Influence of processing conditions on the dynamic modulus of wool: 1. HCl at pH 1

D. W. Dubro*
School of Textile Technology, University of New South Wales, NSW, Australia
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The influence of aqueous HCl at pH 1 upon the structure of wool has been studied by means of dynamic modulus measurements. The most apparent effect is a reduction in stiffness of the matrix. The fitting of a suitable model for the extension of wool suggests that salt links play an important role in the thixotropic transformation of the matrix. With wool equilibrated to 100% r.h. as the reference, HCl at pH 1 lowers the stiffness of the crystalline part of the fibre by 42%.

(Keywords: dynamic modulus; keratin; alpha helices; plasticizers; thixotropic)

INTRODUCTION

In the processing and manufacturing of wool and especially in the laundering and pressing of finished garments wool is often subjected to a variety of physical and chemical environments. Acidic conditions are very common in dyeing and carbonizing. Acid and other plasticizers often wash out of wool without leaving any permanent effect so that structural information can be obtained from measurements carried out in the presence of these plasticizers. Since wool is a nonlinear viscoelastic polymer, measurements of the dynamic modulus[1] yield new information which cannot be obtained by other techniques[2–12].

EXPERIMENTAL PROCEDURE

Wool used in these experiments was supplied by the Sheep Biology Laboratory of CSIRO. The fibres were from penned Lincoln sheep, hand-fed for uniformity of fibre growth, and have been designated SW351 for future identification. All wool was first examined under a projection microscope in order to select undamaged, uniform and medulla-free fibres which were then washed thoroughly in petroleum ether, allowed to dry and rinsed in ethyl alcohol. After equilibrating in room conditions, the fibres were formed into 2 cm loops, tied and secured with a droplet of epoxy resin.

The dynamic modulus was measured as a function of extension using the technique and equipment of Danilatos[13] at 116 Hz and 25°C. A sinusoidal oscillation of 4 μm was superimposed upon a steadily increasing extension of 1% per minute. The oscillating stress was detected by a piezoelectric transducer and a lock-in amplifier referenced to the driving frequency, and a dynamic modulus was computed from the oscillating (complex) stress and the oscillating strain. Load–extension curves were measured on an Instron Tensile Tester at a strain rate of 50% per minute. Between mechanical tests, all fibres were relaxed in water at 52°C for one hour to recover their mechanical properties.

The dynamic modulus of wool was measured in water and compared with that measured in HCl at pH 1. Four tests were carried out on each of a number of single fibres: in water and in acid at two different rates of strain (0.16% $\min^{-1}$ and 1% $\min^{-1}$). The order of tests was varied to see if the tests produced any permanent or cumulative effects. No variation was observed in the results. One hour was allowed for fibres to come to equilibrium with the plasticizers before testing was begun. The error in the dynamic modulus was ±2%.

EXPERIMENTAL RESULTS

A comparison of the dynamic modulus of wool in water and in aqueous HCl is shown in *Figures 1a–c*. In these results, tests were repeated on several different fibres and the results judged to be average are shown.

Figure 1a compares the dynamic modulus of wool in the two plasticizers at a strain rate of 1% per minute. The effect of the second strain rate of 0.16% per minute was very slight: the modulus at a slower rate was only a few percent greater, preserving the same overall shape. Both sets of curves show the characteristic drop in modulus as the fibre is extended, due to the loss of the contribution of the alpha helices which have unfolded into the beta conformation. This drop is quite out of proportion to the amount of alpha material transformed. However, as will be discussed below, the transformed material is similar to a 'weak link in a chain' and must transfer its stress to its neighbouring matrix, which is comparatively weak as well. This drop in modulus is related to the stiffness of the crystalline part of the fibre[1], which has now been lost and which is fairly constant over a range of relative humidities from dry to wet. Acid reduces this drop by a factor of about two. The remnant modulus in the yield region for acid is also about one-half the value obtained in water.

(The Hookean, yield and post-yield regions may be seen in the stress–strain curve shown in *Figure 2*. They are defined in the figure by the intersection of lines drawn tangential to the curve and are nominally defined as 0–2% strain, 2–30% strain and 30% strain to break, respectively. The Hookean region is known to be linear viscoelastic, but the term 'Hookean' will still be used since

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[*] Present address: Memorial Sloan-Kettering Cancer Center, 1275 York Avenue, New York, NY 10021, USA.

