Mercerized and Cross-linked Cotton Yarns I. Effect of Tension During Mercerization on Degree of Cross-linking and Distention Index

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Synopsis

A study of the effect of tension during mercerization on the distention index and distribution of cross-link in cotton yarns cross-linked by different processes with formaldehyde is reported. The yarns were slack mercerized and then restretched to 90–103% of their original lengths. The mercerized samples were then cross-linked with formaldehyde by form W and form D processes. Estimation of sol-gel, distention index (DI), and distribution of cross-links in cotton yarn samples are discussed. The results of these analyses provide important information on the gross uniformity of the distribution of the cross-link in the fiber structure of cotton yarn mercerized under varying tensions and cross-linked.

INTRODUCTION

In our earlier paper,[1] it was reported that formaldehyde cross-linked cotton cellulose and cotton cellulose treated with different swelling and decrystallizing agents and cross-linked with formaldehyde by form W and form D processes were characterized by the estimation of the soluble (sol) and insoluble (gel) fractions in cupriethylenediamine hydroxide (CED). It was found that cotton cellulose that had undergone mercerization and cross-linking with formaldehyde by different processes exhibited varying degrees of cross-linking depending on the process by which they were cross-linked. Cotton yarns mercerized with varying degrees of tension showed a high degree of distribution of cross-links in the network structure, as evidenced by the moles of formaldehyde per glucopyranosyl unit (GPU) in the cellulose.[2]

Based on the development in the studies of sol and gel fractions of chemically modified cottons, a study was reported on the swelling of cross-linked cotton yarn in a cellulose solvent.[3] The apparent cross-link density, as measured by swelling indices, varies characteristically for each of the different processes of introduction of formaldehyde into cotton. These differences were attributed to the differences in the accessibility of different samples at substantially different states of swelling at the time of cross-link development and different structures of formaldehyde units in the cottons.

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Journal of Applied Polymer Science, Vol. 33, 2179–2187 (1987)

CCC 0021-8995/87/062179-09$04.00

The present investigation was taken up with a view to study the effect of tension during mercerization on the distention index (DI) and distribution of cross-links in mercerized and cross-linked cotton yarns and to investigate the heterogenous reactions of the cross-linking agent with the accessible hydroxyls of cotton cellulose, employing advanced research techniques to obtain the basic information needed for better utilization of cotton.

MATERIALS AND METHODS

Combed GIZA-75 cotton was made into 60/2 (20 tex) gray yarn having a twist multiplier of 3.50 in both the singles and ply, with a reverse twist in the ply.

Mercerization with 23% sodium hydroxide containing 1.0% wetting agent was carried out (25°C) for 7 min in the laboratory. The following mercerization treatments were given to the yarns. The yarns were slack mercerized and then restretched to 90, 94, 96, 100, and 103% of their original lengths. These mercerized samples were then cross-linked with formaldehyde by the form D and form W processes. The yarns were slack mercerized for 3 min, then restretched to the desired length for 3 min. The mercerized yarns were given a hot water wash on the mercerization machine itself, to remove excess alkali. Yarns were then removed from the machine, washed with cold water, neutralized with 1% acetic acid, rinsed with distilled water, and then dried at room temperature, during which they remained at the length already established.

Mercerized and unmercerized yarns (scoured and bleached) were then cross-linked by form W and form D processes, to produce cottons having varying degrees of cross-linking.[1]

Yarn samples were cross-linked in an aqueous system[4,5] (form W) consisting of 76% formaldehyde, 12.2% hydrochloric acid, 2.2% methanol, and 78.0% water at a pH of 1.44 and M/L ratio of 1 : 100 for 30 min. In this process, cross-linking takes place when yarn is in a swollen condition. Yarn samples were also cross-linked in an acetic acid system (form D)[4,6] consisting of 5.5% formaldehyde, 5.5% HCl, 71.3% acetic acid, 1.6% methanol, and 16.1% water at a pH of 1.25 and M with $L = 1 : 100$ for 5 min and were then washed in water and dried at room temperature.

