Swelling and Mechanical Properties of Cellulose Hydrogels. I. Preparation, Characterization, and Swelling Behavior

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Synopsis

Cellulose hydrogels have been synthesized by reacting solutions of cellulose xanthate with different amounts of epichlorohydrin (0–24% w/w on cellulose) after which the cellulose was regenerated. The weight fraction of crystalline cellulose, determined by density measurements, decreases with the extent of chemical crosslinking and was estimated to vary between 30 and 42% for dry gels. The degree of equilibrium swelling in water of the prepared hydrogels varied between 3.05 and 6.33 g water/g dry gel (g/g). The degree of swelling decreases with increasing chemical crosslinking. As a result of the irreversible changes occurring during drying, the degree of swelling in water can be reduced down to 0.74 g/g. According to density gradient column measurements, the partial specific volume of water is 0.865 cm^3/g at water contents below 0.13 g/g. It is suggested that water having this partial specific volume is the specific hydration water. At higher water contents, the partial specific volume of gel water equals the specific volume of bulk water. It is implicit in the interpretation of the density data in terms of a two state model of gel water that the crystallinity of cellulose is independent of the water content. Depending on the degree of swelling, heat treatment resulted in either an irreversible increase or decrease of the degree of swelling.

INTRODUCTION

Cellulose is the predominant structural constituent in the cell walls of higher plants and is the most abundant natural polymer. The strength and toughness of cellulose is utilized in a number of materials such as paper, lumber, cotton fabrics, rayon, and regenerated cellulose films. The plasticizing action of water on these materials is of utmost technological importance since it may determine the limit of their usefulness as well as be a prerequisite for successful processing of cellulose, for instance, in papermaking.

In spite of the vast number of publications covering different aspects of the interaction between cellulose and water, few papers have been concerned with the physicochemical properties of highly water-swollen cellulose gels.

Depending on the method of preparation, cellulose hydrogels can display a wide range of structural features. Water can be present at a number of structural levels, from being adsorbed onto the cellulose chain to being present in cavities of colloidal dimensions.

A common feature of gel materials based on cellulose is their semicrystalline nature. Cellulose may crystallize in several polymorphic forms. Native cellulose is found in the cellulose I form, whereas regenerated cellulose usually crystallizes in the thermodynamically more stable cellulose II form.

The separation of cellulose into two distinct constituents, amorphous and crystalline cellulose, is probably a simplified description of the submicroscopic

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morphology.[1] Different methods used for the determination of the fraction of crystalline cellulose often yield different results and may serve only as relative measures of order. A distribution in size, shape, and degree of perfection of the crystalline regions therefore seems more likely. In regenerated cellulose, the transition zones between perfectly crystalline and perfectly amorphous regions are believed to be of particular importance[2] and the reported size of microfibrils is typically 40.0 nm in length and 6.0 nm in width.[3,4]

Water does not penetrate into the crystallites of cellulose I,[5,6] but a small amount of water is believed to penetrate into cellulose II crystals.[5,7,8]

In order to further elucidate the interaction between cellulose and water, the experimental investigations presented in this series of papers have been initiated. As a suitable material for the studies, isotropic cellulose hydrogels were synthesized from sodium cellulose xanthate. To vary the fraction of crystalline cellulose, chemical crosslinking with epichlorohydrin was adopted.

This paper reports the preparation, characterization, and swelling behavior of the hydrogels. In subsequent papers, the relation between rheological and swelling properties as well as the kinetics of water sorption will be discussed.

EXPERIMENTAL

Preparation

Chemical crosslinking was achieved by adding α-epichlorohydrin to an alkaline solution of sodium cellulose xanthate (viscose).[9] The xanthate groups then were removed by hydrolysis in acid solution (regeneration). Possible reaction paths for epichlorohydrin under alkaline conditions have been discussed by Hollinger et al.[10]

The data for the viscose used are given in Table I. The viscose was purified at about 5°C from by-products, mainly anionic sulphur compounds, by forcing it through an anion exchange resin[11] (Amberlite IRA-400) saturated with hydroxyl ions. The solution was then carefully deaerated under vacuum. Freshly distilled epichlorohydrin was added in a 1:1 mixture with isopropanol under stirring. The amount of epichlorohydrin added was varied between 0 and 24% by weight, based on dry cellulose. After another deaeration, the solution was carefully transferred to glass tubes with a diameter of 11 mm.

