Photocatalytic Functional Cotton Fabrics Containing Benzophenone Chromophoric Groups

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ABSTRACT: In preparation of self-decontamination clothing materials in high reactivities against toxic agents, photoactive benzophenone chromophoric groups were incorporated into cotton fabrics. The cotton fabrics were treated by using 4-hydroxybenzophenone as a reagent, 1,2,3,4,-butanetetra carboxylic acid (BTCA) as a crosslinker, and sodium hypophosphite as a catalyst. The fabric treatment was conducted by a pad-dry-cure method. The benzophenone chromophoric group incorporated cotton fabrics were characterized by FTIR, SEM, TGA, and so on. The results confirmed the expected structures of the benzophenone chromophoric group modified and BTCA crosslinked cotton fabrics. The treated cotton fabrics demonstrated radical reactivities and antibacterial activity under UV irradiation. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2661–2667, 2007

Key words: self-decontamination; cotton; antibacterial fabrics; radical; 4-hydroxybenzophenone; 1,2,3,4,-butanetetra carboxylic acid (BTCA)

INTRODUCTION

Recent development in science and technology has generated unprecedented disturbances in global elemental cycles. The use of anthropogenic toxic chemicals, pathogenic bacteria, and the sophisiticated transportation systems have resulted in severe pressure on the existing ecosystems.[1] As a result, environmental and human health has become an urgent challenge to scientists and researchers. More importantly, protection of human body from toxic chemicals and pathogens is an interesting research subject, and development of protective clothing materials, such as chemical resistant membranes,[2,3] antimicrobial finishings,[4–8] is a solution. Especially, the range of applications for antimicrobial surfaces has spawned a number of different synthetic strategies. When applied to textiles, the resultant self-decontaminating fabrics have potential possible benefits of reduced disease transmission among hospital populations, biowarfare protection and other applications.[9]

A wide range of antimicrobial agents have been added to textiles, including silver-based,[4,7] halamine compounds,[5] and quaternary ammonium[6,8] or phosphonium polymers.[8] More recently, through our preliminary experiment, we have found that photo-initiated radicals could be also potential agents for self-decontamination applications. Radicals, being highly reactive chemical species possessing at least one unpaired electron, tend to undergo fast reactions.[10] A large number of significant chemical processes involve the radical reactions, such as biological reduction of O_2 by antioxidants and technologically important production of acrylic polymers via radical addition of unsaturated molecules. In particular, benzophenone chromophoric group, known to undergo light-excitation to n, π^* triplet states are commonly used as photosensitizers in photochemistry. Triplet benzophenone diradical structure can be readily quenched by oxygen, and it can also abstract 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. Therefore, the fabrics containing benzophenone chromophoric group would be easily excited to the radicals that can then decompose not only bacteria but also toxic compounds when activated by UV light. Also, benzophenone structures have been used as an UV absorbent for a long time, and the effect was extensively examined and discussed.[11,12] Thus, the light fastness of the benzophenone chromophoric groups on the fabrics should be durable.

In this study, self-decontamination fabrics containing benzophenone chromophoric groups were

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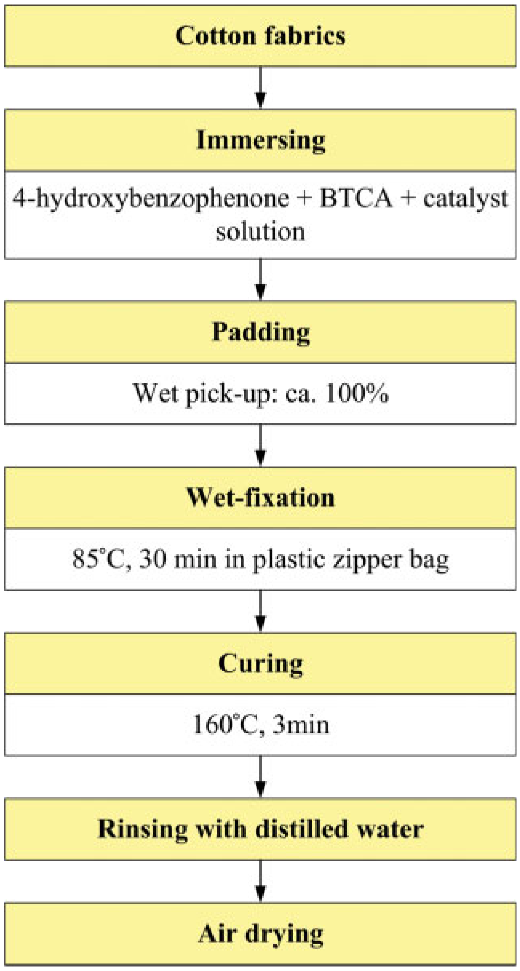


