Dynamic Mechanical Properties of Keratin Fibers during Water Absorption and Desorption

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Synopsis

The dynamic modulus and loss angle of keratin fibers have been measured during changes of relative humidity at a fixed fiber strain, temperature, and frequency of oscillation. From these measurements and the observation of an overshoot in loss angle in particular, certain conclusions about the structure of fibers can be made. This overshoot during absorption can be attributed to an interaction between two phases of keratin fibers. When a fiber at a fixed strain is dried from the wet state, the amount of α helices that have opened up during extension in water remains practically constant. A fiber that has been extended in the dry state contains α helices which open more rapidly than in the wet state for a given strain and rate of strain. When a wet fiber is dried and then rewetted while it is held at a fixed strain, the fiber achieves essentially the same structural state as in its original strained state.

INTRODUCTION

Studies of the dynamic mechanical properties of keratin fibers have been reported previously using a fiber viscoelastometer.[1] These studies refer to the complex modulus (dynamic modulus and loss angle) of fibers during extension[2] or during water absorption at low strains[1,3] (<1%).

The experimental results obtained in the previous work were explained by use of a two-phase model for the keratin structure. According to this model, the water penetrable phase M (associated with matrix) is mainly responsible for the mechanical energy loss during a cycle of oscillation and remains practically invariant during extension. The other phase C (associated with the microfibrils), is practically water impenetrable, elastic (i.e., absorbs negligible energy), and its modulus varies in a similar manner to the variation of the dynamic modulus of the whole fiber.

In this article, the results and theories are reported for an investigation of the variation of complex modulus at different constant levels of extension during both absorption and desorption of water.

EXPERIMENTAL

Apparatus

The apparatus used in the present work has been described elsewhere.[1,2] A brief description of the experimental technique follows.

The fibers under test are mounted in loop form between a vibrating rod and a fixed rod. The vibrating rod is subjected to a sinusoidal oscillation by a vi-

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bration exciter at frequencies in the range 6–1500 Hz. The nonvibrating rod can extend or retract the fiber at a given strain rate. Oscillatory displacements of the order of 4 μm applied at the free end of the fiber loop are detected by a noncontacting strain gauge. Such small oscillatory displacements applied to sample lengths of 2 cm correspond to strains in the order of 0.02%, which can be considered as having a negligible effect on the material under test. The resulting oscillatory force is measured at the fixed end of the fiber loop by using a piezoelectric element.

The ratio of the measured force over the applied strain divided by the cross-sectional area of the fiber is the dynamic modulus. The angle between force and displacement, called the loss angle, is a useful physical parameter of the complex modulus and can be measured by the apparatus. The temperature and relative humidity around the fiber can be controlled with a conditioning chamber.

All tests reported in this article were carried out at 25°C and 116 Hz.

RESULTS

Lincoln wool fibers were used for the tests. Prior to the test, each fiber was conditioned slack at 100% RH for 24 hr and then extended to $X\%$ strain at a strain rate of 1.07%/min. The fiber was held at this extension ($X\%$) for 30 min after which the relative humidity was reduced to 0%. The modulus and loss angle were recorded during desorption until they seemed to have reached an equilibrium value. The drying lasted for 24 hr and the relative humidity was subsequently changed back to 100%. The modulus and loss angle were recorded again until they appeared to have reached an equilibrium value. Six fibers were tested using this procedure, the value of the constant strain level X being 0.6, 5, 10, 20, 30, and 40%, respectively.

