

Stress Relaxation Studies on Wool Fibers

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SYNOPSIS

Stress relaxation studies were made on single fibers of Lincoln, Chokla, and Merino wool in water in the temperature range 2–80°C. Differences in the viscoelasticity of the three wool types were related to differences in their fine structure and morphology. Of the three wools, Merino fibers have the lowest crystalline content and the poorest fibril orientation and packing. This results in greater viscoelastic effects in this wool. Stress relaxation studies have been made in the Hookean, yield, and postyield regions, and the molecular mechanisms of stress relaxation have been discussed.

INTRODUCTION

Starting with the work reported by Speakman in 1928,¹ a number of authors have made important contributions to the understanding of the stress relaxation of wool fibers.^{2–16} This relaxation is attributed to the breaking of various physical and chemical crosslinks on extension and their reformation with the passage of time. Based on the time scale over which they are effective, these bonds are categorized into three main groups:⁸

1. Weak bonds having relaxation times below 0.1 min including hydrogen bonds, salt linkages, and van der Waals and electrostatic forces.
2. Bonds of intermediate strength having relaxation times between 0.1 and 10 min, due to disengagement of bonds between matrix and filament components.
3. Strong bonds having relaxation times above 10 min, consisting of covalent crosslinkages, mainly disulfide bonds.

These three categories of relaxation mechanisms are referred to as low, intermediate, and long time relaxation processes. The intensity and rate of relaxation depends on test conditions such as temperature, humidity, and strain history.

From another viewpoint, it is useful to summarize the prominent molecular processes responsible for relaxation in the three characteristic regions. These are:¹⁷

1. Hookean region: intrahelical bonds and side chain interactions between the helical structure and matrix molecules, mainly disulfide bonds.
2. Yield region: tearing apart of the side chain bonds between matrix molecules and helices with simultaneous alignment of matrix chains.
3. Postyield region: stretching or opening of covalent crosslinkages in globular matrix proteins.

Modification of the fibers leading to an alteration in these bonds by physical and chemical means, has been used to advantage to explain the molecular mechanism *vis-à-vis* mechanical behavior. For example, aging is related to differences in thiol content,¹⁶ second stage recovery to association of water⁷ and settability to disulfide interaction.^{6,11,18} The purposes of the present study are (i) to characterize the stress relaxation behavior of Lincoln, Chokla, and Merino wool fibers, and (ii) to attempt to correlate the stress relaxation characteristics of these three wools to their respective structures. It was hoped that as a result of these studies, some insight will be gained into the structural origin of stress relaxation.

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EXPERIMENTAL

Samples

The stress relaxation studies were conducted on single wool fibers from three different breeds of sheep, viz. Merino (64^s quality, Australian breed), Chokla (44^s quality, Indian breed) and Lincoln (40^s quality, U.K. breed). The procedure used for selection of single fibers for dimensional and structural uniformity has been described elsewhere.¹⁹

Measurements

All the stress relaxation studies were made on an Instron tensile tester. Single fibers of 5 cm gauge

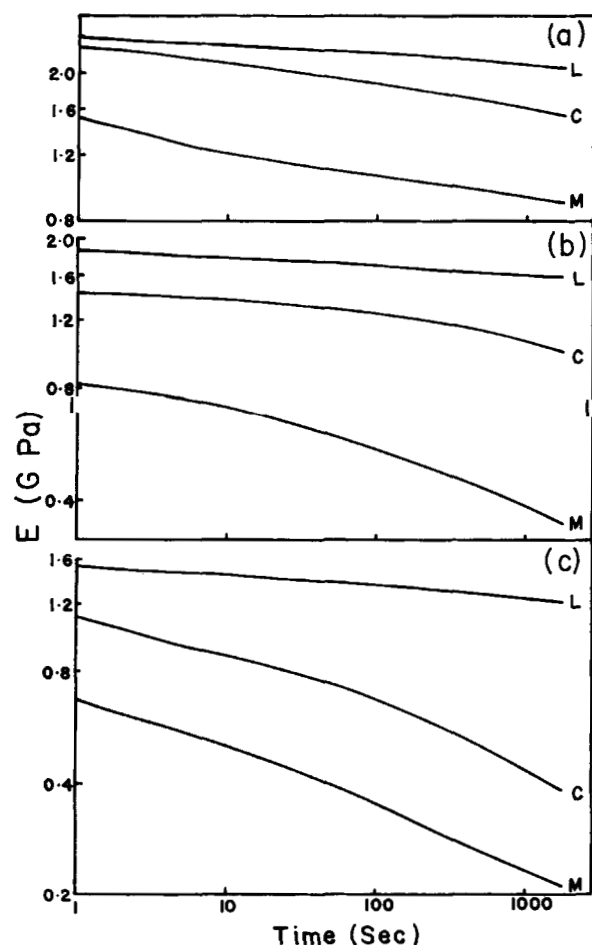


Figure 1 Double logarithmic plot of stress relaxation modulus versus time for relaxation test in water for various temperatures in the Hookean region. Curves: (a) at 2°C; (b) at 50°C; (c) at 70°C. Wool type: L = Lincoln, C = Chokla, and M = Merino.

