Characterization of Cotton Fabrics Treated with Glyoxal and Glutaraldehyde

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ABSTRACT: Comparison was made for glyoxal- and glutaraldehyde-treated cotton fabrics. Crosslinking efficiency between cellulose and dialdehyde measured by wrinkle recovery angle was higher with glutaraldehyde than with glyoxal. This disparity was presumably due to different forms of two dialdehydes in aqueous solution that were confirmed by FTIR and UV-visible spectroscopies. Such difference in hydrated forms along with easy formation of oligomeric and polymeric forms in glyoxal could influence on sorption and reactivity of the dialdehydes with cellulose. Staining and water imbibition values and various thermal parameters, such as percent residue, differential thermogravimetric peak temperature, and maximum rate of weight loss, also supported high crosslinking efficiency of glutaraldehyde. The presence of unreacted aldehyde groups within the treated fabrics was confirmed by FTIR analysis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2691–2699, 1999

Key words: glyoxal; glutaraldehyde, crosslinking; FTIR analysis; thermal parameters

INTRODUCTION

Recent efforts to develop formaldehyde-free reagents in durable press (DP) finishing of cotton focused mainly on the use of polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid (BTCA).[1–3] The BTCA, however, is expensive and requires high curing temperature, 170 to 180°C, to obtain esterified crosslinks with cellulose molecules.[1,2] Moreover, in the presence of sodium hypophosphite, the BTCA-treated cotton showed considerable shade change on certain dyed fabrics.[4] Such limitations in the use of polycarboxylic acid call for reexamination of various other crosslinking agents to substitute N-methylol type reagents.

Many aldehydes have been suggested as crosslinking reagents for cellulose to impart resilience and dimensional stability of the cellulosic fabrics.[5,6] Nevertheless, a literature survey indicated that, in addition to formaldehyde, only dialdehydes such as glyoxal and glutaraldehyde provided improvement in wrinkle recovery angle and DP rating of the treated fabrics.[5] These dialdehydes are one of very few available non-nitrogenous cellulose crosslinking reagents that exhibit high reaction rates required for DP finishing of cotton.[7]

DP finishing of cotton with glyoxal was examined by Welch and his coworkers in the 1980s.[7–9] Unfortunately, no comparison study was made with glutaraldehyde. Furthermore, aside from physical performance, little information is available for cotton fabrics treated with such dialdehydes. Therefore, the present study compares the two most common dialdehydes on the DP treatment of cotton fabrics by using thermal, FTIR spectroscopic, X-ray diffraction analysis, and other methods such as staining and water imbibition.

EXPERIMENTAL

Materials

Scoured, bleached, and mercerized 100% cotton fabrics were used throughout the study. These fabrics were plain weave with 136 and 72 threads per 2.54 cm for warp and weft, respectively. Two dialdehyde crosslinking reagents, glyoxal (40% solution, Yakuri, Japan) and glutaraldehyde (25% solution, Yakuri, Japan), were used. Aluminum sulfate [$Al_2(SO_4)_3 \cdot 16H_2O$, Junsei Chemicals, Japan], which was suggested as the most efficient catalyst for glyoxal crosslinking of cotton in the previous study,[6–8] was employed as a catalyst. A polyethylene-type softener (Siligen VN, BASF, Korea) and a wetting agent (Triton X-100) were also added in the treating bath.

Fabric Treatment and Evaluation

Fabrics were impregnated for 5 min in the pad bath containing dialdehyde, aluminum sulfate, 1% softener, and 0.1% Triton X-100. Fabrics were then padded through a two-bowl vertical laboratory padder (Mathis, Swiss) with two dips and nips to give a wet pick-up of 100 ± 4% on the weight of the fabric. The padded fabric was dried at 85°C for 5 min and cured at 125°C for 2 min, unless otherwise noted. Finally, the fabric was rinsed by warm water at 45 to 55°C for 20 min and redried at 85°C for 5 min.

