Photoactive Antimicrobial Agents/Polyurethane Finished Leather

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ABSTRACT: To prepare antimicrobial coating on leather surfaces with high potency against microbes, photoactive agents such as benzophenone (BP) and rose bengal (RB) were incorporated into polyurethane-based coating solutions, respectively, and then the BP or RB containing solutions were applied onto surfaces of leather by a painting method. The photoactive antimicrobial agents treated leather samples were characterized by FTIR, SEM, and antimicrobial tests. The treated-leather samples demonstrated excellent antibacterial activity under fluorescent light as well as UVA light and also the antimicrobial ability showed the effective durability to abrasion and daylight.
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Key words: photoactive antimicrobial agent; benzophenone; rose bengal; leather finishing; polyurethane

INTRODUCTION

Leather has unique properties such as high strength, durability, breathability, elasticity, plasticity, cushioning comfort, life-like warmth, resistance to water, perspiration, slipperiness, and stiffness, which have not yet completely realized on the man-made materials.[1] Hence, leather is a popular material for fashion items, such as clothing, bags, and shoes, as well as living supplies, such as furniture, and has been widely employed in healthcare and hospitality facilities.

Leather processing involves the following steps: (1) pre-tanning operations to clean the hides or skins; (2) tanning to permanently stabilize the skin or hide matrix; and (3) post-tanning and finishing operation, designed to protect the leather and produce surface effects pleasing to look at and to touch.[2] Therefore, several finishing techniques and coating materials have been developed, which effectively mask the natural defects of leather and improve the surface qualities of leather in various aspects. Hence, it was thought that if some functional additives were applied to the surface of leather during the finishing process, the final leather products would have desired functions on the surface. In particular, we are interested in adding suitable antimicrobial agents onto leather surfaces so as to provide powerful, durable, and washable functions in hospital environment.

Polyurethane (PU) dispersions are the popular coating materials in leather finishing due to their excellent properties against abrasion and chemicals, as well as high-strength and low-temperature flexibility.[1] Therefore, in this study, PU dispersions were used as a basic coating material and two kinds of photoactive antimicrobial agents, benzophenone (BP), and rose bengal (RB) were added into the formulations. BP [Fig. 1(a)] is a good photosensitizer and has been used as a photoinitiator for reactions under ultra-violet radiation. Recently, BP chromophoric groups were found to easily produce radicals under both UVA (365 nm) and fluorescent light irradiation.[3–5] RB [Fig. 1(b)] is a xanthene photosensitizer with high-absorption coefficient in the visible region of the spectrum and a tendency to transfer electrons from its excited triplet state, producing long-lived radicals.[6,7] Therefore, RB has been exploited as a promising sensitizer in water treatment due to its water solubility, absorption in the visible region, good quantum yield of singlet oxygen, and inexpensiveness.[8–10] The BP or RB containing PU leather finishing solutions were applied onto the surface of leather by a painting method.

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EXPERIMENTAL

Materials

Leather sample (cowhide) before finishing process (unfinished leather), and PU-based finishing solution

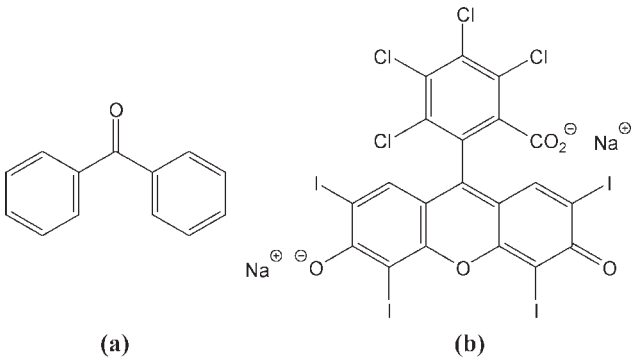

Figure 1 Chemical structures of benzophenone (a) and rose bengal (b).

for leather coating (Material number: 218123, Composition: polyurethane, polyacrylic acid derivative in aqueous dispersion) (Clariant Co., NC, USA) were kindly provided by Conneaut Leather (OH, USA). BP (99% pure), RB (60% pure), and acetone were purchased from Acros Co. (NJ, USA). All the reagents were used as received without any further purification.