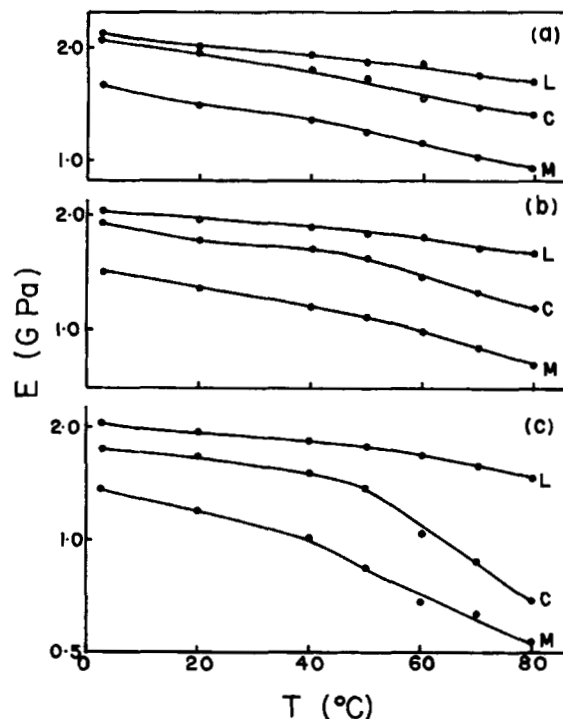


Figure 2 Variation of stress relaxation modulus (logarithmic) with temperature for prestrain in Hookean region at different relaxation times. Time: (a) 6 sec; (b) 600 sec; (c) 1800 sec.

length were used. The samples were maintained at a constant temperature in a standard thermostated cylindrical water bath between 2 and 80°C in water in most cases, and between 2 and 50°C in water in a few cases.

The prestrain levels used corresponded to the Hookean, the yield, and the postyield regions, and were 1%, 20%, and 40% respectively.

The strain rate used for extending the fiber to the above prestrain levels was 25% per min. However, since in the Hookean region, short-time relaxation processes are likely to be operative, a high strain rate of 250% per min was also used for studies at 1% of the prestrain level. The zero time was taken as the time of completion of the application of the prestrain.

RESULTS AND DISCUSSION

Stress Relaxation Data at Low Strain Rate

Hookean Region

The stress relaxation characteristics of the three wool fibers prestrained to the 1% level, at a strain

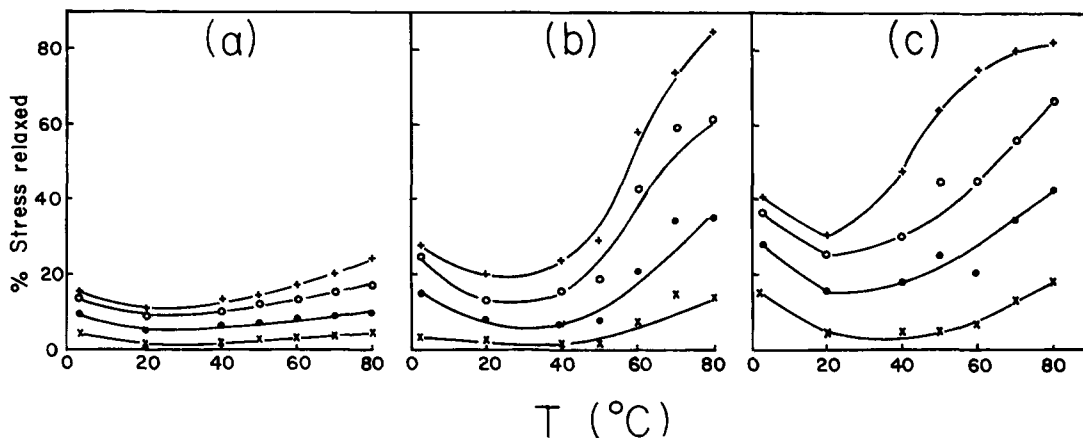


Figure 3 Variation of percent stress relaxation with temperature at different relaxation times for prestrain in Hookean region. Time: × = 2 sec, ● = 60 sec, ○ = 600 sec and + = 1800 sec. Wool type: (a) Lincoln; (b) Chokla; (c) Merino.

rate of 25% per min, in water maintained at different temperatures, are shown in Figure 1 as plots of log stress relaxation modulus versus log time. The same data for the three wools (Fig. 1) are plotted as log stress relaxation modulus versus temperature for different time periods in Figure 2. The percentages of stress relaxation within the experimental time scale, i.e. 1800 sec, for the three wools at various temperatures of measurement are shown in Figure 3 and in Table I. The broad features of these data are as follows:

1. The transitions are more intense in Merino and Chokla fibers and relatively weaker in Lincoln fibers.
2. The data suggest the likelihood of two transitions. First, the tail of the low temperature transition, which apparently occurs below 2°C in water (Fig. 3) is the glass transition. Detailed discussion of this effect will be made

Table I Stress Relaxation in Hookean Region*

Wool Type	Stress Relaxation (%)			
	2°C	20°C	50°C	70°C
Lincoln	15	10	14	20
Chokla	28	20	29	73
Merino	41	30	65	80

* Relaxation time of 1800 sec.

