

Swelling and Mechanical Properties of Cellulose Hydrogels. II. The Relation between the Degree of Swelling and the Creep Compliance*

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Synopsis

The mechanical properties of swollen cellulose hydrogels have been studied. The degree of swelling of the gels was varied between 0.75 and 6.3 g water/g dry gel (g/g) by partial drying followed by re-swelling in water. Creep rate was measured in uniaxial compression in the time interval 15–900 s for gels in equilibrium with water. Isochronous relations between stress and reversible strain were found to be linear, and creep compliance was calculated from the slopes. Both the creep compliance and the creep rate increase with an increased degree of swelling. General observations, such as the high strain limit of linearity in the stress–strain curves and the magnitude of the creep compliance, indicate similarities between swollen cellulose gels and rubbery networks. It is therefore assumed that the statistical theories for swollen networks can describe the amorphous matrix of the gels. In order to obtain creep compliance values representative of the amorphous matrix, the experimental values were corrected for the presence of crystalline regions. It is also suggested that non-load-bearing microvoids are present at high swelling levels. According to calculations based on the theory, the network chains of the amorphous regions in a gel swollen to 2.4 g/g contain about 11 monomer units and the Flory-Huggins interaction parameter χ equals 0.2.

INTRODUCTION

The mechanical properties of cellulose materials have been studied almost exclusively at moisture contents corresponding to air-dry conditions, generally below 20%. This is natural since in their end use these materials are expected to fulfill a role as structural elements at such moisture levels.

However, during the processing of cellulose fibers in the pulp and paper industry, the water uptake is considerably above this level. The occurrence of swelling is then often a prerequisite for a successful result to be obtained.

The extensive reduction of the rigidity of cellulose materials when placed in liquid water is well-known,^{1–3} but detailed studies of the relationship between the mechanical properties and the degree of swelling of cellulose hydrogels appear to be lacking in the literature.

In a previous paper⁴ the preparation of cellulose hydrogels from sodium cellulose xanthate was described as was their characterization. In this paper the effect of the degree of swelling on the mechanical properties is reported.

An attempt is made to describe the properties of the swollen cellulose networks in terms of the statistical theory of rubber elasticity. There are several complications inherent in such an approach since cellulose gels belong to the class of gels where the crosslinks are composed of crystallites and/or hydrogen bonds.

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Hydrogels in this category, such as polyvinylalcohol, gelatine, agarose, and pectin gels, all show characteristic features which originate in the nonpermanent character of the crosslinks.^{5a,6,7} The spontaneous association and dissociation of network junctions leads to hysteresis and other irreversible effects. This implies that the degree of crosslinking cannot be varied independently of the polymer concentration and the temperature. In the case of cellulose, an example of this is the well-known irreversible swelling reduction occurring during drying,^{4,8} which is often referred to as "hornification." Morphological complications also make a theoretical analysis less definite and must thus be treated with appropriate caution. Thus, emphasis will here be laid on the possible application of network theories rather than on a critical assessment of network parameters.

EXPERIMENTAL

The preparation and characterization of the cellulose hydrogels used here have been described in a previous paper.⁴ The same notation for the gels is used here, i.e., a number representing the amount of epichlorohydrin added in the preparation (percent w/w on cellulose) and a subsequent letter showing the batch of preparation.

The degree of swelling of the gels was varied by partial drying followed by reswelling in water.⁴ By means of the irreversible drying effect the water content of the gels in equilibrium with water could be varied between 0.75 and 6.33 g water/g dry gel (g/g). The degree of swelling was determined by oven drying (105°C) and is denoted by Q .

Due to the low rigidity of the swollen gels, uniaxial compression was considered as an appropriate testing configuration. Figure 1 shows the viscoelastometer used to study the mechanical properties. The principle of this apparatus is to load the gels by the application of weights on a rod connected to the core of a linear variable differential transformer (Schaewitz Engineering, Camden, N.J.; LVDT Model 100 DCD). The LVDT was calibrated with precision gauge blocks at the appropriate testing temperature.