The cupriethylenediamine solvent used for distention indices was 1 M in copper and 2 M in amine.[7]

Formaldehyde was determined by colorimetric method.[8] The distention index, that is, the apparent specific volume of the CED-insoluble gel, was determined as described earlier with certain modifications. DI was calculated as

$$\mathrm{DI} = \frac{V_g}{W_g} = \frac{V_g}{C_o G}$$

where V_g is the volume (milliliters) of the swollen gel measured in the centrifuge tube, W_g is the weight (grams) of the recovered gel cellulose free of solvent, C_o is the weight (grams) of the original sample of the yarn, and G is the gel fraction.

RESULTS AND DISCUSSION

Data on mercerized and cross-linked yarns by form W and form D processes, on formaldehyde content, number of cross-links per 100 glucopyranosyl unit (cross-links per GPU), gel fractions, and DI are given in Tables I and II, respectively. Formaldehyde content showed the lowest formaldehyde (0.68%) for scoured and cross-linked yarns and the highest (0.74%) for slack mercerized, with the increase in stretch beyond 90% original dimensions and cross-linked by the form W process. These data show a gradual decrease in formaldehyde content with the increase in stretch during mercerization (Fig. 1). A similar trend is observed in the case of samples cross-linked by the form D process, as

TABLE I
Effect of Mercerization with Varying Degrees of Stretch on the Various Properties of Form W Cross-linked Cotton Yarn *

Serial no.	Samples	Formaldehyde content (%)	No. cross-links per 100 GPU	Gel fraction (G)	DI mL/g
1.	Scoured yarn + cross-linked	0.68	3.68	1.00	15.61
2.	Slack + 90% stretch of OL[a] + cross-linked	0.74	4.01	1.00	16.36
3.	Slack + 94% stretch of OL + cross-linked	0.73	3.96	0.99	21.45
4.	Slack + 96% stretch of OL + cross-linked	0.73	3.96	0.98	23.87
5.	Slack + 100% stretch of OL + cross-linked	0.72	3.90	0.96	27.89
6.	Slack + 103% stretch of OL + cross-linked	0.72	3.90	0.94	29.00

[a] Original length.

TABLE II
Effect of Mercerization with Varying Degrees of Stretch on Various Properties for Form D, Cross-linked Cotton Yarn

Serial no.	Samples	Formaldehyde content (%)	No. cross-links per 100 GPU	Gel fraction (G)	DI mL/g
1.	Scoured yarn + cross-linked	0.46	2.49	0.98	15.04
2.	Slack + 90% stretch of OL + cross-linked	0.65	3.52	0.92	17.00
3.	Slack + 94% stretch of OL + cross-linked	0.63	3.42	0.91	18.50
4.	Slack + 96% stretch of OL + cross-linked	0.59	3.20	0.88	19.90
5.	Slack + 100% stretch of OL + cross-linked	0.58	3.14	0.82	24.50
6.	Slack + 103% stretch of OL + cross-linked	0.56	3.03	0.79	25.20