Figure 1 Preparation process of benzophenone chromophoric group incorporated cotton fabrics. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

prepared by reacting cotton fabrics with 4-hydroxybenzophenone as a reagent, 1,2,3,4,-butanetetra carboxylic acid (BTCA) as a crosslinker, and sodium hypophosphite as a catalyst via a pad-dry-cure method. The structures of the modified fabrics were characterized by using different instrumentations, and the decontaminating properties were evaluated.

EXPERIMENTAL

Materials

Bleached and desized cotton fabrics (no. 400) were purchased from Testfabrics Inc. (West Pittston, PA). 4-hydroxybenzophenone (99+%), BTCA, and sodium hypophosphite hydrate were purchased from Aldrich (Milwaukee, WI). And all other reagents were purchased from Fisher Science (Pittsburgh, PA) or Acros (Fair Lawn, NJ).

Fabric finishing process

The laboratory procedure used to incorporate benzophenone chromophoric groups to cotton fabrics is shown in Figure 1. The cotton fabrics, cut in sizes of around 30 cm × 30 cm, were immersed in a finishing solution containing designated concentrations (0.05–0.2*M*) of 4-hydroxybenzophenone, 0.1*M* of BTCA, and 0.1*M* of sodium hypophosphite hydrate. The fabrics were padded through a laboratory padder to have a wet pick-up rate around 100%. Then the treated fabrics were wet-fixed by putting them in plastic zipper bags and storing them in a convection oven for 30 min at 85°C. Then, the fabrics were cured at 160°C for 3 min, and then 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, Ultraviolet spectonics, NY) was used for photoactivation of the treated cotton fabrics.

Characterization

Add-on of benzophenone chromophoric groups in the treated cotton fabrics was measured by a weighing method on the basis of the weigh changes of the fabrics before and after treatment. Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 6700 FTIR spectrometer (Thermo electron, Madison, WI) with a resolution of 4 cm^{-1}, and the measurements were carried out with an attenuated total reflectance (ATR) technique. UV-VIS absorbance of the chemicals was taken with a

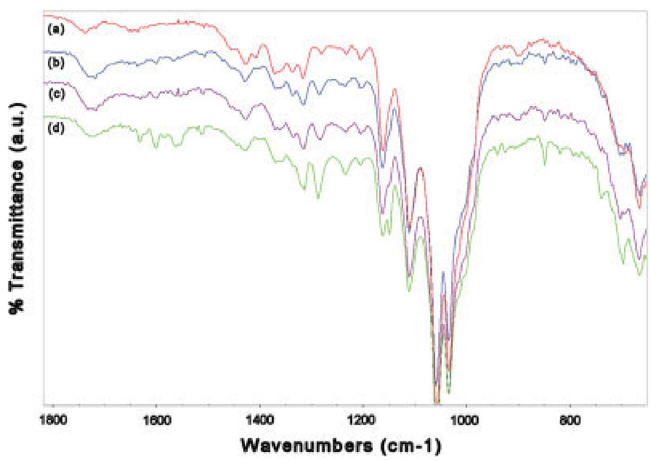
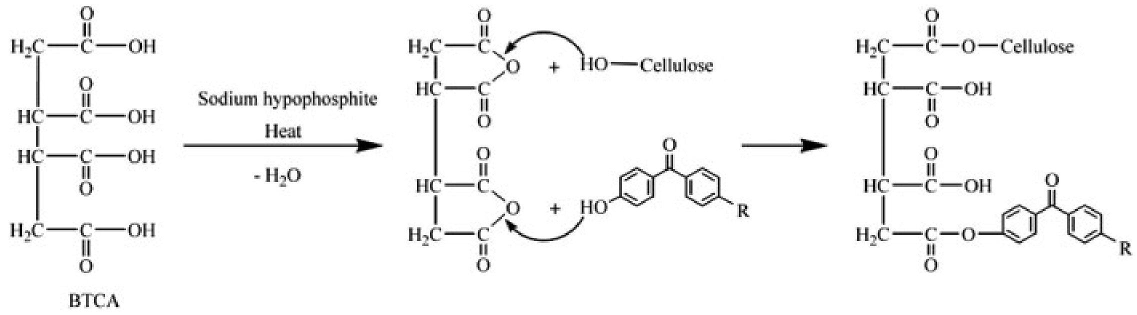