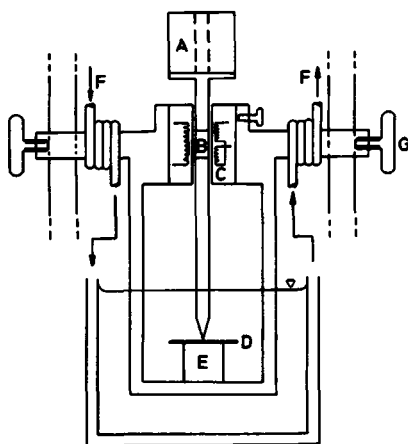


Fig. 1. The viscoelastometer used. (A, weight applied; B, iron core; C, differential transformer; D, glass plate; E, gel surrounded by water; F, thermostated water; G, screw knobs to raise the unit from the bath). The weight holder plus the metal rod weigh 41 g.

The gels were cut into ~5-mm long cylinders. The diameter was 10 mm for fully swollen gels. Since different swelling levels were obtained by drying and reswelling in water, the diameter of the gels varied accordingly. The gels were polished with a fine abrasive before they were inserted into the viscoelastometer. The length was determined by use of the LVDT and the diameter was measured with a sliding caliper. In some cases, the diameter was followed during the experiments by use of a cathetometer. In order to remove sodium azide (the gels were stored in 0.02% sodium azide to prevent bacterial growth), the gels were washed with deionized water at 25°C for 24 h. Finally the gels were equilibrated in the viscoelastometer for 1 h before the measurements were started. The measurements were performed with the gels in equilibrium with deionized water.

The loads were applied by hand and reliable strain data could be collected after 15 s loading time. To obtain isochronous stress-strain data, six successively higher loads were applied for 900 s each, with a recovery period of 900 s between the loading periods. This testing method is illustrated in Figure 2 for a gel 5-A swollen to 6 g/g. The stress is denoted σ (negative in compression) and the strain ($\lambda - 1$), where λ is the ratio of the length when loaded to the initial swollen length.

The initial length in each cycle was corrected for the residual deformation for all previous cycles and the stress was calculated using the unloaded swollen cross-sectional area. Typically, the stress was varied between 0.02 and 0.4 MN/m², and when the degree of swelling was low the stress was varied up to 1.0 MN/m². No mechanical conditioning was carried out before the loading program was started.

RESULTS

In the evaluation of the creep curves obtained, an attempt was made to separate the total compressive strain ($\lambda_{tot} - 1$) into a reversible part ($\lambda - 1$) and an irreversible part ($\lambda_V - 1$), i.e., a permanent set.

Although the recovery period was usually interrupted after 900 s in the testing procedure, substantial evidence was found for the presence of a permanent set. Thus, when the recovery period was extended to 9000 s, it was found that the residual deformation had diminished by only 15% compared with the residual deformation after a recovery period of 900 s.

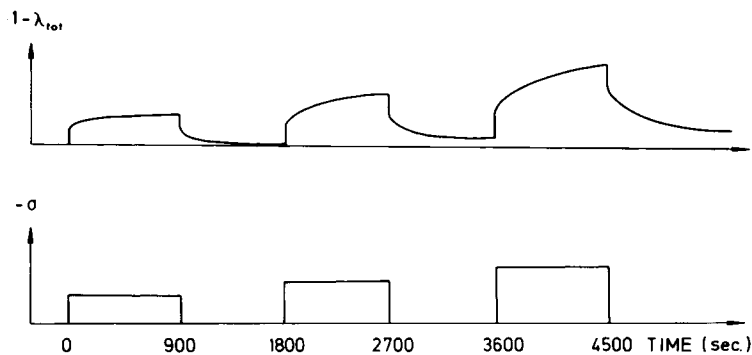


Fig. 2. The testing method is illustrated here for a gel 5-A swollen to 6 g/g (20°C).

In a study of the influence of the loading time and the stress level on the permanent set evaluated after a recovery period of 900 s, it was found that the relation $\lambda_V - 1 = \sigma t / \eta$ holds for loading times up to 2000 s, where t denotes the time under load, σ the stress, and η the viscosity. Thus the permanent set in the time/stress region studied could be described by the mechanical analogy of a Newtonian dashpot with a viscosity η .

