

# STRESS RELAXATION OF WOOL FIBRES IN WATER AT STRAINS OF 5-20 PER CENT.

By B. J. RIGBY\*

[*Manuscript received July 5, 1954*]

## *Summary*

A study has been made of the stress relaxation at fixed longitudinal strains of wool fibres immersed in water, in the post-yield region of their load-strain curves. The fibres were extended at controlled rates up to predetermined strains, particular attention being paid to the first few minutes of the subsequent stress relaxation. It was found that the relaxation curves so obtained could be represented by a sum of one, two, or three negative exponentials, which could, in general, be simplified into two main processes, (a) a relatively fast relaxation of stress occurring in about the first 60 sec and (b) a much slower relaxation. The activation energy of the fast process was found to be approximately 5 kcal/mol. Attempts to calculate activation energies for the slow process showed that the term corresponding to the energy was temperature dependent. Over the range 10-50 °C, the values of this term were found to increase from about 22 to 27 kcal/mol. The fast and slow processes are respectively ascribed to the breakdown of weaker and stronger types of cross-linking bonds in the keratin.

## I. INTRODUCTION

When a keratin fibre is held at a fixed elongation under constant atmospheric conditions the stress decays, appearing to approach an asymptotic value.

According to the generally accepted picture of keratin, it is made up of polypeptide chains joined by a number of different cross-links. The cross-links in keratin include the strong cystine links, involving covalent disulphide bonds, and much weaker links involving hydrogen bonds, van der Waals forces, and electrostatic salt bonds. Speakman and Shah (1941) have attributed stress relaxation in keratin fibres to the breakdown of these cross-links under large strains.

Many conditions affect the rate and amount of stress relaxation, and a number of workers (Speakman 1928; Speakman and Shah 1941; Bull 1945; Katz and Tobolsky 1950) have examined the effect of some of these such as relative humidity, fibre extension, and temperature. Chemical pretreatment aimed at destroying disulphide bonds before relaxation has been carried out (Speakman 1928; Speakman and Shah 1941; Katz and Tobolsky 1950). Further, Katz and Tobolsky (1950) allowed the relaxation rate of an untreated fibre in water to become relatively slow before adding chemicals reagents to break these bonds.

The results of all these studies seem to indicate that the rate of relaxation is accelerated by any process which facilitates bond breakdown.

\* Wool Textile Research Laboratories, C.S.I.R.O., Physics and Engineering Unit, Ryde, N.S.W.

No general equation has been found to fit the experimental curves, although a number of stress-time relationships have been reported which describe parts of them. Little work seems to have been done on the first few minutes of the stress decay, during which time there is a relatively rapid relaxation.

It appears in all of the published work that very rapid strain rates have been employed. The aim seems to have been to extend the fibres as rapidly as possible so as to minimize the relaxation taking place during the straining operation. No stress-strain curves at these high rates seem to have been recorded. Thus, strains, as reported in previous work, cannot be correlated as yet with the well-known regions of the stress-strain diagram, viz. "Hookean", "post-yield", etc. It was thought that useful information could be obtained by examining the phenomenon of stress relaxation in terms of these well-defined regions.

The strains in this work correspond to the post-yield region of the curve, with approximate limits of 5 and 20 per cent. in water. These strains were produced by known strain rates, which then became another parameter, not considered in previous work. Further, the effects of the magnitude of strain and temperature have been investigated with particular reference to the first minute of the relaxation process.

## II. EXPERIMENTAL

In previous work various methods have been adopted to allow for the statistical distribution encountered in the measurement of fibre properties. Bull (1945), for example, used test specimens made up from about 20 fibres. Speakman and Shah (1941) and Katz and Tobolsky (1950) employed half-tension times and relative tensions in order to get a good degree of fibre to fibre reproducibility.

The procedure which has been used in this work is to obtain measurements on a single fibre subjected to various experimental conditions. This was done by immersing the fibre in water at 52 °C for 60 min, after which repetitive relaxation curves could be obtained. The experimental set-up consisted of a Cambridge extensometer as an agent for producing various strains and rates of strain and a Statham electrical resistance strain gauge, galvanometer, lamp, and scale for measuring load. The period of the galvanometer was approximately 2 sec; and it was found possible to read load correct to 0.04 g wt. in the early part of the relaxation, while for the slower portion the load readings were much more accurate. An examination shows that these limitations do not significantly affect the general results given in this paper. The strains were controlled by an automatic switch which could be preset at any desired value.

