Wrinkle Resistant Properties and Antibacterial Efficacy of Cotton Fabrics Treated with Glyoxal System and with Combination of Glyoxal and Chitosan System

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ABSTRACT: This study examined the possibility of using glyoxal and chitosan in one-step finishing to impart both durable press performance and antibacterial efficacy on cotton fabrics. Glyoxal treatment provided good wrinkle resistant property and fair antibacterial activity on the finished fabrics, but the loss of breaking strength retention of the finished fabrics was a main problem of this treatment. Chitosan added in the combination of glyoxal and chitosan system also provided comparable results in wrinkle resistant and antibacterial properties on the finished fabrics as the glyoxal did. The advantage of chitosan in the combination of glyoxal and chitosan system was the improvement of the breaking strength retention of the finished fabrics without affecting the durable press property of the finished fabrics. However, the yellowing of the finished fabric was still a problem when the finished fabrics were treated with the combination of glyoxal and chitosan system. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1372–1377, 2006

Key words: textile finishing; durable press finish; chitosan; glyoxal; antimicrobial finish

INTRODUCTION

Durable press finishing involves the use of chemical crosslinking agents that covalently crosslink with adjacent cellulose polymer chains within cotton fibers. The crosslinks not only result in the fabrics' wrinkle resistance, but also in discoloration and impairment of fabric strength and of other mechanical properties. There are about three types of durable press finishes always mentioned in the research articles. First type is dimethyloldihydroxyethyleneurea (DMDHEU).[1] DMDHEU is the most widely used crosslinking agent because it provides good durable press properties at low cost and is less detrimental to fabric strength, whiteness, and other properties than other *N*-methylol agents. DMDHEU may release formaldehyde vapors during processing, storage, and consumer use. Largely because of concern about formaldehyde hazards to workers in the textile industry and also to consumers, formaldehyde-free crosslinking agents for producing durable press properties are of interest. Second type is polycarboxylic acid nonformaldehyde reactants[2]; i.e., 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid, and a mixture of acrylic acid and citric acid,[3] having been used in durable press finishing of cotton. The main advantages of polycarboxylic acids are that they are formaldehyde-free, do not have a bad odor, and produce a very soft fabric hand. Loss of mechanical properties is a problem; however, BTCA is the most effective in the polycarboxylic acid reactants. BTCA, in the presence of sodium hypophosphite monohydrate as a catalyst, provides the same level of durable press performance and finish durability in laundering as does the conventional DMDHEU. Yet the high cost of BTCA is an obstacle to mills' decisions to use BTCA as a replacement for the conventional DMDHEU reactant. In addition, the hypophosphite monohydrate catalyst used causes some shade changes for dyed fabrics. Citric acid is another candidate to replace DMDHEU. The advantages of citric acid over other PCA are low cost, proven lack of toxicity, and ready availability. The major disadvantage of citric acid is the yellowing of the finished fabric. Moreover, the process for fixing polycarboxylic acids on the cotton fabrics requires a high temperature about 180°C. Third type is glyoxal.[4–6] The low cost, ready availability, high functionality, and high solubility in water due to its dialdehyde make it of considerable interest in formation of formaldehyde-free cellulose. The formation of crosslinks in cotton by glyoxal is through hemiacetal or acetal formation. The two main drawbacks for glyoxal treatment on cotton fabrics are strength loss and yellowing on the treated fabrics. In

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addition, glyoxal has ability of antibacterial efficacy also, but it has not been mentioned much in any research articles. Therefore, the ability of durable press finish and antibacterial finish of glyoxal and effect of chitosan added in the glyoxal system are two main topics studied in this project. Chitosan[7,8] is a polysaccharide obtained by deacetylating chitin. The structure of chitosan is similar to that of cellulose except for the hydroxyl groups on the number two-carbon atom having been replaced by amino groups. Chitosan has been versatilely used in three areas textile manufacture, such as the primary production of human-made fiber, textile fiber finishes, and textile auxiliary chemicals. In this study, chitosan was used as a textile finish for cotton fabrics. The glyoxal as a bridge to fix chitosan on cotton fabric via acetal formation might be possible in the cotton fabrics treated with glyoxal and chitosan system. Therefore, the purpose of this study is to use glyoxal and chitosan in one step treatment for providing durable press and antibacterial properties on cotton fabrics.