The crosslinking reaction was allowed to proceed in a nitrogen atmosphere for 14 h at 40°C, followed by 5 h at 60°C. The gels turned red and macrosyneresis occurred. The xanthogenation reaction is reversed under the prevailing conditions, which also allowed gels to be formed without the addition of epichlorohydrin. The gels were removed from the tubes and transferred to a large beaker for subsequent treatment.

By extensive washing with 2*M* NaOH for 2 h at 20°C and 48 h at 80°C under N_2, by-products formed by the regeneration and causing the red color were removed. The chemical modification due to crosslinking and the use of a nitrogen atmosphere reduces the risk of oxidative degradation of the cellulose. To further minimize this risk, reducing end-groups present in the cellulose were chemically reduced by reacting the gels with a 2*M* NaOH solution containing 0.1% (based on the amount of viscose) sodium borohydride at 20°C for 24 h. The washing

TABLE I
Data on the Viscose[a]

Cellulose source	Sulphite dissolving pulp from MoDoCell AB, Alfredshem, Sweden
Pulp data	
R18[b]	93%
Viscosity[c]	20.5 mPa s
Ethanol extract	0.18%
Ash	0.04%
Viscose data	
Cellulose content	8 ± 0.1% (on total)
NaOH, total	6 ± 0.1% (on total)
CS_2 (xanthation)	32% (on cellulose)
Berol Visco 385[d]	0.1% (on cellulose)
γ number[e]	55
DP[f]	350

[a] Percentage figures are given on a weight basis.
[b] According to SCAN-C 2:61.
[c] According to SCAN-C 15:62.
[d] Manufactured by Berol Kemi AB, Stenungsund, Sweden.
[e] According to Zellcheming-Merkblatt III-21-72.
[f] Degree of polymerization of cellulose chains; according to Zellcheming-Datenblatt B III-1-72.

procedure was finally ended by an additional treatment with 2*M* NaOH for 48 h at 20°C.

To complete the regeneration of the cellulose, the pH was lowered by soaking first in 0.1*M* NaOH for 24 h at room temperature and then in a 10% aqueous solution of acetic acid for 72 h at 4°C. Finally the gels were washed with deionized water for one week. Gels from batch B (see below) were also extracted with a 2% sodium sulphide solution for 96 h in order to remove residual sulphur present in its elementary form.[12] The gels were stored in water containing 0.02% sodium azide, in a refrigerator to prevent the samples from bacterial growth.

The synthesized gels had a diameter of approximately 10 mm and exhibited no visual irregularities. The slow regeneration procedure used is probably a prerequisite for homogeneity to be obtained.[13,14]

The gels prepared were designated, e.g., 5-B, the figure denoting the amount of epichlorohydrin added and the letter the preparation batch. Gel preparations were made on two occasions (A and B). Similar procedures and materials were used except for the sulphide treatment. Before use, the gels were washed with deionized water for 1 day and usually cut into 5-mm long pieces, weighing about 0.5 g, and to avoid skin effects, the gels were polished with a fine abrasive.

Characterization

The fraction of crystalline cellulose was estimated using three different methods: X-ray diffraction, density evaluation, and moisture sorption measurement.

X-ray diffraction tracings were recorded by means of a Philips diffractometer using Cu Kα radiation. The collimated beam was filtered by a Ni-foil to remove Kβ radiation. The transmission configuration was utilized.

To evaluate the tracings, the empirical method suggested by Segal et al.[15] was used. The crystallinity index (CrI) is accordingly determined by internal calibration and is defined (in weight percent[16]) as:

$$\mathrm{CrI} = \frac{I_{cr} - I_{am}}{I_{cr}} \times 100 \tag{1}$$

where I_{cr} is the height of the 002 peak ($2\theta = 21.7°$ in cellulose II[17]) and I_{am} is the corresponding value at the minimum between the $10\bar{1}$ and 101 peaks (between 13° and 15°[18]).

The gels studied were dried over P_2O_5 and care was taken to use dry gels of identical shape and mass.

Density measurements were made using two different methods: by the density gradient technique[19] and by weighing the gels in *n*-heptane or water.

