Three modes of dissociation of H bonds in hydrogen-bond dominated solids

ICE, paper and regenerated cellulose, Nylon (unstretched and lightly stretched), and to a certain extent natural cellulose, lignin and wool are typical examples of hydrogen-bond dominated solids (whose mechanical properties are mostly controlled by the density and characteristics of the hydrogen bond). Previously[1] I have shown that for these materials, Young's modulus E is related to N, the effective number of H bonds per cm^3 responding to unidirectional stress, by $E = kN^{1/3}$. For cellulosics k is $\sim 8 \times 10^2$ when E is in Pa. Two major rheological characteristics of hydrogen-bond dominated solids are their ready softening by water and their relaxation of stress with time under constant strain. Thus, E_w/E_0, the ratio of the modulus at w g H_2O/g solid to the modulus at $w = 0$, drops to very small values for paper at saturation. Similarly, E_t/E_0, the modulus at time t to E at $t = 0$ in a stress relaxation experiment, drops to small ratios at high values of t. I postulate that both types of loss in E arise from reductions in N, through H-bond dissociation. I find this dissociation can be in one of three modes: I, II and III.

Mode I dissociation occurs on wetting a hydrogen-bonded solid within the range, $0 < w < w_c$ where w_c is a critical moisture content designating transition from mode I to mode II. w_c is postulated to be equal to w_m, the moisture content for a monomolecular layer calculated by BET equations[17] applied to the adsorption isotherm of water on the particular polymer. Mode II occurs when $w_c < w < w_{sat}$ where w_{sat} denotes the water saturation value of w. Further, let N_0 be the value of N at $w = 0$ and W be the hypothetical value of w which allows one H_2O molecule for each potential H bond in the solid. (For cellulosics, with potentially six H bonds existing per repeat unit of cellobiose, $W = 1/3$.)

In mode I we begin with

$$d(N_w/N_0)_1 = -(N_w/N_0)_1 d(w/W) \tag{1}$$

and arrive at

$$\ln(E_w/E_0)_1 = (-1/3)(w/W) \tag{2}$$

(The suffix 1 denotes mode I.) Hence, specifically for cellulosics

$$\ln(E_w/E_0)_1 = -w \tag{3}$$

This has been demonstrated for paper for $0 < w < w_m$ (ref. 1).

In mode II, dissociation is cooperatively undertaken by a number of bonds breaking down together. I use here Frank and Wen's hypothesis[2] of H bonds making and breaking cooperatively together in flickering clusters. Thus, I postulate that a molecule of water initiates the cooperative phenomenon by breaking only one bond, but this triggers others to break immediately. The total number is equal to the cooperative index (CI) but the reaction is still unimolecular in N. Thus

$$d(N_w/N_0)_2 = -(\overline{CI})(N_w/N_0)_2 d(w/W) \tag{4}$$

with initial condition at $w = w_c$

$$\ln(N_w/N_0)_2 = \ln(N_w/N_0)_1 = -(w_c/W) \tag{5}$$

Hence

$$\ln(E_w/E_0)_2 = (1/3)\{(w_c/W)[(\overline{CI})-1]-(\overline{CI})(w/W)\} \tag{6}$$

For cellulose, $W = 1/3$, and equation (6) reduces to

$$\ln(E_w/E_0)_2 = w_c[(\overline{CI})-1] - (\overline{CI})w \tag{7}$$

The mean cooperative index $(\overline{CI})$ can be calculated from rheological data, but an *a priori* value was obtained from Starkweather's analysis[3] of the cluster behaviour of water adsorbed on polymers, using Zimm's thermodynamic concepts[4,5], as well as calculations by Némethy and Scheraga[6] for water at room temperature and found, for cellulose and Nylon 66, to be: $(\overline{CI}) = 6.71$.

Comparison of data in the literature on the dependence of E_w on w for paper[7–11] gives the mean for $(\overline{CI})$ as 6.70 ± 0.89 The mean w_c for these experiments was 0.047 ± 0.011, whereas w_m for paper is normally between 0.04 and 0.06. The average for different cellulosics studied by Meredith[12] (ramie, Fortisan, viscose rayon and mercerised cotton) was found to be $(\overline{CI}) = 7.7 \pm 2.7$. The value for w_c was indeterminate because of the large standard deviations in the data, (-0.042 ± 0.09). The average for Nylon 66 studied by Meredith[12] and others[13,14] was $(\overline{CI}) = 6.70 \pm 2.1$. The average w_c was indeterminate but clearly < 0.01 g H_2O/g solid $(0.003 \pm 0.005$; W for Nylon 66 is 0.1593).

Thus, the cooperative dissociation of H bonds in mode II is still 'unimolecular' in N, even though approximately seven bonds are triggered to break down together on average.

In mode III, controlling stress relaxation under constant strain, the dissociation is polymolecular in N. This may be explained by imagining the need for a minimum number of bonds, α, having to dissociate simultaneously before a unit jump leading to stress relaxation becomes possible. Thus, it was found empirically from analysis of rheological data[1]

$$\frac{d(N_t/N_0)}{dt} = -\sum_{i=1}^{i-\alpha} k_i(N_t/N_0)^{\alpha_i} \tag{8}$$

(where $N_0 = N$ at $t = 0$) with explicit interconnections between k_i with k_{i+1} and α_i with α_{i+1} respectively. The infinite series of different reaction rate constants k_i and cooperative indices α_i soon degenerate into a single reaction of rate k_1 and of order α_1, the 'principal cooperative index', which controls the stress relaxation curve for all values of $(N_t/N_0) \lesssim 0.8$.

Analyses of data published by Houghton and Sellen[15] on dry and wet regenerated cellulose at subzero temperatures reveal interesting maxima and minima in α_1 at particular temperatures.

Thus, in mode III the cooperative dissociation of H bonds is different from that in mode II in being truly polymolecular whereas in mode II it is unimolecular in N.

Details of these studies will be published elsewhere[16].

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