The Sorption of Water by Dry Keratin Fibers in Atmospheres above 90% R.H.

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INTRODUCTION

When a dried wool fiber is immersed into liquid water at room temperature, Haly[1,2] has shown that the water entering the fiber produces an advancing front of water. Behind this advancing front the material is swollen relative to the material ahead of the front. In a cylindrical fiber, originally dry, which is absorbing water from the liquid state, the swollen outer annular portion of the fiber, if the *simultaneous length changes are negligible*, must continually change its proportions to accommodate the swelling in progress inside the fiber. Once the whole fiber has completed swelling, this requirement for the outer part of the fiber to change ceases.

The above requirement during the penetration of water from the liquid state or a very high humidity atmosphere into a dry fiber has suggested a model for the behavior of keratin fibers during such absorption.

Further, the variation of mechanical properties (torsional rigidity, and longitudinal stress at a fixed strain) in a swelling fiber can be simply explained in terms of this model.

THE MODEL

Consider a cylindrical fiber consisting of two phases C and M, the phase C consisting of parallel cylinders embedded in a matrix phase M (see Fig. 1). The following properties of the two phases are postulated:

(a) Phase C is impenetrable to water and does not swell when the fiber takes up moisture. (b) Phase M is penetrable to water and swells due to moisture absorption. (c) The water on penetrating phase M dissolves bonds holding together the molecular structure, disorganizing this phase, which at this stage acts as a solution. Subsequently, once movement due to swelling ceases, a rebuilding of bonds occurs converting the matrix into a gel-like structure. In other words, once water has
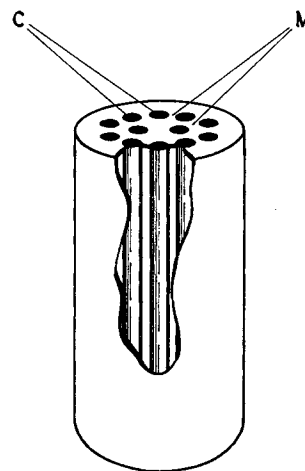

Fig. 1. A diagrammatic representation of the cylinders of the water impenetrable phase C in a matrix M inside a keratin fiber.

penetrated the matrix phase, M, it becomes a thixotropic solution and goes through a sol-gel transformation.

The above model is the same as the two-phase structure that has been proposed for keratin fibers.[3] It was pointed out that the longitudinal force on a wet keratin fiber at any strain is the sum of the longitudinal forces on the two phases C and M. However, for a fiber being twisted most of the shear strain is taken up by the M phase (being very much weaker than the C phase), and the torque due to the fiber is controlled by the shear properties of the M phase.

WATER PENETRATION OF THE MODEL

If the model fiber, dry, is plunged suddenly into a moist atmosphere, a front of water will enter the fiber swelling and dissolving bonds in the matrix M. The swelling of the matrix will cause movement of the cylinders forming phase C. No obstruction, however, to this movement can occur while phase M
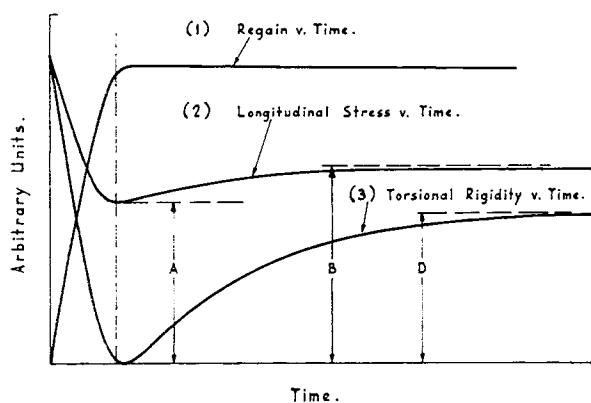
Fig. 2. A comparison of the variation with time of mechanical properties of the proposed model and the increase of water uptake. The mechanical properties chosen are longitudinal stress at a fixed strain and torsional rigidity.

is in a solution state. Water will be taken up by the fiber until all phase M is swollen (see Fig. 2). Then further disorganization in the fiber ceases and a slow buildup of bonds will occur in the completely swollen phase. The matrix M passes from a sol to gel state. This change from sol to gel state must involve little or no change in free energy, otherwise it would be accompanied by a change in moisture content.

