The Time–Temperature Dependence of the Complex Modulus of Keratin Fibers

G. D. DANILATOS and R. POSTLE, *School of Textile Technology, University of New South Wales, Kensington, N.S.W. 2033, Australia*

Synopsis

The dynamic modulus and loss angle of wet keratin fibers have been measured at frequencies between 6 and 1500 Hz in the temperature range 0.2–45°C. Some further measurements were performed at different relative humidities. These results have been compared with other known results, and the agreement or discrepancies found are discussed. A theoretical curve fit has been introduced for a selected set of experimental results.

INTRODUCTION

A fiber viscoelastometer[1,2] has been used by the present authors for the study of the dynamic mechanical properties of keratin fibers. These studies have been performed on fibers during extension,[3,4] or during water sorption.[5-7] This previous work was performed at a constant temperature and frequency whereas the aim of the present paper is to examine the dynamic mechanical behavior of keratin fibers when the temperature or frequency of oscillation is varied.

A comparative presentation of other closely related work is necessary in order to evaluate the results obtained in the present work.

The Tensile Modulus of Keratin Fibers as a Function of Time

Feughelman and Robinson[8] have found that wool fibers behave as linear viscoelastic materials at all water contents for extensions up to 1% in the "Hookean" region. On this basis, they measured the stress relaxation at various humidities at an extension of 0.8% above the zero length of the fiber at the test humidity. Measurements at each humidity were carried out for periods up to 4–5 days. They reported the stress decay, based on the wet cross-sectional area, as a function of log-time (min).

In the present work, the above results were used to find the relaxation modulus as a function of time (s); correction factors for the variation of the cross-sectional area due to swelling at various humidities have been calculated from data presented by Bendit and Feughelman[9] and are given in Table I. Figure 1 shows the values of relaxation modulus calculated in this manner at relative humidities of 0%, 32%, 65%, 91% and 100% (wet), at 20°C. The rate of extension up to 0.8% strain was 10%/min. An examination of the figure suggests that curves at all relative humidities may come together after a long period and may be asymptotic to a value of about 1.4×10^9 Pa. However, it was impractical to demonstrate this more clearly for long periods at 20°C.

It is evident that a major relaxation process occurs within the laboratory time

CCC 0021-8995/83/031221-14$02.40

DANILATOS AND POSTLE

TABLE I

RH (%)	Ratios of ac forces (dry/wet)	Correction factors for swelling	Corrected moduli E' $\times 10^{-9}$ (Pa)	Loss angle (°)
0	2.45	1.352	7.08	1.0
32	2.27	1.270	6.17	1.5
65	1.90	1.202	4.88	2.0
91	1.48	1.105	3.49	2.4
100	1.00	1.00	2.14	2.9

scale for which a pseudo-time constant was obtained by Feughelman and Robinson at each relative humidity, corresponding to the time at which the stress has fallen to half of the initial value. However, it seems that at the higher relative humidities, we are looking at the "tail" of the relaxation of modulus. This view is supported by measurements of dynamic modulus at very short times using different techniques.

Mason[10] obtained a value of 3.5×10^9 Pa for the modulus of horse hair in water at 20 kHz using a wave propagation technique. He also measured the modulus of Lincoln wool at a strain rate of 0.001 s^{-1} and found it to be 1.8×10^9 Pa. Although this corresponds to an equivalent increase in time by a factor of over 10^7, the two values of modulus differ only by a factor of 2. Chaikin and Chamberlain,[11] using a similar technique, measured the modulus of human hair at 100 kHz for 25%, 40%, and 65% RH and found that water had little effect on modulus. They reported values $(8.2 - 7.9 - 7.4) \times 10^9$ Pa, respectively.

In order to compare the dynamic measurements with those obtained by relaxation techniques, the transformation of frequency to time was obtained using the method of Ninomiya and Ferry[12]:

$$E(t) = E'(\omega) - 0.40E''(0.40\omega) + 0.014E''(10\omega)\big|_{\omega=1/t} \tag{1}$$

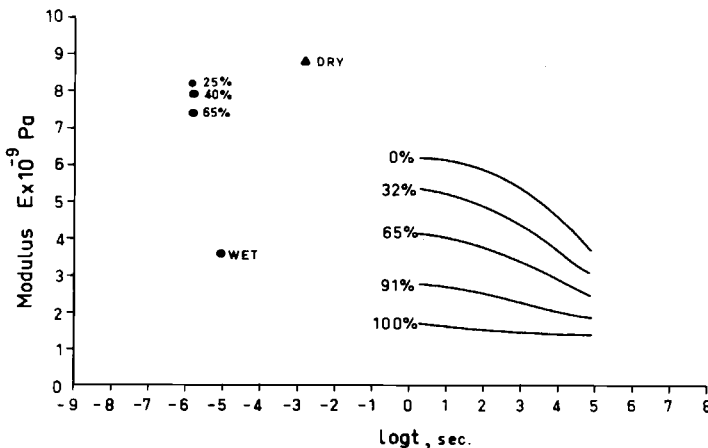where $\omega = 2\pi f$, f is the applied frequency, and E' and E'' are the elastic and lossy

