Carbohydrate Polymers 84 (2011) 1027–1032

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Photoactive antibacterial cotton fabrics treated by 3,3′,4,4′-benzophenonetetracarboxylic dianhydride

Kyung Hwa Hong[a], Gang Sun[b,*]

[a] R&D Division, Korea Textile Inspection & Testing Institute, Seoul 135-935, South Korea
[b] Division of Textiles and Clothing, University of California, Davis, CA 95616, USA

ARTICLE INFO

Article history:
Received 23 March 2010
Received in revised form
20 December 2010
Accepted 21 December 2010
Available online 25 December 2010

Keywords:
Photoactive antimicrobial function
Cotton fabrics
Benzophenone
3,3′,4,4′-Benzophenonetetracarboxylic dianhydride

ABSTRACT

Photoactive antimicrobial cotton fabrics were produced by chemically incorporating 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BPTCD) onto the fibers through a pad-dry-cure finishing process. An esterification reaction between anhydride group of BPTCD and hydroxyl group of cotton cellulose was promoted by a catalyst under elevated temperature. The structural features and functional properties of the BPTCD treated cotton fabrics were investigated by FTIR, XRD, SEM, TGA and antimicrobial testing. Results showed that the BPTCD treated cotton fabrics display excellent antimicrobial functions under UVA (365 nm) light, and also the treatment does not damage the mechanical properties of the cotton fabric.

1. Introduction

A wide range of antimicrobial agents can be applied to textiles, including silver based materials (Klueh, Wagner, Kelly, Johnson, & Bryers, 2000; Yuranova et al., 2003), halamine compounds (Sun & Sun, 2003), quaternary ammonium (Lin, Qiu, Lewis, & Klibanov, 2003; Tashiro, 2001), and phosphonium polymers (Tashiro, 2001), to produce antimicrobial clothing or sanitary textile products. More recently, some photoactive compounds and structures were found to produce radicals under UVA or fluorescent light, which can be potentially employed in self-decontamination applications (Hong & Sun, 2007a,b, 2008a,b, 2010a,b).

Radicals (often referred to as free radicals) are atoms, molecules, or ions with unpaired electrons on an open shell configuration. The unpaired electrons are highly chemically reactive and play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes, including human physiology (Griller & Ingold, 1976; Kochi, 1973). In particular, benzophenone chromophoric group, known to undergo $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ triplet states transition under light-excitation, are commonly used as photosensitizers in photochemistry. The triplet benzophenone diradical structure can be readily quenched by oxygen, and can also attract a hydrogen atom from any active hydrogen source to form a ketyl radical. Most likely, biological agents and toxic chemicals serve as the sources of active hydrogen, which could result in antimicrobial effect and decomposition of the chemicals. In addition, when the radical react with oxygen it could form peroxide or even generate superoxide agents (Görner, 2003; Korchev et al., 2006), which are biocidal and oxidative. Therefore, the benzophenone chromophoric groups incorporated on fabrics can decompose not only bacteria but also toxic compounds under UVA or fluorescent light irradiation (Hong & Sun, 2007a,b, 2008b, 2010a,b).

Benzophenone incorporated cotton fabrics were prepared by using 4-hydroxybenzophenone, 1,2,3,4,-butanetetra carboxylic acid (BTCA), and sodium hypophosphite as a catalyst. And significant antimicrobial functions were observed from the treated cotton fabrics. However, the mechanical properties of cotton fabrics such as tensile strength were also decreased by the treatment because of use of the cross-linker BTCA (polycarboxylic acid) (Hong & Sun, 2007a). Therefore, in this study, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BPTCD) as a benzophenone derivative was incorporated to cotton cellulose without use of any cross-linker since anhydride groups of BPTCD could easily react with hydroxyl groups of cotton cellulose. The treated cotton fabrics demonstrated excellent properties which are discussed here.

