

Crosslinking Cotton Cellulose with Aldehydes

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Synopsis

The relative effectiveness of several aldehydes in crosslinking cellulose of cotton fabric was determined using a pad-dry-cure treatment and a treatment by immersion in a solution at room temperature. Aldehydes ranked in the same order of ability to crosslink in both treatments. Factors related to crosslinking ability are discussed. The aldehydes crosslinking to the greater extent hydrated readily in water because the aldehyde group was activated or because cyclic hydrates could be formed.

INTRODUCTION

Many aldehydes in addition to formaldehyde have been suggested as crosslinking agents for cellulose to impart resiliency and dimensional stability to cellulosic fabric. However, published data demonstrate the effectiveness of only a few of these aldehydes in crosslink finishing.^{1,2} Our experience indicated that only a small number of aldehydes form crosslinks readily enough to be considered as finishing agents for fabric.

The work reported here compares the crosslinking of cotton fabric with a number of aldehydes of diverse structure. It is intended to provide data on specific aldehydes or classes of aldehydes and to show the structural characteristics that are related to their potential as crosslinking agents.

EXPERIMENTAL

Cotton fabric was crosslinked with aldehydes using two treatments. The first was a common pad-dry-cure application. The second allowed the cotton fabric to react at room temperature (20–25°C) while immersed in a solution of aldehyde.

In the pad-dry-cure treatment, a solution of the aldehyde and magnesium chloride hexahydrate was applied to cotton by padding with two dips and two nips to give 80–90% wet add-on. The same solvent and same catalyst concentrations were used for all comparisons. Solvent was water when possible and an ethanol–water mixture when some aldehydes in a series being compared were insoluble in water. Except where specified, pad formulations were adjusted to pH 5 before adding the magnesium chloride catalyst. After padding, the fabric samples were placed on pin frames and then dried and cured in mechanical convection ovens for 7 min at 70°C and 3 min at 160°C. Before testing, samples were washed once by laundry method IIB in the AATCC test method "Appearance of Durable Press Fabrics after Repeated Home Launderings."³

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In the treatment at room temperature the fabric was immersed in an acetic acid solution of aldehyde, water, and hydrogen chloride. This solution was used by Reeves, Perkins, and Chance³ for treatments with formaldehyde. The fabric samples were immersed in these solutions for 60 min while they were lying flat in a shallow pan. The fabric was washed before testing.

Wrinkle recovery angles and durable press ratings after the single wash were by AATCC methods.⁴ Weight add-on from treatment was determined by the change in weight of the air-equilibrated fabric samples and is expressed as percent of original fabric weight. It was recognized that add-on was of dubious value, particularly with low-molecular-weight aldehydes, because material loss in processing and changes in moisture regain could hide part or all of a small weight gain.

The cotton fabric used was a desized, scoured, and bleached printcloth weighing about 110 g/m² (3.2 oz/yd²). All compounds applied to fabric were reagent grade chemicals.

RESULTS AND DISCUSSION

Extent of Crosslinking by Aldehydes

In estimating the ability of aldehydes to crosslink cotton, wrinkle recovery angles were taken as the primary measure. Durable press ratings and weight add-on after the wash were secondary measures of reaction. The weight add-on before washing was used as a measure of retention of applied agent through curing in pad-dry-cure treatments.

Table I shows the results of treating cotton printcloth with a diverse group of aldehydes with the pad-dry-cure method. The pad formulation for these

TABLE I
Crosslinking by Aldehydes in Pad-Dry-Cure Treatment

Aldehyde	Molecular wt	Boiling point (°C)	Applied concn (%)	Fabric properties			
				Wrinkle recovery angle (deg, <i>w + f</i>)	Durable press rating	Add-on (% of original wt)	
						Before wash	After wash
None ^a	—	—	—	199	2.0	0.9	-0.9
Formaldehyde	30	-21	5.4	270	4.3	1.2	-0.2
Acetaldehyde	44	20	7.9	217	2.9	0.2	-0.7
Lauraldehyde (dodecanal)	184	230	33.1	195	2.2	0.7	-0.2
5-Hydroxypentanal	102	(204) ^b	18.4	206	2.5	5.1	1.7
Glyoxal	58	51	10.4	259	3.2	7.5	0.5
Glutaraldehyde (pentanedial)	100	101	18.0	274	4.0	3.5	3.2
Benzaldehyde	106	179	19.1	200	1.7	-0.5	-1.6
<i>p</i> -Anisaldehyde (<i>p</i> -methoxybenzaldehyde)	136	247	24.5	196	2.3	3.3	-1.4
<i>o</i> -Nitrobenzaldehyde	151	(270) ^b	27.2	187	1.7	2.7	-0.9
Phenylacetaldehyde	120	195	21.6	202	2.3	3.6	0.0

^a Treated with 2.0% MgCl₂·6H₂O only.