All the tests were carried out using wool from Corriedale sheep, hand fed for uniform growth. The coefficient of variation of the cross-sectional area along individual fibres was about 5 per cent., the average unstretched diameter, in water, being about 50  $\mu$ . A typical curve is illustrated in Figure 1 which shows the initial load-strain curve (obtained at 10 per cent./min) together with the subsequent relaxation of stress from a fixed strain of 20 per cent. The quantity, rate of straining, has been used in this work rather than "time of straining". The decrimped fibre length was standardized at 40 mm.

Most of the data are for a time range up to 200 sec (not including the time taken to extend the fibre), although some tests had time ranges up to 10 min. All the experiments were carried out with the fibre immersed in distilled water, the temperature of which was maintained constant to within  $\pm 0.1^\circ\text{C}$ .

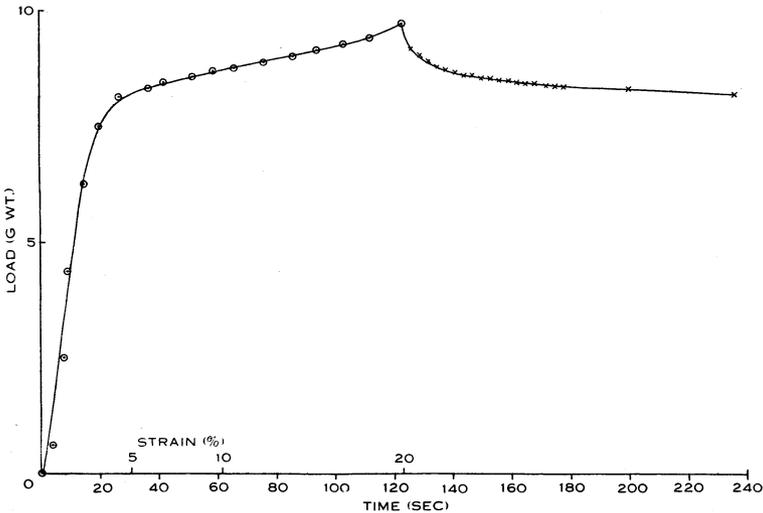


Fig. 1.—A typical curve, showing the initial load-strain curve (obtained at 10 per cent./min) together with the subsequent relaxation of stress from a fixed strain of 20 per cent.

### III. RESULTS

Typical experimental results showing the effect of variation in each of three parameters are given in Figures 2, 3, and 4.

Each of these sets represents the effect upon the relaxation curve of the *variation* of only *one parameter* on a particular fibre. At least five different fibres were examined with each parameter, similar results being obtained for each. The range for each of the variables was as follows :

- Strain, 5–20 per cent.
- Strain rate, 0.75–250 per cent./min
- Temperature, 5–50 °C

Analysis of the relaxation curves obtained, over the time range 0–200 sec, showed that the curves could be represented by a sum of one, two, or three exponential terms, the number depending upon the particular experimental conditions, that is

$$S_t = \sum_i S_i \exp(-g_i t) + S_\infty, \dots\dots\dots (1)$$

where  $S_t$  = stress at time  $t$ ,  $S_\infty$  = asymptotic stress,  $S_i, g_i$  are functions of the parameters,  $i=1, 2, \text{ or } 3$ .

It should be pointed out that it is not known, in analysing into exponentials, whether the expansion is unique, and also that over limited ranges one mathematical expression often closely approximates another. For example, in the

present instance each relaxation curve could be closely fitted by a rectangular hyperbolic law for about the first 60 sec. For these reasons it was not considered advisable to determine each  $S_i$  and  $g_i$  for a given curve. A significant feature

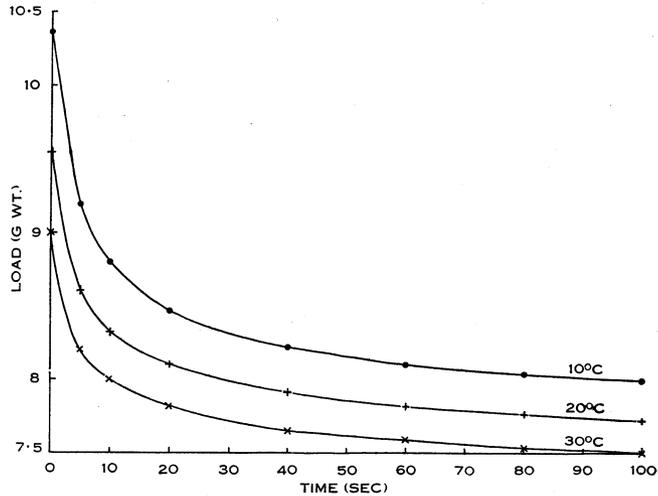


Fig. 2.—A typical set, showing the effect of the variation of temperature on the stress relaxation of a fibre which has been strained at a rate of 55 per cent./min to an extension of 20 per cent.

