A Quantitative Study of Crosslinking Cotton with N-Methylol Acrylamide
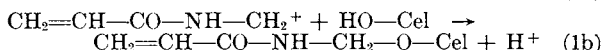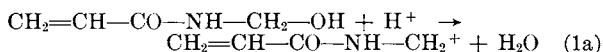
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INTRODUCTION

Commercial processes for improving the resilience of cotton fabrics and imparting wash-wear properties to them involve the use of difunctional reagents which can, at least potentially, etherify cellulose. The evidence that such reagents, e.g., dimethylolethyleneurea, do crosslink cellulose is largely circumstantial, but what we know about the reaction mechanism and the nature of the changes in the mechanical properties of the fabric strongly support the idea that covalent crosslinks are formed.[1] Unfortunately, the conventional reagents can also react with themselves to give polymers or oligomers or they can react with cellulose single-endedly, and it is difficult to establish to what extent they form true crosslinks in the fabric. A way out of this dilemma is to use a reactant having two different functional groups, such as N-methylol acrylamide (MAM), and to control the conditions of reaction so that only one or the other of the groups or both, as desired, react with the cellulose. Strain[2a], has mentioned the reaction of a methylolated acrylamide with rayon cellulose. The reaction, which occurs under the acid conditions Strain has used, has been clarified by the work of Mantell[2b] who points out that under acid catalysis only the N-methylol groups react with cellulose:

$$CH_2=CH—CO—NH—CH_2—OH + H^+ \rightarrow$$
$$CH_2=CH—CO—NH—CH_2^+ + H_2O \quad (1a)$$
$$CH_2=CH—CO—NH—CH_2^+ + HO—Cel \rightarrow$$
$$CH_2=CH—CO—NH—CH_2—O—Cel + H^+ \quad (1b)$$

In a separate alkali-catalyzed second step Mantell reacted suitable active hydrogen compounds, such as thiophenols, with the pendant double bonds of the acrylamidomethylcellulose to render the fabric hydrophobic. He also mentioned, without going into details, that an alkaline catalyst treatment of the acrylamidomethylcellulose in the absence of other reagents caused addition of the cellulosic hydroxyls to the double bonds forming crosslinks of the following nature:

$$Cel—O—CH_2—NH—CO—CH_2—CH_2—O—Cel$$

The present study shows that, under suitable conditions, the pendant acrylamidomethyl groups can homopolymerize through their double bonds to form a new type of polymeric crosslink in cellulose. In this connection it should be mentioned that very recently Kamogawa et al.[3] investigated the reaction of MAM and cellulose with acidic free radical catalysis. Under such conditions homopolymerization of the double bonds and etherification of the cellulose take place simultaneously, leading to crosslinks which in all likelihood are identical to the ones obtained when the acrylamidomethylation and polymerization are carried out in two separate steps. However, the two step crosslinking process described below has some distinct advantages from the standpoint of basic research. It allows the study of the single-ended reaction and the crosslinking reaction separately, giving insight into the nature and extent of each. Furthermore, it allows the separation of effects due to changes in the bulk of the fabric from those due to crosslinking.

Recent research has emphasized the point that the state of swelling of the cellulose during the crosslinking reaction has an important influence upon the nature of the changes in the physical properties.[1,4,5] This effect can be very conveniently studied with the aid of acrylamidomethylcellulose, since the second step crosslinking reactions can be catalyzed either by the conventional pad-cure procedure, i.e., substantially in the dry, nonswollen state, or with the fabric immersed in hot aqueous catalyst solution, i.e., in the wet, swollen state.

In the present work different amounts of MAM were reacted single-endedly on cotton with the aid of a mild acid catalyst using the dry state pad-cure procedure. As will be shown, analysis of the reaction product indicated that the reaction occurred exclusively as described in eq. (1). This single-ended reaction had only a relatively small effect on the mechanical properties of the fabric. The acrylamidomethylated cotton was subsequently crosslinked by three basic procedures. In the "dry

APS" or "dry KOH" treatment a solution of ammonium persulfate or potassium hydroxide was padded on the fabric at room temperature and then the fabric was heated in an oven. In the "wet KOH" process the acrylamidomethylated cotton was immersed in a hot potassium hydroxide solution. The most striking chemical change due to either of these aftertreatments was that a portion of the double bonds disappeared. Since these treatments did not change the weight of the fabric, the double bonds must have been consumed either by a polymerization reaction or by addition of hydroxyl groups to them. These reactions changed the mechanical properties of the fabric in a very spectacular manner, and in particular they substantially increased the crease recovery.

It may be mentioned that the crease recovery test is widely used in the field of wash-wear finishing of textiles. The test involves creasing a small strip of fabric under weight for 5 min., removing the creasing load to allow the strip to recover for 3 or 5 min., as specified by the test, and measuring the angle thus formed. Complete recovery would correspond to 180°, but this is not achieved in practice even when very resilient fabrics are tested because friction between the fibers restricts full realization of the inherent resilience of the fiber forming substance.[6] Although rheological analysis of the crease recovery test is complicated,[7] it is believed that this test measures the same fundamental property as a tensile recovery or work recovery test.[1,6,8,9] In terms of a rheological picture, high crease recovery indicates that the main mode of deformation is elastic, while in materials with low crease recovery a viscous deformation mechanism predominates.

One of the aims of the present study is to establish quantitative relationships between crosslink content and properties such as crease recovery, tensile strength, and breaking elongation. In addition, the effect of swelling during the crosslinking is studied and some evidence is presented pertaining to the changes in supermolecular structure of the cellulose when the crosslinking is carried out in the swollen state. It is also shown that only a portion of the total number of crosslinks contributes to the increment in crease recovery.

EXPERIMENTAL

Preparation of Samples

The discussion is based on two experimental series. To prepare one of these, different amounts of crude, technical MAM were reacted on cotton
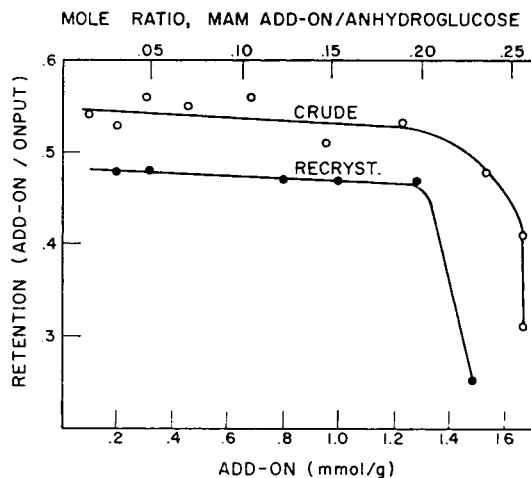

Fig. 1. Variation of retention with add-on in the single-ended reaction of MAM with cotton cellulose.
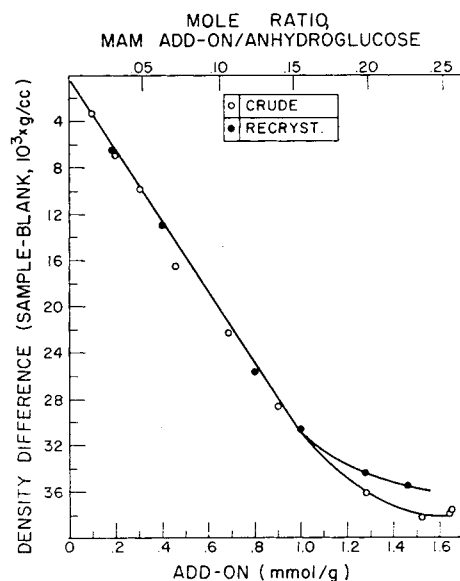

Fig. 2. Density reduction due to single-ended reaction of MAM with cotton cellulose.

under acid conditions, as described below for the single-ended reaction. The data of this experimental series is used only in Figures 1 and 2. In the second series recrystallized MAM was used. In this series four samples were prepared at each of six MAM contents: 1.4, 3.2, 6.9, 8.0, 10.9, or 12.2%. One sample of each set of four received no crosslinking aftertreatment, the other three received three different aftertreatments. The chemical properties of these samples are given in Table I, and the physical properties of one set are given in Table II. The method of preparation used in this second experimental series is given below.

TABLE I
Analytical Data (in mole/g.) of Cotton Printcloth Treated with N-Methyl Acrylamide

Analysis	Single-ended react.	Aftertreatment			Single-ended react.	Aftertreatment		
		Dry APS	Dry KOH	Wet KOH		Dry APS	Dry KOH	Wet KOH
By wt. add-on	0.19	—	—	—	0.39	—	—	—
N	0.20	0.18	0.17	0.19	0.39	0.41	0.41	0.39
Methylene	0.19	0.17	0.19	0.20	0.37	0.37	0.38	0.39
Double bonds	0.20	0.16	0.04	0.07	0.41	0.30	0.11	0.22
By wt. add-on	0.83	—	—	—	0.97	—	—	—
N	0.84	0.82	0.77	0.76	1.02	1.07	0.96	1.03
Methylene	0.75	0.67	0.77	0.76	1.02	0.84	0.83	0.96
Double bonds	0.81	0.50	0.23	0.58	0.99	0.58	0.12	0.75
By wt. add-on	1.31	—	—	—	1.47	—	—	—
N	1.27	1.33	1.27	1.26	1.44	1.39	1.37	1.51
Methylene	1.28	0.97	1.11	1.14	1.46	1.12	1.27	1.43
Double bonds	1.23	0.48	0.11	0.98	1.45	0.47	0.08	1.17

Single-ended reaction. MAM was recrystallized from ethyl acetate solutions containing 1% hydroquinone as a polymerization inhibitor and dissolved in water to obtain 3.5 to 50% (w/w) concentration. Each solution contained 1% (w/w) 2-amino-2-methylpropanol hydrochloride as a catalyst. These solutions were padded on 80^2 cotton printcloth to obtain 95 to 100% wet pick-up. The samples were then placed for 3.5 min. in a well-ventilated oven at 150°C. The unreacted materials were removed by rinsing the samples in an aqueous solution of 2% sodium nitrite polymerization inhibitor at 80°C. and then in cold water.