The modulus and loss angle during desorption are shown in Figures 1 and 2

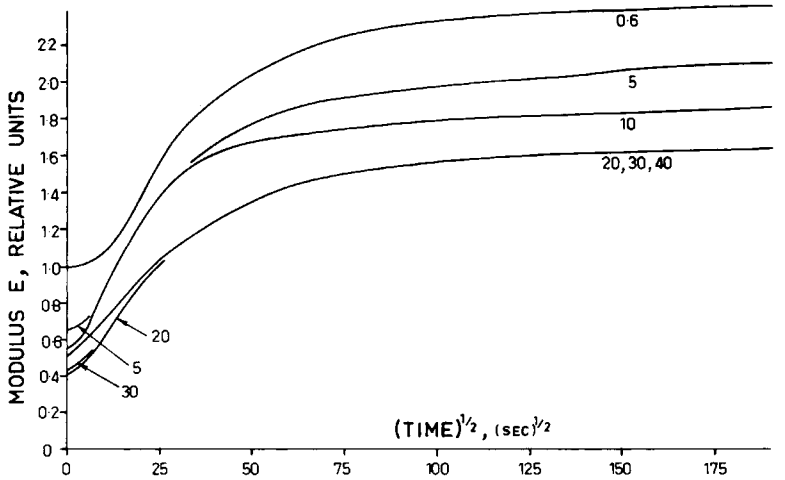

Fig. 1. The modulus E plotted against (time)$^{1/2}$ for fibers during desorption from 100 to 0% RH for the different fixed-extension levels of each fiber shown on each curve. (Relative unit = 2×10^9 N/m^2).

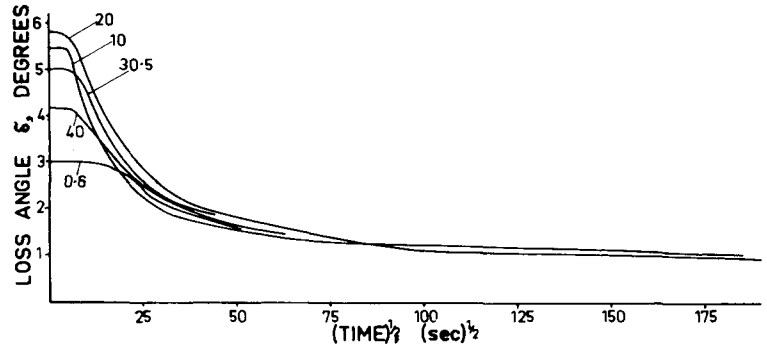

Fig. 2. The loss angle δ plotted against $(\text{time})^{1/2}$ for fibers during desorption from 100 to 0% RH for the different fixed-extension levels of each fiber shown on each curve.

for the constant strain X indicated on each curve. The modulus and loss angle during absorption are shown in Figures 3 and 4 in the same way.

A further Lincoln wool fiber, held at 10% fixed strain, was treated the same way, except that the final conditioning to 100% RH was performed by introducing water into the chamber and not by saturating the atmosphere with vapor. The result during absorption is shown by the dashed lines in Figures 3 and 4. Finally, one Lincoln wool fiber underwent the following treatment: The fiber was conditioned slack at 100% RH for 24 hr, then extended to 11% strain at 1.07%/min and held at 11% strain for the following 30 min. Subsequently, the fiber, while being held at the fixed strain, was dried for 24 hr and eventually extended to break in dry conditions by using a strain rate of 1.07%/min. The dotted curves of Figure 5 show the variation of modulus and loss angle with strain during the final extension in dry conditions.

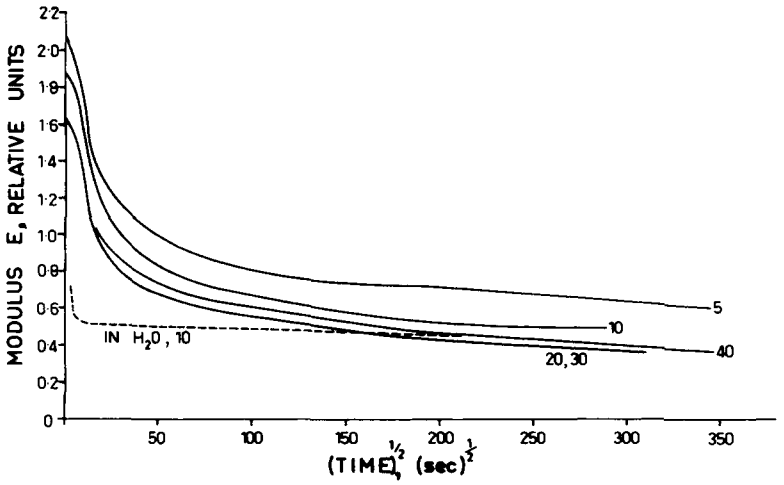

Fig. 3. The modulus E plotted against $(\text{time})^{1/2}$ for fibers during absorption from 0 to 100% RH for the different fixed-extension levels of each fiber shown on each curve.