Mixtures of carbon tetrachloride and toluene, both dried over anhydrous sodium sulphate, gave the desired range of densities. The column was calibrated with glass floats (five significant figures; Davenport Ltd., Welwyn Garden City, Herts., UK). The gradient never exceeded 0.2 g cm^{-3} m^{-1}, and was stable for weeks. The addition of swollen gels did not disturb the gradient. The temperature was kept at 23.0°C. The standard error of the density determinations by this method was estimated to be ±0.0002 g/cm^3.

The weight fraction of crystalline cellulose, X_c, in the dry samples was calculated from[16]

$$X_c = \frac{V_a - V}{V_a - V_c} \tag{2}$$

where V denotes the specific volume of the sample, and V_a and V_c the specific volumes of amorphous and crystalline cellulose, respectively. On the basis of the unit cell of cellulose II, a V_c value of 0.617 cm^3/g can be obtained.[20] A V_a value is harder to establish and the value 0.687 cm^3/g, which is the highest value available, was used. This value was taken from a work where it was determined by an extrapolation technique.[21] A direct determination is less advantageous owing to the difficulties encountered in the preparation of completely amorphous samples.[22]

Both completely and partially dried gels from batch B were studied by the density gradient method. Drying at a pressure of 8 Pa at room temperature for 10 days was needed in order to obtain constant density readings for dry gels. The dry content of partially dried gels was also determined by this drying procedure.

The gels were soaked in the denser liquid of the column before each measurement. Completely dried gels were soaked at reduced pressure.

It is assumed that liquids of the type chosen do not penetrate homogeneous cellulose materials.[5] Density values obtained for dry gels were also found to be independent of in which of the liquids the low-pressure soaking was performed.

Swollen samples lost some water (about 1% of the gel weight) in the column and the density values were matched with swelling levels determined after the measurements.

The densities of gels from batch A at 24°C were determined for dry gels by

weighing in dry *n*-heptane and for water-swollen samples by weighing in water. The swollen samples were in swelling equilibrium with liquid water.

The *moisture sorption* was measured by suspending about 25 mg (dry weight) of a gel sample on a quartz spring and measuring the change in length of the spring by means of a cathetometer. Different relative humidities (RH) were obtained by circulating the air surrounding the gel sample over saturated salt solutions. The moisture sorption at 65% RH was obtained by interpolation of data obtained at 23°C for the interval 11.3–90.5% RH.

According to Valentine,[6] the weight fraction of amorphous cellulose, $1 - X_c$, can be calculated from the relationship

$$1 - X_c = 0.38 \cdot \mathrm{SR} \tag{3}$$

where the sorption ratio (SR) is defined as the ratio of the moisture sorption of the sample studied to that of a cotton sample at a given RH value. At 65% RH, the moisture regain of cotton is 7.4% when equilibrium is approached from the dry side.[23]

The gels were dried with a flow of dry nitrogen before the measurements, and sorption values were always obtained during the adsorption cycle.

The *pore size distribution* of fully swollen, never-dried gels was characterized using the solute-exclusion method.[24] The gels were equilibrated with 1% solutions of dextrans (Pharmacia Fine Chemicals, Uppsala, Sweden) having different relative molecular masses ($10^4 - 2 \times 10^6$). The corresponding Stoke's radii for these polymers were taken from ref. 24. The amount of accessible gel water was calculated from the concentration change in the dextran solution utilizing a Knauer 2000 differential refractometer.

The surface characteristics of a gold-sputter-coated gel 5-A were studied by *scanning electron microscopy* (SEM). To retain the swollen structure, the gel was dried according to the critical point drying method.[25] The volume of the aerogel formed was observed to be about 50% lower than the original swollen volume.

Swelling Measurements

The gels were partially dried in desiccators at 20°C over saturated salt solutions. The degree of swelling is given as g water/g dry gel (abbreviated g/g). The degree of swelling expressed in these units is denoted Q in the following.

Dry gels were obtained by drying (unless otherwise stated) over P_2O_5 at room temperature. Swelling levels were determined by oven drying at 105°C to constant weight.