Conditioned wrinkle recovery angles were measured by Monsanto method (AATCC 66-1992).[10] Fourier transform infrared spectroscopic analysis (KVB/Analet, USA) was carried out with KBr pellet method with 32 scans and 4 cm^{-1} resolution. To determine absorbance of carbonyl groups in aqueous dialdehyde solutions, a UV-visible spectrophotometer (Hewlett Packard, HP8452A, USA) was also employed. Thermal characteristics of the treated fabrics were also evaluated by using thermogravimetric analysis (TG/DTA 6200, Seiko, Japan) under nitrogen atmosphere (100 ml/min). Samples were held isothermally at 80°C for 20 min to evaporate water, and heated at a rate of 10°C/min to 400°C. Percent residue was determined at 400°C. To determine activation energy of the treated fabric at a nonisothermal condition, a rate of temperature increase was changed at 10, 20, 30, 40, and 50°C/min. X-ray diffraction study (Regaku, D/Max IIIB, Japan) was undertaken to evaluate crystalline structural change. The condition for the X-

Scheme 1   Acetal formation of dealdehyde with cellu-ose.

ray analysis included Cu-Ka X-ray, which was filtered by a Ni filter at 40 kV and 30 mA, scan speed 10 degree/min, scan step 0.05, and diffraction angle between 5 and 50 degree range.

In order to evaluate differences in the dialdehyde-treated fabrics, the samples were stained by C. I. Direct Red 80 for 90 min at room temperature.[11] K/S (color strength) values were measured after staining at λ = 540 nm. To measure water imbibition values of the treated fabrics, the samples were immersed in a distilled water bath for 3 hr. The wetted sample was centrifuged for 30 min at 1800 rpm, and then its weight was measured (W_w). The centrifuged sample was dried at 85°C for 1 hr, and its dried weight (W_d) was determined. The water imbibition values were calculated by the following equation:[12]

$$\text{Water imbibition } (\%) = [(W_w - W_d)/W_d] \times 100 \tag{1}$$

RESULTS AND DISCUSSION

Reaction between dialdehyde and cotton cellulose is believed to be an acetal formation as shown in Scheme 1. Since this is a reversible reaction, the presence of acid catalyst will be critical. Also, high temperature curing is needed to eliminate water molecules for completion of the reaction. However in the case of glyoxal, the reaction mechanism between cellulose and dialdehyde would be more complex than a simple acetal formation[8] due to easy formation of five-membered chelate rings with metal ions (M) as shown in Scheme 2. Chelation with M in glutaraldehyde would be much more difficult due to the presence of three additional methylene groups (Scheme 3).

Scheme 2 Possible structures of glyoxal in aqueous solution.

Figure 1 Effect of dialdehyde concentration on conditioned wrinkle recovery angles of the treated cotton cured at 125°C for 2 min. (●) CWRA of the glyoxal-treated, (■) CWRA of the glutaraldehyde-treated, (▲) whiteness index of the glyoxal-treated, (▼) whiteness index of the glutaraldehyde-treated.

Wrinkle Recovery Angle

Figure 1 shows effects of dialdehyde concentration on conditioned wrinkle recovery angle (CWRA). In this set of the experiment, mole ratios between dialdehyde and aluminum sulfate (AS) were kept constant. Surprisingly, CWRAs were consistently higher in glutaraldehyde-treated fabrics than in glyoxal-treated fabrics at the same concentration of dialdehyde. Since glutaraldehyde has larger molecular size than glyoxal, an actual mole of glutaraldehyde used in the treating bath is less than that of glyoxal. Two reasons could be attributed to higher CWRA of the glutaraldehyde-treated fabric even at smaller mole fraction. First, the mole ratio of AS versus glutaraldehyde (0.02:1) was higher than that of AS versus glyoxal (0.013:1) due to large molecular size of glutaraldehyde. The higher mole ratio of AS versus glutaraldehyde could cause greater CWRA of the treated fabric. Secondly, in aqueous solution glyoxal is mainly remained as dimer, trimer, 5- or 6-membered ring, or polymeric forms (Scheme 2).[13] On the other hand, glutaraldehyde retains monomeric forms (Scheme 3).[14] In the case of

Scheme 3 Possbile structures of glutaraldehyde in aqueous solution.

glyoxal, therefore, such easy formation of oligomeric or polymeric structure could adversely affect on its sorption ability to cotton, resulting in low CWRA values.

