the mole fraction F_2 of VDC in the copolymer radicals; the latter quantity is given by the standard relation[11]

$$F_2 = (f_1f_2 + r_2f_2^2)/(r_1f_1^2 + 2f_1f_2 + r_2f_2^2) \qquad (8)$$

The three sets of points and curves correspond to chosen ratios k_{t11}/k_{t22} equal to 2.2, 1, and 0.3. The largest of these is obtained by combining the observed k_{t11} of Burnett and Wright[18] for VC in tetrahydrofuran with our own[1] k_{t22} for VDC and correcting (as required by diffusion control[19]) by the ratio $\eta_1/\eta_2 = 0.25$ of the solvent viscosities.[20] It is seen in Figure 3 that smooth curves for k_t as a function of radical composition can be drawn if the point of lowest VDC content is ignored.

We conclude that an adequate description of the system can be based on the Atherton–North treatment, or equally well on the classical one. Our principal result is that there is no anomalous termination behavior in the homogeneous VC–VDC copolymerization system.

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Density of Hydrogen Bonds in H-Bond Dominated Solids

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ABSTRACT: Hydrogen-bond dominated solids belong to the class of solids the elastic properties of which, either in theoretical analysis or experimental studies, are found to be related in the first approximation to the density and characteristics of the hydrogen bond with only minor or negligible contributions from covalent, ionic, or van der Waals' bonds or from entropic changes. For such solids, previous work determined that $E = kN^{1/3}$ where E is Young's modulus in dyn/cm^2, N is the number of H bonds per cm^3 effectively carrying the load, and k is a constant equal to 7.8×10^3 dyn/cm for OH- - -O bonds occurring in cellulosics based on H-bond dissociation energy of 4.5 kcal/mol, internuclear distance of 2.7 Å, and a Morse function for the bond potential. In this paper, the value of k is determined from an independent source. By using calculations carried out by Dr. Richard E. Mark and his colleagues at Syracuse University for the three moduli of elasticity for cellulose crystallites, k was calculated for a sheet of randomly oriented crystallites and was found to be $(9.7 \pm 1.6) \times 10^3$ dyn/cm. It is concluded that k probably equals 8.7×10^3 dyn/cm, with an uncertainty of approximately 20%.

The elastic properties of solids are, ultimately, manifestations of changes in their molecular free energies brought about by deformation. Thus, Young's modulus E is in principle calculable from changes in the internal energy and entropy of the solid. In general, the elastic properties of all solids must have contributions from all factors which affect the internal energy and entropy of the system when the solids are deformed. However, it often happens that one contribution predominates to such an extent that, to a first approximation, it alone needs to be considered and others may be neglected. For example, although contributions from the energy potentials of covalent, ionic, and dispersion bonds as well as from the entropy of conformation may generally affect the elastic response of actual samples of natural rubber, very useful predictive formulations of elastomeric responses to strain have been made with benefit to the study of this class of materials by considering solely the entropic contributions, neglecting energy changes.

In this restricted sense, certain materials may be defined as H-bond dominated solids. They form a class of solids the elastic properties of which, either in theoretical analysis or experimental studies, are found to be related in a first approximation to the density and characteristics of the hydrogen bond with only minor or negligible contributions from covalent, ionic, or van der Waals' bonds or from entropic changes. Examples are ice, rayon or other relatively disordered or low-stretch cellulosics, paper, low-stretch Nylon and similar H-bonded polymers, as well as, probably, many biological tissues and membranes.