Six samples were prepared at each MAM concentration. Two samples were preweighed, one being used for determining the wet pick-up and the other being heat-treated in a relaxed state, rinsed, and oven-dried to determine the weight add-on. The other four samples were heat-treated on pinframes, care having been taken to maintain their original dimensions. After being cured and rinsed, the samples were dried again on pinframes. One of these samples was dried in the conditioning room at 65% R.H. and 21°C. and kept in the conditioning room until its mechanical properties and moisture regain were determined. The other samples were oven dried and used for the aftertreatments.

"Dry APS" aftertreatment. The acrylamidomethylated samples were padded with 0.5% ammonium persulfate solution, cured on frames, rinsed, and dried in the conditioning room as indicated above.

"Dry KOH" aftertreatment. The procedure was the same except that 2% potassium hydroxide was used as a catalyst and the rinsing step included the use of 2% acetic acid solution prior to the water rinse.

"Wet KOH" aftertreatment. The samples were put on special metal frames and immersed in 2% potassium hydroxide solution at 90°C. for 3 min., soaked in 2% acetic acid, rinsed in cold water, and dried in the conditioning room.

Catalyst controls. Cotton samples were also treated in the same way as indicated above in the absence of MAM. None of the catalysts had any effect on the moisture regain, density, crease recovery, or wash-wear ratings. The alkanolamine hydrochloride and the "wet KOH" or "dry KOH" treatments had no effect on the tensile strength or the breaking elongation, but the "dry APS" treatment significantly reduced these properties (cf. Figs. 12 and 13).

Methods of Analysis

The double bond, methylene, and nitrogen contents were determined and calculated on the basis of millimole per gram of untreated cellulose. The nitrogen contents were determined by the micro Kjeldahl method; the procedures for double bonds and methylene are given below.

Double bonds. It is customary to determine double bonds adjacent to electron-withdrawing groups, e.g., in acrylic esters or in acrylonitrile, by reaction in an alkaline medium with a thiol, such as dodecanethiol, and then titrating the excess of untreated thiol with iodine.[10] The double bonds react much faster with thiols than with aliphatic alcohols since presence of an alcohol was found not to interfere with the results.

TABLE II
Typical Physical Property Data Obtained in One Set of Experiments

In the first step a solution of 1% alkanolamine hydrochloride and 18% MAM was applied to obtain 99% wet pick-up, and 8% (0.97 mmole/g.) add-on. The aftertreatments caused no measurable change in the weight of the fabric.

| Analysis | Single-ended react. | Aftertreatment | | | Blank |
		Dry APS	Dry KOH	Wet KOH	
Dens. diff., blank − sample, $10^3 \times$ g./cc.	30.7	26.3	27.8	31.9	—
Moist. regain, %, at 93% R.H.	12.3	9.6	8.5	14.3	15.4
Crease recovery $(W + F)/2$, °					
Dry	92	133	137	105	72
Wet	84	116	137	132	55
Wash-wear rating					
Tumble dry	1	4	5	3	1
Drip dry	1	3	4	4	1
Tens. strength, lb./0.5 in.					
Dry: warp	20	13	12	13	27
fill	19	11	10	12	24
Wet: warp	23	12	12	13	27
fill	20	11	10	12	24
Breaking elong., %					
Dry: warp	10	8	7	8	10
fill	19	12	13	11	29
Wet: warp	15	8	8	8	16
fill	25	14	13	12	34

This principle of double bond determination has been modified in that a water-soluble thiol, mercaptoethanol, was used. A weighed piece of cotton containing 0.2 to 3 mmole of double bonds was treated under nitrogen in a 125 ml. Erlenmeyer flask with a mixture of 10 ml. of a 5.7% (v/v) solution of mercaptoethanol in water and 2 ml. of 2N NaOH for 15 min. at room temperature. Subsequently 5 ml. of 1N HCl and 20 ml. of 0.15N iodine were pipetted into the flask and the solution was titrated with 0.1N iodine to starch endpoint. A blank was run in identical manner. To check the accuracy of this method, freshly recrystallized acrylamide or MAM was also analyzed. The results agreed to ±2% with the theoretical values.

This titration method was counterchecked in the following manner. The titrated cotton samples were rinsed in cold water, dried, and analyzed for sulfur by Schoniger's semimicro flask combustion method.[11] The sulfate was determined by titration with 0.02N BaCl$_2$ solution using tetrahydroxyquinone as indicator.[12] After correcting the sulfur content values for the increased bulk in the samples due to mercaptoethanol addition, the values obtained in this way agreed very well, usually within ±2%, with the iodimetric titration values.

Methylene. The cotton samples were first hydrolyzed and the formaldehyde in the hydrolyzate was determined by chromotropic acid method.[13] A weighed piece of fabric, containing about 0.05 mmole of methylene groups was hydrolyzed in 50 ml. of 5N H$_2$SO$_4$ at 60°C. for 3 hr. The solution was cooled and its volume was adjusted to 100 ml. with 5N H$_2$SO$_4$. 5 ml. of this hydrolyzate was mixed with 2 ml. of 10% chromotropic acid solution and 25 ml. of concentrated H$_2$SO$_4$. This mixture was kept at 60°C. for 30 min., cooled, and diluted to 100 ml. with 5N H$_2$SO$_4$. The optical density was determined at 570 mμ. The method was calibrated with formaldehyde solutions of known concentrations. Below an optical density of one, the data followed the Lambert-Beer Law. The conversion of optical density to methylene or formaldehyde content is given by formula:

$$\text{mmole/cotton sample} = 7.76 \times \text{optical density}$$

Physical Properties

The average of warp and fill crease recovery of samples conditioned at 65% R.H. and 21°C. was determined in triplicate by the Shirley Institute Monsanto modification of the creasing angle method.[14] For determining wet crease recovery, the method was modified in that the creasing and recovery was carried out under water and the sample was allowed to recover while floating on mercury.

The wash-wear data were obtained by the tenta-

tive AATCC method[15] using the Monsanto plastic models as standards. The rating 5 corresponds to perfectly smooth fabric.

For determination of tensile strength, breaking elongation and modulus, 0.5 in. raveled strip specimens were used at a gage length of 2 in. The rate of strain was 25%/min. and the experiments were carried out in quadruplicate on an Instron tester. The tensile strength values are reported in pounds load per 0.5 in. sample width. For the dry tests the samples were conditioned at 65% R.H. at 21°C. To determine the wet stress–strain properties, the test specimens were soaked for 1 hr. in water and then removed from the water and tested immediately.

For determining moisture regain, the samples were conditioned at 93% R.H. over saturated dibasic ammonium phosphate solutions at 21°C. for 7 to 10 days.

The density values were very sensitive to the MAM content of the fabric (cf. Fig. 2). To evaluate the density differences induced by crosslinking, special sets of samples were prepared. Four small swatches were cut out from each single-endedly reacted sample in such a way that their original positions in the fabric were adjacent. It was reasonable to expect that the MAM content of the four swatches was the same and not subject to the significant sample-to-sample variation within each type of treatment. One of these samples received no further treatment; the other three were treated according to the three typical aftertreatment procedures. Only the densities of these samples are reported in Table II and Figure 11.

Fiber densities were determined in toluene/CCl$_4$ gradient columns.[16] The fibers were oven-dried and treated with boiling toluene for 10 min. prior to entering them into the columns. The determinations were run in duplicate, always in the presence of an untreated cotton sample. The absolute value for the density of untreated cotton varied between 1.5512 and 1.5549 g./cc., but the density difference between treated and untreated samples was reproducible to ±0.0005 g./cc.

RESULTS AND DISCUSSION

Chemistry of the Reactions

The single-ended reaction. The acrylamidomethyl contents calculated from the weight add-on were in reasonable agreement with the other analytical data, as shown in Table I. This indicates that the acid catalyzed first step reaction indeed proceeds as suggested by eq. (1).

The onput is calculated from the wet pick-up and the MAM concentration in the treating solution. The ratio add-on/onput is the fractional retention, and this value is plotted against add-on in Figure 1. At low add-on values the retention does not change appreciably with the add-on or onput because in this concentration range the reactive cellulosic hydroxyls are present in great excess and their concentration does not affect the rate of reaction. Consequently, the reaction is of first order with respect to MAM and its efficiency is independent of the MAM concentration. When the MAM add-on exceeds 1.4 mmole/g., the reaction kinetics change because the reactive hydroxyls are consumed to a sufficient extent that their concentration also influences the results. It is reasonable to assume that only a certain proportion of the hydroxyl groups is potentially available for the reaction. Thus at high MAM onput values the ratio of reactive hydroxyls to MAM is reduced. The probability that an individual MAM molecule can find a reactive site becomes low and the retention is decreased. It may be mentioned that it is not possible to react more than 1.65 mmole/g. MAM single-endedly on cotton with 1% alkanolamine hydrochloride catalyst.

The density of the samples is reduced due to acrylamidomethylation, probably because the density of MAM is lower than that of cotton. Figure 2 shows that the relationship between density and add-on is linear in the add-on range 0 to 1.1 mmole/g. At higher add-on values the density reduction per reacted MAM molecule becomes small, suggesting that the reacted molecules have to form clusters or, in other words, have to be in a state of closer packing.

These results are significant in considering the accessibility of cotton. Cellulose contains 6.18 mmole/g. anhydroglucose units. Deuterium exchange, formylation and water sorption studies indicate that cotton is about 16 to 40% accessible to aqueous systems, while x-ray and hydrolysis experiments indicate that it is 10 to 20% amorphous.[17] This means that about 1.0 to 2.4 mmole/g. anhydroglucose units are accessible. Since each anhydroglucose unit contains three hydroxyl groups, there are three times as many accessible hydroxyl groups.

The present retention and density data indicate that 1.1 to 1.4 mmole/g. hydroxyls have high reactivity toward MAM and that a total of 1.65 mmole/g. of hydroxyl groups is available for reaction. These

values are between the limits given above for the concentration of available anhydroglucose units, and this result strongly suggests that MAM reacts with only one of the three types of hydroxyls in cellulose. If this is so, it is possible to calculate that about $20 \pm 2\%$ of cotton is highly accessible to MAM and that the total accessibility is $26 \pm 2\%$. It is probable that cotton is accessible to the same degree to other nitrogenous reactants, such as urea–formaldehyde or melamine–formaldehyde precondensates.

