Some Mechanical Changes During Sorption of Water by Dry Keratin Fibers in Atmospheres Near Saturation

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It has been pointed out in previous papers[1,2] that in a wool fiber, originally dry, which is absorbing water in an atmosphere at or near saturated vapor pressure, the swollen annular portion of the fiber, if the simultaneous length changes are zero, must continually change its proportions to accommodate the swelling in progress inside the fiber. It was this continuous change of proportions of the swollen part of the fiber which was considered a possible cause of disruption in the fiber. It was also reported[1] that simultaneously with the sorption of water by the fiber, observations were carried out of longitudinal stress at a fixed small strain ($\sim$1%) at which the fiber had previously been held in water until a steady stress value was reached in about 1 hr. and then dried. As the fiber absorbed moisture, the stress in the fiber varied with time as indicated in Figure 1, showing a minimum when the fiber has reached approximately maximum regain at time t_m. Mackay and Downes[3] also have shown that for a single fiber the torsional rigidity falls rapidly to almost zero during sorption from 0% to 94% R.H. and then slowly increases until equilibrium rigidity at 94% R. H. is reached. Their measurements were made with the use of a torsional pendulum to obtain values of the torque per unit angular displacement of the fiber during the experiment. Recently one of the authors (P. N.) remeasured the torsional rigidity of a single wool fiber during a similar absorption step, using a technique (to be described elsewhere) in which the fiber was driven instead of acting as part of a self-oscillating system. The value of the rigidity of the fiber did not fall to zero or near it at time t_m as indicated by Downes and Mackay. In the measurement of rigidity by use of a torsional pendulum (by Downes and Mackay) displacements of the order of one revolution were used. In this later work using the driven system displacements very much lower, of the order of 0.04 of a revolution were

used. As a further test, measurements of torque by techniques[8] described elsewhere were carried out at constant twist level, in which the fiber was held first in water at a fixed twist until torsional relaxation was negligible. The fiber was then dried out at the constant twist, and then rewet. The variation of torque in the fiber at constant twist going from dry to wet showed no signs of collapse of the fiber rigidity at a time t_m as indicated by the torsional pendulum experiment. The difference between the torsional pendulum result and these later results may lie in the high displacements used in the former experiment. The later results appear more appropriate to apply in conjunction with the longitudinal experiments, where no change of extension was made between the dry and wet condition. A discussion of the difference between these experimental results will appear at a later date. However, these new results on the change of rigidity with time no longer showing a collapse in the rigidity modulus at about a time t_m require a reassessment of the interpretation to be put on the longitudinal stress change indicated in Figure 1.

In a previous paper[1] it was suggested that the rise of longitudinal stress beyond time t_m was due to reformation of strained hydrogen bonds in the matrix, the matrix of the wool fiber going from a sol to a gel state beyond time t_m. Recent experiments[4] on the longitudinal and torsional properties both of "permanently" set and chemically modified wool fiber suggest that the hydrogen bonds in the matrix at saturation cannot sustain a stress for an extended period of time. This would cast doubt on the explanation already put forward for the rise of longitudinal stress beyond time t_m, which would require formation of hydrogen bonds under strain. Further, the new measurements on the torsional rigidity variation with time also discounts the explanation given on the basis of
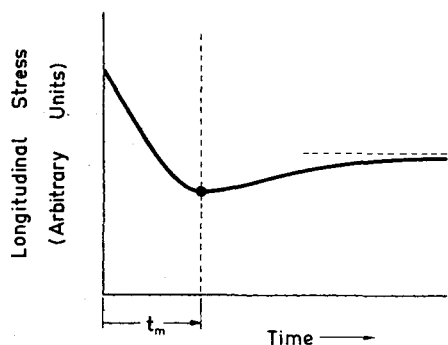
Fig. 1. The change in longitudinal stress (arbitrary units) of a wool fiber at a fixed small extension ($\sim 1\%$), when the fiber is taken from 0% to 100% R.H. Before being taken to 0% R.H. the fiber had been extended to the fixed extension in water and held at this extension for 1 hr.
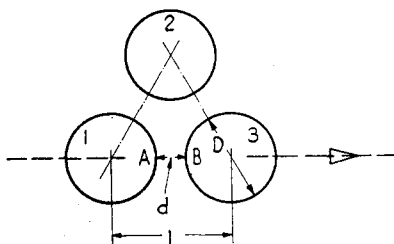