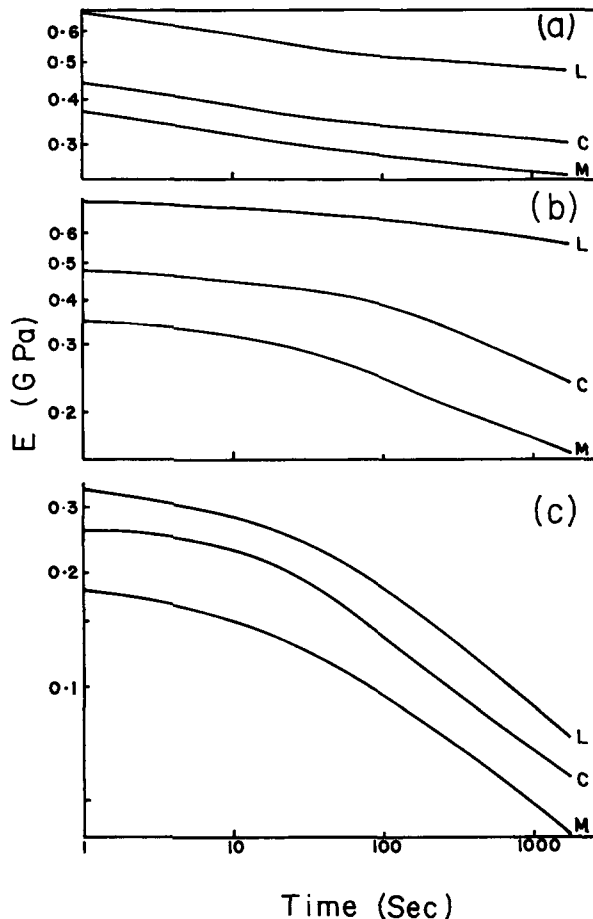


Figure 4 Double logarithmic plot of relaxation modulus versus time for relaxation test in yield region, in water at various temperatures. Curves: (a) at 2°C; (b) at 50°C; (c) at 70°C.

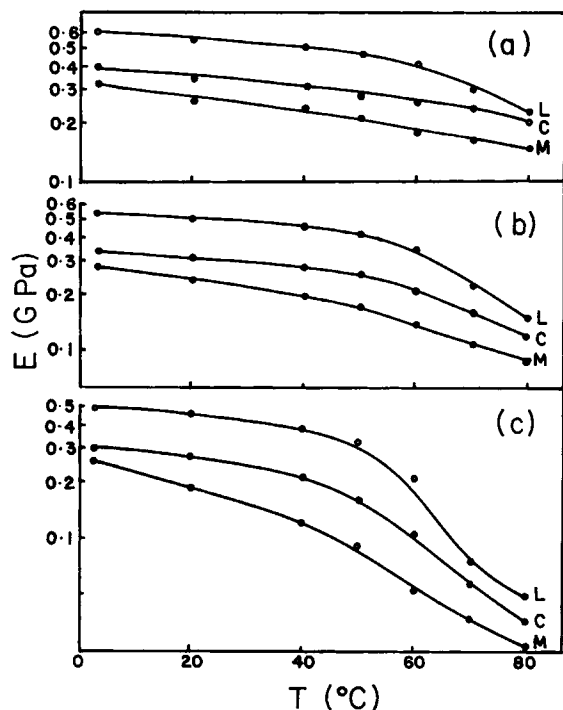


Figure 5 Variation of stress relaxation modulus (logarithmic) with temperature for prestrain in yield region at different relaxation times. Time: (a) 6 sec; (b) 600 sec; (c) 1800 sec.

later. The second transition, which occurs in the region of 50–70°C, is associated with the characteristic disulfide interaction and is characterized as a second order transition in wool.⁶

It was shown elsewhere²⁰ that among the three wools studied the glass transition in Merino occurs at about 5 to 10°C higher than in the other two wools. At room temperature, in the wet state, Merino wool is thus closer to its T_g than the other two wools and consequently more viscoelastic. It is generally believed that up to approximately 2% strain, the deformation of α -helices follows the measured deformation of fiber. The stress generated in the fibers at 1% strain will therefore reside mostly in the α -helices and the intrahelical bonds; the fibril-matrix bonds will be expected to be under considerable strain. The stress will be transferred from the α -helix to the surrounding matrix with the passage of time. Another factor that should be taken in to consideration is the low Hookean modulus of Merino fiber. In addition, it has been shown elsewhere that Merino fibers have low crystalline content, poor crystallite orientation²¹ and birefringence,²² and poor thermal stability.²³ These factors will also contribute to its higher viscoelasticity. These arguments will also apply to the data up to 80°C.

Yield Region

The corresponding stress relaxation data for fibers extended by 20% are presented in Figures 4 to 6, and the data on percentage stress relaxed at different temperatures for the three wool fibers are summarized in Table II. Degree of stress relaxation in the yield region is high, increasing with temperature, and is in the same range for all three fibers; in contrast, for the Hookean region the degree of stress relaxation is lower for Lincoln wool over the whole

