A Study on Distension Index and Distribution of Crosslinks in Formaldehyde-Crosslinked Cotton*

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Synopsis

A study on distension index (*DI*) and distribution of crosslinks is reported for cotton cellulose treated with selected swelling reagents and crosslinked by different processes with formaldehyde. Details of estimation of the distension index are also described. Distribution of crosslinks under different conditions of crosslinking has also been shown by electron microscopy. Marked differences in *DI* values and distribution of crosslinks in cellulose samples crosslinked under different conditions of treatments are discussed. The results of these analysis provide quantitative information on the gross uniformity of distribution of crosslinkages in the fiber structure of cotton celluloses.

INTRODUCTION

In a previous paper[1] it was reported that formaldehyde-crosslinked cotton cellulose and cotton celluloses treated with selected swelling and decrystallizing agents and crosslinked with formaldehyde by form W and form D processes were characterised by estimation of soluble (sol) and insoluble (gel) fractions in cupriethylenediamine hydroxide solvent (CED). Substantial differences in network structure among these samples were brought to light by the sol–gel analysis. The results also showed a high degree of accessibility of formaldehyde to the molecular units of the cellulose and a degree of randomness of distribution of crosslinkages throughout the fiber structure, which was hardly expected on the basis of the heterogeneous nature of the reactions. The form W process was found more efficient, as was evident from gel fraction data, and these results were in conformity with the findings of other workers.[2] It was also shown that cotton cellulose treated with different reagents and crosslinked by form W and form D processes exhibited varying degrees of crosslinking depending on the type of chemical modifications of treatments. Highly decrystallized celluloses (treated with NaOH and $ZnCl_2$) showed higher degrees of distribution of crosslinks in cellulose network structures as evidenced by the moles of formaldehyde per glucopyranosyl unit (GPU) in celluloses.

Based on the developments in studies of gel and sol fractions of chemically modified cottons, a study was reported on swelling of crosslinked cottons in a cellulose solvent.[3] The apparent crosslink 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 accessibility of different samples, substantially different states of swelling at the time of crosslink developments, and different structures of formaldehyde

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units in crosslinks. From the foregoing it will be seen that no information is available in the literature on the swelling characteristics of gels of the variety of treated cottons.

In view of the above, the present investigation was undertaken with the object to study the swelling characteristics of gel fractions (G) of cotton cellulose modified with selected swelling reagents before crosslinking, to provide more detailed information on distribution of crosslinkages and the swelling characteristics of the crosslinked celluloses. In this paper sol–gel and distension index analysis of cotton celluloses treated with selected swelling and decrystallizing reagents and then crosslinked with formaldehyde by different processes for different periods of time to provide different degrees of crosslinking is reported. The relationship between *DI* and G fraction and *DI* and crosslink distribution in cellulose is also discussed.

EXPERIMENTAL

Purified lint sample of MCU.3 cotton was used in this study. Lint samples were treated with the following swelling and decrystallizing reagents before crosslinking: NaOH, 20% at 5°C for 16 hr; $ZnCl_2$, 63% at 28°C for 1 hr; H_3PO_4, 80% at 28°C for 5 min; H_2SO_4, 60% at 28°C for 1 min.

After the treatments, all the swollen samples were washed thoroughly with tap water to remove the swelling reagents and finally with distilled water and then dried at room temperature. Treated and untreated cellulose samples were crosslinked with formaldehyde by form W and form D processes for varying periods to produce modified cottons having varying degrees of crosslinking.[1]

Cotton was crosslinked in an aqueous system,[4] form W consisting of 7.6% formaldehyde, 12.2% hydrochloric acid, 2.2% methanol, and 78.0% water. In this process crosslinking takes place when cotton is in the swollen condition. Cotton was crosslinked in an acetic acid system,[5] form D, consisting of 5.5% formaldehyde, 5.5% hydrochloric acid, 71.3% acetic acid, 1.6% methanol, and 16.1% water.