The difference between high and total accessibility is either due to variation in order within the accessible region or, what may be the same thing, due to the difference in reactivity between the amorphous regions and the accessible surface of the crystallites.

It should be emphasized that single-endedly reacted monomers have only little effect on the crease recovery. The highest dry crease recovery was 92° and the highest wet crease recovery was 84° when 1% alkanolamine hydrochloride was used as catalyst. The properties of the sample having these crease recovery values are shown in Table II. It may be mentioned that N,N'-dimethylol diamides of dibasic acids are known to increase the crease recovery of cellulosic fabrics substantially when applied with acid catalysts.[18]

The crosslinking by "dry APS" aftertreatment. The data of Table I show a random small variation in nitrogen content among samples which received the same single-ended treatment. This variation is mostly due to the fact that it was not possible to apply MAM to the fabrics completely reproducibly in the single-ended reaction. In separate experiments the nitrogen contents of samples were determined before and after the crosslinking reactions, and no significant reduction in the nitrogen content could be observed. Thus it is reasonable to equate the nitrogen content with the original MAM content of each individual sample and discuss the aftertreatment induced changes in the analytical data relative to the nitrogen content.

It is striking that all aftertreatments substantially reduce the double bond content and somewhat reduce the methylene content. At present it may be convenient to confine the discussion to changes in the double bond content. Since the aftertreatments do not change the bulk of the samples, the loss of low molecular weight methylene groups being hardly measurable by simple weighing, disappearance of double bonds can only be due to reactions leading to their saturation.

In the free radical catalyzed "dry APS" treatment the reaction can occur only between the double bonds because it is unlikely that hydroxyls would add to the double bonds by chain transfer. The chain transfer properties of cellulose should be poor, since the O—H bond is strong and alkoxy free radicals are known to be unstable. Furthermore, if hydroxyls would add to the double bonds in appreciable amounts, a difunctional vinyl compound of a structure similar to MAM, methylenebisacrylamide, would crosslink cellulose and increase the crease recovery when catalyzed with APS. Table III shows that this is not the case. It may also be mentioned that polymerization of up to 15% acrylamide into cotton did not change the mechanical properties of the fabric.

TABLE III
Application of Methylenebisacrylamide to
Cotton Printcloth

$$CH_2{=}CH_2{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}CH{=}CH_2$$

Padded on the fabric in solution, heat-treated for 10 min. at 150°C., washed

Catalyst onput	Methylenebisacrylamide		Dry crease recovery, W, °
	Onput, %	Add-on, %	
None	24	0	66
0.6% NH₄Cl	19.5	1.1	66
0.5% APS	24	4.4	76
0.6% K₂S₂O₈	19.5	4.8	68
2% KOH	24	3.3	100

It should be realized that polymerization of double bonds grafted to long chain polymers must be to a certain extent sterically hindered. No prediction can be made as to the mode of termination, although the initiation and propagation probably proceeds by the well known mechanism of free radical polymerization. Some idea about the nature of the polymerization reaction can be obtained from the conversion data presented in Figure 3. The conversion is defined as follows:

$$\text{conversion} = \frac{\text{converted monomers}}{\text{total monomers}} = \frac{\text{nitrogen} - \text{double bonds}}{\text{nitrogen}}$$

Points lying on the same curve in Figure 3 were obtained at identical reaction conditions, i.e., at the same catalyst concentration, reaction time, and temperature. Generally, free radical catalyzed polymerizations are of first order with respect to
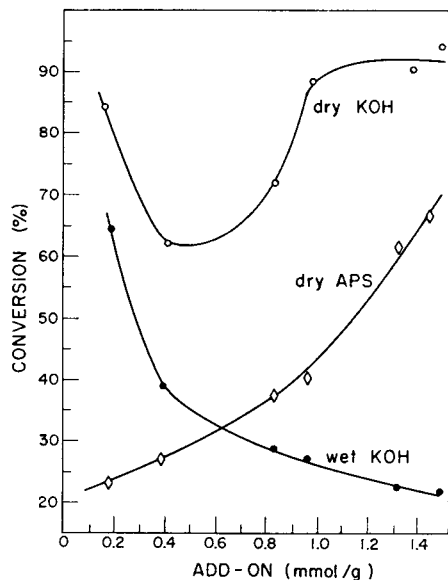
Fig. 3. Dependence of conversion upon MAM concentration of the fabric under different catalysis conditions. The points lying on each curve were obtained at identical reaction time and temperature and with the same catalyst concentration.
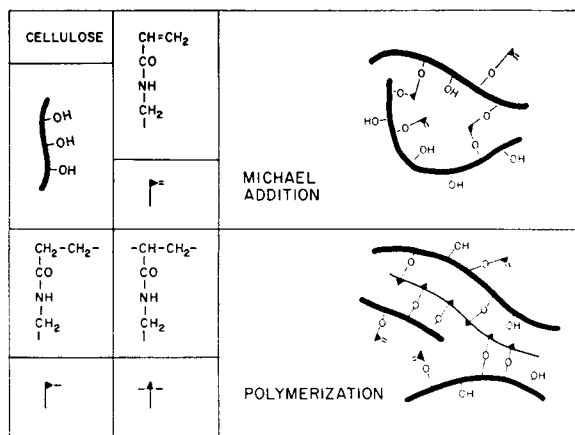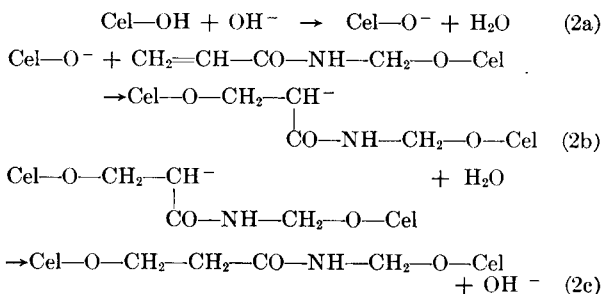

Fig. 4. Schematic structures of crosslinked cellulose.

monomer, i.e., in such a reaction the conversion is independent of the initial monomer concentration. In the present case, however, the conversion in the "dry APS" treatment increases with initial monomer concentration. The reason for this is that the higher the monomer content of the fabric, the higher is the probability that there is a monomer close enough to any given monomer to be able to react with it. Thus the main difference between solution polymerization and the present case is that in solution polymerization each monomer is potentially available for reaction with any other monomer while in the present case this is not so. It also follows that it is unlikely that the present polymerization method leads to high molecular weights.

The evidence reviewed above indicates that the "dry APS" treatment leads to an acrylic polymer with each or most of the monomer units of the acrylic polymer attached to a cellulose molecule by a methylene bridge. An idealized picture of this structure is given in the lower half of Figure 4.

Crosslinking acrylamidomethylcellulose by treating it with a free radical catalyst is thus essentially a *homo*polymerization of the pendant double bonds. It may be noted that it has been previously known that unsaturated esters or ethers of cellulose can be crosslinked by *co*polymerizing the pendant double bonds with reactive monomers.[19]
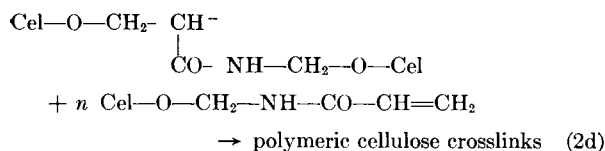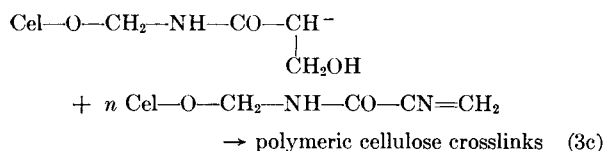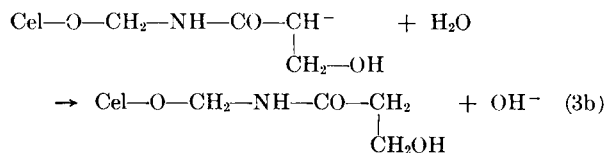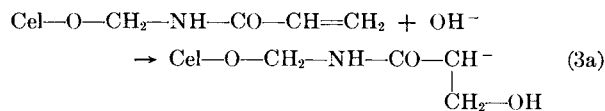
Crosslinking by alkaline aftertreatments. It is well known that cellulose reacts in an alkaline medium with compounds having double bonds in the α position to electron withdrawing groups. When monofunctional compounds such as acrylonitrile, acrylic acid, or acrylamide are used,[20] the crease recovery is unaffected, but similar difunctional compounds such as divinyl sulfone[21] and methylenebisacrylamide (reference 20, cf. Table III) improve the crease recovery. It should also be noted that cotton pretreated with acrylamide in alkaline medium is more responsive than untreated cotton to acid-catalyzed formaldehyde crosslinking.[22] Such crosslinking treatment, i.e., carbamoylethylation followed by methylenation, is similar to the present method but involves a reverse sequence of forming the crosslinks. A similar reverse order two-step crosslinking reaction has been carried out by Geiger,[23] who applied methylol vinyl ketone to cellulose with alkaline catalysts and aftertreated with an acid catalyst to increase the crease recovery.