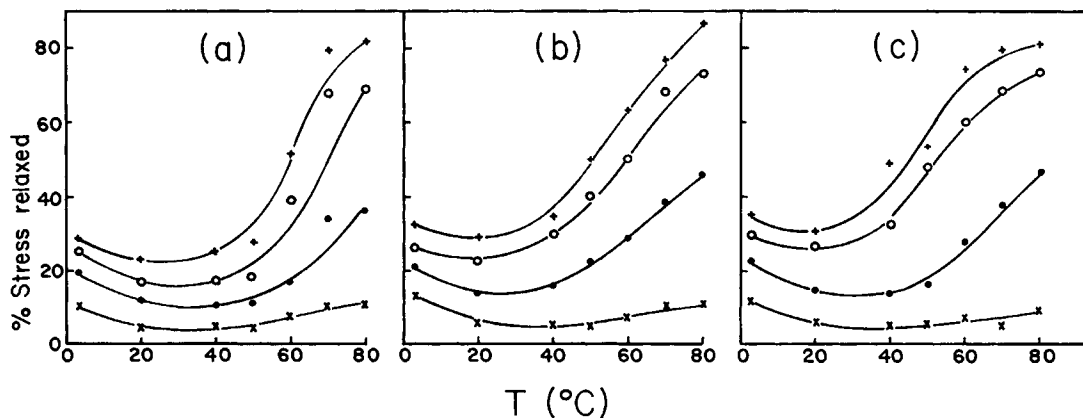


Figure 6 Variation of percent stress relaxation with temperature at different relaxation times for prestrain in yield region. Time: \times = 2 sec; \bullet = 60 sec; \circ = 600 sec; $+$ = 1800 sec. Wool type: (a) Lincoln; (b) Chokla; (c) Merino.

Table II Stress Relaxation in Yield Region^a

Wool Type	Stress Relaxation (%)			
	2°C	20°C	50°C	70°C
Lincoln	28	23	27	80
Chokla	33	29	50	76
Merino	35	31	54	79

^a Relaxation time of 1800 sec.

temperature range. The effect of glass transition can be seen from stress relaxation curves at low temperatures, but the effect is much smaller than in the Hookean case.

To explain these results, it may be recalled that up to 50°C, at this high strain level, hydrogen bonds

and salt linkages can break and re-form and thus provide a mechanism for regrouping of structural units. The relatively higher rate of decrease of modulus with temperature in Merino fibers reflects its high viscoelasticity. Above 50°C, the breakage and re-formation of the chemical crosslinks can likewise provide a mechanism for stress relaxation. In addition, the absolute value of the stress developed in the fiber at 20% strain will also play a role. For temperatures above the second order transition temperature the mobility of molecular segments in the matrix increases. The deformation is consequently relatively larger as the matrix approaches the rubberlike state and the percentage of stress relaxation decreases. It would appear that the results at 80°C can be explained principally in terms of the relatively higher stress generated in Lincoln fiber; the bond breakage and re-formation would perhaps not play an equally important role.

It may also be noted (Fig. 5) that the rate of change of modulus with temperature varies with time and temperature and also with the wool type. At short times, the second order transition appears at high temperature in all cases. For Lincoln wool, this transition occurs around 10°C higher than for the other two wools.

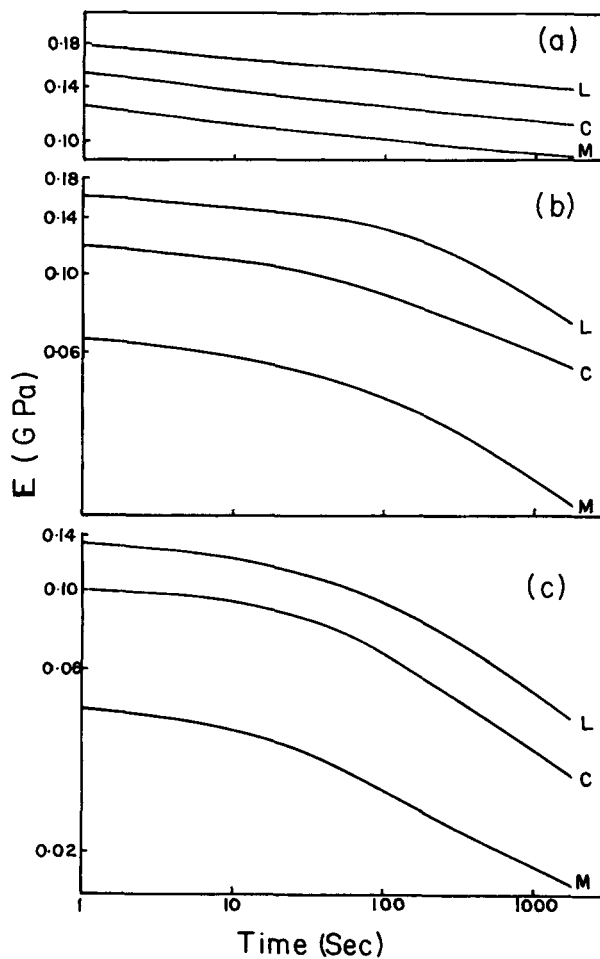


Figure 7 Double logarithmic plot of relaxation modulus versus time for relaxation test in postyield region, in water. Curves: (a) at 2°C; (b) at 50°C curves; (c) at 70°C curves.

