Influence of processing conditions on the dynamic modulus of wool: 2. Set

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Heat setting of wool at 10% strain in boiling water produces specific damage to the different parts of the wool fibre. A new model has been used to fit the data and test the conclusions. Some of the alpha helical material unfolded to the beta conformation in the crystalline part of the fibre is stabilized into a lower energy configuration which is stiffer than the rest of the material. The dynamic modulus is seen to serve as a convenient measure of the amount of set acquired by a fibre. The matrix, once set, is restructured into a conformation less susceptible to mechanical loss.

(Keywords: dynamic modulus; keratin; alpha helices; set)

INTRODUCTION

Various thermal transitions have been observed in wool: from 60 to 70°C in water there is a second-order transition[1]; the alpha helical part melts in water between 120 and 130°C[2]; and dry wool decomposes above 250°C[3]. Elevated temperatures and mechanical straining are common in industrial processing of wool and can lead to set. A considerable amount of research has already been carried out on set in keratin[4-7] but new measurements on set wool obtained by observing the dynamic modulus are reported below.

EXPERIMENTAL PROCEDURE

Fibre preparation and the technique for measuring the dynamic modulus have been explained in a previous paper[8].

A series of measurements were carried out on 30 fibres set at 10% strain and 100°C (in boiling distilled water) for varying periods of time. After setting, each fibre was released and allowed to relax in the boiling water for a time at least as long as the setting time. The setting times used and the relaxation allowed are shown in *Table 1*.

Since fibre-to-fibre variation is often quite pronounced, some of the fibres were tested and re-set successively to obtain a standard for comparison. Load–extension curves were also measured to ascertain the amount of set and to compare the results with those of previous workers. Fibres set at 10% strain suffer only a negligible change in length or cross-sectional area, and the use of geometrical corrections was not necessary.

EXPERIMENTAL RESULTS

The results are shown in *Figure 1*. Load–extension curves are shown in *Figure 1a* for a normal fibre and for the same fibre set for 30 min. The effects of a 15 min set are similar to, but not as pronounced as, those of a 30 min set and in all cases the curves are the same as those obtained in more extensive studies[4]. The results for a fibre set for 1 min are erratic and are not shown. It would appear that 1 min is not long enough for a fibre subjected to the thermal shock of boiling to reform a stable and reproducible structure.

The load–extension curve of the normal fibre shows the three characteristic regions: Hookean, yield and post-yield. In the set fibre there is a clear loss of stiffness in the Hookean region, the end of the Hookean region is not as sharply defined, and the yield region, as such, does not exist. It is possible to define a fourth region in the load–extension curve, an eroded region. At the end of this eroded region is a continuation of what remains of the yield region followed by the post-yield region.

The dynamic modulus of the set fibre in *Figure 1b* shows a strong loss in the initial modulus and a small inflexion point in the middle of the yield region. For comparison, the moduli for a fibre set for 60 min have been included in the figures. This fibre shows a much smaller value of Hookean modulus and the inflexion point actually becomes a maximum, moving to higher values of strain.

The derivatives of the load–extension curves of *Figure 1a* have been calculated and plotted in *Figure 1b*. These slope (or slope modulus) curves accentuate the changes in the load–extension curve and are compared with the dynamic modulus curves. In theory, these slope curves should be similar to the dynamic modulus curves (for small loss angles), but due to non-linear effects they differ substantially except in the Hookean region[9]. None the less, they still reflect the same structural changes shown by the dynamic modulus curves.

