Swelling and Mechanical Properties of Cellulose Hydrogels. III. Temperature Effects on the Swelling and Compliance Levels Studied by Dilatometry and ^{1}H-NMR Spectroscopy

LENNART WESTMAN and TOM LINDSTRÖM, *Swedish Forest Products Research Laboratory, Box 5604, S-114 86, Stockholm, Sweden*

Synopsis

The temperature dependence of the swelling and the creep compliance has been investigated for swollen isotropic cellulose hydrogels. The measurements were performed in a high precision type of dilatometer between 5 and 65°C. The thermal expansion of the gels in silicone oil (closed system) and the temperature dependence of the equilibrium swelling in water (open system) were studied. The influence of compressive stress in these experiments was also evaluated. The swelling level in equilibrium with water diminishes slightly with increasing temperature due to migration of water from the gel phase to the surrounding water phase. A secondary transition was found at 35°C where the temperature dependence of the swelling level is changed. When measured at constant gel composition the creep compliance of a highly swollen gel decreases with increasing temperature. The decrease is not, however, large enough for entropy elasticity to dominate over energetic elasticity. The energetic contribution f_U/f was determined to be 0.61 for a gel swollen to 3.9 g water/g dry gel (g/g) and 1.24 for a gel swollen to 1.05 g/g. The swelling and compliance data have also been analyzed in terms of a model where the gels are assumed to behave as a filler-reinforced rubbery network. The amorphous parts of the hydrogels are thus assumed to be described by the statistical theory for polymeric networks. In proton magnetic resonance studies of a gel swollen to 4.4 g/g the spin-lattice relaxation time T_1 was determined to be considerably longer than the spin–spin relaxation time T_2. T_2 has a maximum at 30°C. This maximum marks the onset (on the NMR time scale) of an exchange process between two types of proton species. These species are suggested to be specific hydration water and free gel water, respectively.

INTRODUCTION

In a previous communication,[1b] the applicability to cellulose hydrogels of the statistical theory for swollen rubbery networks was discussed. Support for such an approach was found in the magnitude of the creep compliance, in the observed relation between stress and strain, and finally in the relationship between the creep compliance and the degree of swelling.

A model for the swollen gels was suggested in which crystallites and microvoids are distributed in an amorphous gel matrix. The properties of the matrix were assumed to be described by the theory for swollen polymeric gels.[2] The role of the crystalline regions in such a model will be to act *both* as filler particles and as crosslinks.

The main object of the work described in this paper has been to investigate the thermoelastic relation between creep compliance and temperature. A high precision dilatometer was constructed in which the temperature dependence of both the degree of swelling and the creep compliance could be studied.

A secondary transition in the temperature dependence of the swelling degree

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is also discussed. Several other authors[3–6] have discussed a secondary transition in cellulose occurring at room temperature. The transition is generally thought to be associated with the cellulose–water interaction.[4,7] To investigate this interaction further, proton relaxation times were measured by NMR spectroscopy over the same temperature interval as investigated in the dilatometer experiments (5–65°C).

EXPERIMENTAL

Dilatometry

The dilatometer used in this investigation is shown in Figure 1. The principle is to use a rod to follow the dimensional change in one direction of the gel under study. The rod and a linear variable differential transformer (LVDT Model 100 DCD; Schaewitz Engineering, Camden, N.J.) were thermostated at 24.7°C, while the temperature in the solution surrounding the gel could be varied stepwise both upward and downward. The thermocouple voltage and the signal output from the LVDT were followed continuously on a recorder. The load of the rod (21 g; length 40 cm) was evenly distributed by a glass plate over the gel surface, which ensured good contact between the glass plate and the gel. The load could be increased by applying weights to the rod. The maximum load used was 220 g.

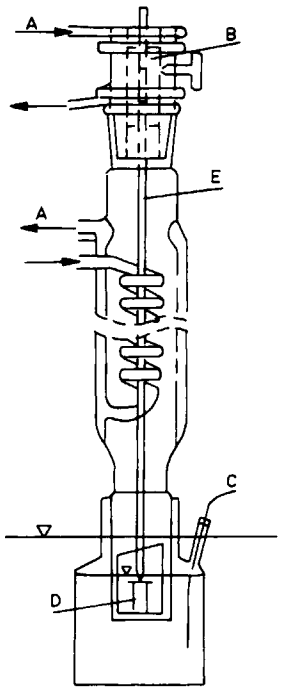

Fig. 1. The dilatometer shown here was made from Pyrex glass, except from the LVDT-holder (B), which was made from a nickel alloy of low thermal expansivity (A: thermostated water, C: thermocouple, D: gel, and E: glass rod).