If during the above uptake of moisture the model is under a small fixed strain, as the water dissolves the bonds in the matrix it will cause the longitudinal stress in the matrix to fall to zero, the overall longitudinal stress falling to a minimum value A, corresponding to the stress produced by the impenetrable phase C (see Fig. 2). Once full regain is reached the minimum longitudinal stress is also observed and from then on the longitudinal stress builds up slowly to a value B, where $(B - A)$ corresponds to the force produced by the structure of M going from a sol to a gel state.

If, simultaneously with the above events, observations are made on the torsional rigidity of the fiber, the following results will be obtained. The portion of the fiber for which the matrix M is in a sol state will offer no resistance to shear. (It is assumed that the cylinders forming phase C are of such small diameter relative to the whole fiber as to offer no opposition to bending.) It follows that for the whole fiber model the rigidity falls with increase of regain until the complete phase M is in a sol state, when the rigidity falls to zero. This point will correspond (in time) to the fiber reaching full regain. Thence the matrix transforms slowly from a sol to a gel state and a buildup of torsional rigidity

will result until some equilibrium value D is reached (see Fig. 2).

DISCUSSION

Experiments on single wool fibers corresponding to the ones described above for the model structure have been carried out. Mackay and Downes[4] have shown that, when a single fiber has the atmosphere around it changed from 0% to 94% R.H., the torsional rigidity of the fiber falls rapidly to almost zero and then slowly increases until the equilibrium rigidity at 94% R.H. is reached. They also showed that the rigidity reaches its lowest value approximately, when the increase in regain of the fiber has ceased. Further, Feughelman and Robinson[5] have shown that the longitudinal stress in a single fiber with the strain at about 2%, when taken from 0% R.H. to the wet state, changes with time in the same manner as curve 2 in Figure 2. These two experiments indicate that for wool fibers going from a dry state to one of high moisture content, the mechanism of moisture absorption can be explained by a front of water entering the fiber, swelling the water accessible regions, and converting them to a
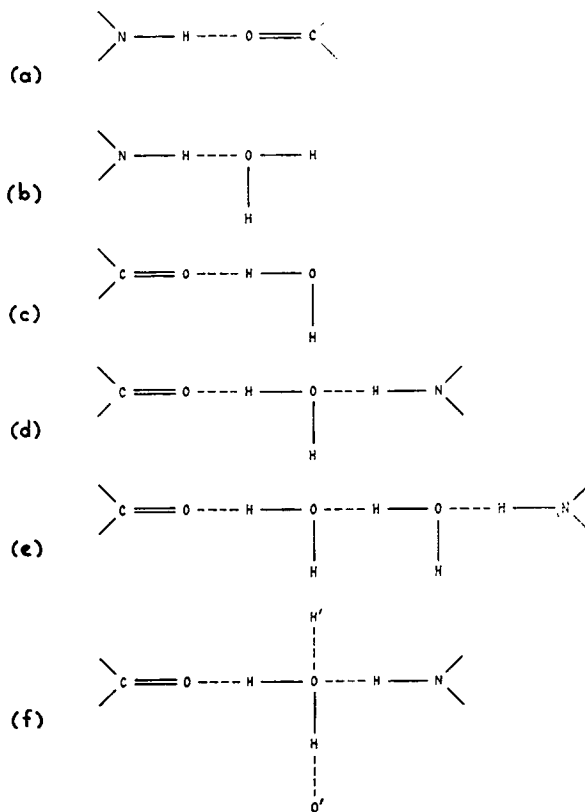

Fig. 3. A series of possible hydrogen bond associations: (a), in the dry fiber between amide groups; (b) to (f), in the fiber absorbing water.

sol state. Once disorganization caused by the swelling has ceased, a slow conversion from the sol to gel state occurs. This sol state of the water accessible regions of wool would correspond to a relatively unrestricted elastomer, the polypeptide chains being joined at intervals by covalent links, which are unaffected by the presence of water. The gel process for these same regions corresponds to the polypeptide chains becoming limited in their movement by the formation of new bonds which convert the regions into restricted elastomers.