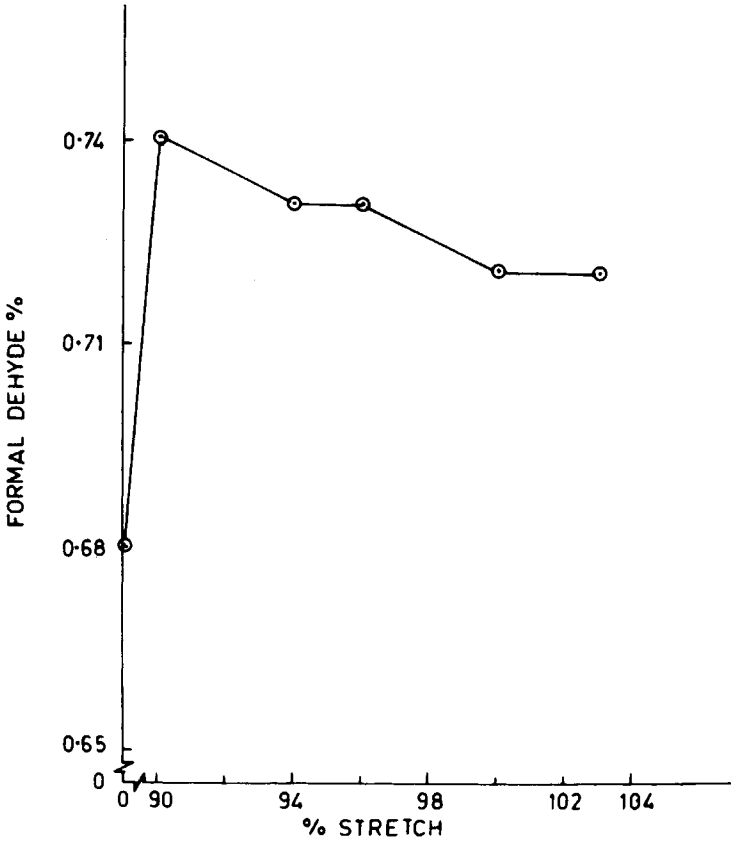

Fig. 1. Effect of tension during mercerization on the percentage of formaldehyde of cotton cross-linked by the form W process.

may be seen in Table II. These data also show a gradual decrease in the percentage of formaldehyde with an increase in stretch during mercerization (Fig. 2). On comparing the percentage of formaldehyde of the two processes, it is seen that formaldehyde values are higher in the samples cross-linked by the form W process than the corresponding samples of the form D process. However, this comparison is not valid as the treatments were not to the same level of cross-linking, as may be seen from nonmercerized cross-linked samples.

Data on the number of cross-links per 100 GPU, and the DI of the yarn samples that had been mercerized and cross-linked by form D and form W processes were obtained. Calculation of the number of cross-links is based on the assumption that all the formaldehyde present is participating in the cross-links and the cross-links formed are single methylene bridges.[9] The results on the number of cross-links per 100 GPU for the samples mercerized and cross-linked by the form W and form D processes are shown in Tables I and II, respectively. These data show a similar trend, a gradual decrease with an increase in stretch during mercerization as observed in the case of formaldehyde content for both processes. The number of cross-links per 100 GPU in samples cross-linked by the form W process varied from 3.68 for scoured and cross-linked yarn to 4.01 for slack mercerized yarn, with the increase in

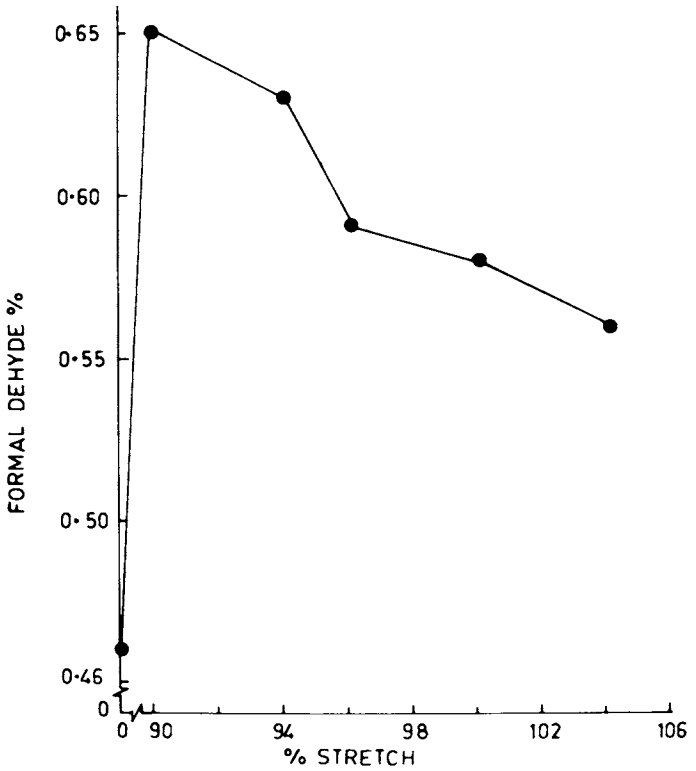

Fig. 2. Effect of tension during mercerization on the percentage of formaldehyde of cotton cross-linked by the form D process.

stretch beyond 90%, of the original dimensions (sample 2 in Table I). The remaining yarn samples, which were given higher stretch, beyond 90% showed almost a similar value within the above range. The samples cross-linked by the form D process showed almost a similar trend, indicating a lower value of cross-links per 100 GPU (2.49) for scoured and cross-linked yarn compared with mercerized yarn with varying stretch and cross-linked thereafter (Table II), where the number of cross-links per 100 GPU varied from 3.03 to 3.52.