The effect on the swelling levels of heat treatment at temperatures in the range of 30–80°C was determined in equilibrium with liquid water by heating for periods of up to several days on a thermostated water bath. The degree of swelling was followed by withdrawing the gel, quickly blotting the surface with an absorbent paper, weighing the gel, and replacing it in the thermostated water.

It was noted that the swelling of the hydrogels was independent of pH and sodium chloride concentrations in the investigated intervals, 3–10 and up to 2M, respectively.

RESULTS AND DISCUSSION

Characterization

Table II gives the results of the *chemical analysis* of the gels. From Table II it is evident that the gels contain substantial amounts of sulphur if the added amount of epichlorohydrin is high. The sulphur content is only marginally lowered by the extraction with sodium sulphide. Thus, the sulphur is probably not present in its elementary form. Since the xanthate groups are powerful nucleophiles, they can compete with the cellulose hydroxyls for the epichlorohydrin. The increase in the amount of sulphur can then be explained by the formation of reaction products between xanthate groups and epichlorohydrin, which are resistent to acid hydrolysis. However, it can be expected that most of the epichlorohydrin attached to sulphur is removed during the hydrolysis.

As is usually found to be the case, the methods used for the determination of the *crystallinity* of the completely dried gels give different results. These are summarized in Table III where density and moisture sorption data are also given.

Figure 1 shows X-ray diffraction tracings for a series of gels differing in degree of chemical crosslinking. Addition of more epichlorohydrin during the preparation leads to a reduction in the diffraction peak intensity. No peak-broadening effects can be observed although peak overlap makes the change in width less clear. The calculated CrI values decrease somewhat with the amount of epichlorohydrin added (Table III). This crystallinity index does not give a quantitative estimate of the amount of crystalline material, but it is, however, useful for rating a series of samples with respect to their crystallinity.[17] A reduction

TABLE II
Chemical Analysis of the Cellulose Gels[a]

Gel	Sulphur content[b] (%)	
	Before Na_2S	After Na_2S
0-B	<0.02	0.03
2-A	0.06	—
2-B	0.08	0.06
5-A	0.36	—
5-B	0.67	0.61
10-A	1.26	—
10-B	2.19	2.07
20-A	4.41	—
24-B	6.81	6.58
5-A	Ash[c]	<0.1%
	Na[d]	420 ppm
	Fe[d]	25 ppm
	Cu[d]	10 ppm
	Ca[d]	15 ppm
	Acidic groups[e]	27 meqv/kg

[a] All figures are based on dry weight.

[b] From Schöniger combustion[26] followed by oxidation with H_2O_2 to SO_4^{2-}, which was determined by titration with Pb^{2+} using a Pb^{2+} sensitive ion electrode.

[c] From combustion at 600°C.

[d] From atomic absorption spectroscopy.

[e] According to the ion-exchange procedure recommended by Wilson.[27]

TABLE III
Weight Fraction of Crystalline Material in the Cellulose Gels as Determined from Density, Moisture Sorption, and X-Ray Diffraction Data[a]

Gel	X_c (%) Density	X_c (%) Moisture	CrI (%) X ray	Density (g/cm³)	Q (g/g) at 65% RH
0-B	41	34	67	1.5180	0.128
2-A	42	—	—	1.520	—
2-B	41	34	69	1.5179	0.128
5-A	39	—	—	1.515	—
5-B	41	29	67	1.5181	0.138
10-A	39	—	—	1.516	—
10-B	39	37	64	1.5148	0.123
20-A	34	—	—	1.508	—
24-B	30	41	59	1.5005	0.115

[a] Moisture sorption data and the densities of dry gels are also included.

in crystallinity is also expected as a result of the chemical crosslinking, because of the reduced tendency of a less regular structure to crystallize.

