Durable Antimicrobial Finish of Cotton Fabrics

Eun S. Bang,[1] Eui S. Lee,[1] Seung I. Kim,[1] Young H. Yu,[1] Soon E. Bae[2]

[1]*Department of Textile Engineering, Inha University, Incheon 402-751, Korea*
[2]*Department of Fashion and Design, Hanseo University, Seosan 356-706, Korea*

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ABSTRACT: Cotton fabrics were treated with Biopag, which does not have any functional groups that are reactive toward cellulose, using crosslinking agents or a binder, for the purpose of imparting a durable antimicrobial finish. In this respect, it was found that the crosslinking agents were more effective than the binder. It was confirmed by FT-IR that the characteristic split peaks of Biopag were still seen even after repeated launderings. The crosslinking agents deteriorated the whiteness and tensile strength of the Biopag-treated cotton fabrics, while the wrinkle recovery angles (WRAs) were significantly improved. The one-step padding of Biopag and the crosslinking agent was found to be superior to the two-step padding method in which Biopag padding was followed by padding of crosslinking agent in respect of WRA, whereas the whiteness and tensile strength were vice versa. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 938–943, 2007

Key words: antimicrobial; crosslinking; whiteness; wrinkle recovery angle

INTRODUCTION

Wastes secreted from the human body such as sweat and sebum cause the microorganisms that adhere to clothes to grow more easily, and cause an offensive odor and unpleasantness. Also, they alter the shade of the fabric and lower its strength. Treating clothes with an antimicrobial finish suppresses the growth of these microorganisms, thereby preventing the aforementioned problems from occurring. Recently, because of the rapid increase in the number of antibiotic resistant viruses such as MRSA and concerns about healthy living, research into antimicrobial finishes has been growing in importance. The chemicals used for antimicrobial finishes are organic compounds such as amines or quaternary ammonium compounds,[1] biguanide,[2-4] alcohols,[5] phenols,[6] and aldehydes, mineral compounds[7] such as metal ions, oxides, photocatalysts, organometallic compounds,[8,9] and natural compounds.[10-12] One of the most important factors to consider for the antimicrobial finish of cotton fabrics is its durability against repeated launderings.[13] One of the desirable methods endowing cotton fabrics with a durable antimicrobial finish using a topical finishing method is to have the antimicrobial agent bind or react with cellulose.[14]

This study was focused on improving the durability of the antimicrobial properties of cotton fabrics treated with an antimicrobial agent having no functional groups. A crosslinking agent used for producing a durable-press finish or a binder was added to the padding bath and its effects were investigated.

Correspondence to: E. S. Lee (eslee@inha.ac.kr).
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EXPERIMENTAL

Fabrics

Desized, scoured, bleached, and mercerized cotton cloth (84 × 64), weighing 118.9 g/m^2, was used.

Chemicals

The chemicals used in this study were biocide polymer (Biopag, Institute of Ecotechnologies, Russsia), binder (Helizarin FWT, BASF, Switzerland), glyoxal (Aldrich Chemical Co., Milwaukee, WI), dimethyloldihydroxyethylene urea (DMDHEU) (Fixapret CL, 75% aqueous solution, BASF, Switzerland), 1,2,3,4-butanetetracarboxylic acid (BTCA, Aldrich Chemical Co.), aluminum ammonium sulfate (Shinyo Pure Chemical Co., Japan), magnesium chloride (Aldrich Chemical Co.), sodium hypophosphite (Shinyo Pure Chemical Co.), Nutrient Broth (Becton Dickinson and Company Sparks, MD), and Bacto Agar (Becton Dickinson and Company Sparks).

Treatment of fabrics

The cotton fabrics were treated by the pad–dry–cure process.[15] The fabrics were padded with the 2 dip-2 nip method[16] using a padder (horizontal and vertical type HVP, 1 bar, 1 m/min, Werner Mathis AG,

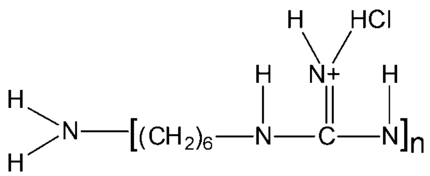

Figure 1 Chemical structure of Biopag (n = 30–50).

