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Swelling Characteristics of Gel Fractions of Formaldehyde-Modified Cotton Celluloses*

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Synopsis

A method for assessing extent of swelling of the gel fraction of formaldehyde-modified cottons, employing cupriethylenediamine hydroxide as the swelling agent, is described. Substantial differences in apparent specific volumes of swollen gel fractions are observed for cottons crosslinked by different processes to the same level of agent. The apparent crosslink density measured by the swelling of gel fraction increases with formaldehyde content of the cotton; at 0.20% formaldehyde the order of increasing crosslink density in the various processes of reaction is as follows: nonaqueous system (forms D and D′) < aqueous system (forms W and W′) < swelling system (form F) < vapor system (form V) < bake–cure system (form C).

INTRODUCTION

In preceding studies it has been shown that cotton cellulose crosslinked with formaldehyde under a variety of conditions differs markedly in number of effective elastic units,[1] in heterogeneity of distribution of crosslinks,[2] and in extent of accumulation of agent per accessible hydroxyl group.[2] In view of the many complications in the network structures of fibrous cotton cellulose, it is essential to obtain additional characterizations of these structures.

One of the best techniques for characterizing network structures involves swelling the crosslinked polymer in a liquid which is a solvent for the uncrosslinked material. Under these conditions, uncrosslinked polymer will dissolve, and the crosslinked portion will swell until the osmotic forces of dissolution are balanced by elastic forces of the stretched segments of the crosslinked chains.[3] Thus, simple swelling measurements can be employed for estimates of crosslink densities. While the degree of swelling of crosslinked elastomers provides an inverse measure of crosslink density, the numerous differences between amorphous, homogeneously crosslinked elastomers and semicrystalline, heterogeneously crosslinked cotton cellu-

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loses, have complicated the application of this approach to crosslinked cotton celluloses. The fibrous nature of cotton has added further complications to meaningful measurements of swelling.

In view of the recent development of a simple, reliable technique for determining sol and gel fractions of chemically modified cottons,[4] we were encouraged to investigate the swelling of various crosslinked cottons in a cellulose solvent. This paper describes a method for measuring and assigning an empirical numerical value, designated distention index, to the swelling characteristics of formaldehyde-crosslinked cottons in cupriethylenediamine hydroxide (cuene). Interrelationships among the amount of crosslinking agent, the gel fraction, and distention index (i.e., apparent specific volume of gel fraction in cuene) have been studied for cotton fabric crosslinked with formaldehyde under a variety of conditions of reaction.

EXPERIMENTAL

Materials and Reagents

The cotton cellulose employed as a starting material was the conventional desized, scoured, bleached 80 × 80 print cloth weighing approximately 3.5 oz./sq. yd. The cotton fabric was crosslinked with formaldehyde by 5 different processes (designated forms C, D, F, V, and W) which produce fabrics having generally different combinations of physical performance properties.[5–9] Each treatment was conducted to yield a series of samples having increasing formaldehyde contents.

Form W cotton was produced in an aqueous system[9] consisting of 7.6% formaldehyde, 12.2% hydrochloric acid, 2.2% methanol, and 78.0% water. The product is representative of crosslinking in a system in which the cotton is in a swollen condition. This type of reaction develops wet wrinkle recovery with little or no increase in dry wrinkle recovery.

Form W′ cotton was also produced in an aqueous system; this consisted of 16.0% formaldehyde, 14.6% hydrochloric acid, and 69.4% water. Performance of form W′ cotton is generally similar to that of form W cotton, less change occurring per unit of agent in the former case. It has been proposed by Guthrie[10] that longer crosslinks (and, therefore, at a specific level of formaldehyde, fewer crosslinks) may be introduced into cotton as the concentration of formaldehyde is increased in the reagent bath.