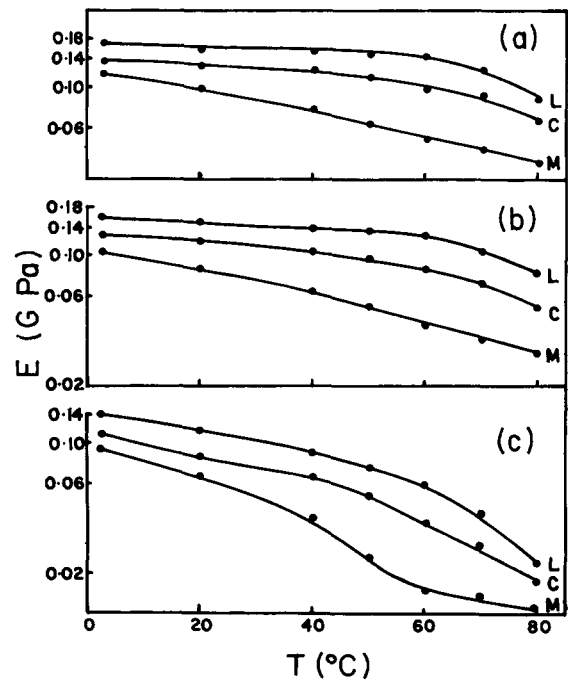


Figure 8 Variation of stress relaxation modulus (logarithmic) with temperature at different relaxation times for prestrain in postyield region. Time: (a) 6 sec; (b) 600 sec; (c) 1800 sec.

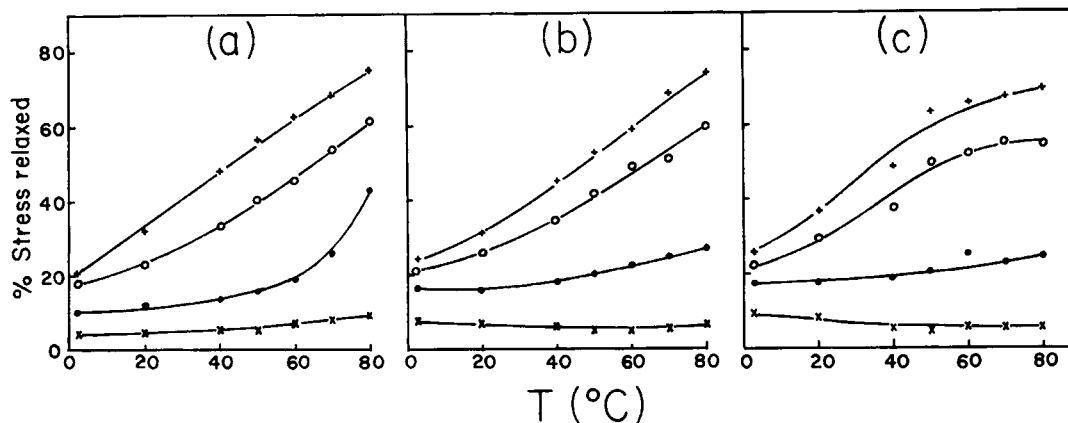


Figure 9 Variation of percent stress relaxation with temperature at different relaxation times for prestrain in postyield region. Time: \times = 2 sec; \bullet = 60 sec; \circ = 600 sec; $+$ = 1800 sec. Wool type: (a) Lincoln; (b) Chokla; (c) Merino.

Since stress relaxation through covalent bond breakage would not be expected to be different to any significant degree in the three wools, the percentage of stress relaxation at high temperatures is almost the same in the three wools.

Postyield Region

The stress relaxation data are shown in Figures 7 to 9 and the data on percentage stress relaxation at different temperatures are summarized in Table III.

The data are broadly similar to the data in the yield region, though when they are examined in detail, there are some differences. For example, the effect of the glass transition is not seen, and the stress relaxation is mainly due to the second order transition. Further, the second order transitions now occur at slightly lower temperatures in all cases (Fig. 7). This difference is particularly marked for Chokla and Merino wools, as shown in Table III.

Shift of Relaxation Curves

Relaxation curves obtained at different strains shift to low times with an increase in strain. A similar

Table III Stress Relaxation in Postyield Region^a

Wool Type	Stress Relaxation (%)			
	2°C	20°C	50°C	70°C
Lincoln	20	28	51	73
Chokla	24	31	53	69
Merino	26	37	60	67

^a Relaxation time of 1800 sec.

observation was reported by Chapman¹⁵ and Weighman et al.⁹ The relatively large deformation at high strain releases more —SH groups during the straining step, and decay due to thiol-disulfide interchange interaction shifts to shorter times. Among the three wools the shift is more pronounced in Merino than in the other two wools.

Activation Energy

The activation energy, E_a , in the yield and postyield region was calculated using the approach suggested by Rigby⁴ according to which for a long time stress relaxation curve at a particular temperature, T , the activation energy is given by

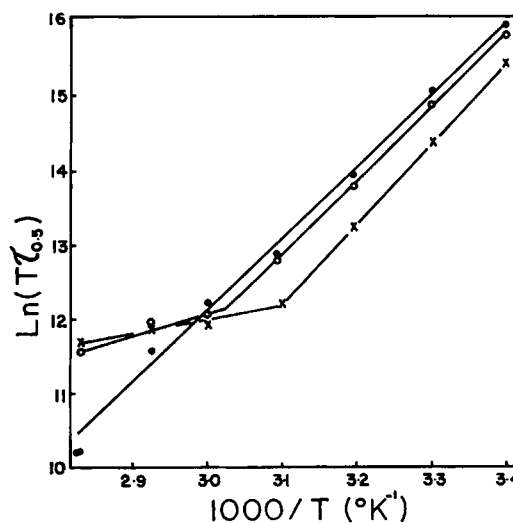


Figure 10 Plot between $\ln(T t_{0.5})$ against inverse of absolute temperature for data in postyield region. Wool types: \bullet Lincoln; \circ Chokla; \times Merino.

