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Modification of Crosslinking Effects in Cotton Fabrics by Swelling and Methylation

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Synopsis

The effects of crosslinking on cotton fabric are changed when the cotton has been chemically modified before crosslinking with an inert substituent, such as the methyl group. The main action of the inert substituent is to preserve swelling ability by hindering fiber deswelling after methylation and during crosslinking. At the levels of modification used, the crosslinking reaction appears to proceed normally, with no effects from reduction in the number of reactive cellulosic hydroxyl groups.

Introduction

In previous investigations at this laboratory the crosslinking of chemically modified cotton fabric has been studied to determine the effects of various modifications on properties imparted or changed by cellulose crosslinking.[1,2] The present study is a continuation of this research in which cotton is modified with an inert substituent under a range of reaction conditions. Since the substituent group is inert to modification or removal, chemical activity by the group is absent and a previously reactive site is blocked. Any effects produced by the modification, therefore, are from a change in the reactivity of the cellulose or from a physical action on the structure of the cotton.

For this investigation, the modification of cotton fabric employed was partial methylation. The methyl group is inert, and methylation can be accomplished with the cotton in different degrees of swelling. In the methylation procedure, cotton fabric was treated with dimethyl sulfate in the presence of sodium hydroxide solution varying in concentration from 7 to 45%. Dimethylol ethyleneurea was selected for use as the crosslinking agent because it reacts readily and is obtainable in a fairly pure state.

The dry and wet wrinkle recovery angles, nitrogen content, moisture regain, and water of imbibition of the treated fabrics were determined. The last two properties are considered to be a measure of the degree of swelling of the fabric or, as is probably more correct, the ability of the cotton to swell in water.

Experimental Procedures

A desized, scoured, and bleached cotton 80 × 80 printcloth was used in all experiments.

The fabric was methylated essentially by the technique of Reeves and co-workers.[3] Reactions were carried out at 86–87°C. in a glass reactor in which dimethyl sulfate in toluene was circulated through fabric impregnated with an aqueous solution of sodium hydroxide. Various times were used to obtain different degrees of substitution. Repeated methylations were necessary to achieve comparable degrees of substitution when 7% sodium hydroxide was employed instead of 20% and 45% solutions.

Samples were crosslinked by impregnating with a solution containing 8 wt.-% of dimethylol ethyleneurea (DMEU) and a commercial zinc nitrate catalyst preparation, placing the fabric on pin frames, drying for 7 min. at 60°C., and curing for 3 min. at 160°C. After curing the samples were washed with a nonionic detergent.

Methoxyl content was determined by the Zeisel procedure and nitrogen by the Kjeldahl method. Moisture regain was determined by ASTM method D 629-59T.[4] Wrinkle resistance, as measured by dry wrinkle recovery angles was determined by ASTM method D 1295-60T.[4] Wet wrinkle recovery angles were determined by using the procedure for dry wrinkle recovery angles on samples that were soaked for 5 min. in water containing a nonionic wetting agent at 65°C. and blotted to remove excess water. Water of imbibition is the amount of water, as per cent of dry sample weight, retained after the sample was dried in a desiccator 24 hr., weighed, soaked in distilled water 1 hr., centrifuged at 1000 *g* for 40 min., and weighed again.

Results and Discussion

Because of the paucity of existing data, preliminary experiments were run to show the effects of methylation on the fabric properties under consideration. A series of samples were prepared with increasing degree of methyl substitution (DS methyl, average number of methyl groups per anhydroglucose unit in the cellulose chain) by varying the reaction time on fabric impregnated with 45% sodium hydroxide solution. Test data for this series are given in Table I.

TABLE I
Properties of Cotton Fabrics Methylated with the Use of 45% Sodium Hydroxide

DS methyl	Moisture regain, %	Wrinkle recovery angles (W + F)	
		Dry	Wet
Nil[a]	8.7	175°	203°
0.22	9.7	174°	194°
0.75	9.5	165°	188°
0.93	9.2	132°	170°

[a] Treated with sodium hydroxide solution but not with dimethyl sulfate.