When partially substituted acrylamidomethylcellulose is treated with an alkaline catalyst, reaction can be initiated by ionizing either the free hydroxyl groups or the acrylic groups. In the first instance, the following sequence of reactions is possible:

$$Cel—OH + OH^- \rightarrow Cel—O^- + H_2O \qquad (2a)$$

$$Cel—O^- + CH_2{=}CH—CO—NH—CH_2—O—Cel$$

$$\rightarrow Cel—O—CH_2—CH^-$$
$$\qquad\qquad\qquad CO—NH—CH_2—O—Cel \quad (2b)$$

$$Cel—O—CH_2—CH^- \qquad\qquad + H_2O$$
$$\qquad\quad CO—NH—CH_2—O—Cel$$

$$\rightarrow Cel—O—CH_2—CH_2—CO—NH—CH_2—O—Cel$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad + OH^- \quad (2c)$$

Cel—O—CH$_2$- CH$^-$
   |
   CO- NH—CH$_2$—O—Cel

   + n Cel—O—CH$_2$—NH—CO—CH=CH$_2$

$\rightarrow$ polymeric cellulose crosslinks   (2d)

If the initiation involves the double bonds, the following sequence of reactions can occur:

Cel—O—CH$_2$—NH—CO—CH=CH$_2$ + OH$^-$

$\rightarrow$ Cel—O—CH$_2$—NH—CO—CH$^-$ (3a)
            |
            CH$_2$—OH

Cel—O—CH$_2$—NH—CO—CH$^-$ + H$_2$O
            |
            CH$_2$—OH

$\rightarrow$ Cel—O—CH$_2$—NH—CO—CH$_2$ + OH$^-$ (3b)
            |
            CH$_2$OH

Cel—O—CH$_2$—NH—CO—CH$^-$
            |
            CH$_2$OH

   + n Cel—O—CH$_2$—NH—CO—CN=CH$_2$

$\rightarrow$ polymeric cellulose crosslinks   (3c)

In the presence of water the ionic intermediates formed in reactions (2b) and (3a) cannot initiate polymerization because they immediately exchange protons with water. Thus in "wet KOH" aftertreatments the crosslinks are formed exclusively through reaction (2c). In the dry state cure, however, crosslinks can also be obtained by reactions (2d) and (3c). Actually, it is reasonable to assume that the two reactions, Michael condensation and polymerization, compete with each other under such conditions.

These chemical considerations are supported by the conversion data of Figure 3. If the predominant reaction is between the double bonds and the hydroxyls by a Michael mechanism, high conversions are obtained when there are many potentially reactive hydroxyls near enough to any given double bond so that they react with it. Even if different types of hydroxyls were used in the acid catalyzed single-ended reaction and in the Michael reaction, the ratio of double bond-reactive hydroxyls to monomers decreases with increasing monomer content and so does the probability for reaction and conversion. The data show that the conversion indeed decreases with increasing monomer content for the "wet KOH" aftertreatment, indicating that the prevalent reaction is between the hydroxyls and double bonds. A schematic picture of the structure thus obtained is given on the upper half of Figure 4.

The conversion/add-on plot corresponding to the "dry KOH" aftertreatment passes through a minimum. It would seem that, as predicted from chemical considerations, the Michael addition and anionic polymerization indeed compete with each other in this reaction. At low add-on values, where the probability for polymerization is low but the probability for Michael reaction is high, the latter predominates and the conversion decreases with increasing add-on. The reverse is true for high add-on values. This finding implies that the reaction proceeds to an appreciable extent even before all water in the fabric is evaporated, and is probably completed when the fabric is substantially dry. Thus if a Michael reaction is favored, most of the double bonds are consumed while water is present in the fabric. If the probability for a Michael reaction is low, very few double bonds are consumed while water is present and the reaction takes place almost exclusively in the dry state.

In discussing the single-ended reaction, it was shown that in all probability this reaction involves only one of the three types of hydroxyl groups in cellulose. It is of interest that even at the highest degree of acrylamidomethylation, where most of hydroxyls accessible to the single-ended reaction are occupied, it is possible to obtain as high as 18% conversion in the "wet KOH" treatment. Thus it is likely that the Michael reaction involves a type of hydroxyl group different from the one involved in the single-ended reaction. Carter[24] showed that the 2-hydroxyl is the most reactive cellulosic hydroxyl in the alkali-catalyzed Michael condensation with acrylonitrile. Cyanoethylation is analogous to the reaction at "wet KOH" catalysis in the present system and thus it is likely that the latter reaction also involves the 2-hydroxyl group. Since the 3-hydroxyl groups are known to be very inert, it follows that the single-ended reaction involves the 6-hydroxyl groups. It must be emphasized that this assignment of the 6- and 2-hydroxyls for the single-ended and Michael reaction, respectively, is based on circumstantial evidence and further work would be needed to clarify this matter.

In the presence of water the reaction according to eq. (3b), leading to the formation of β-hydroxypropionamidomethyl groups, could be possible. However, the reversability of this reaction and the higher reactivity of the alkoxy than the hydroxy ions makes it probable that the extent of this reaction is small. This reaction, if it occurs, would saturate double bonds without leading to crosslinks. As will be shown below, the

crosslink content can be calculated from the converted monomer content and in such calculations β-hydroxypropionamidomethyl groups would be counted as crosslinks. Jacobs,[25] investigating the temperature dependence of the "wet KOH" aftertreatments, found that the dependence of the crease recovery upon crosslink content was independent of the temperature of the treatment. It is unlikely that the activation energy for alkoxy and for hydroxy addition should be the same. Since only alkoxy addition leads to increased crease recovery, the fact that the same crease recovery/crosslink relationships were obtained at different reaction temperatures again strongly indicates that the prevalent reaction in the presence of water is alkoxy addition. If this were not so, at some reaction temperature the β-hydroxypropionamidomethyl groups would have seriously interfered with the calculation of crosslink contents. It should also be mentioned that, since hydroxy ions are present in great excess, the formation of β-hydroxypropionamidomethyl groups would be a first order reaction with respect to the acrylamidomethyl content of the fabric and, if this reaction were prevalent, the conversion would be independent of add-on. Again, this was not found to be the case. In summary, the consideration of the chemistry of the reactions, crease recovery/crosslink relationships obtained at different temperatures and the dependence of conversion upon add-on all strongly indicate that β-hydroxypropionamidomethyl groups are not formed to an appreciable extent. It is thus justified to disregard this reaction in calculating crosslink contents.
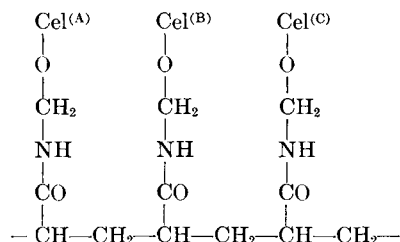
Calculation of crosslink contents. As will be shown below, the crosslink content in millimoles per gram can be calculated by the following formula:

$$\text{crosslinks} = \text{methylene} - \text{double bonds}$$

If the "wet KOH" treatment did not cause losses in methylene, the crosslink content of fabrics treated in this fashion would be equal to the converted monomer content, i.e., to the difference between the molal nitrogen and double bond contents. Unfortunately, some methylene is hydrolyzed from the fabric. However, this loss in methylene can occur only on converted monomers, since the nitrogen contents remain unchanged. If unconverted monomers lost methylene, the link between the monomer and cellulose would be broken and the monomer would be washed out resulting in loss of nitrogen and reduction of bulk,

contrary to experimental evidence. Thus two types of *converted* monomers exist in cellulose after the "wet KOH" catalysis: crosslinks and carbamoylethyl ether groups. The number of double bonds is a measure of the unconverted monomers, each necessarily carrying methylene. The difference between methylene and double bonds is the amount of methylene on converted monomers, i.e., this value is the true crosslink content. By calculating the crosslinks in this manner the carbamoylethyl groups are disregarded.

The situation is more complicated when polymeric crosslinks are formed. Polymeric crosslinks are multifunctional, i.e., they connect a number of different sites of cellulose. It may be convenient to define as effective crosslinks the shortest possible bridges between cellulose sites. For example, the structure below would represent two effective crosslinks spanning between sites A and B and between sites B and C. The link between sites A and C would not be separately counted.

$$
\begin{array}{ccc}
\text{Cel}^{(A)} & \text{Cel}^{(B)} & \text{Cel}^{(C)} \\
| & | & | \\
O & O & O \\
| & | & | \\
CH_2 & CH_2 & CH_2 \\
| & | & | \\
NH & NH & NH \\
| & | & | \\
CO & CO & CO \\
| & | & | \\
-CH-CH_2- & CH-CH_2- & CH-CH_2-
\end{array}
$$

It can be readily seen that the so-defined effective crosslink content would be equal to the converted monomer content if the degree of polymerization of the crosslinks were infinitely large and if no methylene were lost in the reaction. Since some methylene and no nitrogen is lost, the crosslink content can be calculated from the difference between methylene and double bond contents in the same way as for monomeric crosslinks. This calculation would lead to a result twice as high as the actual value if the polymerization stopped at dimerization. However, the magnitude of the error is very rapidly reduced as the degree of polymerization increases. For example, at a degree of polymerization of 6 the error involved would be 17%.

The "dry APS" aftertreatment, being acidic, could involve a noncrosslinking side reaction that could interfere with the calculations. It is possible that the amide groups bared when methylene is lost could react with N-methylol groups formed when additional methylene-cellulose bonds are broken. The polymeric methylenebisacrylamide

thus formed would be counted as a crosslink. The highest possible error due to this reaction can be estimated from the deficiency of formaldehyde with respect to nitrogen. In most cases this error would be 10% or less, but in one sample it could amount to as much as 30%.

Another source of error would arise if in any of the aftertreatment reactions the methylene-cellulose or the methylene-nitrogen bonds were broken in such a way that the methylol groups thus formed would stay single-endedly attached. However, this is extremely unlikely since such groups are unstable and would be easily hydrolyzed when the fabric is washed.

Relationship between Chemical and Physical Properties of the Treated Fabrics

Crease recovery and crosslink content. As can be seen in Figure 5, the crease recovery levels off at a maximum value typical for each type of after-treatment when the crosslink concentration reaches about 0.2 mmole/g. If we assume that cotton is 20% accessible, it can be calculated that the leveling-off value of the crease recovery is reached when the ratio of accessible anhydroglucose units to crosslinks is about 4 or 5.

It is of interest to compare this result with other available data. It has been shown[26-28] that it is possible to determine the crosslinking efficiency for dimethylolurea and dimethylolethyleneurea from the ratio of formaldehyde to nitrogen. From available data it was estimated[1] that the molal concentration of crosslinks is half that of the urea residues on the treated fabric. It is also known that 5%

dimethylolethyleneurea is needed to obtain the leveling-off value of crease recovery in cotton. It follows from these data that for urea-based cross-linkers the leveling-off value of crease recovery is reached when the cotton contains about 1 crosslink per 4 anhydroglucose units in the accessible portion. These estimates have recently been confirmed by Frick et al.[29] who determined the crease recovery, nitrogen, and formaldehyde contents of cotton at different dimethylolurea and dimethylolethylene-urea add-ons.