The CED solvent which was used for the measurement of gel fractions and for distension indices (*DI*) was 1*M* in copper and 2*M* in amine.[6]

Formaldehyde in crosslinked samples was determined by colorimetric method.[7] Sol–gel fractions of crosslinked cottons were measured in CED.[1]

Distension index (*DI*), i.e., the apparent specific volume of the CED-insoluble fraction of the crosslinked cotton, was measured according to the method of Stark and Rowland[3] with certain modifications described below:

Modified cotton was finely cut, dried in an oven for 4 hr at 100°C, weighed accurately to about 100 mg, and transferred to a specifically fabricated 50-ml glass-stoppered, graduated centrifuge tube. Air in the tube and the sample was displaced by passing nitrogen through several times. A 20-ml portion of 0.05% solution of a wetting agent was added to the finely cut sample in each tube and each tube was thoroughly shaken to wet and disperse the sample. Then 20 ml 1*M* CED solvent was added to each tube from a buret (by keeping CED solvent under nitrogen pressure) to produce CED solution of 0.5*M* concentration, and the tubes were shaken thoroughly to mix the contents. As the CED is sensitive to light, each tube was wrapped with black cloth and placed on a horizontal shaker and agitated for 18 hr (overnight period). At the end of the period, each tube was centrifuged for 1 hr at 2500 rpm. This period was found sufficient to reach

a stable volume of swollen gel and to develop a horizontal interface between the swollen gel and the CED solution after numerous preliminary trial operations of various centrifuging periods. The volume of swollen gel in the graduated tube was recorded. The interface between gel and CED solvent could be easily recorded in fluorescent light. *DI* is calculated as

$$DI = V_g/W_g = V_g/(C_0G)$$

where V_g is the volume (ml) of swollen gel measured in the centrifuge tube, W_g is the weight (g) of recovered gel free of solvent, C_0 is the weight (g) of the original sample of cotton, and G is the gel fraction.

Electron micrographs of a few selected samples were obtained as described earlier.[8]

RESULTS AND DISCUSSION

Data on formaldehyde content, number of crosslinks (moles of formaldehyde) per GPU, gel fractions, and *DI* of five series of chemically treated crosslinked cotton celluloses by form W and form D processes were obtained. The calculation of the number of crosslinks is based on the assumptions that all of the formaldehyde present is participating in crosslinks and that all crosslinks formed are single methylene bridges. The relationship between *DI* values and number of crosslinks per GPU unit for the samples crosslinked by form W process is shown in Figure 1. It will be seen from the data shown in Figure 1 for any single series of sample that *DI* decreases regularly as the formaldehyde content or number of crosslinks per GPU increases. Data also show that at the same level of crosslinks in cellulose for different series of crosslinked samples, *DI* values differ and gel fraction of decrystallized celluloses exhibit lower *DI* values (less swelling) in cellulose solvent as compared to untreated crosslinked celluloses

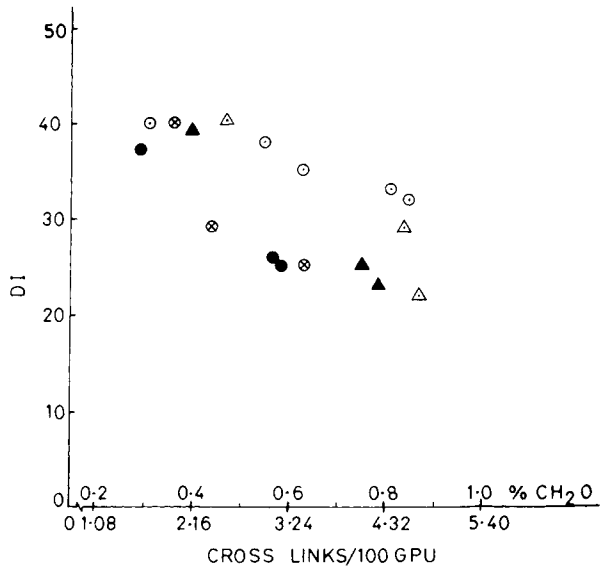


Fig. 1. Relationship of *DI* to formaldehyde content of cotton crosslinked by form W process: (⊙) crosslinked; (⊗) H_3PO_4, crosslinked; (●) H_2SO_4, crosslinked; (△) $ZnCl_2$, crosslinked; (▲) NaOH, crosslinked.