A quantitative figure for the crystallinity can be obtained from density values. The evaluation of crystallinity on the basis of density measurements is, however, complicated for gels crosslinked with epichlorohydrin because the density contribution from the crosslinks is not known. However, the values for the weight fraction of crystalline cellulose (X_c) computed on the basis of the density data follow the same trend as do the CrI values. It is only by virtue of this comparison

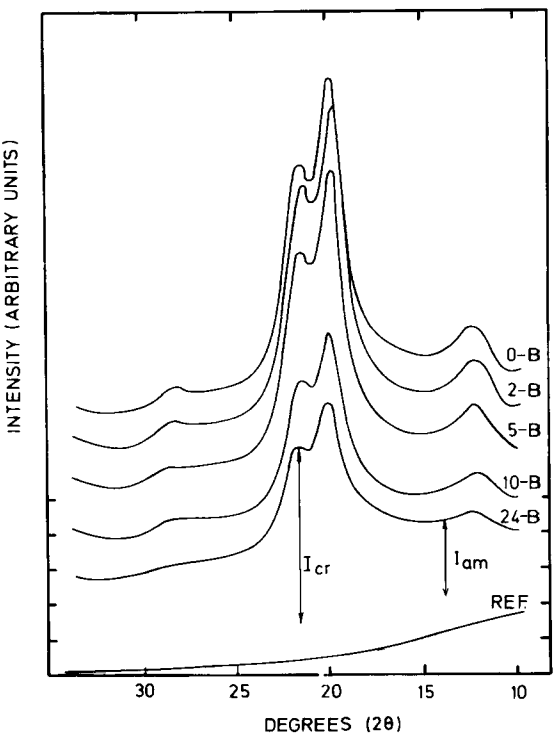

Fig. 1. X-ray diffraction tracings of dry cellulose gels from batch B. Note that the base line is shifted upwards for each curve. REF shows the result obtained in the absence of any sample.

that the use of X_c values from density data can be motivated for the more modified gels.

The X_c values calculated from the sorption ratio and eq. (3) were found to increase at high levels of epichlorohydrin addition. The X_c values are determined at 65% RH. The same pattern of variation between the gels is obtained irrespective of the RH value chosen. The result could be expected if crystallinity and/or crystallite size increases but this result is not supported by the X-ray diffraction data. Therefore it is suggested that the decrease in moisture sorption at higher levels of epichlorohydrin addition is due to a lower adsorption capacity of the (unknown) species formed from xanthate groups and epichlorohydrin.

The value of 1.5180 g/cm^3 for the density of the unmodified gel, type 0-B, and the X_c value of 41% calculated from this value compare well with literature data on density[5] and also on crystallinity values obtained from quantitative X-ray diffraction data on regenerated cellulose.[1]

Accordingly, the crystallinity values derived from density data are considered to be the best available estimates of crystallinity for samples dried from the water-swollen state at the present time.

Figure 2 shows the accessibility of gel water for different dextran molecules determined by the solute exclusion technique for never-dried gels from batch A. This is a measure of the *pore size distribution.* No significant difference can be discerned between the gel types. The fraction of water which is accessible to dextran molecules larger than 50.0 nm in diameter is high, ~20%. ~50% of the gel water is found to be present in pores having diameters exceeding 10.0 nm. These pores are here designated microvoids.

The heterogeneity of the pore structure is probably a result of separation of the gel and water phases during the crosslinking and regeneration reactions (microsyneresis[28]). The dispersion of pores in the gel matrix is stabilized by the formation of a gel network.

The swollen gel structure is best described as a three-phase system containing regions of high and low order as well as voids. This structural view of cellulose gels was also suggested by Beebe et al.[14] based on light scattering studies.

It was noted that gels formed by adding no epichlorohydrin or only a few

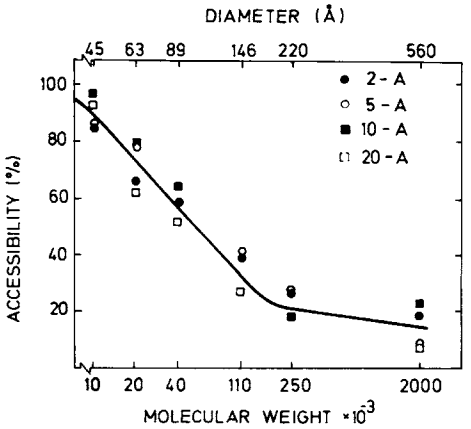

Fig. 2. Fraction of water in cellulose gels accessible to dextran molecules of different molecular weights (never-dried gels).