The error in the LVDT-output signal due to temperature effects on the dilatometer setup was found to be very small, max ±0.3 μm over the temperature interval 5–65°C. This value was determined by running the apparatus without any sample. The coefficient of linear thermal expansion, α, for a cylindrical piece (10 mm in length) of brass containing 65.2% Cu and 33.3% Zn was determined to be 1.84×10^{-5} K^{-1}, which can be compared with the literature value of 1.77×10^{-5} K^{-1} at 35°C for brass containing 67% Cu and 33% Zn.[8]

The gels were surrounded either by the swelling medium (open system) or by an inert, high viscosity, silicone oil (Dow Corning 200 Fluid; Dow Corning Ltd., Glamorgan, UK) (closed system). The length–temperature data were found to be linear and will be given as coefficients of linear thermal expansion (for both the open and the closed system) defined by $\alpha = \Delta L/(L\Delta T)$, where L denotes the gel length and T the temperature. α was generally determined as the average of results obtained for both increasing and decreasing temperature changes. The standard deviation of the mean values α was determined to be ±10%. The standard deviation for the mean transition temperature T_k (see "Results") was ±4°C.

The experiments performed in silicone oil were disturbed by a slow loss of water from the gels at higher temperatures (>45°C). This effect was observable as a baseline drift, which was linear in time. In this case, α values were calculated as averages of the results from increasing temperature changes exclusively and, through the use of baseline extrapolations, corrections were made for the small loss of water.

The same batches of cellulose hydrogels were used as described earlier.[1a] The same notation is also used for the gels, i.e., a figure denoting the amount of epichlorohydrin added in the preparation and a letter denoting the preparation batch. The degree of swelling is given as g water/g dry gel (g/g).

The swelling level of the gels was varied by partial drying of the gels followed by reswelling in water.[1a] The length of the gels was typically 10 mm and the diameter varied with the degree of swelling, being 10 mm at the highest swelling levels. Initial length and diameter was measured with a sliding caliper and the degree of swelling was determined by weighing the gels before and after oven drying (105°C). To remove skin, the surfaces of the gels were polished with a fine abrasive.

The gels were heat treated under load at 80°C in the dilatometer for 4 h before the experiments were started. This heat treatment reduced the irreversible temperature effects described previously[1a] and the mechanical creep during the measurements so that, for the open system, only reversible length changes were recorded in the temperature interval 5–65°C. The time between each temperature step was adjusted to allow for the development of a stable baseline, i.e., the length data were apparently determined at equilibrium.

NMR

Proton spin-lattice relaxation times, T_1, and spin–spin relaxation times, T_2, were measured in a Bruker pulsed spectrometer CXP-100 at 90 MHz. One measurement was performed at 200 MHz using another Bruker spectrometer, WP-200. T_1 was determined by the inversion recovery method[9] (180°-τ-90°) and T_2 by the Meiboom–Gill[10] modification of the Carr–Purcell[11] pulse sequence,

which reduces the possible disturbances from sample heterogeneity and diffusion. The separation between the 180° pulses was 200 μs. The relaxation plots were single exponentials and no sign of two-phase behavior could be detected. T_1 and T_2 were evaluated by nonlinear least-square fits of observed intensities to the integrated Bloch equations. From these fits, the standard deviations of the mean relaxation times were estimated to be ±6% in T_1 and ±2% in T_2.

The temperature was varied by a flow of thermostated dry air. A thermocouple near the sample was used for temperature control. The temperature difference between sample and thermocouple was compensated for by a calibration series. To investigate water loss or other hysteresis effects, the temperature was varied both upward and downward.

A heat treated gel of type 0-B (pure regenerated cellulose) swollen to 4.4 g/g (determined after the experiment) was studied. The gel was first equilibrated in distilled and deionized water with a specific conductivity less than 2×10^{-4} Ω^{-1} m^{-1}. Oxygen was removed from the water using nitrogen gas. The gel was then transferred into a probe tube containing deuterated cyclohexane (>99% D, Ciba-Geigy), which reduced the loss of water during the experiment to <10%.

RESULTS

Dilatometry

Results from dilatometry for gels 2-B are given in Table I. Data from both open and closed system runs are included as well as from studies of the stress dependence of the coefficients of linear thermal expansion, α. α is positive if the composition of the gel phase is kept constant while the temperature is changed. On the other hand, in swelling equilibrium with an excess of water, α is negative. This difference is shown in Figure 2, which also shows that the magnitude of the temperature effects is rather small. If the temperature is increased, the swelling level of a gel in equilibrium with water thus decreases slightly due to a lowering of the water content.

An exchange of water between the gel phase and the adjacent water phase was also detected at low swelling levels where the diffusion rate of water in the gels is low. For a short period of time after a temperature increase, the gel behaved as if it was a closed system, i.e., its length increased. Then the length slowly decreased due to a loss of water by diffusion from the gel phase. The opposite behavior was observed when the temperature was decreased.

A decrease in the swelling level of cellulose as a result of a temperature increase has also been noted by other authors,[12] although the magnitude of the effect reported here is much smaller.

In a previous study of the irreversibilities observed in the drying of cellulose,[1a] it was found that the dimensional changes were isotropic and isotropy is also expected from the method of gel preparation. Gravimetrically estimated α values also agreed reasonably well with the dilatometrically obtained values.

Isotropy can only be expected to hold for values of α obtained by extrapolation to zero stress. As is shown in Table I, these extrapolated values do not deviate markedly from α values determined at the lowest stress levels.