Table IV Activation Energy for Long-Time Relaxation in Postyield Region

Wool Type	E_a (K cal/mol)	
	2-50°C	50-80°C
Lincoln	22	22
Chokla	26	8
Merino	23	6

$$T \cdot \tau_{0.5} = A \exp(-E_a/RT) \quad (1)$$

where, $\tau_{0.5}$ is the arbitrarily selected relaxation time during which the stress decreases to half its maximum value, A is a constant, and R the universal gas constant.

The yield region data lead to activation energies in the range between 18 and 22 Kcal/mol which is typical of covalent bond cleavage. In the postyield region the activation energy showed temperature dependence. The plots for Equation 1 for the postyield region are shown in Figure 10 and the values of E_a are shown in Table IV. At high temperatures, both Merino and Chokla wool show the low activation energy typical of rubberlike relaxation, while at low temperatures they show activation energy representative of covalent bond cleavage in wool. This difference is not shown by Lincoln wool which does not appear to develop a typical rubbery state below 80°C (Fig. 9).

The above results indicate that the onset of the characteristic disulfide interaction depends on three factors, namely temperature, strain level, and relax-

ation time. Certain treatments which affect the concentration of these bonds alter the transition temperature but do not affect the character of stress relaxation; stability is thus directly related to the presence of these bonds. In the experimental time scale of about 1800 sec, this interaction becomes the controlling mechanism at very short times and low temperatures in the postyield region and at longer times and lower temperatures or shorter times and higher temperatures in the yield region. In the Hookean region this reaction is intense in Merino and Chokla fibers and is practically absent in Lincoln fibers. Since the thermal stability of wool is associated with this interaction, among the three wools studied, Lincoln fibers show higher stability than Chokla with Merino fibers showing the lowest stability.

Stress Relaxation Data in the Hookean Region at High Strain Rate

In the Hookean region, the relaxation characteristics are largely affected by breakage and re-formation of weak bonds having low relaxation times. At a strain rate of 25% per min, the time taken for 1% strain would be over 2 sec. Thus in this case considerable stress relaxation could have occurred during the application of the extension itself. By using a strain rate of 250% per min, this time was reduced by a factor of 10; the extension of the sample was now complete in 0.25 sec.

The stress relaxation curves for the three wools are shown in Figure 11. The basic features of the data are similar to the earlier data at low strain rate, though the curves now extend to shorter time pe-

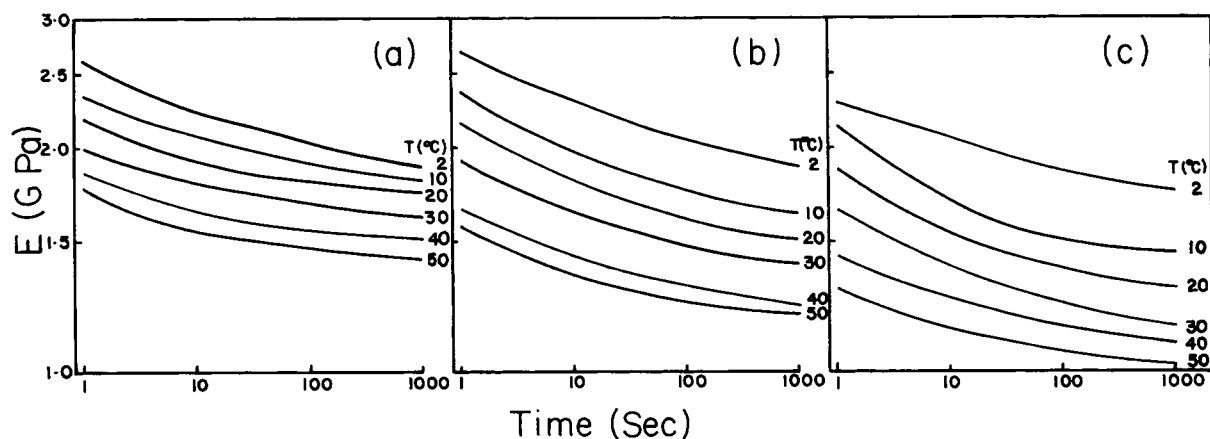


Figure 11 Double logarithmic plot of stress relaxation modulus versus time in water for various temperatures (indicated) in the Hookean region, when prestrain is applied at 250% per min. Wool type: (a) Lincoln; (b) Chokla; (c) Merino.