Furthermore, different hydrated forms of two dialdehydes in aqueous solution can be an important factor in determining their reactivity with cellulose molecules. To confirm hydrated forms of glyoxal and glutaraldehyde in an aqueous solution, FTIR analysis was undertaken. Characteristic FTIR spectrum for normal aldehydes consists of a carbonyl stretching peak at approximately 1725 cm^{-1} and a pair of weak aldehyde C–H stretching peaks at 2750 cm^{-1} and 2850 cm^{-1}.[15] As shown in Figure 2, no such peaks were observed in aqueous glyoxal solution. This suggested that glyoxal molecules mainly remained in hydrated forms as shown in Scheme 2. On the other hand, in an aqueous glutaraldehyde solution, a small but a definite peak at 1700 cm^{-1} appeared. A pair of aldehyde C–H stretching peaks also appeared at a range of 2800 cm^{-1} and 3000 cm^{-1}. This suggested that at least some fractions of aldehyde groups in glutaraldehyde remained as nonhydrated state or hemihydrated state (III in Scheme 3) in an aqueous solution.

The presence of aldehyde carbonyl in aqueous solution can also be confirmed by UV-visible spectroscopic analysis. It was known that in the absence of conjugated system aldehyde molecules can be represented by low intensity absorption

Figure 2 FTIR analysis of aqueous solutions of dialdehydes. (a) 40% glyoxal solution, (b) 25% glutaraldehyde solution.

band at around 290 nm due to $n - \pi^*$ transition.[15] As shown in Figure 3, 40% aqueous glyoxal solution clearly showed aldehyde absorption band at 264 nm. In the case of glutaraldehyde, however, an absorption peak at 276 nm was much stronger than the peak of glyoxal at 264 nm even in diluted condition. Note that concentration of glutaraldehyde solution for UV-visible spectroscopic analysis was only a quarter of glyoxal concentration. Therefore, this again substantiated that nonhydrated or hemihydrated forms of glutaraldehyde molecules in aqueous solution were more abundant than those of glyoxal. Glutaraldehyde has about 20% of nonhydrated forms in an aqueous solution.[5]

Thermal Analysis

It has been reported that by using thermal parameters, such as percent residue, rate of weight loss,

Figure 3 UV-visible spectra of aqueous solutions of glyoxal (40%) and glutaraldehyde (10%). (a) glyoxal, (b) glutaraldehyde.

Figure 4 Effect of dialdehyde concentration on DTG peak temperature and percent residue of the treated cotton. (●) DTG peak temperature of the glyoxal-treated, (■) DTG peak temperature of glutaraldehyde-treated, (▲) percent residue of the glyoxal-treated, (▼) percent residue of the glutaraldehyde-treated.

and residue/rate factors, thermal analysis can predict performance of DP reagents in cotton cellulose.[16] Figure 4 represents percent residue and differential thermogravimetric (DTG) peak temperature of the cotton fabrics treated at different concentrations of dialdehyde. After an initial decrease, percent residue continually increased with increase in concentration of dialdehyde. It should be

Figure 5 Effect of dialdehyde concentration on maximum rate of weight loss of the cotton cured at 125°C for 2 min. (●) glyoxal-treated, (■) glutaraldehyde-treated.

Table I   Effect of Washing on Thermal Analysis Data of the Fabrics Treated with 4.8% Dialdehyde and 0.38% Aluminum Sulfate[a]

Dialdehyde	Washing	% Residue	Maximum Rate of Weight Loss (%/min)	DTG Peak Temperature (°C)
Control	—	12.0	28.0	368.0
Glyoxal	no	24.8	9.6	341.3
Glyoxal	yes	9.6	22.8	325.4
Glutaraldehyde	no	19.4	11.0	341.4
Glutaraldehyde	yes	12.5	21.8	339.9

[a] Glyoxal-treated fabric was cured at 125°C, and glutaraldehyde-treated fabric was cured at 110°C.

noted that at low concentrations of dialdehyde, percent residues were lower than that of untreated control sample (12%). Our previous study showed that high residues and low DTG peak temperatures were indicative of good DP performance in a maleic acid-itaconic acid system.[16] Thermal stability of the DP treated fabrics could be related to two separate factors that act in opposite directions: acid degradation during the treatment, which could reduce thermal stability, and crosslinking effect, which could enhance the stability. At low dialdehyde concentrations, therefore, acid degradation effect seems to surpass the crosslinking effect, resulting in lower percent residue.