Fig. 1. Published results on the modulus of α-keratin plotted against log-time t (s): ($\oplus$) by Chaikin and Chamberlain; ($\bullet$) by Mason; ($\blacktriangle$) by Druhala; solid curves by Feughelman; figures indicate RH.

components of the complex modulus with magnitude E at time t. In practice it was found that

$$E(t) \simeq E'(\omega)|_{\omega=1/t} \qquad (2)$$

Using the relation (2), Mason's result is shown in Figure 1 together with those of Chaikin and Chamberlain for three relative humidities. Comparing these points, it seems that there must be an abrupt decrease of modulus from the value at 100 kHz and 65% RH to the value at 20 kHz and 100% RH. This observation remains to be explained.

Makinson[13,14] reported a value of 1.01×10^{10} Pa for ram's horn and 1.09×10^{10} for rhinoceros horn at 5 Mkz in room conditions. However, these values refer to the dilatational modulus c_{11}, which is somewhat higher than the longitudinal dynamic modulus depending on the Poisson's ratio. Makinson reported that the dynamic modulus should be 17% less than the dilatational modulus of isotropic solids with Poisson's ratio 0.25. However, lack of information on the dependence of the Poisson's ratio on the water content makes the estimation of the dynamic modulus from the dilatational modulus impossible. Druhala and Feughelman[15] found a value of 8.8×10^9 Pa for dry horse hair, at 110 Hz.

It can be seen that there is a considerable gap in our knowledge of the modulus of keratin at short times, and the provision of data to fill this gap forms the basis of the present work.

EXPERIMENTAL

A horse hair, medulla-free, washed with petroleum ether, was tested at frequencies between 6 and 1500 Hz in the temperature range 0.2–45°C. The average diameter of the dry fiber measured at 10 different points was found to
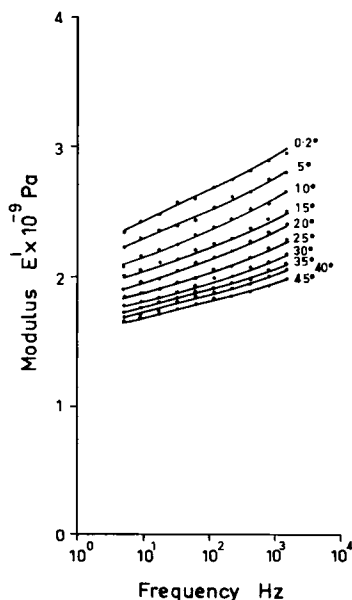
Fig. 2. The modulus E' of wet α-keratin plotted against frequency on a log scale at different temperatures as shown on each curve.
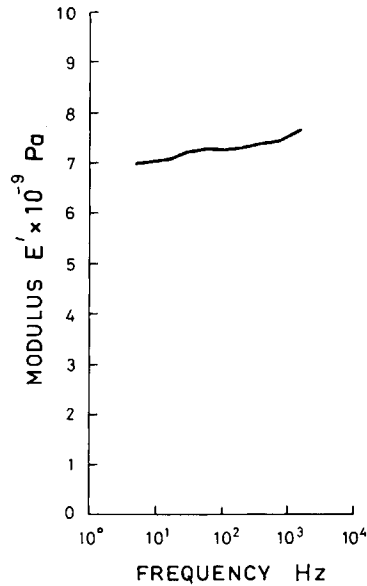
Fig. 3. The modulus E' of dry α-keratin plotted against frequency on a log-scale at 20°C.

be 155 μm. Horse hair was chosen in this experiment, because it produces a high ac output from the piezoelectric element, thus minimizing the effects of background noise in the viscoelastometer apparatus used.[1,2]

The fiber was left in distilled water in the conditioning chamber overnight and then tested in water by scanning the frequency, while keeping the temperature constant. This procedure was repeated for various temperatures starting from 45°C and decreasing the temperature by steps of 5°C. The lowest temperature achieved was 0.2°C, close to the freezing point of water. The use of water was the best way to ensure 100% RH around the sample during these changes. The use of saturated vapor was shown to be impractical, not giving reproducible results. The results for the dynamic modulus are presented in graphical form in Figure 2. Those for the loss angle are given as a "master curve" in the following section, because these results are too scattered to give as clear a picture as shown in Figure 2 for the modulus. The fiber was then dried in a dry atmosphere for 48 h and tested over the same frequency range at 20°C only, as shown in Figure 3. The reduction of diameter in the dry fiber has been taken into account in plotting the modulus (for correction factor see Table I).