Preparation

Unfinished leather was cut into 10 × 10 cm^2, and the surfaces of the small squares were cleaned by dry cotton fabrics. PU coating solutions were prepared just before the application with formulations displayed in Table I. The solution was applied to the surface of the cut leathers by a painting manner in an approximate amount of 0.9 g per 100 cm^2. Then, the leather patches coated by the polymer were placed in a convection oven set at 35°C for 3 min, and then left in atmospheric condition for 2 days to cure the coating.

On the other hand, an ultra-violet (UV) lamp (BLE-8 T365 (bandwidth: ≈ 365 nm); five 8W lamps (12″); sample to bulb distance: 15.8 cm), fluorescent lamps (light output: 400 lm; fiber 8W lamps (12″); sample to bulb distance: 15.8 cm), or the just daylight was used for the photoactivation.

Characterization

Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet 6700 FTIR spectrometer (Thermo Electron Co.) with a resolution of 4 cm^{-1}. The measurements of the materials were carried out by using KBr pellets, and the measurements of the coating layers on leather samples were carried with an attenuated total reflectance (ATR) device. Color differences of the leather samples were evaluated according to the CIELAB system using a spectrophotometer (GretagMacbeth™ Color-Eye 7000A, USA) under CIE illuminant D65 with the 10° standard observer. Hydrogen peroxide (H_2O_2) production analyses were conducted by irradiating the finished leather sample under UVA light for 1 h, and then immediately dripping distilled water (0.1 mL) on the surface of the leather sample. The sample in wet was kept in dark chamber for 1 h. Subsequently, H_2O_2 produced and dissolved in water was detected by a peroxide test strip (Code 2984LR, LaMotte Co., MD). The photoactive antimicrobial properties of the coated leather samples were tested against *Staphylococcus aureus* (*S. aureus*) (ATCC 12600, 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 films (DOW 0923).[11] The modified procedures are as follows: (1) the back

TABLE I
Formulations of Leather Coating Solution

	BP added coating solutions				
	BP-0	BP-1	BP-2	BP-3	BP-4
PU-based coating solution (g)	5	5	5	5	5
BP/*n*-propanol solution (0.15g/mL; 15.733 wt %) (g)	0	0.0625	0.125	0.25	0.5
n-propanol (g)	0.5	0.4375	0.375	0.25	0
BP concentration (wt %)	0	0.179	0.358	0.715	1.430
	RB added coating solutions				
	RB-0	RB-1	RB-2	RB-3	RB-4
PU-based coating solution (g)	5	5	5	5	5
RB/*n*-propanol solution (0.15g/mL; 15.733 wt %) (g)	0	0.0625	0.125	0.25	0.5
n-propanol (g)	0.5	0.4375	0.375	0.25	0
RB concentration (wt %)	0	0.179	0.358	0.715	1.430

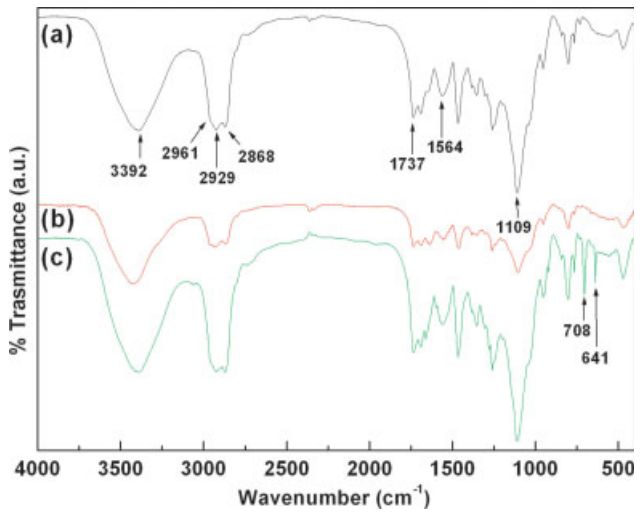

Figure 2 FTIR spectra of PU-based coating material (a), BP-4 incorporated PU coating material (b), and RB-4 incorporated PU coating material (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