Tesoro[30] found that the reaction of cellulose with pyridine salts of bischloromethyl ethers of ethylene glycol homologues is clearcut and free of side reactions. By following the extent of these reactions and the changes in crease recovery, this author estimated that the leveling-off value of crease recovery was reached when every accessible anhydroglucose unit is crosslinked or when the ratio of accessible anhydroglucose units to crosslinks is 2.

It is reasonable to assume that the order of magnitude of these values is applicable to any type of crosslinker since Cooke et al.[31] found that equimolar amounts of different crosslinkers produced about the same crease recovery increment.

It may be worth while to discuss the theoretical significance of the high crosslink densities. The primary aim of cellulose crosslinking is to improve resilience by eliminating the viscous portion of the deformation process. In uncrosslinked polymers the occurrence of creep or irrecoverable deformations is generally due to chain slippage. If, however, the condition for the formation of an infinite molecular network is fulfilled by introduction of
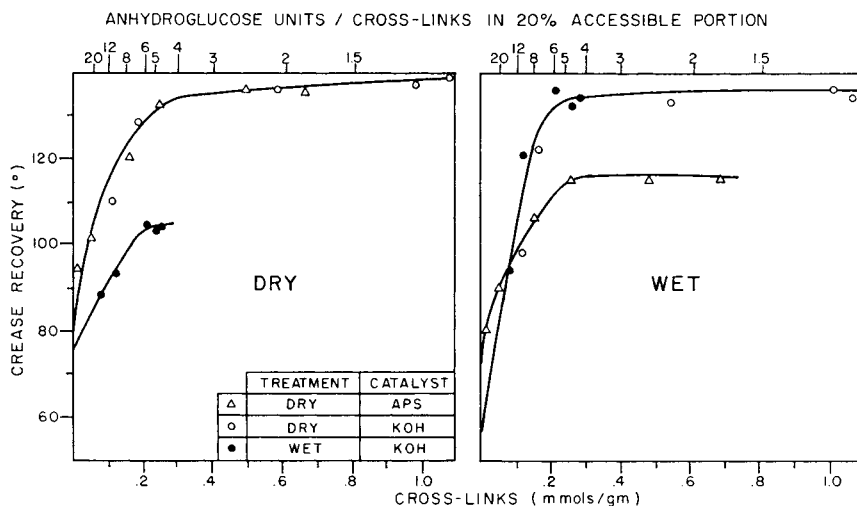

Fig. 5. Variation of dry and wet crease recovery with crosslink content.
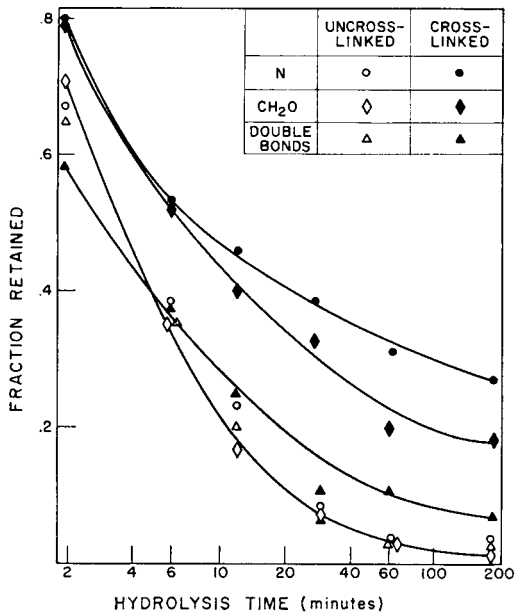
Fig. 6. Comparison of single-endedly substituted and dry APS crosslinked samples in their resistance to hydrolysis. Both samples contained 12.2% MAM. Hydrolysis conditions: 0.044N HCl, 80°C.

one crosslink per number-average molecule, chain slippage is normally inhibited. In rubbers, striking changes in the rheological properties do indeed start to occur in the region in which the degree of crosslinking reaches the postulated level. In cotton this level would correspond to 1 intermolecular crosslink per 3000 glucose units. This condition may be fulfilled at an even lower level due to the polycrystalline nature of cellulose.

The present data indicate that the degree of crosslinking necessary to suppress irrecoverable deformation in cotton is about 600 times higher than that required for the formation of an infinite network. To obtain high crease recovery it is apparently not enough merely to prevent long range chain slippage. Short range readjustment of chain segments in new positions of lower stress due to formation and breaking of hydrogen bonds also seems to be important. In crosslinked nonpolar polymers this latter type of irrecoverable deformation is unimportant because the interchain forces are weak.

Differentiation between effective and ineffective crosslinks. Some of the cotton samples were treated with alkaline mercaptoethanol solutions to block free double bonds and subsequently washed to remove the excess of mercaptoethanol. After this treatment the sulfur contents corresponded to the double bond contents of the original samples.

These samples were hydrolyzed, and analytical and crease recovery data were obtained at different hydrolysis times. As shown in Figure 6, formaldehyde, nitrogen, and sulfur are stripped off at the same rate when an uncrosslinked sample is hydrolyzed. This indicates that the weakest link in the acrylamidomethyl ether of cellulose is the bond between cellulose and the methylol group. When an aftertreated sample is hydrolyzed, the rate of sulfur removal is about the same as the rate of hydrolysis for uncrosslinked samples. This is to be expected, since the rate of sulfur removal corresponds to single-endedly reacted monomers. The rate of hydrolysis of nitrogen and formaldehyde from the crosslinked samples is significantly slower than that of the single-ended monomers. The converted monomer contents were calculated from the differences between the molal nitrogen and sulfur contents, and the number of crosslinks from the difference between the molal formaldehyde and sulfur contents. These values and the dry crease recovery are plotted against hydrolysis time in Figures 7 and 8.

Figure 7 shows hydrolysis of a "wet KOH" crosslinked sample at 80°C. in 0.044N HCl. Similar although somewhat displaced curves are obtained with "dry KOH" and "dry APS" crosslinked samples. The converted monomer content and crosslink content drops very rapidly in the first few minutes, coinciding with a very sudden reduction
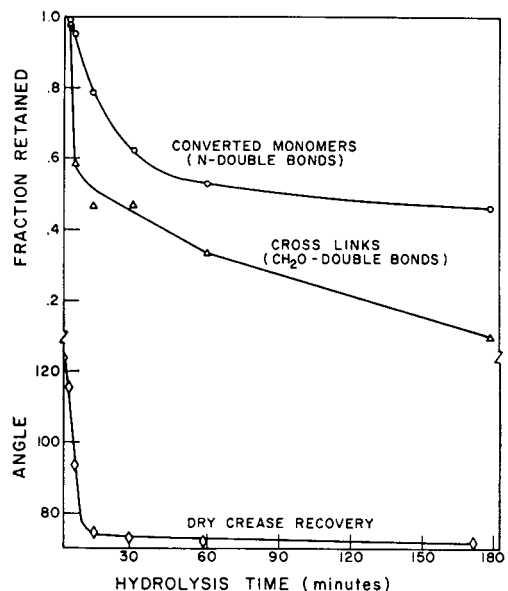

Fig. 7. Hydrolysis of a sample containing 12.2% MAM and crosslinked by "wet KOH" treatment. Hydrolysis conditions: 0.044N HCl, 80°C.
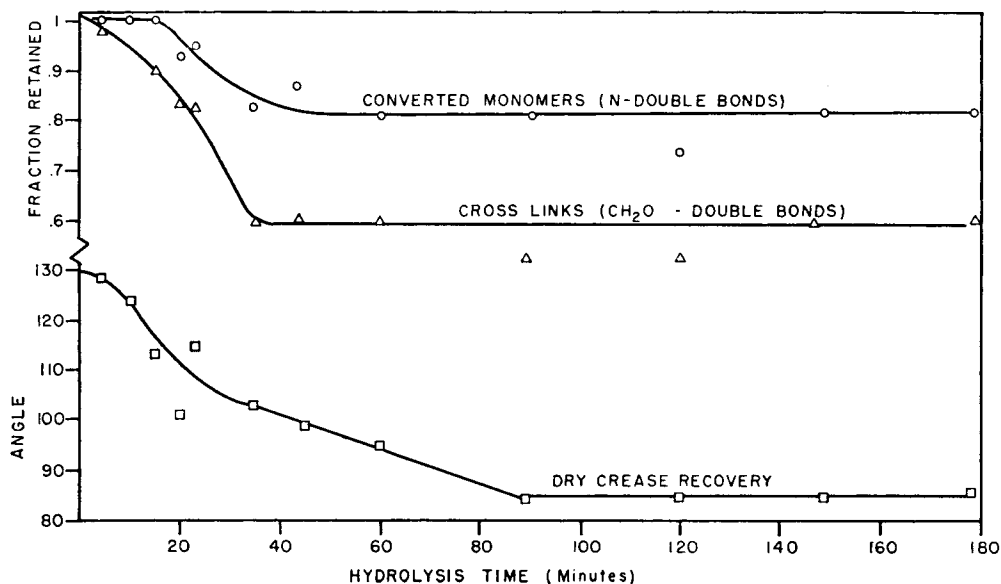
Fig. 8. Hydrolysis of a sample containing 8% MAM and crosslinked by "dry APS" aftertreatment. Hydrolysis conditions: 0.044N HCl, 60°C.

of dry crease recovery. When the crosslink content is reduced by 40 to 60%, the crease recovery has dropped to practically the same value as that of uncrosslinked cotton. The crosslinks eliminated in the first rapid phase of hydrolysis are the ones which contribute to the crease recovery, and the ineffective crosslinks are less sensitive to hydrolytic attack. It may be mentioned that Lineken et al.[32] found that, when melamine–formaldehyde resin was stripped from cotton, the crease recovery decreased faster than the nitrogen content, in accordance with the present results.

The hydrolysis data obtained at 80°C. are not well suited for quantitative differentiation between effective and ineffective crosslinks because it is uncertain whether the extrapolation of a plot relating crosslink content to time on a linear scale is justified. This difficulty was eliminated by reducing the hydrolysis temperature to 60°C. As shown in Figure 8, the crosslinks and the converted monomers which do not contribute to crease recovery are stable at this temperature, allowing unequivocal extrapolation. Accordingly, about 58% of the original crosslinks do not contribute to crease recovery for the "dry APS" crosslinked sample containing 8% MAM.