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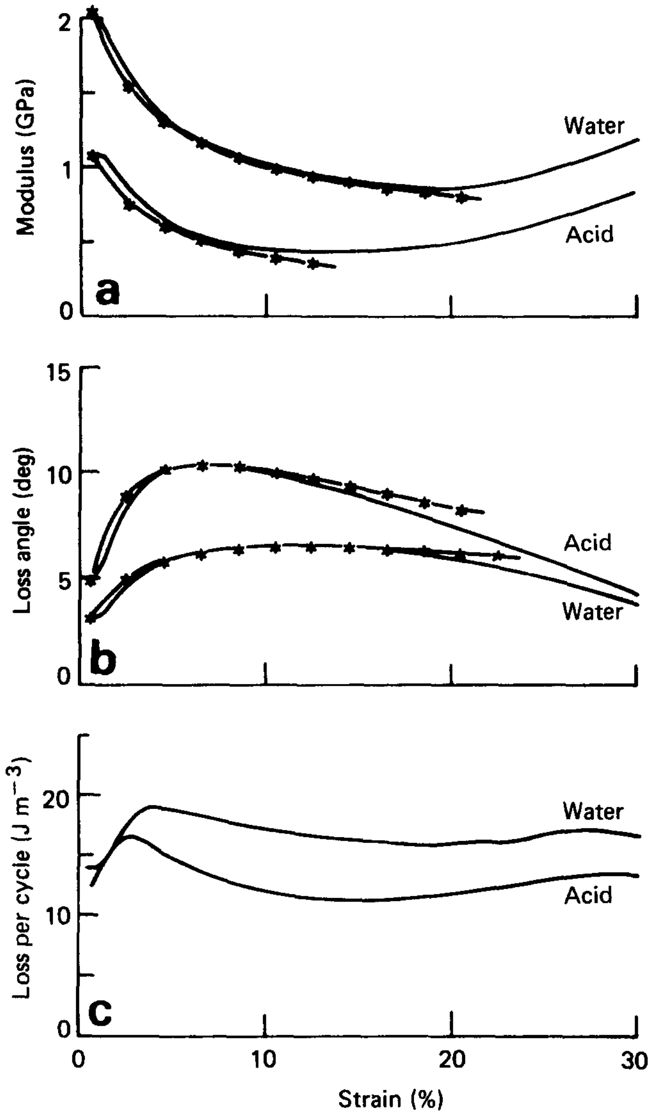

Figure 1 (a) Dynamic modulus, (b) loss angle, and (c) loss per cycle of vibration of a wool fibre immersed in water and in HCl at pH 1. ★, Fitted curve

all load–extension curves were made at a constant rate of extension.)

Figure 1b shows the loss angle for the fibre in both the water and the acid. The acid curve shows a much higher loss angle at low extensions, but at the onset of the post-yield region, the two curves tend to come together. *Figure 1c* shows the loss per cycle of mechanical vibration per unit volume[1] for the plasticizers. The water curve shows greater losses. The loss per cycle in water has a shallow maximum at about 5% strain. The maximum in HCl is sharper and occurs at a smaller strain.

DISCUSSION

A simple examination of the dynamic modulus curves in *Figure 1a* indicates that the HCl at pH 1 is reducing the stiffness of the wool fibre. The influence in the Hookean and yield regions is a little complicated; however, in the post-yield region the two modulus curves differ only by a constant and the loss angles approach each other. Since one of these effects is multiplicative and the other is additive, these two facts can only be reconciled within experimental error because the loss angles are small.

Wool is a complex structure and the extension mechanism in the Hookean and yield regions is the result of an interplay of many influences. To get a better understanding of the influence of HCl at pH 1 on wool, a model for extension[14] was fitted to the experimental curves. The results of this fitting are also shown in *Figure 1a* and *b*. The model itself is sketched in *Figure 3* for a partially extended fibre. The above comparison of a transformed section to a 'weak link in a chain' is extremely deceptive. All textbooks on viscoelasticity introduce spring and dashpot models, which can prejudice one's manner of thinking. For a chain of springs, the spring constant of the whole chain *is* limited to the spring constant of the weakest section. But a physical material such as wool must be discussed in terms of its physical properties. Hence one must discuss moduli, and how they combine. The modulus of a longitudinal structure is *not* limited to the modulus of its weakest section[14].

The extension process in wool is assumed to consist of two parallel structures extending together. One structure is crystalline, containing the alpha helices, which exhibit sufficient long-range order to give X-ray reflections; the other structure is the amorphous matrix, which is a much more open structure. It is a crosslinked polymer held together by disulphide covalent bonds, a network of polar bonds such as hydrogen bonds and salt links, as well as van der Waal interactions. It is readily plasticized by a number of materials. Each part of the model is represented by a characteristic value of modulus.