EXPERIMENTAL

Materials

Desized, scoured, and bleached plain weave cotton woven fabric was used for this study and was purchased from BekerTex Co., Ltd. The fabric count was 65 × 60, 2.5 cm^2 and the fabric weight was 4.04 oz/yd^2, as measured by the researcher. Acetic acid was purchased from Merck (Bangkok, Thailand). Glyoxal (obtained as its 40% aqueous solution) and aluminum sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$) were purchased from A.C.S. Xenon (Bangkok, Thailand). All chemicals were laboratory reagent grade. Chitosan with a molecular weight of 111,000 g/mol and 95% degree of deacetylation was purchased from Seafresh Chitosan (Lab) Company Limited.

Fabric treatment

Glyoxal treatment

The cotton fabric was impregnated in an aqueous finishing solution containing glyoxal and aluminum sulfate catalyst. Each glyoxal finishing formulation varied in the reactant concentrations, the catalyst, and curing temperature. The fabric was immersed and padded to give a wet pick-up of 80–90% on weight of fabric (o.w.f.), then mounted on a pin frame, and predried at 100°C for 5 min. The predried mounted fabric was removed from the oven, the temperature was raised to curing temperature and the fabric was once again placed in the oven for curing at this temperature for 2 min. After curing, the finished fabric was removed from the frame and rinsed in running, hot tap water for 10 min, remounted on the frame and redried at 100°C for 5 min.

A total of 18 glyoxal durable press finish formulations were studied. Three durable press finishing variables in the study were: (a) three concentrations, 4, 6, and 8%, of glyoxal, (b) two concentrations, 1 and 2%, of aluminum sulfate catalyst, (c) three curing temperature at 130, 140, and 150°C.

Chitosan treatment

Chitosan solution was prepared by dissolving chitosan in 1% dilute acetic acid solution. Two concentrations, 0.5 and 0.8%, of chitosan were studied. The cotton fabric was treated with chitosan solution by pad-dry method. The fabric was impregnated in chitosan solution and padded to give a wet pick-up of 80–90% o.w.f., and then mounted on a pin frame, and dried at 100°C for 5 min. After drying, the finished fabric was removed from the frame and rinsed in running, hot tap water for 10 min, remounted on the frame and redried at 100°C for 5 min.

Combination of glyoxal and chitosan treatment

Each combination of glyoxal and chitosan finishing formulation varied in the glyoxal and chitosan concentrations, and curing temperature. Aluminum sulfate (1%) catalyst was used throughout in the study. The fabric was immersed and padded to give a wet pick-up of 80–90% o.w.f., then mounted on a pin frame, and predried at 100°C for 5 min. The predried mounted fabric was removed from the oven, the temperature was raised to curing temperature and the fabric was once again placed in the oven for curing at this temperature for 2 min. After curing, the finished fabric was removed from the frame and rinsed in running hot tap water for 10 min, remounted on the frame and redried at 100°C for 5 min.

A total of 18 combination of glyoxal and chitosan durable press formulations was studied. Three durable press finishing variables in the study were: (a) three concentrations, 4, 6, and 8%, of glyoxal, (b) two concentrations, 0.5% and 0.8%, of chitosan, (c) three curing temperature at 130, 140, and 150°C.

Fabric evaluation

Dry wrinkle recovery angle (DWRA), breaking strength (BS), whiteness index, and durable press (DP) rating were four properties of the finished cotton fabric that were evaluated. Standard methods were used to measure DWRA (AATCC 66–1990), BS (ASTM D 5035–95; for strip method), whiteness index (AATCC 110-1989), and DP rating (AATCC Test Method 124-1989). The whiteness index was measured by using Spectrophotometer Spectraflash 500 Instrument. The

TABLE I
Effect of Glyoxal Concentration and Curing Temperature with 1% Catalyst on Performance Properties of Cotton Fabrics Treated with Glyoxal Only

Glyoxal (%)	Curing temp. (°C)	Dry wrinkle recovery angle (w + f)°	Breaking strength retention (%)	Whiteness index retention (%)	Durable press rating cycles		% Bacterial reduction	
					1st	5th	*K. pneumoniae*	*S. aureus*
4	130	249	50.8	98.2	2.00	2.00	68.1	54.7
4	140	259	55.9	97.6	2.50	2.33	68.3	56.0
4	150	275	39.6	93.4	2.83	2.83	68.8	55.4
6	130	262	55.6	97.7	2.00	2.33	73.5	58.8
6	140	273	55.1	96.8	2.83	2.66	64.9	57.9
6	150	281	44.7	89.6	3.00	3.00	57.9	62.8
8	130	268	65.2	99.7	2.50	2.66	70.5	70.8
8	140	287	54.9	94.6	3.08	3.08	55.8	76.4
8	150	295	45.7	87.0	3.33	3.33	58.5	72.0

BS was carried out in the warp direction. BS and whiteness index results were reported as BS retention and whiteness index retention comparing with those of untreated fabrics.