There are two possible explanations for differences between effective and ineffective crosslinks. If the effective crosslinks are intermolecular and the ineffective ones intramolecular, it could be assumed that the higher stability of the intramolecular

crosslinks is due to their more stable cyclic structure or to their less strained position. On the other hand, the efficient crosslinks may be in the least ordered and most accessible portion of cotton and be more susceptible to hydrolytic attack for this reason.

Difference between wet and dry state crosslinking. The fact that wet state crosslinking improves the wet crease recovery to a greater extent than the dry crease recovery has been attributed to the stabilization of the open, swollen structure of the cellulose and to an increased degree of intramolecular crosslinking.[1,4] As can be seen in Figure 5, the "dry APS" aftertreatment leads to higher dry than wet crease recovery, while the opposite is true for the "wet KOH" aftertreatment, in line with these theories. The results of the "dry KOH" aftertreatment require further explanation. The dry and wet crease recoveries are about equal and the dependence of dry crease recovery on crosslink density is the same as for the "dry APS" aftertreatment, while the wet crease recovery–crosslink relationship is identical to that of the "wet KOH" aftertreatment. This may be related to the critical water content of the fabric at the time the reaction starts. In the "dry KOH" cure the critical water content may be high, causing the reaction product to have features typical of both dry and wet state reactions. The conversion data of Figure 3 confirm this argument by showing that two types of reactions occur in the dry state cure, anionic poly-
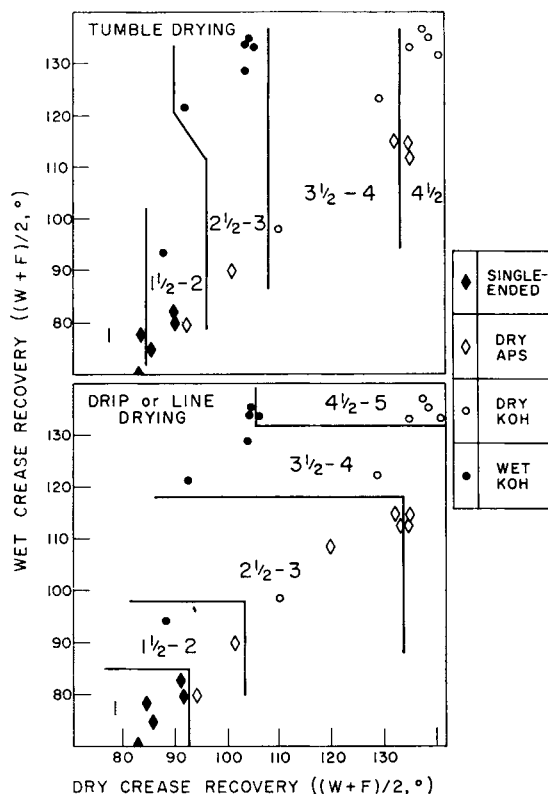
Fig. 9. Variation of wash-wear ratings with wet and dry crease recovery. The numbers indicate the ratings corresponding to points lying between the solid lines.

Fig. 10. Dependence of 93% R.H. moisture regain upon add-on after single-ended and three different crosslinking reactions.

merization, which is characterized by anhydrous reaction conditions, and the Michael reaction, which is typical for aqueous reaction medium.

The variation of wash-wear rating with the dry and wet crease recovery is presented in Figure 9, showing that tumble dry ratings are related primarily do the dry crease recovery, while the line and drip dry ratings are related both to the dry and wet crease recovery. Steele[4] prepared similar mappings of wash-wear and crease recovery values and found that the drip dry ratings were related solely to the wet, while the tumble dry ratings were related to both wet and dry crease recovery. The present data, compared to Steele's, cover a narrower range of wet to dry crease recovery ratio and are probably a less sensitive indication of the interdependence between wash-wear rating and crease recovery. However, both sets of data are in agreement on one basic point: higher wet than dry crease recovery is associated with higher line or drip dry than tumble dry wash-wear rating and the opposite is true for higher dry than wet crease recovery.

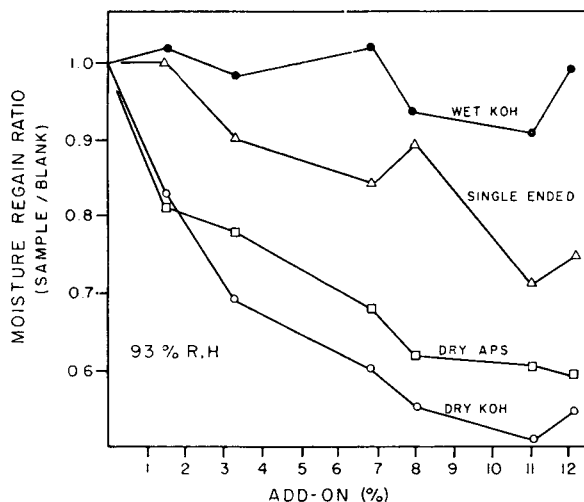It is shown in Figure 10 that the single-ended reaction reduces the moisture regain. Dry state crosslinking causes further reductions, contrary to wet state aftertreatments, which increase the moisture regain relative to the single-endedly reacted samples. This increased moisture regain could be due to stabilization of the open, swollen structure of cellulose and is contrary to the general experience that the swellability of polymers is reduced by crosslinking.

As can be seen in Figure 11, the aftertreatments change the density of the single-endedly reacted samples. The dry treatments increase the density, probably due to the fact that in a reaction of the type A + B → C, the density of the product is generally higher than the average density of the adducts. This effect becomes predominant for the "wet KOH" aftertreatment only at high add-ons. At low add-ons density reductions are produced by the opening up of the cellulose structure.

The indication from moisture regain and density data that wet state aftertreatments change the supermolecular structure of cellulose was consistent with powder diagrams of samples containing 10.9% MAM. The diagrams were practically identical for blank cotton, the single-endedly reacted sample, and the sample that received "dry APS" aftertreatment. The main 002 reflection peak determined by a Geiger counter diffractometer was, however, significantly shorter and broader for the "wet KOH" aftertreated sample. This indicates the existence of smaller or more strained crystalline regions.

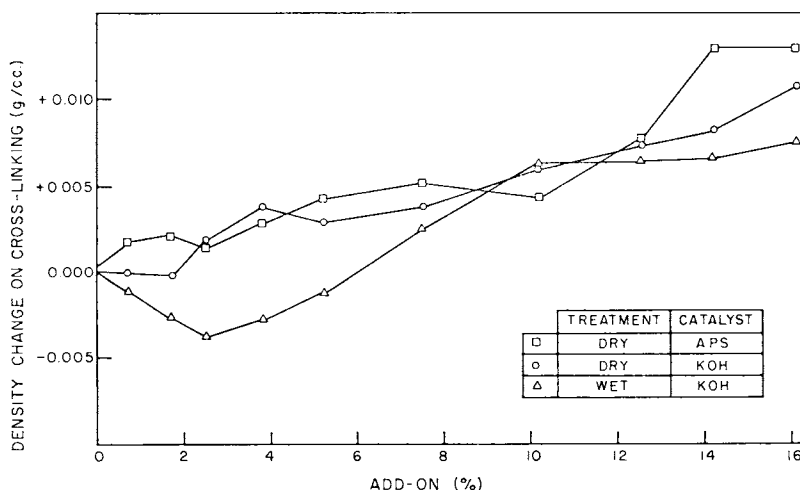The question may arise as to why wet state crosslinking increases the amorphous portion of

Fig. 11. Density changes in cotton reacted single-endedly with MAM and crosslinked by various aftertreatments.
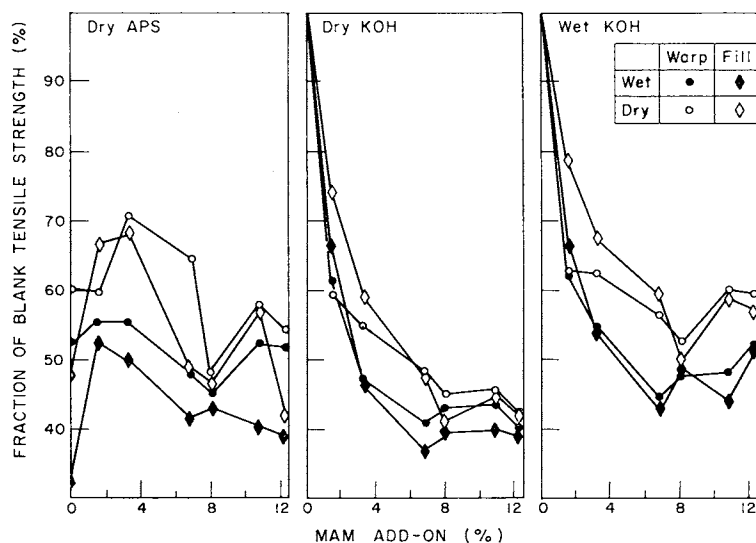

Fig. 12. Variation of tensile strength with add-on after different crosslinking treatments.

cotton. This could happen because the cotton swells in the catalyst solution and the crosslinks cause the amorphous/crystalline ratio characteristic to the swollen state to persist after the sample is dried. However, it is also possible that the effect of wet state crosslinking goes beyond that and, when the crosslinks are introduced in the presence of the swelling medium, the amorphous portion is increased to a greater extent than when the cellulose is swollen without simultaneous crosslinking treatment. If this is so, we can visualize that in the presence of a swelling medium there exists a dynamic equilibrium between melting of crystallites and ordering of the amorphous region to crystallites. When a crystallite near to a single-endedly

reacted molecule is melted and then a crosslink is formed, the conformation of the chains is restricted to some distance from the crosslink and the crystallite cannot re-form, resulting in an increase of the amorphous portion. It must be emphasized that this explanation is tentative and better data than the present ones are needed to evaluate the effect of swollen state crosslinking on the supermolecular structure.

