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N-halamine Modified Polyester Fabrics: Preparation and Biocidal Functions

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Abstract: A cyclic N-halamine precursor, 1-glycidyl-s-triazine-2,4,6-trione (GTT), was synthesized and grafted onto polyester fibers. The tricarbimide rings could be transferred to N-halamine structure upon exposure to dilute sodium hypochlorite solution. Structural and surface characterizations of the polyester (PET) fabrics treated with GTT were accomplished using FT-IR, SEM, and DSC. The antimicrobial efficacy test showed that the N-halamine modified PET could inactivate 6-log of *Staphylococcus aureus* (Gram-positive) and *E. coli* O157:H7 (Gram-negative) within 10 min of contact time. The antimicrobial fabrics exhibited good durability and stability to washing and storage.

Keywords: Antimicrobial, N-halamine, Polyester, Finishing

Introduction

Textile materials are good media for growth of bacteria, and may be responsible for some cross-infection in the healthcare-associated industry [1-5]. In order to reduce the risk of transmission of diseases caused by pathogenic microorganisms, antimicrobial finishing of textiles has been extensively studied [6-16].

In the past two decades, the researchers showed their interest of applications of N-halamines to produce antimicrobial fabrics [10-16]. N-Halamines are the compounds that contain one or more nitrogen-halogen bonds. N-Halamines have antimicrobial mechanisms similar to hypochlorite bleach, but N-Halamines are more stable. Fabrics modified by N-halamine showed powerful biocide efficacy in inactivating both Gram-negative and Gram-positive bacteria. More importantly, the antibacterial properties of the N-Halamines are regenerable, and the active halogen lost during washing and wearing can be regenerated by simple exposure to household bleach during the washing process.

Recently, many studies reported the preparation of antimicrobial PET fabrics modified by N-Halamines. Admicellar polymerization technique was used to coat 3-(4'-vinylbenzyl)-5,5-dimethylhydantoin onto the surface of PET by Ren *et al*. [17]. Some N-halamine siloxanes were prepared and coated PET using a pad-dry-cure technique [18]. Sun and Sun had used similar technique to introduce N-halamine compounds into PET fibers to render them biocidal [19,20]. Unfortunately, most of the mentioned N-halamine precursors are water insoluble, and organic solvents are need to prepare the treatment solution. The use of the organic solvents will increase the cost and limits their industrial application.

To solve this problem, a water-soluble N-halamine precursor, 1-glycidyl-s-triazine-2,4,6-trione (GTT), was synthesized through the reaction of cyanuric acid with epichlorohydrin in a facile condition in our previous study [21]. Cyanuric acid, a very cheap and easy available cyclic N-halamine precursor containing three imide groups, can react with epichlorohydrin to form 1-glycidyl-s-triazine-2,4,6-trione (GTT). The epoxide was successfully grafted onto cellulose to produce a powerful and durable antimicrobial cotton fabrics. In this study, we demonstrated the preparation of biocidal polyester by using 1-glycidyl-s-triazine-2,4,6-trione. Different from cellulose, PET fibers have fewer reactive groups, such as hydroxyl groups. Therefore, in this study NaOH was emplyed to hydrolyze some ester linkages on the surfaces of polyester fibers and enhance the reaction efficiency between PET and GTT as shown in Scheme 1. The GTT modified PET was characterized by FTIR, DSC, and SEM. After exposure to dilute household bleach, the GTT coated PET fabrics could be rendered biocidal. Biocidal efficacy tests showed that the chlorinated fabrics could completely inactivate *Staphylococcus aureus* and *Escherichia coli* O157:H7 in 10 min of contact time, respectively. Stability of the N-Cl bonds to standard washing and storage was also evaluated in this study.

Experimental

Materials

PET fabric was provided by Wujiang Zhongpeng Textiles Co., Ltd., China. The bacteria used in the tests were *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* O157:H7 ATCC 43895 (American Type Culture Collection, Rockville, MD). Cyanuric acid was purchased from J&K Chemicals, Shanghai, China. Other chemicals used in this research were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All the chemicals were used without further purification.