Lastly, Lincoln wool fibers were tested for relative humidities of 0%, 32%, 65%, 91%, and 100%, at a constant frequency of 116 Hz, at 20°C. The fibers were left slack for 24 h at 100% RH and 20°C, then dried, and finally brought up to the required RH before testing. Feughelman and Robinson relaxed their fibers between tests by leaving them for 1 h and 52°C in water prior to conditioning at the required relative humidity, but it has been shown that the same effect is achieved if the fibers are left at 100% RH at room temperature for 24 h.[16] Lincoln wool was chosen for this test because it required considerably less time for conditioning, while the moduli for wet horse hair and Lincoln wool did not differ more than the experimental error of the apparatus. The results from this test are given in Table I. The table includes the measured ratios of dry/wet ac force,

the correction factors used for swelling, the corrected moduli, and the loss angle. The coverage of a wider range of humidities and temperatures is left for future work.

ANALYSIS OF RESULTS

Construction of Master Curves

From Figure 2 it can be seen that there is an overall change in the slope of the modulus–frequency curve as the temperature varies. At high temperatures the value of the slope is low, while around 5°C the slope has achieved its maximum value. This behavior is expected from a viscoelastic material, in which the processes are activation controlled [as described by Williams, Landel, and Ferry[12] (WLF)]. To analyze the results, the assumption is made that the time–temperature equivalence of WLF holds for this case. It follows that it is possible to produce a "master modulus curve" by choosing one particular temperature and applying a horizontal shift on a logarithmic time scale to make the modulus curves for other temperatures join as smoothly as possible onto the curve at this particular temperature; 20°C was chosen as the reference temperature. The molecular theories of viscoelasticity suggest that there should be an additional small vertical shift factor $T_0\rho_0/T\rho$ in changing from the actual temperature T K and density ρ to the reference temperature T_0 K and density ρ_0. The shift factor is taken into account here, and the correction factor can be expressed in equivalent terms as

$$[1 + \beta(T - T_0)]T_0/T \tag{3}$$

where β is the coefficient of thermal expansion, which has been taken from Mason's work[17] to be equal to 5×10^{-4} deg^{-1}. From the results of Figure 2, the modulus master curve obtained is shown in Figure 4.

An important criterion of the applicability of the technique of forming the
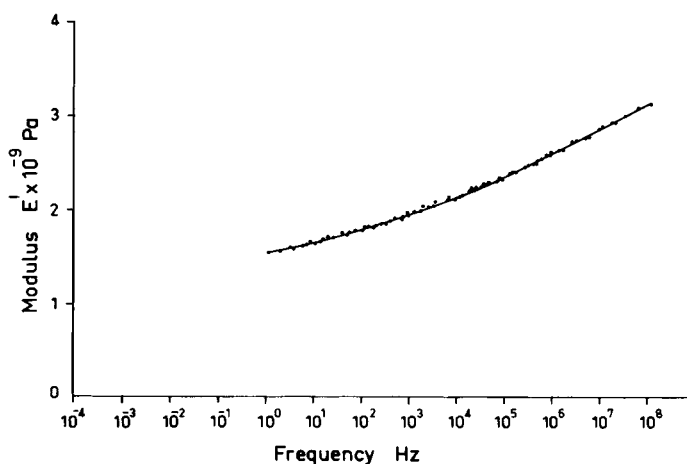

Fig. 4. The "master curve" for modulus obtained by plotting the data of Figure 2 with reduced variables, representing the behavior of modulus of α-keratin over an extended frequency scale at 20°C.
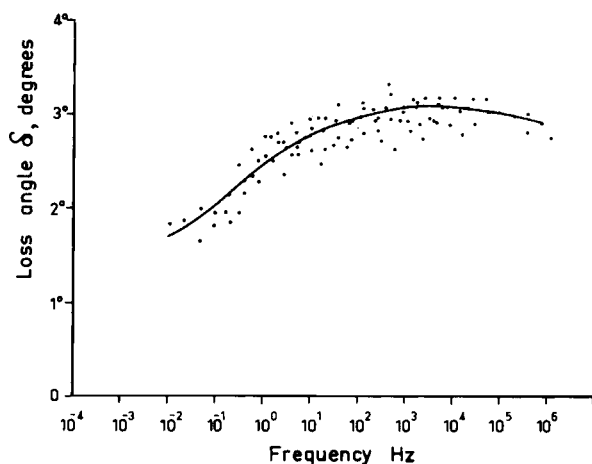
Fig. 5. The "master curve" for loss angle representing the behavior of loss angle of α-keratin over an extended frequency range at 20°C.

reduced curve is that the shapes of the original curves at different temperatures must match over a substantial range of frequencies. This appears to hold in the present case. One other general criterion is that the same horizontal shift factor must superpose all the viscoelastic functions. Unfortunately, the measurement of the loss angle (which is a viscoelastic function) resulted in a considerable scatter of points, which did not allow a reliable independent estimation of the shift factors. Because of this effect, the assumption is made that the viscoelasticity of the keratin fiber complies with the WLF theory, and the shift factors obtained from the modulus measurements are used to construct the "master curve" for the loss angle. The result is presented in Figure 5.