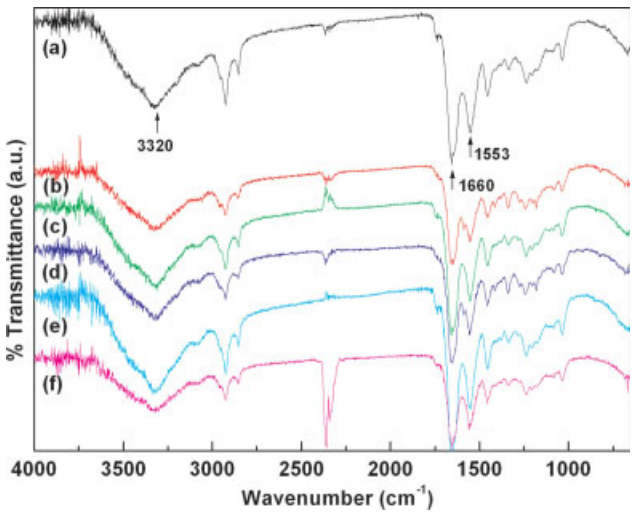

Figure 3 FTIR-ATR spectra of surface of BP/PU-coated leather samples with increasing BP concentration; (a) uncoated, (b) PU coated, (c) BP-1/PU coated, (d) BP-2/PU coated, (e) BP-3/PU coated, and (f) BP-4/PU coated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sides of the leather samples were irradiated by UVC (254 nm wavelength light) to sterilize them before the tests; (2) the surfaces (front sides) of the leather samples were inoculated by dropping and spreading 0.5 mL of diluted microbial aqueous solution onto the same areas on each surface of the leather samples; (3) following the inoculation, UVA light or fluorescent light was irradiated on the surface of leather samples covered by microbial solution for 1.5 h; (4) the leather samples were each immersed in quenching solution (distilled water) in sterilized containers, and the containers were placed in a shaker for 5 min to detach the microbes from the surfaces of leather samples to quenching solution; and then (5) 0.1 mL of microbial suspension (the quenching solution with microbes) was taken from the container, and then the suspension was diluted to 10^1, 10^2, 10^3, and 10^4 in series. One hundred microliters of the dilution was placed onto agar plates and incubated at 37°C for 18 h. 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 test polymer and control samples, respectively.

To evaluate the durability of the photoactive agents in the coated leather samples, the following two experiments were conducted. First, to investigate the durability against daylight, the leather samples were placed under daylight for 40 days (from 11 February 2009 to 23 March 2009), and then their antimicrobial abilities were tested. Second, to investigate the durability against abrasion, the surface of leather samples were imposed to abrasion by a manual crock meter (contact face was covered by 100% Dacron fabrics (Type 54, Testfabrics, Inc.)), and then the antimicrobial abilities of the abraded samples were tested.

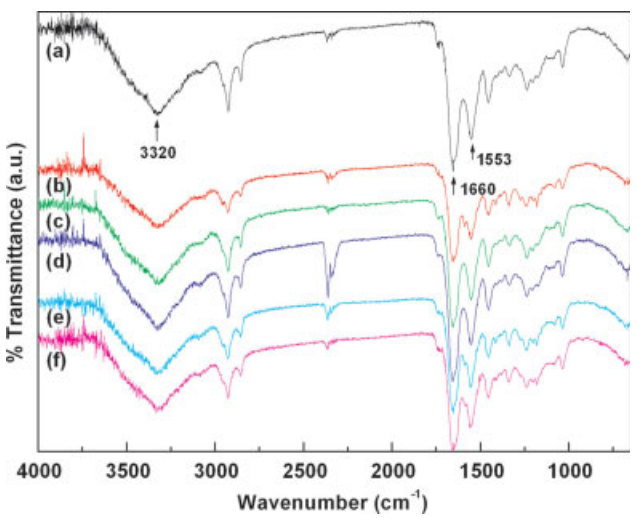

Figure 4 FTIR-ATR spectra of surface of RB/PU coated leather samples with increasing RB concentration; (a) uncoated, (b) PU coated, (c) RB-1/PU coated, (d) RB-2/PU coated, (e) RB-3/PU coated, and (f) RB-4/PU coated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