* Corresponding author. Tel.: +1 530 752 0840; fax: +1 530 752 7584.
E-mail address: gysun@ucdavis.edu (G. Sun).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.12.062

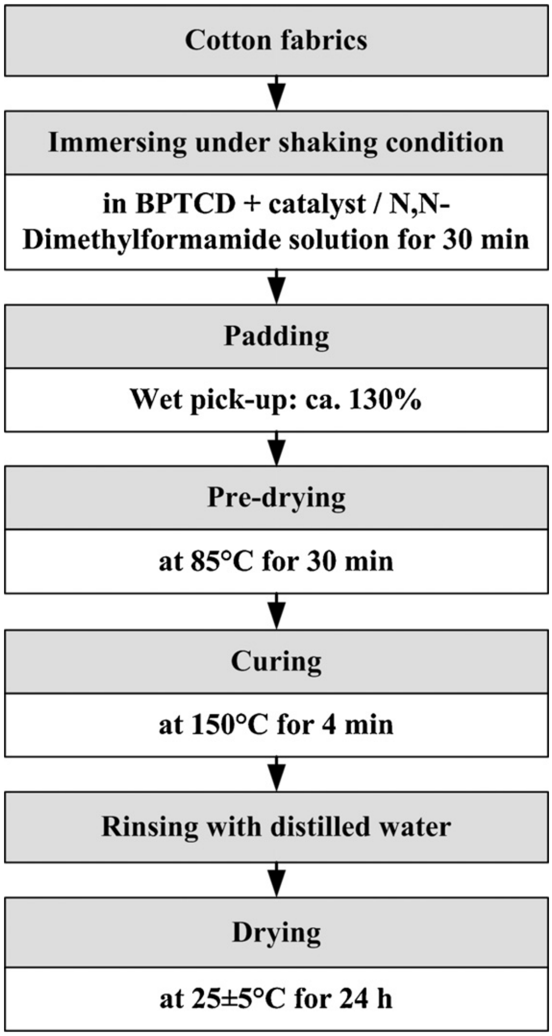


Fig. 1. Preparation process of BPTCD incorporated cotton fabrics.

2. Experimental

2.1. Materials

Bleached and desized cotton fabrics (#400) were purchased from Testfabrics, Inc. (West Pittston, PA). BPTCD, sodium hypophosphite hydrate, and N,N-dimethylformamide were purchased from Aldrich Co. (MO, USA). All reagents were used as received without any further purification.

2.2. Fabric finishing process

The laboratory procedure used to incorporate benzophenone chromophoric groups to cotton fabrics is shown in Fig. 1. The cotton fabrics, cut in sizes of around 30 cm × 30 cm, were immersed in a finishing solution containing designated concentrations (0.0125–0.2 mole) of BPTCD and 0.05 mole of sodium hypophosphite hydrate, and then the baths were gently shaken for 30 min. After that, the fabrics were padded through a laboratory padder to have a wet pick-up rate around 130%, and the treated fabrics were dried at 85 °C for 30 min. Subsequently, the fabrics were cured at 150 °C for 4 min, and then they were washed with distilled water and air-dried in a conditioning room (25 °C, 65%R.H.) for 24 h. The ultra-violet (UV) lamp (BLE-8 T365 (bandwidth: ≈365 nm); sample to bulb distance: 15.8 cm) was used for photo-activation of the treated cotton fabrics.

2.3. Characterization

Add-on (%) of benzophenone chromophoric groups in the treated cotton fabrics was measured by a weighing method on the basis of the weight changes of the fabrics before and after treatment. Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 6700 FTIR spectrometer (Thermo Electron Co., USA) with a resolution of 4 cm^{-1}, measurements were carried out by using KBr pellets. Crease angles were measured according to AATCC standard Test Method 66, Wrinkle Recovery of Fabrics: Recovery Angle Method. Thermogravimetric analysis (TGA) was carried out with a Shimadzu TGA-50 apparatus (Shimadzu science instruments, Inc., USA) at a heating rate of 10 °C/min from 30 °C to 600 °C under a nitrogen atmosphere. The surface morphologies of cotton fabrics were examined using a scanning electron microscope (SEM; Philips XL30, USA). The tensile strength of the fabrics was measured by the cut strip method (KS K 0520-1995) with an Instron 5566. Chromophores incorporated on the cotton fibers were observed by fluorescent microscope Leica DM 2500 (Leica Microsystems, Germany). The antimicrobial activities of the fabrics were tested against *Staphylococcus aureus* (*S. aureus*) (12,600, a gram-positive bacterium) and *Escherichia coli* (*E. coli*) (K-12, a gram-negative bacterium) according to a modified testing method for antibacterial activity of textiles (AATCC 100). During the antimicrobial test, all cotton fabrics were inoculated by bacteria and then immediately illuminated under UV light (365 nm wavelength light) in a container for 2 h. After the UVA light contact time, the inoculated cotton fabrics were each immersed in 100 mL of quenching solution (distilled water) and the containers were shaken well to move all bacteria from the cotton fabrics to distilled water. And then, 0.1 mL of the microbial suspension in the container was taken and was diluted to 10^1, 10^2, and 10^3 in series with distilled water. One hundred microliter of the dilution was placed onto agar plates and incubated at 37 °C for 18 h. The same testing procedure was employed for a bacterial solution for no BPTCD treated cotton fabric, serving as a control. The reduction of bacteria was calculated according to the following Eq. (1):