From Figure 5, it appears that there is a maximum value of the loss angle δ at

TABLE II

$\log f$ (f in Hz)	$E' \times 10^{-9}$ (Pa)	δ (°)	$E'' \times 10^{-7}$ (Pa)
−2.0	1.54	1.7	4.57
−1.5	1.60	1.83	5.11
−1.0	1.65	2.02	5.83
−0.5	1.72	2.25	6.76
−0.0	1.78	2.45	7.62
0.5	1.86	2.63	8.53
1.0	1.95	2.75	9.37
1.5	2.04	2.87	10.23
2.0	2.14	2.95	11.03
2.5	2.25	3.02	11.87
3.0	2.35	3.05	12.52
3.5	2.47	3.07	13.27
4.0	2.60	3.07	13.94
4.5	2.74	3.05	14.60
5.0	2.86	3.01	15.04
5.5	3.00	2.95	15.46
6.0	3.14	2.88	15.80

a frequency around 10 kHz at 20°C. To deduce a frequency-dependent transition temperature corresponding to the loss maximum, one has to consider the loss modulus E'', for which the maximum lies to the right of that of δ on the frequency scale. This difference on the frequency scale usually amounts to a few decades.[12] From Table II in which the values of E'' are given ($E'' = E' \tan \delta$), it appears that the latter difference must be greater than three decades. Table II contains also the values of E' and δ used for the calculation of E'' at different frequencies.

Comparison with Published Data

One aspect of the dynamic measuring technique has to be considered, before any comparison is attempted, in order to establish the thermodynamic conditions, under which an experiment is to be conducted. In particular, it must be clarified whether we have adiabatic or isothermal conditions.

Following the work by Algie and Watt,[18] it is assumed that the experiments reported in this work were conducted mainly under adiabatic conditions and to a lesser extent under isothermal conditions. The difference, however, between adiabatic E_{ad} and isothermal E_{is} moduli is, in practice, negligible. This can be shown to be the case by using the formula[12]

$$E_{ad} = E_{is} + (\partial E/\partial T)^2 \, T/C_a a^2 \qquad (4)$$

where a is the oscillating strain and C_a the heat capacity per gram at constant strain. The above formula holds for the case in which the modulus E is directly proportional to T, which is approximately true in the present case. From Feughelman and Robinson's work,[19] the factor $\partial E/\partial T$ for a 10%/min strain rate is 1.1×10^7 Pa·grad^{-1}, or from the present work at 116 Hz, $\partial E/\partial T$ is 1.9×10^7 Pa·grad^{-1}. Using the latter value and $a = 0.02\%$, we find the second term of eq. (4) to be of the order 10^3 Pa, which is really negligible relative to E_{is}.

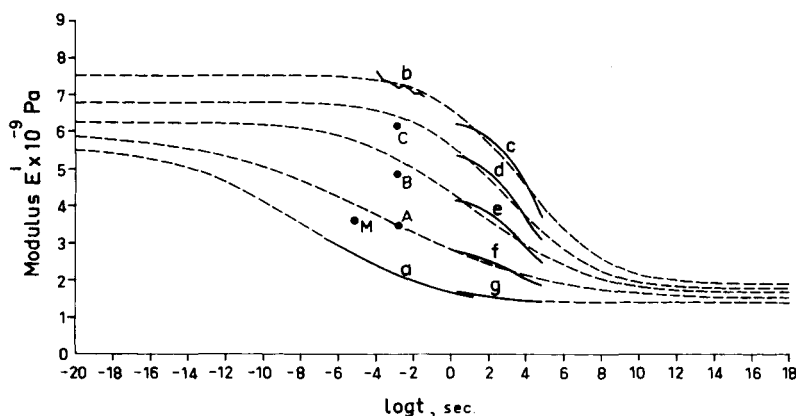Another point in the comparison of published data on keratin is that various

Fig. 6. The modulus E' vs. time (s) on a log scale: Solid curve (a) for wet keratin, solid curve (b) for dry, and points A,B,C for intermediate relative humidities (see text) have been obtained in the present work. Solid curves (c), (d), (e), (f), (g), and point M have been replotted from Figure 1; (- - -) theoretical fits.

authors have used different types of keratins as well as different techniques which may account for some discrepancies.