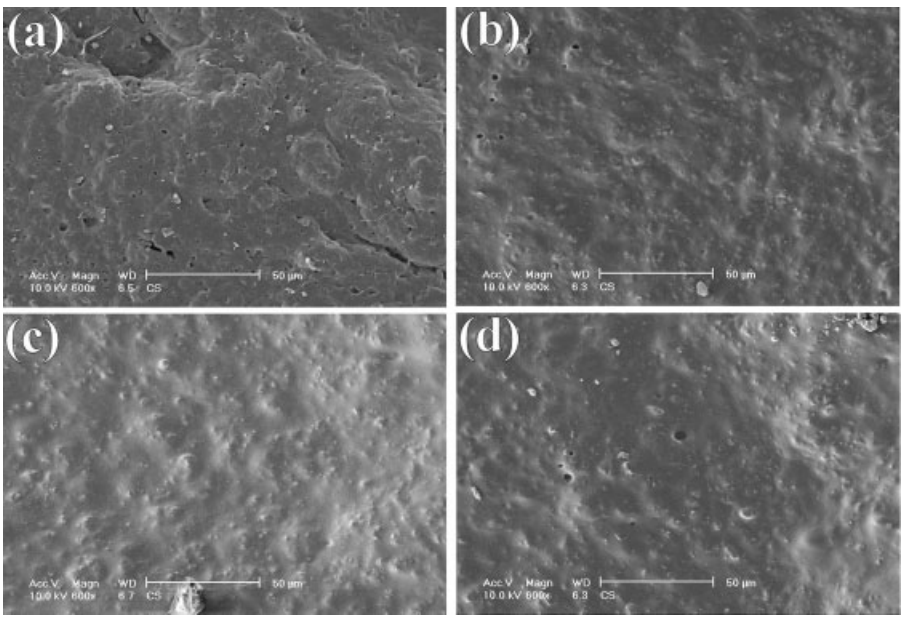

Figure 5 Surface morphologies of uncoated-leather (a), PU-coated leather (b), BP-4/PU-coated leather (c), and RB-4/PU-coated leather (d).

RESULTS AND DISCUSSION

Spectroscopic property

FTIR spectra of initial PU-based coating material, BP (1.43 wt %) containing PU coating material, and RB (1.43 wt %) containing PU coating material are given in Figure 2. The initial PU-based coating material shows PU characteristic peaks: N—H stretching vibration at 3392 cm^{-1}, C—H stretching band of CH_2 and CH_3 groups in PU at 2868, 2929, and 2961 cm^{-1}, C=O stretching at 1737 cm^{-1}, C—N stretching and NH deformation at 1564 cm^{-1}, C—O—C stretching bands at 1109 cm^{-1}.[1,12] Also, other photoactive antimicrobial agents added PU materials show almost the same characteristic peaks as the initial PU-based coating material. However, just in the spectrum of the RB added PU coating material [Fig. 2(c)], C—Cl stretching peaks due to RB structure are observed at 641 and 708 cm^{-1}.[13] Therefore, it seems that 1.43 wt % of BP or RB dose not have any significant effect on the PU-based coating material. Figures 3 and 4 each show FTIR-ATR spectra of the surfaces of the leather samples coated by BP containing PU (BP/PU finished leather samples) and RB containing PU (RB/PU finished leather samples), versus the concentration of the agent concentrations. The spectrum (a) in Figures 3 and 4 is bovine-tanned leather, mainly showing the bands due to polypeptide chains of the collagen: N—H stretching at 3320 cm^{-1}, C=O stretching at 1660 cm^{-1} and the amide II band