On the other hand, DTG peak temperatures (Fig. 4) and maximum rate of weight loss data (Fig. 5) were continuously decreased with an increase in dialdehyde concentration. Unlike percent residue that showed some deviations, that is, lower residue than control, both DTG peak temperatures and maximum rate of weight loss data were consistently lower than those of the untreated control sample. Note that the glutaralde-hyde-treated fabrics showed consistently lower DTG peak temperatures and maximum rate of weight loss than the glyoxal-treated fabrics at the same dialdehyde concentration. Also, percent residues of the glutaraldehyde-treated fabrics tended to be higher than the glyoxal-treated fabrics. The glutaraldehyde-treated fabric showed consistently higher CWRA than the glyoxal-treated fabric at the same concentration (Fig. 1). Therefore, high crosslinking efficiency of glutaraldehyde with cellulose accounts for high percent residue, low DTG peak temperature, and maximum rate of weight loss.

The samples discussed in the previous section were washed samples, and thus there were no unfixed reagents on the fabric. Once the unwashed samples were used for thermal analysis, both increase in percent residues and decrease in maximum rate of weight loss were substantial as shown in Table I. This indicated that the presence of unfixed reagents on the fabric surface could considerably delay thermal decomposition of the treated fabric.

Table II   Effect of Curing Temperatures on Thermal Properties of the Finished Fabrics

Curing Temperature (°C)	% Add-on		% Residue		Maximum Rate of Weight Loss (%/min)		DTG Peak Temperature (°C)	
	A[a]	B[b]	A	B	A	B	A	B
100	2.0	2.5	13.3	17.8	25.1	24.8	345.3	330.8
110	2.6	2.6	14.6	17.2	18.9	22.7	329.0	330.2
125	3.3	2.6	22.4	18.2	17.8	27.2	327.2	355.1
140	3.6	3.1	17.7	20.8	17.8	16.7	324.6	334.4
Untreated Control	—		12		28		368	

[a] The fabrics were treated with 6% glyoxal and 0.475% AS.
[b] The fabrics were treated with 6% glutaraldehyde and 0.475% AS.

Figure 6 X-ray diffraction curves of the untreated control and treated cotton fabrics. (a) untreated control, (b) glyoxal treated, (c) glutaraldehyde treated.

Table II showed TGA results obtained from varying curing temperatures at constant dialdehyde (6%) and catalyst (0.475%) concentration. Even though there are some deviations, effects of curing temperatures on various thermal parameters are very similar to concentration study; that is, with increase in curing temperatures, percent residue increased, DTG peak temperature decreased, and maximum rate of weight loss decreased. Obviously, at higher curing temperatures, increase in crosslinking of cotton cellulose resulted in such increase in percent residue and

decrease in DTG peak temperature and maximum rate of weight loss.

By using five different heating rates (10, 20, 30, 40, and 50°C/min) at nonisothermal conditions, activation energies of the dialdehyde-treated fabrics were obtained according to the following equations:[17]

$$g(\alpha) = (AE_d/qP)P(x) \qquad (2)$$

Table III   K/S and Water Imbibition Values of Dialdehyde-Treated Cotton Fabrics[a]

Dialdehyde Concentration (% owb)	K/S Values After Staining		Water Imbibition Values (%)	
	Glyoxal	Glutaraldehyde	Glyoxal	Glutaraldehyde
3.6	1.42	0.80	17.6	16.3
4.8	1.17	0.68	19.9	15.6
6.0	1.12	0.66	22.9	14.4
7.2	1.04	0.60	17.0	13.8
Untreated Control	3.887		24.8	

[a] Curing was carried out at 125°C.

Figure 7 FTIR spectra of the cotton fabrics treated with glyoxal at various conditions. (a) padding, drying, curing at 125°C, washing; (b) padding, drying at 25°C; (c) padding, drying at 85°C; (d) padding, drying, curing; (e) padding, drying, curing, pellet drying.

$$P(x) = \int_{\infty}^{x} [\exp(-x)/x^2] \, dx, \, x = E_d/RT \quad (3)$$

$$\log q = \log[AE_d/g(\alpha) \, R]$$
$$- 2.315 - [0.457 \, E_d/RT] \quad (4)$$

where A is a preexponential factor and E_d is activation energy for decomposition. At various decomposition rates (5, 15, 30, and 40%), linear relationships were obtained in plots of log q and temperature (1000T, K^{-1}) by equation (3), and then activation energy was calculated from a slope of the linear line. Results showed that activation energies of the untreated control, glyoxal-treated sample (3.8% add-on), and glutaraldehyde-treated sample (2.6% add-on) were 170 kJ/mol, 262 to 270 kJ/mol, and 180 to 210 kJ/mol, respectively. The dialdehyde treatment, there-fore, generally increased thermal stability of the cotton cellulose.