Since the recovery period was usually limited to 900 s, η values are underestimated by approximately 15%.

Isochronous relations between σ and $(\lambda - 1)$ were found to be linear (Fig. 3), with the exception of the results of some preliminary experiments that were performed with highly swollen gels above 45°C. The creep compliance was calculated from the slope in accordance with the definition

$$D(t) = \{(\lambda_{\text{tot}} - 1)/\sigma\} - t/\eta = (\lambda - 1)/\sigma \quad (1)$$

with the time t in seconds. $D(900)$ was underestimated by about 3% due to the procedure chosen for the evaluation of η . The standard error of the creep compliance values was estimated to be $\pm 10\%$.

The mechanical testing method used was critically studied. The results are given in Table I. When the length of the recovery period or the aspect ratio length/diameter was varied, no substantial changes in $D(t)$ and η could be found. Thus the results obtained are not disturbed by the short recovery period that was used and no barreling due to friction at the gel ends interferes with the measurements. There is an indication in Table I, however, that when a new gel sample is used for each stress level, the $D(15)$ value is significantly higher than when the same gel is used for all stress levels. Since the $D(900)$ value is apparently unaffected by this difference in evaluation method, only the data obtained at short times may be questioned on this ground.

The gel volumes during loading were calculated from strain data and cathetometer readings of the diameters. It was found that within the experimental resolution the volume was constant for gels swollen up to 4 g/g, i.e., Poisson's ratio was near 0.5. However, significant reductions in gel volume were recorded for gels with higher swelling degrees. This compressibility of highly swollen gels was also found to lead to an irreversible reduction in the degree of swelling in equilibrium with water after the testing procedure.

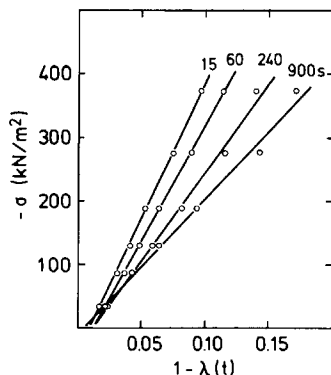


Fig. 3. Isochronous relations between stress and strain determined at 20°C for a gel 10-B swollen to 4.6 g/g.

TABLE I
Study of the Mechancial Testing Method Performed (20°C)

Gel ^a	Recovery time (s)	Aspect ratio	New gel for each cycle	$D(15)$ (m ² /MN)	$D(900)$ (m ² /MN)	η^b (GNs/m ²)
5-B	900	0.31	No	0.30	0.74	5.3
5-B	900	0.42	No	0.32	0.64	4.9
5-B	900	0.45	No	0.31	0.65	4.7
5-B	900	0.58	No	0.36	0.77	3.8
5-B	900	0.82	No	0.31	0.66	5.4
5-B	900	0.45	Yes, six gels	0.43	0.71	3.5
20-A	900	0.48	No	0.31	0.63	19
20-A	900	0.41	No	0.34	0.67	15
20-A	4500	0.36	No	0.30	0.60	16
20-A	4500	0.39	No	0.31	0.55	16
20-A	9000	0.41	No	0.28	0.52	16
20-A	9000	0.42	No	0.32	0.61	18

^a Degrees of swelling: 5-B 5.15 g/g, 20-A 5.11 g/g.

^b Evaluated from the residual deformation after 900-s recovery time in all cases.

Some typical creep curves are shown in Figure 4. The creep compliance, $D(t)$, is approximately a linear function of time in a double logarithmic diagram. Since this finding was established throughout this experimental investigation, only $D(15)$ and $D(900)$ values are reported in the following. If the creep rate is defined as $dD(t)/d \ln t$, it can also be used as an approximation for the retardation spectrum.^{5b} From Figure 4 it is clear that the creep rate defined in this way increases with the degree of swelling, which implies that the retardation spectrum will show a considerably higher amplitude at higher swelling levels. Molecular mobility characterized by relaxation times between 10 and 10³ s thus rapidly increases as the degree of swelling increases. However, from the approximately parallel nature of the curves in Figure 4 it can be concluded that a mean retardation time characteristic for each creep curve appears to be independent of the degree of swelling.