Swiss), and the wet pickup was (102 ± 2)%. The dry and cure process was carried out using a Laboratory Drying and Curing Machine (CH-815, Werner Mathis AG, Swiss). The treated fabrics were thoroughly washed with frequent stirring in water at 50°C for 30 min, and then dried.[17] All of the samples were conditioned at 20°C, under 65% relative humidity atmosphere.

Tests and analysis

Bactericidal activity test

The durable bactericidal properties were quantitatively evaluated with the Gram-negative bacteria, *Klebsiella pneumoniae* ATCC No. 4352 according to AATCC Test Method 100. The activity of the bacteria used in this test should be sufficiently high as to increase in number more than 31.6 times after 18 h of cultivation. The bacteriostatic ratio (%) was calculated from the following equation:

$$\text{Bacteriostatic ratio (\%)} = (M_b - M_c)/M_c \times 100$$

where M_b and M_c are the numbers of bacteria recovered from the inoculated control and treated specimen after 18 h of incubation, respectively.

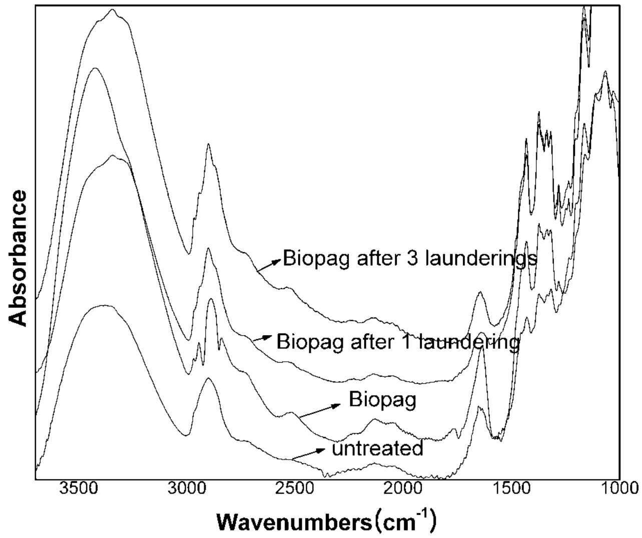

Figure 3 FT-IR spectra of fabrics treated with Biopag alone after laundering cycles.

Laundering durability test

The reduction in the number of bacteria (%) after repeated home launderings (1, 3, 5, 10 cycles) was evaluated by AATCC Test Method 124-1996 (permanent press, liquor ratio 50:1, laundering for 10 min at 50°C—rinsing–screen drying for 4 min at 60°C).

Other properties

The wrinkle recovery angle (WRA) was tested according to AATCC 66-1998. The tensile strength was tested according to ASTM D 1682-64 (1-in. raveled strip). The whiteness index was measured with

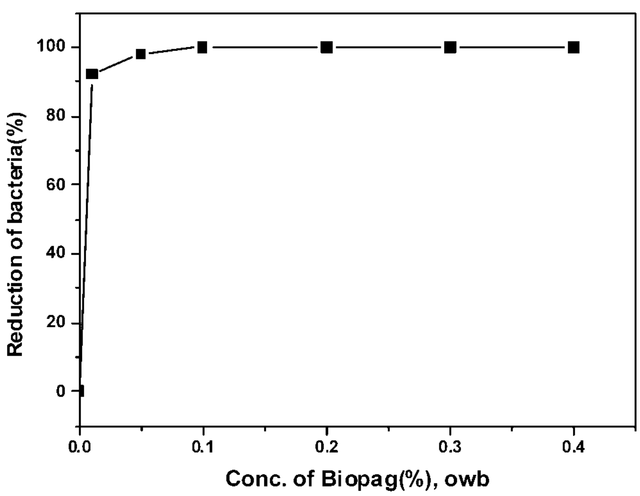

Figure 2 Reduction of bacteria (%) on cotton fabrics treated with different crosslinking agents (Biopag 0.1%, owb).