Instruments

Fourier transform infrared (FTIR) spectra of PET, GTT modified PET, and chlorinated GTT modified PET were

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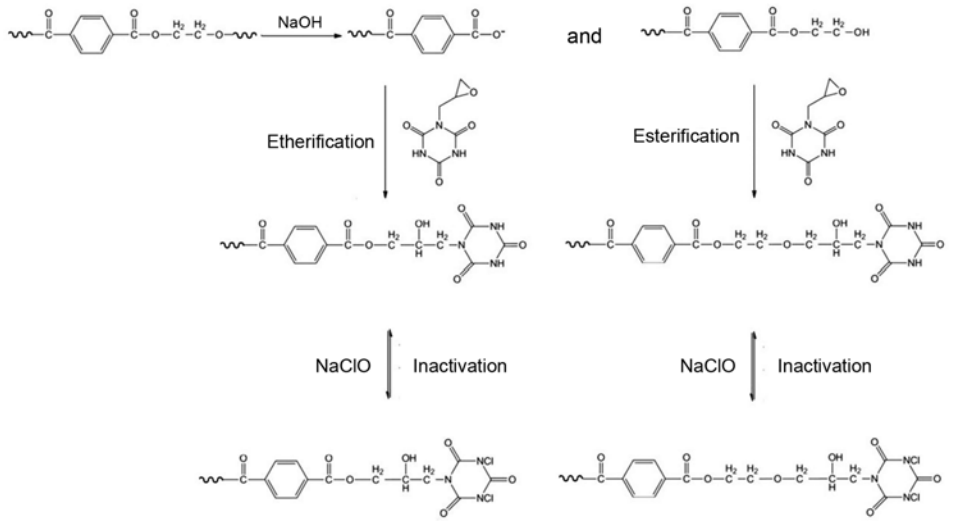

Scheme 1. The production of antimicrobial polyester.

obtained with a Nicolet NEXUS 470 spectrometer (Nicolet Instrument Corporation, Madison, WI). An SU-1510 field-emission scanning electron microscope (Hitachi, Tokyo, Japan) was used to characterize the surface morphology of fabrics. Differential scanning calorimetry (DSC) studies of the samples were performed on a TA Q200 DSC at a heating rate of 10 °C/min under nitrogen atmosphere. The washing stabilities of chlorinated PET fabrics were measured using a Launder-Ometer (Darong Textile Instrument Co., Ltd., Zhejiang, China).

Synthesis of GTT

GTT was synthesized according to a method reported previously [21]. In brief, a mixture of 0.05 mol of cyanuric acid and 0.1 mol of sodium hydroxide in 150 m*l* water was stirred for 10 min to get a uniform solution. Then, 0.05 mol of epichlorohydrin was added to the solution, and the solution was stirred for 24 h at ambient temperature. After the reaction, the solution was neutralized (pH 6.8-7.0) with 10 % sulfuric acid. Water was removed by evaporation under reduced pressure, and 100 m*l* of N,N-dimethylformamide (DMF) were added to the flask to dissolve the product. Sodium salts produced in the reaction were removed by filtration. The solvent of DMF was evaporated under vacuum producing the desired white solid in a yield of 85 %. The product was used to graft fabric directly without furthur purification.

Grafting of GTT onto PET

The PET swatches were soaked in an aqueous solution containing 10 wt% of GTT and 2 wt% of NaOH for 10 min. Then, PET fabrics were padded through a laboratory wringer to get a wet pickup of 100 %, dried at 100 °C for 10 min, and cured at 170 °C for 20 min. After the curing process, the fabrics were soaked in a 0.5 % detergent solution for 15 min, then rinsed with distilled water to remove any unbonded GTT, and dried in air.

Chlorination and Analytical Titration

The GTT modified PET fabric swatches were soaked in 10 % solution of aqueous bleach solution (NaOCl, pH 7) at room temperature for 1 h. The chlorinated PET samples were rinsed thoroughly with distilled water and dried at 45 °C for 1 h to remove unreacted free chlorine. The weight percentage of oxidative chlorine of the samples was determined by the iodometric/thiosulfate titration method. The Cl^+ % on the polyester swatches was calculated from the following equation:

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

where, N and V are the normality (equiv/*l*) and volume (*l*) of the titrant sodium thiosulfate, respectively, and W is the weight of the PET samples in grams.