The temperature dependence of the equilibrium swelling levels shows a dis-

TABLE I
Stress (σ) Dependence of the Coefficients of Linear Thermal Expansion (α)[a]

Degree of swelling at 65°C (g/g)	Surrounding medium	$-\sigma$ at 65°C (kN/m^2)	$\alpha_1 \times 10^5$ (K^{-1})	$\alpha_2 \times 10^5$ (K^{-1})	T_k (°C)	Number of experiments	Temperature steps (°C/h)	$1 - \lambda$ at 65°C
3.9	H_2O	4.1	−5.5[b]	−3.1[f]	29	6	4.5/1	—
3.9	H_2O	14.4	−3.6	−2.5	32	4	4.5/1.3	—
3.9	H_2O	43.8	−1.1	−1.6	(40)	8	4/1.3	—
3.9	Silicone oil	3.6	8.5[c]	—	—	5	4/1.3	0.002
3.9	Silicone oil	12.8	8.7	—	—	2	4/1.3	0.007
3.9	Silicone oil	38.8	10.7	—	—	3	4/1.3	0.019
1.05	H_2O	7.5	−6.4[d]	−4.0[g]	35	4	6.4/1.7	—
1.05	H_2O	26.6	−5.0	−3.1	38	6	6.4/1.7	—
1.05	H_2O	80.4	−4.4	−2.8	40	4	6.4/1.7	—
1.05	Silicone oil	7.7	8.0[e]	—	—	3	4.5/0.7	0.001
1.05	Silicone oil	27.0	7.4	—	—	4	4.5/0.7	0.003
1.05	Silicone oil	81.8	7.5	—	—	4	4.5/0.7	0.007

[a] The data were obtained for gels 2-B. The strain levels, $(\lambda - 1)$, were estimated from $D(900)$ in our earlier work (ref. 1b) at the lowest stress levels and were determined experimentally at higher stress levels. Errors in strain data are on the order of ±20%.

[b] Extrapolation to zero stress yields −5.6.

[c] Extrapolation to zero stress yields 8.0.

[d] Extrapolation to zero stress yields −6.3.

[e] Extrapolation to zero stress yields 7.9.

[f] Extrapolation to zero stress yields 3.1.

[g] Extrapolation to zero stress yields −3.9.

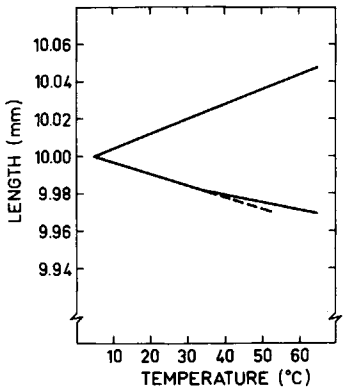

Fig. 2. Influence of temperature on the length of a gel 2-B swollen to 1.05 g/g (based on Table I; data extrapolated to zero stress). The length was arbitrarily taken to be equal to 10 mm at 5°C. The upper curve is obtained at constant gel composition, the curve below for measurements performed in equilibrium with water.

continuity at a point (T_k) in the vicinity of 35°C (Table I and Fig. 2). α is denoted α_1 at temperatures below T_k and α_2 above. This point thus represents a secondary transition. No transition was, however, found in experiments performed in silicone oil. Hence, the transition is associated with the partitioning of water between the gel phase and the surrounding bulk phase.

Further dilatometric experiments were performed in order to investigate the mechanism underlying the transition. The results are shown in Table II. It is evident that neither a replacement of deionized water by aqueous solutions of 0.1*M* KBr or 6*M* LiCl nor a solvent exchange to deuterated water significantly changes the value of T_k. Also, the value is independent of the swelling level or the epichlorohydrin addition in the preparation of the gels. Since no transition was found for dry cellulose gels or for gels equilibrated in the aprotic solvent DMF, the transition can be ascribed to a change in the interaction between cellulose and water.

The creep compliance, $D(t_{eq}) = (\lambda - 1)/\sigma$, was determined from stress (σ) and strain ($\lambda - 1$) data calculated from Table I. λ equals the ratio between deformed and initial length. λ was calculated at different temperatures from the known values of λ at 65°C and α. The temperature dependence of the initial diameter and initial length were both taken from α values extrapolated to zero stress. The calculations of the stress were based on the swollen initial area. Note that it was the force, not the stress level, that was constant during the experiment. t_{eq} marks that the measurements apparently were made at equilibrium. It was noted that the results obtained for α were independent of whether the gels were run at a higher stress before a lower or vice versa.

The thermoelastic relationship between the mechanical properties and temperature is more easily analyzed in thermodynamic terms if the composition of the gel phase is kept constant.[13] Thus the creep compliance data given in Figure 3 refer to the closed system. For the more swollen gel, $D(t_{eq})$, in agreement with the kinetic theory of rubber elasticity[2] decreases with temperature whereas $D(t_{eq})$ increases slightly for the less swollen gel.