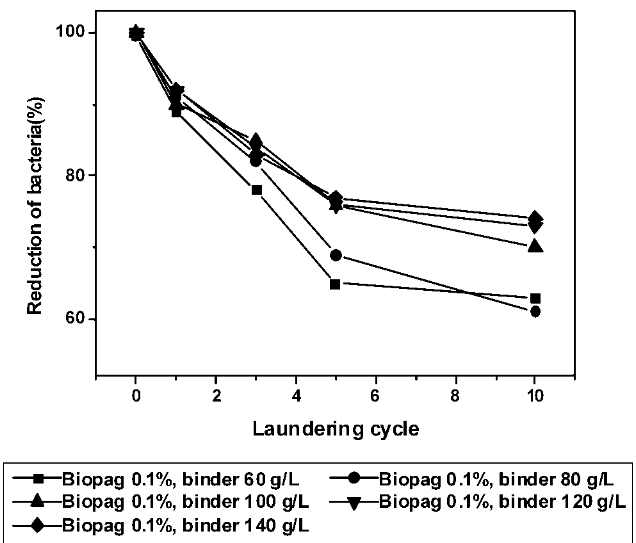

Figure 4 Reduction of bacteria (%) on cotton fabric treated with Biopag (0.1%, owb)/binder by one-bath method.

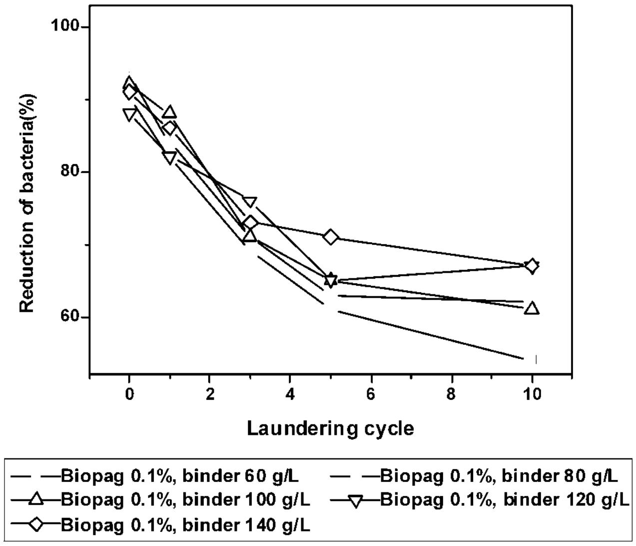

Figure 5 Reduction of bacteria (%) on cotton fabric treated with Biopag (0.1%, owb)/binder by two-bath method.

an X-Rite spectrophotometer with illuminant D_{65} and a 10° field according to AATCC 110-2000. The FT-IR spectra of the treated fabrics were obtained with a Nicolet 520 spectrometer.[16]

RESULTS AND DISCUSSION

Effect of Biopag concentration

Biopag is a nonreactive quaternary ammonium compound whose chemical structure is shown in Figure 1. The reduction in the number of bacteria (%) in the treated fabrics was analyzed as a function of the Biopag concentration. The biocidal properties appeared at a concentration of as low as 0.01%, reached a maximum at a concentration of 0.1%, and did not increase any further at higher concentrations, as shown in Figure 2.

TABLE I
Reduction of Bacteria (%) on Cotton Fabric Treated with Biopag (0.1%, owb) and Crosslinking Agents

	Laundering cycles				
	0	1	3	5	10
Biopag 0.1%	100	–	–	–	–
Glyoxal 6%, $AlNH_4(SO_4)_2$ 0.006[a] mol (curing 160°C, 3 min)	100	100	100	100	100
DMDHEU 4%, $MgCl_2$ 15%[b] (curing 160°C, 4 min)	100	100	100	100	100
BTCA 8%, NaH_2PO_2 0.4 mol (curing 180°C, 3 min)	100	100	100	100	100

[a] Catalyst/crosslinking agent mole ratio.
[b] Catalyst/DMDHEU wt %.