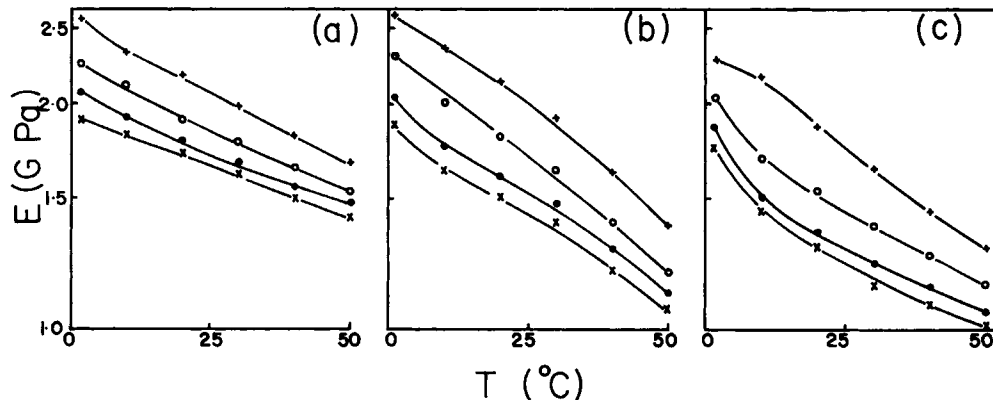


Figure 12 Variation of stress relaxation modulus with temperature at different relaxation times for strain in the Hookean region. Prestrain is applied at an extension rate of 250% per min. Time: × = 1 sec; ○ = 10 sec; ● = 100 sec; + = 1000 sec. Wool type: (a) Lincoln; (b) Chokla; (c) Merino.

riods. The data are plotted in the form of stress relaxation modulus versus temperature in Figure 12 and again the similarity with the earlier data is obvious.

The master stress relaxation modulus curves were constructed by simple horizontal shift, taking 2°C as the reference temperature. The shift factor data are shown in Figure 13. These data are similar to the shift factors reported for stress relaxation data in the linear viscoelastic region for wool by Wortmann and de Jong.^{24,25} The shift of the relaxation curves is known to be linearly dependent on the water content.²⁴ In the present experiments all the tests were carried out in water and hence the observed shift factors correspond to a temperature change of about 50°C above T_g . This gives rise to a shift rate

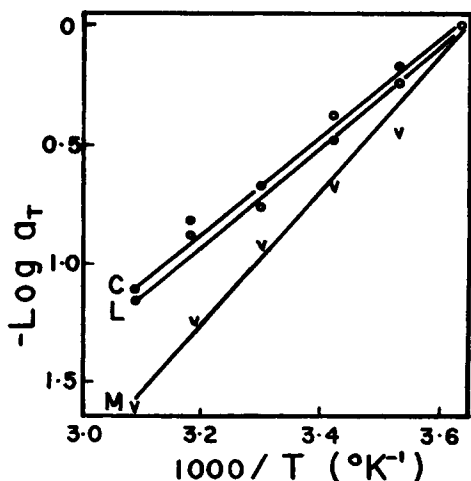


Figure 13 Plot of log of shift factor versus reciprocal of absolute temperature.

of about 0.05 decade/°C. This is in good agreement with the shift rate of 0.06 decade/% moisture regain reported by Stootman²⁶ from torsion relaxation data, and by Wortmann and de Jong²⁴ from stress relaxation data. The correspondence indicates the similarities between the change in properties of wool with temperature and that with moisture.

The activation energy was determined from the Arrhenius plots of log of shift factor versus $1/T$ (Fig. 13), and the activation energy values obtained were (in kcal/mol): Merino 8.2, Chokla 8.9, and Lincoln 9.8. These values are much smaller than expected for a T_g -like process in semicrystalline polymers. These values are slightly higher than the values expected for dissociation of weak bonds which would be around 5 kcal/mol. This would also include a small part from the covalent crosslinked network of chains which contribute mainly to the equilibrium modulus of the matrix. It should be remembered that unlike in other polymers the magnitude of shift factors in wool is small and the calculation of E_a from this method will be sensitive to the superposition technique. Since the methodology is successful in providing a single composite curve, the E_a can be formally interpreted as a heat of dissociation. However, such low values of E_a have also been reported for undiluted methacrylate polymers.²⁷ For temperatures above T_g , the free volume increases with increasing temperature and the relaxation times of some sub- T_g processes, such as side chain and backbone motions, decrease; as a consequence E_a decreases with temperature.

Master Curves and Distribution Spectra

The master stress relaxation modulus curves (Fig. 14) show the viscoelastic regions in the three wool

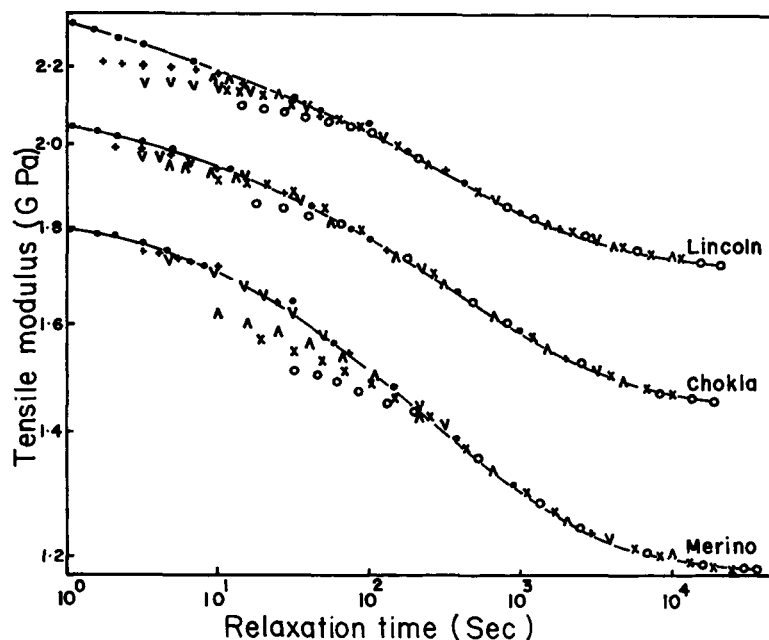


Figure 14 Master relaxation curves obtained from the superposition of data in Figure 11. The various points are from the relaxation curves for the temperature indicated: ● at 2°C; + at 10°C; v at 20°C; ^ at 30°C; x at 40°C; ○ at 50°C.

fibers quite clearly, with the glassy and the rubbery regions on either side.