Figure 2 FTIR-ATR spectra of cotton fabrics; (a) pristine, (b) 0.05*M* 4-hydroxybenzophenone treated, (c) 0.1*M* 4-hydroxybenzophenone treated, and (d) 0.2*M* 4-hydroxybenzophenone treated; the other agents in the finishing bath: 0.1*M* BTCA and 0.1*M* sodium hypophosphite hydrate; curing condition: 160°C/3 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 1 Esterification mechanism of BTCA with cellulosic substrate and 4-hydroxybenzophenone.

Hitachi U-2000 spectrophotometer (Hitachi instruments, Santa Clara, CA) in a wavelength range of 200–800 nm. Thermogravimetric analysis (TGA) was carried out with a Shimadzu TGA-50 apparatus (Shimadzu science instruments, Columbia, MD) at a heating rate of 10°C/min from 30 to 550°C under a nitrogen atmosphere. A field emission scanning electron microscope (FE-SEM) (Philips XL30, USA) was used for high-magnification observation. Color difference of the fabrics was evaluated in terms of Yellowness (ASTM E 313 73 D 1925) and Whiteness (CIE Ganz 82) with a spectrophotometer (GretagMacbeth™ Color-Eye 7000A, USA) under CIE illuminant D65 with the 10° standard observer. The tensile strength of the fabrics was measured by the cut strip method (KS K 0520-1995) with an Instron 4465. 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 modified testing method for antibacterial activity of textiles (AATCC 100). During the antimicrobial test, both 4-hydroxybenzophenone/BTCA-treated and pristine cotton fabrics were inoculated by bacteria and then illuminated under UV light (≈ 365 nm) in a container for 1 h at room temperature. In addition, 4-hydroxybenzophenone/BTCA-treated cotton fabric that was bacteria inoculated but not irradiated by UV light was also used as a reference. After the contact time (1 h), 0.1 mL of microbial suspension was taken from the container and then the suspension was diluted to 10^1, 10^2, 10^3, and 10^4 in series. 100 μL of the dilution was placed onto agar plates and incubated at 37°C for 18 h. The reductions of bacteria were calculated according to the following equation.

$$\text{Reduction (\%)} = \frac{(B - A)}{B} \times 100 \tag{1}$$

where, A and B are the surviving bacterial cells (colony forming unit mL^{-1}) for the plates containing test samples (treated cotton fabrics) and the control (pristine cotton fabric), respectively.

RESULTS AND DISCUSSION

Preparation of benzophenone chromophoric group incorporated cotton fabrics

Crosslinking cotton cellulose with polycarboxylic acids, such as BTCA, is well known.[13,14] The reaction of polycarboxylic acid with cellulosic polymers occurs through esterification of hydroxyl groups, although not all the carboxylic acids will be able to react with the cellulosic substrate. The effective polycarboxylic acids contain three or more carboxylic groups and those groups are capable of forming five- or six-member cyclic anhydride rings. Researchers have suggested that polycarboxylic acids react with cellulosic hydroxyl groups by formation of cyclic anhydride as reaction intermediates.[13,14] Therefore, when cellulose fabrics were treated with a solution containing 4-hydroxybenzophenone, BTCA, and sodium hypophosphite via a pad-dry-cure method, BTCA could serve as crosslinking unit to connect 4-hydroxybenzophenone to the cellulosic substrate through esterification, as shown in Scheme 1.