Form D and form D′ cottons were produced in acetic acid systems;[6] the reagent for form D cotton consisted of 5.5% formaldehyde, 5.5% hydrochloric acid, 71.3% acetic acid, 1.6% methanol, and 16.1% water and the form D′ reagent contained 9.8% formaldehyde, 6.6% hydrochloric acid, 66.0% acetic acid, and 17.6% water. Form D cotton is characterized by substantial increases in both wet and dry wrinkle recoveries over the original cotton.

Form F cotton was prepared by reaction with formaldehyde in a formic acid solution consisting of 8.6% formaldehyde, 90.0% formic acid, and 1.4% water.[7] Formic acid is indicated to be a stronger swelling agent than water for cotton;[11] therefore, this medium is expected to represent crosslinking under the highest degree of swelling in this series. This treated fabric exhibits increased wet wrinkle recovery with little increase in dry wrinkle recovery over that of the original cotton.

Form V cotton was prepared by treating the fabric, containing ambient moisture, in an atmosphere of formaldehyde–hydrochloric acid vapors.[10] Form V cotton fabric exhibits high levels of wet and dry wrinkle recoveries.

Form C cotton was prepared by the pad-dry-cure process;[5] in this series of samples, the fabric was padded to approximately 100% wet pickup in aqueous reagent baths consisting of formaldehyde (1.0–7.5% concentration) and magnesium chloride (0.2–0.5% concentration). The cure was conducted in an oven at 180°C. for 1 min. The fabrics exhibited high wet and dry wrinkle recoveries, generally approaching those of form V cotton. Each of the fabrics described above was subjected to conventional laundering, rinsing in hot water, and/or treating with dilute alkali prior to our studies.

The stock solution of cuene which was employed for measurements of sol and gel fractions and for distention indices was 1*M* in copper and 2*M* in amine.[12] In conjugation with this cuene solution, a 0.04% solution of Aerosol OT was used as a wetting agent for the cotton and as basis for dilution of the cuene to 0.5*M*.

Methods

Sol fraction was measured by the method described by Bullock et al.[4] and gel fraction was obtained by difference. Gel fractions of some samples of formaldehyde-modified cotton celluloses (especially those having gel fractions above 0.95) were checked by isolation and gravimetric determination of the insoluble material.

The distention index (DI, i.e., the apparent specific volume of the cuene-insoluble fraction of the formaldehyde-modified cotton) was determined by the following procedure which evolved as the result of various exploratory trials. Fabric was ground in a Wiley mill to pass a 20-mesh screen and samples weighing between 30 and 100 mg. (dried 2 hr. at 105°C.) were transferred to centrifuge tubes which were API-ASTM 100-ml. oil centrifuge tubes modified to 50-ml. capacity and to introduce threaded necks for plastic screw cap closures. The air space in each tube was filled with nitrogen by applying vacuum and nitrogen alternately several times. A 20-ml. portion of 0.04% solution of Aerosol OT was added to the ground sample in each tube and each tube was shaken to wet and disperse the sample. Then 20.0 ml. of 1*M* cuene was introduced into each tube to produce a cuene solution of 0.5*M* concentration, and the tube was shaken again thoroughly. Each tube was placed on a shaking machine and subjected to agitation for an overnight period; since cuene is sensitive to light, the contents of the tube were shielded from light by a black paper cover. At the end of this period, each tube was centrifuged for 50 min. at 2000 rpm, the tube was rotated in the centrifuge cup 180° on its axis, and centrifuging was continued for another 50-min. period. In the course of numerous operations which employed shorter and longer periods of centrifuging, it was established that this sequence of operations was adequate to reach a minimum or stable volume of swollen gel and to develop a horizontal interface between the swollen gel and the cuene solution. The volume of swollen gel in the lower, constant-diameter portion of the tube was recorded. The interface between the gel and solvent may be accentuated by addition of a little mercuric oxide which settles rapidly and marks the top of the gel with a contrasting color.