Breaking Strength Testing

The breaking strengths of untreated PET fabrics (control) and GTT treated PET fabrics with/without chlorination were measured according to the GB/T3923-1997 method. The breaking strength testing was performed at ambient temperature. The PET swatches (5×20 cm) were tested for five times, and their averages were reported.

Biocidal Efficacy Testing

Both modified PET fabrics with/without chlorination were challenged with *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC 43895) using a modified AATCC 100-1999 Test Method. An aliqot of 25 μl bacterial suspensions was added to the center of two pieces of 1 square inch PET swatches, which were held in place by sterile weights. After contact

times of 10, 20, and 30 min, the PET samples were quenched with 5.0 m*l* of sterile 0.02 N sodium thiosulfate solution to neutralize any active chlorine. The mixture was vortexed vigorously for 2 min. A 10-fold serial dilutions of the quenched samples were made using phosphate buffer (pH 7) and placed onto Trypticase soy agar. The plates were incubated at 37 °C for 24 h. After incubation, bacterial colonies were counted for biocidal efficacy analysis.

Standard Washing Testing

The stability and rechargeability of chlorine loadings of the PET samples were evaluated by a standard washing test according to AATCC Test Method 61. The chlorinated GTT treated PET samples were washed for the equivalents of 5, 10, 25, and 50 machine washes in a Launder-Ometer. The chlorine content of samples after washings with or without rechlorination treaments were measured by the titration procedure outlined above.

Storage Stability Testing

The storage stability of choloinated PET fabrics at room temperature was evaluated. Chlorinated GTT treated PET samples in sealed plastic bags were stored in dark place. After a period of time, the samples were titrated, or rechlorinated and titrated to assess the stability of active chlorine to storage.

Results and Discussion

Characterization of Polyester Treated with GTT

The FTIR spectra of the PET, PET treated with GTT, and chlorinated PET treated with GTT were shown in Figure 1. The characteristic vibrational band of samples treated with GTT appears at 1770 cm^{-1} in Figure 2(B), which corresponds to the tricarbimide carbonyl vibrational modes [21]. This band was not observed in Figure 2(A) for the untreated PET. After chlorination, the carbonyl vibrational band at 1770 cm^{-1} shifts to 1775 cm^{-1}. The shifts to higher wavenumber of carbonyl bands of the N-halamine precursors upon chlorination have been reported in former studies [18,21,22]. The FTIR spectra clearly confirmed that GTT has been covalently bonded onto PET, and the unreacted water-soluble GTT could be easily washed off from the surface of fibers.

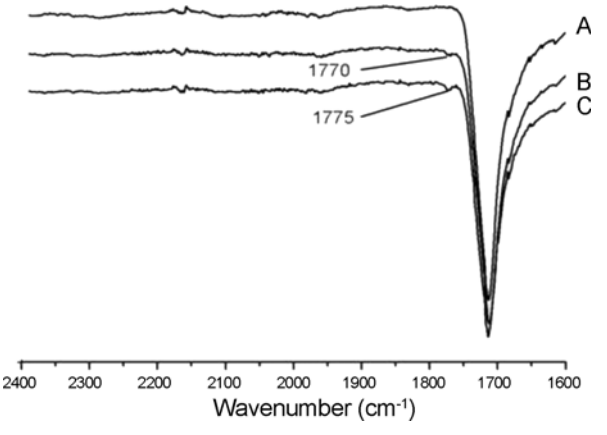

Figure 1. FTIR spectra of (A) PET, (B) PET treated with GTT, and (C) chlorinated PET treated with GTT.