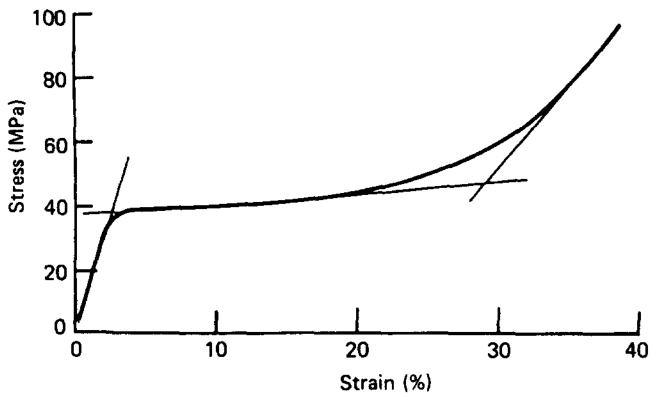

Figure 2 Stress–strain behaviour of a normal wool fibre in water. The intersections of the tangents define the Hookean, yield and post-yield regions

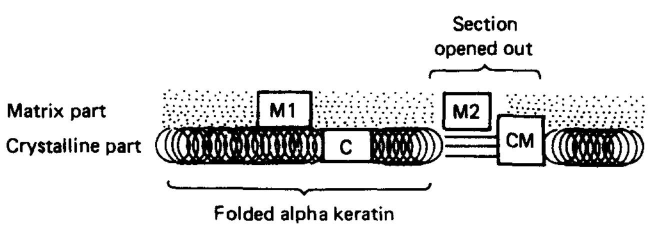

Figure 3 Diagram of the model for non-linear extension for a partially extended wool fibre. The values represented by the boxes are the crystalline modulus (C) of the alpha helices, the coupling modulus (CM) of the extended (beta) material coupled to the neighbouring material, the ordinary matrix modulus (M1) and the modulus of the thixotropically modified matrix (M2)

Table 1 Moduli measured by fitting the model to experimental data

	Water		HCl	
	Modulus (GPa)	Loss angle (deg)	Modulus (GPa)	Loss angle (deg)
C	1.40	0.0	0.8	0
CM	0.045	4.3	0.035	12
M1	0.66	9.8	0.3	18
M2	0.35	0.0	0.07	0
Fraction of alpha material transformed at 30% extension	0.27		0.43	

The model takes into account the stress transfer from the crystalline alpha helices (C) to the amorphous matrix (M1) when the alpha helices unfold to the beta conformation during extension. The unfolded section of the fibre is coupled to the neighbouring areas (represented by a coupling modulus (CM)). The transferred stress then is assumed to produce a thixotropic change (i.e. a change in which a bonded network goes from a 'gel' to a 'sol' situation) in the parallel matrix, which is then represented as a second matrix (M2). This model only explains the change in modulus in the yield region. The stiffening of the fibre in the post-yield region is due to other phenomena, which are beyond the present scope of the model. The moduli measured by fitting the model to experimental data are shown in *Table 1*.

The fitting procedure has been modified to allow the rate of the alpha to beta transformation to be included as a fitting parameter. This rate is assumed to be linear and is represented in the table by the fraction of alpha material unfolded at 30% extension of the fibre. The alpha to beta transformation is slightly faster in the HCl. This is readily seen by inspection since the minimum of the acid (modulus) curve occurs at a smaller value of strain than that of the water curve.

These results give a quantitative feel for the influence of the acid on the fibre. The value of the crystalline modulus (C), which is interpreted as being essentially the stiffness of the alpha helices, drops to about 58% of its value in water. The stiffness of the alpha helices, to a first approximation, does not depend upon water content[1].

This weakening of the alpha helices indicates that the pH 1 HCl solution is affecting the alpha helices and causing some weakening of the structure before extension begins, possibly by the penetration of H^+ ions, resulting in the rupture of salt links. The structure would appear to be too tightly bound to admit the larger H_2O molecules. The loss of the salt links in acid solutions and the general weakening of the alpha keratin in other plasticizers is understandable in terms of the recent exposure of the nature of the alpha helices and their interaction with each other. It has been shown[15] from X-ray diffraction studies that alcohol penetration of the crystalline part of the fibre, particularly the inter-helical spacing, was probably a result of hydrophobic bonds being involved in the interhelical interactions. Recent work[16] on the sequence of amino acid residues in alpha helices indicates the presence of heptad repeats of the form

$$(a–b–c–d–e–f–g)_n$$

along the polypeptide chain, in which the residues 'a' and 'd' are apolar groups capable of being involved in hydrophobic interactions and the 'g' and 'e' residues are charged as indicated in *Figure 4*. In the helical situation these sequences result in a combined stabilization of the interhelical forces by hydrophobic and coulombic interactions. Further, in the presence of water, when the hydrophobic interactions are effective, the stability of these interactions between alpha helices helps in the stabilization of the salt links by preventing water molecules from coming between the alpha helices and interacting with the charged groups. Such a lateral orientation of the salt links would do a great deal to bind the crystalline structure together, giving longitudinal strength only indirectly.