$$\text{Reduction of bacteria}\,(\%) = \frac{B - A}{B} \times 100 \qquad (1)$$

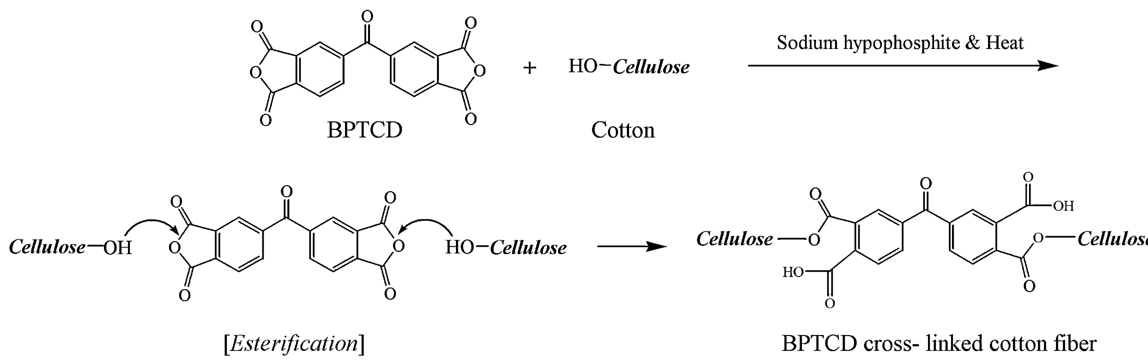
where A and B are the surviving cells (colony forming unit mL^{-1}) on the agar plates corresponding to the treated cotton fabrics and the control, respectively.

3. Results and discussion

3.1. Preparation of BPTCD incorporated cotton fabrics

It is well known that anhydride structure is able to react with the hydroxyl group in cellulose to form ester (Yang, 2003). In particular, the effective polycarboxylic anhydride can be used as a cross-linker for preparing wrinkle-resistant cellulosic fabrics due to the two anhydride rings, which are more reactive to form ester bonds with hydroxyl groups (El-Tahlawy, El-Bendary, Elhendawy, & Hudson, 2005; Sricharussin, Ryo-Aree, Intasen, & Poungraksakirt, 2004). Therefore, when cellulose fabrics were treated with a solution containing BPTCD and sodium hypophosphite via a pad-dry-cure method, BPTCD cross links cellulose and undergoes the reactions shown in Scheme 1.

Through the treatment, the add-on percentage of BPTCD on cotton fabrics increased with increasing the BPTCD concentration in finishing baths, as shown in Fig. 2. The chemical structures of the BPTCD treated cotton fabrics with increasing BPTCD concentration were evaluated by using FTIR spectroscopy, shown in Fig. 3. All the spectra of cotton fabrics show a 1317 cm^{-1} band associated with the bending vibration mode of hydrocarbon structures as well as



Scheme 1. Esterification mechanism between BPTCD and cotton fabric.

1370 and 1430 cm^{-1} bands associated with symmetric stretching of carboxylate groups, which are originated from cellulosic molecules. There were almost no differences among the FTIR spectra (Fig. 2) except the samples treated with higher concentrations of BPTCD. A new peak attributed to ester band at 1727 cm^{-1} could only be observed in the spectra of the samples treated with 0.1 and 0.2 mole of BPTCD (Fig. 2(e) and (f)), indicating that incorporation of BPTCD on the cotton fabrics was successful. At low concentration of BPTCD in the finishing baths, the amount of incorporated BPTCD groups on cotton was very low, almost having no add-on rate on the treated fabrics (Fig. 2), and thus the FTIR spectra were unable to show the characteristic band of BPTCD from these samples.

