

***The Role of Water in the Segmental Mobility of
Hydrophilic Fibers***

Water absorbed by hydrophilic fibers such as α -keratin (wool, hair etc.), nylon, viscose, and acetate rayons has a profound effect on the mechanical properties of these fibers. To a large extent the action of water on these properties is that of a "plasticizer," that is, an agent reducing the internal viscosity of the molecular structure of the fiber. This has recently been well illustrated for wool fibers¹ in the variation of stress at a fixed extension over a range of moisture content in equilibrium with zero to 100% relative humidity. For extensions in the Hookean region (<2%), the stress in a fiber at equilibrium with a fixed relative humidity decays to a steady value independent of the relative humidity. The relaxation time τ of the stress decay is very sensitive to the water content of the wool fiber (see Table I), indicating that the segmental movement within the

TABLE I
Relaxation Time of Stress Relaxation of Wool Fiber Held Extended at a Strain within the Hookean Region of the Load Extension Curve for the Fiber

Relative humidity, %	Water content, %	Relaxation time, τ , min ^a
0	0	5.2×10^2
14	5	2.4×10^2
32	8.3	1.85×10^2
65	14.5	1.25×10^2
91	23	4.2×10^1
100 (wet)	33	6.6×10^{-1}

^a Value of τ corresponds to the fiber in equilibrium with a range of relative humidities and hence with various water contents.

fiber's molecular structure is controlled by the presence of water. The rate of length recovery from cohesive set observed by Haly and Feughelman² for Corriedale wool fibers at various water contents further illustrates the control of the internal viscosity of these fibers by their moisture content.

This ability of water to greatly modify the internal viscosity of a hydrophilic fiber may be understood in terms of some basic properties of the water molecule, namely its strong polarizability and therefore large inducible dipole moment, its ability to form associations via hydrogen bonding, and its small molecular diameter ($\sim 2.7 \text{ \AA}$).

A dry fiber consists of molecular chains and side chains with a large number of localized electrically charged and polar groups. The electric field inside the fiber structure will be determined by the nature and distribution of these charged groups, which can form strong localized interchain interactions. The nonuniform electrostatic fields so formed would be most intense in the neighborhood of the charged groups, leading to a series of potential maxima and minima for an isolated charge or electric dipole moving through the fiber. If the fiber is extended, interchain interactions are stressed. This stress is relaxed by the rupture of the interchains followed by relative movement of the chains which allow the charged groups to form new interactions in more energetically favored circumstances. The process involves a movement of the individual charged groups through the nonuniform internal electric field of the fiber from one potential energy minimum over potential maxima to another potential minimum.

This situation is greatly altered by the introduction of water into the structure. Because of their small size, water molecules can gain access to the internal structure of the fiber where, through their polarizability and ability to form polar interactions, they distribute themselves in the fiber so as to concentrate in regions of high electric field in-

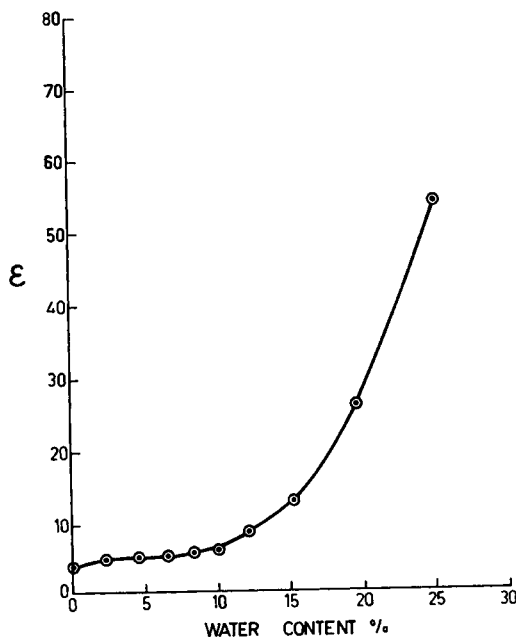


Fig. 1. Equilibrium dielectric constant ϵ versus water content at 35°C and 1592 Hertz for Corriedale wool fibers. (From Algie.⁴)

tensity. They concentrate around accessible charged and polar groups and, being highly polarizable, tend to attenuate the electric fields associated with these groups. The result is to reduce the interaction between neighboring polar groups, that is, to produce shielding. The overall effect of the water is to moderate and average out the internal electric fields in the fiber.

This shielding effect of the water on a region in the fiber of high electric field intensity can be understood as a conversion of such a region to one of relatively high dielectric constant so that the Coulombic interaction between charged groups is weakened. Some idea of the degree of this effect can be gained by considering the expression³ for the reduction in the association constant K_a with increase in dielectric constant ϵ for rigid charged spheres of diameter a in a continuum,

$$K_a = K^0 \exp \{ l^2 / a \epsilon k T \} \quad (1)$$

where K^0 is a geometrical factor accounting for excluded volume, l is the unit charge, k is the Boltzmann constant, and T is absolute temperature. This expression may be compared with the variation of the equilibrium dielectric constant of wool with water content⁴ (Fig. 1). The observed dielectric constant is seen to rise with water content and, if eq. (1) applies, K_a and hence the interaction forces must decrease with increasing water content. The reduction of interaction forces produced by the water that concentrates in the regions of high electric field strength reduces the energy differences between the potential minima and maxima, thus increasing the mobility of chain movement from one potential energy minimum to another.

Bull and Breese⁵ have explained the apparent freezing of egg albumin in its native configuration and also its increased thermal stability with dehydration in terms of the strengthening of intra- and interchain interactions between the ions in molecular ion

pairs when the medium is transformed from one of high dielectric constant (wet) to one of low dielectric constant (dry).

For a hydrophilic fiber in water, once the interaction of an interchain molecular polar pair has been interrupted owing to an applied stress, the exposed polar groups would quickly become associated with water molecules. This is facilitated by the smallness and therefore high mobility of the water molecules, which also enables them to quickly reposition themselves to moderate any newly created region of high electric field strength. The water molecules can move rapidly to new positions of minimum free energy within the fiber. It is therefore possible that the rate of bond breakdown and reformation, as reflected in the relaxation of stress in a fiber at fixed extension, may be in part determined by the rate of molecular transport of the absorbed water.

References

1. M. Feughelman and M. S. Robinson in preparation.
2. A. R. Haly and M. Feughelman, *Text. Res. J.*, **31**, 135 (1961).
3. R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).
4. J. E. Algie, *Text. Res. J.*, **34**, 477 (1964).
5. H. B. Bull and K. Breese, *Ach. Biochem. Biophys.*, **128**, 488 (1968).

L. J. LYNCH*

M. FEUGHELMAN†

Received October 22, 1969

* CSIRO, Division of Textile Physics, 338 Blaxland Road Ryde, Sydney, Australia.

† School of Textile Technology, University of N.S.W. Kensington, Sydney, Australia.