Both the creep compliance values and the viscosities obtained are summarized in Table II. As expected, the creep compliance increases and the viscosity decreases monotonously as the degree of swelling increases. A closer inspection

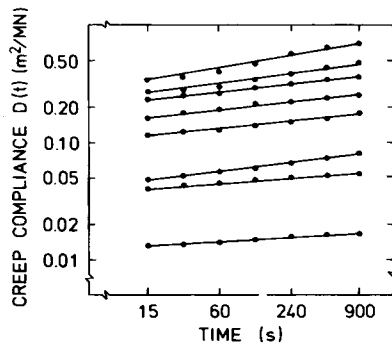


Fig. 4. Some creep curves obtained for gels 5-A and 5-B at 20°C. From the upper curve to the lower, the gels are: 5-A swollen to 6.0 g/g, 5-A 4.7, 5-A 2.9, 5-A 2.4, 5-B 1.9, 5-A 1.2, 5-A 0.95, and finally 5-B to 0.75 g/g.

TABLE II
Mechanical Properties of the Gels Studied (20°C)

Gel	Degree of swelling Q (g/g)	$D(15)$ (m ² /MN)	$D(900)$ (m ² /MN)	η (GNs/m ²)
2-A	6.33	0.31	0.65	6.7
5-A	0.95	0.040	0.054	120
5-A	0.96	0.033	0.078	46
5-A	1.18	0.048	0.081	200
5-A	2.40	0.16	0.25	60
5-A	2.87	0.23	0.36	26
5-A	4.16	0.40	0.66	12
5-A	4.68	0.27	0.48	25
5-A	4.87	0.31	0.54	21
5-A	5.33	0.33	0.54	14
5-A	6.00	0.34	0.64	7.0
10-A	5.64	0.30	0.74	10
20-A	5.11	0.32	0.65	18
0-B	5.67	0.29	0.71	4.4
2-B	5.57	0.30	0.71	5.0
5-B	0.75	0.013	0.017	— ^a
5-B	0.88	0.040	0.056	300
5-B	1.16	0.049	0.065	310
5-B	1.89	0.12	0.17	62
5-B	4.16	0.31	0.55	9.3
5-B	4.92	0.28	0.63	5.1
5-B	5.15	0.33	0.67	4.5
10-B	4.60	0.24	0.48	14
24-B	3.05	0.20	0.35	22

^a Too high to be measured.

of the data reveals that the effects of different degrees of chemical crosslinking and crystallinity of the cellulose⁴ are insignificant compared with the effect of the degree of swelling. This result is believed to illustrate the importance of secondary bonds in these hydrogels.

Experiments were also performed in which the temperature was increased up to 65°C. Gels heat treated⁴ at 80°C were studied in this case. It was usually found that the creep compliance increases with temperature. Thus for gels 5-B swollen to 2.4 g/g, the creep compliance $D(900)$ increased from 0.22 at 20°C to 0.30 m²/MN at 65°C. However, a closer examination of related data for highly swollen samples revealed that the stress-strain curves were concave toward the strain axis at high temperatures, suggesting strain-induced bond breakage. This type of bond breakage appears to be a common feature of many hydrogels.⁷ A study of the influence of the temperature on creep compliance was therefore undertaken in which the strain was kept at considerably lower magnitudes. This study will be reported in a subsequent paper.

DISCUSSION

The possible application to cellulose hydrogels of the statistical theories for the swelling and elastic properties of rubbery networks is here considered.

There are a number of general experimental observations that indicate that

these semicrystalline hydrogels have properties in common with rubbery networks. Firstly, the strain limit of the linearity in the stress-strain curves is higher than 20%, which exceeds what is observed for materials in their glassy or transition state.⁹ Secondly, the ultimate tensile strain was estimated to be at least 40%. Thirdly, the stress is separable into a function of λ , i.e., $(\lambda - 1)$, and a function of time, $D(t)$, which has been suggested as a characteristic feature for crosslinked rubbers.¹⁰ Finally, the magnitude of the creep compliance is similar to that observed for elastomers.¹¹