at the same level of distribution of crosslinks in cellulose structure. Further, it is interesting to see (Fig. 1) that the cellulose samples untreated and crosslinked with formaldehyde show the least change in *DI* values, specially when the number of crosslinks are at the highest level in cellulose samples of this series. All the treated samples showed almost similar relationships between *DI* and number of crosslinks per GPU in cellulose, that is, as *DI* decreases, the number of crosslinks per GPU increases. If all the points for different series of samples are joined with separate straight curves, the curve for H_2SO_4-treated samples lies at the bottom and indicates maximum change in *DI* with increase in the number of crosslinks per mole of GPU, which is followed by the H_3PO_4, NaOH, and $ZnCl_2$ curves in decreasing order.

The relationship between *DI* and number of crosslinks per mole of GPU for the samples crosslinked by the form D process is shown in Figure 2. These data also show somewhat similar relationships as observed in the case of samples treated by the form W process, i.e., as the number of crosslinks per mole of GPU in cellulose increases, the *DI* value of G decreases. However, there are specific differences between each series of samples. *DI* values of NaOH-treated samples are the lowest at the same level of crosslinks, compared to other series of samples. Similarly, other treated samples also showed lower *DI* values compared to untreated and crosslinked samples. These results indicate that gel fraction of decrystallized celluloses swell to a lesser extent in cellulose solvents compared to crystalline (native) cellulose treated under similar reaction conditions.

Comparison of data in Figures 1 and 2 indicates that the same series of samples crosslinked by the form W process show lower *DI* values compared to the same series of sample crosslinked by the D process, with a few exceptions, although the number of crosslinks per mole of GPU is higher in the case of samples crosslinked by the form D process. This indicates that the distribution of crosslinks in the network structure of cellulose is more uniform in the case of samples treated by the W process than the samples treated by the D process. However, in case of NaOH- and $ZnCl_2$-treated samples, *DI* values of samples treated by the form D process are much lower as compared to other samples, and

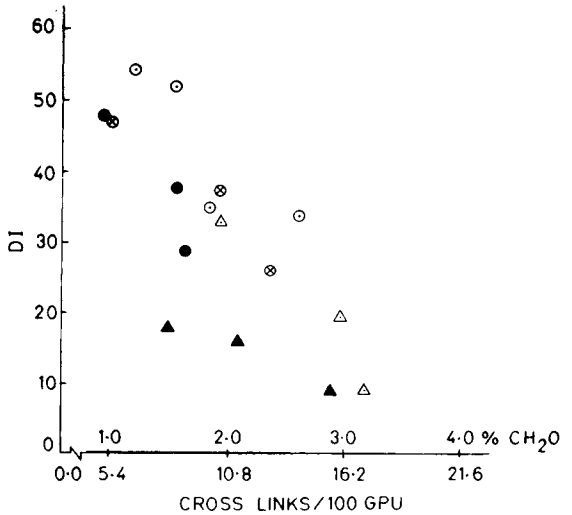


Fig. 2. Relationship of *DI* to formaldehyde content of cotton crosslinked by form D process. Designations are the same as those of Figure 1.

this indicates high degrees of uniformity of distribution of crosslinks in these samples.

Data on the G fraction and the *DI* of five series of crosslinked celluloses (by form W process) at varying levels of crosslinks are shown in Figure 3. It may be seen from the figure that for each series of samples a specific but linear relationship develops. The linear relationship is consistent with, and perhaps a confirmation of, the control of the amount of gel and the density of crosslinks in the gel by diffusion. It is interesting to note the large differences in *DI* values at a specific level of gel fraction for each series of sample. Except in the case of H_2SO_4-treated samples, where the *DI* showed the least change over a wide range of G values, other samples showed sharp decrease in *DI* values, even when G values were in a very narrow range. This indicates that depending on crosslink density in the gel, *DI* of the different series of samples varies. Introduction of additional crosslinks in the gel further decreases the *DI*. Extent of swelling as measured by *DI* in these samples decreases throughout the course of incorporation of the crosslinks.