The loss of stiffness of the alpha helices is also reflected in the faster rate of unfolding of the alpha helices as well as in the greater loss angles measured in acid. The loss angle is a measure of the ratio of the loss modulus to the storage modulus, and the decrease of the crystalline stiffness increases the loss angle. The matrix, both stressed and unstressed, is further plasticized by HCl at pH 1 by swelling the structure and eliminating bonds not solved by water. The matrix moduli M1 and M2 in acid are 45% and 20% of the water values, respectively. The amorphous matrix is the lossy part of the fibre. Feughelman and Mitchell[5] have proposed the breaking and remaking of hydrogen bonds as the chief mechanism for mechanical loss in a fibre. When water enters the structure, it disturbs the existing hydrogen bonded network, but reforms one of its own. This would explain why the wetting of a dry fibre does not influence the losses as much[1] as the addition of HCl at pH 1. HCl breaks salt links, but does not exert as strong an influence on a hydrogen bonded network and only reduces the losses slightly. Although most of the loss occurs in the matrix, it is quite reasonable to expect some loss in the crystalline part of the fibre, as is suggested by the loss angle of the CM, at about 2% strain when the alpha helices begin to unfold. Many hydrogen bonds in the alpha helices are oriented axially, providing support for the successive turns of the alpha helices. When the fibre is strained, the hydrogen bonds would extend together and reach their breaking limit at about the same time. This can explain the fairly sharp maximum at 2% strain in the loss per cycle in acid. When the acid is not present, other bonds

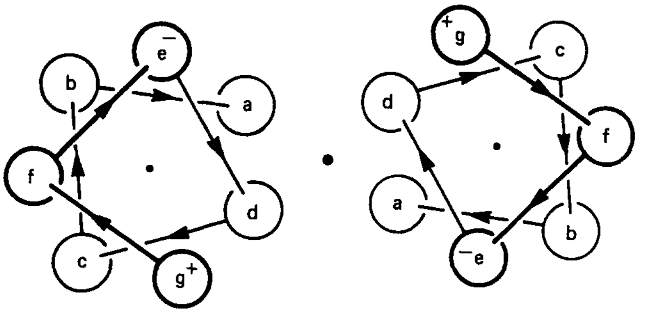

Figure 4 Diagrammatic representation of the relative position of the repeating heptad (a–b–c–d–e–f–g) of amino acid residues in two neighbouring alpha helices. Residues 'a' and 'd' are apolar and result in hydrophobic interaction between the helices along their area of contact. Residues 'e' and 'g' are charged groups which result in salt links (coulombic interaction) between the two alpha helices

which have no particular orientation may contribute to loss, and they would not line up and break simultaneously. This can explain the broader maximum at around 5% in the loss per cycle in water. It should be borne in mind that viscoelastic loss is not characterized by a single breaking of a bond. In oscillating experiments, bonds may break on the positive-going cycle and remake on the negative-going cycle. Bonds which are all aligned will make and break in unison, giving greater losses than bonds which are not so well aligned and do not make and break together.

The influence of the acid on the M2 modulus is also interesting for what can be gleaned about the thixotropic transformation. Both in water and in acid the M2 moduli are less than the M1 moduli, as would be expected for the thixotropic transformation. The loss angles for the M2 moduli are not particularly significant because the M2 are coupled to the CM, which have quite a substantial loss angle. But the M2 matrix in acid almost disappears, whereas the M1 is reduced to only 45% of its value in water. This seems to be a clear indication that the salt links play an important role in the thixotropic change.

CONCLUSION

Wool is a linear viscoelastic polymer up to about 1% strain. Beyond that strain, the extension process is a complex interaction between the crystalline part of the fibre, which contains the alpha helices, and the amorphous matrix, which is in parallel with the crystalline part. The influence of a physical treatment has been studied by means of the dynamic modulus, and the effects discussed in terms of the parallel structure of wool and a new model for the extension of wool.

Aqueous HCl at pH 1 has a strong influence on the dynamic modulus of wool. It weakens both the matrix and the alpha helices, but the mechanism for doing so is different for each case. In the alpha helices, the HCl affects salt links in a region already strengthened by hydrophobic interaction. These salt links bind the alpha helices together laterally and combine with hydrophobic interactions to stabilize the longitudinal structure.

HCl weakens the matrix by swelling it, eliminating salt links, which contribute directly to the stiffness, and interfering slightly with loss mechanisms. The salt links appear to play a significant role in the thixotropic transformation which occurs in the matrix.

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