Thus a model may be considered in which the cellulose hydrogel is visualized as a swollen rubbery network in which inaccessible zones, crystallites, are present. It was earlier shown that the weight fraction of crystalline cellulose depends on the degree of chemical crosslinking but is approximately 40% and is independent of the degree of swelling.⁴

With this model in mind the relationship between the rigidity of the gels and the degree of swelling can be subjected to a closer examination. In Figure 5, the experimentally determined compliance values are given in a double-logarithmic graph versus the volume fraction of cellulose in the amorphous regions of the gels, ϕ_{2a} , which was calculated by assuming volume additivity. This graph reveals that in the region $0.12 < \phi_{2a} < 0.35$ both $D(15)$ and $D(900)$ are proportional to $\phi_{2a}^{-2.1}$. It is interesting to note that a quadratic relationship of this type is predicted from the statistical theory of rubber elasticity provided that the equilibrium swelling degree is changed by varying the degree of crosslinking.^{12,13} This finding also supports the use of the statistical theory for the system under consideration.

The influence on the creep compliance of the crystallites in the cellulose gels has so far been ignored in this comparison.

Moduli have also been shown to be approximately proportional to the square of the polymer concentration in a number of hydrogels such as agarose, alginate, and gelatine gels.⁷ These systems all have in common that secondary bonds can be formed when the polymer concentration increases.

Thus it is suggested that the irreversibilities occurring during drying of cel-

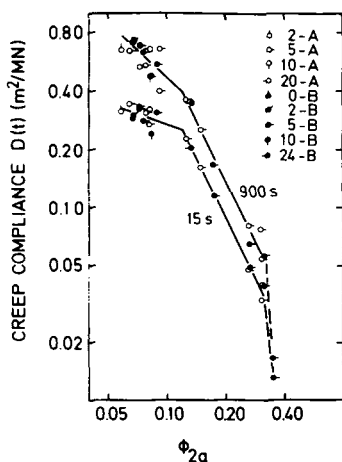


Fig. 5. Creep compliances, $D(15)$ and $D(900)$, versus the volume fraction of polymer in the amorphous parts of the gels (20°C). Note the logarithmic axes.

lulose can be described by an increase in the degree of crosslinking of the gels due to the formation of secondary bonds. Some of these crosslinks, or junction zones, formed during drying may form structures that will resist rupture when the gels are reswollen.

From Figure 5 it is also clear that there are deviations from the quadratic concentration dependence at high swelling levels ($\phi_{2a} < 0.12$). Further, there is another deviation at the lowest swelling degree investigated indicating that the cellulose gels enter the transition zone.

When an attempt is made to make a more quantitative analysis, two basic problems are immediately encountered. Firstly, the compliance data are not equilibrium data and, secondly, the structural role of the crystallites has to be clarified so that compliance data representative of the amorphous regions of the gels, $D_a(t)$, can be obtained.

The application of the extrapolation method suggested by Chasset and Thirion¹⁰ to determine equilibrium creep compliance values was not successful as finite values were not usually obtained. The difficulty of obtaining equilibrium stress-strain data for gels formed by secondary bonds is also well-recognized.^{5a} The compliance values obtained at 900 s, $D(900)$, were therefore used in the calculations.

The transformation of this pseudoequilibrium compliance into a compliance representative of the amorphous regions of the gels was performed with the aid of relationships developed for filled elastomers. It has been shown by Payne¹⁴ that the effect of carbon black on the modulus of natural rubber vulcanizate can be separated into two contributions. The first of these is hydrodynamic in origin (pure filler effect), while the second is due to the formation of links between the matrix and the filler material. By analogy with this result, the crystallites in cellulose hydrogels are assumed to function both as crosslinks and as a filler material.

The crosslinking effect of crystallites in semicrystalline polymers has been discussed in a number of papers.¹⁵⁻¹⁸ If the number of crystallites or the overall crystallinity increases, the elastic constraints on the amorphous regions will increase and the swelling level decrease.¹⁵ Thus the crystallites act as crosslinks and the amorphous phase will contain the thermodynamically required amount of solvent. However, to recalculate $D(900)$ into $D_a(900)$ values that only take the crosslinking effect of the crystallites into account, the filler effect of crystallites has to be corrected for. It is here assumed that the crosslinking and filler effects of the crystallites are separable.