Fig. 2. A diagrammatic representation of the relative position of three microfibrils (1, 2, 3) in transverse section in the wool fiber. If the direction of the arrow is radial during sorption, regions A and B of the microfibrils will come under temporary stress above that experienced by the fiber at equilibrium in the wet state (see text).

a sol–gel transformation of the hydrogen bonding in the matrix, since this transformation would require the torsional rigidity of the fiber, which depends mainly on the matrix elasticity, to fall to a very low value, while the fiber is in the sol state. The fiber was claimed to be in the sol state at time about t_m. The stress in the fiber at saturation beyond time t_m appears therefore to be sustained by the microfibrils, the increase of stress indicating a reformation of components of the microfibril in a stressed state. This suggestion is supported by evidence reported elsewhere[5] of the amount of D $\rightarrow$ H exchange (a) in D_2O until no further exchange is measured and (b) after drying and wetting in D_2O five hundred times. In the former case about 70% of the peptide hydrogen is exchanged, and, in the latter, well above this figure of 70% (in fact 90%). This result indicates that during the sorption process from dry to saturation a transient increase of the accessibility of the wool fiber is obtained. Such a transient increase of accessibility would result if, during the sorption,

a process of disruption occurred in the microfibrils, followed by a reformation. In a previous paper[7] evidence was discussed of the relationship between microfibrils, the matrix and the mechanical properties of a keratin fiber. It will be assumed in this discussion that the microfibrils embrace the organized and relatively water-impenetrable regions, the matrix the disorganized and the relatively penetrable regions of the keratin fiber. In the wet state the longitudinal stress of an extended keratin fiber may be assumed to be completely due to the microfibrils. Hence any disruption of the microfibrils followed by a reformation would have two effects: (a) a weakening of the fiber followed by a restrengthening, as indicated by the longitudinal stress measurement at a fixed small strain; (b) a temporary increase in the accessibility of the fiber as indicated by D $\rightarrow$ H exchange during multiple drying and wetting in D_2O. A suggested possible mechanism for creating the temporary disruption of the microfibrils during moisture sorption will now be discussed. This mechanism depends on the continuous change of proportions of the swollen part of fiber during moisture uptake, and the effect this has on the mechanical relations between microfibril and matrix.

Figure 2 shows in section three microfibrils 1, 2, and 3 embedded in a matrix. Electron microscope and x-ray evidence[5] show that the center-to-center distance L of the microfibrils in the dry keratin fiber is 100 A. and the diameter is 60–80 A. The boundary between the microfibril and matrix will be rather indefinite. Fraser and Macrae[6] claim the change in L at saturation to be the same as the diametral swelling of the fiber, i.e., about 16%. If we assume the microfibril swelling corresponds to the change measured by the high-angle x-ray pattern of 5%, the distance d between the two neighboring microfibrils must increase from dry to wet about 42% if we assume the microfibril diameter is 70 A. During sorption to saturation some microfibrils in the outside annulus of the fiber must be separated during the early stages of absorption by a distance d even greater than that indicated for equilibrium conditions. This situation arises if their center-to-center line (as indicated in Figure 2 between microfibrils 1 and 3) is in the radial direction. At the early stages of sorption because of the restriction in the tangential direction to swelling, most of the swelling of the annulus must be radial. Any swelling pressure produced by the absorbed water will be opposed by bonds under strain due to the swelling. In a wet wool

fiber, since the matrix is the main swelling medium, it might be expected that the regions of most strain would be those where neighboring microfibrils are closest, as the matrix between A and B in Figure 2. In this region any crosslinkage network of main chains or side chains between the two microfibrils 1 and 3 would be extended to result in 42% increase of d from dry to wet. The extensions of these networks creates a stress opposing the swelling of the matrix. In the wet fiber at equilibrium such a situation would exist for all networks between each microfibril. However, during moisture absorption, swelling is limited more to the radial direction. Bonds in networks between neighboring microfibrils with center-to-center lines in the radial direction will come under greater strain than at equilibrium, since they are now the bonds mainly opposing the swelling pressure. This means that the microfibrils in the vicinity of A and B (in Fig. 2), if the microfibrils 1 and 3 are in the radial direction, will experience a lateral stress above that at equilibrium. This increased stress may cause disruption in the microfibril, in particular to the polypeptide chains at A and B, thus increasing the water accessibility of these parts of the microfibrils. As the fiber becomes uniformly swollen the stress due to swelling will drop in the regions A and B, resulting in a reformation of the microfibrils and a reduction of water accessibility.