We now proceed to compare the experimental data obtained from this work with some of the results obtained by others. The curve of Figure 4, the modulus master curve for wet keratin, has been replotted on a log-time scale in Figure 6 as a solid curve (a). The moduli for intermediate regains are shown as points A, B, C taken from Table I. The modulus for the dry horse hair is shown as solid curve (b) for times corresponding to frequencies between 6 Hz and 1500 Hz at 20°C. The conversion of frequency to time was made by using the relation (2). The results by Feughelman and Robinson[8] have been plotted in the same Figure 6 as solid curves (c), (d), (e), (f), and (g) for 0%, 32%, 65%, 91%, and 100% RH; Mason's point (M) for wet keratin is also shown.

The curve (a) matches curve (g) very well; it does not, however, agree well with Mason's point for wet keratin. Mason's results over seven decades of time show a similar change of modulus to that obtained in this work; only the absolute value of modulus differs. Also, the curve (b) for the dry fiber does not seem to match the corresponding curve (c).

To understand the above observations, an appreciation of the role of water in keratin must be made. Water in keratin can be considered as a plasticizer which associates with the polymer. The effect of plasticizers generally is to lower the temperature of the glass transition by making it easier for changes in molecular conformation to occur. Plasticizers can make the loss peak broader, and this broadening depends on the nature of the interaction between the polymer and the plasticizer. Thus, because of the strong interaction between water and keratin, a very broad loss peak is expected. This is the case as shown in Figure 5.

In the case of an ideal plasticizer in a polymer, the initial (unrelaxed) modulus for very short times and the final (relaxed) modulus for very long times are independent of the plasticizer content, provided that the plasticizer does not swell the polymer. The question now arises whether this is applicable to the keratin–water system. From existing data,[15] it is expected that the relaxation of the water itself would show up as well as the relaxation of other small units of the main chain. Thus, a considerable portion of the relaxation spectrum of times for the main chain must overlap with the relaxation spectrum of smaller units and that of the water. Druhala[20] found that the water loss maximum occurs for 18% regain in the fiber at −95°C and at 110 Hz, and is much less well defined than for the lower water contents. This is because of a transition at a higher temperature occurring in the vicinity of 0°C. This transition may arise from the motion of bulky side chains. Druhala also found that the modulus of the keratin–water system for temperatures below the transition temperature for the water loss is higher at higher water contents, because of the contribution to the modulus of the water *per se*. This result could partly explain the very high modulus reported by other authors,[11,13,14] since their results were measured at very high frequencies.

Theoretical Curve Fitting

In the following, an attempt is made to fit the results obtained in this work with those of Feughelman and Robinson by use of a relaxation function derived

from a log-normal distribution of relaxation times τ. The same function was used successfully by Stootman[21] to fit his data on the modulus of rigidity. The distribution function is given by

$$F(\tau)\, d\tau = \frac{1}{\beta\sqrt{2\pi}} \exp\left[-\frac{(\ln\tau - \alpha)^2}{2\beta^2}\right] d\ln\tau \tag{5}$$

which satisfies the condition

$$\int_0^\infty F(\tau)\, d\tau = 1$$

where α is the mean $\langle \ln\tau \rangle$ and β is the width of the distribution. Gross[22] gives the normalized relaxation function $\psi(t)$ as

$$\psi(t) = \int_{-\infty}^\infty F(\tau) \exp(-t/\tau)\, d\tau \tag{6}$$

By applying the transformation

$$(\ln\tau - \alpha)^2/2\beta^2 = u^2$$

and combining eqs. (5) and (6), we obtain

$$\psi(t) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^\infty \exp[-u^2 - t\exp(-u\beta\sqrt{2} - \alpha)]\, du. \tag{7}$$

If E_i is the initial (unrelaxed) modulus and E_f is the final (relaxed) modulus, then the modulus $E(t)$ as a function of time is given as follows:

$$E(t) = (E_f - E_i)\psi(t) + E_f \tag{8}$$

Equation (8) can be made to fit the experimental data and depends on four parameters, E_i, E_f, α, and β. The parameters E_i and E_f were fixed and α and β were calculated via a computer program (used by Stootman) for the best fit employing the method of "least squares." The parameter E_f was taken to be equal to 1.4×10^9 Pa for the case of 100% RH, while, for the other relative humidities, the above value was multiplied by the correction factors of Table I to allow for diametral swelling. The parameter E_i was fixed as follows. Initially, the program was run for only one fixed parameter, i.e., $E_f = 1.9 \times 10^9$ Pa corresponding to the relaxed modulus for dry keratin and the initial dry modulus E_i was predicted to be equal to 7.5×10^9 Pa. This value was taken as the value to which all the moduli would converge for very short times regardless of the water content; but, to allow again for diametral swelling, the above value was divided by the correction factors of Table I, in order to fix the initial modulus for the