The influence of setting on the loss angle, shown in

Table 1 Setting and relaxtion times used in the experiments

Setting time (min)	Relaxation time (min)
1	15
15	15
30	30
60	60

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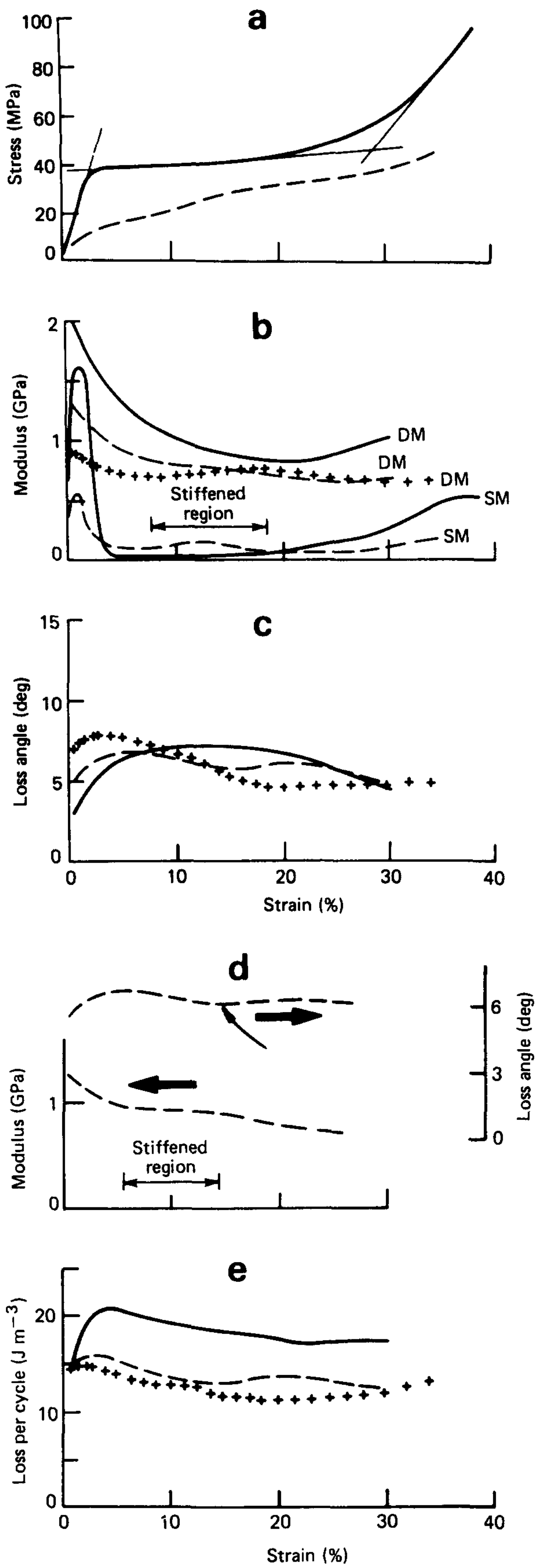

Figure 1 Experimental and fitted curves of normal and set wool fibres in water: (a) stress–strain behaviour; (b) dynamic modulus (DM), slope modulus (SM) and extent of visually defined stiffened region; (c) loss angle; (d) dynamic modulus and loss angle of model fitted to the 30 min set fibre; the stiffened region was selected to give the best fit; arrow on upper curve indicates a cusp which the model fits very well; (e) loss per cycle of vibration. ———, Normal; – – –, 30 min set; + + +, 60 min set

Figure 1c, is to give a larger and narrowing concentration of loss angle at the low values of extension. The fibre set for 30 min shows the process partly completed, with a local maximum at low extension, another maximum at higher extensions, and a sharp distinction between the two. The 60 min set fibre shows a sharper maximum at fairly low extension, which then falls away to a relatively flat or slightly inclined region at about 20% strain. *Figure 1e* shows the loss per cycle for set fibres. Normal fibres are more lossy than set ones.

The load–extension curves in *Figure 1a* show substantial changes in the late Hookean to mid-yield regions of the curves. Both the initial Hookean and post-yield regions show the same familiar shape, although the slope and extent of the regions is a little different. These results show that certain discrete parts of the fibre are damaged, whereas other parts, which are much less affected by setting, still show their original behaviour. In this case of a load–extension experiment, the curve shows large modifications when the damaged portion is being extended, but the remainder of the fibre acts quite normally. The Hookean region is gradually affected by the setting treatment, but even after 60 min boiling at 10% strain, a wool fibre still shows (results not shown) a small linear 'Hookean' region. The post-yield region is probably affected slightly by the setting treatment, but since the damaged material is a little weaker (judging from the smaller forces in the yield region) the fibre extends more easily, which postpones the start of the post-yield region. If the set curves of *Figure 1a* are transposed up and to the left, to compensate for the lower stress and longer extension of the yield region, the post-yield region appears to be much less affected by setting.