Similarly, the data on gel fraction of mercerized and cross-linked samples by the form W and form D processes are shown in Tables I and II, respectively. The gel value in the case of samples cross-linked by the form W process show the same values of 1.0 for scoured cross-linked samples and slack mercerized with the increase in stretch beyond 90% of original dimensions. Other samples showed slightly lower values and decreasing trend. These data clearly indicate that the network structure of cotton fibers in yarn is uniformly cross-linked. Therefore, the cellulose solvent CED has very little effect on the samples, as the cross-linked samples are unaffected by such solvents. A similar trend is noted in the case of G values of the samples cross-linked by the form D process, but these samples showed lower G values and higher dissolution in CED compared with the corresponding samples treated by the form W process (Table II). This may be because the reaction period for samples

cross-linked by the form D process was kept to a minimum; therefore, the degree of cross-linking was restricted in these samples. This may also be partly due to less uniform cross-link distribution.

Data on DI values (which indicates extent of swelling) of mercerized and cross-linked samples treated by the form W process showed the lowest DI value (15.6) for scoured and cross-linked yarn and other samples showed a gradual increase in DI values with an increase in stretch during mercerization. The DI value was highest (29.0) in the case of a sample mercerized slack and stretched to 103% of OL (Table I). This shows that the samples given higher stretch during mercerization have higher swelling capacity in CED and give higher DI values. A similar trend is observed in the case of DI values of the samples cross-linked with the form D process, as may be seen from Table II, except that DI values of these samples are lower than those of the corresponding samples of the form W process. An explanation for this has been given earlier. The relationship between DI values and number of cross-links per GPU for the samples cross-linked by form W is shown in Figure 3. It may be seen from Figure 3 that in the case of samples cross-linked by the form W process, the DI is independent of substitution (the number of cross-links per 100 GPU). On the other hand (Fig. 4), results of mercerized samples cross-linked by the form D process showed a somewhat different relationship between the DI and number of cross-links per 100 GPU, indicating a gradual decrease in DI with increase in degree of substitutions. The data also show that the DI values differ in the yarn samples cross-linked by the processes. Futher, it is observed that the DI values of the yarn samples cross-linked by