From the superposed master curves of the three wools obtained at various temperatures in water, the relaxation spectrum, $H(\tau)$, was calculated using Alfrey's approximation:²⁸

$$H(\tau) = \log E(t) \frac{d \log E(t)}{d \log(t/a_r)}, \quad (2)$$

where, $E(t)$ is the relaxation modulus at time t , and a_r is the horizontal shift factor. The relaxation time

spectra for the three wools (Fig. 15), show similar features, with a preponderance of relaxation at short times in the case of Merino and Chokla fibers and of even shorter times in the case of Lincoln fibers. The sharp and intense relaxation peak for Merino wool compared to the broad peaks for the Lincoln wool is noteworthy. This can be attributed to the fact that all these studies have been made above T_g . Of the three wools, Merino fibers show the lowest modulus throughout the time and temperature range studied and this is attributed to low degree of orientation and low crystallinity. Therefore, intense

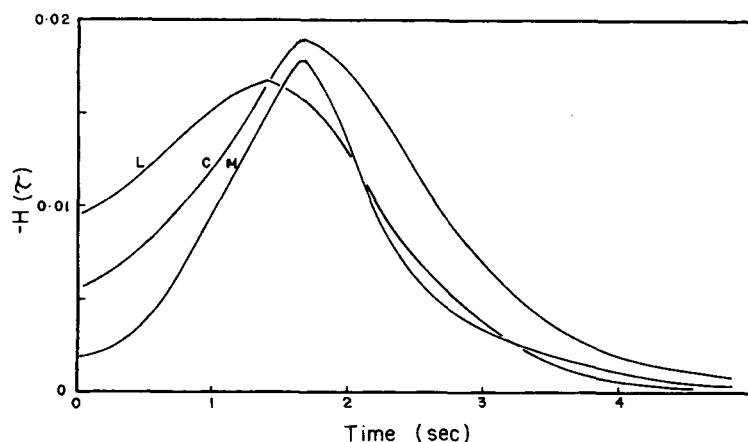


Figure 15 Relaxation distribution spectra (for data in Fig. 14).

and narrow distribution of relaxation spectra for Merino wool indicates distinct phase separation of crystalline and amorphous phases.

Equilibrium Moduli

Since the absolute stress values are different in the three wool types it would be interesting to compare their fibril phase moduli or equilibrium moduli. Data on viscoelastic relaxation of wool fibers were analysed by two phase models using the cumulative log-normal distribution for the relaxation function.²⁴⁻²⁶ Since the shape of the relaxation function is independent of the structure and composition of the material, this method was successfully used to predict the phase moduli.^{24,25} This model is represented by Equation 3:

$$E(t) = (E_0 - E_a)\phi(t) + E_a \quad (3)$$

where E_a and $(E_0 - E_1)$ are the moduli of the elastic and the viscoelastic phases respectively. $E(t)$ is the relaxation modulus and $\phi(t)$ the relaxation function. The relaxation function can be expressed as

$$\phi(t) = 1 \vee (2\pi\sigma) \int \exp[-1/2\{(x - \mu)/\sigma\}^2] dx \quad (4)$$

where μ and σ are the mean and standard deviation of the cumulative log-normal distribution. Assuming constancy of shape of the relaxation function, and applying the two phase model²⁴ to the relaxation curves, E_a can be estimated through a simple curve-fitting procedure. For the present data the predicted values for E_a are: 1.4 GPa for Lincoln, 1.2 GPa for Chokla and 0.8 GPa for Merino fiber. Since the process controlling the relaxation mechanism is expected to be the same in the three wools the differences in the E_a values have a physical meaning in molecular terms reflecting the intrinsic differences in the fibril phase.

Structural Differences in the Three Wools

The pronounced viscoelastic effects in Merino wool compared to those of Lincoln could arise, amongst other factors, from structural differences, viz. relatively poor organization of the fibrils.

The stress relaxation studies have, in the main, been made with the wool fiber immersed in water. In this condition at room temperature, the fiber is very close to its T_g and as the temperature is raised, the matrix becomes much more compliant as it

passes from the viscoelastic to the rubberlike state. The principal feature which distinguishes Merino from the other two wools is its bilateral structure. The ortho regions have relatively more disoriented fibrils²⁹ and a higher density of bulky side groups.³⁰ It is interesting to note that the relatively higher T_g of Merino wool fiber arises from the presence of a relatively higher proportion of bulky groups in the matrix, which will require higher thermal energy for motion to commence and result in a high glass transition temperature.

In the dry state, the matrix is glassy due to good molecular bonding. With the ingress of moisture, the bonds are loosened or break and the bulky groups in ortho-rich Merino fibers generate more free volume and thus enhance the freedom of motion in other molecular segments. The higher accessibility of the ortho regions in the wet state has been well established.³¹ Relatively low thermal stability of Merino fibers thus follows from its higher accessibility and poor organization in the fibril phase.

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