Antibacterial efficacy testing

Antibacterial efficacy of the treated fabrics was assessed according to the shake flask method.[9] It is a standard test method to measure a percent reduction of bacteria calculated as following equation:

$$\textit{The percent reduction of bacteria} = (B - A)/B \times 100$$

where A, the number of bacteria after 1 h shaking; B, the number of bacteria before shaking.

Gram-positive *Staphylococcus aureus* (ATCC 6538) and Gram-negative *Klebsiella pneumoniae* (ATCC 4352) were used as the test microorganisms.

RESULTS AND DISCUSSION

Cotton fabrics treated with glyoxal only

By examining the results of fabric properties given in Table I, it was apparent that the fabrics treated with glyoxal solutions had better results in wrinkle recovery angles and DP rating and had worse results in BS retention and whiteness index retention than those of the untreated fabrics.

Effect on glyoxal concentration and curing temperature with 1% catalyst on performance properties of cotton fabrics treated with glyoxal only

As shown in Table I, the DWRA of the treated fabrics was better when the glyoxal concentration or curing temperature increased.

The BS retention of the treated fabrics decreased when the glyoxal concentration or curing temperature increased. A finishing condition consisting of high glyoxal concentration and high curing temperature at the same time affects the BS retention more severe than a finishing condition consisting of high glyoxal concentration and low curing temperature. Normally, the loss in BS of the treated fabrics is directly related to the number of crosslinks. In addition, the catalyst can also damage the BS property of the cotton fabrics as well. The glyoxal molecule can from four linkages to cellulose, whereas formaldehyde is difunctional. The glyoxal may be regarded as tetra-functional crosslinking agent. Therefore, the number of crosslinks of glyoxal may be more than that of formaldehyde. This may cause the severe loss of BS of the cotton fabric treated with glyoxal only.

The whiteness index retention of the treated fabrics only slightly decreased when curing temperature increased. Increasing curing temperature affected the whiteness index of the treated fabrics than that of increasing glyoxal concentration.

The DP rating of the finished fabrics got better when any factor of glyoxal concentration or curing temperature used in the finishing formulation increased. To get at least three of DP rating, the cotton fabric needed to be treated with 6 or 8% of glyoxal concentration and curing temperature at 140 or 150°C. The DP ratings after one and five wash cycles of the finished fabrics were different slightly.

Effect on glyoxal concentration and curing temperature with 2% catalyst on performance properties of cotton fabrics treated with glyoxal only

As shown in Table II, the DWRA of the treated fabrics was quite stable when the glyoxal concentrations increased or curing temperature increased, with 2% aluminum sulfate catalyst. This may be implied that the

TABLE II
Effect of Glyoxal Concentration and Curing Temperature with 2% Catalyst on Performance Properties of Cotton Fabrics Treated with Glyoxal Only

Glyoxal (%)	Curing temp. (°C)	Dry wrinkle recovery angle (w + f)°	Breaking strength retention (%)	Whiteness index retention (%)	Durable press rating cycles	
					1st	5th
4	130	286	48.3	96.3	2.83	3.00
4	140	287	33.4	85.0	3.25	3.25
4	150	286	30.9	74.0	3.50	3.50
6	130	287	53.9	97.7	3.17	3.00
6	140	290	42.8	90.1	3.50	3.33
6	150	288	33.0	78.0	3.50	3.42
8	130	288	50.0	96.9	3.00	3.00
8	140	294	43.8	92.5	3.50	3.33
8	150	296	36.4	69.6	3.50	3.42

DWRA was not affected by glyoxal concentration and curing temperature at 2% catalyst.

The BS retention of the treated fabrics decreased when the glyoxal concentration or curing temperature increased with 2% catalyst as well. It could be concluded that the 2% aluminum sulfate catalyst affected the strength loss of the treated fabrics more than the 1% aluminum sulfate catalyst did. It has been known that the acid catalyst will damage the BS of the treated fabrics. The stronger the acid is, the greater is the damage.

The whiteness index retention of the treated fabrics treated decreased when curing temperature or glyoxal concentration increased. The curing temperature factor affected the whiteness index more than the glyoxal concentration factor did. The 2% aluminum sulfate catalyst affected the whiteness index retention more than the 1% aluminum catalyst did.

The 2% aluminum sulfate catalyst affected the BS retention severely, and also affected whiteness index of the treated fabrics more than the 1% aluminum sulfate catalyst did. Therefore, the 2% aluminum sulfate catalyst was not studied further in the combination of glyoxal and chitosan system.