^b Indicated boiling points at 760 torr from 120° at 15 torr and 153° at 23 torr.

aldehydes contained 0.18 mole aldehyde and 2.0 g magnesium chloride hexahydrate for 100 g of solution, in a solvent of 75% ethanol and 25% water by weight. This is the concentration of water obtained when preparing the formulation with glutaraldehyde, which was supplied as a 50% solution, and was diluted with absolute ethanol in preparation of the pad formulation. This solvent ratio was effective for making solutions of all the aldehydes listed.

Among the aldehydes listed in Table I, formaldehyde and glutaraldehyde crosslinked to a large extent, glyoxal to a moderate extent, acetaldehyde and hydroxypentanal to a small extent, and other aldehydes only slightly or not at all.

Table II shows results from treatments for 60 min at 20–25°C in solutions of 0.12 mol aldehyde, 3.7 g hydrogen chloride, and 18 g water in 100 g acetic acid solution. Only formaldehyde and glutaraldehyde crosslinked to a noticeable extent, although some reaction would be expected by glyoxal because of its crosslinking ability in the pad-dry-cure treatment.

Crosslinking in the solution at room temperature seems to follow the order of reaction in the pad-dry-cure treatment. However, crosslinking in the acetic acid solution was less, so only those aldehydes with the greatest extent of crosslinking in the pad-dry-cure treatment showed any indication of reaction.

Relation of Crosslinking to Properties of Aldehydes

Boiling Point

To react the aldehyde must remain on the cotton long enough for the reaction to proceed. Therefore, volatility of the aldehyde may be a factor in the pad-dry-cure treatment. In treatment with solution at room temperature, volatility is unlikely to be a factor.

The data in Table I show no relation between crosslinking in the pad-dry-cure treatment and boiling point. One of the most reactive aldehydes, formaldehyde, has the lowest boiling point. The reactive aldehydes were retained through curing to a greater extent than they reacted. However, some of the high-boiling aldehydes were retained through curing and showed no evidence of reaction. Absorption of the aldehydes appears necessary for crosslinking because of reasons over and above retention of the aldehyde on the fabric.

Although catalyst is necessary for acetalization and crosslinking, formaldehyde is absorbed on cotton even without catalyst.^{5,6} Absorption seems to result from formation of a cellulose hemiformal.⁷ The other reactive aldehydes probably behave in a similar manner.

TABLE II
Crosslinking by Aldehydes in Solution at Room Temperature

Aldehyde	Fabric properties		
	Wrinkle recovery angle (deg, $w + f$)	Durable press rating	Add-on after wash (% of original wt)
Formaldehyde	242	3.4	1.6
Acetaldehyde	182	2.3	0.0
Glyoxal	195	2.3	-1.1
Glutaraldehyde	237	3.3	2.2
Benzaldehyde	188	1.8	0.0
Glyoxylic acid	189	1.3	-1.1

Molecular Size

To react extensively with cotton, aldehydes must penetrate the fiber structure. There should be, therefore, a limit on the molecular size that allows crosslinking. However, with molecular weight as the indicator of molecular size, there is no correlation between crosslinking and molecular size within the range tested. Glutaraldehyde has one of the higher molecular weights among the aldehydes tested and showed one of the highest levels of crosslinking. Acetaldehyde showed little reaction although its molecular weight is low.

Stability of Acetals

Because the reaction of aldehydes with alcohols to form acetals is reversible, aldehydes forming acetals with higher resistance to hydrolysis would be expected to crosslink cotton to a greater extent. However, this hypothesis is not supported by available data on the rates of hydrolysis of ethyl acetals.⁸

Of the aldehydes tested in the referenced work and here, formaldehyde forms the acetal with the slowest rate of hydrolysis and shows one of the highest extents of crosslinking. However, phenylacetaldehyde forms an ethyl acetal with a relatively low rate of hydrolysis and yet showed no more than slight reaction. The reactive glutaraldehyde is not noted in the referenced work but would be expected to form acetals with a relatively rapid rate of hydrolysis like those in acetals of acetaldehyde or propionaldehyde.

This proposal regarding the lack of a relationship between hydrolysis resistance and extent of crosslinking must be tempered with some caution. The aromatic group in phenylacetaldehyde may be a deterrent to fiber penetration. Acetals of glutaraldehyde and cellulose may have a higher resistance to hydrolysis than expected by virtue of a cyclic structure, that is, 2,6-dialkoxytetrahydropyrans.

