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Characterization of the Internal Pore Structures of Cotton and Chemically Modified Cottons by Gel Permeation*

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Summary

The pore structures of cotton and formaldehyde-modified cottons have been characterized by applying the principles of gel permeation to chromatographic columns formed of the finely divided fibrous cottons. Measurements were made of the relative elution volumes of suitable solutes which cover a range of known, discrete molecular weights. The solutes chosen were sugars ranging in molecular weight from 198 to 738, the elution volumes of which are in an inverse linear relationship to their molecular weights. Extrapolations of this linear relationship provide measures of the effective internal solvent volumes and the permeability limits of the cotton celluloses. Changes in these parameters are indicative of the nature and extent of the alterations of the pore structure produced by cross-linking.

Marked differences have been found in the pore structures of cotton cross-linked to progressively higher levels with the fibers in a collapsed state by a bake-cure process and with the fibers in a semidistended state by reaction in an acetic hydrochloric acid medium. The technique will be useful for relating changes in pore structure to the modifications of physical and performance characteristics of fabrics produced by various chemical treatments.

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INTRODUCTION

Cotton cellulose strongly sorbs water and in doing so undergoes swelling to permit permeation by an appreciable volume of liquid; there is an extensive system of pores within the supramolecular organization of its elementary and microfibrillar units (*1*). The presence of such a pore structure provides access of chemical reagents to the microstructural units which exhibit the crystalline organization of the cotton cellulose. Techniques of gel permeation chromatography are useful in determining certain characteristics of this pore structure. For this purpose, finely divided samples of cellulose are employed as the media in chromatographic columns and the elution volumes of suitable solutes of a range of known, discrete molecular weights are measured. It has been shown by this method (*2*) that cotton cellulose decrystallized by ball-milling is permeated by (sugar) solutes up to a molecular weight of approximately 1900. Chopped fibrous cotton contains some larger pores as indicated by a permeability to approximately 2900 molecular weight. However, the specific internal pore volume of water-swollen, fibrous cotton is only one-third of that of the decrystallized cotton. This technique has proven effective for investigating changes in pore structure caused by cross-linking decrystallized cotton (*2*), by mercerizing fibrous cotton (*3*), and by cross-linking fibrous cotton (*4*).

The object of the present work was to study the relation of changes in gel permeation characteristics of fibrous cotton as a function of the levels of formaldehyde cross-linking achieved under two different sets of reaction conditions. In one process, the bake-cure conditions effect reaction of formaldehyde with the collapsed fibers of the cotton. The second process employs an acetic–hydrochloric acid medium in which the cellulosic structure is semidistended, but the fibers are not as swollen as in the aqueous wet-cure process.

EXPERIMENTAL

Preparation of Cross-linked Cottons

Cross-linking with formaldehyde in the acetic–hydrochloric acid medium and by the bake-cure process was applied to cotton fabric. The fabric used was 80 × 80 printcloth, 3.2 oz/sq yd; it had been desized, scoured, and bleached.

The procedure described by Chance et al. (*5*) was used for the cross-linking in the acetic–hydrochloric acid medium. In this case, the fabric was cut into 6 in. × 10 in. pieces, and approximately 70 g batches of fabric were treated with the reagent solution in shallow pans at room temperature for each cross-linked sample. The reagent composition was: CH_2O (paraformaldehyde) 5.5%, HCl 5.5%, CH_3COOH 72.9% and H_2O 16.1%. Proportions of 13.5 ml of solution/g of cotton (air dried) were used for all four samples, D-1 through D-4, and progressively higher levels of cross-linking were obtained by increasing the times of reaction as shown in Table 1. After thorough washing and air drying, the batches of fabric were cut into 1-in. squares and reduced to the particle size required for column packing by Wiley milling successively through the 20- and 60-mesh filter screens. Untreated fabric was milled similarly for the control sample, WM-6.