We have described above a possible mechanism to explain the mechanical changes proceeding through a keratin fiber during sorption from a dry to a saturated or near saturated state. It was assumed throughout that the microfibrils included the organized and relatively water-impenetrable regions, the matrix the disorganized and the relatively water-penetrable regions. Obviously, a zone of gradation may exist between the two. However, such a gradation would not change the points raised here in explaining the experimental observations made. In the previous paper on these observations it had been suggested that the bond breakdown and reformation occurred in the matrix. In this paper we suggest the shift of this mechanism of breakdown and reformation to the microfibrils.

References

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Synopsis

If a wool fiber is held at a small. fixed strain in water ($\sim$1%) the stress in the fiber relaxes and reaches a steady value in about 1 hr. If, while the fiber is still held extended, it is dried and subsequently rewetted, the stress in the fiber after rewetting drops rapidly to a minimum and then slowly rises. This rise in stress in the fiber was previously interpreted as a rebuilding of hydrogen bonds under strain in the matrix of the wool fiber. Recent torsional measurements on fibers during the absorption of moisture from dry to a high humidity throw doubt on this conclusion. It appears that the rise in stress after moisture sorption is due to the reformation of the structure of the microfibrils, which have been partially disrupted by the swelling of the keratin structure due to the entrance of moisture. Infrared evidence of increased deuterium oxide penetration of the keratin structure during sorption of deuterium oxide agrees with this interpretation. A mechanism is suggested for this disruption of the microfibrils based on the difference of swelling of matrix and microfibril with the sorption of water into the wool fiber.

Résumé

Si une fibre de laine est maintenue dans l'eau ($\sim$1%) dans une faible tension déterminée, la force dans la fibre se relâche et atteint une valeur constante après une heure environ. Si, alors que la fibre est encore maintenue en extension, on la sèche et ensuite on la réhumidifie, la force dans la fibre après la réhumidification passe rapidement par un minimum et augmente ensuite lentement. Cette augmentation de force dans la fibre a été antérieurement interprétée comme étant due à une reformation des liaisons hydrogènes sous l'action de la tension au sein de la fibre de laine. Des récentes mesures de torsion effectuées sur les fibres pendant l'absorption d'humidité depuis l'état sec jusqu'à une humidité élevée jette un doute sur cette conclusion. Il semble que l'augmentation de la force après adsorption d'humidité soit due à la reformation de la structure des microfibriles qui ont été partiellement rompus lors du gonflement de la kératine provoqué par l'humidité. Cette interprétation s'accorde avec la mise en évidence par spectrographie infrarouge d'une augmentation de la pénétration d'oxyde de deuterium dans la kératine pendant l'absorption d'oxyde de deutérium. On propose un mécanisme pour expliquer cette rupture des microfibriles, mécanisme basé sur la différence de gonflement de la matrice et du microfibrile lors de l'absorption d'eau par la fibre de laine.

Zusammenfassung

Wird eine Wollfaser bei einer kleinen konstanten Dehnung ($\sim$1%) unter Wasser gehalten, so nimmt die Spannung in der Faser ab und erreicht in etwa einer Stunde einen sta-

tionären Wert. Wird nun die Faser bei aufrecht erhaltener Dehnung getrocknet und dann wieder befeuchtet, so fällt die Spannung in der Faser nach der Befeuchtung rasch auf eine Minimum ab und steigt dann langsam wieder an. Dieser Spannunganstieg in der Faser wurde früher als Folge der neuerlichen Bildung von Wasserstoffbindungen unter Verformung in der Wollfasermatrix gedeutet. Neuere Torsionsmessungen an Fasern während der Feuchtigkeitsaufnahme vom trockenen bis zum hochgradig feuchten Zustand lassen diesen Schlusszweifelhaft erscheinen. Es scheint, dass der Spannungsanstieg nach der Feuchtigkeitsaufnahme durch die Rückbildung der Struktur der

Mikrofibrillen bedingt ist, die durch das Eindringen der Feuchtigkeit und die damit verbundene Quellung der Keratinstruktur zum Teil gespalten wurden. Das im Infrarot erkennbare, erhöhte Eindringen von Deuteriumoxyd in die Keratinstruktur während der Sorption von Deuteriumoxyd stimmt damit überein. Es wird ein Mechanismus für diese Aufspaltung der Mikrofibrillen vorgeschlagen, der auf der verschiedenen Quellung von Matrix und Mikrofibrille bei der Sorption von Wasser durch die Wollfaser beruht.