Hydration of Aldehydes

It was noted that absorption of the aldehyde by cotton seems necessary before formation of acetal crosslinks and that the absorption likely occurs by formation of a cellulose hemiacetal.⁷ An aldehyde that reacts readily to form a hemiacetal is also likely to hydrate readily. In line with this consideration, the reactive aldehydes formaldehyde and glyoxal in water solution gave PMR spectra without the signals in the 9–10 ppm region that are characteristic of hydrogen in aldehyde groups. The poorly reactive acetaldehyde and unreactive benzaldehyde in the presence of water showed the characteristic signal at 9–10 ppm that integrates in the theoretical ratio with the signals from the remaining hydrogens in the molecules. Glutaraldehyde, although it crosslinked cotton readily, also showed a signal at 9.7 ppm. However, this signal was no more than 5% of the integration of all hydrogen signals instead of the theoretical 25%. This indicates that about 80% of the aldehyde groups in glutaraldehyde are hydrated. Also indicative of a high degree of hydration is the high water solubility of glutaraldehyde; solubility is much higher than expected from its molecular or equivalent weight.

Glyoxylic acid is an apparent exception to a generalization that all aldehydes with hydrated aldehyde groups crosslink cotton readily. The only signal in the PMR spectrum from glyoxylic acid in water was at 5.4 ppm, an indication that

aldehyde groups as such are absent. However, as seen from Table III, glyoxylic acid was unreactive when applied in a pad-dry-cure treatment from solution at pH 5 like the other aldehydes. With application at lower pH, glyoxylic acid became reactive (see Table III). The change in response with change in pH was unique with glyoxylic acid. Application of acetaldehyde or benzaldehyde at pH 2 gave no more crosslinking than application at pH 5 (Table I). Nor did application of these aldehydes with magnesium chloride and citric acid as catalyst increase crosslinking as would be expected if the increased reactivity of glyoxylic acid at low pH was caused by increased catalytic activity from the salt-acid combination.⁹

The response of crosslinking to changing pH suggests that glyoxylic acid reacted only in the unionized form. Again, some caution is required with this hypothesis. As the solution is dried on fabric, there will be a change in acidity to an unknown value. In an acetic acid solution at room temperature (as used with other aldehydes for the results in Table II), glyoxylic acid showed no crosslinking even though acidity was quite high.

SUMMARY AND CONCLUSIONS

The extents that aldehydes crosslink cellulose of cotton in a pad-dry-cure treatment with a high curing temperature and in an acidic solution at room temperature was related. The same order of crosslinking ability among the aldehydes occurs in both treatments, although crosslinking at room temperature is less. Glyoxylic acid is an exception to this statement, but another factor comes into play, i.e., the change in reactivity of glyoxylic acid with change in acidity of the pad formulation.

For an aldehyde to crosslink with cotton it must readily form a hemiacetal with cellulose. This not only prevents complete volatilization from the fabric before the crosslinking reaction but keeps the aldehyde at reactive sites in the cellulose molecule. Hemiacetal formation is closely related to hydration and the existence of the aldehyde as a hydrate in water solution is therefore an indication of the ability to crosslink cotton.

Structural features that indicate potential as a crosslinking agent are hard to define. Three aldehydes that crosslink readily, formaldehyde, glyoxal, and unionized glyoxylic acid, have an isolated carbonyl group or another carbonyl group adjacent to the aldehyde group. The carbonyl group is electron-withdrawing. However, the electron-withdrawing phenyl group, even when substituted with a nitro group to augment the effect, gave no noticeable crosslinking.

TABLE III
Crosslinking by Glyoxylic Acid in Pad-Dry-Cure Treatment

pH of formulation ^a	Wrinkle recovery angle (deg, $w + f$)	Durable press rating
2	267	3.7
4	212	2.3
5	201	2.3

^a Formulation: 8.0% glyoxylic acid, 1.8% magnesium chloride hexahydrate, and triethylamine to adjust pH in water.

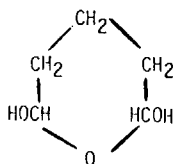


Fig. 1. 2,6-Dihydroxytetrahydropyran.

Glutaraldehyde is an active crosslinking agent, and yet with the separation of the aldehyde groups, appears to be closely related to aliphatic monoaldehydes such as the poorly reactive acetaldehyde. However, the glutaraldehyde molecule is of a size to form a cyclic monohydrate with a six-membered ring, 2,6-dihydroxytetrahydropyran (Fig. 1), and is reported to form such rings.¹⁰ Because of the favorable ring size, glutaraldehyde may form hydrates more readily than other unactivated aliphatic aldehydes. Similarly, α -hydroxyadipaldehyde can form an internal hemiacetal with a six-membered ring, 2-formyl-6-hydroxytetrahydropyran, and is reported to be reactive to cotton.² Also, the acetal 2,5-dimethoxytetrahydrofuran has a similar cyclic structure with a five-membered ring and crosslinks cotton more readily than most acetals.¹¹

The preceding examples of reactive aldehyde derivatives are based on dialdehydes. 5-Hydroxypentanal is a monoaldehyde that exists predominantly as a cyclic hemiacetal, 2-hydroxytetrahydropyran.¹² However, 5-hydroxypentanal did not crosslink to a greater extent than acetaldehyde, an unsubstituted aldehyde. The cyclic structure seems to give an ability to crosslink by bringing two aldehyde or potential aldehyde groups close together.

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