Durable Antimicrobial Finish of PET with 6-(1-anthraquinonyl amino) Hexyldimethylammonium Bromide

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Abstract: New quaternary ammonium compound, 6-(1-anthraquinonylamino) hexyldi methylammonium bromide (AHDDAB) was synthesized by 1-aminoanthraquinone with dimethyl dodecyl amine via hexamethylene spacer, antimicrobial activity was investigated. Results indicate that the new quaternary ammonium salt was successfully treated on PET surfaces by exhaustion method as in dyeing, and durable antimicrobial finish of PET was also investigated.

New QAC was exhausted on PET fabric without any aid of chemical auxiliary even though it is water-soluble. Since AHDDAB is soluble in water, and the anthraquinonyl moiety of compound could anchor on PET surface, and the antimicrobial part orientates outwards, the results indicate that the durability of PET treated with AHDDAB was good enough to maintain the initial properties even after 30 repeated launderings. The fastness of PET treated with AHDDAB after 30 repeated launderings in anionic commercial detergent is good enough to show colony reduction above 70% against S, *aureus* and K, *pneumoniae*.

The results mentioned above would suggest that test fabrics finished with AHDDAB could be valuable in the development of the field of antimicrobial fabrics, and could contribute considerably to better hygiene of all textiles in general.

Keywords: Durable, antimicrobial finish, poly (ethylene terephthalate), exhaustion, quaternary ammonium compound, antimicrobial agent.

1. Introduction

Quaternary ammonium compound (QAC), which has the ammonium or pyridinium cation moiety in its molecular composition, has been used widely as general disinfectants. Since QAC has a comparatively lower toxicity and an excellent antimicrobial effect against various kinds of bacteria, they are being used broadly in food industries, textile industries and medical fields.

In textile industries, currently, there is increasing necessity for antimicrobial finishing due to consumer's huge interest in health care. Many antimicrobial finishing agents contain quaternary ammonium groups. Many studies have examined QAC as an antimicrobial finish for textile materials, and attaching such a group to QAC could improve its antimicrobial activity. Possibly the aqueous solubility of a quaternary ammonium derivative would increase, thus further improving its use as an antimicrobial finishing agent.

There have been many reports on the synthesis and antimicrobial characteristics of various kinds of mono-QACs. The activities of mono-QACs are generally influenced by structural features, such as the N-alkyl chain length and the kind of substituent groups and their positions on the pyridine ring. Furthermore, quantitative structure-activity relationship analysis indicated that the antibacterial activity of mono-QACs depends on the molecular hydrophobicity, adsorbability, the cell surface activity and the bacterioclastic activity.

Munehiro studied a bis-quaternary ammonium compound, N, N'-hexamethylenebis, which has 6 carbon atoms in the connecting methylene chain and 10 carbon atoms in the N-alkyl chain, was synthesized and characterized [1]. Kiyo synthesized N-Alkyl-2-benzylaminopyridinum iodides from 2-benzylaminopyridine and n-alkyl iodide, and investigated their bactericidal characteristics [2].KIM synthesized N-(2-hydroxy) propyl-3-trimethy lammonium chitosan chloride as an antimicrobial finish for cotton using a reaction of glycidyltrmethylammonium chloride and chitosan [3]. Shin treated PP nonwoven fabric with chitosan solution of different molecular weight by pad-dry method and investigated its bactericidal activities [4].

On the other hand, because of the inherent low reactivity of (poly ethylene terephthalate) (PET) towards chemicals, somewhat complicated processes are adopted for value-added properties of PET in textile finishing; co-spinning [5], physical coating [6], plasma discharge [7] and graft polymerization [8, 9]. However, some of these methods have limited

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practical use, and are frequently accompanied hardening due to the touch of PET or elevated production cost.

In the present study, we reported that ethoxylated hexylaminoanthraquinone was successfully applied on PET by usual exhaustion method as in dyeing, and found that it anchors on PET surface with ethoxylated hydrophilic moiety outwards.The durability of PET treated with ethoxylated hexylaminoanthraquinone was good enough so as to maintain the initial properties even after 30 repeated laundering [10-12].