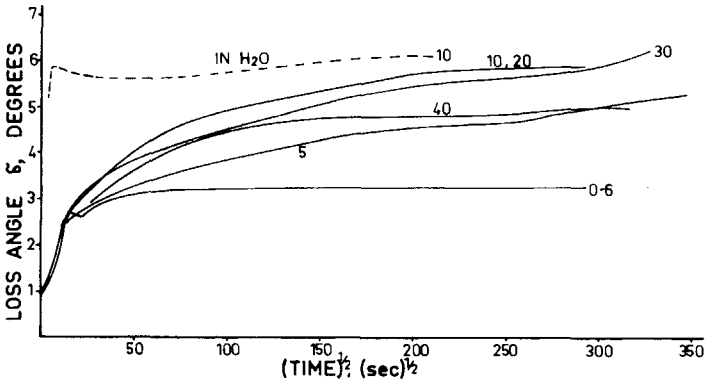

Fig. 4. The loss angle δ plotted against $(\text{time})^{1/2}$ for fibers during absorption from 0 to 100% RH for the different fixed-extension levels of each fiber shown on each curve.

DISCUSSION

Desorption

It is observed that the modulus during desorption generally increases with time to some equilibrium value depending on the fixed strain level at which the fiber is held. Wherever portions of the various curves almost overlap with one another, the curves have been drawn discontinuously for the sake of clarity. The exact equilibrium values of the modulus for dry fibers at various constant strain levels is shown as curve d in Figure 5, from which it is observed that the equilibrium dynamic modulus decreases with strain up to 20%, beyond which it remains practically constant. During desorption, the loss angle decreases with time and it reaches practically the same low level regardless of strain.

Curve d for the modulus in Figure 5 has the same general shape as that for a modulus plotted against extension for a fiber stretched in water.[2] This last

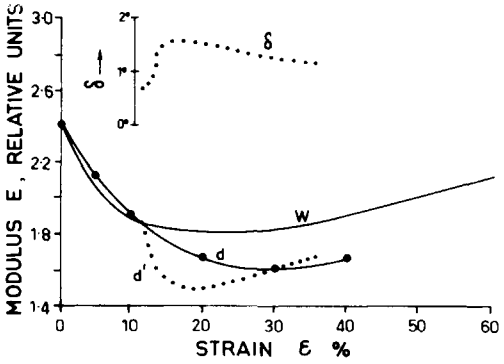

Fig. 5. The modulus vs. strain for Lincoln wool fibers under the following conditions: Curve d is the modulus of a dry fiber after extension in water to the plotted strain. Curve w is the modulus of a wet fiber for which a fixed vertical shift has been applied to equate the modulus at near zero strain ($\simeq$0.6%) with that of the dry fiber of curve d. Curve d′ is the modulus of a dry fiber extended dry to various strains greater than 11%, after the fiber had been previously extended wet to 11% strain and dried. The loss angle for the fiber corresponding to the conditions for curve d′ is plotted as curve δ.

modulus has been redrawn (neglecting the absolute level) as curve w in Figure 5 to be compared with curve d. Curve w has been plotted so that the initial level at zero strain coincides with curve d. It is observed that the two curves are close to each other for fixed strain levels up to $\simeq 15\%$. This result implies that the phase C (microfibril) remains basically unaltered upon drying the fiber from the wet state for fixed strains up to $\simeq 15\%$. Beyond this strain level, phase C appears to become weaker upon drying, which is compatible with the fact that the modulus decreases with time when a wet fiber is held at a fixed strain level higher than 15%.[1] Thus, the effect of the phase M (matrix) upon drying a wet fiber is to raise the modulus of the total fiber by a component which is practically invariant with strain; this component corresponds to the increase of modulus of the M phase itself.

