

CELLULOSE AS A VISCOELASTIC MATERIAL

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INTRODUCTION

The complex problem of viscoelasticity can be treated from a purely mathematical point of view. Gross¹ has given a concise summary on this type of analysis. Such an approach is not without merit, even for those whose interests transcend the mathematical techniques, since it clarifies our understanding of the behaviour of viscoelastic materials when subjected to various types of stress. However, the molecular interpretation of the mechanical properties of cellulose, and of all other materials, must remain the primary aim of physical chemists. To obtain such interpretations from the various phenomenological functions (*e.g.* the distribution of relaxation times) used to describe viscoelastic behaviour can be extremely difficult.

The viscoelasticity of cellulosic materials is known to be the product of many factors, interacting in complicated and, as yet, not completely understood ways; there is much evidence to indicate that these mechanical properties are strongly influenced, or even governed, by hydrogen bonds, particularly those bonds which exist in the amorphous regions of cellulose. It is reasonable to expect that a molecular theory based on the *known* properties of the hydrogen bond would be a logical first approximation to the viscoelastic behaviour of cellulose. The authors believe that such an approach is intrinsically more desirable than an attempt to translate the somewhat abstract nature of a distribution of relaxation times into molecular reality. Nevertheless, some aspects of the phenomenological problem and their interpretation should always be borne in mind since any attempt to predict viscoelastic behaviour from a molecular model must not contradict these findings.

Most attempts to treat the viscoelastic behaviour of cellulose quantitatively have been primarily concerned with the phenomenological aspects of the problem. It is well known that a single Maxwell element cannot describe, adequately, the relaxation of cellulose. Thus, many investigators have been concerned with the problem of obtaining a spectrum of relaxation times for cellulosic materials. Such an approach is tantamount to assuming that a large or infinite number of relaxation units exist in cellulose, each with a characteristic relaxation time. For example, Passaglia and Koppehele² used a modified, strain-dependent distribution function of relaxation times in order to solve the problem of non-linear viscoelastic behaviour exhibited by isotropic and oriented cellulose filaments.

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The effects of humidity and frequency on the dynamic mechanical properties of viscose rayon have been studied by Price, McIntyre, Pattison, and Dunell³. These investigators found that the dynamic moduli of rayons were constant with frequency (5–100 c/s) at constant relative humidity, while the dynamic viscosities varied with frequency, but were unaffected by changes in relative humidity. Theoretically, it is possible to relate dynamic moduli and viscosities to a distribution of relaxation times, but the non-linearity of cellulose viscoelasticity makes such an interpretation of doubtful significance.

If we choose to explain cellulose viscoelasticity in terms of the phenomenological theory, then we must explain the non-linear effects observed experimentally. Such effects can be interpreted in two ways: (i) celluloses *cannot* be considered as composed of linear springs and Newtonian dashpots; (ii) if the linear element model is to be used, then we must explain the non-linear effects as due to a continuous variation in the distribution of relaxation times induced by structural changes that occur on straining cellulose. There does not appear to be, at present, any means by which to distinguish between the two interpretations given above.

A notable attempt to describe the non-linear behaviour of polymeric and fibrous systems in terms of a semi-molecular model is that by Eyring and Halsey⁴. They propose a model consisting of two Hookean springs in combination with a viscous element obeying the Eyring hyperbolic-sine flow law. This model has been successful in describing viscoelastic phenomena in cellulosic systems (see Wakeham⁵, and also Meredith⁶). However, there is still a phenomenological point of view involved in the Eyring and Halsey model, namely, the Hookean springs, and also in the analytical separation of *elastic elements* from a *viscous element*.

MORE DEFINITELY MOLECULAR APPROACHES

Macroscopic deformation of cellulose may involve several of the following microscopic deformations: valence bond length and angle deformation, secondary bond deformation, re-orientation of macromolecules in amorphous regions, re-orientation of crystalline regions, and configurational entropy effects. Generally, when discussing the effects of these molecular processes on mechanical properties, it is convenient to classify them in somewhat arbitrary ways and consider gross changes in these properties rather than small variations with strain. Thus, the over-all effects of crystallinity, orientation (or stretch), side group additions, degree of polymerization, *etc.*, are used to classify the behaviour of cellulosic materials, bearing in mind that one or several of these properties may be changing during the straining process. It is, therefore, not always possible to assign an unequivocal value to all of these factors for a material undergoing strain. Meredith⁶ has summarized the mechanical properties of natural and regenerated cellulose and discusses various effects which supermolecular structure have on these properties, as do Tripp, Orr, Ziifle, and Conrad⁷ for native and chemically modified cottons.

Many investigators of the mechanical properties of cellulose and its derivatives have recognized the importance of the hydrogen bonds which exist in cellulose and of their profound effect on the behaviour of cellulosic materials.