Moisture regain rises as methyl substitution increases, reaches a maximum, and then falls as substitution increases further. These results indicate that the methylated cottons are more swollen or have greater swelling ability than the cotton treated with sodium hydroxide only. This should be expected, since the substituent groups are introduced when the cotton fiber is swollen with alkali, and their physical presence can block the return of molecular segments of cellulose to the positions they held when the fiber was in the unswollen state. Deswelling on removal of the alkali by water or on drying is thereby reduced to some extent. The resulting increase in number of accessible hydroxyl groups causes the increased moisture regain. Increasing methyl substitution, however, reduces the total number of hydroxyl groups and therefore reduces the amount of water that can be held as regain if all hydroxyl groups were accessible. A substitution is reached where the effect of reduction in total number of hydroxyl groups increases faster than the effect of greater accessibility, and moisture regain starts to decline.

In the series of Table I, both dry and wet wrinkle recovery angles are decreased at the higher degrees of methyl substitution. This is indicative of a decrease in the natural recovery forces in the cotton fiber, presumably because of a decrease in intermolecular hydrogen bonding or other interchain attractions. This can be ascribed also to the retention of a higher degree of swelling after methylation. However, an expected increase in wet wrinkle recovery in relation to dry wrinkle recovery from the increased ability to swell[5] appears small, if existent at all, in Table I.

Another series of methylated cotton fabrics was prepared with the use of 45% sodium hydroxide to determine how the degree of methyl substitution affected properties after crosslinking. This series is shown in Table II. The range of degree of substitution goes to 0.57, at which level dry wrinkle recovery angles have not yet declined. Wet wrinkle recovery angles in this series show a marked increase as substitution increases and an apparent sharp drop at the highest substitution. Moisture regain and water of imbibition values increase over the range of this series, with a particularly large increase in the latter.

The effects of crosslinking on the methylated fabrics are qualitatively the same as those produced on unmodified cotton but with significant changes in quantity as degree of substitution increases. Crosslinking results in higher dry wrinkle recovery angles, but the increase produced by a given solution of crosslinking agent becomes smaller as substitution increases. This occurs even though the nitrogen contents indicate that more agent reacts with increasing substitution. Two possible explanations are offered for this phenomenon. The increased swelling ability of the methylated cotton permits more dimethylol ethyleneurea to react with the cellulose, but the methyl substitution, by blocking hydroxyl groups, makes completion of crosslinks more difficult. Alternatively, the higher degree of swelling permits more agent to react and crosslink, but this is accompanied by enough decrystallization that an even greater increase in degree of cross-

TABLE II
Properties of Cotton Fabrics Methylated with the Use of 45% Sodium Hydroxide, Before and After Crosslinking

DS methyl	Not crosslinked: Wrinkle recovery angles (W + F), Dry	Not crosslinked: Wrinkle recovery angles (W + F), Wet	Not crosslinked: Moisture regain, %	Not crosslinked: Water of imbibition, %	Crosslinked[a]: Wrinkle recovery angles (W + F), Dry	Crosslinked[a]: Wrinkle recovery angles (W + F), Wet	Crosslinked[a]: Moisture regain, %	Crosslinked[a]: Water of imbibition, %	Crosslinked[a]: Nitrogen content, %
Nil[b]	181°	224°	8.7	40	259°	255°	7.8	25	0.98
0.09	182°	246°	9.2	—	262°	280°	8.6	—	1.13
0.34	181°	266°	9.6	52	239°	273°	9.5	38	1.13
0.57	179°	163°	10.7	80	235°	266°	10.5	36	1.28
					281°[c]	264°	9.3	—	2.59

[a] Treated with 8% dimethylol ethyleneurea except where otherwise noted.
[b] Treated with sodium hydroxide solution but not with dimethyl sulfate.
[c] D.S. 0.57 treated with 16% dimethylol ethyleneurea.

linking is required to produce a given wrinkle recovery angle. Previous work indicated degree of crosslinking is not reduced by methylation and therefore supports the latter explanation.[1] This explanation is also supported by the lack of chlorine retention in the crosslinked methylated cotton. Any dimethylol ethyleneurea that is bound but does not crosslink should provide sites for retaining chlorine from hypochlorites. All of the crosslinked methylated samples of Table II suffered less than 10% strength loss in the test for damage from retained chlorine.[6] On the other hand, a noticeable reduction in dry wrinkle recovery from methylation without crosslinking would be expected if decrystallization, the alternate, was the true explanation. In any event, increasing the concentration of crosslinking agent in solution gives a treatment in which enough crosslinks are formed to give high dry wrinkle recovery angles. This indicates that methylation, unlike acetylation in nonswelling media,[2] does not occur preferentially in regions of the cotton fiber where crosslinking is required for large increases in dry wrinkle recovery angles.