TABLE III

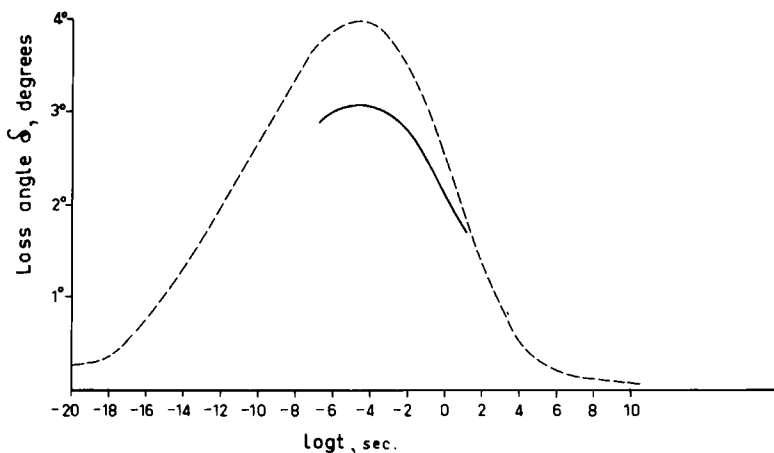| RH (%)	$E_i \times 19^{-9}$ (Pa)	$E_f \times 10^{-9}$ (Pa)	α	β	$\alpha/2.303$	$\beta/2.303$
0	7.50	1.90	9.18	8.54	3.99	3.71
32	6.79	1.78	7.23	8.90	3.14	3.86
65	6.24	1.68	3.06	11.51	1.33	5.00
91	5.91	1.55	−8.37	16.37	−3.63	7.11
100	5.55	1.40	−17.36	12.19	−7.54	5.29

Fig. 7. The loss angle vs. time (s) on a log scale for wet α-keratin obtained experimentally (——) and predicted from the theoretical fit for the wet case in Figure 6 (- - -).

program at the corresponding relative humidities. The fixed pairs of E_i and E_f for the different relative humidities are given in Table III. In the same table, the calculated parameters α and β for the distribution function are given. These values for α and β apply for the variable $\ln \tau$ and, since the results are plotted against $\log_{10} \tau$, an additional two columns are given in the table, where the values of α and β have been converted to this variable. Modified values and new curve fits should be recalculated by including new experimental data in future work.

The Loss Angle

It is possible to calculate the loss angle from the theoretical fits shown in Figure 6 by using the formula[23]

$$\tan \delta = \frac{\pi}{2} \frac{d \ln E'}{d \ln \tau} \tag{9}$$

In this work, the loss angle has been calculated from the curve corresponding to 100% RH only, in order to compare it with the experimentally obtained loss angle as shown in Figure 5. Thus, in Figure 7, the experimentally obtained loss angle has been replotted as a solid curve together with the calculated loss angle (dashed curve) using eq. (9).

The Loss Modulus Dependence on RH

Some further observations are made in this section of the variation of the loss modulus E'' with change of RH. Values for the dynamic modulus E' and loss angle δ at a constant frequency of 116 Hz have been extracted from previous work of the present authors[2,3] and are shown in Table IV. These values have been used to calculate the loss modulus as shown in Figure 8 [curve (b)]. From this figure, it is observed that the loss modulus has a maximum value around 80% RH.

TABLE IV

RH (%)	$E' \times 10^{-9}$ (Pa)	δ (°)	$E'' \times 10^{-7}$ (Pa)	Fibre swelling factors
0	6.72	1.10	12.90	1.352
11	6.34	1.20	13.28	1.310
33	5.63	1.40	13.76	1.268
52.9	5.06	1.55	13.68	1.228
73.8	4.20	2.00	14.64	1.179
85	3.40	2.25	13.34	1.140
92.5	2.67	2.70	12.58	1.095
98	2.23	2.95	11.49	1.044
100	2.00	3.10	10.82	1.000

From Table III, it is observed that the parameter β also has a maximum value around 80% RH.

Numerous workers have also observed a marked change of many mechanical properties around 80% RH. Therefore, it could be postulated that there may be a correlation between E'' and β. However, this is not necessarily the case, since E'' is essentially a function of time, and, as such, if E'' is plotted against relative humidity, the plot should vary according to the time at which E'' is measured.