Concentration of 4-hydroxybenzophenone concentration on the treated cotton fabrics would affect chemical reactivities of the products. Figure 2 shows the FTIR-ATR spectra of pristine cotton fabric [Fig. 2(a)] and the 4-hydroxybenzophenone/BTCA-treated cotton fabrics with increasing concentration of 4-hydroxybenzophenone [Fig. 2(b–d)], respectively. All the cotton fabrics show a 1317 cm^{-1} band associated with the bending vibration mode of hydrocarbon structures as well as 1370 and 1430 cm^{-1} bands associated with symmetric stretching of carboxylate groups, which are originated from cellulosic molecules. However, the 4-hydroxybenzophenone/BTCA-treated cotton fabrics only show relatively narrow and distinct peaks at 1560 and 1602 cm^{-1} assigned to aromatic C=C stretch. Also, the 4-hydroxybenzophenone/BTCA-treated cotton fabrics reveal a peak at 1635 cm^{-1} assigned to carbonyl stretching, which seemed to be originated from the benzophenone chromophoric groups. Moreover, a peak at 850 cm^{-1} attributed to out-of-plane C—H vibration of *para*-substituted benzene ring and a peak at 1290 cm^{-1}

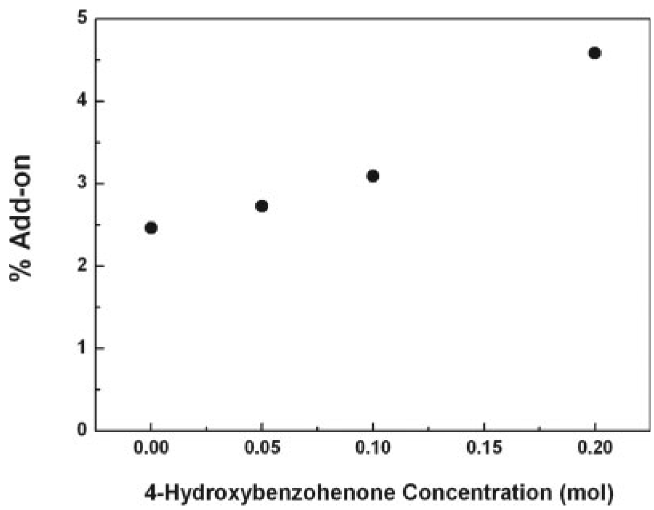


Figure 3 Percent add-on of treated cotton fabrics with increasing 4-hydroxybenzophenone concentration; the other agents in the finishing bath: 0.1*M* BTCA and 0.1*M* sodium hypophosphite hydrate; curing condition: 160°C/3 min.

attributed to ester C—O stretching were observed in the 4-hydroxybenzophenone/BTCA-treated cotton fabrics. These findings could serve as a proof of the linkage between BTCA and 4-hydroxybenzophenone. On the other hand, Yang[15] reported that the 1725 cm^{-1} band indicated the ester groups in the BTCA finished cotton fabrics, which includes both ester groups between the cotton cellulose and the acid molecules and the groups crosslinking the cotton cellulose molecules. Therefore, the linkages of cellulose molecule-BTCA-benzophenone chromophoric group could also form in the 4-hydroxybenzophenone/BTCA-treated cotton fabrics. On the other hand, it was observed that the peaks originated from benzophenone chromophoric groups increased as the 4-hydroxybenzophenone concentration in the finishing bath was increased, consistent with the increase of add-on of the treated cotton fabrics as shown in Figure 3.