TABLE II
Color Differences of Coated-Leather Samples Under D65 Light

	L^*	a^*	b^*	ΔE
Pristine leather	24.259	0.133	0.005	–
BP-0 or RB-0	24.658	0.010	−0.445	0.601514
BP-1	24.748	−0.018	−0.468	0.696887
BP-2	24.725	−0.041	−0.440	0.498213
BP-3	24.714	−0.059	−0.490	0.496376
BP-4	24.793	−0.090	−0.431	0.581692
RB-1	24.688	1.812	0.007	1.787436
RB-2	24.964	3.320	0.211	3.270414
RB-3	24.881	3.928	0.036	3.849615
RB-4	24.431	4.187	−0.012	4.057931

TABLE III
Antimicrobial Abilities of BP/PU-Coated Leather Samples Under UVA light; Colony Numbers of *E.coli* and *S.aureus* after Placement of 0.1 mL Bacteria Suspension on Agar Plates and Incubation at 37°C for 18 h

	Dilution ratio of bacteria solution after contact time				Reduction of bacteria (%)
	10	10^2	10^3	10^4	
E.coli					
Blank	∞	∞	∞	26	–
BP-0	∞	19	3	1	–
BP-1	∞	17	4	0	0
BP-2	∞	28	1	0	0
BP-3	87	6	2	0	54.21
BP-4	1	0	0	0	99.47
S.aureus					
Blank	∞	∞	∞	∞	–
BP-0	32	6	0	0	–
BP-1	19	3	0	0	40.63
BP-2	7	1	0	0	78.13
BP-3	0	0	0	0	>99.9999
BP-4	0	0	0	0	>99.9999

TABLE IV
Antimicrobial Abilities of RB/PU-Coated Leather Samples Under UVA light; Colony Numbers of *E.coli* and *S.aureus* after Placement of 0.1 mL Bacteria Suspension on Agar Plates and Incubation at 37°C for 18 h

	Dilution ratio of bacteria solution after contact time				Reduction of bacteria (%)
	10	10^2	10^3	10^4	
E.coli					
Blank	∞	∞	∞	26	–
RB-0	∞	19	3	1	–
RB-1	∞	21	2	0	0
RB-2	∞	13	1	0	31.58
RB-3	∞	7	0	0	63.16
RB-4	0	0	0	0	>99.9999
S.aureus					
Blank	∞	∞	∞	∞	–
RB-0	32	6	0	0	–
RB-1	11	1	0	0	65.63
RB-2	4	0	0	0	87.50
RB-3	0	0	0	0	>99.9999
RB-4	0	0	0	0	>99.9999

(N—C=O stretching) at 1553 cm^{-1}.[12] Meanwhile, all other spectra in Figures 3 and 4 display almost the same pattern as the first spectrum of untreated-bovine leather. It was assumed that PU characteristic peaks mostly overlapped with the polypeptide peaks, and thus the spectroscopic peaks of the coating materials could not be separated from the polypeptide characteristic peaks.

Surface observation

Figure 5 shows the surface morphologies of pristine leather, PU only coated, BP/PU coated, and RB/PU-coated leather samples, respectively. It was observed that after PU coating on the pristine leather, the surface of leather became uniform and smooth, as shown in Figure 5(b). Even when the amount of BP or RB incorporated in the PU was increased to 1.43 wt %, the coating surfaces of the leather samples did not show any significant change compared with the surface of the PU-coated leather. However, RB added surface shows a little aggregation and this phenomenon agrees with a previous study.[10] On the other hand, Table II shows the color differences of the surfaces of the finished leather samples. The three coordinates of CIELAB represent the lightness of the color ($L^* = 0$ yields black and $L^* = 100$ indicates diffuse white; specular white may be higher), its position between red/magenta and green (a^*, negative values indicate green, whereas positive values indicate magenta) and its position between yellow and blue (b^*, negative values indicate blue and positive values indicate yellow).[14] RB is a naturally red colorant with absorption at around 550 nm.[15] Hence, even though we used black leather as a substrate in this study, the RB/PU finished leather still became reddish after the treatment, and