It is believed that the strain levels used in this investigation are sufficiently

TABLE II
Dilatometric Data Obtained for Cellulose Gels in Open Systems

Gel	Degree of swelling (g/g)	Surrounding medium	$-\sigma$ (kN/m^2)	$\alpha_1 \times 10^5$ (K^{-1})	$\alpha_2 \times 10^5$ (K^{-1})	T_k (°C)	Number of experiments	Temperature steps (°C/h)
0-B	5.33	H_2O	2.8	−3.5	−2.4	36	6	3.5/1.3
2-A	5.89	H_2O	2.6	−4.1	−2.4	36	5	3.5/1.3
5-A	5.52	H_2O	2.7	−4.2	−2.0	35	2	3.5/1.3
10-A	5.13	H_2O	2.9	−4.0	−2.4	35	7	3.5/1.3
20-A	4.60	H_2O	3.0	−4.7	−2.9	35	7	3.5/1.3
2-A	4.58	H_2O	3.1	−3.6	−2.4	32	7	3.5/1.3
2-A	3.09	H_2O	3.8	−4.3	−2.6	32	3	6/2.5
2-A	0.75	H_2O	7.4	−6.7	−4.0	31	6	5/2
2-A	0.75	0.1*M* KBr	7.4	−6.8	−3.7	34	3	5/2
2-A	0.85	6*M* LiCl	7.0	−7.0	−4.0	38	5	8/3.3
2-A	~0[a]	*n*-Heptane	12.2	+3.0	—	—	5	5/2
2-B	~0[a]	Silicone oil[b]	12.2	+3.7	—	—	12	5/1
10-A	5.17	D_2O[c]	2.8	−3.6	−2.3	35	5	5/2
10-A	1.32[d]	DMF	5.9	−3.7	—	—	2	10/4
10-A	3.79[e]	DMF	3.4	−2.9	—	—	3	5/2

[a] Dried over P_2O_5 at 0.01 Pa.
[b] Dried over $CaCl_2$.
[c] From Norsk Hydro A/S (99.8%D).
[d] Dried *in vacuo* after solvent exchange to acetone, then equilibrated in dimethyl formamide (DMF).
[e] Obtained by solvent exchange to DMF from water.

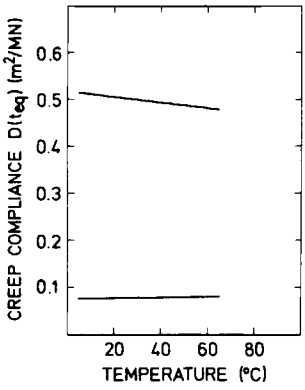

Fig. 3. Relation between temperature and compliance level at constant gel composition for gels swollen to 3.9 (upper curve) and 1.05 g/g (lower curve), respectively (based on Table I; gels 2-B).

small to avoid interference from strain-induced bond breakage at high temperatures as discussed for these gels in a previous communication.[1b] Disturbances of this type are a common feature of many other hydrogel systems, as has been pointed out by Mitchell.[14]

NMR

The relaxation times obtained, T_1 and T_2, are shown in Figure 4 in an Arrhenius type of diagram. T_1 is considerably longer than T_2. T_1 increases with temperature, while T_2 has a maximum at 30°C. No hysteresis was found in the results.

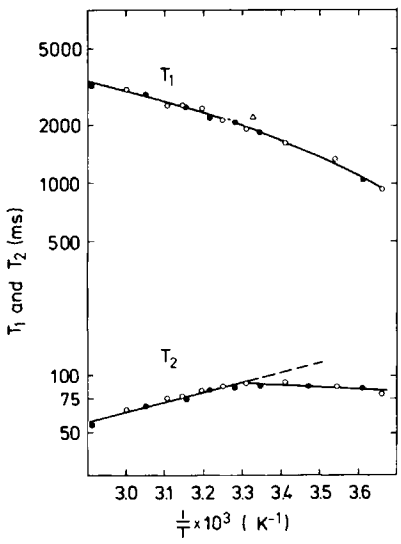

Fig. 4. Relaxation times determined at 90 MHz for a gel 0-B containing 4.4-g/g water are here shown in an Arrhenius-type diagram. ● denote rising temperature, ○ descending temperature. The triangle shows the average of two measurements of T_1 at 200 MHz for the same gel.

DISCUSSION

Dilatometry

The relation between compliance level, $D(t_{eq})$, and temperature, T, can be analyzed in terms of thermoelasticity. From classical thermodynamics[13] it is found that the strain-dependent elastic force, f, is given by

$$f = \left(\frac{\partial U}{\partial L}\right)_{V,T,n} - T\left(\frac{\partial S}{\partial L}\right)_{V,T,n} \tag{1}$$

which is to be identified with $f = f_U + f_S$, where f_U and f_S are, respectively, the energy and entropy contributions to the force. All the symbols used here have their customary meaning, n implying that the composition is constant. The ratio between f_U and f can be found from[13]

$$\frac{f_U}{f} = 1 - \left(\frac{\partial \ln f}{\partial \ln T}\right)_{V,L,n} \tag{2}$$

which suggests that the main problem in the theoretical analysis is to convert data obtained at constant pressure to isochoric data. Shen[15] has shown that the ratio f_U/f can be obtained from the temperature dependence of the shear modulus G since

$$\frac{f_U}{f} = 1 - \left(\frac{\partial \ln G}{\partial \ln T}\right)_{n} - \alpha_n T \tag{3}$$

where the derivative is not subject to the constraints of constant V and L. α_n is the coefficient of linear thermal expansion (closed system) of an unstrained sample. G is a material property and thus independent of the length L. From the statistical theory of rubber elasticity it follows that G depends only on the initial volume and *not* on the volume when strained.