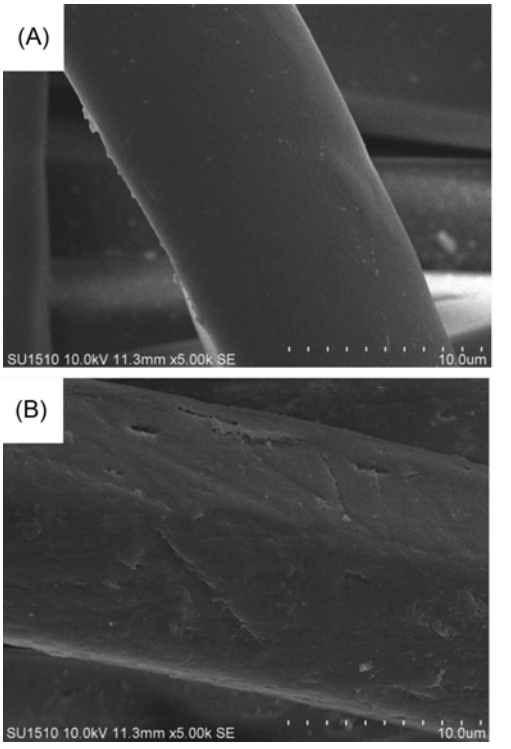

Figure 2. SEM images of (A) PET and (B) PET after the treatment with 5,000× magnification.

SEM micrographs of the untreated PET fibers and treated PET fibers are shown in Figure 2 with magnification of 5,000×. The surfaces of the untreated PET fibers were smooth. However, the GTT and NaOH treated PET fibers

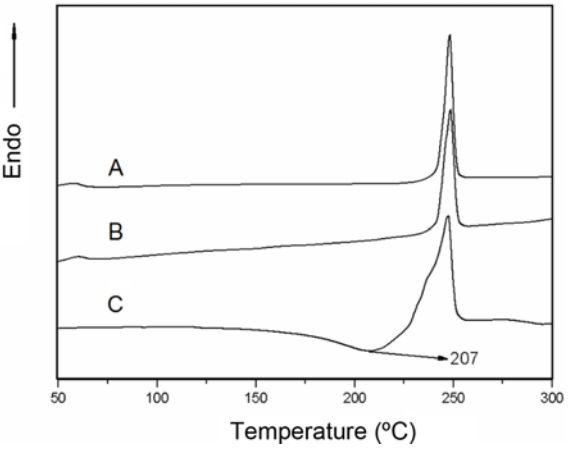

Figure 3. DSC curves of PET samples; (A) PET, (B) PET treated with GTT, and (C) chlorinated PET treated with GTT.

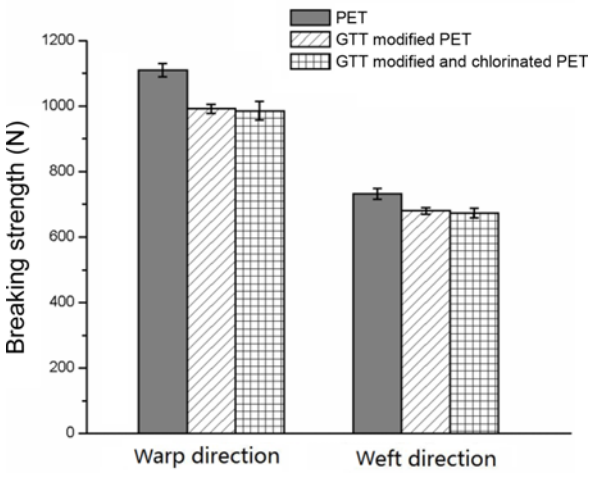

Figure 4. Breaking strengths of PET samples.

Table 1. Stability to washing

Washing cycles	A (Cl^+ % wt)	B (Cl^+ % wt)
0	0.20	0.20
5	0.15	0.20
10	0.10	0.18
25	0.08	0.16
50	0.04	0.16

(A) chlorinated before washing and (B) chlorinated before washing and rechlorinated after washing.

show a rough surface, which is due to the hydrolyzing of ester linkages on the surfaces of polyester fibers caused by NaOH and the coating of GTT. The hydrolyzing process causes the decrease of the tensile strength of PET fabrics and enhances the reaction efficiency between PET and GTT.

The DSC curves of PET, GTT modified PET, GTT modified and chlorinated PET are shown in Figure 3. The DSC curves of PET, GTT modified PET are very similar to each other. The DSC curve of chlorinated GTT modified PET, a new exothermic peak around 207 °C could be clearly observed as the characteristic peak of thermal decomposition of the N-Cl bond. This is in agreement with previous studies [22,23]. The DSC data further confirms the formation of N-halamine structure upon the chlorination treatment, as shown in Scheme 1.