Surface and mechanical properties of benzophenone chromophoric group incorporated cotton fabrics

Surface morphologies of pristine cotton fabric and the 4-hydroxybenzophenone/BTCA-treated cotton fabrics with increasing 4-hydroxybenzophenone concentration are shown in Figure 4. The SEM reveals that a layer of relatively thin and uniformed coating formed on the fabrics treated with up to the 0.1*M* of 4-hydroxybenzophenone/BTCA [Fig. 4(c)], but when the concentration was increased to 0.2*M* some flakes formed on the fibers [Fig. 4(d)]. It seems that excess amount of 4-hydroxybenzophenone did not react with BTCA and thus formed some hard masses on the surfaces of the fibers when the concentration of

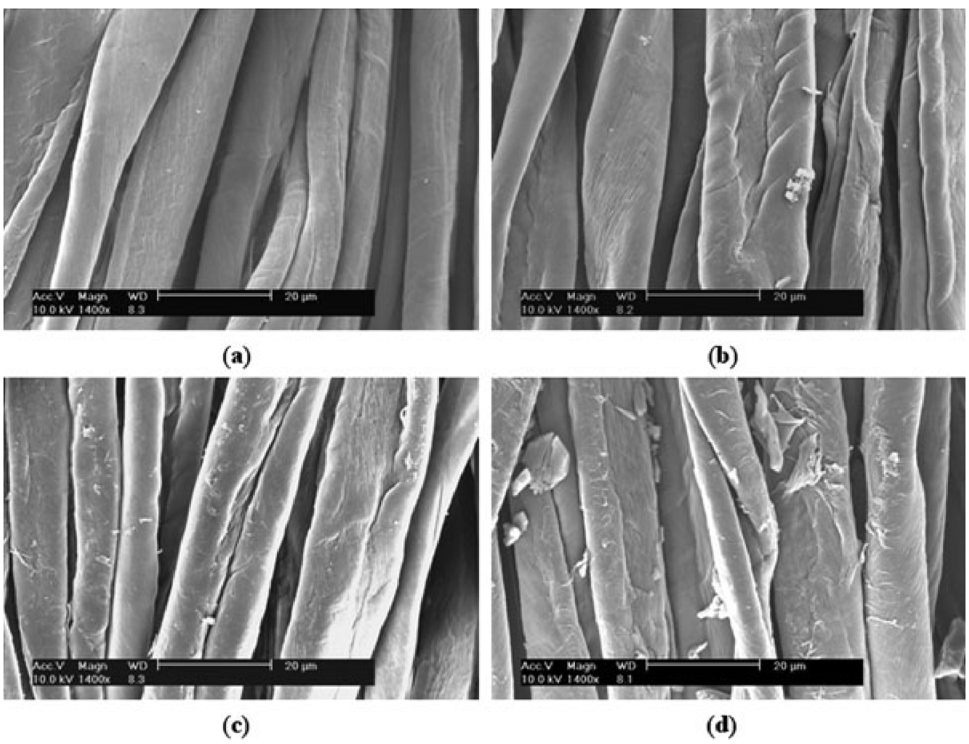


Figure 4 SEM morphologies of cotton fabrics; (a) pristine, (b) 0.05*M* 4-hydroxybenzophenone treated, (c) 0.1*M* 4-hydroxybenzophenone treated, and (d) 0.2*M* 4-hydroxybenzophenone treated; the other agents in the finishing bath: 0.1*M* BTCA and 0.1*M* sodium hypophosphite hydrate; curing condition: 160°C/3 min.

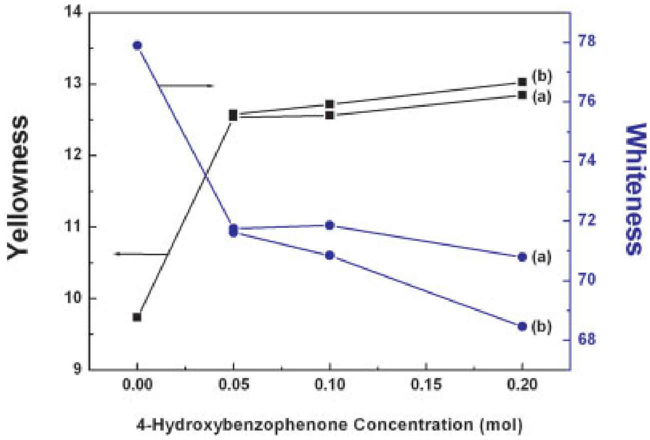


Figure 5 Whiteness and yellowness of treated cotton fabrics with increasing 4-hydroxybenzophenone concentration; (a) before UV illumination and (b) after UV illumination for 3 h; the other agents in the finishing bath: 0.1*M* BTCA and 0.1*M* sodium hypophosphite hydrate; curing condition: 160°C/3 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

4-hydroxybenzophenone was at 0.2*M* in the solution. These flakes could be removed by some mechanical forces or laundering.