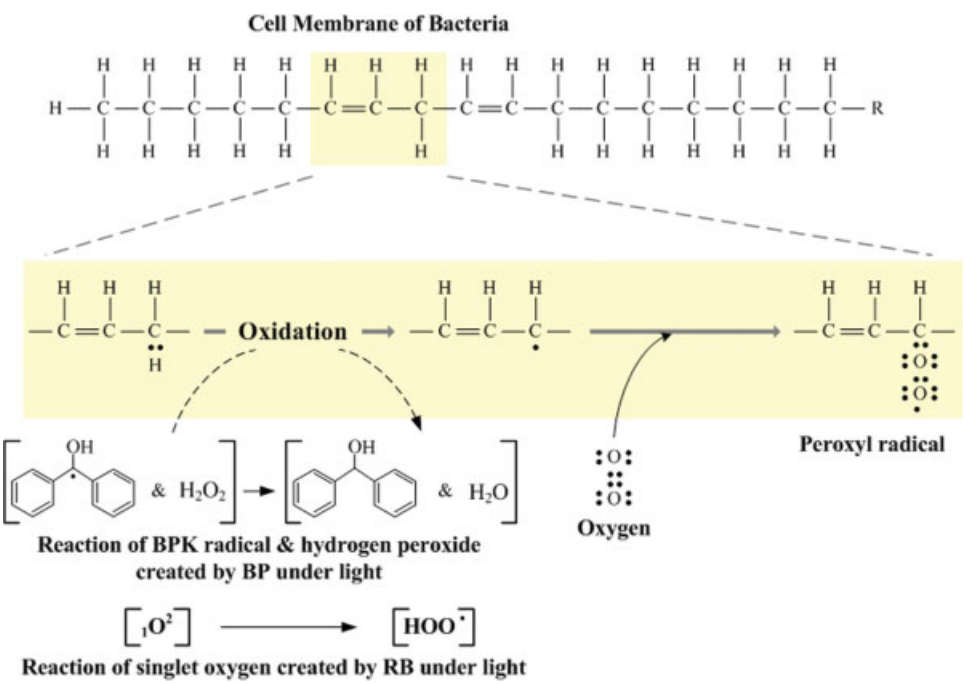

Figure 6 Potential peroxidation reaction involving the photoactive agents (BP and RB) and a fatty acid in cell membrane of bacteria. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Antimicrobial Abilities of BP/PU- and RB/PU-Coated Leather Samples Under Fluorescent Light; Colony Numbers of *E.coli* after Placement of 0.1 mL Bacteria Suspension on Agar Plates and Incubation at 37°C for 18 h

E.coli	Dilution ratio of bacteria solution after contact time 10	10^2	10^3	10^4	Reduction of bacteria (%)
Blank	∞	∞	164	21	–
BP-0 or RB-0	∞	79	7	3	–
BP-4	0	0	0	0	>99.9999
RB-4	0	0	0	0	>99.9999

TABLE VI
Antimicrobial Abilities of BP/PU- and RB/PU-Coated Leather Samples after Day Light Irradiation for 40 days; Colony Numbers of *E. coli* after Placement of 0.1 mL Bacteria Suspension on Agar Plates and Incubation at 37°C for 18 h

E.coli	Dilution ratio of bacteria solution after contact time 10	10^2	10^3	10^4	Reduction of bacteria (%)
Blank	∞	∞	∞	44	–
BP-0 or RB-0	∞	∞	132	16	–
BP-4	∞	9	1	0	99.32
RB-4	11	4	0	0	99.70

the redness increased as the amount of RB in the coating increased. Therefore, due to the strong color RB has certain color limitations to be used as a photoactive agent in some applications.