The bake-cure cross-linking reaction with formaldehyde was carried out as described by Fujimoto et al. (*6*) with 12 in. × 18 in. pieces of fabric which were padded with a solution of paraformaldehyde and magnesium chloride catalyst. In this case, progressively higher levels of cross-linking were obtained by increasing the concentration of the reagent solution while maintaining the ratio of $CH_2O:MgCl_2 \cdot 6H_2O$ at 3.75:1. All of the batches of fabric were padded to a wet pickup of approximately 130%. Drying and curing were effected in a single step, employing a forced draft oven preheated 175–178°C. Introduction of six fabric pieces, suspended to permit adequate circulation, reduced the temperature to 135–140°C. The temperature reached 161–163°C in 2 min and was maintained at this temperature for 3 min for curing. The treated fabrics were rinsed immediately in hot, running tap water,

TABLE 1

Gel Permeation Characteristics of Cotton Cross-Linked in the Acetic–Hydrochloric Acid Medium

Samples	Reaction time (min)	CH_2O (%)	Total internal H_2O (V_r)(ml/g)	Internal solvent volume (V_i)(ml/g)	V_i/V_r	Permeability limit (M_x) MW
WM-6	0	0	0.351	0.303	0.86	2830
D-1	5	0.49	0.344	0.291	0.85	1810
D-2	10	0.74	0.347	0.228	0.66	1400
D-3	15	0.81	0.239	0.206	0.86	1500
D-4	30	1.39	0.232	0.163	0.70	1180

followed by several rinses in distilled water, and finally by 15 min boiling to remove hemiformals and unreacted formaldehyde.

The samples of fabric were reduced to fine fiber particles by milling successively through the 20-, 60-, and 80-mesh screens in the Wiley mill. An untreated control sample, WM-13, was similarly prepared for packing the chromatographic column. A control sample, C-C, which was subjected to the bake-cure in the presence of the catalyst (no formaldehyde) was also included in this series. The paraformaldehyde concentrations of the padding solutions and the resulting formaldehyde contents of the fabrics, C-1 through C-4 are given in Table 2.

TABLE 2

Gel Permeation Characteristics of Cotton Cross-Linked in the Bake-Cure Process

Samples	Reagent concn CH_2O (%)	Sample CH_2O (%)	Total internal H_2O (V_r) (ml/g)	Internal solvent volume (V_i) (ml/g)	V_i/V_r	Permeability limit (M_x) MW
WM-13	0	0	0.334	0.289	0.87	2430
C-C	0	0	0.249	0.237	0.95	2130
C-1	2.5	0.47	0.231	0.170	0.74	1280
C-2	4.5	1.21	0.167	0.096	0.60	1120
C-3	6.0	1.47	0.152	0.069	0.45	1290
C-4	7.5	2.20	0.107	0.047	0.44	1280

Gel Permeation Chromatographic Measurements

Details of the instrumentation, of the packing of sample columns, and of the techniques for making the gel permeation measurements have been described previously (*7*). Adaptation of the method for the study of chopped fibrous cotton also has been reported (*3*). The sugars used as solutes were glucose monohydrate, maltose monohydrate, raffinose pentahydrate, and stachyose tetrahydrate; they covered the range of molecular weight from 198 to 738. Relative peak elution volumes were determined with reference to the column void volumes measured by dextran of molecular weight $\bar{M}_w = 10{,}000$. The dextran and each of the four sugars were eluted individually at intervals sufficiently spaced to prevent overlapping of the elution peaks. They were injected from a sample loop of 0.25 ml volume as 4% solutions (solutions containing 40 mg/ml). Elution with distilled water was carried out at a linear flow rate of approximately 3 cm/hr. The inverse linear relationship of peak elution volumes to molecular weights of the characteristic hydrates of these sugars was found to apply in chromatography of the samples of cotton investigated in these experiments.