Relationship between *DI* and G values for the different series of samples treated by the D process is shown in Figure 4. In general, a similar relationship is seen as observed in the case of the W process, i.e., for each series of sample, *DI* decreases as G value increases. It is interesting to see that G fractions of NaOH-treated samples showed least swelling in CED compared to the similar G fractions of samples treated with other reagents. G fractions obtained from $ZnCl_2$-treated samples showed the next-lowest *DI* values. Other samples showed almost similar values as untreated crosslinked samples. On comparing Figures 3 and 4, it is observed that the samples treated by the form W process have higher G values and lower *DI* than the sample treated by the form D process for the same series of sample. This shows that the treatment by the form W process produces more efficient crosslinking, and crosslinks are stable to CED treatment due to which *DI* values are lower compared to the samples treated by the form D process.

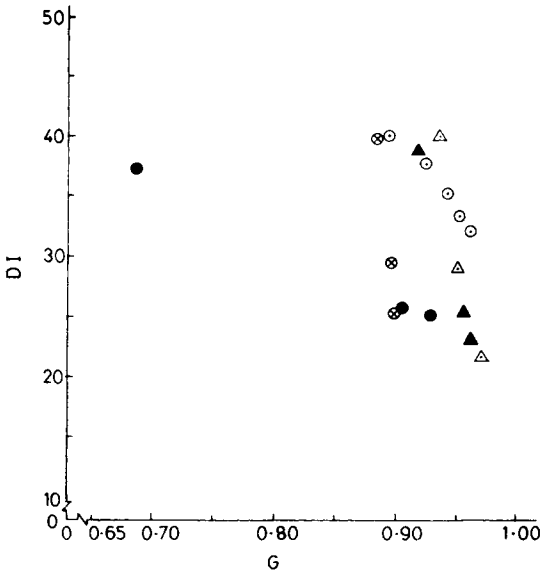


Fig. 3. Relationship of *DI* to gel fraction (G) of cotton crosslinked by the form W process. Designations are the same as those of Figure 1.

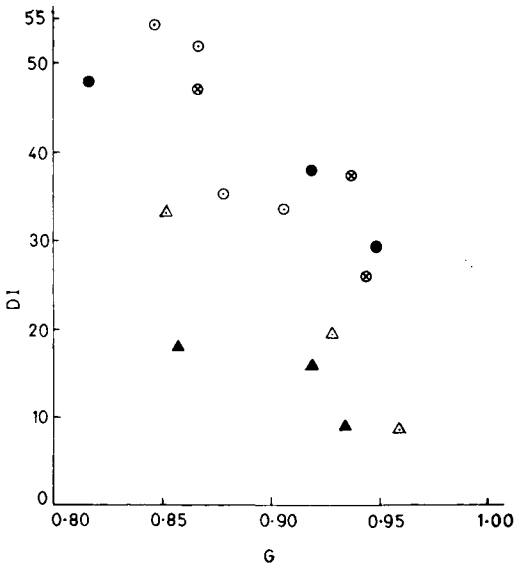


Fig. 4. Relationship of DI to gel fraction (G) of cotton crosslinked by the form D process. Designations are the same as those of Figure 1.