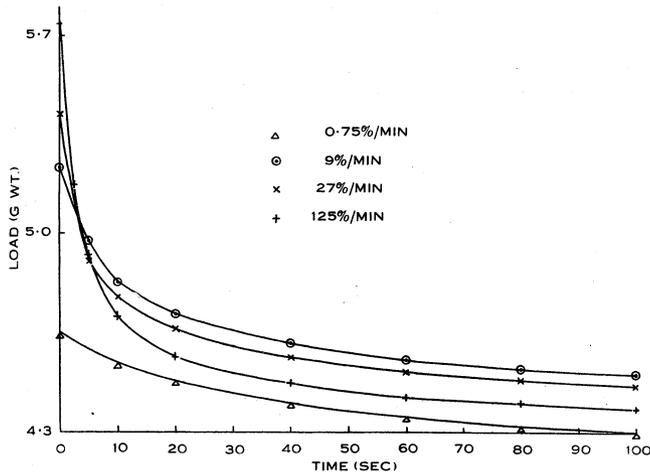


Fig. 3.—A typical set, showing the effect of the variation of strain rate upon stress relaxation. The temperature and total strain were maintained at 20 °C and 12.5 per cent. respectively.

of the present results, which will be discussed fully later, was that it was found possible to separate each curve into a *rapid* process of decay lasting about 40–60 sec followed by a considerably slower one (see Figs. 2, 3, and 4).

The effect of each parameter (the other two being kept constant) on the properties of the relaxation curve was as follows.

(a) *Relaxation as a Function of Initial Strain*

Examination of Figure 4, a typical set of curves, shows that :

- (i) Increasing the initial strain brought about a proportional increase in the initial stress.
- (ii) The relaxation curves were identical in shape, i.e. for any given period of time the stress decayed by the same amount.

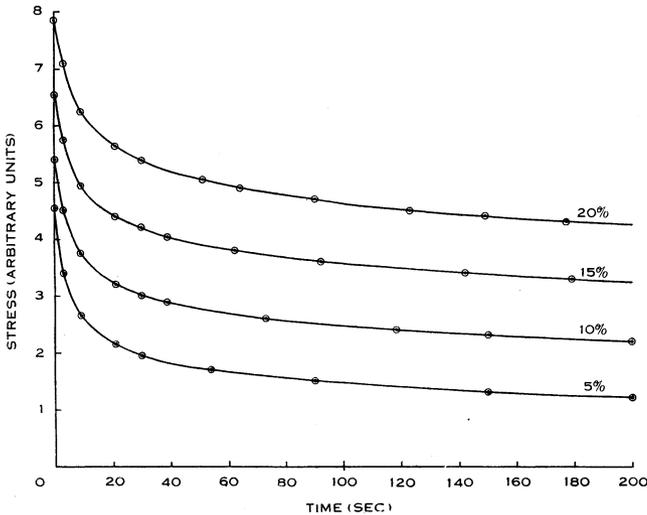


Fig. 4.—A set of curves showing the effect of the variation of total strain on the subsequent stress relaxation. The strain rate was 10 per cent./min and the temperature 19 °C.

(b) *Relaxation as a Function of Strain Rate*

(i) Referring to Figures 3 and 4, both the initial stress  $S_0$  and  $S_0 - S_t$  were found to vary linearly with  $\ln \rho$  where  $\rho$  is the rate of straining up to the fixed strain (see Fig. 5).

$$S_0 = a \ln \rho + C_1, \quad \dots \dots \dots (2)$$

$$S_0 - S_t = a \ln \rho + C_2. \quad \dots \dots \dots (3)$$

(ii) The slope  $a$  of the lines (2) and (3) has a value in agreement with that predicted by a recent theory of viscoelasticity by Burte and Halsey (1947).