The results of breaking strength testing of the PET treated with GTT and NaOH before and after chlorination are shown in Figure 4. The treated PET leads to about 7-10 % of strength loss in weft and warp direction compared with untreated samples due to the hydrolysis of some ester linkages on the surface of PET fibers by the sodium hydroxide added in treatment solution [17]. The small loss of tensile strength is acceptable in practical textile finishing given the value added by antimicrobial finishing. Interestingly, the chlorination treatment does not weaken the strength of the fabrics.

Table 2. Stability to storage

Time of storage (weeks)	Cl^+ % wt
0	0.20
2	0.18
4	0.16
6	0.16
13	0.12
13 (rechlorination)	0.20

Table 1 shows the results of washing testing of PET fabric swatches treated with GTT. The chlorine loadings of the PET swatches coated with chlorinated GTT decreased from original 0.20 % to 0.15 % after 5 washing cycles. After 50 washing cycles, there are still 0.04 % of the active chlorine remained. The washing stability of GTT treated PET is better than other N-halamine modified cotton fabrics. The hydrophobic surfaces of PET fabrics protect the hydrolysis of N-Cl bonds during washing [17,18]. After 50 washing cycles and rechlorination, 80 % of the initial chlorine loading regained, indicating that most of the GTT moieties are still bonded on the PET fabrics.

Previous study showed that moistures in the air could affect shelf lives of the N-halamine products [16]. To estimate the stability of N-halamine structure bonded to PET fabrics, the storage test was performed at room temperature. The storage stability of the chlorinated fabrics is shown in Table 2. After 13 weeks' storage, the PET samples retained 60 % of the initial chlorine loading which is still effective in inactivating bacteria. All of the lost chlorine could be restored by rechlorination, which indicated that the chlorine losses were due to the dissociation of the N-Cl bonds rather than the departure of the GTT moieties from fabrics. The results showed that the imide N-Cl bonds on PET fabrics and covalent bonds between GTT and PET fabrics are very stable at room temperature. The antimicrobial properties of the PET fabrics after storage will be discussed in the antimicrobial testing section.

Table 3. Biocidal efficacy of the fabric with 0.12 % active chlorine content

Sample	Contact time (min)	*S. aureus*[a]	*E.coli* 0.157:H7[b]
		Bacterial reduction	Bacterial reduction
Unchlorinated	30	1.52	0.28
Chlorinated	10	5.99	6.05
	20	5.99	6.05
	30	5.99	6.05

[a]Total bacteria: 9.67×10^5 (cfu/sample) and [b]total bacteria: 1.13×10^6 (cfu/sample).

Antimicrobial Testing

Both unchlorinated and chlorinated PET samples treated with GTT were challenged with *S.aureus* (gram-positive) and *E.coli* O157:H7 (gram-negative) at concentrations of about 10^6 CFU/sample. The results of antimicrobial tests are shown in Table 3. The unchlorinated samples showed some degree of log reductions of *S.aureus* and *E.coli* O157:H7 within 30 min of contact time. The small reductions were mainly due to adhesion of bacteria to the samples. The log reduction of unchlorinated PET samples for *S.aureus* is larger than that for *E.coli* O157:H7, probably due to the different shapes and surface structures of *S.aureus* compared with *E.coli* O157:H7, which cause the *Saureus* more easily to be adsorbed onto the surface of fiber as reported in previous study [18]. The chlorinated samples with 0.12 % active chlorine loading demonstrated a total inactivation against *S.aureus* and *E.coli* O157: H7 with 6 log reduction in 10 min of contact time. The imide halamine structures in the chlorinated GTT might kill bacteria faster than the amide halamines in chlorinated hydantoin derivatives [17,18,21].

Conclusion

An N-halamine precursor, 1-glycidyl-s-triazine-2,4,6-trione (GTT), has been successfully grafted onto the surfaces of the PET via epoxide group. The process employed in this study only caused a small damage to the breaking strength of the fabrics. The washing test results showed that the GTT bonded to PET was very stable and that the lost chlorine could be regenerated by rechlorination. The storage test indicated that 0.12 % wt active chlorine remained on the surface of chlorinated GTT treated PET fabrics after 13 weeks' storage. The GTT modified PET fabrics after chlorination demonstrated excellent biocidal efficacy against *S.aureus* and *E.coli* O157: H7. With advantages mentioned above, the antimicrobial PET fabrics will have great potential applications in healthcare-associated industry.

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