Since the elastic retractive forces that counteract complete expansion (and dissolution) during the swelling process are inversely proportional to the molecular weight of polymer between points of crosslinking, the decrease in swelling with progressive reaction in the form W process is evidence of an increasing number of crosslinks. Thus, it is apparent that both G fraction and number of crosslinks in the G fraction increase throughout the course of the form W process of crosslinking.[3]

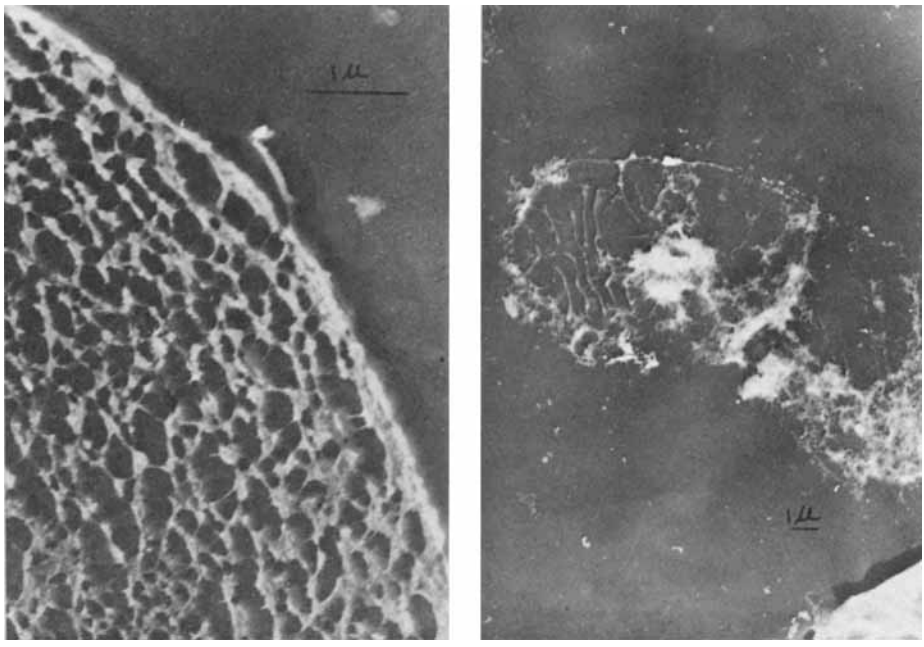
The relationship between *DI* and the G fraction of the series of cellulose samples reported in this study are in conformity with others,[3] and increasing order of crosslink density in G fraction is indicated by *DI* as follows: form D < form W. At a 0.20% level of formaldehyde in the total sample, increasing order of crosslink density in the gel fraction, as indicated by *DI* for different processes, was found as follows[3]: form D < form W < form F < form V ≤ form C. The consistently higher level of swelling observed for the gel fraction from the form D cotton compared to form W cotton suggests that the former is characterized by fewer and longer crosslinks as a result of high concentration of formaldehyde in the reagent system.

The variation in degree of swelling of G fractions of different series of cottons at the same level of agent under form W and form D processes can also be attributed to some extent to the distributions or structures of the crosslinks. Similarly, at the same level of reagent, the lower *DI* values of gel fractions in the case of NaOH- and $ZnCl_2$-treated samples of both the processes indicate that the decrystallized cellulose samples swell to a lesser extent than the crosslinked crystalline (native) cellulose crosslinked under similar conditions. The results are interpreted to be the consequence of more uniform distribution of crosslinkages along the chain of the swollen and decrystallized cellulose as a result of more random reaction. In crystalline cellulose, crosslinking is restricted to the fraction of glucopyranosyl units in the accessible segment of the cellulose chain. Thus, the crystalline regions, which are without crosslinks (except on the sur-

faces), are free to swell when these chain segments are solvated in CED; the swelling in CED of chain segments in crystalline regions is limited only by the crosslinks on the extremities of these regions. This appears to be one of the important reasons why the *DI* of crosslinked crystalline cellulose approaches a common value at high levels of crosslinking with formaldehyde.[3] The "tighter" crosslinking structure in the decrystallized cellulose is also suggested[9] to be responsible for the lower *DI* value.