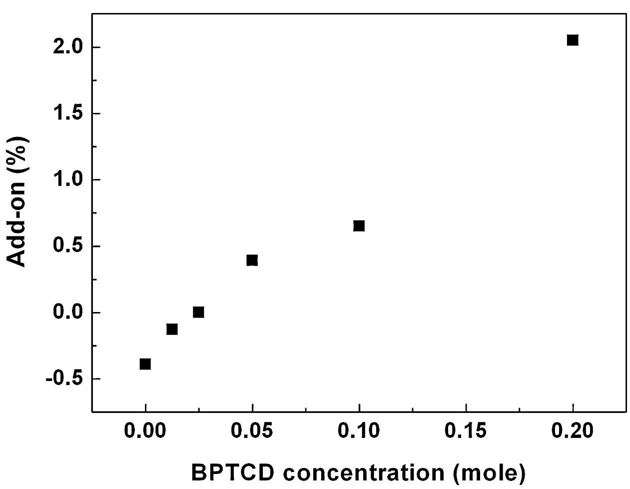


Fig. 2. Add-on (%) of BPTCD treated cotton fabrics as a function of BPTCD concentration.

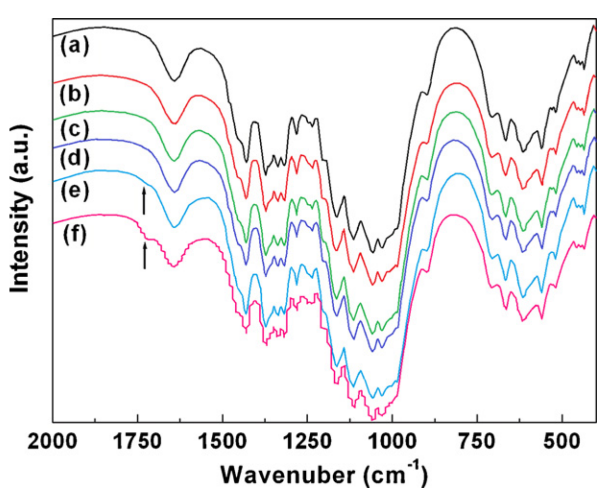


Fig. 3. FTIR spectra of cotton fabrics: (a) no BPTCD, (b) 0.0125 mole BPTCD treated, (c) 0.025 mole BPTCD treated, (d) 0.05 mole BPTCD treated, (e) 0.1 mole BPTCD treated, and (f) 0.2 mole BPTCD treated.

Due to the existence of multiple anhydride groups in BPTCD which can form ester bonds as cross-linking units between cellulose molecules, this treatment could consequently provide durable press effect on the cotton fabrics. In order to prove this a recovery angle test was conducted on the treated cotton, and the wrinkle resistant properties can be demonstrated in Fig. 4. Again, since the add-on rates of BPTCD on the fabric were quite low at low finishing concentrations of the treatment, only the samples treated with higher concentrations of BPTCD showed good performance.

3.2. Surface and mechanical properties of BPTCD incorporated cotton fabrics

Fig. 5 shows the surface morphologies of the BPTCD treated cotton fabrics. The SEM images reveal that the BPTCD treated fibers were almost same from the concentration changes of BPTCD, a sign of penetration of the chemical into the fibers. On the other hand, durable press finished cotton fabrics always lose their tensile strength significantly after the treatment. Such strength losses are caused by acid catalyzed depolymerization of cellulose by the chemical agent and catalyst, especially under high temperature (Meyer, Mueller, & Zollinger, 1976; Segal & Timpa, 1973; Yang & Bakshi, 1996; Zeronian et al., 1989). Cross-linking of cellulose molecules increases the brittleness of cotton fibers and reduces the strength of the cross-linked fabrics as well (Kang, Yang, Wei, & Lickfield, 1998). However, in this treatment, the BPTCD did not

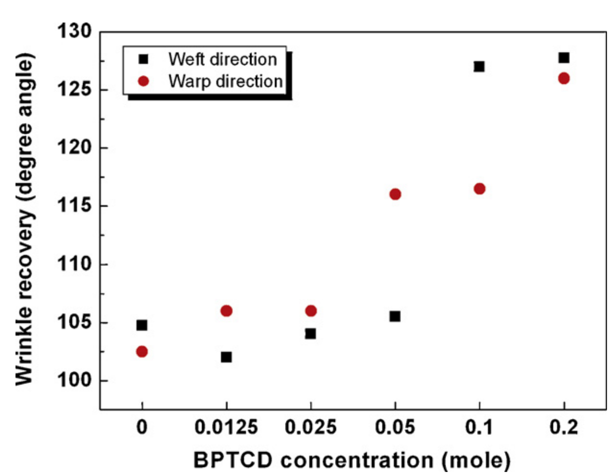


Fig. 4. Wrinkle recovery of BPTCD treated cotton fabrics as a function of BPTCD concentration.