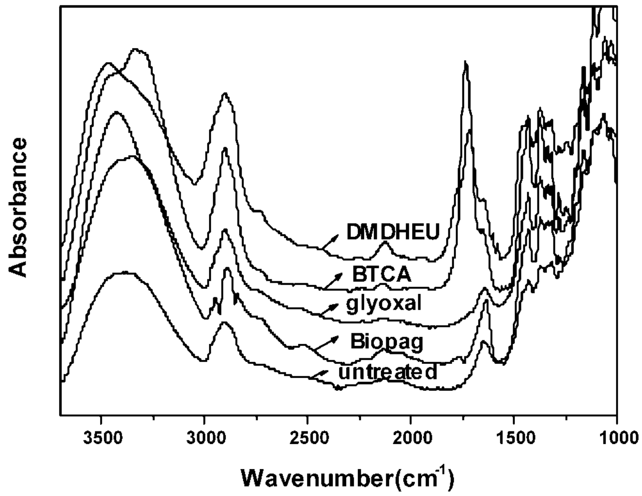

Figure 6 FT-IR spectra of fabrics untreated or treated with Biopag or crosslinking agents.

Effect of binder

As shown in Figure 3, the peak of Biopag at around 2780 cm^{-1} disappeared even after one laundering, which means that fabrics treated with Biopag only was not durable to repeated launderings. The fabrics were treated with a padding solution containing 0.1% Biopag and a binder at various concentrations (80, 100, 120, 140 g/L), in order to improve the durability of the finish. The durability to repeated launderings increased as the amount of binder added was increased (Fig. 4). The cotton fabrics were also treated using the two-bath method, with the Biopag treatment being carried out in the first bath followed by the treatment with the binder in the second bath. The reduction in the number of bacteria on the treated fabrics was higher when the one-bath method was used than when the two-bath method

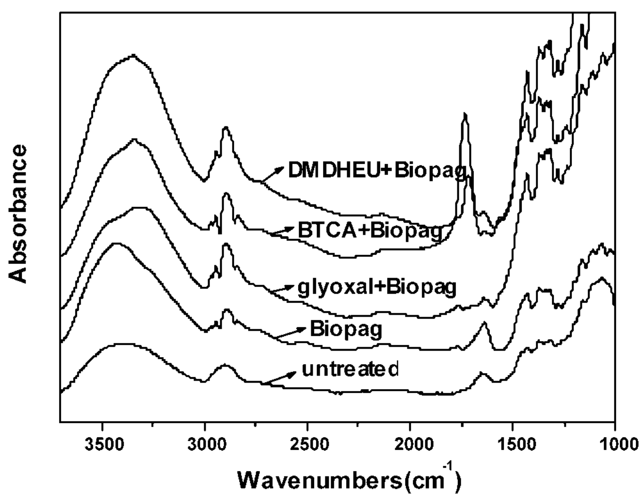

Figure 7 FT-IR spectra of fabrics untreated or treated with Biopag with or without crosslinking agents.

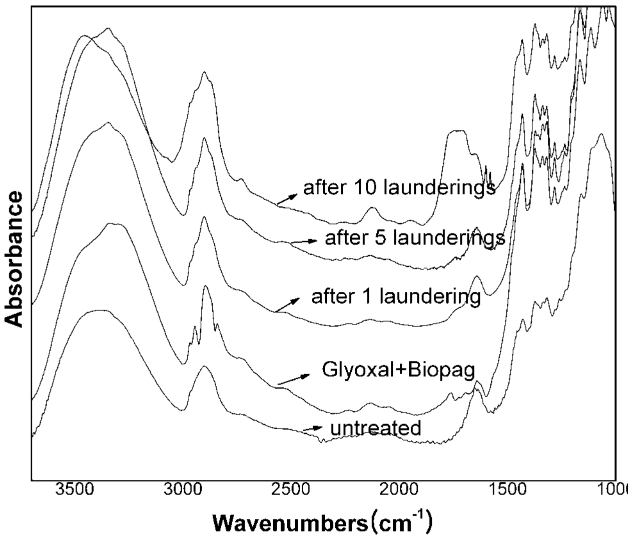

Figure 8 FT-IR spectra of fabrics treated with glyoxal/Biopag after laundering cycles.