The conclusion from the similarity of curves d and w is further supported by the behavior of modulus E (curve d′) and loss angle δ (curve δ) plotted against extension as shown by the dotted curves of Figure 5. This result was obtained by continuously extending a dry fiber from 11% strain to the breaking point, after the fiber was extended to a fixed strain (11%) at 100% RH, relaxed for 30 min, and subsequently dried at 0% RH. The dotted curves present all the characteristics of a normal unextended dry fiber[2] with an abrupt decrease of the dynamic modulus and a corresponding increase of the loss angle. The marked increase of the initial slope of the curve d′ is inhibited by a dry matrix. For a dry fiber, α helices do not open up completely into the β configurations because of steric hindrances; hence, more helices must be partially unfolded to obtain the same strain level when compared with the unfolding of α helices to obtain β chains in a wool fiber extended in water.[4]

The fact, however, that the loss angle (curve δ) starts from the same low value as that of an unextended fiber needs closer consideration. Upon drying a fiber from the wet state at any fixed extension, the loss angle achieves the same final low value as that of an unextended dry fiber, as pointed out earlier. This result suggests that the structural state of the wool fiber dried from the wet condition at any extension is similar to the initial state of the unextended dry fiber. As far as the matrix M is concerned, drying from the wet condition at any strain certainly achieves a dry matrix set in a state similar to an unextended dry fiber. Further extension of the latter set fiber when dry would create stresses in a network of bonds similar to that when straining an unextended dry fiber.

Absorption

It is observed that the modulus during absorption generally decreases with time to some equilibrium value depending on the fixed strain, at which the fiber is held. Wherever portions of the various curves almost overlap with one another, the curves have again been drawn with discontinuities for clarity.

The equilibrium values of modulus at 100% RH have been plotted against (fixed) strain as curve $E(2)$ in Figure 6; for comparison purposes, the modulus just prior to the commencement of desorption is also plotted against (fixed) strain as curve $E(1)$. During absorption, the loss angle generally increases with time (Fig. 4) to some equilibrium value depending on the fixed strain at which the fiber is held. The loss angle plotted against (fixed) strain is also shown in Figure 6 immediately prior to the commencement of desorption [curve $\delta(1)$] as well as

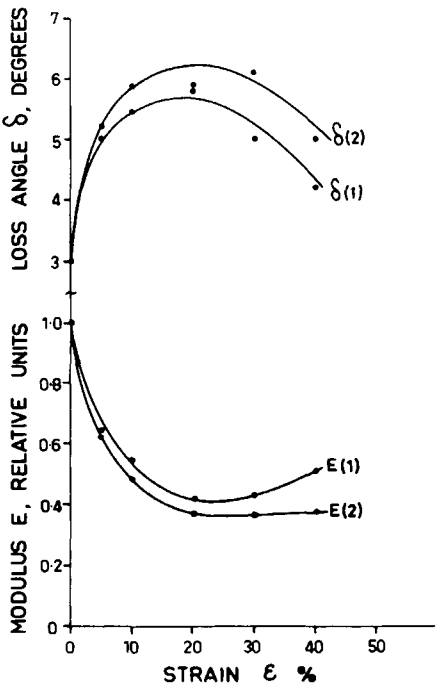

Fig. 6. The equilibrium dynamic modulus $E(2)$ and loss angle $\delta(2)$ plotted against strain for a fiber at 100% RH and the modulus $E(1)$ and loss angle $\delta(1)$ against strain just before desorption, at 100% RH.

when equilibrium was nearly achieved at 100% RH after absorption [curve $\delta(2)$]. From Figure 6, it is observed that in general $E(2) < E(1)$ and $\delta(2) > \delta(1)$, the inequalities becoming more pronounced with increasing strain. The important feature, though, is that the fiber recovers, in the main, its previous structural state, as though the desorption cycling had no major effect, except for the small inequalities just stated.

When the relative humidity is changed from 0 to 100% using water vapor, the loss-angle change with $(\text{time})^{1/2}$ shows an abrupt increase and subsequently a slow increase. The magnitude and speed of the abrupt increase is almost independent of the fixed strain level, while the slow increase is strongly dependent on the fixed strain level. When the initially dry fiber (at 11% fixed strain) is wetted with water, the loss angle shows a pronounced overshoot, slowly increasing again by a final small amount as shown by the dashed line in Figure 4.