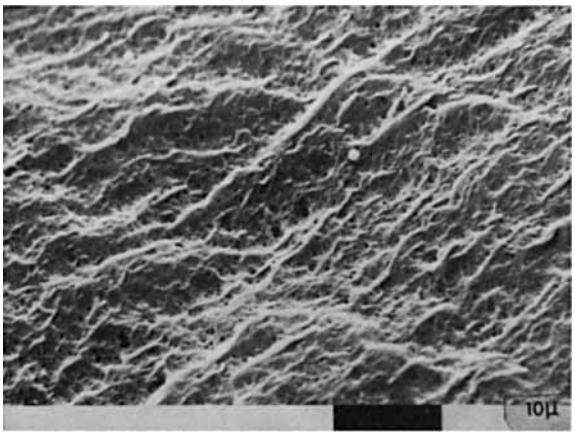

Fig. 3. SEM picture of the surface of a cellulose aero-gel 5-A. The black strip at the bottom represents 10 μm in the horizontal direction.

percent were only slightly opaque. The opacity increased with the level of epichlorohydrin addition. This difference between the gel types persisted even in the dry state. It has been found for cellulose hydrogels that the scattering of light is not due to fluctuations in the degree of crystallinity.[14] Thus the microvoids and sulphur-containing components are probably the main contributors to the turbidity of the chemically crosslinked gels.

Finally, the *SEM picture* of a dried gel (Fig. 3) also gives the impression of a heterogeneous structure. However, it is believed that the heterogeneity is overemphasized in this picture by the collapse of the structure during the critical point drying.

Swelling Behavior

The swelling levels of the prepared gels in equilibrium with water are shown in Figure 4 as a function of the amount of epichlorohydrin added. As expected, chemical crosslinking decreases the degree of swelling of the gels. As the crys-

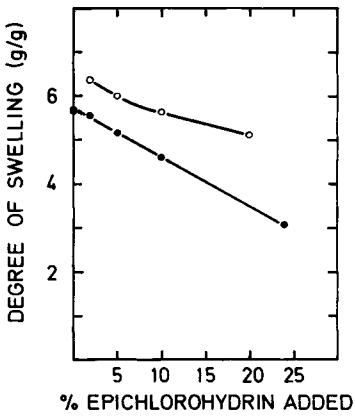

Fig. 4. Degree of swelling of never-dried cellulose gels as a function of the amount of epichlorohydrin added during preparation (○ batch A; ● batch B).

tallinity also decreases it must be concluded that shortening of network chains in the amorphous regions due to chemical crosslinking overshadows the effect of a decreased crystallinity. The gels from batch A are more swollen than gels from batch B. The reason for this may be a difference in the concentration of sodium cellulose xanthate in the viscose batches.

After the hydrogels have been dried to different extents, the equilibrium degree of swelling on reswelling in water can be reduced by as much as a factor of 8 (Fig. 5). The effect of partial drying to intermediate swelling levels is less pronounced, however. The first quantities of water leaving a gel most likely originate from the microvoids since that water will be retained only by capillary forces. Then it is not difficult to conceive that these partially collapsed microvoids can be reopened again, as total pore closure is presumably required in order to induce an irreversible change in the structure. When regenerated cellulose is completely dried, pores with sizes exceeding 4.0 nm in diameter are apparently eliminated in the reswollen structure.[29]

This irreversible swelling reduction, or hornification, resulting from the drying of cellulose is well-known and is of great importance in cellulose and paper technology. Haskell[30] interpreted the irreversible effect as being a result of the formation of new junctions between microfibrils. It was also pointed out that during the last stages of drying the junction point density increases rapidly.

The junctions formed during drying then will act as crosslinks in the structure and probably consists of hydrogen bonds between the cellulose chains. Some of the junctions formed will be stable during rewetting. It may be noted that once dried, the influence of the different degrees of chemical crosslinking on the degree of swelling of the gels is diminished, probably due to the dominance of other crosslinking effects.