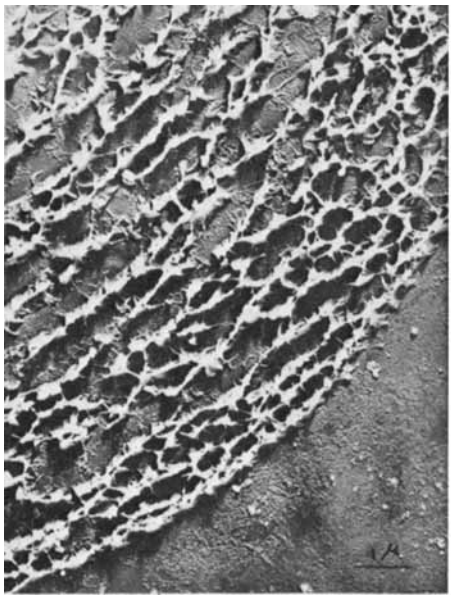
Electron micrographs of ultrathin sections of fibers prepared by layer expansion technique of a few samples were examined to explain the extent of crosslinking and distribution of crosslinks in the network structures of cellulose. Electron micrographs (Fig. 5) of normal cotton show characteristic layers. The electron micrographs (Fig. 6) of the sample crosslinked by form W process (0.0167 crosslinks/GPU) appear to be somewhat similar to control with some loss of discrete microfibrillar pattern, and some fusion of microfibrils is evident at high magnification [Fig. 6(c)]. The electron micrograph [Fig. 6(d)] of the same sample after CED treatment shows distribution of crosslinks in network structure and partial dissolution of the uncrosslinked portion.

Electron micrographs (Fig. 7) of cotton fiber treated with NaOH and crosslinked by form W process showed partial fusion due to crosslinking and honeycomb structure typical of mercerized cotton. This sample contained 0.0405 crosslinks/GPU and showed a very high degree of insolubility (0.96) in CED. This is confirmed by Figure 7(d), which indicates intact section after CED treatment and uniform distribution of crosslinks in the network structure of the fiber. The electron micrograph (Fig. 8) of cotton treated with NaOH and crosslinked by form D process, on the other hand, showed complete fusion, indicating a high degree of crosslinking (0.154 crosslinks/GPU, CH_2O, 2.85%). This sample also showed a high degree of insolubility (0.93) in CED solvent, which confirms a high degree of crosslinking.

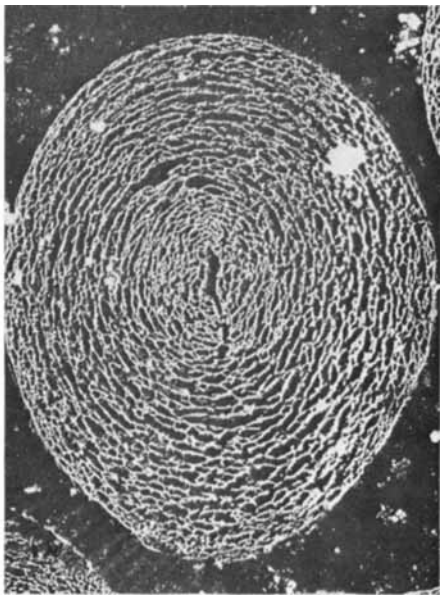


(a) (b)

Fig. 5. Electron micrographs of expansion patterns of normal cotton: (a) low magnification and (b) high magnification.



(a)