Change in wet wrinkle recovery angles on crosslinked fabric as methyl substitution increases is less noticeable. The increased swelling ability offsets any reduction in the effectiveness of the crosslinking reaction.

The higher moisture regain and water of imbibition of the crosslinked, methylated cottons compared to the crosslinked control show that the effect of increased swelling ability persists through crosslinking. As methyl substitution increases, less loss of moisture regain occurs on crosslinking. At the highest substitution, the crosslinked fabric, even with a high dry wrinkle recovery angle, has greater moisture regain than the uncrosslinked, unmethylated fabric. Water of imbibition, however, shows an unchanging or increasing loss on crosslinking as methyl substitution approaches the highest values. At the highest substitution, the water of imbibition of the crosslinked fabric is greater than that of the crosslinked, ummethylated fabric but is less than half that of the uncrosslinked fabric with the same methyl substitution. These data show that methylation makes more accessible water-retaining regions in the cotton fiber to increase both moisture regain and water of imbibition. Crosslinking affects these two properties differently, either because different regions of the cotton fiber are responsible for each property or because the crosslinking can restrict the entry of liquid water more than it restricts the entry of water vapor to the water-retaining regions of the fiber. As there seems no evidence for any preferential distribution of substituents, either methyl groups or crosslinks, the latter explanation seems the more likely.

To determine the effects of extent of swelling during methylation, the series of fabrics listed in Table III was prepared. This series is composed of three fabrics methylated to DS 0.30–0.35 by using 7, 20, and 45% sodium hydroxide solutions and three control fabrics treated with the sodium hydroxide solutions only. These three concentrations of sodium hydroxide include one below mercerizing strength and two above. It was found impossible by the methods used to get a significant degree of methylation with

TABLE III
Properties of Cotton Fabrics Methylated with the Use of Different Concentrations of Sodium Hydroxide Before and After Crosslinking

NaOH used, %	DS methyl	Wrinkle recovery angles (W + F)		Moisture regain, %	Water of imbibition, %	Nitrogen content, %
		Dry	Wet			
		Before crosslinking				
7	Nil[a]	164°	193°	7.1	—	—
7	0.33	143°	212°	6.4	47	—
20	Nil	182°	250°	9.0	—	—
20	0.33	180°	264°	10.1	58	—
45	Nil	181°	224°	8.7	—	—
45	0.34	181°	266°	9.6	52	—
		After crosslinking[b]				
7	Nil	292°	275°	5.5	—	1.44
7	0.33	282°	290°	5.5	24	1.21
20	Nil	266°	270°	8.0	—	1.26
20	0.33	255°	274°	9.5	34	1.23
45	Nil	259°	255°	7.8	—	0.98
45	0.34	239°	273°	9.5	38	1.13

[a] Treated with sodium hydroxide solution but not with dimethyl sulfate.
[b] Treated with 8% dimethylol ethyleneurea.

a sodium hydroxide concentration less than 7%. Even at 7% repeated treatments were required to give a substitution above 0.3.

Examination of data from the uncrosslinked fabric samples in Table III shows that swelling effects, indicated by moisture regain, water of imbibition, and wet wrinkle recovery angles, increase sharply on going from below (7%) to above mercerizing strength hydroxide (20%). No further increase, and possibly a decrease, in these effects occurs on going from 20 to 45% concentration. Methylation with the use of mercerizing strength hydroxide accentuates these swelling effects by reducing the amount of deswelling on removal of caustic and drying. This accentuation occurs to a much smaller extent, if at all, when less than mercerizing strength hydroxide is used in methylation. At the low hydroxide concentration, not enough swelling occurs to make the reduction in deswelling a significant factor.