We also investigated color variation of the 4-hydroxybenzophenone/BTCA-treated cotton fabrics with increasing the 4-hydroxybenzophenone concentration, and observed the color differences of the fabrics before and after UV irradiation. Figure 5 shows the increase in yellowness index and the decrease of whiteness index in the treated cotton fabrics with increasing the 4-hydroxybenzophenone concentration. Also, the discoloration is deteriorated after UV

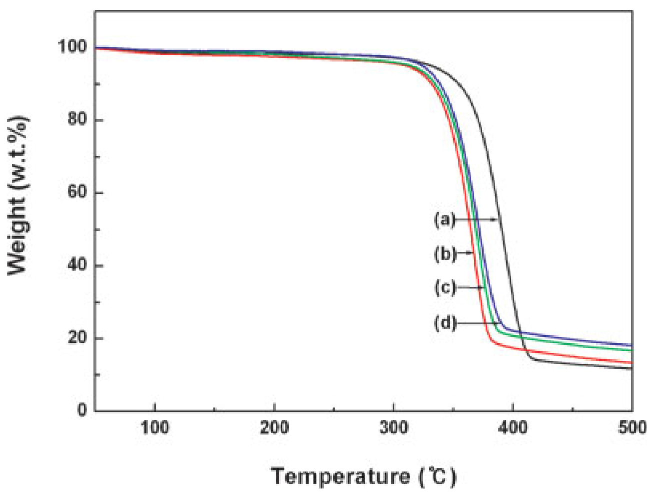


Figure 6 TGA curves of cotton fabrics; (a) pristine, (b) 0.05*M* 4-hydroxybenzophenone treated, (c) 0.1*M* 4-hydroxybenzophenone treated, and (d) 0.2*M* 4-hydroxybenzophenone treated; the other agents in the finishing bath: 0.1*M* BTCA and 0.1*M* sodium hypophosphite hydrate; curing condition: 160°C/3 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

irradiation. Similar results were observed in Yang and Naarani's studies,[11] in which UV absorbants with benzophenone structures were applied in various fabrics.

Figure 6 shows that thermo degradation residue (%) of the cotton fabrics increases with increasing the 4-hydroxybenzophenone concentration. The benzophenone chromophoric groups in the treated cotton fabrics increase carbonization rate of the treated fabrics under thermodegradation. However, pristine cotton fabric showed the highest decomposition onset temperature, followed by a decreasing order of 0.2*M* 4-hydroxybenzophenone/BTCA-treated cotton fabric >0.1*M* 4-hydroxybenzophenone/BTCA-treated cotton fabric >0.05*M* 4-hydroxybenzophenone/BTCA-treated cotton fabric. This result indicates that the decomposition onset temperature of cotton fabrics was affected by the finishing process, because the decomposition of cellulosic substrate is catalyzed by the low acidity of BTCA at an elevated temperature. The 0.2*M* 4-hydroxybenzophenone/BTCA-treated cotton fabric shows the highest decomposition onset temperature among the treated cotton fabrics. It seems that the 0.2*M* 4-hydroxybenzophenone/BTCA-treated cotton fabric has most amount of aromatic structure originated from benzophenone chromophoric groups, and so the aromatic structure intrinsically shows a good heat resistance character.