A study of the infra-red region of dry cellulose by Marrinan and Mann⁸ indicates that there are *no* free hydroxyl groups in cellulosic materials. Since each cellobiose unit is capable of forming six hydrogen bonds, it seems reasonable to postulate that any viscoelastic phenomenon is accompanied by a breakdown, re-arrangement, bending, and stretching of these hydrogen bonds. There is ample evidence to support this belief.

In a summary of the mechanical properties of cellulose, Wakeham⁵ has pointed out that the hydrogen-bonding capabilities of cellulose play an important rôle in determining the properties of cellulose. Thus, the adsorption of water by cellulose leads to a marked decrease in the dynamic elastic modulus.

The effect of temperature on the elastic modulus of wet rayon is due to the number and lifetime of crosslinks which exist between cellulose chains, as postulated by Roseveare and Poore⁹. Rubber elasticity theory cannot account fully for the entropy decrease which occurs on stretching wet and room air-conditioned (50 per cent R.H.) rayon because of the observed decrease of modulus of elasticity with temperature. Roseveare and Poore postulate that the entropy decrease may be due to the increase in equilibrium moisture content which occurs on stretching rayon, as reported by Treloar¹⁰.

It should be noted that Gabrail and Prins¹¹ have analysed force, temperature, and length data for rayon, using the rigorous forms of the various thermodynamic relationships involved. These investigators point out that correction of constant pressure data to constant volume is of more importance than generally considered, and that energy effects on the stresses which are observed on stretching rayon are by no means negligible, even in the wet state. These authors suggest that the short range elasticity of dry cellulose may be due to interchain hydrogen bonding.

The effects of temperature on degree of swelling, extension at break, breaking load, and relaxation of wet viscose rayon have been studied by Clark and Preston¹². These investigators found that the variation of these properties with temperature changes markedly in the range 50–60°. Clark and Preston postulate that these changes are the net result of several reaction mechanisms, namely, the dissociation of cellulose–cellulose crosslinks, the formation of cellulose–water bonds, and the dissociation of cellulose–water bonds; each of these reactions has a characteristic reaction rate.

The effects of humidity, crystallization, and drawing on the dynamic mechanical properties of fibres have been studied by Tokita¹³, who found that the dispersion of the loss factor for rayon shifted to lower temperatures with increase in humidity. Tokita suggests that these dispersions originate in the amorphous regions since these regions are most sensitive to humidity changes. It was also noted that increased drawing tended to raise the dynamic moduli, probably because of orientation effects, while the loss factor remained independent of degree of crystallinity and of orientation.

The dispersion of mechanical properties of viscose rayon at low temperatures (0 to –80°) in the frequency range 8–80 c/s has been studied by Dunell and Price¹⁴. They found that the dynamic modulus and loss factor are independent of frequency in this range of frequencies. From the maximum slopes of the dynamic modulus and loss factor *v.* temperature

curves, the activation energies for these viscoelastic parameters were calculated to be 400 and 1100 cal/mole, respectively. Dunell and Price note that Mark's estimate of the molar cohesion energy for the cellulose chain is 6200 cal/mole per 5 Å of chain length, based on a co-ordination number of 4 for each chain. Thus, they conclude that the low activation energies found for viscose rayon suggest that the relaxation unit is a single glucose unit in the amorphous regions with co-ordination number much less than 4, or a CH₂OH side chain whose flow motion does not involve the breaking of a hydrogen bond.

The effects of degree of polymerization and molecular orientation on the ultimate mechanical properties of rayon monofilaments have been studied comprehensively by Cumberbirch and Harland¹⁵. They explain the increase of tenacity with degree of polymerization, at constant orientation (measured by birefringence), in terms of the fringe-micellar theory. It is postulated that, as the degree of polymerization increases, the probability that a given cellulose chain will connect two crystalline regions increases. Cumberbirch and Harland showed that the tenacity approaches a nearly constant value as the degree of polymerization increases beyond a certain value. Also, the increase of tenacity and the increased ratio of wet to dry strength due to higher orientation, at constant degree of polymerization, is considered to be due to an increase in the number of hydrogen bonds in the amorphous regions and in the number of minor crystallites formed. In a later paper Cumberbirch¹⁶ has investigated the effects of distribution of degree of polymerization on the mechanical properties of rayon monofilaments, and finds that a simple average D.P. is not sufficient to characterize the fibre.

Cumberbirch and Mack¹⁷ have investigated the tenacity and breaking extension of cellulose monofilaments and have developed a quantitative theory based on the concepts of statistical chain configurations. It is postulated that in the completely wet state the cellulose chains connecting crystallites are mobile due to the adsorption of water on the hydrogen bonding sites of the glucose units. The tenacity of the filament is then calculated in terms of the rupture energy of a cellulose chain and the number and distribution of chain lengths connecting adjacent crystallites.