Previous studies by the author on H-bond dominated solids based on a Morse function for the potential of the hydrogen bonds resulted in the following principal equations.[1]

(1) For a body containing a total of N_T randomly oriented hydrogen bonds, distributed with uniform density and taking part in resisting uniaxial small tensile strains, the effective number of bonds N which may be considered to resist the

uniaxial strains in the body is given by:

$$N = (N_T/3) \tag{1}$$

(2) For such a body the stress σ is related to the strain ϵ by:

$$\sigma = (2a\Delta H N^{2/3}/r_e) \times [1 - \exp(-a\epsilon/r_0 N^{1/3})][\exp(-a\epsilon/r_0 N^{1/3})] \tag{2}$$

or

$$\sigma = E\epsilon - K\epsilon^2 + \text{(higher order terms)} \tag{3}$$

where

$$E = \lim_{\epsilon \to 0} (\sigma/\epsilon) = -(2a^2\Delta H/r_e r_0)N^{1/3} \tag{4}$$

or

$$E = kN^{1/3} \qquad (k = \text{species constant}) \tag{5}$$

and

$$K = -3a^3\Delta H/r_e r_0^2 \tag{6}$$

with a = universal constant in the Morse function for H-bond potential; ΔH = hydrogen bond energy; r_e = the equilibrium distance between O and the distant H in the hydrogen bond H–O- - -H; $r_0 = r_e(1 + k_2/k_1)$ where k_2/k_1 is the ratio of the force constants of the weak, long O- - -H limb to the strong O–H limb of the H-bond, respectively.

(3) Furthermore, after these primary equations were found, several secondary equations predicting the influence of temperature, moisture, and stress relaxation on E were derived in the general form:

$$\ln (E_2/E_1) = f(T,w,t) \tag{7}$$

where subscript 2 referred to the condition being studied and subscript 1 referred to a standard condition, of temperature T, of water content w as g H_2O/g solid, and of time t. An example, which will be used in the present paper, was the temperature function given in:

$$\mathrm{d} \ln E/\mathrm{d}T = -0.0039(°\mathrm{C})^{-1} \tag{8}$$

for cellulose when T was measured in °C. These equations were checked against as many data as could be found in the literature[2] and found to be, generally, valid.

It will be noticed that in the equations of type 7 ratios of E are used. Therefore, k in eq 5 disappears. In most situations, this fact is of minor importance, but sometimes the absolute value of k is required. (An example is the determination of H-bond dissociation rate constant from stress relaxation.[2]) Besides, if the value of k as calculated from reasonable value of a, ΔH, r_e, r_0 could be checked against materials where both E and N were either known or calculated by independent, reasonably exact methods, the theory advanced would receive a good measure of validation of the principal assumptions. The purpose of this communication is to present such a comparison.

Validation of the Constant k

In the theory described in ref 1 k was calculated for cellulose by assigning the following values: $a = 2.0$; $\Delta H = 4.5$ kcal/mol or 3.1×10^{-13} ergs/bond; $r_e = 1.7 \times 10^{-8}$; and $k_2/k_1 = 0.12$. Then when σ, the stress, is in dyn/cm^2,

$$k = 7.78 \times 10^3 \text{ dyn/cm} \tag{9}$$

To check this value, I propose to use the results of the more exact calculations made by Jaswon, Gillis, and Mark[3] of the three moduli of elasticity of a cellulose crystallite. The calculations were based on the geometry of all the atoms in the crystallite and taking force constants for interatomic bonds and bond angles. A chair conformation was assigned to the cellulose molecule, and the unit cell of Meyer and Misch was adopted. Dr Richard Mark has very kindly sent me a correction sheet (private communication) from which I quote the following values:

$$E_{11} = 2.54 \times 10^{11};\ 2.57 \times 10^{11}$$
$$\therefore \bar{E}_{11} = 2.56 \times 10^{11} \pm 0.02 \times 10^{11}$$
$$E_{22} = 5.65 \times 10^{11};\ 5.65 \times 10^{11}$$
$$\therefore \bar{E}_{22} = 5.65 \times 10^{11} \pm 0.00 \times 10^{11}$$
$$E_{33} = 3.80 \times 10^{11};\ 1.68 \times 10^{11}$$
$$\therefore \bar{E}_{33} = 2.74 \times 10^{11} \pm 1.50 \times 10^{11}$$

All values are in dyn/cm^2 and are at 0 K. The two values of each E_{ii} are calculated by making different assumptions for the force constants of the hydrogen bonds. It is seen that E_{22}, the modulus along the b axis of the Meyer and Misch unit cell or parallel to the cellulose chain, is on the low side, and the authors are rightly puzzled by its being so low, since ramie and other highly oriented cellulosic fibers give higher values for E along the fiber axis. Therefore, they assumed that these calculations set a lower bound for E_{22}.