(iii) Analysis of one set of curves (Fig. 3) into exponentials, showed that the curve produced by the slowest rate of straining (0.75 per cent./min) reduced to a single exponential term. The curves due to the higher rates appeared to have this basic component plus others.

(c) *Relaxation as a Function of Temperature (see Fig. 2)*

(i) The initial stress  $S_0$  was found to decrease almost uniformly with an increase in temperature.

(ii) As mentioned earlier, the relaxation curves can be separated into an initial rapid process, followed by a much slower one. Activation energies were calculated for each of these processes in the following manner (Glasstone, Laidler, and Eyring 1941).

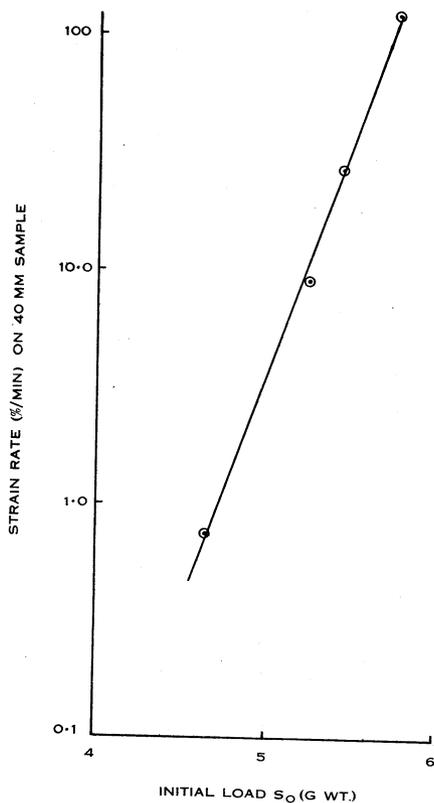


Fig. 5.

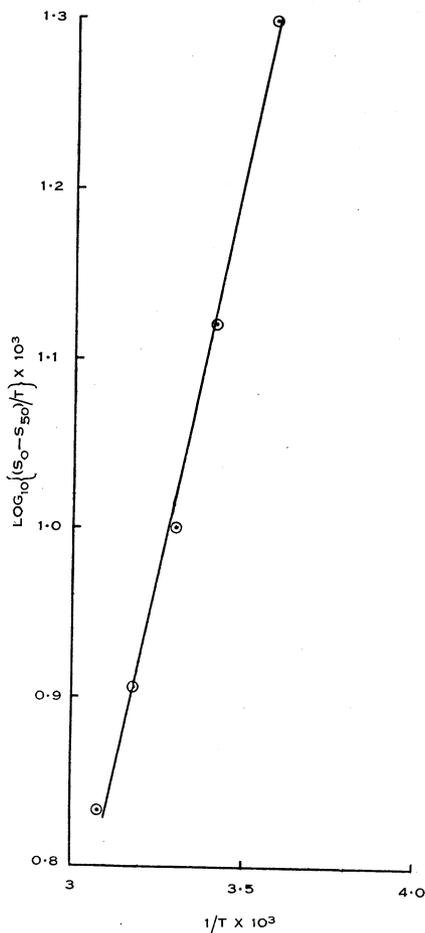


Fig. 6.

Fig. 5.—A plot of the initial stress  $S_0$ , against the logarithm of the strain rate, with the temperature and total strain held at 20 °C and 12.5 per cent. respectively.

Fig. 6.—A plot of  $\log_{10}\{(S_0 - S_{50})/T\}$  against  $1/T$ . The slope of this line is a measure of the activation energy of the fast relaxation process (see text).

*The fast process.*—It was assumed that the amount of stress decay in a given time was proportional to the specific rate constant ( $k'$ ) for the process ;

$$k' = \frac{kT}{h} \exp(-E_1/RT),$$

that is,

$$S_0 - S_t \propto T \exp(-E_1/RT),$$

where  $S_0$  and  $S_t$  are defined above,  $T$  is the absolute temperature,  $k$  is Boltzmann's constant,  $h$  is Planck's constant,  $E_1$  is the activation energy for the process,  $R$  is the universal gas constant.

Thus a plot of  $\ln \{(S_0 - S_t)/T\}$  against  $1/T$  should give a straight line, with a slope equal to  $E_1/R$ . Five fibres were studied in the temperature range 5–50 °C and straight lines were in fact obtained. A typical plot is shown in Figure 6. These straight lines were plotted for values of time up to 50 sec since the fast process is practically completed by this time. The value of  $E_1$  calculated from these lines varied from 4 to 7 kcal/mol, the average value being 5 kcal/mol.