RESULTS

Data obtained by the successive elution of dextran and each of the four sugars from columns containing cottons cross-linked by the bake-cure process are presented in Fig. 1, together with results of measurements of an uncross-linked control sample, WM-13. The spread of triplicate measurements with each of the four sugars on each sample

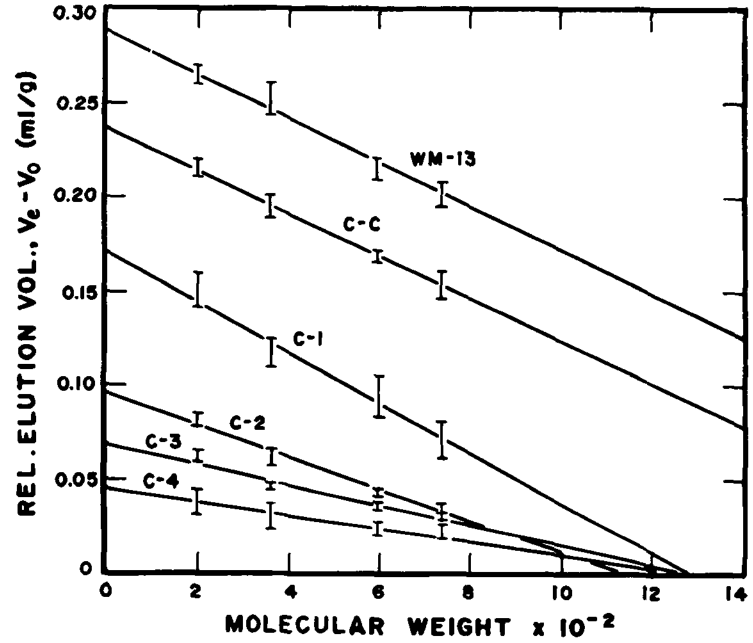

FIG. 1. Relationship of relative elution volumes to molecular weights of the hydrates of glucose (198), maltose (360), raffinose (594), and stachyose (738) for the bake-cure cross-linked cottons, C-1 to C-4, for uncross-linked sample, C-C, and for unmodified cotton sample, WM-13. Bars show spread of triplicate measurements of the specific elution volumes of the four sugars, relative to the void volumes, V_0, measured by dextran, on each of the cellulose sample columns.

column shows the reproducibility of determinations of these volumes. The lines are plotted from the best fit by least squares of the combined data for each sample to an inverse linear equation relating relative elution volumes to molecular weights. Comparable results were obtained from the samples of cotton cross-linked in the acetic–hydrochloric acid medium.

The volume occupied by the water-swollen fibrous cotton particles is readily calculated (on a specific basis) from the difference between the known total column volume occupied by sample material and the void volume measured by the peak elution volume of dextran. It is assumed that the molecular chains of cellulose forming the "gel" have the specific volume 0.629 which is calculated from the dimensions of the unit cell of crystalline cellulose (*8*). Substracting this value from the specific gel volume yields the total internal water content, V_r, given in the fourth columns of Tables 1 and 2.

Extrapolation of the chromatographic measurements relating relative elution volumes to molecular weights (e.g., see Fig. 1) provides values for the specific internal solvent volume of the cellulose, V_i (at zero molecular weight), and the limit of permeability in terms of molecular weight, M_x (at zero relative elution volume). Changes in these parameters with increasing modification of the cellulose structure by cross-linking reveal the nature of alterations of the supramolecular structure and internal pore volume distributions produced by cross-linking under the two different reaction conditions.

Cotton Cross-linked in the Acetic–Hydrochloric Acid Medium

The relation of the internal volumes and permeability limits to the levels of cross-linking carried out in the acetic–hydrochloric acid medium are shown graphically in Fig. 2. Under these conditions, there is a progressive elimination of larger pores, i.e., a reduction of the size of internal spaces available to larger solutes. This is shown by the continuing decrease of the permeability limit, M_x, with increasing formaldehyde content of the cotton samples. Little reduction of the internal volumes, either total water content, V_r, or effective solvent water, V_i, occurs until a formaldehyde content of 0.6% is reached. At a formaldehyde content of 0.7% both of these volumes decreased markedly and tended to level off. There is not much more reduction in V_r or V_i up to a formaldehyde content of 1.4%. Since these samples were prepared by reaction for periods of time ranging from 5 to 30

