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The Elastic Modulus of Lignin as Related to Moisture Content

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Summary. In previous papers, a theory was developed relating Young's modulus of hydrogen-bond dominated solids to the density of this bond and to its parameters, and also to the moisture content of the solid. In this paper, the theory is applied to experimental results reported by Cousins on periodate lignin. The theory fits the observations and, furthermore, predicts that this particular lignin has 6.84 potential H-bonding sites per repeating unit of an assumed molecular weight of 1,000. No data for periodate lignin exist, but a Freudenberg constitutional scheme for lignin postulates a little over 7 potential sites for H-bonding per repeating unit of 1,000 molecular weight.

The paper by W. J. Cousins [1976] on the above subject provides a very welcome set of data in an almost barren field. These data will be particularly appreciated by theoreticians struggling to fit observations to underlying structures and mechanisms. The present communication aims to illustrate such an attempt.

In a paper [Nissan 1976], I have developed a theory relating the modulus of elasticity of H-bond dominated solids, E, to their regain w (i.e., gms H_2O/gm solid). The theory is based on a previous formulation of E in terms of the characteristics of the hydrogen bond and its density N (i.e., number of effective H-bonds/cm^3) [Nissan 1957] and utilizes the ideas of Frank and Wen [1957] on the cooperative behavior of H-bonds and calculations by Starkweather [1975] and Némethy and Scheraga [1962] on the clustering of H_2O molecules on cellulose and in liquid water. The derivation will not be repeated here, but the results are

$$\text{Regime 1:} \quad \ln (E/E_0)_1 = -(\tfrac{1}{3})\,(w/W) \quad \text{when } 0 \leqslant w \leqslant w_m \tag{1}$$

$$\text{Regime 2:} \quad \ln (E/E_0)_2 = (\tfrac{1}{3})\,\{(w_m/W)\,[(\overline{C.I.}) - 1] - (\overline{C.I.})\,(w/W)\} \quad \text{when } w_m \leqslant w \leqslant w_{\text{saturation}} \tag{2}$$

At

$$w = w_m, \quad \ln (E/E_0)_1 = \ln (E/E_0)_2 = -w_m/W \tag{3}$$

In these equations:

Suffix 1 denotes behavior in regime 1
Suffix 2 denotes behavior in regime 2
w_m = value of w at the B.E.T. monomolecular layer adsorbed on the solid
W = value of w which would hypothetically give 1 H_2O molecule per potential hydrogen bonding group in the solid.

$$= 18\,n/(M.W.) \tag{4}$$

n = number of potential sites for hydrogen bonding on repeating unit of (M.W.) molecular weight
$\overline{(C.I.)}$ = the average cooperative index or total number of dissociating H-bonds when one of the bonds dissociates on adsorbing a molecule of water.

These equations appear to describe well the behavior of paper, ramie, fortisan, mercerized cotton, rayon, nylon and wool.
To use these equations in analyses for n and $\overline{(C.I.)}$, the two important parameters in this theory, normally the following steps may be followed:
(1) From measured values of E_0 (E at w = 0) and E at a low regain (i.e., $w < 0.05$), Eq. (1) is used to yield W and hence, through Eq. (4), n is calculated.
(2) From a regression of $\ln(E/E_0)$ on w, two constants, the intercept at w = 0 and the slope, are used together with W from (1) to calculate w_m and $\overline{(C.I.)}$. w_m is then checked against experimental w_m, if an adsorption curve is available. If it checks, then $\overline{(C.I.)}$ appears credible, and the cooperative dissociation of H-bonds in that particular solid is elucidated.
This approach is unfortunately not available here, since E_0 was not a measured value but an estimate by R. E. Mark on E_0 for "lignin" which was adopted by Cousins. Hence, its influence on W and the other parameters is too great to be an acceptable risk.
A second approach, which I had adopted in the analysis of cellulosics, paper, nylon, etc., where the chemical composition is precisely known, is to calculate W from the structural formula and then follow step (2) above. This approach is not quite available to us with lignin either as its formula is not precisely known although, as I shall show, I use it later to check the "credibility" of the value for W calculated by the third method available to us.
The third method, adopted here, is to determine w_m from a B.E.T. analysis of water adsorption curve for lignin and then use it in Eq. (2) to obtain values for W and $\overline{(C.I.)}$ from the regression of $\ln(E/E_0)$ on w. W is then checked against what is known of lignin structure. This method will be illustrated in what follows. Because E_0 is estimated for the periodate lignin, I have taken the curve for this lignin giving E vs. moisture on Fig. 4 of Cousin's paper [1976]. The mean values of E, read off the curve, are the following.