DP rating of the treated fabrics was better than that of 1% catalyst. To get the DP rating at least three could be done in two ways. One was to treat the cotton fabrics with 6 or 8% of glyoxal concentration and curing temperature at 140 or 150°C with 1% catalyst. The other was to treat the cotton fabrics with at least 4% of glyoxal concentration and curing temperature at 140–160°C with 2% catalyst.

Cotton fabrics treated with the combination of glyoxal and chitosan system in one step

Comparing the results of fabric properties given in Tables I and III, it was apparent that the fabrics treated with glyoxal and chitosan in one step had better result in BS retention and DP rating than those of the fabrics treated with glyoxal only. The DWRA of finished fabrics treated with the combination of glyoxal and chitosan at 4% glyoxal decreased slightly compared with that of the finished fabrics treated with 4% glyoxal only. But, the DWRA of finished fabrics treating with the combination of glyoxal and chitosan at 6 or 8% glyoxal was comparable with that of the finished fabrics treated with the same concentration of glyoxal at 6 or 8%. Overall, cotton fabrics treated with the combination of glyoxal and chitosan had better results in BS retention and DP rating. The DWRA results were comparable. The cotton fabrics treated with the combination of glyoxal and chitosan had the whiteness index worse than those of the cotton fabrics treated with glyoxal only.

It could be concluded that the DP finishing formulations in the glyoxal and chitosan system provided the better results in BS retention and DP rating of the finished fabrics and worse results in whiteness index than those in the glyoxal system. The two different systems of fabric treatment provided comparable results in DWRA of the finished fabrics.

It has been known that the chitosan has been used as antibacterial agent for cotton fabric. In this study, antibacterial efficacy of the finished fabrics was measured by shake flash method. Antibacterial efficacy on the finished fabrics treated with chitosan only is reported in Table IV, and antibacterial efficacy on the finished fabrics treated with glyoxal system and combination of glyoxal and chitosan system are reported in Table I and III, respectively.

Cotton fabrics treated with chitosan only

By examining the results of fabric properties in Table IV, it was apparent that the fabrics treated with chitosan solutions at 0.5 or 0.8% had better results only in DP rating both after one and five washes. This might be because of stronger hydrogen bonds formed be-

TABLE III
Effect of Glyoxal Concentration and Curing Temperature with 1% Catalyst on Performance Properties of Cotton Fabrics Treated with Glyoxal and Chitosan System in One Step

Chitosan (%)	Glyoxal (%)	Curing temp. (°C)	Dry wrinkle recovery angle (w + f)°	Breaking strength retention (%)	Whiteness index retention (%)	Durable press rating cycles		% Bacterial reduction	
						1st	5th	*K. pneumoniae*	*S. aureus*
0.8	4	130	226	82.6	76.3	2.61	3.36	56.6	46.3
0.8	4	140	239	86.3	67.6	3.14	3.42	53.3	42.9
0.8	4	150	242	90.1	58.6	2.67	3.42	58.9	43.4
0.5	4	130	237	92.8	85.3	2.94	3.36	45.0	48.2
0.5	4	140	256	88.7	77.6	3.25	3.36	46.0	44.2
0.5	4	150	256	91.5	67.0	3.28	3.39	42.8	39.2
0.8	6	130	278	75.3	65.8	2.81	3.19	61.1	63.3
0.8	6	140	278	75.9	50.1	3.25	3.19	56.5	58.3
0.8	6	150	275	79.2	42.4	2.72	2.97	52.5	58.3
0.5	6	130	271	87.5	82.3	2.72	3.47	58.8	43.1
0.5	6	140	274	81.8	77.7	3.03	3.42	57.3	51.4
0.5	6	150	270	82.3	61.4	3.27	3.25	58.3	45.3
0.8	8	130	278	70.2	74.2	2.06	2.69	70.0	45.5
0.8	8	140	290	59.1	55.6	2.44	3.00	71.3	50.0
0.8	8	150	287	62.2	63.3	3.00	3.25	76.1	55.4
0.5	8	130	293	66.8	81.2	2.83	3.14	63.8	44.9
0.5	8	140	295	52.6	70.7	3.25	3.25	65.0	51.2
0.5	8	150	299	50.1	63.7	3.42	3.36	64.3	49.0

tween chitosan and cotton, preventing the bond slip under laundering condition. The DP rating after five washes was better than that after one wash. This might be because of the loss of some chitosan on the finished fabrics after 5-times washing. This might provide fabric softer than that of 1-time washed fabrics. The BS retention of the chitosan treated fabrics was slightly different from that of untreated fabric. But it could be concluded that there was no change on the BS retention on the chitosan finished fabrics. Whiteness index retention of the finished fabric decreased when the concentration of chitosan increased. Chitosan solution is not a clear solution. It is slightly yellow solution, therefore, treatment with chitosan solution could cause a yellowing problem on the white cotton fabrics. The DWRA of the cotton fabric treated with 0.5% chitosan was better than that of untreated fabric, while the DWRA of the cotton fabric treated with 0.8% of chitosan was worse than that of untreated fabric. In addition, the fabric treated with 0.5% chitosan felt the same as that of untreated fabric, while the fabric treated with 0.8% chitosan felt much stiffness than that of untreated fabric. The stiffness property of fabric might affect the DWRA property directly.