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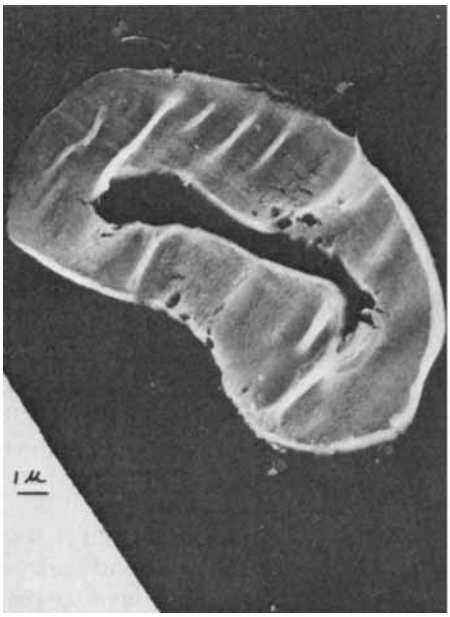
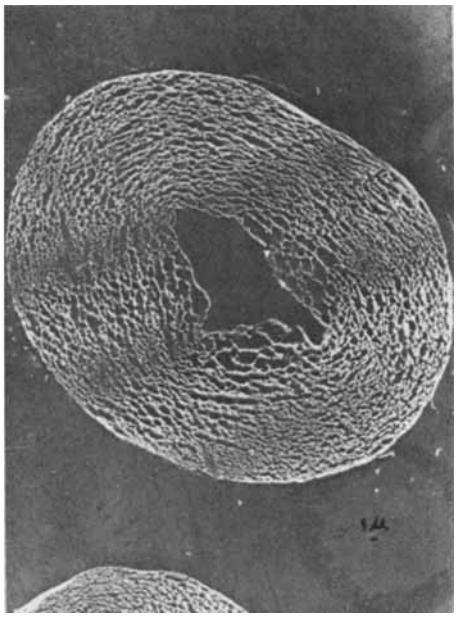


(c)



(d)

Fig. 6. Electron micrographs of cotton cross section of form W cotton. CH_2O, 0.31%; crosslinks, 0.0167/GPU; G = 0.89. (a) Dry embedding control, layer expansion pattern; (b) low magnification; (c) high magnification; and (d) after treatment with 0.5*M* CED.