Antimicrobial ability

Tables III and IV show antimicrobial abilities of BP/PU and RB/PU-coated leather samples with increasing concentrations of the photoactive agents under UVA light irradiation. We already proved that the UVA light with 365 nm wavelength does not affect microbial growth.[3–5] Both of the BP/PU- and RB/PU-coated leather samples demonstrated excellent antimicrobial abilities against *E.coli* and *S.aureus* when the contents of the photoactive agents were at 1.43 wt %. BP can be excited into radical structures under UVA light, and at above 1.43 wt % of BP in the coating system, the radicals generated in BP/PU system provided antimicrobial functions. Also, BP is known as a photosensitizer that can attract hydrogen atoms from suitable donors, such as amines and alcohol, and form corresponding benzophenone ketyl (BPK) radicals under light.[16] It seems that the BPK radicals in PU coating material might attack bacteria as the free radicals could induce many unwanted side reactions in biological process (e.g., the classic free radical syndrome, such as skin aging).[17]

Also, when exposed to oxygen, the BPK can be rapidly oxidized back to BP (initial state) with an accompanying formation of H_2O_2. Both BP radical structures and H_2O_2 could provide antimicrobial functions. Thus, the carbamate group in PU could be an effective hydrogen donor to form BPK radicals from the BP/PU system and consequently producing H_2O_2. A peroxide strip test easily indicated the presence of H_2O_2 in the system after exposure to light, revealing that H_2O_2 could be a biocide to kill the bacteria in the BP/PU system. On the other hand, RB is well known to effectively generate singlet oxygen ($^1O_2$, Reactive oxygen species) under light.[18] Therefore, the singlet oxygen generated from the RB/PU system under UVA light could be another biocide in the RB/PU system, or it could result H_2O_2 in existence of oxygen. Proposed formation of the biocides by BP and RB under UVA light is suggested in Figure 6.

Table V displays the antimicrobial abilities of BP/PU- and RB/PU-coated leather samples, under fluorescent light irradiation. This result indicates that the photoactive agents/PU-coated leather samples could provide antimicrobial functions under very low energy irradiation. This is advantageous since these materials can provide antimicrobial functions under almost all potential daily light sources.

Durability of antimicrobial function

The durability of the photoactive antimicrobial agents/PU finished leather samples against daylight

TABLE VII
Antimicrobial Abilities of BP/PU- and RB/PU-Coated Leather Samples after Imposing Abrasion on Surface; Colony Numbers of *E.coli* after Placement of 0.1 mL Bacteria Suspension on Agar Plates and Incubation at 37°C for 18 h

E.coli	Dilution ratio of bacteria solution after contact time 10	10^2	10^3	10^4	Reduction of bacteria (%)
Blank	∞	∞	∞	32	–
BP-0 or RB-0	∞	∞	76	6	–
BP-4 (0)	0	0	0	0	>99.9999
BP-4 (20)	0	0	0	0	>99.9999
BP-4 (100)	0	0	0	0	>99.9999
BP-4 (500)	0	0	1	0	98.68
BP-4 (1000)	0	0	4	0	94.74
RB-4 (0)	0	0	0	0	>99.9999
RB-4 (20)	0	0	0	0	>99.9999
RB-4 (100)	0	0	0	0	>99.9999
RB-4 (500)	0	0	0	0	>99.9999
RB-4 (1000)	0	0	0	0	>99.9999

Numbers in parentheses are abrasion cycles.

and abrasion was investigated. No significant changes in the antimicrobial abilities of both BP/PU- and RB/PU-coated leather samples were observed after leaving the leather samples for 40 days under daylight, as shown in Table VI. On the other hand, the antimicrobial function of the photoactive agents/PU finished leather samples demonstrated relatively effective resistance to abrasion even though slight decrease in antimicrobial ability was observed in BP/PU finished leather samples over 500 cycles, as shown in Table VII.

CONCLUSIONS

Photoactive agents, BP, and RB were incorporated into PU dispersions, and the PU mixtures were coated onto leather samples. The surface of PU-coated leather samples became uniform and smooth, and the addition of the photoactive agents did not significantly affect the finishing effect of PU on leather in terms of surface morphology and touch. However, RB/PU coating made the surface of leather reddish due to the instinct color of RB. On the other hand, the photoactive agents/PU-coated leather samples showed excellent antimicrobial abilities against *E.coli* and *S.aureus*, and the antimicrobial functions demonstrated effective durability to abrasion and daylight.

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