The tenacity of wet and dry filaments correlate with degree of polymerization, as predicted by the Cumberbirch and Mack theory. The explanation given is that the increased tenacity of dry filaments, which was found to be greater by a constant amount than the tenacity of the wet filament with the same degree of polymerization, is due to the energy required to rupture the hydrogen bonds existing in the amorphous regions. Cumberbirch and Mack postulate that the degree of hydrogen bonding may be nearly independent of degree of polymerization, at constant orientation, as indicated by the constant difference of dry and wet tenacity with degree of polymerization.

The various relationships which exist between humidity (*i.e.* accessibility) and relaxation, breaking strength and length, dynamic modulus, stress-strain curve, *etc.*, indicate that the hydrogen bond is of even more importance in determining the viscoelasticity of cellulose than was previously considered. In this connection it is interesting to note that there is a positive

increase in the entropic force component with water content for various cellulosic materials, as reported in a summary by Wakeham⁵. The fact that the modulus of elasticity decreases with temperature, and also that the entropic force component remains negative and smaller in value than the energy force component, leads to the belief that even in the wet state, cellulose deformation is primarily controlled by inter- and intra-chain forces of energetic origin. If this is a valid deduction then some modification may be necessary in the finer details of Cumberbirch and Mack's theory. The principal conclusions, however, appear to contribute a major advance in the understanding of the problem.

H. Krässig and W. Kitchen¹⁸ discuss quantitatively the simultaneous influences of DP, of DP_L (the effective length of the morphological units expressed in number of glucose units), of crystallinity index and of an orientation parameter on the tensile strength of wet and air conditioned yarns and fibres. They demonstrate effectively that in previous work it was a mistaken assumption that these parameters could be changed singly: changing one inevitably changed the others. By considering them simultaneously, the true relations became clear.

It will be noticed that in both of these extensive and quantitatively checked works—by Cumberbirch and Mack¹⁷, and by Krässig and Kitchen¹⁸—the morphological units are of great significance to the ultimate properties of the fibre. It is no criticism of this approach to state that it should prove of some interest and possible value to look at even a lower level than the interconnections of the morphological units, *i.e.* to look at individual intermolecular bonds as the ultimate basis of mechanical properties. While the proper approach to a bridge design is in terms of the strengths, numbers, and geometrical relationships of the struts, beams and other morphological units which, in the aggregate, make up the bridge, it is still profitable to look at the crystallography and molecular arrangements which give the struts their peculiar properties. This is particularly true if we do not concentrate our attention on ultimate properties, but endeavour to learn the mechanism of elastic and plastic yielding at small strains.

Cellulosic materials are governed by a number of bond types: covalent, hydrogen, Van der Waals' and possibly ionic. However, if we choose a region of rigidity and yielding which is neither too high nor too low, and if we select materials which are not too highly crystalline nor too well oriented, *i.e.* if we limit ourselves to regenerated cellulose of low draw-ratios and to paper, the H-bond appears to predominate.

THE APPROACH THROUGH THE H-BOND

There is a large amount of evidence which indicates that the hydrogen bond may be the primary parameter governing the viscoelastic behaviour of cellulosic systems. Hence it appears justified to choose a *specific* model based on the properties of this bond as the logical, molecular starting point from which to elucidate the viscoelastic behaviour of cellulose. Undoubtedly, in dry regenerated cellulose with high amorphous ratio, and in strong paper, the hydrogen bond is of greater significance than in weak paper, where Van der Waals' forces are significant, or in highly crystalline or oriented

cellulose such as cotton, flax, and ramie where valence bonds are a major factor. It is likely that the hydrogen bond is of varying significance even in regenerated cellulose, depending on the degree of crystallinity, orientation, and regain. Nevertheless, it will be instructive to consider the viscoelastic dictates of a system which is completely controlled by hydrogen bonding effects, realizing that such a system is probably a first approximation to reality for some cellulosic materials, while for other cellulose (e.g. regenerated cellulose) it may prove to be a very good approximation.

In a first approach to the hydrogen bond problem, Nissan^{19, 20} made several simplifying assumptions to arrive at a working model for the viscoelastic properties of hydrogen-bonded solids. Nissan assumed that (a) the macroscopic body was isotropic and non-interacting, *i.e.* that one-third of the hydrogen bonds in the body acted along each of three principal axes, (b) no re-orientation of bonds occurred as a result of straining, (c) configurational entropy effects could be neglected.