The average tensile strength of pristine cotton fabrics, BTCA-treated cotton fabrics, and 0.1*M* 4-hydroxybenzophenone/BTCA-treated cotton fabrics are shown in Figure 7. The tensile strengths of the cotton fabrics before and after UV illumination were also measured to investigate the effect of benzophenone chromophoric radicals on the mechanical strength of cellulosic substrate. The tensile strengths

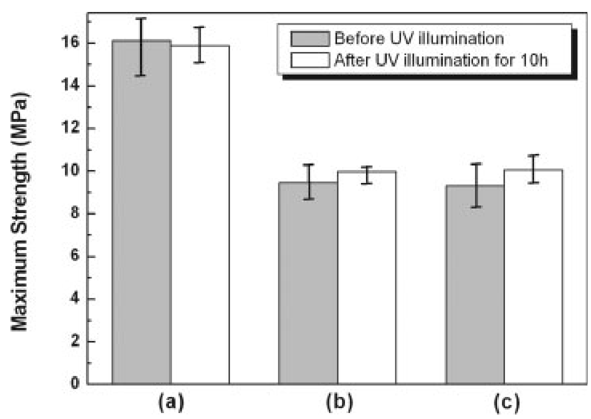


Figure 7 Tensile strength of cotton fabrics before and after UV illumination; (a) pristine, (b) 0.1*M* BTCA treated, (c) 0.1*M* 4-hydroxybenzophenone/0.1*M* BTCA-treated cotton fabrics; the other agent in the finishing bath: 0.1*M* sodium hypophosphite hydrate; curing condition: 160°C/3 min.

TABLE I
The Colony Numbers of *S. aureus* and *E. coli* After Injecting the 0.1 mL Bacterial Aqueous Solution on the Agar Plates and Incubating them at 37°C for 18 h

	Dilution ratio of *S. aureus* solution after contact time				Dilution ratio of *E.coli* solution after contact time			
	(10)	(10^2)	(10^3)	(10^4)	(10)	(10^2)	(10^3)	(10^4)
[UV treated] Pristine cotton fabrics	∞	57	5	0	∞	∞	∞	561
[No_UV treated] 0.1*M* 4-hydroxybenzophenone-treated cotton fabrics	∞	12	1	0	∞	∞	∞	47
[UV treated] 0.1*M* 4-hydroxybenzophenone-treated cotton fabrics	0	0	0	0	8	0	0	0

of the BTCA only treated cotton fabrics and the 0.1*M* 4-hydroxybenzophenone/BTCA-treated cotton fabrics were obviously lower than that of pristine cotton fabric. In general, BTCA-treated cellulosic fabrics suffer a major loss of such mechanical properties as tensile strength, tear strength, and abrasion resistance because of two key contributing factors; the acidity of the polycarboxylic acid at high temperature and the restriction of stress distribution within the fibers because of the crosslinking between cellulosic polymers.[14,16] However, there was no significant difference in the tensile strengths between the BTCA-treated cotton fabrics and the 0.1*M* 4-hydroxybenzophenone/BTCA-treated cotton fabrics. Also it was observed that the average tensile strength of the 0.1*M* 4-hydroxybenzophenone/BTCA-treated cotton fabrics hardly changed after 10 h UV illumination [Fig. 7(c)]. Therefore, the benzophenone chromophoric radicals seemed to have limited effect the mechanical strength of the cotton fabrics.

Antibacterial effect and UV-absorbing activity of benzophenone chromophoric group incorporated cotton fabrics

Antibacterial effect of the 4-hydroxybenzophenone/BTCA-treated cotton fabrics were examined against *S. aureus* and *E. coli* as shown in Table I. When UV light irradiated the 4-hydroxybenzophenone/BTCA-treated cotton fabrics during the contact with bacteria, the colony forming numbers of *S. aureus* and *E. coli* were significantly reduced, in a reduction rate of 99.99%; however, when UV light did not irradiate the treated cotton fabrics, the colony forming numbers of the bacteria little reduced. Therefore, it confirmed that the benzophenone chromophoric group incorporated cotton fabrics could inhibit the growth of the bacteria. It seems that the benzophenone chromophoric radicals on the treated cotton fabrics attacked the bacteria as if free radicals induce many unwanted side reactions in biological process (e.g.,