During the uptake of water into a dry fiber involving a large sorption step, Mackay and Downes[6] have postulated the formation of a "stress front" between the unswollen and swollen parts of the fiber. However, if the two-phase model is accepted, during the penetration of water into the fiber, the swollen portion of the fiber is greatly weakened mechanically. Because of this weakening, the swollen material behind the front entering the wool fiber could not react on the unswollen part ahead of the front to create the "stress front."

The molecular forces holding the wool structure together, which are affected by the presence of water are (a) Van der Waal's forces, (b) Salt-linkages, and (c) hydrogen bonds.

Of the above groups of intermolecular bonds, the hydrogen bonds provide a possible simple mechanism for a sol-gel transformation in the matrix structure, after the penetration of water into the structure. In the dry fiber, inter- and intra-molecular hydrogen bonding will occur between the amide—NH and —CO groups in the polypeptide chains [see Fig. 3(a)]. With the first penetration of water into the matrix of the wool fiber, these hydrogen bonds are disrupted with the formation of new hydrogen bonds between the penetrating water molecules and the amide—NH and —CO of the keratin molecule (see Figs. 3(b) and 3(c)). At this stage, the polypeptide chains of the keratin structure are not restricted by the hydrogen bonds. With time the water molecules will form more associations such as in Figures 3(d) and 3(e) and eventually as in Figure 3(f). In the last case the hydrogen H' and oxygen O' may belong to other water molecules or to amide groups. When the stage shown in Figure 3(f) is reached the water molecule is fully associated in the structure in a manner similar to that in ice.[7] At this stage the polypeptide chains forming the matrix become restricted in their movements. The matrix mechanically becomes stiffer, and equivalent to a gel-like structure.

References

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Synopsis

Use is made of the basic concepts of a two-phase model structure for keratin fibers, consisting of a water impenetrable phase embedded in a water penetrable matrix phase. The mechanism of water sorption of a dry fiber in liquid water or in a high humidity atmosphere is discussed. It is assumed that during moisture uptake the matrix goes into a sol-state. Once moisture uptake is complete the matrix goes through a sol-gel transformation. Both the torsional rigidity and longitudinal stress at low strain vary during the sorption process, and subsequently, in a manner compatible with this model.

Résumé

On fait usage pour les fibres de kératine du concept fondamental d'une structure modèle à deux phases conprenant une phase impénétrable à l'eau occlue dans une phase matricielle pénétrable à l'eau. On discute du mécanisme d'absorption de l'eau sur les fibres sèches en phase aqueuse ou en atmosphère fortement humide. On présume que durant l'absorption d'humidité la matrice passe à l'état de sol. Lorsque l'absorption de l'eau est complète la matrice subit une transformation sol-gel. La rigidité à la torsion et la torsion longitudinale à faible contrainte varient toutes les deux durant le phénomène d'absorption d'une manière compatible avec ce modèle.

Zusammenfassung

Für Keratinfasern werden die Grundannahmen einer Zweiphasen-Modellstruktur benützt, die aus einer wasserundurchlässigen Phase besteht, welche in eine wasserdurchlässige Matrixphase eingebettet ist. Der Mechanismus der Sorption von Wasser durch eine trockene Faser in flüssigem Wasser oder in einer Atmosphäre hoher Feuchtigkeit wird diskutiert. Es wird angenommen, dass während der Feuchtigkeitsaufnahme die Matrix in einen Solzustand übergeht. Sobald einmal die Feuchtigkeitsaufnahme vollständig ist, erleidet die Matrix eine Sol-gelumwandlung. Sowohl die Torsionsfestigkeit als auch die Longitudinalspannung bei geringer Verformung ändern sich während des Sorptionsprozesses und in der Folge in einer Weise, die mit diesem Modell verträglich ist.