Moisture content, %	0.0	3.6	7.5	9.8	11.9
w, g H_2O/g solids	0.000	0.037	0.081	0.109	0.135
$\bar{E} \times 10^9$, Pa	7.0	6.6	5.2	4.3	3.2

Using Eq. (2) in the form

$$\ln (\bar{E}/E) = A - Bw \tag{5}$$

a regression of $\ln (\bar{E}/E_0)$ on w yielded:

$$\ln (\bar{E}/E_0) = 0.2433 - 7.1803\,w; \quad r^2 = 0.9682 \tag{6}$$

Hence,

$$(\tfrac{1}{3})\,\{(w_m/W)\,[\overline{(C.I.)} - 1]\} = 0.2433 \tag{7}$$

and

$$(\tfrac{1}{3})\,\overline{(C.I.)}/W = 7.1803$$

(It will be noted that $\ln \bar{E}$ vs. w yields a straight line with $r^2 = 0.9682$ even though the original data of E can also be plotted directly against moisture content to yield a straight line with $r^2 = 0.88$. Of course, in using $\bar{E}$ instead of E, r^2 tends to rise; it is not argued that $\ln \bar{E}$ is a better empirical function than E is of w as both straight lines may be of equal fit to the data; it is proposed as a more useful theoretical function.)

Next, the data of moisture content (changed to w) vs. relative humidity (changed to relative pressure) of Fig. 1 in Cousins' paper was read off the curve as follows:

Relative pressure, P	0.12	0.33	0.54	0.76	0.975
w	0.0384	0.0811	0.1086	0.1364	0.2165
$\frac{P}{w(1-P)}$	3.55	6.07	10.81	23.22	180.14

A B.E.T. analysis was performed to extract w_m, the value of w at a monomolecular layer. Thus, it was found that up to P = 0.54 a straight line was obtained when $P/w(1 - P)$ was plotted against P with

$$P/w(1 - P) = 1.1057 + 17.2857\,P; \quad r^2 = 0.9698$$

The B.E.T. equation was used in the form

$$P/w(1 - P) = (1/w_m C) + [(C - 1)/w_m C]\,P \tag{8}$$

Thus

$$w_m = 1/\{\text{slope} + [P/w(1 - P)]_{P=0}\} \tag{9}$$

$$= 1/(17.2857 + 1.1057)$$

$$= 0.0544 \text{ gms } H_2O/\text{gm solid} \tag{10}$$

Stamm [1964] states that a general or average value for w_m for "lignin" is of the order of 0.05 in agreement with these data. Eq. (5) then yields

$$[\overline{(C.I.)} - 1]/W = 0.2433 \times 3/0.0544 = 13.4173 \tag{11}$$

Eq. (6)

$$\overline{(C.I.)}/W = 3 \times 7.1803 = 21.5409 \tag{12}$$

Hence

$W = 0.1231$ gms H_2O/gm solid

and

$\overline{(C.I.)}$ = 2.65 H-bonds dissociating cooperatively on adsorption of 1 molecule of H_2O

Using Eq. (4)

$$n = \frac{W \times M.W.}{18} \tag{13}$$

For a repeating unit of 1000 molecular weight assumed for the lignin,

n = 6.84 potential H-bonding sites for H_2O/repeating unit.