Nissan assumed that the potential energy (U) of the hydrogen bond could be described adequately by the Morse Function*

$$U = \frac{\Delta H}{N} \left[1 - \exp(-a)(r - r_e)/r_e \right]^2 \quad (1)$$

where ΔH is the heat of dissociation of one mole of hydrogen bonds, N is Avogadro's number, a is a constant obtainable from spectroscopic data, and r and r_e are the H \cdots O distances at energy U and at equilibrium, respectively. The force on a hydrogen bond is given by dU/dr , and this force acts on an area l^2 where $3/l^3$ is the *effective* hydrogen bond density, *i.e.* the number of hydrogen bonds being strained per unit volume. (The details of the derivation have been presented in a paper by Sternstein and Nissan²¹ and only the results will be given here.) The final equation relating the macroscopic, unidirectional stress (σ) to the macroscopic strain (ϵ) is as follows:

$$\frac{Nr_e l^2 \sigma}{2a\Delta H} = \left[1 - \exp\left(\frac{-a\epsilon}{r_0}\right) \right] \left[\exp\left(\frac{-a\epsilon}{r_0}\right) \right] \quad (2)$$

where r_0 is equal to $r_e(1 + K_2/K_1)$ and K_2 and K_1 are the force constants of the H \cdots O and O—H bonds, respectively. Equation (2) is plotted in *Figure 1* and labelled "one-dimensional theory". Before considering the applications and interpretation of the hydrogen bond theory as applied to stress-relaxation, it will be useful to remove one of the limiting assumptions made by Nissan.

In any real body, the hydrogen bonds of the system will exist in various orientations with respect to the principal axes. If a unidirectional stress is applied to the body, then some distribution of strains (or stresses) will exist among the hydrogen bonds of the system. We shall refer to this effect as "interaction". In a treatment of the interaction effect for isotropic systems^{21, 22}, Sternstein and Nissan have deduced the stress-strain law for hydrogen-bonded networks which do not exhibit re-orientation or

* See p. 145 for full nomenclature.

configurational entropy effects. The problem was couched in terms of generalized stress-energy relationships, and the distribution of stresses was obtained by using the *Principle of Least Work* in conjunction with the calculus of variations. The resultant stress-strain law for unidirectional applied stress is shown in *Figure 1*, and is labelled "three-dimensional theory". It is evident that the effect of interaction is to increase the stress for any given strain; the increase in stress is due to the increased energy stored in the system due to the distribution of stress among the randomly-oriented hydrogen bonds. For example, those bonds at right angles to the direction of macroscopic strain will be in compression—the energy associated with these bonds is neglected in the one-dimensional theory.

The three-dimensional theory is not an *ad hoc* addition to the hydrogen bond theory but rather, as the authors believe it to be, the solution to the hydrogen bond network problem within the stated limitations of *isotropy*, absence of re-orientation of bonds and configurational entropy effects. The hydrogen bond theory has been checked against experimental evidence in

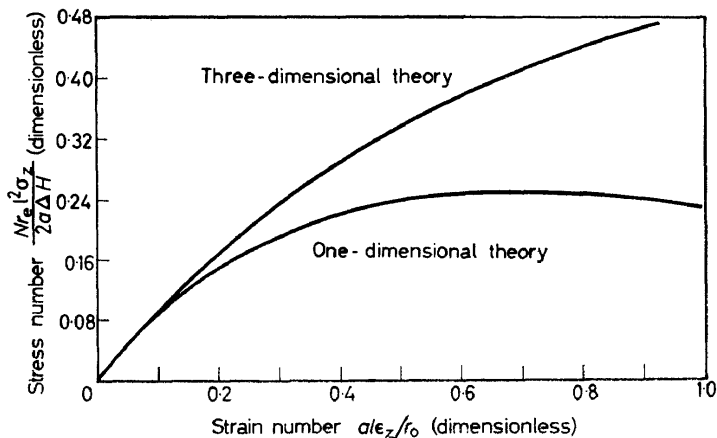


Figure 1

a number of ways and the reader is referred to other papers¹⁹⁻²² for a review of these verifications. It is our purpose here to demonstrate the application of the theory to stress relaxation as an example of viscoelasticity.

In view of the effect hydrogen bonding is believed to have on the viscoelasticity of cellulose, it is plausible to expect that a time-dependent phenomenon, such as stress-relaxation, can be studied by following the process of hydrogen bond breakdown. Thus, a strained solid will undergo a time-dependent change in the *effective* number of hydrogen bonds which results in a decay of stress; those hydrogen bonds which reform do so in a state of no stress. This interpretation is not in disagreement with the Eyring treatment if one accepts the postulate that movement of a flow unit must involve the destruction of one or several hydrogen bonds, and that there is a fundamental relationship between the number and rate of flow of these units and the number and rate of breakdown of effective hydrogen bonds in the system.

A divergence of opinion occurs when one compares the basic hypothesis presented here with the accepted principles of phenomenological viscoelasticity. We postulate that the primary elastic elements in the system are the hydrogen bonds in the amorphous regions; hence, the elastic elements *cannot* be considered Hookean in nature. Secondly, we need not postulate the existence of separate viscous elements to account for time-dependent phenomena but, instead, we consider the possibility that a change in the number of elastic elements can occur with time.