In this study, we attempted the synthesis of a new QAC,6-(1-anthraquinonylamino) hexyldimethylammo-nium bromide for the surface modification of PET, where the anthraquinonyl moiety of compound could anchor on PET surface and the antimicrobial part orientates outwards, making the surface antimicrobial.

The purpose of this study is to investigate the antimicrobial activities of PET finished with new QAC after repeated laundering.

2. Experimental

2.1 Materials

1-Aminoanthraquinone (Aldrich) was recrystallized from ethanol. Sodium hydride (Kanto) was used after removing paraffin oil using hexane. Reagent grade of 1,6-dibromohexane (Aldlich) was used without further purification.

PET fabric (plain, 100 % PET) was washed with acetone repeatedly and dried in vacuum.

2.2 Instruments

^{1}H-NMR spectrometer (Bruker Advance Digital 400, USA), UV-visible spectro-photometer (Shimadzu UV-2100, Japan), LC-MS spectrometer (HP 1100 LC/MSD, USA)and Auto textile dyeing machine (Daelim, Korea),

2.3 Synthesis of 1-(6-bromo hexylamino) anthraquinones

To an ice-cooled 1-aminoanthraquinone (10.00g, 44.8 mmol) in THF (200ml) was added sodium hydride (1.29g, 53.80 mmol) in THF in small portions for over 30min. After 1, 6-dibromohexane (43.72 g, 180 mmol) was added to the system, the reaction mixture was refluxed for 20 hrs. The reaction mixture was filtered and concentrated under reduced pressure. The residual mixture was extracted with hexane to eliminate unreacted 1-aminoanthraquinone. The concentrated extract was subsequently separated by silica gel column chromatography to remove 1, 6-dibromohexane (hexane) and to give 1-(6-bromohexylamino) anthraquinone (dichloromethane/hexane mixture) (11.82g, 68% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.53-1.59 (m, 4H), 1.77-1.81 (m, 2H), 1.90-1.93 (m, 2H), 3.32-3.37 (m, 2H), 3.40-3.45 (m, 2H), 7.05 (d, J = 8.4Hz, 1H), 7.54-7.60 (m, 2H), 7.70-7.76 (m, 2H), 8.23-8.28 (m, 2H), 9.71 (s, 1H)

2.4 Synthesis of 6-(1-anthraquinonylamino) hexyldimethylammonium bromide

6-(1-anthraquinonylamino) hexyldimethylammoni-um bromide (AHDDAB) was prepared by the reaction of 1-(6-bromohexylamino)anthraquinones with dimethyl dodecylamine. To a solution of dimethyldodecylamin (0.069g, 0.324mmol) in isopropanol (10ml) was added 1-(6-bromo hexylamino) anthraquinone (0.15g, 0.389mmol) in isopropanol (20ml) by stirring. The reaction mixture was heated at reflux for 10hrs and filtered. The filtrate was concentrated under reduced pressure. Unreacted residual1-(6-bromo hexylamino) anthraquinone was eliminated by washing with n-hexane.

2.5 Antimicrobial finish of PET

Desized and scoured PET fabrics were treated with AHDDAB by usual exhaustion method as in dyeing under the bath ratio of 85:1 at 130℃ for 60 mins. The treated PET was dried for 30 minutes at 60℃ in a laboratory oven.

2.6 Dye uptake

PET fabric was dyed with AHDDAB at 130℃ for 60 mins under the bath ratio of 85:1.The dyed fabric was rinsed with sufficient water, and then extracted with dimethylformamide (DMF). The adsorbed amounts of the compounds were calculated from their absorbance and previously prepared calibration curve.

2.7 Evaluation of antimicrobial activity

Antimicrobial activity of the treated fabric was evaluated by Shake Flask Method in terms of bacteria reduction rate. Two strains of bacteria were used, Staphylococcus *aureus* (ATTCC 6538) and Klebsiella *pneumoniae* (ATCC 4352).