G will be approximately equal to $[3D(t_{eq})]^{-1}$ since Poisson's ratio for gels swollen to between 1 and 4 g/g is close to 0.5.[1b] From the data in Table I and Figure 3, $f_U/f = 1.24$ at 1.05 g/g and $f_U/f = 0.61$ at 3.9 g/g are obtained as mean values over the temperature and strain intervals studied. Hence, the elasticity is dominated by the energetic contribution f_U. However, for the more swollen sample, the elasticity is at least partly entropic in origin.

The ratio f_U/f has also been determined for swollen filaments of regenerated cellulose by Gabrail and Prins.[16] f_U/f was found to equal 4.0 at 30°C and −4.5 at 90°C. They noted that the filaments behaved anisotropically, a factor known to influence the thermoelastic behavior. It should also be noted that the preparation procedure of the gels used in this investigation[1a] is quite different from that used by Gabrail and Prins. Stöckmann[17] reported the derivative $(\partial \ln f/\partial \ln T)_{V,L,n}$ to be negative for water-swollen ramie fibers. Both of these investigations were performed in open systems which lead to the introduction of large correction terms. The possible influence of water structure rearrangements on the results was also discussed.

In order further to analyze the compliance and swelling data, the structural model for the gels suggested earlier[1b] was used. This model is based on an amorphous matrix described by the creep compliance $D_a(t_{eq})$ and the swelling level $q_i = \phi_{2a}^{-1}$, where ϕ_{2a} is the volume fraction of polymer in the amorphous regions. $D_a(t_{eq})$ can be calculated from the experimental $D(t_{eq})$ values if they

are corrected for contributions from non-load-bearing microvoids and the presence of crystallites according to the following formula[1b]

$$D_a(t_{eq}) = D(t_{eq})[1 + 1.25\phi_c/(1 - 1.28\phi_c)]^2(1 - \phi_p) \quad (4)$$

where ϕ_p is the volume fraction of microvoids and ϕ_c is the volume fraction of crystallites. Swelling water in excess of $\phi_{2a} = 0.12$ was earlier found to be present in microvoids.[1b] From the temperature dependence of $D_a(t_{eq})$ and ϕ_{2a}, the degree of polymerization of the network chains, DP_n (the number of anhydroglucopyranose units), and the Flory–Huggins interaction parameter χ can be calculated at various temperatures according to the following equations[1b]

$$D_a(t_{eq}) = \frac{162 q_o^{2/3} q_i^{1/3} DP_n}{3\rho_a RT} \quad (5)$$

$$\frac{\rho_a \bar{V}_1 q_o^{-2/3} q_i^{-1/3}}{162 DP_n} + \ln(1 - q_i^{-1}) + q_i^{-1} + \chi q_i^{-2} = 0 \quad (6)$$

where q_o is the reference swelling level which has been set equal to unity, ρ_a = 1.455 g/cm^3 is the density of amorphous cellulose,[18] 162 is the molecular weight of an anhydroglucopyranose unit, R is the gas constant, $\bar{V}_1$ the molar volume of water, and T the absolute temperature. A more detailed discussion of the application of these network formulae to cellulose gels is given in the preceding paper.[1b]

The temperature dependence of ϕ_{2a} was calculated using the α values given in Table I for the open system extrapolated to zero stress and the α value for dry cellulose (gel 2-B in Table II). These calculations were based on the following simplifying assumptions: (i) volume additivity, (ii) the value of ϕ_p is independent of temperature, and (iii) α has the same value for both amorphous and crystalline cellulose.

Along these lines, the data given in Table III were calculated. The total correction factor in eq. (4) was taken to be independent of temperature and was calculated to be 0.96 for the gel swollen to 3.9 g/g and 1.51 for the gel swollen to

TABLE III
Parameters Describing the Properties of the Amorphous Networks of the Gels 2-B Swollen to 3.9 and 1.05 g/g Water, Respectively[a]

T (K)	ϕ_{2a}	DP_n	χ	$-\chi_H$	χ_S
278	0.1181	15.0	0.164	0.312	0.476
288	0.1185	15.3	0.173	0.303	0.476
298	0.1188	15.7	0.184	0.292	0.476
308	0.1192	16.0	0.194	0.282	0.476
318	0.1195	16.4	0.203	0.273	0.476
328	0.1197	16.7	0.211	0.265	0.476
338	0.1200	17.1	0.219	0.257	0.476
278	0.2728	4.6	0.311	0.438	0.749
288	0.2738	4.9	0.327	0.422	0.749
298	0.2748	5.1	0.341	0.408	0.749
308	0.2758	5.3	0.355	0.394	0.749
318	0.2765	5.5	0.367	0.382	0.749
328	0.2773	5.7	0.378	0.371	0.749
338	0.2780	6.0	0.388	0.361	0.749

[a] The calculations were based on the structural model suggested earlier (ref. 1b).