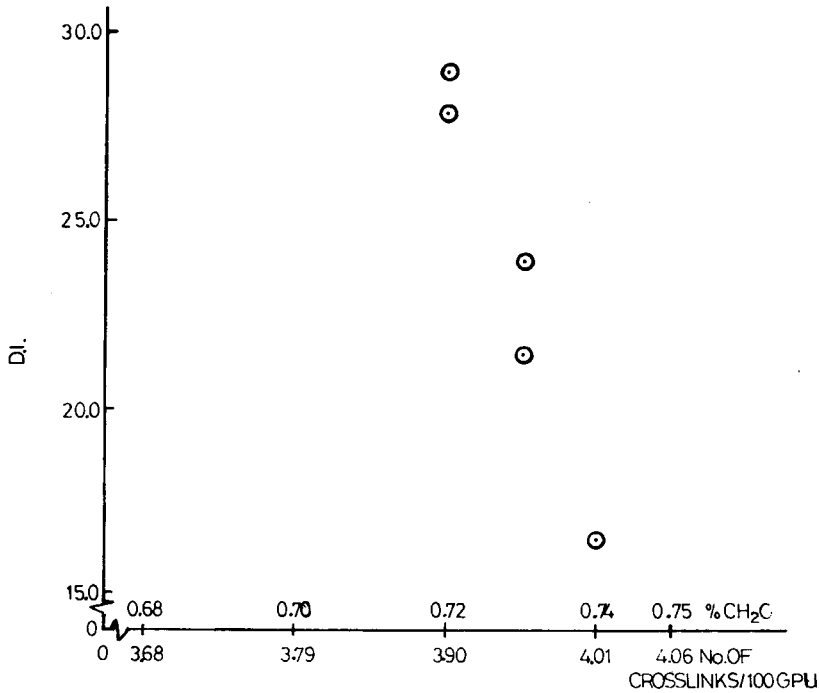

Fig. 3. Relationship of the DI to the formaldehyde content and cross-links per 100 GPU of cotton cross-linked by the form W process.

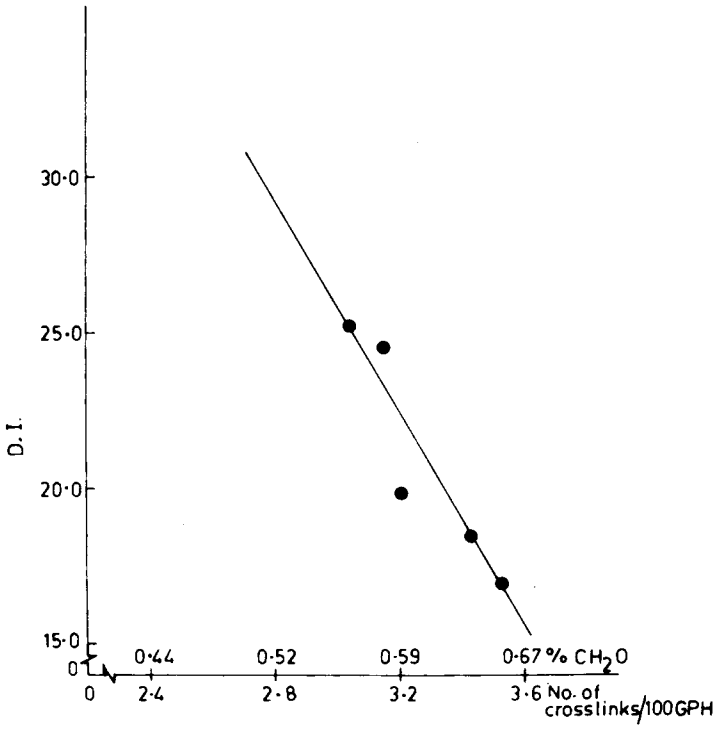

Fig. 4. Relationship of the DI to the formaldehyde content and cross-links per 100 GPU of cotton cross-linked by the form D process.

the form W process are slightly higher than the corresponding sample cross-linked by the form D process. This is probably due to the treatments that were not given to the same level of cross-linking.

All the treated samples showed almost a similar relationship between the DI and number of cross-links per 100 GPU in the cellulose; that is, the DI is dependent on the number of cross-links per 100 GPU—the degree of substitution. A somewhat different trend is noted in the samples cross-linked by the form D process. A lower DI indicates more uniformity in the distribution of cross-links in the samples.[4] In the present study, however, the DI values of the samples cross-linked by the form D process are slightly lower than the DI values of the samples cross-linked by the form W process. This may be because the samples treated by the form D process were given less time to prevent a higher degree of cross-linking, which would otherwise decrease the strength of the yarn samples. Since the elastic forces that counteract complete expansion (dissolution) during the swelling process are inversely proportional to the molecular weight of the polymer between points of cross-linking,[4] a decrease in the swelling with progressive reaction in both processes is evidence of an increasing number of cross-links per GPU. Thus it is apparent that the number of cross-links in the samples increases throughout the course of the form W and form D processes of cross-linking.