In other words, there are $6.84 \times 6.02 \times 10^{23} = 4.12 \times 10^{24}$ sites for potential H-bonding (alcoholic OH, phenolic OH, COOH) per 1000 g of the periodate lignin of *Pinus radiata* analyzed.

Discussion

The purpose of this communication was to illustrate the utility of the theory and equations discussed in shedding light on the inner structures and mechanisms of the phenomena: It appears then:

(1) A cooperative phenomenon wherein H-bonds break together exists when periodate lignin adsorbs water. The average cooperative index $\overline{(C.I.)}$ is 2.65 for this lignin compared to 6.71 for paper, several cellulosics and Nylon 66 [Nissan 1976]. The difference is, at present, without rigorous explanation but could be due to different degrees of steric hindrances to cooperative action of the H-bonds existing in lignin and the other materials respectively.

(2) n for this periodate lignin is 6.84 per 1000 molecular weight repeating unit as calculated by the present method. This represents the total number of phenolic OH, alcoholic OH and COOH groups per repeating unit (assumed to be 1000 molecular weight). This value of n, as can be seen from Eqs. (11), (12) and (13) is influenced by both the slope and the intercept of the straight line connecting $\ln (E/E_0)$ with w. The slope is not influenced by the value adopted for E_0; the intercept is affected directly by this value. From above, E_0 was taken as 7.0×10^9 Pa, which was, unlike the other means of measured values, an estimate by Mark quoted and plotted by Cousins in Fig. 4. This figure may, therefore, not be applicable to the particular periodate lignin studied by Cousins. I was interested to determine E_0 by Eq. (1) using W = 0.1231. Thus,

$$\ln (E/E_0)_1 = -(\tfrac{1}{3})\,(w/0.1231) \tag{14}$$

Using $E = 6.6 \times 10^9$ Pa at $w = 0.037$, $E_0 = 7.3 \times 10^9$ Pa instead of 7.0×10^9. Thus, uncertainties exist in the values of n, W and $\overline{(C.I.)}$ calculated here. It is necessary to determine not only w_m (as was done above) but also W (or n) by independent means, e.g. chemical analysis, in order to fix definitely the true value of the intriguing parameter, $\overline{(C.I.)}$, the average cooperative index. It would then be possible to compare more meaningfully $\overline{(C.I.)}$ for lignin with $\overline{(C.I.)}$ values for other H-bond dominated solids such as cellulosics, paper and nylon which give a single value of $7 (\pm 2)$ and wool which appears to give a lower value.

In an attempt to check these findings against experimental results, I failed to find data on periodate lignin of *Pinus radiata*. However, I have used a generalized, constitutional scheme for lignin propounded by Freudenberg [1964] for native softwood lignins. Periodate lignin should on the one hand, have more H-bonding sites as it oxidizes some of the groups into such sites and, on the other, less sites than Freudenberg's lignin as it might change phenolic OH and other groups to non-hydrogen-bonding groups. I have assumed that, on balance, W for periodate lignin would not differ greatly from that for Freudenberg's hypothetical structure for softwood lignins. A count of potential sites for H-bonding and subsequent dissociation on adsorption in Freudenberg's structure gave either 23.5 potential sites for 3,305 molecular weight repeating unit or 24.5 potential sites for a 3,321 molecular weight repeating unit, depending upon the choice of an H atom or an OH group at an equivocal position in the lignin molecule where it joins a carbohydrate. This gives n of 7.11 or 7.38. These figures are in good, possibly fortuitously too good, agreement with $n = 6.84$ calculated above. (Formula $W = 0.1280$ or 0.1328 respectively vs. modulus W of 0.1231.) It does, however, serve to illustrate the possible use of these analytical schemes based on the H-bond theory of the mechanical properties of H-bond dominated solids.

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