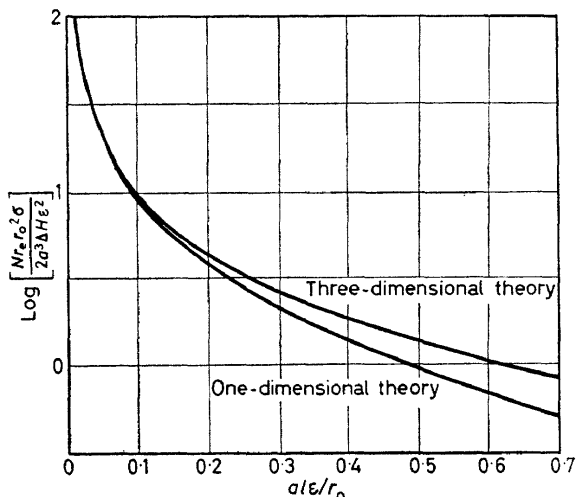


Figure 2

For convenience in dealing with stress relaxation we shall define a dimensionless quantity called the relaxation number (Σ) which is defined as follows:

$$\Sigma = \frac{Nr_e l^2 \sigma}{2a \Delta H} \left(\frac{r_0}{a l \epsilon} \right)^2 \quad (3)$$

$$\Sigma = \frac{3\sigma}{2K \epsilon^2} \quad (3a)$$

where

$$K = \frac{3a^3 \Delta H}{Nr_e r_0^2} \quad (3b)$$

The relaxation number is plotted *v.* strain number ($a l \epsilon / r_0$) in *Figure 2* for the one and three-dimensional theories. In a stress-relaxation experiment the relaxation number varies because of changes in l and we have the following relationship:

$$\Sigma / \Sigma_0 = \sigma / \sigma_0 = f(a l \epsilon / r_0) / f(a l_0 \epsilon / r_0) \quad (4)$$

where f is the functional relationship indicated graphically in *Figure 2*. Making use of known values of the molecular constants in equations (3) and (4), it is possible to construct a plot of *effective* hydrogen bond density

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($n = 3/l^3$) *v.* time, given a stress-relaxation curve. From this plot, a molecular interpretation of the stress-relaxation process is obtained.

A stress-relaxation curve for rayon at 25° and 65 per cent R.H. over a time interval 10^{-1} to 10^{16} sec has been obtained by Meredith⁶ by use of the superposition principle. This curve has been transformed to a plot of hydrogen-bond density *v.* time by Nissan¹⁹, with the use of the one-dimensional theory. Nissan's results (in slightly modified form) are plotted

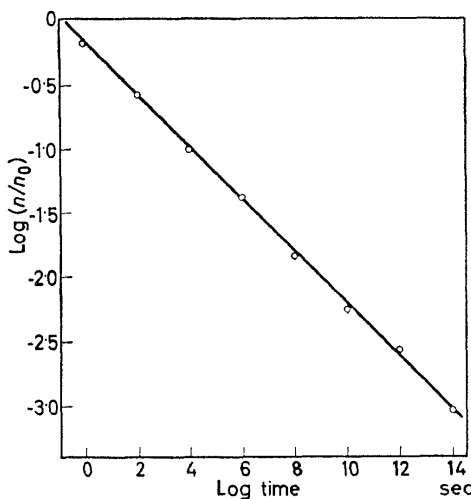


Figure 3

in Figure 3 as $\log(n/n_0)$ *v.* $\log t$ where n_0 is the effective hydrogen bond density at time zero, and t is time. To analyse Figure 3, we proceed as follows:

If we assume that a co-operative phenomenon is occurring whereby α hydrogen bonds must break simultaneously, or co-operatively, in order for a relaxation unit to pass from a stress supporting state to an unstressed state, then

$$-\frac{d(n/n_0)}{dt} = k(n/n_0)^\alpha \quad (5)$$

where k is a reaction rate constant and α is a co-operative index. Integration of equation (5) gives

$$(n/n_0)^{1-\alpha} - 1 = k(\alpha - 1)t \quad (5a)$$

The co-operative index α is assumed to be greater than unity; hence, for all values of n/n_0 less than a particular value, the following condition is fulfilled (note that $0 \leq n/n_0 \leq 1$):

$$(n/n_0)^{1-\alpha} \gg \text{unity} \quad (5b)$$

Equation (5a) may then be written:

$$\frac{d \log (n/n_0)}{d \log t} = \frac{1}{1 - \alpha} = \beta \text{ (a constant)} \quad (5c)$$

Thus, we see that Nissan's results obey equation (5c), and since $\beta = -0.2$, we calculate α to be 6.0. A co-operative index of six is not unacceptable, but is in fact corroborated by other considerations. A study of regain phenomena, in terms of the hydrogen bond theory, led Nissan¹⁹ to conclude that, at 65 per cent R.H., 5.8 hydrogen bonds, on the average, are grouped together in a structural unit. Thus, the regain and relaxation mechanisms predicted by the theory are in agreement as to the structure of the amorphous, or low order, regions in regenerated cellulose.