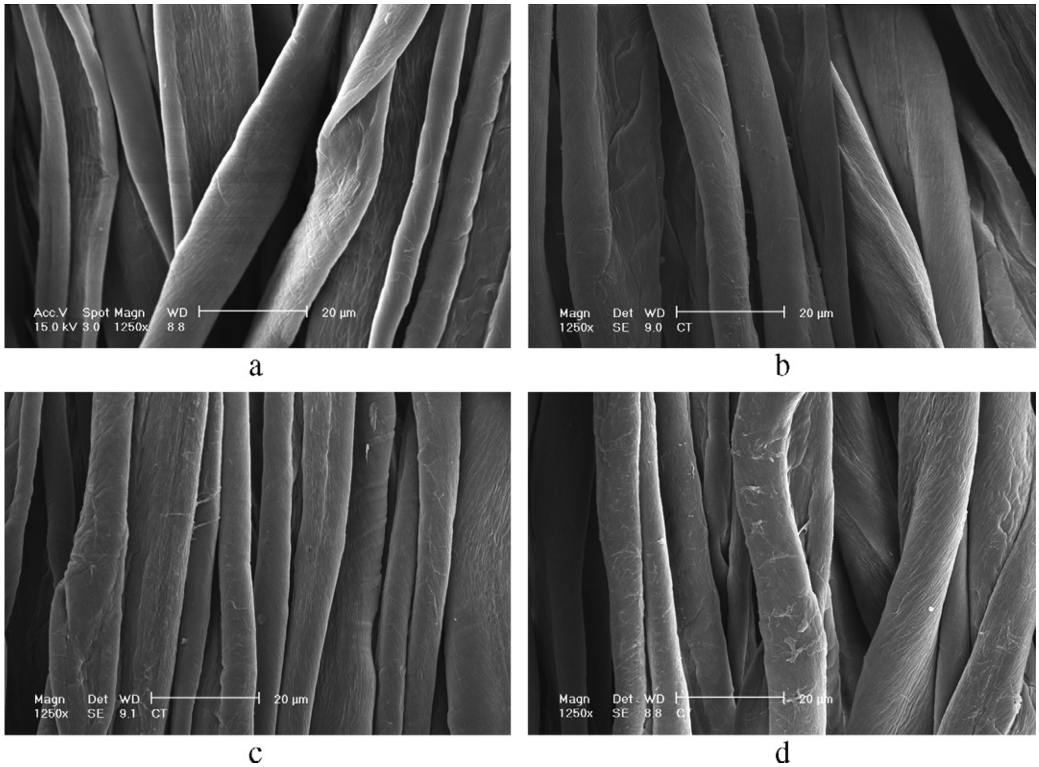


Fig. 5. SEM images of cotton fabrics: (a) pristine, (b) 0.025 mole BPTCD treated, (c) 0.025 mole BPTCD treated, and (d) 0.2 mole BPTCD treated.

impair the mechanical properties of cotton fabrics, as shown in Fig. 6, which was probably due to low acidity (pH is close to neutral) of the finishing solution. Increased BPTCD concentration in the finishing baths did not affect the tensile strength significantly. This is advantageous compared to other cross-linking agents on cellulose fiber, such as polycarboxylic acids and urea derivatives.

Thermal properties of the BPTCD treated cotton fabrics were evaluated by TGA. Fig. 7 shows that thermal degradation residue (%) of the cotton fabrics increases with increasing BPTCD concentration, while the decomposition temperature was decreased slightly. The BPTCD serving as crosslinking groups in the treated cotton fabrics increased carbonization rate of the treated fabrics during the thermal degradation, leading to high degradation residues. The pristine cotton fabric showed the highest decomposition onset temperature and lowest degradation residues.