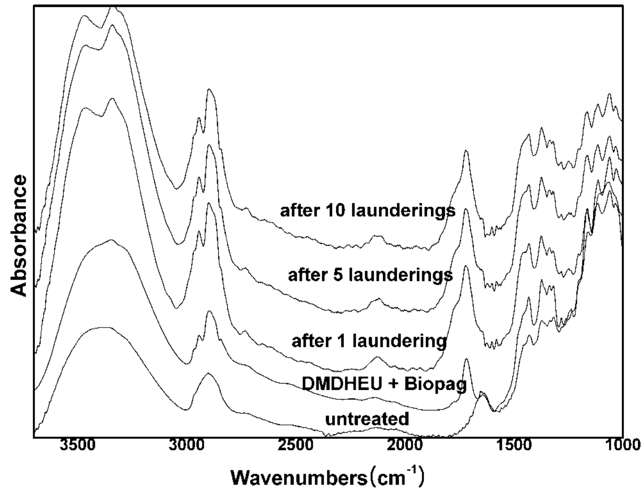

Figure 10 FT-IR spectra of fabrics treated with DMDHEU/Biopag after laundering cycles.

was used, as shown in Figures 4 and 5. However, neither of these two methods gave the treated fabrics adequate durability to repeated launderings. It is considered that the applied binder with Biopag adheres physically to the surface of fibers, and consequently it may be detached easily by laundering actions.

Effect of crosslinking agents

Table I shows the influence of the crosslinking agents on the antimicrobial properties and their durability to repeated launderings, when the cotton fabrics were treated in a 0.1% Biopag padding solution containing one of the three crosslinking agents, viz. glyoxal, DMDHEU, and BTCA, and its catalyst.[13] It was found that crosslinking the treated fabrics increased the durability of the antimicrobial finish using Biopag, which is unreactive to cellulose. It is considered that the Biopag molecules are bound in between the crosslinking networks of the cellulose chains with the crosslinking agent, and consequently the Biopag molecules become less liable to be washed off by repeated launderings. Figure 6 shows the IR spectra of the untreated cotton fabrics and those treated with each of the chemicals used in the experiments. The characteristic split peak (—CH_2— stretch peak) appeared at around 2780 cm^{-1} only in Biopag. The split peaks of Biopag were also seen in the cotton fabrics treated with the padding solution containing Biopag and the crosslinking agent, as shown in Figure 7. These characteristic split peaks of Biopag were still seen even after repeated launderings, as shown in Figures 8–10.

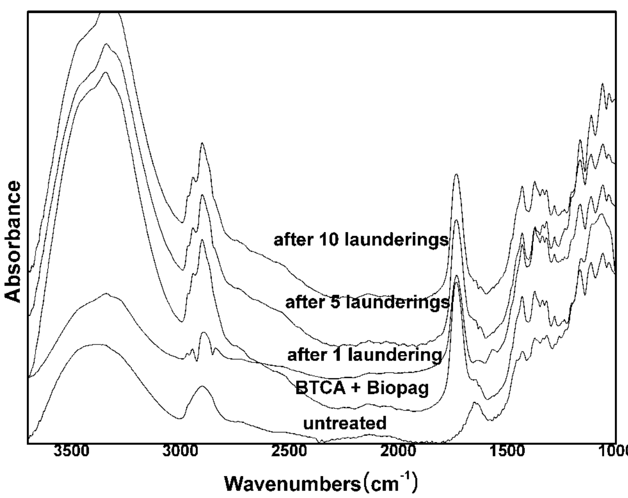

Figure 9 FT-IR spectra of fabrics treated with BTCA/Biopag after laundering cycles.