The loss modulus E'' can also be derived from the theoretical values of the fits for the modulus at a fixed time for different relative humidities. Curve (a) in Figure 8 shows the loss modulus plotted against relative humidity for $\tau = 10^{-2.8}$ s (i.e., $f = 116$ Hz), obtained in this way. The two curves (a) and (b), having been constructed quite independently, compare with each other satisfactorily. This result is another indication that the theoretical fits for the modulus may be close to reality.
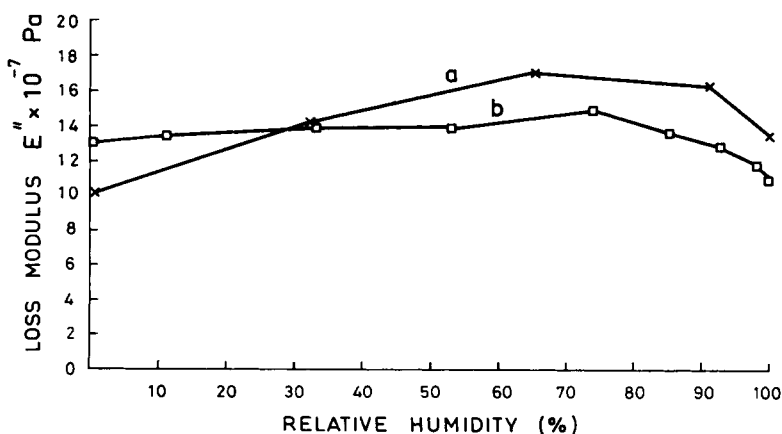

Fig. 8. The loss modulus E'' plotted against relative humidity for keratin at 116 Hz and 20°C. Curve (a) predicted from the theoretical fits in Figure 6; curve (b) plotted from experimental data in Table IV.

DISCUSSION

When a polymer is subjected to an oscillatory strain at a particular frequency and temperature, the material absorbs a certain amount of energy per cycle per unit volume. This energy is absorbed by specific structural units of which the time of response is equivalent to the applied frequency. McCall[24] has classified the various relaxation processes or absorption bands as follows:

(i) primary main chain motion in crystals;

(ii) primary main chain motion in amorphous materials;

(iii) secondary main chain motion in crystals;

(iv) secondary main chain in amorphous materials;

(v) side group motions;

(vi) impurity motions.

The results shown in Figure 6 are indicative of a major relaxation process occurring in the keratin structure. This process is characterized by a mean relaxation time varying by more than 11 decades, when the atmosphere surrounding the keratin is varied between dry and wet conditions. The width of the distribution function of the relaxation times is large and varies considerably with RH.

The values for α and β given in Table III, however, must not be considered as the final and accurate characteristic constants for keratin. Rather these values represent a reasonable approximation, because the theoretical fit is satisfactory but not excellent owing to the fact that the experimental data have been obtained using different techniques, for different fibers, under nonidentical conditions. For example, application of a step function of strain is not identical to the application of a sinusoidal strain. Besides, the application of a step function of strain in practice is inevitably accompanied by an error in the definition of zero time.

Furthermore, when starting an experiment, the initial structure of keratin has not been identical in all cases. For example, the dry or near-dry fiber may not be in an internally stress-free condition, or, in other words, the fiber may be at a different state of "aging" prior to a test. The results of Feughelman and Robinson were obtained after 17 h of equilibrium following drying from the water saturated state, while relaxation effects still occur after 10^9 s, i.e., after 32 years, in the dry fiber. The initial part of the sigmoidal curves obtained by these authors can be attributed to an initial weakening of the structure upon extension to 0.8% as found during measurements of the dynamic modulus as a function of extension.[3] It has also been found that the dynamic modulus increases as a function of time at fixed strains below 15%,[4] which is indicative of a strengthening of the molecular structure with time. These two effects superimposed could account for the sigmoidal shape reported. Thus, it is proposed that the Feughelman–Robinson work should be repeated for lower levels of initial fixed strain.

In addition to these observations, it must be clarified that the theoretical fits shown in Figure 6 are meaningless for very short times: by the time the visible region is reached (very high frequencies), all molecular absorption bands have been passed and any energy absorption arises simply from electronic polarization. Furthermore, in the short time range, where molecular absorption is possible, the fits should not vary as smoothly as predicted, because of special absorption

bands due to small side chain units or the reorientation of the water molecules themselves.[20]

The fits for times greater than approximately 10^{-7} s are believed to represent reality reasonably closely. They appear to have the characteristics describing a typical viscoelastic material. The relaxation process indicated by the abrupt change of slope of the curves in Figure 6 is thought to arise from the primary main chain motion in the "lossy" phase M of the keratin fiber. In general, the longer and more ordered the structural units are, the larger will be their relaxation times; therefore, the long relaxation times for low relative humidities must be characteristic of macromolecules. These relaxation times for the macromolecules change markedly because of the action of water.