1.05 g/g. From these calculations, both the DP_n values and the Flory–Huggins interaction parameter χ were found to increase with temperature.

Thus according to the network model discussed here, energy elasticity is due to a decreasing degree of crosslinking (increased DP_n) with increasing temperature, which may be interpreted in terms of a decreased hydrogen bonding between the network chains at higher temperatures.

In these calculations, the reference degree of swelling, q_o, has been assumed to equal unity and to be independent of the temperature. q_o is defined[2] from $q_o^{2/3} = \langle r^2 \rangle_{0,s} / \langle r^2 \rangle_d$, where $\langle r^2 \rangle_{0,s}$ is the mean square end-to-end distance the network chains would attain in the absence of constraints imposed by network junctions (reference dimensions) and $\langle r^2 \rangle_d$ is the corresponding actual distance in the dry network.

For ideal rubbers, the energetic contribution to the force is of intramolecular origin[19] and given by $f_U/f = d \ln \langle r^2 \rangle_{0,s} / d \ln T$. For a number of cellulose derivatives, the temperature coefficient of the intrinsic viscosity $d \ln [\eta]/dT$ is known to be large and negative.[20] Thus, with increasing temperature, a more flexible conformation is possible and $\langle r^2 \rangle_{0,s}$ is diminished. The backbone chain stiffness of cellulose is probably the reason for this result. This situation was also believed to hold for unsubstituted cellulose in strongly solvating media such as water.[20] There is thus evidence that the quantity $d \ln \langle r^2 \rangle_{0,s}/dT$ is negative for cellulose and does not show any temperature anomaly. A negative contribution to f_U/f is then expected from the derivative $d \ln \langle r^2 \rangle_{0,s}/d \ln T$. Therefore, it is likely that the positive contribution to f_U/f originates from the intermolecular hydrogen bonding as suggested above.

χ is usually interpreted as representing a reduced residual free energy of mixing and can be further divided into an enthalpic and an entropic component, $\chi = \chi_H + \chi_S$, from which it follows that[21]

$$\chi_H = -T \left(\frac{\partial \chi}{\partial T} \right)_{P,n} \tag{7}$$

and

$$\chi_S = \left(\frac{\partial (\chi T)}{\partial T} \right)_{P,n} \tag{8}$$

In Table III, it is shown that χ_H is slightly negative, while χ_S is positive, temperature independent, and the dominant contributor to χ. The combination of a slightly negative χ_H, a positive χ_S, and an increasing χ with polymer concentration[1b] is common in many polymer–solvent systems.[21] χ_S will include effects from a nonideal combinatorial entropy of mixing between solvent and polymer which probably originates from a nonideal volume change on mixing.[22] The positive values of χ_S can then be explained since volume contraction was earlier found on mixing in the cellulose–water system.[1a] The residual partial molar entropy of water $\overline{\Delta S}_1 = -\chi_S R \phi_{2a}^2$ is thus negative and structuring of the water near the cellulose chains may also contribute to this result.

χ_H gives the partial molar enthalpy of the solvent from $\overline{\Delta H}_1 = \chi_H RT \phi_{2a}^2$. Since χ_H is negative, the mixing process is exothermic. $\overline{\Delta H}_1$ is more negative for the less swollen gel, in agreement with calorimetric data.[23] $\overline{\Delta H}_1$ is approximately constant over the temperature interval. It is interesting to note here certain similarities in the interaction parameter χ between polyvinyl alcohol

(PVA) and cellulose hydrogels. For PVA gels, χ_H is negative, χ_S positive, and χ increases with temperature.[24,25] A transition in the swelling level of PVA gels around 35°C has also been recorded by Ogasawara et al.[26] Whether or not these similarities reflect common fundamental features on a molecular level for these systems is at the present time difficult to assess. In other types of hydrogels, both increases and decreases in the swelling level with increasing temperature have been reported,[27] depending on the sign of $\overline{\Delta H_1}$.

NMR

The NMR study was undertaken as a supplement to the dilatometric study to investigate further the temperature effects on the interaction between cellulose and water. The data obtained are discussed in relation to similar studies of water in gels or of water adsorbed on surfaces.

T_1 is considerably longer than T_2. Since the spin-lattice relaxation time T_1 is less sensitive than T_2 to low-frequency thermal motion, the difference between T_1 and T_2 is an indication either of the presence of a less mobile proton species or that the distribution in molecular mobilities is broad.

The observed relation between T_1 and T_2, and especially the maximum in T_2 at 30°C, cannot be described by the classical BPP theory[28] of magnetic relaxation and a single correlation time. Child[29] has also found an indication of a broad maximum in T_2 at about 20°C in cellulose containing 0.073 g water/g dry cellulose.