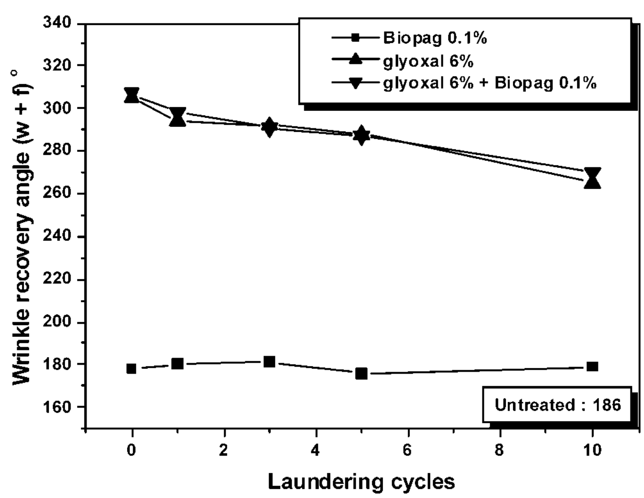

Figure 11 Effects of Biopag on wrinkle recovery angles of treated fabrics.

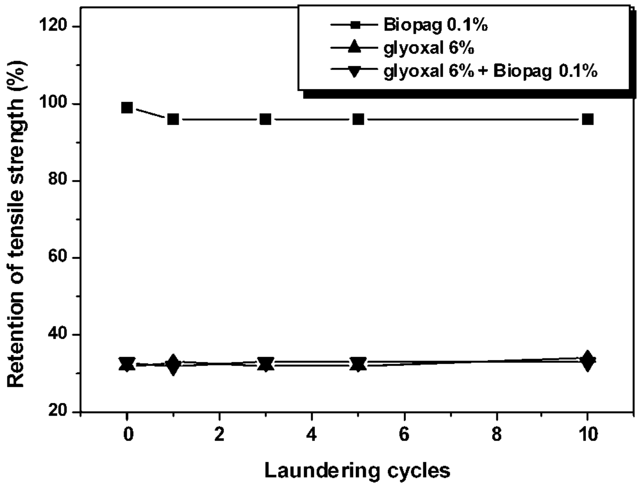

Figure 12 Effects of Biopag on whiteness of treated fabrics.

Effect of Biopag on WRA, whiteness, and strength

The cotton fabrics were treated in three different padding solutions, viz. 0.1% Biopag alone, 6% glyoxal alone, or 6% glyoxal with 0.1% Biopag. The WRAs were not affected by Biopag, as shown in Figure 11. Biopag slightly deteriorated the whiteness of the treated cotton fabrics, while glyoxal greatly deteriorated it (Fig. 12). The whiteness of the cotton fabrics treated with Biopag alone was increased after repeated launderings. This was attributed to the removal of Biopag from the cotton fabrics by laundering. Biopag did not affect the tensile strength of the cotton fabrics with or without the crosslinking agent treatment, as shown in Figure 13.

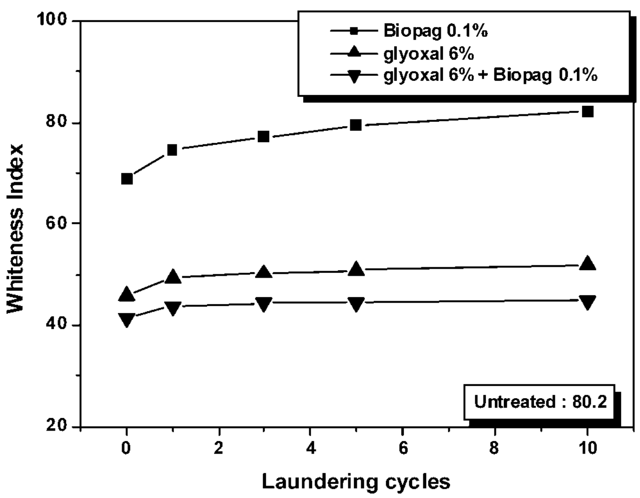

Figure 13 Effects of Biopag on retention of tensile strength of treated fabrics.