Distention index (DI) is calculated as follows:

$$\mathrm{DI} = V_g/W_g = V_g/(C_0G).$$

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

RESULTS

Gel fraction and distention index (DI) data are summarized in Table I for seven series of formaldehyde-crosslinked cottons at varying levels of agent. It is evident from examination of data for any single process of introduction of formaldehyde that DI decreases regularly throughout the course of the reaction and that DI is a function of gel fraction and formaldehyde content. The interdependencies in the case of the form W cotton are illustrated in an isometric drawing in Figure 1. The projection of the three-dimensional curve to the left face of the block shows the inverse and almost linear relationship between DI and gel fraction. Since the elastic retractive forces which counteract complete expansion (and dissolution) during the swelling process are inversely proportional to the molecular weight of po'ymer between points of crosslinking, the decrease in swelling with progressive reaction in the form W process is evidence of increasing number of crosslinks. Thus, it is apparent that both gel fraction and number of crosslinks in the gel fraction increase throughout the course of the form W process of crosslinking.

The differences in relationship between DI and gel fraction for the cottons crosslinked by various processes are shown in Figure 2. For each process a specific, but generally linear, relationship develops. The linear relationship is consistent with, and perhaps a confirmation of, the control of amount of gel and the density of crosslinks in the gel by the same factor, i.e., diffusion. While the large differences in DI at a specific level of gel fraction are interesting, it is perhaps most important to consider the near convergence of lines in the lower right corner of Figure 2 as an indication of the differing courses by which the various processes approach the same ultimate product. Yet, complete convergence is not realized at a gel fraction of 1.0; as additional crosslinks are introduced there is still a decrease in DI which differs in extent for the individual processes.

Extent of swelling, as measured by DI, in these crosslinked cottons decreases throughout the course of incorporation of the crosslinking agent, but most notably in the initial stage of each specific process of reaction. This is

TABLE I
Chemical and Physical Measurements of Crosslinking

Fabric	Formaldehyde content, %	Gel fraction	Distention index, ml./g.	
			Individual values	Average
Form W	0.05	0.647	54.9–61.1	58.1
	0.08	0.829	35.9,30.9	33.4
	0.14	0.910	21.9,22.8	22.4
	0.20	0.940	21.2,19.6	20.4
	0.27	0.985	17.6,18.0	17.8
	0.34	0.990	17.9,16.4	17.2
Form W′	0.11	0.973	23.3,23.2	23.2
	0.32	0.985	16.6 17.5	17.0
	0.76	0.992	13.9,15.0	14.4
	1.09	1.000	13.1,13.4	13.3
Form D	0.17	0.386	28.2,33.5	30.9
	0.30	0.714	19.4,22.0[a]	20.5
	0.59	0.875	17.1,17.3	17.2
	0.84	0.911	14.7,15.2	15.0
	1.22	0.992	13.4,13.8	13.6
	1.90	0.985	14.2–12.1[a]	13.4
	2.09	0.987	9.6, 9.7	9.6
Form D′	0.21	0.302	33.3,32.7	33.0
	0.40	0.408	25.9,24.3	25.1
	0.63	0.571	21.3 23.3	22.3
	1.04	0.681	17.8,16.9	17.4
	1.44	0.792	13.8,14.6	14.2
	2.08	0.912	11.6,10.6	11.1
Form F	0.08	0.853	24.8,24.4	24.6
	0.34	1.000	14.8,15.4	15.1
	0.86	1.000	15.0,14.9	15.0
	1.16	1.000	14.6,14.7	14.6
	1.44	1.000	13.8,12.1	13.0
	1.69	1.000	12.6,12.7	12.7
Form V	0.06	0.848	22.6,22.1	22.3
	0.14	0.980	15.4,17.0	16.2
	0.44	1.000	14.3,15.5	14.9
	0.58	1.000	17.0–12.9[a]	14.7
	0.76	1.000	15.1,15.5	15.3
Form C	0.09	0.887	20.4 20.8	20.6
	0.18	0.926	15.2,14.5	14.9
	1.05	0.970	12.5,12.1	12.3
	1.90	0.973	8.6, 8.9	8.8

[a] These represent maximum and minimum values which were obtained. Additional values were employed in determining the average.