Later, Dr. Mark suggested to Dr. Gillis that a higher value for E_{22} would be calculated if certain geometric factors were taken into account. Dr. Gillis did this and recalculated the moduli. But because he did not take full account of other restraints, he concluded that he had calculated an *upper* limit for E_{22}. His values[4] were:

$$E_{11} = 2.492 \times 10^{11};\ 2.516 \times 10^{11}$$
$$\therefore \bar{E}_{11} = 2.504 \times 10^{11} \pm 0.017 \times 10^{11}$$
$$E_{22} = 31.906 \times 10^{11};\ 24.641 \times 10^{11}$$
$$\therefore \bar{E}_{22} = 28.274 \times 10^{11} \pm 5.137 \times 10^{11}$$
$$E_{33} = 3.726 \times 10^{11};\ 1.644 \times 10^{11}$$
$$\therefore \bar{E}_{33} = 2.685 \times 10^{11} \pm 1.472 \times 10^{11}$$

Again, all values are in dyn/cm^2 and at 0 K.

An overall average $\bar{E}$ for isotropic cellulose cannot be calculated by simply taking the arithmetic mean of these values. It is necessary to use a physical model to help us average properly. The simplest model for calculating $\bar{E}$ would be based on an isotropic sheet of cellulose composed of a large number of cubes joined across their faces to each other with hydrogen bonds and each made up of bundles of microcrystals oriented along one of the three principal dimensions of the cube. The cubes would be assumed to be randomly oriented with respect to each other but with sides along X, Y, and Z dimensions of the sheet, and the sheet would be subjected to tensile stretch in the X direction. In such a case, the cubes would have $\bar{E}_{11}$, $\bar{E}_{22}$, and $\bar{E}_{33}$ as their moduli and sides $l_{11} = l_{22} = l_{33}$. To relate the modulus of the sheet in direction X to the moduli E_{ii}, consider a sheet 1 cm thick. Isolate a cube within the sheet with a 1 cm side in each of the principal axes X, Y, Z and let it be subjected to force F in the direction X. It will stretch by ΔL cm given by $\Delta L = F/\bar{E}$, where $\bar{E}$ is the modulus of the sheet in direction X. Let this 1-cm cube be divided into n smaller cubes with $(n/3)$ having E_{11}, $(n/3)$ having E_{22}, and $(n/3)$ having E_{33} moduli in the direction X. Thus, there will be $(n^{1/3})$ of these smaller cubes in series along the X axis and $(n^{2/3})$ cubes in parallel across the face YZ of the 1-cm cube. The length l_{ii} of each side of the small cubes will be $(1/n^{1/3})$ cm. The force experienced by each small cube will be $(F/n^{2/3})$. Each small cube will, therefore, stretch by Δl_{ii} in direction X given by $\Delta l_{ii} = [(n^{2/3}f)/E_{ii}](1/n^{1/3}) = n^{1/3}f/E_{ii}$. There are $(n^{1/3}/3)$ of each type in series and the total stretch in direction X, $\Delta L = (n^{1/3}/3)\Sigma\Delta l_{ii}$. Hence,

$$(1/\bar{E}) = \Delta L/F = (n^{1/3}/3)(n^{1/3}\mathrm{f})[\Sigma(1/E_{ii})/n^{2/3}f]$$

or

$$(1/\bar{E}) = \tfrac{1}{3}(1/\bar{E}_{11} + 1/\bar{E}_{22} + 1/\bar{E}_{33}) \qquad (10)$$