The relationship between the DI and the gel fraction for the samples cross-linked by the form W process are shown in Figure 5. There is a linear

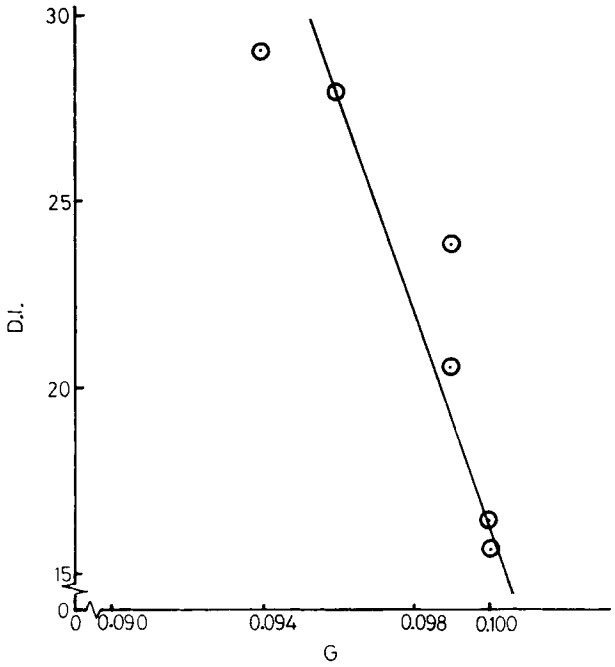

Fig. 5. Relationship of the DI to the gel fraction G of cotton cross-linked by the form W process.

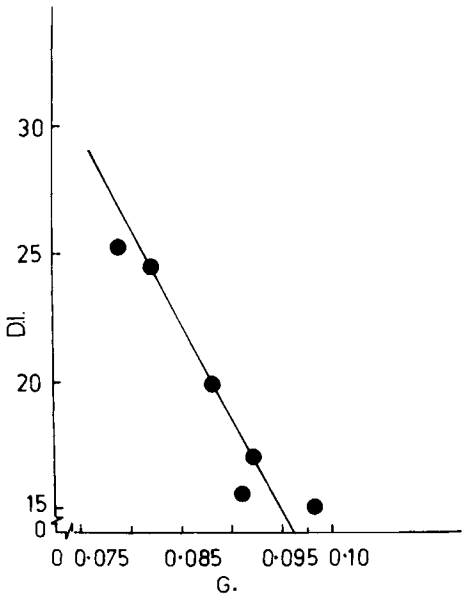

Fig. 6. Relationship of the DI to the gel fraction G of cotton cross-linked by the form D process.

relationship between the two properties. It is seen that as the DI decreases the gel fraction increases. A similar trend between the two properties is also observed in the case of samples cross-linked by the form D process (Fig. 6). When the two figures are compared, it is seen that the DI and the gel values are lower for samples cross-linked by the form D process compared with corresponding samples of form W process. These data corroborate our earlier observation[4] that the DI decreases as G increases. It is interesting to see that G fractions from samples given higher stretch and cross-linked showed higher swelling in CED compared with similar G fractions of samples treated without or with less stretch for form W and form D processes.

CONCLUSION

This study provides information on cross-link density, number and distribution of cross-links in native, mercerized cotton with varying stretch and cross-linked cotton yarn by form W and form D processes. From the study it is concluded that the samples given varying stretch during mercerization show marked differences in swelling capacity in CED solvent and distribution of cross-links in the network structure of the fiber. The samples given higher stretch during mercerization showed a higher swelling capacity in CED solvent and gave higher DI values for both the form W and form D processes. Further, it is observed that the DI is independent of substitution in form W samples, but the trend for form D samples showed a decrease in the DI with an increase in the degree of substitution. It is also observed that there is an inverse linear relationship between the DI and the gel fraction. The G fractions from samples given higher stretch and cross-linked by form W or form D processes showed higher swelling in CED compared with similar samples treated without or with less stretch for both processes.

The authors wish to express their sincere thanks to Dr. S. P. Rowland, Research Leader (Retired), Cotton Chemical Reaction Research, Southern Regional Research Centre, New Orleans, for his interest in this work, Prof. A. Hebeish, National Research Centre, Dokki, Cairo, for supplying mercerized yarn samples, and Dr. V. Sundaram, Director, Cotton Technological Research Laboratory, for his permission to publish this paper.

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Received August 12, 1985
Accepted July 31, 1986