The dynamic modulus of the set fibre in *Figure 1b* appears to show a slight increase in stiffness in the region of 18–20% strain. The additional stiffness is also seen in the slope modulus. As the setting time increases, this stiffening becomes more and more pronounced. When a fibre is set, the unfolded material is stabilized in a new configuration and many crosslinks are formed. The data seem to indicate that there now exist sufficient additional molecular entanglements in the set fibre to make it a little more difficult to initiate the extension of the modified material. However, once this is overcome, (the rest of) the fibre acts normally and the stiffness falls away.

Details of the shape of the load–extension curve are accentuated in the slope modulus curves of *Figure 1b*. The difference in the Hookean region between the dynamic modulus and the slope modulus of the normal fibre can be attributed to the viscoelastic effects resulting from the difference in time scale of the two experiments[10]. The difference in the yield region has already been explained by the non-linear extension model in terms of a non-linear phenomenon associated with the unfolding of the alpha helical material and a coupling to the matrix[8,9]. In the case of the set fibre, this drop is smaller in magnitude, indicating that a set fibre has already lost some alpha material from the setting process. In fact, the magnitude of the dynamic modulus of the unextended fibre gives a ready quantitative measure of the extent of the set. The normal fibre has an initial modulus of 1 GPa. The 30 min set fibre has a modulus of 1.3 GPa and the 60 min set fibre has one of 0.932 GPa. Studies on birefringence, longitudinal swelling and X-ray diffraction have indicated that there is considerable disruption to the ordered crystalline part of the fibre during setting[11]. When bonds are broken in thermal setting, they reform in a new configuration. X-ray diffraction studies[1] have shown that upon release sufficiently set fibres show a reduction in the alpha reflection and the emergence of a beta reflection. At the same time, much more amorphous material appears to be introduced into the structure.

The model for the extension of wool discussed in a previous paper[8] was modified to allow for a stiffened region. In the extension region from 6 to 15%, the coupling modulus (CM) was increased by a factor of eight. The parameters obtained in the fitting (shown in *Figure 1d*) would not be considered as reliable as those from a normal fibre, since many of the assumptions of the model are no longer valid; however, the stiffening does provide an inflection point in the dynamic modulus curve, as shown in *Figure 1d*, and a sharp cusp in the loss angle (also *Figure 1d*), both of which may be seen in the experimental curves of *Figure 1b* and *c*. Many chemical bonds in the alpha helices have been disturbed during setting. On reformation, bonds in the alpha-material which had been opened out by extension reform in such a way that they stabilize the beta structure[12], and thus, when the fibre is released, it does not return completely to the alpha helix. Since some of the fibre is now stabilized in a slightly longer configuration (beta material), the onset of the post-yield region is delayed; it is shifted to higher strains with the result that the post-yield slope appears smaller at a given level of strain. The matrix is also affected. The reformation of bonds in the matrix forms a structure which is less susceptible to loss. Whether this is effected by forming stronger bonds, or by forming an aggregate consisting of domains of highly bonded material bonded loosely to other domains, is an open question; the latter would appear to be more likely.

CONCLUSION

Beyond 1% strain, the extension process in wool is a complex interaction between the crystalline part of the fibre and the amorphous matrix. The influence of setting changes the interaction of the two components. The dynamic modulus of set wool as a function of extension has been successfully described in the Hookean and yield regions by a new model.

The most obvious influence of heat setting is a loss in stiffness of the Hookean modulus. This is due to a disruption of the alpha helices. The initial disruption is followed by the formation of new bonds which appear to form into a region of slightly stiffer material than in a normal fibre and which still shows a stabilized form of beta material. The matrix is also constituted into a structure in which bonds are not as available to loss mechanisms.

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