TABLE II
Effects of Laundering on Wrinkle Recovery Angles (w + f)° of Fabrics Treated with One-Bath and Two-Bath Method

Padding solution		Laundering cycles 0	1	3	5	10
One-bath	DMDHEU 4% + Biopag 0.1%	307	298	291	287	270
	BTCA 8% + Biopag 0.1%	303	292	282	280	272
	Glyoxal 6% + Biopag 0.1%	291	278	274	272	267
Two-bath	DMDHEU 4% + Biopag 0.1%	304	298	275	270	256
	BTCA 8% + Biopag 0.1%	300	293	289	284	281
	Glyoxal 6% + Biopag 0.1%	282	268	262	264	260

TABLE III
Effects of Laundering on Whiteness of Fabrics Treated with One-Bath and Two-Bath Method

Padding solution		Laundering cycles 0	1	3	5	10
One-bath	DMDHEU 4% + Biopag 0.1%	41	44	44	44	45
	BTCA 8% + Biopag 0.1%	59	61	61	62	62
	Glyoxal 6% + Biopag 0.1%	72	66	67	67	67
Two-bath	DMDHEU 4% + Biopag 0.1%	47	45	45	45	45
	BTCA 8% + Biopag 0.1%	61	62	63	64	63
	Glyoxal 6% + Biopag 0.1%	68	71	71	72	72

Effect of finishing processes

The cotton fabrics were treated either in a padding bath containing Biopag and crosslinking agent together (one-bath method) or two padding baths, the first one containing Biopag and the second one containing the crosslinking agent (two-bath method). The WRAs of the cotton fabrics treated using the one-bath method were better than those of the cotton fabrics treated using the two-bath method (Table II), whereas the opposite results were obtained for the whiteness (Table III). The two-bath method was superior to the one-bath method with respect to the tensile strength retention of the treated cotton fabrics (Table IV). This was attributed to the fact that the reaction of the crosslinking agents with cellulose was

TABLE IV
Effects of Laundering on Retention of Tensile Strength (%) of Fabrics Treated with One-Bath and Two-Bath Method

Padding solution		Laundering cycles 0	1	3	5	10
One-bath	DMDHEU 4% + Biopag 0.1%	33	32	33	33	33
	BTCA 8% + Biopag 0.1%	42	42	44	43	44
	Glyoxal 6% + Biopag 0.1%	51	53	54	55	56
Two-bath	DMDHEU 4% + Biopag 0.1%	37	35	35	36	35
	BTCA 8% + Biopag 0.1%	54	55	56	57	56
	Glyoxal 6% + Biopag 0.1%	44	50	49	48	48

disturbed by the Biopag that was incorporated into the fabric in the first bath in the two-bath method.

CONCLUSION

The addition of a crosslinking agent to the padding solution significantly improved the durability of the antimicrobial properties of cotton fabrics treated with Biopag, which itself has no reactive group. The effect of the crosslinking agent was better than that of the binder, because the former crosslinked chemically with cellulose and entrapped the Biopag molecules more firmly, whereas the latter adhered physically to the surface of fibers and might be easily detached by repeated laundering actions. Using this procedure, both an antimicrobial finish and a durable press finish can be successfully imparted on cotton fabrics by the one-bath method. Biopag did not influence the WRA or tensile strength of the treated fabrics, but did affect their whiteness. When Biopag and a crosslinking agent were applied to the cotton fabrics, their WRA was better in the case of the one-bath method, while their whiteness and tensile strength were higher in the case of the two-bath method. It was confirmed by FT-IR that the characteristic split peaks of Biopag were still seen even after repeated launderings.

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