X-Ray Diffraction Study

Figure 6 shows X-ray diffraction curves of the untreated and dialdehyde-treated samples. All three diffraction patterns were practically the same as a typical cellulose I structure[18]: weak peaks of (101) and (101) at a range of $2\theta = 15$–17, and (021) and (002) peaks at a range of $2\theta = 20$–25. Also, the (021) reflection appears as a weak shoulder on the strong (002) peak. This result confirmed that the reaction occurred mainly in an amorphous area of the cotton.

Staining and Water Imbibition

As shown in Table III, K/S values of the dialdehyde-treated samples after staining were considerably lower than that of the untreated control.

Figure 8   FTIR spectra of the cotton fabrics treated with glutaraldehyde at various conditions. (a) padding, drying, curing at 125°C, washing, (b) padding, drying at 25°C; (c) padding, drying at 85°C; (d) padding, drying, curing; (e) padding, drying, curing, pellet drying.

Moreover, K/S values of the glutaraldehyde-treated fabrics were lower than the glyoxal-treated fabrics at the same dialdehyde concentration, supporting higher efficiency of glutaraldehyde treatment. We also carried out water imbibition study by using centrifuge. The trend of water imbibition value was the same as that of direct dye staining.

FTIR Analysis

To evaluate the cotton fabrics treated with dialdehydes, KBr pellets were prepared by using five different fabrics as follows: Sample A (padding, drying, curing, and washing), Sample B (drying at 25°C after padding), Sample C (padding, drying at 85°C for 5 min), Sample D (padding, drying at 85°C for 5 min, and curing at 125°C), and Sample E (padding, drying, curing, and KBr pellet made was redried in a vacuum oven at 70°C for 8 hr).

Analyses of the spectra revealed that clear differences were shown between the glyoxal- and glutaraldehyde-treated cotton fabrics (Figs. 7 and 8). In the glyoxal-treated samples, no free aldehyde carbonyl peaks were shown, with the exception of a vacuum-dried KBr pellet, indicating the glyoxal tended to be remained as hydrated forms within the fabric. Contrarily, in the glutaraldehyde-treated fabrics all the samples showed definite aldehyde carbonyl peaks at 1699 cm^{-1} in the spectra. No aldehyde C–H stretching peaks were shown for the glutaraldehyde-treated fabrics due to overlapping (not shown). This evidence consistently ratified that, between the two dialdehydes, hydrated formation in glyoxal was much more common not only in aqueous solution but also in residual unreacted aldehyde groups within the treated fabric. We believe that such different forms of residual aldehyde carbonyl groups in the dialdehyde-treated cotton could be directly related to the whiteness of the fabric. As

shown in Figure 1, the glutaraldehyde-treated fabrics generally showed low whiteness index, especially at curing temperature 125°C or higher. Even though it was not shown here, curing at 110°C was able to eliminate such yellowing effect in the glutaraldehyde-treated fabric.

CONCLUSIONS

Crosslinking of cotton cellulose with two common dialdehydes, glyoxal and glutaraldehyde, was investigated. Results revealed that reactivity of glyoxal and glutaraldehyde with cellulose was quite different. This difference was mainly due to the molecular states of two aldehydes in aqueous solution, which were confirmed by FTIR and UV-visible spectroscopic analyses. Glyoxal retained more hydrated forms, whereas in glutaraldehyde some fraction of aldehyde groups retained nonhydrated forms. Such difference in hydrated forms along with easy formation of oligomeric and polymeric forms in glyoxal could influence on sorption and reactivity of the dialdehydes with cellulose. In addition, FTIR analysis indicated that unreacted residual aldehydes of glutaraldehyde in the treated fabric retained free aldehyde forms, rather than hydrated forms, affecting whiteness of the treated fabric. In general, crosslinking efficiency was higher with glutaraldehyde than glyoxal, and this was confirmed by wrinkle recovery angle, staining, and water imbibition techniques. Various thermal factors, such as percent residue, DTG peak temperature, and maximum rate of weight loss, also supported high reactivity of glutaraldehyde with cellulose.

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