Using the figures of Jaswon et al., the lower value for $\bar{E}$ would be $\bar{E} = 3.217 \times 10^{11}$ dyn/cm^2 at 0 K. Using the results of Gillis, the upper value would be $\bar{E} = 3.717 \times 10^{11}$ dyn/cm^2 at 0 K. In the absence of further information, the best estimate of $\bar{E}$ would be $\bar{E} = 3.467 \times 10^{11} \pm 0.35 \times 10^{11}$ dyn/cm^2 at 0 K. Nissan's equations are for $\bar{E}$ at 20 °C and there are no theoretical formulas for the change of E for cellulosics with temperature other than eq 8 above which, when integrated, gives:

$$\bar{E}_{20\,^\circ\mathrm{C}} = \bar{E}_{0\,\mathrm{K}} \exp(-0.0039 \times 293)$$

or

$$\bar{E}_{20\,^\circ\mathrm{C}} = 1.1 \times 10^{11} \pm 0.1 \times 10^{11}\ \mathrm{dyn/cm^2} \qquad (11)$$

These calculations were based on isometric unit cubes forming the sheet. The size of the cube was not defined and could be relatively large in terms of the sample dimensions. The larger the elementary unit is the less the uniformity of the sample. To produce the most uniform isotropic sheet, the dimensions of the elementary unit should be a minimum. An absolute minimum exists when the unit is of the size of the Meyer and Misch unit cell. Thus, another and a more general way of forming the sheet is out of single Meyer and Misch unit cells, which are anisotropic, all laid out with the cell axes (assumed normal to each other) parallel with X, Y, and Z dimensions of the sheet, but randomly distributed with respect to each other. Here $L_1 = 8.35 \times 10^{-8}$ cm, $L_2 = 10.3 \times 10^{-8}$ cm, and $L_3 = 7.90 \times 10^{-8}$ cm. Thus the values of E_{ii} will have to be weighted differently in calculating $\bar{E}$. The calculations of $\bar{E}$ from $\bar{E}_{11}$, $\bar{E}_{22}$, $\bar{E}_{33}$ and L_1, L_2, and L_3 follow essentially the same path as for $\bar{E}$ from a sheet made up of unit cubes with $L_1 = L_2 = L_3$ except that the values are somewhat complicated by geometric factors. These appear as ratios of the different L's. For such an isotropic sheet made up of a large number of anisotropic unit cells randomly and uniformly distributed but with all axes parallel to either X, Y, or Z, we get

$$(1/\bar{E}) = \tfrac{1}{3}[1/\bar{E}_{11} + (1/\bar{E}_{22})(L_2/L_1)^2 + (1/\bar{E}_{33})(L_3/L_1)^2] \times \{[(L_1/L_3) + (L_1/L_2) + 1]/[(L_3/L_1) + (L_2/L_1) + 1]\} \qquad (12)$$

It will be noticed that when $L_1 = L_2 = L_3$ eq 12 reduces to eq 10. Here, if we substitute the lower values for $\bar{E}_{ii}$ and L_i, we obtain $\bar{E} = 3.372 \times 10^{11}$ dyn/cm^2 at 0 K. If we then substitute the higher values, we obtain $\bar{E} = 4.228 \times 10^{11}$ dyn/cm^2 at 0 K. In the absence of further information favoring either of the two sets of values, the best estimate of $\bar{E}$ is the arithmetical mean of these two values. Thus, $\bar{E} = 3.880 \times 10^{11} \pm 0.61 \times 10^{11}$ dyn/cm^2 at 0 K.

Again we must change $\bar{E}_{0\,\mathrm{K}}$ to $\bar{E}_{20\,^\circ\mathrm{C}}$ by using the exponential eq 11. Thus, we finally arrive at $\bar{E}_{20\,^\circ\mathrm{C}} = (1.2 \pm 0.2) \times 10^{11}$ dyn/cm^2 at 20 °C.