Stress–strain properties. Alkaline treatments identical to the "wet KOH" or "dry KOH" catalysis have no effect on the tensile strength of the fabric in the absence of MAM. However, with increasing MAM add-on the tensile strength is substantially reduced due to crosslinking, as shown
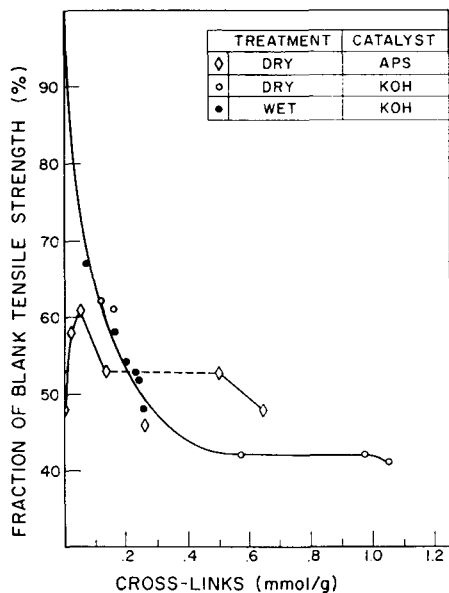
Fig. 13. Variation of the average warp-fill–wet-dry tensile strength with crosslink concentration. The plotted value is the average of the warp-dry, warp-wet, fill-dry and fill-wet values.

in Figure 12. The results for "dry APS" treatment follow a different pattern. Ammonium persulfate strongly degrades the fabric in the absence of MAM but with increasing MAM add-on the tensile strength passes through a maximum. This initial rise in tensile strength may be due to compensation of the degradation by crosslinking or to a reduced degrading effect of the catalyst in the presence of MAM. The latter explanation is, however, unlikely because separate experiments showed that the tensile strength loss in "dry APS" treatments in the presence and absence of acrylamide (in both cases without MAM) was about the same.

Figure 12 also shows that for each aftertreatment the magnitude of tensile strength loss is in the following increasing order: dry-warp, dry-fill, wet-warp, wet-fill. However, all four tensile strength losses follow the same trend with increasing degree of crosslinking. To obtain higher precision for comparison purposes, it is justifiable to average the four different tensile strength values. These averages are plotted against crosslink density in Figure 13. The data indicate that the "dry KOH" and "wet KOH" aftertreatments lead to comparable tensile strength loss, while the "dry APS" aftertreatment at high crosslink density is associated with higher tensile strength than the alkaline aftertreatments. Separate experiments not reported here showed that this difference could be

magnified when the concentration of the free radical catalyst was reduced but a change in alkaline catalysis conditions had no significant effect on the crosslink dependence of tensile strength. These results indicate that the tensile strength losses due to crosslinking alone are lower for free radical than for alkaline catalysis. There are a number of possible explanations for this effect:

(1) The shortest effective crosslink in a polymeric crosslink spans two MAM monomers, while the crosslink produced by Michael condensation is only one monomer unit long.

(2) If only the 6-hydroxyl is etherified in the single-ended reaction, this would be the only type of hydroxyl which is involved in "dry APS" crosslinking since this method of catalysis affects only the double bonds and not the hydroxyls. Alkaline catalysis furthers the reaction between double bonds and probably the 2-hydroxyl. Crosslinks attached to this secondary hydroxyl may have lower freedom of movement and excessively reduce tensile strength due to their greater rigidity.

(3) The reaction in "dry APS" catalysis occurs when the fabric is substantially dry and thus the crosslinks introduced by this reaction have the least disordering effect on cellulose.

As already mentioned, the alkanolamine hydrochloride catalyst used for the single-ended reaction
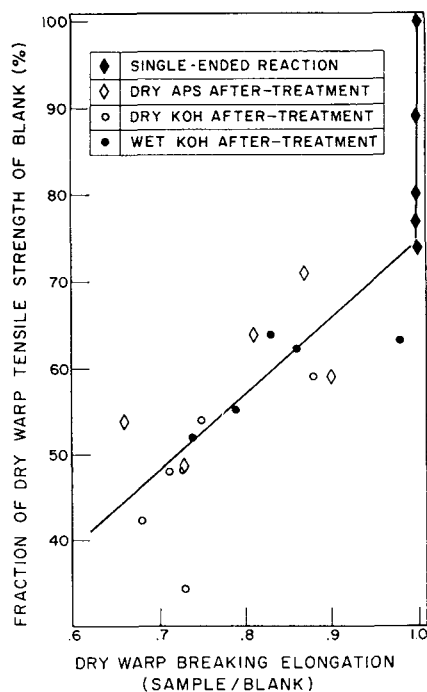

Fig. 14. Correlation between warp-dry tensile strength and breaking elongation.

has no effect on tensile strength. However, the single-ended reaction itself reduces the tensile strength occasionally as much as 28%. This effect may be related to the lowering of swellability causing reduction in plasticization. In spite of the tensile strength losses, the single-ended reaction has no effect on the breaking elongation. On the other hand, the crosslinking aftertreatments reduce the breaking elongation in proportion to the reduction in tensile strength. As an illustration, the warp dry tensile strength is plotted against the warp dry breaking elongation in Figure 14.

In the present experiments the modulus of each sample was determined from the slope of the stress–strain curve near the break and it was found that the modulus did not change with the single-ended reaction or with crosslinking. The wet and dry warp modulus was about 3.5 lb./0.5 in./% and the wet and dry fill modulus was about 2 lb./0.5 in./%. It is probable that the modulus is insensitive to crosslinking because of the highly oriented molecular structure of cotton. Flory[33] has shown that the crosslink induced increment in modulus is much greater in random than in oriented polymeric structures.

CONCLUSIONS

1. Acid-catalyzed application of MAM to cellulose leads to formation of acrylamidomethyl ether groups. Circumstantial evidence indicates that only the 6-hydroxyl is etherified and that cotton is about 20% accessible to this reaction.

2. Partially acrylamidomethylated cotton can be crosslinked without changing the bulk of the sample by saturating the pendant double bonds either through alkali catalyzed addition of cellulosic hydroxyls or by anionic or free radical catalyzed homopolymerization.

3. The dependence of conversion upon increasing acrylamidomethyl content is a sensitive indication of the nature of the crosslinking reaction. Increasing conversion indicates reaction between double bonds and decreasing conversion indicates reaction of double bonds with cellulosic hydroxyls. Accordingly, a free radical catalyst, such as ammonium persulfate, causes homopolymerization of the acrylamidomethyl ether groups, wet state treatment with an alkaline catalyst causes addition of hydroxyls to double bonds, and dry state treatment with alkaline catalysts can result in either or both of these reactions. It is likely that the 2-hydroxyl is the one that is involved in the alkali catalyzed hydroxyl addition to double bonds.

4. The molal crosslink content can be calculated from the difference of the molal methylene and double bond contents.

5. To obtain highest attainable crease recoveries in cotton, it is necessary to introduce 1 crosslink per 4 to 5 accessible anhydroglucose units.

6. About half of the MAM crosslinks are ineffective in increasing the crease recovery, probably because of intramolecular crosslinking. The ineffective crosslinks are more stable to hydrolytic attack than the effective crosslinks.

7. The wet to dry crease recovery ratio is the higher, the greater the extent of swelling of the cellulose during the crosslinking reaction. The ratio of line or drip dry to tumble dry wash-wear rating increases with the wet to dry crease recovery ratio.

8. Density, moisture regain, and x-ray data indicate that swollen state crosslinking causes disordering of the cellulose. Dry state crosslinking increases the density, reduces the moisture regain, and has no effect upon the x-ray pattern. Wet state crosslinking increases the moisture regain, changes the x-ray pattern, and, under certain conditions, reduces the density.

9. Crosslinks produced by alkaline catalysis cause greater losses in tensile strength than those produced by free radical catalysis.

10. Wet and dry tensile strength losses with increasing degree of crosslinking follow the same trend but the wet strength losses are larger than the dry ones.

11. The reduction in the breaking elongation due to crosslinking is roughly proportional to the tensile strength loss.

12. The modulus of cotton is not changed by crosslinking.

References

1. Gardon, J. L., and R. Steele, *Textile Research J.*, **31**, 160–171 (1961).

2. (a) Strain, D. E., U. S. Pat. 2,173,005 (Sept. 12, (1939). (b) Mantell, G. S., U. S. Pats. 2,837,511 and 2,837,512 (June 3, 1958).

3. Kamogawa, H., R. Murase, and T. Sekiya, *Textile*

Research J., **30,** 774–781 (1960); *Bull. Textile Research Inst.* (Japan), **52,** 108–116 (1960).

4. Steele, R., *Textile Research J.*, **30,** 37–46 (1960).

5. Reeves, W. A., R. M. Perkins, and L. H. Chance, *Textile Research J.*, **30,** 179–192 (1960).

6. Daniels, W. W., *Textile Research J.*, **30,** 656–661 (1960).

7. Sobue, H., and K. Murakami, *Textile Research J.*, **29,** 251–259 (1959).

8. Gagliardi, D. D., and I. J. Gruntfest, *Textile Research J.*, **20,** 180–188 (1950).

9. Krasny, J. F., and A. M. Sookne, Textile Research J., **25,** 493–498 (1955).

10. Beesing, D. W., W. P. Tyler, D. M. Kurtz, and S. A. Harrison, *Anal. Chem.*, **21,** 1073–1076 (1949).

11. Schoniger, W., *Mikrochem. Acta,* **1956,** 869–876.

12. Ogg, C. L., C. O. Willits, and F. J. Cooper, *Anal. Chem.*, **20,** 83–85 (1948).

13. Bricker, C. E., and W. A. Vail, *Anal. Chem.*, **22,** 720–722 (1950).

14. Buck, G. S., Jr., and F. A. McCord, *Textile Research J.*, **19,** 216–247 (1949).

15. American Association of Textile Chemists and Colorists, Tentative Test Method 88-1958, *Am. Dyestuff Reptr.*, **47,** P578–P580 (1958).

16. Preston, J. M., and M. V. Nimkar, *J. Textile Inst.,* **41,** T446–T545 (1950).

17. Howsman, J. A., and W. A. Sisson, in *Cellulose and Cellulose Derivatives*, Vol. I, Ott, E., H. M. Spurlin, and M. W. Grafflin, Eds., Interscience, New York–London, 1954, pp. 231–315.