However, another possibility is that the crystallinity increases during the

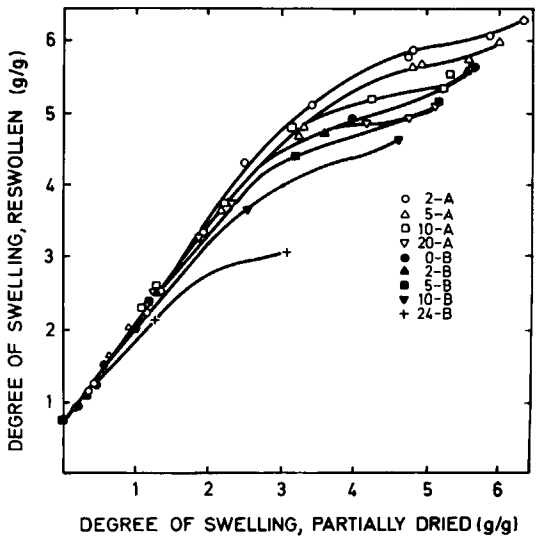

Fig. 5. Degree of swelling of a reswollen gel as a function of the degree of swelling after partial drying. All points refer to 20°C. The end points to the right of each curve denote the initial degree of swelling of the prepared gels before partial drying. The swelling of the reswollen gels is always lower than this initial level.

drying of cellulose. In order to investigate this alternative, the specific volume was determined for cellulose samples containing different amounts of water.

The standard way to determine the partial specific volume of the components in a binary mixture is to plot the volume per unit weight of the mixture versus the weight fraction of one of the components. The diagram shown in Figure 6 was constructed according to this well-known intercept method. Two linear regions can be discerned in Figure 6. The linearity implies that the partial specific volumes of the two components are constant throughout each region. The point of intersection is at a weight fraction of water of 0.116, which corresponds to 0.131 g/g. Cellulose containing this quantity of water mixes in an ideal way with both water and dry cellulose. From the intercepts a value for the partial specific volume of water of 0.865 cm^3/g is obtained at low water contents and a value of 1.001 cm^3/g at high water contents. The corresponding figures for cellulose are 0.659 and 0.642 cm^3/g, respectively.

The volume contraction occurring in the cellulose–water system has been known for a long time and has been ascribed to a contraction of the water[5,31] or to the presence of free space in cellulose.[32] If the mixing process is exothermic, as is found for cellulose–water,[33] negative volume changes are generally found.[34] For polymer–solvent mixtures, volume contraction due to mixing has been explained as resulting from a decrease in the available total hole free-volume.[35] Since the glass transition temperature of dry cellulose is about 220°C,[36] its hole free-volume is expected to be very low at 23–24°C. The decrease in volume on mixing is thus here interpreted as being due to a contraction of the water component, although it originates from the interaction between cellulose and water.

If the volume contraction is due to a contraction of the water component, the two values obtained for the partial specific volume of cellulose can be interpreted as follows. When 1 g of dry cellulose is added to a hypothetical large gel containing less than 0.131 g/g of water, the gel volume will increase by 0.659 cm^3.

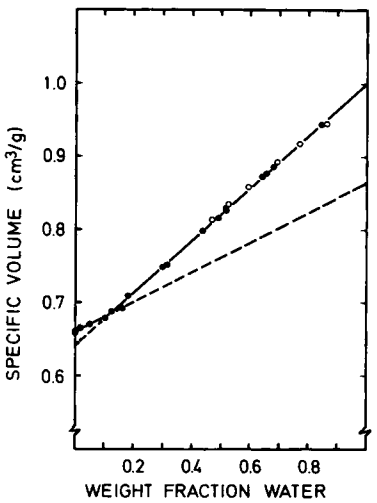

Fig. 6. Specific volume of gels 0-B (pure regenerated cellulose) at different water contents (●, 23.0°C). Each of the first two points to the left are based on three independent determinations. (○, corresponding values for gels 2-A at 24°C). The point of intersection of the straight lines as determined by least-square fits is at the weight fraction of water 0.116.

If the large gel initially contains more water than 0.131 g/g, the corresponding addition will again result in a volume increase of 0.659 cm^3. In addition, however, 0.131 g of water will become associated with the added cellulose and will change its specific volume from 1.001 to 0.865 cm^3/g. The net effect of adding 1 g of cellulose and the contraction of water is accordingly equal to the volume increase of 0.642 cm^3/g.

The linearity in the specific volume data above 0.131 g/g was analyzed by a least-square fit to a second-order polynomial. The change in the intercept of the tangent to this curve was found to be negligible over the concentration interval. This linearity supports the view that the overall crystallinity of cellulose (X_c) remains constant during dehydration since its inherent specific volume is constant. The effects of drying on the crystallinity of cellulose has been studied by several authors, but it is difficult to draw any definite conclusion from the papers published. The conflicting results reported may be due to two effects, which balance each other.[37] According to this view, amorphous regions may become more ordered while at the same time highly ordered regions are distorted during dehydration. Such structural changes may take place without changing the mean specific volume of the cellulose.