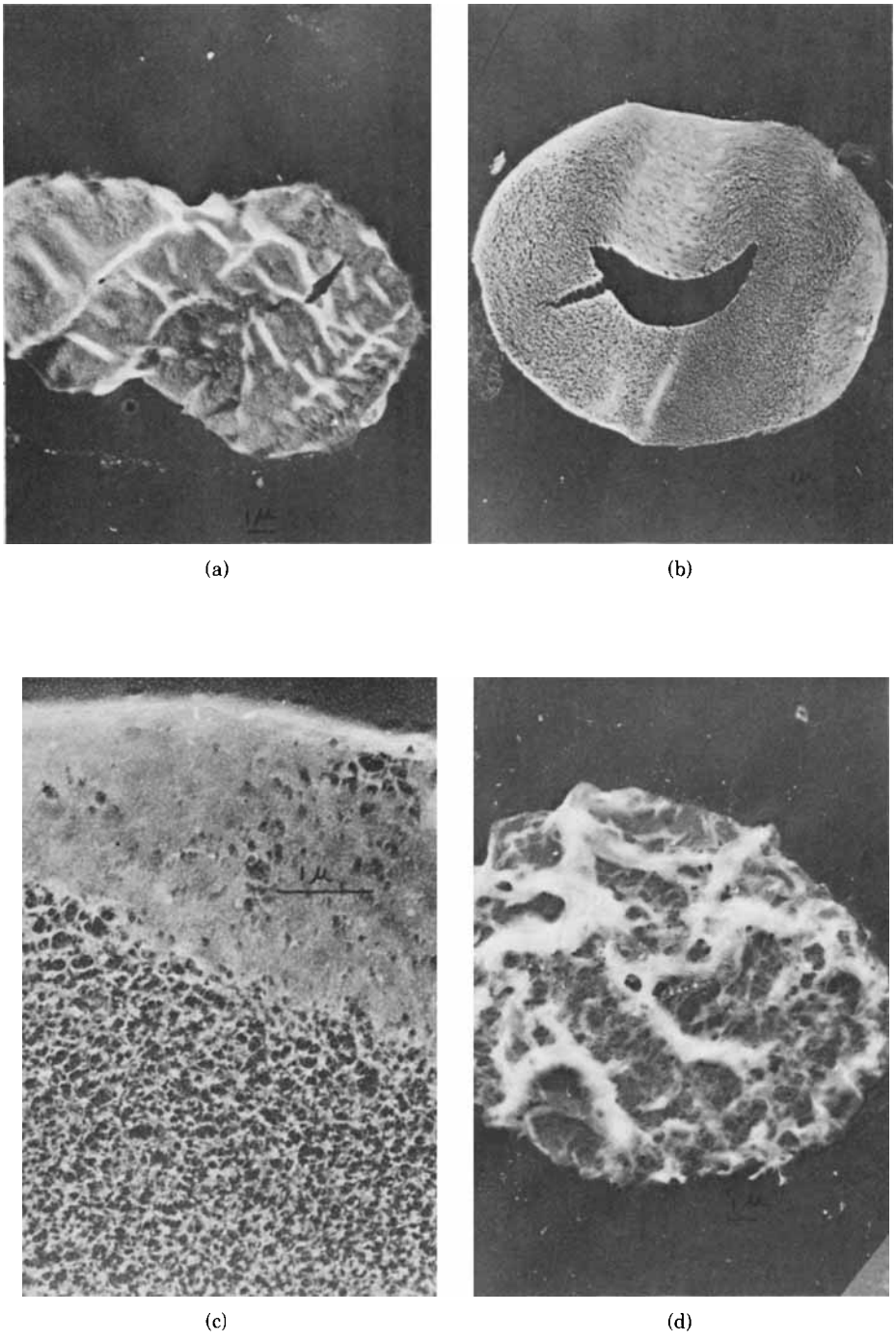


Fig. 7. Electron micrographs of cotton cross section of form W cotton treated with NaOH and then crosslinked with formaldehyde. CH_2O, 0.75% crosslinks 0.0405/GPU, G = 0.96, (a) Dry embedding control, layer-expansion pattern; (b) low magnification; (c) high magnification; and (d) after treatment with 0.5*M* CED.

Fig. 8. Electron micrograph of expansion patterns of cross section of form D cotton, treated with NaOH and then crosslinked with formaldehyde. CH_2O, 2.85%, crosslinks, 0.1540/GPU; G = 0.93.

From these figures it is clear that distribution of crosslinks in network structures depends on condition of treatment. Similarly, a wide range in heterogeneity of distribution of crosslinks was reported by Rowland et al.[10] who observed that the most heterogeneous distribution appeared in a high concentration of crosslinks in peripheral regions of the fiber. In the very early stage of reaction of CH_2O with cotton by form W, crosslinked regions were limited to the periphery and isolated interior portions, the latter suggesting diffusion through pores or channels. They also reported pronounced nonuniform distribution of crosslinks in case of samples crosslinked by form D process.

CONCLUSIONS

This study provides information on apparent crosslink density and number and distribution of crosslinks in native and chemically treated cotton. The apparent crosslink density, as measured by swelling of the gel fraction, i.e., *DI*, varies characteristically for the different processes of introduction of crosslinks into cotton. At the different levels of formaldehyde content of the cellulose, the increasing order of apparent crosslink density in the gel fraction is: form D < form W, and it follows the same trend obtained by sol–gel analysis.[1] For each series of cellulose the volume of swollen gel and *DI* decreases as the number of crosslinks per GPU increases. The volume of swollen gel in case of native cotton (crystalline cellulose) is higher than the volume of decrystallized celluloses such as in the case of $ZnCl_2$- and NaOH-treated samples. Similarly decrystallized crosslinked samples showed lower *DI* as compared to the crosslinked crystalline cellulose at the same level of crosslinks.

DI values showed different levels of apparent crosslink density in the network structure depending upon the conditions of treatment at the time of crosslink development, different accessibilities, and different structure of formaldehyde units in crosslinks. These techniques can be used with greater confidence, despite the heterogeneity in crosslinking reactions, and the results of these analyses provide quantitative information on the gross uniformity of distribution of crosslinkages in cellulose. Heterogeneity and uniform distribution of crosslinkages in network structure of a few selected samples is also explained by electron micrographs.

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