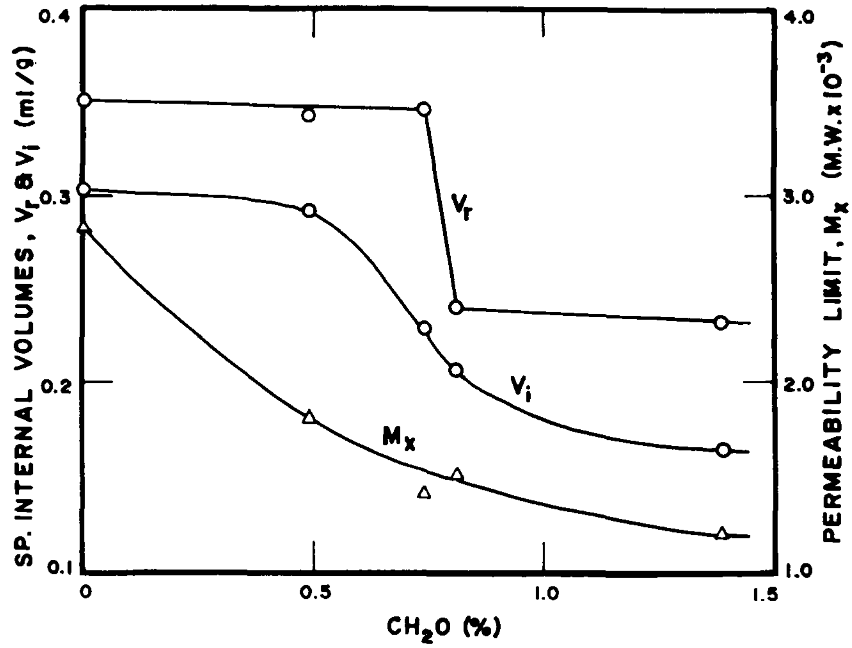

FIG. 2. Changes produced in the specific internal volumes, V_r and V_i, and in the permeability limit, M_x, of fibrous cotton by acetic-hydrochloric acid cross-linking to progressively higher levels of CH_2O content.

min, the marked decreases of the internal pore volumes above 0.6% formaldehyde content are a function of the time of exposure to the medium as well as to the progressively increasing extent of cross-linking.

Cotton Cross-linked in the Bake-Cure Process

Reduction of the values of the gel permeation parameters relative to the percentages of formaldehyde introduced by the bake-cure reaction conditions are shown in Fig. 3. These changes are not a function of reaction time, as all of the samples were cured for the same length of time under the same conditions. As higher percentages of formaldehyde are introduced, there is a progressive and uniform decrease of the total internal water content, V_r, and a roughly parallel reduction of the effective internal solvent volume, V_i. This set of reaction conditions produces a striking change in the permeability

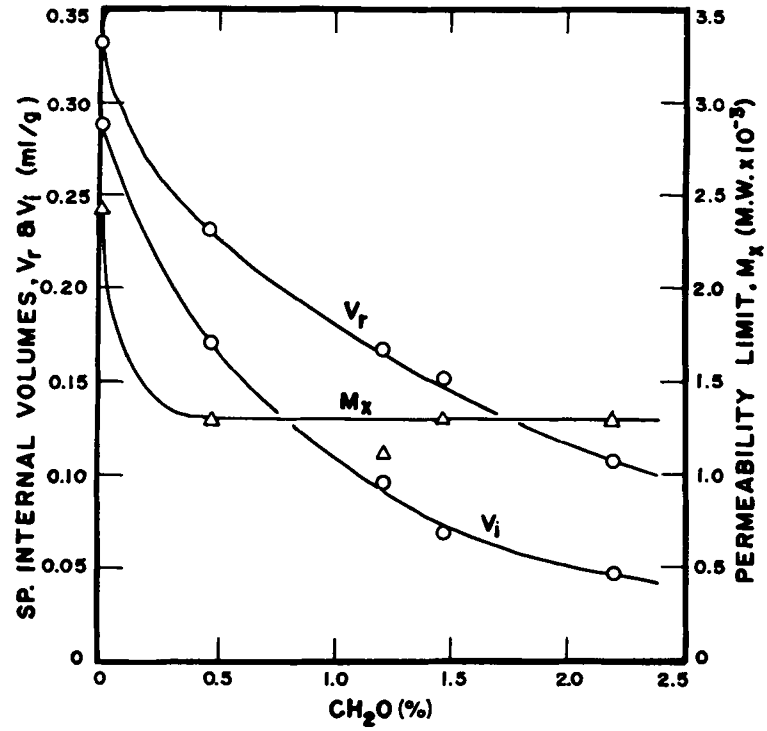

FIG. 3. Changes produced in the specific internal volumes, V_r and V_i, and in the permeability limit, M_x, of fibrous cotton by cross-linking to progressively higher levels of CH_2O content in the bake-cure acid medium.