The latter result shows that the structural behavior of keratin during absorption at high extensions is similar to its behavior at low extensions. However, the structural changes during absorption depend strongly on the way the conditioning is performed. Thus, the overshoots in loss angle were not observed when water vapor was used, probably because the secondary slow increase overshadows a possible tendency for an overshoot. This secondary slow increase is probably of the same origin as the one described during absorption at low extensions.[1,3]

In summary, there are three phenomena occurring during absorption: one responsible for the initial abrupt increase of loss angle, a second responsible for

the decrease of loss angle after the overshoot occurs, and a third responsible for the secondary increase in loss angle. The relative importance of these three phenomena depends on the path followed by the environmental changes.

The main factor likely to be decisive in relation to the structural behavior of keratin during absorption is the heat evolution. The important role of temperature in the wool–water sorption system is not always fully appreciated. Two examples may serve to emphasize the magnitude of the effect[5]: (1) if the water content of a wool sample near saturation is changed under adiabatic conditions by 1%, then the temperature of the sample will change by about 12°C; and (2), in a system initially containing water vapor at saturation pressure at 20°C, if the temperature is increased by 1°C while the vapor pressure is maintained constant, then the relative pressure is reduced to 94% and the corresponding equilibrium water content of wool is reduced from 33 to ~26%.

When keratin absorbs water vapor, the total quantity of heat liberated consists of the heat of condensation of the water vapor plus the heat of reaction of the water with keratin. The heat of reaction varies with the water content of the keratin. When the dry keratin is saturated (33%) from the liquid phase, the heat evolved amounts to approximately 220 cal/g of wool,[6] while the heat of absorption from the vapor phase is 660 cal/g of wool. It appears, thus, that the heat effects are minimized, when the water is absorbed from the liquid phase, both because the heat evolution is considerably lower and because of the higher heat capacity of the liquid water (compared to water vapor).

A higher rate of water absorption (e.g., for liquid water compared to water vapor) results in a higher rate of swelling, i.e., in a higher rate of extension due to swelling. It has been reported elsewhere[1,2] that the rate of extension is responsible for significant structural changes in the fiber. This observation provides an explanation for the different behavior of the dynamic mechanical properties of keratin during absorption of water from the liquid as compared to the vapor phase.

CONCLUSION

It has been observed that, when the relative humidity around a keratin fiber is increased abruptly by any given amount, the loss angle exhibits a maximum value with time, while the rate of change of the modulus shows an abrupt variation at the time of maximum loss angle. These phenomena appear when the fiber is held at a low fixed extension. They are also present when the fiber is held at a higher fixed-strain level, provided that the relative humidity increase is extremely fast and that the temperature effects are eliminated; such is the case, for example, when the fiber is immersed in water.

The characteristic change in the complex modulus with time during absorption of water has been interpreted to mean a general increase of mobility in keratin at the molecular level. This mobility must take place in both phases: The matrix phase M must achieve maximum mobility, since it has to accommodate a large degree of swelling mainly in the lateral direction, the longitudinal swelling being inhibited by the microfibril C phase. The latter phase C also passes through a state of maximum mobility, since it undergoes a transient extension induced by the swelling forces of the M phase. Thus, the transient increase in mobility of the whole fiber combined with the transient weakening of the C phase

result in the maximum of the loss angle and the abrupt change of the rate of decrease of modulus with time.

When a keratin fiber, held at a fixed strain level, is dried from the wet state, the modulus increases to a value above that which it would have if the fiber were extended in the dry state to the particular fixed strain level; the loss angle decreases correspondingly to the value exhibited by the unextended dry fiber. The proposed explanation for this observation is that the fiber, dried at the fixed strain, has less α helices opened out than it would otherwise have if the fiber were extended in the dry state from zero to this particular strain. This effect arises from the steric hindrance imposed upon the unfolding of α helices to form β chains when a fiber is extended in the dry state (as opposed to fiber extension in the wet state). This steric hindrance means that in order to obtain the same strain level, more α helices must be unfolded for the fiber extended in the dry state.

Finally, it has been found that when a wet fiber is dried and then rewetted while it is held at a fixed strain, the fiber achieves essentially the same structural state as it had in the original strained wet state; the modulus, however, is slightly less and the loss angle slightly higher than their corresponding values for the initial wet fiber.

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