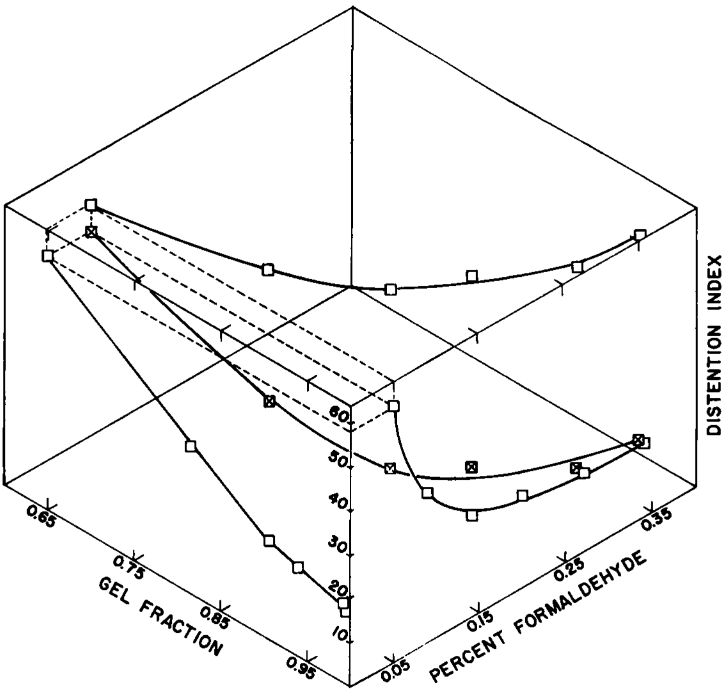

Fig. 1. Three-dimensional relationship of distention index to formaldehyde content and gel fraction of cotton crosslinked by the form W process; (⊠) three-dimensional curve; (□) projections of this onto planes of the cube.

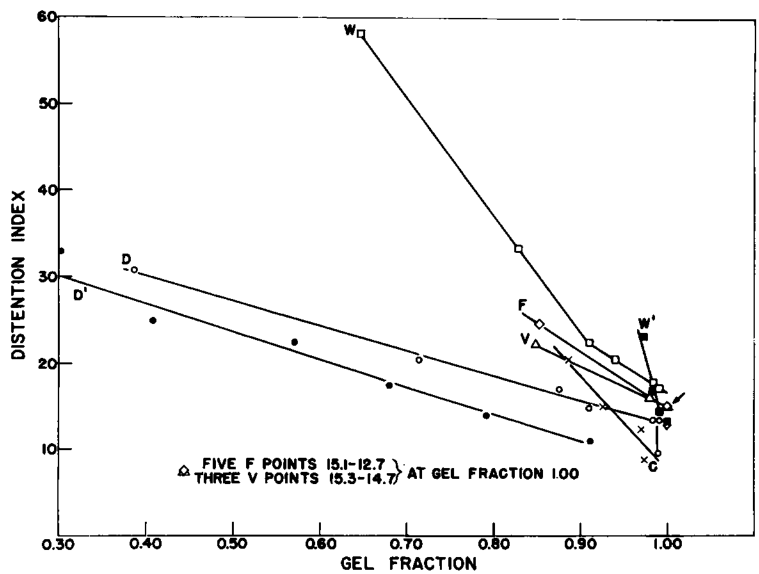

Fig. 2. Distention index as a function of gel fraction for various processes of crosslinking cotton with formaldehyde. (■) form W′; (□) form W; (◊) form F; (Δ) form V; (O) form D; (●) form D′; (×) form C.