The filler effect may be regarded as hydrodynamic in origin,¹⁹ since the local strains in the amorphous regions will be amplified compared with the macroscopic strain, thus increasing the measured rigidity.

Fedors²⁰ has reviewed equations describing the influence of filler particles on the moduli of filled elastomers. These relations have originally been derived for the relative viscosity of suspensions but can also be used for moduli²¹ if Poisson's ratio is 0.5. According to the empirical Eilers-van Dijk equation,^{5c,14,20,21} a factor $[1 + 1.25\phi_c/(1 - \phi_c/\phi_m)]^2$ describes the relative moduli, where ϕ_c is here the volume fraction of crystallites in the swollen gel, which can be calculated by assuming volume additivity, and ϕ_m is the maximum volume fraction to which the crystallites can pack. ϕ_m was set equal to 0.78, a value which was originally found by Eilers. The particular choice of correction factor for the filler effect is, however, not critical for the following discussion.

The relation between $D(900)$ and $D_a(900)$ is then

$$D_a(900) = D(900) [1 + 1.25\phi_c/(1 - 1.28\phi_c)]^2 \quad (2)$$

The correction factor approximately equals 1.2 at $\phi_{2a} = 0.12$ and 1.7 at $\phi_{2a} = 0.35$. The calculated $D_a(900)$ values are found to be proportional to $\phi_{2a}^{-1.8}$ in the region $0.12 < \phi_{2a} < 0.35$.

The $D_a(900)$ and ϕ_{2a} values thus obtained may then be inserted into the following equations^{22,23}

$$D_a(900) = \frac{q_o^{2/3} q_i^{1/3}}{3\nu_e RT} \quad (3)$$

$$\nu_e \bar{V}_1 \left(q_o^{-2/3} q_i^{-1/3} - \frac{2}{h} q_i^{-1} \right) + \ln(1 - q_i^{-1}) + q_i^{-1} + \chi q_i^{-2} = 0 \quad (4)$$

where the first equation describes the equilibrium compliance of a swollen network and the second equation yields the degree of swelling, $q_i = \phi_{2a}^{-1}$, in equilibrium with pure diluent. q_o denotes the reference swelling level where no elastic forces are present in the network, ν_e is the concentration of elastically active network chains in the dry network, which equals $\rho_a/(162DP_n)$, where DP_n is the degree of polymerization of a network chain, 162 is the relative molecular mass of an anhydroglucopyranose unit, and ρ_a is the density of amorphous cellulose which has been determined²⁴ to be 1.455 g/cm³. Furthermore, R is the gas constant, T the absolute temperature, \bar{V}_1 the molar volume of the diluent, χ the Flory-Huggins interaction parameter and h the functionality of the network. The digit 3 in the denominator of eq. (3) originates from the choice of strain function, since the theoretically derived function $[\lambda - (q/q_i)\lambda^{-2}]$, where q is the degree of swelling during loading is here approximated by $3(\lambda - 1)$. Strictly the strain function $(\lambda - 1)$ can only be used for gels swollen to up to about 4 g/g since for these swelling levels the Poisson's ratio equals 0.5, implying that the degree of swelling during loading is equal to the initial degree of swelling.

The functionality h can be taken to be large for a network where crystallites function as crosslinks¹⁷ and the term containing the functionality in eq. (4) can therefore be neglected.

q_o , the memory parameter, is generally assumed to be related to the state of dilution at which crosslinks have been introduced. As the precursor in the crosslinking reaction was sodium cellulose xanthate, an anionic polyelectrolyte, and the cellulose was formed by regeneration it can be expected that q_o will be considerably lower than the state of dilution during crosslinking. q_o was rather arbitrarily taken to be unity, i.e., the reference state where no elastic forces are present in the network was taken to be the dry state.

In this way, DP_n values and χ values could be calculated, and the results are given in Table III for swollen gels in the region $0.12 < \phi_{2a} < 0.35$. The DP_n values are found to increase and the χ values to decrease as the degree of swelling is increased.