Antibacterial efficacy on the finished fabrics

By examining the results of fabric properties given in Table I, III, and IV, the results of the percent bacterial reduction of fabrics treated with chitosan only were not better than those of the finished fabrics treated with either glyoxal only or the combination of chitosan and glyoxal. The cotton fabrics treated with chitosan only had the low percent bacterial reduction. This may be because the cotton fabrics treated with chitosan were not cured. Therefore, the chitosan on the surface of the treated fabrics may be washed out in the step of washing. The results of the percent bacterial reduction of fabrics treated either with glyoxal system or combination of glyoxal and chitosan system were found to be quite similar to each other.

TABLE IV
Properties of Cotton Fabrics Treated with Chitosan Only

Chitosan concentration (%)	Dry wrinkle recovery angle (w + f)°	Breaking strength retention (%)	Whiteness index retention (%)	Durable press rating cycles		% Bacterial reduction	
				1st	5th	*K. pneumoniae*	*S. aureus*
Untreated fabrics	191	100.0	100.0	1.50	1.75	0.0	0.0
0.5	196	103.5	92.8	2.50	2.72	44.4	29.2
0.8	182	96.6	89.6	2.06	2.72	40.9	36.7

For the glyoxal system, the average percent bacterial reduction of *K. pneumoniae* was 65% for the finished fabrics. The average percent bacterial reduction of *S. aureus* was 63% for the finished fabrics. The mechanism of antibacterial activity of glyoxal has not been known in detail yet. Since the chemical structure of glyoxal was similar to formaldehyde. Therefore, the glyoxal treated on the cotton fabric might be decomposed under certain condition and released the formaldehyde to inhibit the growth of microorganisms. This was just a hypothesis of mechanism of antibacterial activity of glyoxal. However, there was no any evidence to proof it yet.

For the combination of glyoxal and chitosan system, the average percent bacterial reduction of *K. pneumoniae* was 62% for the finished fabrics treated with the combination of glyoxal and chitosan at 0.8%, and 56% for the finished fabrics treated with the combination of glyoxal and chitosan at 0.5%. The average percent bacterial reduction of *S. aureus* was 51% for fabrics treated with the combination of glyoxal and chitosan at 0.8%, and 47% for fabrics treated with the combination of glyoxal and chitosan at 0.5%. It could be concluded that the fabrics treated with glyoxal only had a slightly better result in antibacterial property than that of the fabrics treated with combination of glyoxal and chitosan system. According to the average results of percent bacterial reduction, the addition of chitosan into the glyoxal system did not much affect the antibacterial ability of glyoxal. In other words, chitosan did not improve antibacterial ability of the fabrics treated with combination of glyoxal and chitosan system. The main advantage of adding chitosan into the glyoxal system was to improve BS retention of the finished fabrics.

CONCLUSIONS

Glyoxal treatment provided both DP performance and antibacterial properties on the finished fabrics. The disadvantage of fabrics treated with glyoxal was the loss of BS retention. The antibacterial efficacy of the fabrics treated with glyoxal only was better than that of the fabrics treated with chitosan only and slightly better than that of the fabrics treated with the combination of glyoxal and chitosan. Chitosan treatment provided a better DP rating than that of untreated fabric, but the chitosan finished fabrics had the same wrinkle recovery angle and strength retention as the untreated fabric had. The disadvantage of fabrics treated with chitosan only was a yellowing problem. The fabrics treated with chitosan did not have good results in DP performance and antibacterial properties as the fabric treated with glyoxal only had. Combination of glyoxal and chitosan treatment had a better result in strength retention than that of glyoxal treatment. Chitosan added in the glyoxal system improved the BS retention of the finished fabrics without affecting wrinkle recovery angle and DP rating, but it did affect the antibacterial efficacy of glyoxal a little bit and did cause the yellowing on the finished fabrics. Adding chitosan in glyoxal treatment could improve the drawback of strength loss on the finished fabrics treated with glyoxal system.

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