*The slow process.*—The stress decay over a long period of time is predominantly due to the slower process, and in this case the time  $t'$  taken for the stress to fall to a given value should be inversely proportional to the rate constant ( $k'$ ).

Thus  $t'T \propto \exp(-E_2/RT)$  where  $E_2$  is the activation energy for the process.

A plot of  $\ln(t'T)$  against  $1/T$  should give a straight line with a slope equal to  $E_2/R$ . Seven fibres were studied over the range 10–50 °C, but the value of  $E_2$  was found to be temperature dependent, varying from 22 to 27 kcal/mol.

#### IV. DISCUSSION OF RESULTS AND CONCLUSIONS

Most of the results can be interpreted using a simple extension of a suggestion made by Speakman and Shah (1941). They suggested that the breaking of cross-linking bonds in keratin followed by molecular rearrangement is responsible for stress relaxation. An equation of the form (1) could, for instance, be reasoned in the following manner. Suppose that after a longitudinal strain has been produced on a fibre there will be a certain number of cross-links in a strained state. Some may have broken, and re-formed during the straining period—this number will depend upon the rate of straining, but whatever has happened during the extension it should only affect the amounts of stress decay and the initial stress in the stress relaxation test. This very simple picture explains the form of the relaxation curves by only requiring that at the completion of any fibre extension there are a number of strained cross-links. It seems reasonable to assume that the total stress energy which can relax will be proportional to the number of these strained bonds. These bonds will immediately begin to revert to their stable energy state and this energy decrease will be manifested by a stress relaxation. Now, if these bonds revert with a rate which is proportional to the total number  $n$  strained at any time, thus

$$\frac{dn}{dt} = -gn,$$

then, in view of the statement that the number  $n$  is proportional to the stress which can relax, we get upon integration,

$$S_t = \text{const.} \times \exp(-gt).$$

If there are a number of distinct cross-links, each having its own value of  $g$ , then

$$S_t = \sum_i S_i \exp(-g_i t).$$

In the equation given earlier, viz.

$$S_t = \sum_i S_i \exp(-g_i t) + S_\infty,$$

$S_\infty$  would represent the stress energy contained in the main chains.

This exponential equation explains why the relaxation curves with strain as the only parameter are identical in shape but displaced along the stress axis. Bull (1945) shows this effect quite clearly graphically.

When the rate or time of straining is varied this simple theory would require that the amount of relaxable stress should increase with the strain rate  $\rho$ . This is verified by the data summarized in equations (2) and (3), but it would be difficult to derive equation (2) from the theory discussed above, because the stress  $S_0$  is determined by other factors as well as the relaxation which occurs during straining.

Figure 3 is interesting for in this particular fibre it appears as though the slow process has been isolated. The bottom curve in this set can be represented by a single exponential term and, since it was obtained after a very slow rate of straining, it seems probable that the weak bond breakdown (which would give other exponential terms) has been in equilibrium with the molecular adjustments due to straining at all times. Further it will be noticed that the curve representing this slow process is parallel to the other three curves, after about 25 sec; indeed, analysis shows it to be a component of each of the four curves.

Because of the dependence upon temperature of  $E_2$  there is strictly no justification in calling it an activation energy. However, the large difference between  $E_1$  and  $E_2$  supports the contention that the fast and slow processes are due to weaker and stronger bonds respectively. It may be noted that the value of 5 kcal/mol for  $E_1$  could be ascribed to hydrogen bonds.

#### V. ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of Mr. T. W. Mitchell in these experiments.

#### VI. REFERENCES

- BULL, H. B. (1945).—*J. Amer. Chem. Soc.* **67**: 533.  
 BURTE, H., and HALSEY, G. (1947).—*Text. Res. J.* **17**: 465.  
 GLASSTONE, S., LAIDLER, K. G., and EYRING, H. (1941).—“*Theory of Rate Processes.*” 1st Ed. (McGraw-Hill: New York.)  
 KATZ, J. M., and TOBOLSKY, A. V. (1950).—*Text. Res. J.* **20**: 87.  
 SPEAKMAN, J. B. (1928).—*Proc. Roy. Soc. B* **103**: 377.  
 SPEAKMAN, J. B., and SHAH, S. Y. (1941).—*J. Soc. Dy. Col.* **57**: 108.