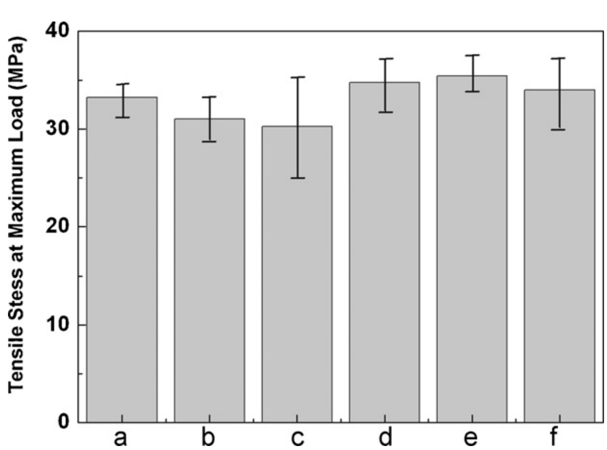


Fig. 6. Tensile strength of cotton fabrics: (a) no BPTCD, (b) 0.0125 mole BPTCD treated, (c) 0.025 mole BPTCD treated, (d) 0.05 mole BPTCD treated, (e) 0.1 mole BPTCD treated, and (f) 0.2 mole BPTCD treated.

3.3. Photo-reactivity of BPTCD incorporated cotton fabrics

BPTCD compound may have a fluorescent effect under light irradiation. Chromophoric reactions of pristine cotton fabric and the BPTCD treated cotton fabric were observed by using a fluorescent microscope, as shown in Fig. 8. It confirmed that benzophenone chromophoric groups were on the treated cotton fabrics, since we already observed that benzophenone chromophoric groups were activated by fluorescent as well as UVA light through our previous study (Hong & Sun, 2008a). On the other hand, antibacterial functions of BPTCD treated cotton fabrics were examined against *E. coli* and *S. aureus*, as shown in Table 1. When UVA light irradiated the BPTCD treated cotton fabrics inoculated by *E. coli and S. aureus*, the

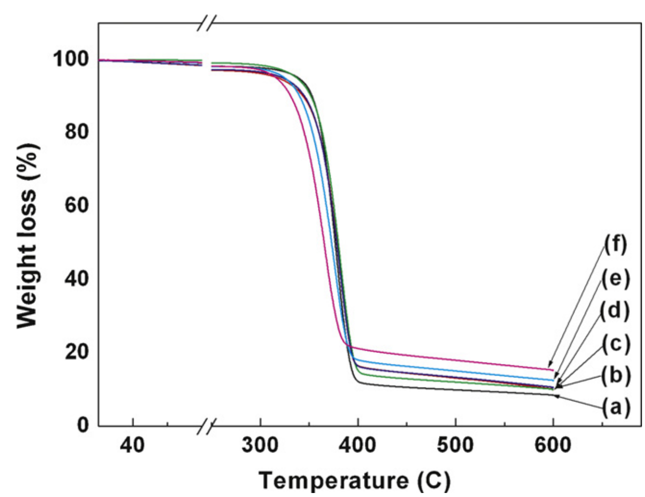


Fig. 7. TGA curves of cotton fabrics: (a) no BPTCD, (b) 0.0125 mole BPTCD treated, (c) 0.025 mole BPTCD treated, (d) 0.05 mole BPTCD treated, (e) 0.1 mole BPTCD treated, and (f) 0.2 mole BPTCD treated.