It should also be noted that Burleigh and Wakeham²³ have analysed stress-relaxation data for cellulose in terms of the Eyring and Halsey model. Assuming that the average distance through which a flow unit moves was equal to the length of a cellobiose unit, Burleigh and Wakeham were able to obtain reasonable results for the number of flow units per unit cross section of sample. Since a cellobiose unit is capable of forming *six* hydrogen bonds, the results obtained by Nissan appear to be compatible with these findings.

The interesting results obtained by Nissan have prompted further investigation by the authors along similar paths. Stress-relaxation experiments were carried out on regenerated cellulose (cellophane) at various temperatures under dry conditions (dew point *ca.* -100°F). The experiments were performed on an Instron tester specially fitted with a sample conditioning chamber through which dry air at the desired temperature could be passed. The stress-relaxation experiments were performed on samples 1 inch wide and 7 inches long cut on a precision sample cutter to ensure smooth and parallel edges. The samples were mechanically conditioned by cyclic loading and stress-relaxation under dry conditions at the highest temperature at which they were to be tested. Some of the experimental results are shown in *Figure 4*, for a sample which was mechanically conditioned at 41° .

The stress-relaxation curve can be converted to a curve of n/n_0 *v.* time by means of equations (3) and (4), using the measured values of

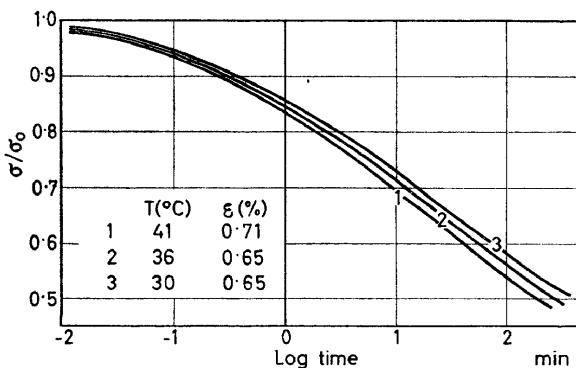


Figure 4

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initial stress (σ_0), strain (ϵ), and a value of K , the relaxation constant, equal to 1.1×10^{12} dynes/cm². This value of K is the same as the value for the "second coefficient of elasticity", as defined by Nissan¹⁹. Thus, for an initial stress of approximately 6×10^8 dynes/cm², Σ_0 is ca. 16. Inspection of *Figure 2* reveals that the one- and three-dimensional theories are indistinguishable for this value of Σ ; hence, the following results are not dependent on the model used. For further discussion of the significance of the one- and three-dimensional theories at large strains, the reader is referred to papers by Sternstein and Nissan²¹, and Sternstein²².

The results of the calculations for experiment 1 are shown in *Figure 5*; it is seen that the rate equation given by equation (5c) is not applicable for

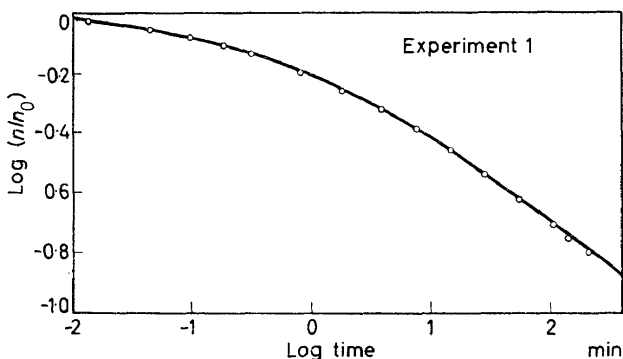


Figure 5

n/n_0 values near unity as can also be seen by inspection of equation (5c) for values of time approaching zero. A correct test of the applicability of the postulated rate mechanism, equation (5), is given by a plot of equation (5a) on logarithmic co-ordinates. This test is shown in *Figure 6* and it is seen that for a value of $\alpha = 3$, a straight line is obtained, but *not* of unit slope as predicted by equation (5a). (*Figure 6* also shows the effect on n/n_0 values as calculated by the one- and three-dimensional theories.)

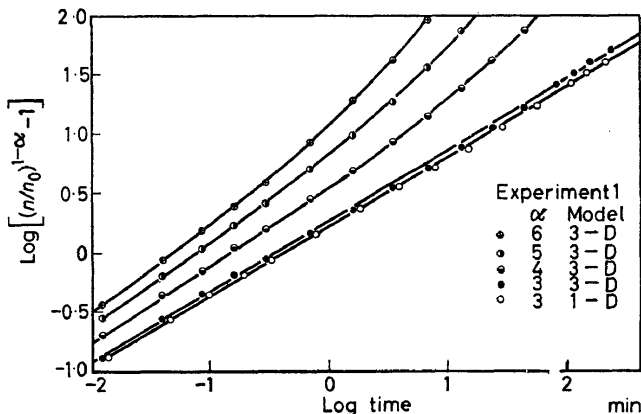


Figure 6

Thus, from *Figure 6*, we have that

$$\frac{d \log[(n/n_0)^{1-\alpha} - 1]}{d \log t} = m = 0.59 \quad (6)$$

Equation (6) can be written as follows:

$$-\frac{d(n/n_0)}{dt} = k'(n/n_0)^\alpha [(n/n_0)^{1-\alpha} - 1]^{\frac{m-1}{m}} \quad (7)$$

where

$$k' = m[(n/n_0)^{1-\alpha} - 1]_1^{1/m} / (\alpha - 1)$$

and $[(n/n_0)^{1-\alpha} - 1]_1$ is to be evaluated at $t = \text{unity}$.

Equation (7) reduces to equation (5) if $m = \text{unity}$. Expanding the above equation in a Taylor series gives

$$\begin{aligned} -\frac{d(n/n_0)}{dt} = k' & \left\{ (n/n_0)^{\alpha_1} + \frac{1-m}{m} (n/n_0)^{\alpha_2} \right. \\ & + \frac{1-m}{2!m^2} (n/n_0)^{\alpha_3} + \frac{(1-m)(1+m)}{3!m^3} (n/n_0)^{\alpha_4} \\ & \left. + \dots + \frac{(1-m) \prod_{q=0}^{p-2} (1+qm)}{m^p p!} (n/n_0)^{\alpha_{p+1}} \right\} \quad (8) \end{aligned}$$

where

$$\alpha_1 = \frac{m + \alpha - 1}{m}, \quad \alpha_2 = \frac{m\alpha + \alpha - 1}{m},$$

$$\alpha_3 = \frac{m(2\alpha - 1) + \alpha - 1}{m}, \quad \alpha_4 = \frac{m(3\alpha - 2) + \alpha - 1}{m},$$

and

$$\alpha_{p+1} = \frac{m(\alpha - p + 1) + \alpha - 1}{m}$$

The experimental results indicated in *Figure 4* are plotted according to equation (6) in *Figure 7*, and it is seen that a value of $\alpha = 3$ and a slope $m = 0.59$ describe all the experimental results reasonably well. Thus the "multiple index mechanism" given by equation (8) (or equation (7)) appears to be a valid representation of the stress-relaxation mechanism in dry cellulose. We shall attempt to give a possible explanation of the significance of equation (8) in terms of the energetics of the breakdown mechanism.

The reduction of the multiple index mechanism to a mechanism controlled by a single co-operative index for a value of m equal to unity, or for n/n_0 values somewhat less than unity (*ca.* $n/n_0 < 0.8$), can be seen

by inspection of equation (8). Thus, the single co-operative index mechanism, equation (5), is a special case of the more general multiple index mechanism, equation (8). Whether or not the relaxation data on rayon at 65 per cent R.H., as used by Nissan¹⁹ for construction of *Figure 3*, would indicate a multiple index mechanism for very small times is a matter of conjecture; however, Nissan's treatment of the data definitely establishes the single co-operative index effect over many decades of time. The data for cellophane as presented in *Figures 4* and *5* confirm Nissan's findings for larger times, and in addition, lead to a generalization of the stress relaxation process in terms of a distribution of co-operative indices for small times (see *Figure 7* and equation (8)).

The primary co-operative index predicted by equation (8) is given by $\alpha_1 = (m + \alpha - 1)/m$ and is equal to 4.4 for the cellophane studied ($\alpha = 3$, m (slope) = 0.59; see *Figure 7*). This is the limiting co-operative

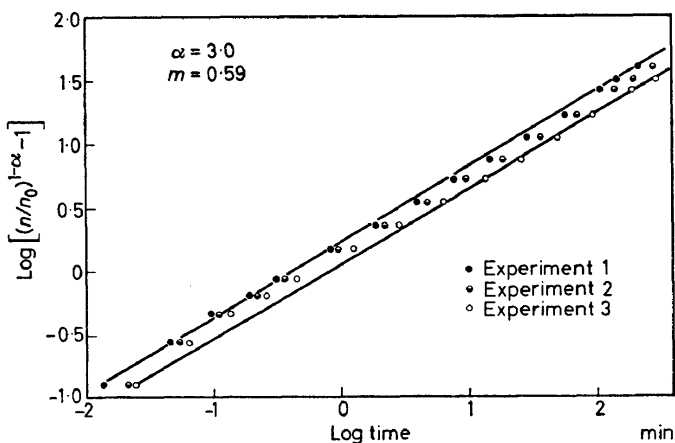


Figure 7

index which governs the hydrogen-bond relaxation process at large times (small values of n/n_0).