18. Desson, R. G., and E. S. Nicholson, Brit. Pat. 790,796 (June 15, 1956).

19. (a) Malm, J., and C. R. Fordyce, U. S. Pat. 1,973,493 (Sept. 11, 1934). (b) Berlin, A. A., and T. A. M. Makarova, *J. Gen. Chem. U.S.S.R.*, **21,** 1383–1389 (1951); *Chem. Abstr.*, **46,** 1996c (1952). (c) Hewson, W. M., U. S. Pat. 2,682,481 (June 29, 1954). (d) Ernsberger, M. L., and A. S. Gregory, U. S. Pat. 2,364,165 (Mar. 5, 1946). (e) Ushakov, S. N., *Fiz. Nat. Mauk.*, **1,** 35–36 (1943, published 1945); *Chem. Abstr.*, **40,** 458⁵ (1946). (f) Fletcher, C. A., U. S. Pat. 2,789,030 (Apr. 16, 1957). (g) Musser, D. M., U. S. Pat. 2,455,083 (Nov. 30, 1948). (h) Tochinami, H., Japan Pat. 246 (1960); *Chem. Abstr.*, **54,** 18975ᵈ (1960). (i) Tonami, H., *J. Soc. Textile Ind. Japan,* **14,** 100-105 (1958).

20. Frick, J. W., W. A. Reeves, and J. D. Guthrie, *Textile Research J.*, **27,** 92–99, 294–299 (1957).

21. Schoene, D. L., and V. S. Chambers, U. S. Pat. 2,524,399 (Oct. 13, 1950).

22. Negishi, M., and N. Aida, *Textile Research J.*, **29,** 982–989 (1959).

23. Geiger, A., *Textil-Rundschau,* **12,** 494–502, 560–576 (1957).

24. Carter, M. E., paper presented at the Third Cellulose Conference, Syracuse, N. Y., October 27, 1960.

25. Jacobs, H., Rohm and Haas Co., unpublished data.

26. Steele, R., and L. E. Giddings, Jr., *Textile Research J.*, **26,** 116–123 (1956).

27. Steele, R., and L. E. Giddings, Jr., *Ind. Eng. Chem.*, **48,** 110–114 (1956).

28. Frick, J. G., Jr., B. A. Kottes, and J. D. Reid, *Textile Research J.*, **29,** 314-322 (1959).

29. Frick, J. G., Jr., B. W. K. Andrews, and J. D. Reid, *Textile Research J.*, **30,** 495–504 (1960).

30. Tesoro, G. C., *Textile Research J.*, **30,** 192–201 (1960).

31. Cooke, T. F., P. B. Roth, J. M. Salisbury, G. Switlyk, and W. J. van Loo, *Textile Research J.*, **27,** 150–165 (1957).

32. Lineken, E. E., S. M. Davis, and C. M. Jorgensen, *Textile Research J.*, **26,** 940–947 (1956).

33. Flory, P. J., *J. Am. Chem. Soc.*, **78,** 5222–5235 (1956); *Science*, **124,** 53–60 (1956).

Synopsis

Cotton was acrylamidomethylated by applying *N*-methylol acrylamide to it with the aid of a mild acid catalyst. When the molal ratio of *N*-methylol acrylamide to anhydroglucose exceeded about 0.2, the efficiency of this reaction was suddenly reduced and the variation of density with add-on departed from linearity. These and other available facts indicated that only one of the three hydroxyls in cellulose, probably the one in the 6-position, was involved in the acrylamidomethyl ether formation and that cotton was about 20% accessible to this reagent. When acrylamidomethylated cotton was treated with free radical or alkaline catalysts, the double bonds became partially saturated and the mechanical properties changed in a spectacular manner. In particular, the resilience of the fabric, as measured by crease recovery, was improved. Analysis of double bond reaction at various levels of acrylamidomethyl content of the fabric indicated that free radical catalysis caused homopolymerization of the pendant double bonds, that alkaline catalysis in the presence of water resulted in Michael condensation between double bonds and the hydroxyls of cellulose, and that these two reactions competed with each other when the alkaline aftertreatment was conducted in dry state. These reactions crosslinked the fabric, and the crosslink content could be calculated from the difference of molal methylene and double bond contents.

The crease recovery reached the maximum attainable value characteristic for the method of catalysis when the ratio of accessible anhydroglucose units to crosslinks was 4 to 5. When the crosslinked fabrics were hydrolyzed in acid, the crease recovery increment produced by crosslinking was eliminated after about half of the crosslinks were broken. The residual crosslinks did not contribute to crease recovery. Dry state crosslinking treatments reduced the moisture regain, increased the density, and had no effect on the x-ray pattern. In contrast to this, wet state crosslinking increased the moisture regain, changed the x-ray pattern, and, under certain conditions, reduced the density. These results indicate that wet state crosslinking increased the amorphous portion of cotton. Wet state crosslinking lead to higher wet than dry crease recovery whereas the opposite was true for dry state crosslinking. Although the alkaline catalyst did not degrade the fabric, alkali catalyzed crosslinking substantially reduced the tensile strength. Free radical catalysis was more favorable for tensile strength, in spite of the fact that it degraded the fabric in the absence of crosslinking agent.

Résumé

La réaction du *N*-méthylol-acrylamide en présence d'acide gras comme catalyseur a permis l'acrylamido-méthylation du coton. Quand le rapport molaire du

N-méthylolacrylamide et de l'anhydro-glucose dépasse 0.2, l'efficacité de la réaction diminue rapidement et la variation de la densité avec la quantité ajoutée s'écarte de la linéarité. Ce résultat, ainsi que les autres données expérimentales, montre qu'un seul des trois hydroxyles de la cellulose, probablement celui qui est situé en position 6, participe à la formation d'un lieu éther avec le *N*-méthylol-acrylamide. Le coton n'est donc accessible à ce réactif qu'à 20%. Lorsqu'on traite le coton acrylamido-méthylé avec des catalyseurs radicalaires ou des catalyseurs alcalins, les doubles liaisons deviennent particulement saturées; les propriétés mécaniques du polymère changent alors de manière spectaculaire. L'élasticité du tissu mesurée par recouvrement des plis est améliorée. L'analyse de la réaction des doubles liaisons à divers taux de produit acrylamidométhylé dans le tissue montre que les catalyseurs radicalaires causent une homopolymérisation des doubles liaisons latérales et que les catalyseurs alcalins en présence d'eau provoquent la condensation de Michael entre les doubles liaisons et l'hydroxyle de la cellulose. Ces deux réactions peuvent cependant entrer en compétition si le traitement secondaire est effectué en absence d'humidité. Ces réactions produisent un pontage du tissu, la densité de pontage pouvant se calculer à partir des différences molaires entre les groupements méthyliques et les doubles liaisons. Le recouvrement des plis atteint sa valeur maximale caractéristique de la méthode catalytique lorsque le rapport des unités anhydroglucosiques aux unités pontées varie de 4 à 5. Lorsque les tissus pontés sont hydrolysés en milieu acide, l'augmentation de recouvrement des plis produite par le pontage est éliminée lorsque la moitié des ponts est rompue. Les ponts résiduels ne contribuent pas au recouvrement des plis. Des traitements provoquant le pontage à l'état sec diminuent la quantité d'eau absorbable, augmente la densité et n'a pas d'effet sur le diagramme aux rayons-X. Contrairement à ces résultats, un pontage en milieu humide augmente la quantité d'eau retenue, modifie le spectre aux rayons-X et dans certaines conditions réduit la densité. Ces résultats montrent que le pontage en présence d'humidité augmente la fraction amorphe du coton et conduit à un pouvoir de recouvrement des plis à l'état humide meilleur qu'à sec, tandis que le contraire est réalisé pour le pontage à sec. Quoique la catalyse alcaline ne dégrade pas le tissu, un pontage catalysé par les alcalins réduit la résistance à la traction. Un catalyseur radicalaire est plus favorable à la force de traction malgré le fait que ces catalyseurs dégradent le tissu en l'absence d'agent de pontage.

Zusammenfassung

Baumwolle wurde unter Verwendung von *N*-Methylolacrylamid und Zusatz eines milden sauren Katalysators acrylamidomethyliert. Sobald das Molverhältnis von *N*-Methylolacrylamid zu Anhydroglukose 0,2 überstieg, wurde die Ausbeute der Reaktion plötzlich vermindert und die Dichteänderung bei weiterem Zusatz wich von der Linearität ab. Dieser und andere ähnliche Umstände weisen darauf hin, dass nur eine der drei Hydroxylgruppen der Cellulose, wahrscheinlich die in 6-Stellung, den Acrylamidomethyläther bildet und dass Baumwolle zu ungefähr 20% auf dieses Reagens anspricht. Behandelt man acrylamidomethylierte Baumwolle mit Radikal- oder alkalischen Katalysatoren, so werden die Doppelbindungen teilweise abgesättigt und die mechanischen Eigenschaften änderten sich in auffallender Art. Im besonderen wurde die Elastizität des Gewebes verbessert, wie die Bestimmung der Knitterfestigkeit zeigt. Untersuchungen der Doppelbindungereaktion in verschiedenen Stadien der Acrylamidomethylierung des Gewebes zeigten, dass Katalyse durch Radikale eine Homopolymerisation der freien Doppelbindungen, alkalische Katalyse in Gegenwart von Wasser eine Michaelkondensation zwischen den Doppelbindungen und den Hydroxylgruppen der Cellulose hervorruft, während bei einer alkalischen Nachbehandlung in trockenem Zustand diese beiden Reaktionen miteinander konkurrieren. Diese Reaktionen vernetzen das Gewebe; der Vernetzungsgrad konnte aus der Differenz zwischen molaren Methylen- und Doppelbindungsgehalt berechnet werden. Die Knitterfestigkeit erreichte den höchstmöglichen, für die katalytische Methode charakteristischen Wert bei einem Verhältnis von reaktionsfähigen Anhydroglukoseeinheiten zu Vernetzungsstellen von 4–5. Wurden die vernetzten Gewebe in Säure hydrolysiert, so verloren sie die durch die Vernetzung erzeugte Zunahme der Knitterfestigkeit nach der Spaltung von ungefähr der Hälfte der Vernetzungsstellen. Die verbleibenden Vernetzungsstellen trugen zur Knitterfestigkeit nicht bei.