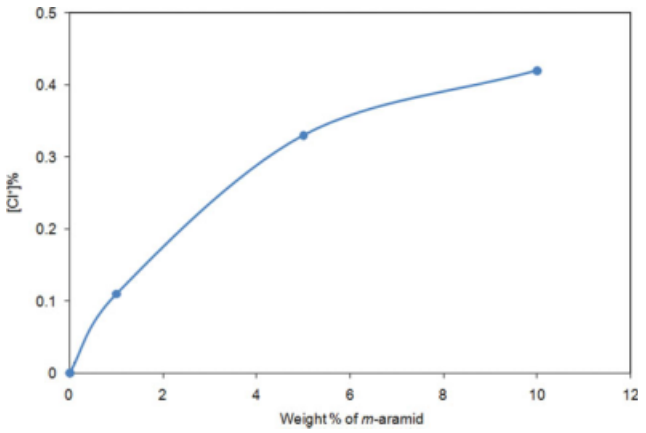

Figure 6 Oxidative chlorine content of *m*-aramid treated onto PET fabrics. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

the other hand, the samples which are chlorinated after 5, 10, and 25 washing cycles recovered their original antimicrobial functions to about 85, 57, and 33% of the oxidative chlorine, respectively. It is presumed that the small amount of oxidative chlorine should be sufficient to inactivate bacteria after recharging of the antimicrobial PET fibers. Therefore, it may be proven that 0.1% of the oxidative chlorine is sufficient to inactivate bacteria, shown by Lee et al.[19]

Antimicrobial efficacy

The biocidal test results of the *m*-aramid coated PET against *Staphylococcus aureus* (Gram-positive bacteria) and *E. coli* O157:H7 (Gram-negative bacteria) after different contact times are shown in Table II. The unchlorinated PET samples provided about 0.4 log reduction of *S. aureus* even at the highest contact time, 120 min. The chlorinated PET samples coated with *m*-aramid showed about 6 log reductions of *S. aureus* and *E. coli* O157:H7 at a contact time of 10 and 30 min, respectively. It indicates that the efficacy of the chlorinated PET sample against *S. aureus* is superior to those of against *E. coli* O157:H7. Gram-negative bacteria possess one more cell wall, as compared with Gram-positive bacteria. It is called outer membrane which is filled with water.[20] *N*-halamines enhanced hydrophobicity after chlorination since N—H bonds in *N*-halamines were converted into N—Cl bonds. Therefore, enhanced hydrophobicity could result in less antibacterial efficacy against Gram-negative bacteria of *E. coli* O157:H7.

TABLE I
Durability and Rechargeability of the *m*-aramid (10%) Treated Onto PET Fabrics Unit: [Cl^+]%

Washing cycles	Group 1[a]	Group 2[b]
0	0.42	0.42
5	0.28	0.36
10	0.17	0.24
25	0.08	0.14

[a] Prechlorinated samples.
[b] Prechlorinated samples, which after each cycle were rechlorinated.

CONCLUSIONS

Commercial *m*-aramid coated onto PET fabric surface shows great potential as *N*-halamine precursors. This study may demonstrate an alternative way of creating the *N*-halamine bicidal functionality on PET without synthesis of *N*-halamine precursors. The PET coated with *m*-aramid was characterized using FTIR-ATR, XPS, and SEM. FTIR shows new bands in the 1645 and 1524 cm^{-1} regions as characteristic of *m*-aramid bands, which means that *m*-aramid is coated onto the PET surface. The result in XPS exhibits a distinguishable peak at binding energy 398.7 eV, indicating the existence of nitrogen atom

TABLE II
Antimicrobial Efficacy Against Microorganisms

		Staphylococcus aureus[b]			*E. coli* O157:H7[c]		
Samples[a]	Contact time (min)	Bacterial No. (cfu/mL)	Total bacteria (cfu/sample)	Log reduction	Bacterial No. (cfu/mL)	Total bacteria (cfu/sample)	Log reduction
Control	10	2.40×10^5	1.32×10^6	0.11	2.40×10^5	1.40×10^6	0.04
	30	2.27×10^5	1.18×10^6	0.16	1.21×10^5	8.87×10^5	0.24
	60	1.87×10^5	9.88×10^5	0.24	1.15×10^5	7.85×10^5	0.29
	120	1.29×10^5	7.44×10^5	0.36	1.07×10^5	6.12×10^5	0.40
Chlorinated	10	0	0	6.12	9.30×10^1	2.78×10^2	3.70
	30	0	0	6.07	0	0	5.94
	60	0	0	5.99	0	0	5.89
	120	0	0	5.87	0	0	5.78

[a] The samples were treated with *m*-aramid (10%).
[b] Total bacteria: 1.73×10^6 cfu/sample.
[c] Total bacteria: 1.54×10^6 cfu/sample.

of the PET surface coated with *m*-aramid. In addition, SEM image shows a layer of coating onto the PET surfaces, implying the coating of *m*-aramid. Hence, these observations confirm that *m*-aramid is coated onto PET fabric surfaces. Oxidative chlorine content varied with the concentration of *m*-aramid. Higher concentration of *m*-aramid on the PET fabrics indicates more capable of generating chlorine charge on the surface of the PET fabrics. The chlorinated PET exhibited high antimicrobial activity against *S. aureus* and *E. coli* O157:H7. The chlorinated PET samples coated with 10% *m*-aramid showed about 6 log reductions of *S. aureus* and *E. coli* O157:H7 at a contact time of 10 and 30 min, respectively. In addition, the antimicrobial activity was durable and rechargeable after 25 wash cycles.

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