The existence of a maximum in T_2 can be explained if two types of proton species are present: a more mobile water phase that is here denoted A and a less mobile phase denoted B. The corresponding weight fractions, average lifetimes in the states, relaxation and correlation times are here denoted $p_A, p_B, C_A^{-1}, C_B^{-1}$, T_A, T_B, and τ_A, τ_B.

Zimmerman and Brittin[30] have derived expressions for relaxation times in such a two-phase system. A maximum in T_2 can be found in the temperature interval where a very slow change between the phases ($T_{2i} \ll C_i^{-1}$, $i = A$ or B) is gradually succeeded by a slow exchange condition ($T_{2B} \ll C_B^{-1}$).[31] The experimentally determined T_2 value, T_{2A}', is then given by[32]

$$\frac{1}{T_{2A}'} = \frac{1}{T_{2A}} + C_A \tag{9}$$

At the maximum point, $T_{2A} = C_A^{-1}$. At higher temperatures, the observed T_{2A}' will be shorter than T_{2A} and approximately equal to C_A^{-1} (exchange broadening). However, the exchange rate will not affect T_{2B} until it is rapid ($T_{2i} \gg C_i^{-1}$). The transfer from slow to rapid exchange will give a minimum in the observed T_2 values.

Thus, the observed T_2 is T_{2A}' given by eq. (9). The relaxation rate T_{2B}^{-1} is probably too large and its intensity too low for T_{2B} to be detected. The value of T_{2B} is determined by τ_B, which reflects the motion of the macromolecule.

A similar maximum in T_2 and/or a subsequent minimum at a higher temperature has been observed for a number of water-containing systems. In agarose gels a T_2 maximum is found at about 0°C and a minimum at 30°C,[33] for keratin there is a maximum at 40°C,[34] for kappa-carrageenan hydrogels a minimum is found at 50°C as well as for iota-carrageenan gels at 20°C.[35]

In a review of NMR in the most extensively studied hydrogel, agarose, Ablett et al.[33] found the proton exchange to take place within that part of the water that does not freeze at 0°C. To explain all the NMR data available they had to include four kinds of protons: free water, nonfreezing (bound) water, a very tightly bound species, and nonexchangeable agarose protons. They were unable to decide whether the tightly bound species was a water fraction (about 0.1 g/g in that case) or exchangeable agarose protons.

A value of 0.1 g/g corresponds well to the figure of 0.13 g/g obtained at 23°C for the water of specific hydration in the cellulose hydrogels.[1a] The tightly bound species B will thus be identified with the specific hydration water. Support for this identification can be found from an investigation of oriented rayon samples.[36] A singlet, due to a mobile species, appears in a region around 40°C. At temperatures above 40°C, a doublet due to bound water molecules slowly disappears and the intensity of the singlet peak increases. The intensity of another singlet assigned to the cellulose hydroxyls remains constant over the temperature interval. Thus it appears as though water is the tightly bound species. The presence of tightly bound water in cellulose has also been reported by Forslind[37] as well as by Froix and Nelson.[38]

From eq. (9) and the T_2 data in Figure 4, the lifetime C_A^{-1} can be determined to be 180 ms at 30°C. The ratio p_B/p_A can be estimated from the values for the amount of specific hydration water and the total amount of water to be 0.03. From the mass balance

$$p_A C_A = p_B C_B \tag{10}$$

the average lifetime for water species in the tighly bound phase is found to be 5.4 ms. In agarose gels, this lifetime has been estimated to a few hundred microseconds at 30°C.[33] Also the T_1 data can be analyzed in terms of a two-phase model for the gel water. The observed T_1 increases with temperature and is considerably longer than any of the calculated lifetimes. τ_B is probably long enough for T_{1B} to have passed its minimum since τ_B in agarose gels is about 4×10^{-6} s at 25°C.[39] T_{1B} will then be frequency dependent. An indication of a small frequency dependence can be found from the T_1 value determined at 200 MHz. The exchange is then rapid ($T_{1i} \gg C_i^{-1}$) and the equation

$$\frac{1}{T_1} = \frac{p_A}{T_{1A}} + \frac{p_B}{T_{1B}} \tag{11}$$

holds where the first term probably dominates since $p_A \gg p_B$. Thus T_1 approximately equals T_{1A}/p_A. T_{1A} will then according to the T_1 data have a temperature dependence near that of T_1 in bulk water.[40]

This reasoning becomes more complicated if distributions in correlation times are assumed.

FINAL COMMENT

The molecular mechanism underlying the 35°C transition observed in the dilatometer data has so far not been discussed. According to the dilatometer data, the interaction between cellulose and water is changed at the transition temperature. The maximum in T_2 from NMR data is found near this temperature but it should be noted that the presence of such a maximum is not necessarily coupled to any secondary transition.

p_B, and thus also p_A, probably vary with temperature since the amount of specific hydration water is known to decrease with increasing temperature in glucose solutions.[5,41,42] Thus it is suggested that the secondary transition is associated with a change in the temperature dependence of the amount of specific hydration water.

Even in pure water, however, structural changes occur in the vicinity of 35°C. From Raman spectra, Forslind[43] could compute the temperature dependence of various coordination species in water and found break points around 38°C.