Crosslinking the cottons methylated by using 7% sodium hydroxide gives about the same dry wrinkle recovery angles as crosslinking the unmethylated control. When higher concentrations of sodium hydroxide are used, however, subsequent crosslinking produces lower wrinkle recovery angles. Apparently this level of methyl substitution does not hinder crosslink formation. This conclusion is in accord with the concept that with methylation under high swelling conditions more crosslinking is required for a given wrinkle recovery angle. Other work at this laboratory has shown that increased swelling conditions at time of crosslinking up to the level of swelling caused by water does not affect the dry wrinkle recovery produced by a given degree of crosslinking.[7] Here, however, we are concerned with a much higher extent of swelling that, as postulated, involves a lower degree of crystallinity.

Any tendency to lose wet wrinkle recovery from the above effect is apparently offset by the tendency of increased swelling ability to improve it.

The fabrics methylated with the use of the higher hydroxide concentrations show less decrease in moisture regain than the controls do as a result of crosslinking. This also demonstrates their higher swelling ability and the smaller amount of deswelling they undergo in the dry-cure crosslinking treatment. The fabric methylated by use of the 7% hydroxide again shows no such effect, because swelling was not extensive enough when the methyl substituents were introduced. Water of imbibition data are less complete but show a similar trend.

Summary and Conclusions

The effects of crosslinking treatments on cotton fabric are modified when the cellulose is etherified with an inert substituent such as in methylation. This modification is due mainly to the preservation of a swollen state or swelling ability in the cotton. This occurs because the substituent prevents deswelling after the etherification treatment by physically blocking molecular segments in the cellulose chains from returning to their original positions.

When mercerizing concentrations of sodium hydroxide are used in methylation, the high degree of swelling is probably accompanied by extensive decrystallization. The methyl substituents also hinder any recrystallization. Reduced crystallinity seems the likely reason that crosslinking treatments produce a smaller improvement in dry wrinkle recovery in the methylated fabric. More crosslinks are then needed to produce a given resiliency. High wrinkle recovery angles can be obtained if enough crosslinking is accomplished. Inactivation of reaction sites by methyl groups, whereby the number of crosslinks is reduced, does not seem to be the major factor in causing reduced dry wrinkle recovery at the levels of methyl substitution studied. In samples methylated without high swelling, the effect of the substituent is small or nonexistent.

Methylation of the cotton has less effect on the improvement in wet than on dry wrinkle recovery angle after crosslinking. This is because the increased swelling ability partially offsets the reduced effectiveness of the crosslinks in directly improving resiliency.

The effects of swelling persist after crosslinking. Noticeably higher moisture regains and water of imbibition values are observed in crosslinked, methylated fabric than in crosslinked, unmethylated fabric. The methyl groups apparently prevent deswelling on drying during the crosslinking treatment much as they prevent deswelling after methylation. Methylated cotton, from treatments with mercerizing strength sodium hydroxide, has a higher moisture regain than unmethylated cotton before crosslinking and a smaller drop in regain on crosslinking. Water of imbibition is greatly increased by methylation, but crosslinking causes a correspondingly large decrease. Crosslinking the swollen cotton seems to make a proportionately greater barrier to liquid water than it does to water vapor.

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Résumé

Les influences du pontage sur les fibres de coton sont changées lorsque le coton a été modifié chimiquement avant pontage au moyen d'un substituant inerte tel que le groupe méthyle. L'action principale du substituant inerte est de préserver l'aptitude au gonflement en empêchant le dégonflement de la fibre après méthylation et pendant le pontage. Avec cette modification, la réaction de pontage semble s'effectuer normalement sans diminution du nombre de groupes hydroxyles réactionnels de la cellulose.

Zusammenfassung

Der Vernetzungseffekt bei Baumwollgewebe ändert sich, wenn die Baumwolle vor der Vernetzung mit einem inerten Substituenten, wie die Methylgruppe, chemisch modifiziert wurde. Die Hauptwirkung des inerten Substituenten besteht in der Beibehaltung der Quellfähigkeit durch die Verhinderung der Faserentquellung nach der Methylierung und während der Vernetzung. Bei dem verwendeten Modifizierungsgrad scheint die Vernetzungsreaktion normal ohne Beeinflussung durch die Herabsetzung der Zahl der reaktiven Zellulose-hydroxylgruppen zu verlaufen.

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