limit, M_x; this parameter is reduced to half of the value found for untreated cotton at the lowest level of formaldehyde examined in these compositions. As cross-linking proceeds to higher levels of formaldehyde, the permeability limit remains essentially constant (to formaldehyde contents of 2.2%). These changes of the supramolecular structure of the cotton cellulose polymer as a result of cross-linking of fibers in the collapsed state are in marked contrast to those shown in Fig. 2 for comparable levels of cross-linking of the fibers in a semidistended state.

DISCUSSION

The pattern of changes in gel permeation parameters illustrated in Figs. 2 and 3 are indicative of different behavior of the cellulose and perhaps the introduction of different reagent residues during cross-linking of the cellulose polymer under the two sets of reaction conditions. In the acetic–hydrochloric acid medium, formaldehyde reacts with accessible hydroxyl groups on surfaces of the larger pores, progressively reducing the permeability limit of the cellulose. Since there is little reduction of the internal volumes, V_r and V_i, up to about 0.6% formaldehyde content, cross-links must be entering in such a manner that large pores are subdivided or that spaces between surfaces of large pores are progressively reduced. Beyond this level of reaction, the structure appears to undergo a rather rapid transition either as the result of cross-linking of the microfibrillar units or the effect of the reagent solution in collapsing the structure after reaction for 5–10 min. In the earlier stages of reaction, there is a redistribution of pore sizes with little decrease in the total internal pore volume. When sufficient cross-linking has occurred to cause a large decrease in the internal volumes, rapid reduction in the volume distributed in small pores occurs as there is only small additional diminution of the limit of permeability.

The marked difference in the progress of alteration of the pore structure of cotton with progressive cross-linking by the bake-cure process is illustrated by the data presented in Fig. 3. In this case there is a uniform decrease in the internal volumes, V_r and V_i, as the percentage of formaldehyde increases. On the other hand, the reduction of the permeability limit occurs in the very early stages of the cross-linking. All of the decrease does not occur as a result of collapse of the cellulose polymer structure by heating and drying, as shown by the relatively small change in this parameter from the control sample, C-C, which was subjected to curing with the catalyst alone. The limit of permeability is reduced to approximately half the value found for untreated cotton at some percentage of formaldehyde equal to or less than 0.47%. With progressively higher levels of cross-linking, the limit of permeability remains essentially unaltered, while both the total internal water content and the effective internal solvent volume are reduced progressively. These results indicate that half of the internal volume comprised of large pores is eliminated by the heating and drying and a minimal level of formaldehyde, which fixes the value of the permeability limit. Further reaction proceeds randomly in the pores and there is no selectivity of the reduction of volume composed of small pores by the cross-linking process. While the internal pore volumes decrease progressively, the distribution of pore sizes within this internal volume remains unaltered. This is true of the pores of sizes accessible to solutes such as the sugars, constituting the effective internal solvent volume. It is also true of the total internal water content which includes pores accessible only to water, i.e., pores too small to accommodate molecules of the nature of the solutes used.

The results of these experiments demonstrate that the gel permeation technique provides detailed information for characterizing pore structure of cotton cellulose and changes in pore structure of cotton cellulose; this information is not obtainable from other methods of measurement such as water of imbibition. Water of imbibition measures only the total water content in and on and between the particles of water-swollen cellulose. The values obtained by water of imbibition are high by comparison with chromatographic determinations of total internal water content, V_r (*3*). The gel permeation method is expected to provide a means of developing a better understanding of changes in the supramolecular structure of cotton. It is expected also to provide a means for investigating the dependence of physical and performance properties of modified cottons upon the nature of the supramolecular structure and its alteration by chemical treatment.

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