It is now possible to check the results of our theory against these figures. The theory states

$$E_{20\,^\circ\mathrm{C}} = 7.78 \times 10^3 N^{1/3} \qquad (5), (9)$$

where

$$N = (N_\mathrm{T}/3) \qquad (1)$$

and N_T is the total number of bonds, randomly and uniformly distributed in 1 cm^3 of a cellulosic sheet. The Meyer and Misch unit cell considered by Mark and his colleagues in their calculations had a volume of 676 Å^3 and was assumed to possess four intermolecular hydrogen bonds. (The remaining H bonds are intramolecular and contribute to the stiffening of the chain, i.e., to E_{22}.) Thus, taking the same unit cell as a basis here, one hydrogen bond will be found, on average, in 169×10^{-24} cm^3 and $N_\mathrm{T} = 5.92 \times 10^{21}$ bonds per cm^3. This is equivalent to $N = 1.973 \times 10^{21}$ and $N^{1/3} = 1.254 \times 10^7$ bonds/cm. Thus, according to the theory, such an isotropic cellulosic body would have:

$$E_{20\,^\circ\mathrm{C}} = 7780 \times 1.254 \times 10^7 = 1.0 \times 10^{11}\ \mathrm{dyn/cm^2} \qquad (13)$$

vs. the higher figure of

$$\bar{E}_{20\,^\circ\mathrm{C}} = (1.2 \pm 0.2) \times 10^{11}\ \mathrm{dyn/cm^2} \qquad (14)$$

calculated directly from the elastic constants of the Meyer–Misch unit cells and their geometry. As has already been explained, the second model is the most general for uniformly distributed, randomly oriented unit crystallites since it reduces the size of the crystallite to the unit cell; it includes the first model as a special case. Hence, it is the preferred model. It happens also to have the larger difference from the predicted value. Therefore, it will be adopted here to study the magnitude of the deviation and its implication to the theory.

$$\Delta\bar{E} = (\bar{E} - E) = (1.2 - 1.0) \times 10^{11} = 0.2 \times 10^{11}\ \mathrm{dyn/cm^2} \qquad (15)$$

vs. a standard deviation in the estimate of $\bar{E}_{20\,^\circ\mathrm{C}}$ of 0.2×10^{11} dyn/cm^2. In other words, the difference between the two calculations is one standard deviation of the more exact calculation. Considering the very different approaches of the two methods and the need to extrapolate from 0 K to 20 °C, the agreement may not be too bad.

It is not as yet possible to state definitely what the actual values of E_{ii} for the crystallite are. But if we accept the above calculations and adopt $\bar{E}_{20\,^\circ\mathrm{C}} = 1.21 \times 10^{11}$ dyn/cm^2, we can recalculate k as

$$k = (1.2 \times 10^{11})/(1.254 \times 10^7) = 9.65 \times 10^3 \qquad (16)$$

instead of 7.78×10^3 adopted in our theory.

Summary and Conclusions

In H-bond dominated solids, $E = kN^{1/3}$ and k is of order of 7.8×10^3 dyn/cm for cellulosics as calculated from assigning reasonable values to the parameters in the controlling Morse function originally assumed in developing the theory for cellulosics of relatively low order. Later, relatively more exact calculations of the moduli of cellulose crystallites used in developing an isotropic body of randomly oriented crystallites yielded a value for k of the order of 9.65×10^3. The standard deviations of both methods of calculation are of the same order as the difference between them; hence, the difference is probably not significant.

Thus, it is concluded that $N^{1/3}$ for cellulosics (i.e., the effective number of H bonds per cm) can be calculated from E, by taking either of the two values, or their mean 8.7×10^3, with an uncertainty of approximately 20%. For other H-bond dominated solids, appropriate values for ΔH, r_e, and r_0 (or for k_2/k_1) have to be used in calculating the appropriate value of k.

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