An apparent correlation between the co-operative index obtained from stress-relaxation studies and a parameter obtained from regain studies has been given by Nissan¹⁹. Nissan finds that for low or zero regain, in cellulose, the co-operative index should approach unity. This is not an unreasonable assumption since it might be expected that, at zero water content, the hydrogen bonds act individually. At higher water content, the cellulose in the amorphous regions of regenerated cellulose may behave as if groups of various sizes (and hence of varying number of hydrogen bonds linking the group to the surrounding structure) are present, thus resulting in a higher co-operative index or a *spectrum* of indices.

The primary index of 4.4 found for the cellophane studied may be due to the fact that a small amount of plasticizer is present in the cellophane. It is reasonable to expect that the primary co-operative index will vary with regain, plasticizer content, density or any other factor which affects the degree of association in the amorphous regions.

Inspection of equation (8) reveals that, for $0.5 < m < 1$ and $\alpha > 1$, the co-operative index *increases* for each term in the series, and the coefficient of each term *decreases*. Thus, the reaction rate constant associated with the index α_1 is k' , and the constant associated with α_2 is $k'(1 - m)/m$, which is less than k' . If the free energy of activation for k' is calculated from equation (7), *Figure 7*, and the Eyring absolute reaction rate theory, a value of 21.2 kcal per mole of relaxation units is obtained (at 41°), each relaxation unit containing α_1 hydrogen bonds. The energies of activation for the reaction rate constants of all other terms in equation (8) will be *larger* than 21.2 kcal, as can be verified by inspection of equation (8) and the absolute reaction rate equation.

At very small times, *i.e.* at n/n_0 near *unity*, there are a large number of active hydrogen bonds in the system, and the stress on the system is high. In this condition, it is possible for groups with high co-operative indices, *i.e.* a large number of hydrogen bond links to the surrounding structure, to "relax" by a co-operative hydrogen bond breakdown. This is only possible when the strain energy in the system is high. As the number of stress-supporting hydrogen bonds decreases, the stress on the system also decays. The system then approaches the breakdown mechanism whereby a *minimum* free energy of activation is required per *co-operative group*—this corresponds to the primary reaction order of the system (α_1), where the value of α_1 depends on the degree of association in the amorphous regions, as discussed above. All other mechanisms require a higher free energy of activation which becomes increasingly more difficult (less probable) to obtain since the stored strain-energy in the system has decreased.

The basic hypothesis on which interpretation of stress relaxation given above is based, is that first advanced by Nissan¹⁹—that the viscoelastic properties of hydrogen-bond controlled solids can be interpreted in terms of a single non-Hookean element, the hydrogen bond. Thus, viscous effects are a result of a time-dependent change in the active number of hydrogen bonds, and are not caused by elements which are purely viscous in their behaviour.

While the basic hypothesis of the hydrogen bond theory is markedly different from the concepts of phenomenological viscoelasticity theory, there are some interesting, but not completely understood, consonant findings which result from the application of the two theories.

The energy of activation found for the primary co-operative index mechanism of equation (8) is 21.2 kcal, and this result is comparable to the values of 25 kcal as quoted by Meredith⁶ for stress-relaxation of dry viscose filaments. The value quoted was obtained from an analysis of the stress-relaxation process in terms of the Eyring theory of viscoelastic behaviour.

The apparent distribution of co-operative indices found in this investigation may be considered analogous to the distribution of relaxation times obtained from linear viscoelasticity theory. Thus, if in equation (8), m is unity, a single co-operative index describes the relaxation process, and if $m = 1/2$, all of the coefficients in equation (8) are equal—this results in a "box" distribution of reaction rate constants. Further experimental and theoretical investigation is required to establish a quantitative link between

the hydrogen bond theory and the phenomenological approach—however, the hydrogen bond theory appears to present a logical, self-consistent approach to the viscoelasticity of regenerated cellulose, and although an interpretation of the theory in terms of the well-established phenomenological approach is highly desirable, the absence of a quantitative link between the two methods does not detract from the plausible *molecular* interpretation of viscoelasticity afforded by the hydrogen bond theory.

Nomenclature

a	Morse function constant	n	Effective hydrogen bond density, $3/l^3$
ΔH	Energy of dissociation per mole of hydrogen bonds	n_0	Effective hydrogen bond density at zero time of relaxation
K	Relaxation constant, $3a^3\Delta H/Nr_e r_0^2$	r	Hydrogen bond length, H · · O
K_1	O—H force constant	r_e	Hydrogen bond length at equilibrium
K_2	H · · O force constant	r_0	$r_e(1 + K_2/K_1)$
k	Reaction rate constant	t	Time
k'	Reaction rate constant, multiple co-operative index mechanism	U	Potential energy of a hydrogen bond
l	Hydrogen bond repeat distance	α	Co-operative index
l^3	Volume containing 3 non-interacting hydrogen bonds	β	Slope, equation (5c)
m	Slope, equations (6, 7, 8)	ϵ	Strain
N	Avogadro's number	Σ	Relaxation number
		σ	Stress

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