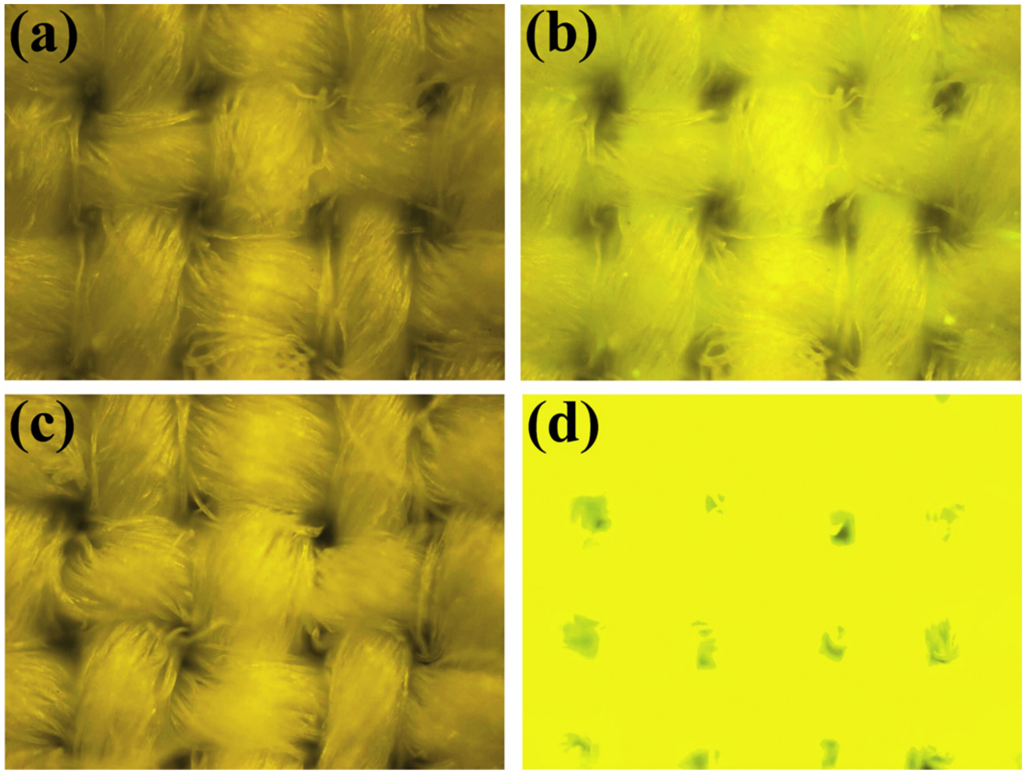


Fig. 8. Fluorescent images of cotton fabrics (magnification: 100×): (a) pristine cotton fabrics before fluorescent light irradiation, (b) pristine cotton fabrics after fluorescent light irradiation, (c) 0.2 mole BPTCD treated cotton fabrics before fluorescent light irradiation, and (d) 0.2 mole BPTCD treated cotton fabrics after fluorescent light irradiation.

Table 1
Antimicrobial abilities of BPTCD treated cotton fabrics as a function of BPTCD concentration against *E. coli* and *S. aureus*. (UVA exposure to all of the following samples for 2 h).

BPTCD concentration (mole)	*E. coli*					*S. aureus*				
	Dilution ratio of microbial solution after contact time				Bacterial reduction %	Dilution ratio of microbial solution after contact time				Bacterial reduction %
	1	10^{-1}	10^{-2}	10^{-3}		1	10^{-1}	10^{-2}	10^{-3}	
No BPTCD	110	14	1	0	–	164	21	6	2	–
0.0125	57	6	1	0	48.18	32	7	4	1	80.49
0.025	34	6	0	0	69.09	16	3	1	0	90.24
0.05	19	3	1	0	82.73	10	2	0	0	93.90
0.1	1	0	0	0	99.09	0	0	0	0	>99.99
0.2	0	0	0	0	>99.99	0	0	0	0	>99.99

colony forming numbers of the bacteria were significantly reduced, in a reduction rate of 99.99% for the sample treated with 0.2 mole of BPTCD. Therefore, we found that the BPTCD treated cotton fabrics have the excellent antimicrobial functions against both gram positive and gram negative bacteria under UVA light.

4. Conclusion

Benzophenone chromophoric groups were incorporated onto cellulose by treating cotton fabrics with BPTCD via a pad-dry-cure method. Through the spectroscopic analysis of the BPTCD treated cotton fabrics, formation of the esterification between BPTCD and cellulosic polymer was verified. And the BPTCD treated cotton fabrics showed wrinkle resistant properties just like any cross-linker treated cotton fabrics for durable press finishing, nevertheless the mechanical strength of the cotton fabrics remained after the treatment. Also the antibacterial effect of the treated cotton fabrics was manifested only when it was irradiated by UVA light, indicating that the benzophenone chromophoric group in the treated cotton fabrics was activated to form radicals under UVA illumination.

Acknowledgement

This work was supported by the National Science Foundation (CTS-0424716).

References

El-Tahlawy, K. F., El-Bendary, M. A., Elhendawy, A. G., & Hudson, S. M. (2005). The antimicrobial activity of cotton fabrics treated with different crosslinking agents and chitosan. *Carbohydrate Polymers*, *60*, 421–430.

Görner, H. (2003). Photoreduction of 9,10-anthraquinone derivatives: Transient spectroscopy and effects of alcohols and amines on reactivity in solution. *Photochemistry and Photobiology*, *77*, 171–179.

Griller, D., & Ingold, K. U. (1976). Persistent carbon-centered radicals. *Accounts of Chemical Research*, *9*, 13–19.

Hong, K. H., & Sun, G. (2007a). Photocatalytic functional cotton fabrics containing benzophenone chromophoric groups. *Journal of Applied Polymer Science*, *106*, 2661–2667.