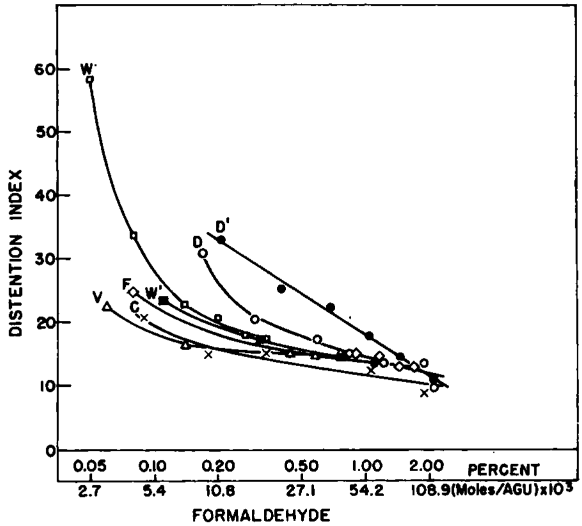

Fig. 3. Distention index as a function of formaldehyde content of the crosslinked cotton. Designations are the same as those in Fig. 2.

illustrated on the right face of the block of Figure 1 for form W cotton and in Figure 3 for all of the materials investigated. Below formaldehyde contents of 0.5% there is considerable divergence among the curves representing the various processes of reaction. At higher levels of formaldehyde

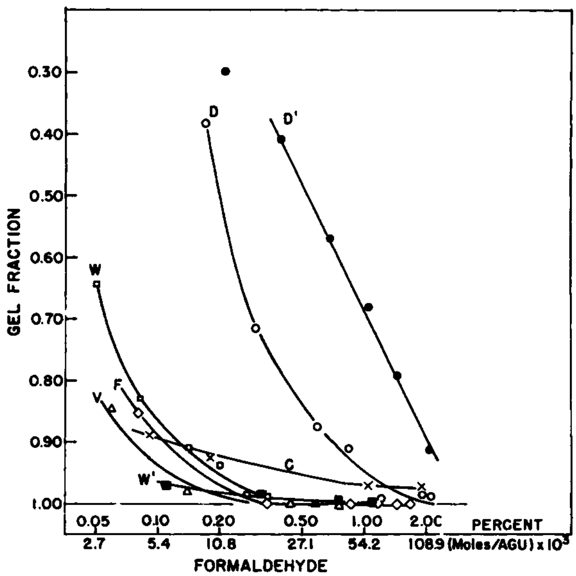

Fig. 4. Relationship of gel fraction of crosslinked cotton to formaldehyde content of the total sample. Designations are the same as those of Fig. 2.

there is a tendency toward convergence; yet, even at the highest levels of agent, there are distinct and reproducible differences among the DI values.

In proceeding toward more detailed comparisons, it must be emphasized that density of crosslinks in the gel fraction only is under consideration on the basis of the relationships presented here. For those compositions for which the gel fraction has reached 0.95 at the particular level of comparison, there is little alteration of conclusions from consideration of gel fraction or total composition. The relationship between gel fraction and formaldehyde content is shown in Figure 4. This figure is essentially a projection of the three-dimensional plot illustrated in Figure 1 to the upper face of the block. A semilogarithmic plot is used in Figure 4 to cover the wide range of formaldehyde content.

DISCUSSION

At a 0.20% level of formaldehyde in the total fabric, increasing order of crosslink density in the gel fraction is indicated by DI as follows: form D′ < form D < form W ⩽ form W′ < form F < form V ⩽ form C. The order which Rowland and Post[1] found for increasing number of effective elastic elements in these crosslinked cottons at the same level of formaldehyde was form D′ < form D < form W < form C < form V < form W′. Except for the positions of forms C and W′ cottons in these series, the orders of apparent crosslink densities in the gels from DI measurements and numbers of effective elastic units in the total composition from sol-gel analysis are the same.

The consistently higher level of swelling observed for the gel from the form D′ cotton (prepared with a reagent system having higher concentration of formaldehyde) compared to form D cotton suggests that the former is characterized by fewer and longer crosslinks, as has been suggested by Guthrie[10] to occur as a result of high concentration of formaldehyde in a reagent system. On the other hand, there is no evidence for this type of difference between the form W′ and form W cottons, since DI is actually slightly lower for the former. This latter difference is consistent with the higher efficiency of formaldehyde for insolubilizing all the molecular species in the form W′ process.