The modulus relaxes with time to an equilibrium level of 1.4×10^9 Pa, which does not change at ambient conditions in the laboratory time scale. The latter equilibrium value of modulus has been attributed mainly to the elastic phase C of keratin. Algie found (private communication) that the relaxation in the C phase (which he terms the α-process) for wool fibers in water has a relaxation time of 100 h at 100°C. From this fact, Algie calculated a relaxation time of 10^{10} years at 20°C using an activation enthalpy of 77 kcal/g·mol for the α-process. Therefore, if the main chain relaxation does not occur in the C phase of keratin in the laboratory time scale, the main chain motion, to which the results of Figure 6 have been attributed, must occur in the M phase. The marked effect of the water being absorbed in the M phase of keratin is further corroborative evidence of the above suggestion.

Lastly, the comment is made that Sikorski and Woods[25] have reported that the Young's modulus varies linearly with log (rate of straining). From Figure 6, it is observed that these findings hold for a few decades of time only, but not over the complete time range for which the modulus curve has a sigmoidal shape.

CONCLUSION

A relaxation process with a very broad spectrum of relaxation times has been found for keratin. The modulus and loss angle have been measured experimentally in the time range between $10^{-6.8}$ s and $10^{1.2}$ s by varying the frequency from 6 Hz to 1500 Hz, and the temperature from 0°C to 45°C, and employing the WLF principle.

The experimentally covered times consist of only part of the whole spectrum of times of the relaxation process. For this reason, the present results have been combined with results of other workers, and together have been fitted with a theoretical function of modulus. Some measurements of complex modulus have been performed at different relative humidities, and a theoretical modulus as a function of time has been derived in the same way.

The relaxation process established depends markedly on the RH. With increasing RH, the relaxation times decrease by more than 11 decades, and the width of the distribution function of the relaxation times varies considerably. This process was attributed to the M phase of keratin.

References

1. G. D. Danilatos, *J. Phys. E: Sci. Instrum.*, **13**, 1093 (1980).

2. G. D. Danilatos, "The Dynamic Mechanical Properties of Keratin Fibers," Ph.D. thesis, University of New South Wales, Australia 1977.

3. G. D. Danilatos and M. Feughelman, *J. Macromol. Sci. Phys.*, **B16**(4), 581 (1979).

4. G. Danilatos and M. Feughelman, *Text. Res. J.*, **50**, 568 (1980).

5. G. D. Danilatos and R. Postle, *J. Appl. Polym. Sci.*, **26**, 193 (1981).

6. G. D. Danilatos and R. Postle, *J. Macromol. Sci. Phys.*, **B19**(1), 153 (1981).

7. G. D. Danilatos and R. Postle, *J. Text. Inst.*, **72**, 90 (1981).

8. M. Feughelman and M. S. Robinson, *Text. Res. J.*, **41**, 469 (1971).

9. E. G. Bendit and M. Feughelman, *Encycl. Polym. Sci. Technol.*, **8**, 1 (1968).

10. P. Mason, *Kolloid Z. Z. Polym.*, **202**, 139 (1965).

11. M. Chaikin and N. H. Chamberlain, *J. Text. Inst.*, **46**, T25 (1955).

12. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1970.

13. K. R. Makinson, *Aust. J. Biol. Sci.*, **7**, 336 (1954).

14. K. R. Makinson, *Aust. J. Biol. Sci.*, **8**, 225 (1955).

15. M. Druhala and M. Feughelman, *Colloid Polym. Sci.*, **252**, 381 (1974).

16. J. B. Speakman, *J. Text. Inst.*, **18**, T431 (1927).

17. P. Mason, *Text. Res. J.*, **34**, 913 (1964).

18. J. E. Algie and I. C. Watt, *Text. Res. J.*, **35**, 922 (1965).

19. M. Feughelman and M. S. Robinson, *Text. Res. J.*, **39**, 196 (1969).

20. M. Druhala, "The Mechanical Properties of Single Keratin Fibers," Ph.D. thesis, University of New South Wales, Australia, 1973.

21. F. Stootman, "The Self-Diffusion of Plasticizers in Wool Keratin," Ph.D. thesis, University of New South Wales, Australia, 1977.

22. B. Gross, *Mathematical Structure of the Theories of Viscoelasticity*, Herman, Paris, 1953.

23. C. Zener, *Elasticity and Anelasticity of Metals*, University of Chicago Press, Chicago, 1948.

24. D. W. McCall, U.S. N.B.S. Special Pub. 301, *Molecular Dynamics and Structure of Solids*, R. S. Carter and J. J. Rush, Eds., Natl. Bur. Stds., Washington, D.C., 1969.

25. J. Sikorski and H. J. Woods, *Leeds Phil. Soc. (Sci. Sec.) Proc.*, **5**, 313 (1950).