Hong, K. H., & Sun, G. (2007b). Preparation and properties of benzophenone chromophoric group branched polymer for self-decontamination. *Polymer Engineering and Science*, *47*, 1750–1755.

Hong, K. H., & Sun, G. (2008a). Antimicrobial and chemical detoxifying functions of cotton fabrics containing different benzophenone derivatives. *Carbohydrate Polymers*, *71*, 598–605.

Hong, K. H., & Sun, G. (2008b). Structures and photoactive properties of poly(styrene-co-vinylbenzophenone). *Journal of Polymer Science: Part B: Polymer Physics*, *46*, 2423–2430.

Hong, K. H., & Sun, G. (2010a). Photoactive antimicrobial agents/polyurethane finished leather. *Journal of Applied Polymer Science*, *115*, 1138–1144.

Hong, K. H., & Sun, G. (2010b). Photoactive antimicrobial PVA hydrogel prepared by freeze-thawing process for wound dressing. *Polymer Science and Engineering*, *50*, 1780–1787.

Kang, I. S., Yang, C. Q., Wei, W., & Lickfield, G. C. (1998). Mechanical strength of durable press finished cotton fabrics: Part I: Effects of acid degradation and crosslinking of cellulose by polycarboxylic acids. *Textile Research Journal*, *68*, 865–870.

Klueh, U., Wagner, V., Kelly, S., Johnson, A., & Bryers, J. D. (2000). Efficacy of silver-coated fabric to prevent bacterial colonization and subsequent device-based biofilm formation. *Journal of Biomedical Materials Research B: Applied Biomaterials*, *53*, 621–631.

Kochi, J. K. (1973). *Free radical*. New York: J. Wiley.

Korchev, A. S., Konovalova, T., Cammarata, V., Kispert, L., Slaten, L., & Mills, G. (2006). Radical-induced generation small silver particles in SPEEK/PVA polymer films and solutions: UV–vis, EPR, and FT-IR studies. *Langmuir*, *22*, 375–384.

Lin, J., Qiu, S., Lewis, K., & Klibanov, A. M. (2003). Mechanism of bactericidal and fungicidal activities of textiles covalently modified with alkylated polyethylenimine. *Biotechnology and Bioengineering*, *83*, 168–172.

Meyer, U., Mueller, K., & Zollinger, H. (1976). Comparison of textile mechanical properties of cotton in crosslinking with dimethylolethyleneurea and formaldehyde. *Textile Research Journal*, *46*, 813–817.

Segal, L., & Timpa, J. D. (1973). Strength losses and structural changes in cotton fabric crosslinked with dimethylolethyleneurea. *Textile Research Journal*, *43*, 185–194.

Sricharussin, W., Ryo-Aree, W., Intasen, W., & Poungraksakirt, S. (2004). Effect of boric acid and BTCA on tensile strength loss of finished cotton fabrics. *Textile Research Journal*, *74*, 475–480.

Sun, Y., & Sun, G. (2003). Novel refreshable N-halamine polymeric biocides: Grafting hydantoin-containing monomers onto high performance fibers by a continuous process. *Journal of Applied Polymer Science*, *88*, 1032–1039.

Yang, C. Q., & Bakshi, G. (1996). Quantitative analysis of the nonformaldehyde durable press finish on cotton fabric: Acid–base titration and infrared spectroscopy. *Textile Research Journal*, *66*, 377–384.

Yang, C. Q. (2003). Infrared spectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. I. Identification of the cyclic anhydride intermediate. *Journal of Polymer Science Part A: Polymer Chemistry*, *31*, 1187–1193.

Yuranova, T., Rincon, A. G., Bozzi, A., Parra, S., Pulgarin, C., Albers, P., et al. (2003). Antibacterial textiles prepared by RF-plasma and vacuum-UV mediated deposition of silver. *Journal of Photochemistry and Photobiology A: Chemistry*, *161*, 27–34.

Tashiro, T. (2001). Antibacterial and bacterium adsorbing macromolecules. *Macromolecular Materials and Engineering*, *286*, 63–87.

Zeronian, S. H., Bertoniere, N. R., Alger, K. W., Duffin, K. W., Kim, M. S., Dubuque, L. K., et al. (1989). Effect of dimethyloldihydroxyethyleneurea on the properties of cellulosic fibers. *Textile Research Journal*, *59*, 484–492.