If the only difference between the form F and form W (or form W′) processes were the degree of swelling during the process of crosslinking, the high swelling activity of formic acid would provide basis for expecting higher DI values for the form F cotton at the same levels of agent. Actually, form F cotton exhibits slightly, but significantly, lower DI values than form W (or form W′) cotton; thus, the factors accounting for differences between these cottons may be distributions or structures of crosslinks.

The swelling which has been measured in terms of DI may be considered to be the sum of DI values which are representative of several regions of the fiber. Thus the total swelling (DI_{Σ}) is the sum of the components from the crystalline regions (DI_c) and from the noncrystalline regions (DI_{nc}); however, the noncrystalline region is not wholly accessible and very likely the extent of accessibility varies with the reagent system. Upon treatment with formaldehyde, the accessible region of the cotton becomes the crosslinked region which responds in swelling (DI_x) according to the crosslink density and distribution of crosslinks; the nonaccessible portion (DI_{na}) of the noncrystalline region responds in swelling according to its peculiar features.

$$DI_{\Sigma} = DI_c + DI_{na} + DI_x$$

Since the swelling values which have been evaluated in the preceding discussion are DI_{Σ}, it is apparent that they are reflections of the amount of swelling of the accessible region (restricted by the density of crosslinks in this region) and that of the noncrosslinked regions ($DI_c + DI_{na}$). In order to obtain a more specific measure of density of crosslinks, it is essential to clarify DI_c and DI_{na} for each process or to eliminate these from consideration by study of a substrate which is completely accessible.

CONCLUSIONS

The gross effectiveness of crosslink development in formaldehyde-modified cottons can be evaluated by means of a measure of the extent of swelling of the gel fraction. The apparent crosslink density, as measured by distention index, varies characteristically for each of the different processes of introduction of formaldehyde into cotton. At 0.20% formaldehyde content of the total fabric, the increasing order of apparent crosslink density in the gel fractions is form D′ < form D < form W $\leqslant$ form W′ < form F < form V $\leqslant$ form C. Except for the positions of forms C and W′ cottons in this series, this order agrees with that obtained by sol-gel analysis by Rowland and Post. Such differences appear to be reflections of different accessibilities, substantially different states of swelling at the time of crosslink development, and different structures (numbers) of formaldehyde units in crosslinks (intra versus inter).

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Résumé

On décrit une méthode pour évaluer le degré de gonflement de fractions gelifiées de coton modifié au formaldéhyde, en employant l'hydroxyde de cupriéthylènediamine comme agent gonflant. Des différences substantielles de volume spécifique apparent des fractions de gel gonflé ont été observées pour des cotons pontés au même taux par divers processus. La densité apparente de pontage mesurée par gonflement de la fraction gelifiée croît avec la teneur en formaldéhyde du coton; à 0.2% de formaldéhyde, l'ordre de densité de pontage croissante au cours des divers processus se présente comme suit: système non-aqueux (formes D et D') < systéme aqueux (forme W et W') < système gonflant (forme F) < système vapeur (forme V) < système recuit (forme C).

Zusammenfassung

Eine Methode zur Ermittlung des Quellungsausmasses der Gelfraktion von formaldehyd-modifizierter Baumwolle mit Kupferhydroxd-Äthylendiamin als Quellungsmittel wird beschrieben. Es werden wesentliche Unterschiede im scheinbaren spezifischen Volumen der gequollenen Gelfraktionen an nach verschiedenen Verfahren mit gleichen Vernetzungsmittelgehalt vernetzten Baumwollen beobachtet. Die durch die Quellung der Gelfraktion gemessene scheinbare Vernetzungsdichte nimmt mit dem Formaldehydgehalt der Baumwolle zu; bei 0,20% Formaldehyd besteht folgende Reihenfolge zunehmen der Vernetzungsdichte bei den verschiedenen Reaktionsverfahren: nichtwässirges System (Form D und D') < wässriges System (Form W und W') < Quellungssystem (Form F) < Dampfsystem (Form V) < Backhärtungssystem (Form C).

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