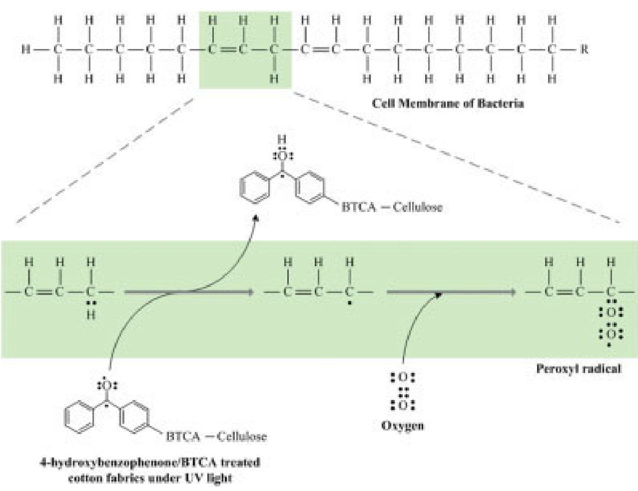


Figure 8 Potential peroxidation reaction involving a fatty acid in cell membrane of bacteria. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

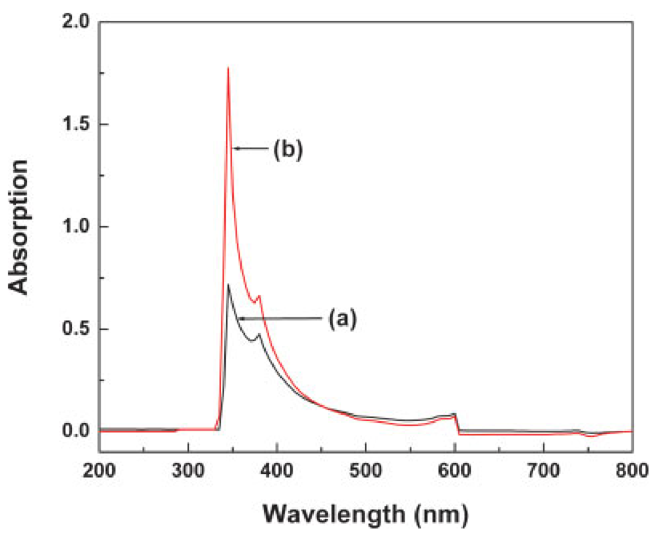


Figure 9 UV-VIS spectra of (a) pristine and (b) 0.1*M* 4-hydroxybenzophenone/0.1*M* BTCA-treated cotton fabrics. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the classic free radical syndrome, the free radical theory of aging).[17] One of the best known toxic effects of the free radicals is the damage to cellular membranes, which is initiated by a process known as lipid peroxidation, as shown in Figure 8. The peroxidation of membrane lipid can have numerous effects, including increased membrane rigidity, decreased activity of membrane-bound enzymes, altered activity of membrane receptors, and altered permeability. In addition to this effect, radicals can also directly attack membrane proteins and induce lipid–lipid, lipid–protein, and protein–protein crosslinking, all of which obviously have effects on membrane function.[18] On the other hand, it was observed that the 4-hydroxybenzophenone/BTCA-treated cotton fabrics absorbed more significantly around 340–400 nm than pristine cotton fabric did as shown in Figure 9.

CONCLUSIONS

Benzophenone chromophoric group incorporated cotton fabrics were successfully prepared by treating cotton fabrics in a finishing solution containing 4-hydroxybenzophenone, BTCA, and sodium hypophosphite via a pad-dry-cure method. Through the spectroscopic analysis of the 4-hydroxybenzophenone/BTCA-treated cotton fabrics, formation of the cellulosic polymer-BTCA-benzophenone chromophoric group was verified. Also the antibacterial effect of the treated cotton fabrics was manifested only when it was irradiated by UV light, and this indicates that the benzophenone chromophoric group in the treated cotton fabrics was activated to form radicals under UV illumination. Moreover UV absorbing ability of the treated cotton fabrics was observed and so light fastness might be expected in the treated cotton fabrics. On the other hand, the color of the 4-hydroxybenzophenone/BTCA-treated cotton fabrics turned to be yellowish by increasing the 4-hydroxybenzophenone concentration, and also the discoloration was deteriorated after UV irradiation. However, the mechanical strength of the treated cotton fabrics was not affected by the activated benzophenone chromophoric radicals.

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