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References

1. (a) L. Westman and T. Lindström, *J. Appl. Polym. Sci.*, **26,** 2519 (1981); (b) L. Westman and T. Lindström, *J. Appl. Polym. Sci.*, **26,** 2533 (1981).
2. K. Dušek and W. Prins, *Adv. Polym. Sci.*, **6,** 1 (1969).
3. S. A. Bradley and S. H. Carr, *J. Polym. Sci. Polym. Phys. Ed.*, **14,** 111 (1976).
4. C. Klason and J. Kubát, *Sv. Papperstidn.*, **79,** 494 (1976).
5. M. V. Ramiah and D. A. I. Goring, *J. Polym. Sci.C*, **11,** 27 (1965).
6. M. Wahba and K. Aziz, *Chem. Scr.*, **7,** 233 (1975).
7. W. Drost-Hansen, *Ind. Eng. Chem.*, **61,** (11), 10 (1969).
8. *Thermophysical Properties of Matter. Vol. 12. Thermal Expansion—Metallic Elements and Alloys*, Series Ed., Y. S. Touloukian, IFI/Plenum Data, New York/Washington, 1975, p. 796.
9. R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48,** 3831 (1968).
10. S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **29,** 688 (1958).
11. H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94,** 630 (1954).
12. K. Chitumbo, W. Brown, and A. de Ruvo, *J. Polym. Sci, Polym. Symp.*, **47,** 261 (1974).
13. J. E. Mark, *Rubber Chem. Technol.*, **46,** 593 (1973).
14. J. R. Mitchell, *J. Text. Stud.*, **7,** 313 (1976).
15. M. Shen, *Macromolecules*, **2,** 358 (1969).
16. S. Gabrail and W. Prins, *J. Polym. Sci.*, **51,** 279 (1961).
17. V. E. Stöckmann, *J. Polym. Sci. C*, **36,** 363 (1971).
18. D. N. Tyler and N. S. Wooding, *J. Soc. Dyers Colour.*, **74,** 283 (1958).
19. P. J. Flory, A. Ciferri, and C. A. J. Hoeve, *J. Polym. Sci.*, **45,** 235 (1960).
20. K. D. Goebel, C. E. Harvie, and D. A. Brant, *Appl. Polym. Symp.*, **28,** 671 (1976).
21. P. J. Flory, *Discuss. Faraday Soc.*, **49,** 7 (1970).
22. I. C. Sanchez and R. H. Lacombe, *Macromolecules*, **11,** 1145 (1978).
23. J. L. Morrison and M. A. Dzieciuch, *Can. J. Chem.*, **37,** 1379 (1959).
24. I. Sakurada, A. Nakajima, and H. Fujiwara, *J. Polym. Sci.*, **35,** 497 (1959).
25. N. A. Peppas and E. W. Merrill, *J. Polym. Sci. Polym. Chem. Ed.*, **14,** 459 (1976).
26. K. Ogasawara, T. Nakajima, K. Yamaura, and S. Matsuzawa, *Colloid Polym. Sci.*, **254,** 456 (1976).
27. W. Nierzwicki and W. Prins, *J. Appl. Polym. Sci.*, **19,** 1885 (1975).
28. N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73,** 679 (1948).
29. T. F. Child, *Polymer*, **13,** 259 (1972).
30. J. R. Zimmerman and W. E. Brittin, *J. Phys. Chem.*, **61,** 1328 (1957).
31. H. A. Resing, *Adv. Mol. Relaxation Processes*, **3,** 199 (1972).
32. D. E. Woessner and J. R. Zimmerman, *J. Phys. Chem.*, **67,** 1590 (1963).
33. S. Ablett, P. J. Lillford, S. M. A. Baghdadi, and W. Derbyshire, *J. Colloid Interface Sci.*, **67,** 355 (1978).
34. L. J. Lynch and K. H. Marsden, *J. Colloid Interface Sci.*, **42,** 209 (1973).
35. S. Ablett, P. J. Lillford, S. M. A. Baghdadi, and W. Derbyshire, *ACS Symp. Ser.*, **34,** 344 (1976).

36. W. W. Fleming, R. E. Fornes, and J. D. Memory, *J. Polym. Sci. Polym. Phys. Ed.*, **17,** 199 (1979).
37. E. Forslind, in *NMR-Basic Principles and Progress*, Vol. 4, Springer Verlag, Heidelberg, 1971, p. 145.
38. M. F. Froix and R. Nelson, *Macromolecules*, **8,** 726 (1975).
39. J. Andrasko, *Biophys. J.*, **15,** 1235 (1975).
40. J. C. Hindman, A. Svirmickas, and M. Wood, *J. Chem. Phys.*, **59,** 1517 (1973).
41. M. J. Tait, A. Suggett, F. Franks, S. Ablett, and P. A. Quickenden, *J. Solution Chem.*, **1,** 131 (1972).
42. M. Ihnat, A. Szabo, and D. A. I. Goring, *J. Chem. Soc. A*, **1968**(7), 1500.
43. E. Forslind, *Prog. Colloid Polym. Sci.*, **56,** 12 (1975).

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