The value 0.131 g/g is in accordance with reported values for the amount of specific hydration water in cellulose at room temperature.[38,39] The point of completion of the first hydration layer is associated with a local minimum in the partial molar entropy of water.[33] If it is assumed that the cellulose hydrate I, $C_6H_{10}O_5 \cdot \frac{1}{3} H_2O$, is formed in the crystalline regions,[5,7,8] while the rest of the water is restricted to amorphous regions, an average of 1.8 water molecules are bound to each amorphous glucopyranose unit. Water present above this water content exhibits a partial specific volume almost identical to its bulk value, 1.002 cm^3/g at 23°C.[40]

It was found that when the temperature was increased, the degree of swelling of the gels slowly decreased with time, indicating that syneresis occurs. Figure 7 shows that the effect of such a heat treatment is partly irreversible.

The irreversible change in the degree of swelling during heat treatment is positive if the initial degree of swelling is low and negative if the swelling is high. The point of indifference towards heat treatments is at 3.2 g/g for heat treatment at 80°C and at 4.4 g/g at 30°C.

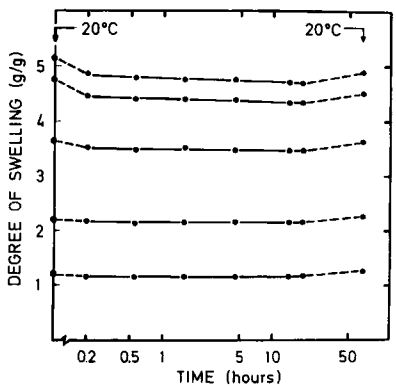

Fig. 7. Effect of heat treatment at 80°C on the degree of swelling of cellulose gels 5-B. The broken lines indicate transition periods between 20° and 80° and back to 20°C.

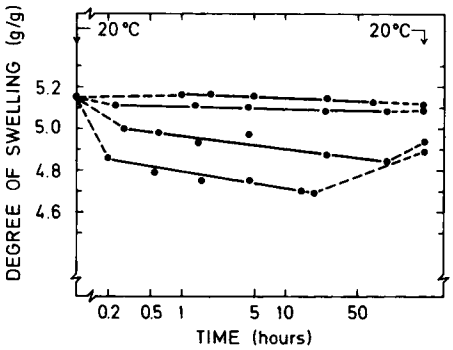

Fig. 8. Time dependence of the degree of swelling for never-dried cellulose gels 5-B at different temperatures (the upper curve at 20°C, followed by 30°, 55°, and 80°C).

Although the time dependence of the decrease in swelling level at the elevated temperature is negligible at the lowest swelling levels, the rate of syneresis, defined as $-dQ/d_{10} \log t$, increases with the degree of swelling.

Figure 8 shows the temperature dependence of the rate of syneresis for never-dried gels 5-B. The rate of syneresis increases at higher temperatures. The apparent activation energy for the syneresis process, calculated from this graph, was found to be 26 kJ/mol.

Presently it is only possible to speculate over the mechanisms yielding the irreversible effects observed after the heat treatments. However, it is interesting to notice that syneresis effects have been reported for a number of hydrogels, e.g., for alginate,[41] polyvinylalcohol,[42] vinyl copolymer,[28] and kraft lignin[43] gels. The mechanisms suggested include the formation of network junctions[41,43] or crystallites[42] and a transition from microsyneresis to macrosyneresis.[28]

The syneresis of the cellulose gels is not associated with any visual change in turbidity, suggesting that it is not due to a transition from microsyneresis to macrosyneresis. Furthermore, such a process cannot explain the irreversible increase in swelling as a result of heat treatment of gels with a low degree of swelling. It is known that the crystallinity of cellulose can be increased by annealing,[44] an effect which could produce the syneresis effects at high swelling levels, but again it is difficult to imagine how the swelling can increase at low swelling degrees. Thus it appears as though the results are best interpreted in terms of a thermally induced stress relaxation mechanism yielding rearrangements of network chains and bonds.

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