The DP_n values obtained are of the order of 10. A critical issue is then whether this rather low value may invalidate the use of Gaussian chain statistics, which is the basis of the theoretical expressions in eqs. (3) and (4). Since cellulose is insoluble in water, the length of a Kuhn statistical segment for cellulose can only be estimated for cellulose derivatives or for cellulose dissolved in water by the use of complexing agents. Brown²⁵ concluded in a review paper that cellulose

TABLE III
Results of Calculations Based on the Structural Model Suggested (20°C)^a

Gel	Q (g/g)	ϕ_{2a}	DP _n	χ
5-A	0.95	0.306	3.6	0.31
5-A	0.96	0.303	5.2	0.40
5-A	1.18	0.262	4.8	0.30
5-A	2.40	0.149	10.9	0.20
5-A	2.87	0.127	14.3	0.19
5-B	0.88	0.315	3.9	0.35
5-B	1.16	0.266	4.0	0.24
5-B	1.89	0.174	7.8	0.18
24-B	3.05	0.136	14.1	0.23

^a Corresponding $D(900)$ values are given in Table II.

chains have a flexibility similar to that of polystyrene. The Kuhn statistical segment was estimated to include 14 monomer units whereas Rijke and Prins²⁶ estimated the figure to be 10 monomers for cellulose acetate.

These values may also be used for cellulose swollen in pure water, provided that the intramolecular hydrogen bonding in cellulose is suppressed by the interaction with water. Since two Kuhn statistical segments are sufficient to yield approximately Gaussian statistics,²⁶ the network chains at least have to contain 20 monomer units. Thus it appears as though the DP_n values are too low for the application of Gaussian chain statistics on these networks.

However, the DP_n values given in Table III are minimum values for several reasons. Firstly, the equilibrium creep compliance is higher than the $D(900)$ values used in these calculations. Secondly, the hydrodynamic correction for crystallites will probably lead to an underestimation of $D_a(900)$ because of an immobilization of the amorphous matrix near the crystallite surfaces, which will increase effective ϕ_c values. In analogy with swollen filled elastomers,²⁷ the swelling level will accordingly be lower near the crystallite interface than on the average. Finally, the microfibrils of regenerated cellulose are rodlike²⁸ from which it is obvious that the value used for ϕ_m is too high. A lower value than 0.78 is to be expected for the random packing of polydisperse asymmetric particles.

For other semicrystalline polymers, the molecular weights of network chains determined are also comparatively low.^{16,17,29}

The interaction parameter χ is often found to be positive and to increase with polymer concentration.³⁰ This result is also found here, as is evident from Table III. Naturally, only a few estimations of χ in the cellulose-water system have appeared in the literature. Kawai³¹ found, based on a similar approach as used here, χ to equal 0.44 at 25°C for rayon samples. Pennings³² used a value 0.35 that was based on data from glucose and sucrose solutions. Thus the χ values determined here are in line with the scanty literature data.

It was earlier mentioned that at high degrees of swelling corresponding to ϕ_{2a} values lower than 0.12, the slope in Figure 5 was lower than in the region $0.12 < \phi_{2a} < 0.35$. In a preceding paper, the occurrence of microvoids in these gels at high swelling levels was shown by the accessibility to large molecules.⁴

Thus it is assumed that non-load-bearing microvoids are present in the gel structure at ϕ_{2a} values below 0.12, a point that approximately corresponds to

$Q = 3 \text{ g/g}$. Thus $Q = 3 \text{ g/g}$ can be taken as the onset of uniform segment distribution in these gels. If it is assumed that all water in excess of this Q -value is present in microvoids, the volume fraction of microvoids in the structure, ϕ_p , can be calculated.

The presence of spherical microvoids in elastomers²⁰ may be corrected for by multiplying the compliance values with a factor $(1 - \phi_p)$. Fairly constant values are here obtained for corrected $D(900)$ values by use of this factor which shows that the presence of microvoids can explain the relation between $D(900)$ and ϕ_{2a} at ϕ_{2a} values below 0.12.

From this discussion, the conclusion can be drawn that the description of the properties of cellulose hydrogels in terms of the theories for swollen networks seems promising, although a more critical assessment of the theory must be postponed until crystallinity corrections are established and methods of obtaining equilibrium compliance data are available.

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