

Linear Superposition of Viscoelastic Responses in Nonequilibrium Systems

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Synopsis

A generalized form of the equations of linear viscoelasticity is presented which enables theoretical treatment of situations where a material is not at equilibrium with its environment and/or is subjected to a changing environment. These generalized equations are used successfully to predict the recovery behavior of wool and nylon fibers from bending deformations in experiments involving conditions of changing temperature and relative humidity.

INTRODUCTION

Linear viscoelastic theory^{1,2} has been used successfully in the study of the mechanical behavior of certain materials at low strains (generally < 1%). The theory can be based on the assumption that linear superposition holds for both stress and strain (the Boltzmann superposition principle). This can be expressed in the following Stieltjes integral forms:

$$f(t) = \int_0^t G(t - \tau) d\epsilon(\tau) \quad (\text{superposition of stress}) \quad (1)$$

$$\epsilon(t) = \int_0^t J(t - \tau) df(\tau) \quad (\text{superposition of strain}) \quad (2)$$

where f and ϵ are the stress and strain at any time t and $G(t)$ and $J(t)$ are functions of time which are unique for the material under specified conditions. These equations describe a linear superposition of responses and imply that a response to a given input is invariant with the time at which this input is applied.

The functions $G(t)$ and $J(t)$ are known as the stress relaxation modulus and creep compliance, respectively. A knowledge of one of these functions determines completely the viscoelastic behavior of the material under the specified conditions. These functions are related through equations

$$\int_0^t G(t - \tau) \frac{dJ(\tau)}{d\tau} d\tau = 1 \quad (3)$$

$$\int_0^t J(t - \tau) \frac{dG(\tau)}{d\tau} d\tau = 1. \quad (4)$$

Convenient numerical methods³⁻⁶ are available for calculating one function from the other.

This theory can be applied to certain systems which are at equilibrium with a constant environment. The applicability of the theory is, however, somewhat restricted since for many practical purposes we are interested in the behavior of the material not at equilibrium with its environment and/or subjected to a changing environment.

It has been shown that keratin fibers, wet out in water and allowed to recondition in air at constant conditions, exhibit mechanical properties which change with time after reconditioning.^{7,8} During this process, which is known as aging, stress relaxation curves obtained by imposing a step strain at increasing times after reconditioning, shift progressively to greater relaxation times. Thus, the stress relaxation function is not invariant with time of testing.

To describe these phenomena, the following generalized forms of eqs. (1) and (2) were proposed:

$$f(t) = \int_0^t G(\tau, t - \tau) d\epsilon(\tau) \quad (5)$$

$$\epsilon(t) = \int_0^t J(\tau, t - \tau) df(\tau) \quad (6)$$

where $G(t_A, T)$ and $J(t_A, T)$ are unique functions of two variables. Thus, the stress relaxation modulus and the creep compliance are unique functions of the absolute (or aging) time t_A and the stress relaxation time T . These equations, which describe a linear superposition of responses that are not time invariant, were used successfully to predict the bending creep and recovery behavior of aging wool fibers.

In the present work, the applicability of this type of equation is tested for wool and nylon fibers in bending in situations where temperature and/or relative humidity are changing with absolute time. This is of considerable practical relevance to the wrinkling of textile materials.^{9,10}

THEORY

Because of complications likely to arise due to changes in the dimensions of the specimen with absolute time, eqs. (5) and (6) must be modified.

Firstly, changes in cross-sectional area of a specimen are likely to occur during environmental changes, and this will result in complicated changes in calculating actual stress. Therefore, for convenience we will define $f(t)$, $\epsilon(t)$, $G(t_A, T)$, and $J(t_A, T)$ to be nominal values^{6,11} calculated from the dimensions of the specimen measured under some standard conditions (say, 20°C and 65% R.H.). In this manner, complex changes in specimen dimensions will not have to be determined independently but will automatically be taken into account.¹² Hereafter, all stresses, strains, moduli, and compliances will be understood to be nominal values.

Secondly, the environmental changes may produce changes in the strain parameter of the stress-free specimen during the course of the experiment, and these changes must be allowed for. For example, in a tensile experiment involving increasing humidity, the length of a keratin specimen would increase¹³ in the absence of tensile stress due to longitudinal swelling. This would produce an increase in strain. Alternatively, if the specimen were held at constant length (zero strain), a compressive stress would be built up during the course of the experiment. Assuming that these "background" effects are additive with the viscoelastic effects, we modify the previous eqs. (5) and (6) as follows:

$$f(t) = \phi_e(t) + \int_0^t G_e(\tau, t - \tau) d\epsilon(\tau) \quad (7)$$

$$\epsilon(t) = \eta_e(t) + \int_0^t J_e(\tau, t - \tau) df(\tau) \quad (8)$$

where $\phi_e(t)$ and $\eta_e(t)$ are the background stress function and background strain function, respectively. They represent the stress or strain changes that would be observed in an experimental sequence with the specimen maintained at zero strain or zero stress, respectively. (It is convenient for most purposes to define $\phi_e(t)$ and $\eta_e(t) = 0$ at $t = 0$.) It is easy to show that they are related by the following expressions:

$$\eta_e(t) = - \int_0^t J_e(\tau, t - \tau) d\phi_e(\tau) \quad (9)$$

$$\phi_e(t) = - \int_0^t G_e(\tau, t - \tau) d\eta_e(\tau). \quad (10)$$

Furthermore, the stress relaxation modulus and creep compliance can be shown from their definitions to be related via relations⁸ which are generalizations of the previously given relations eqs. (3) and (4):

$$\int_{t_A}^t G_e(\tau, t - \tau) \frac{dJ_e(t_A, \tau - t_A)}{d\tau} d\tau = 1 \quad (11)$$

$$\int_{t_A}^t J_e(\tau, t - \tau) \frac{dG_e(t_A, \tau - t_A)}{d\tau} d\tau = 1. \quad (12)$$

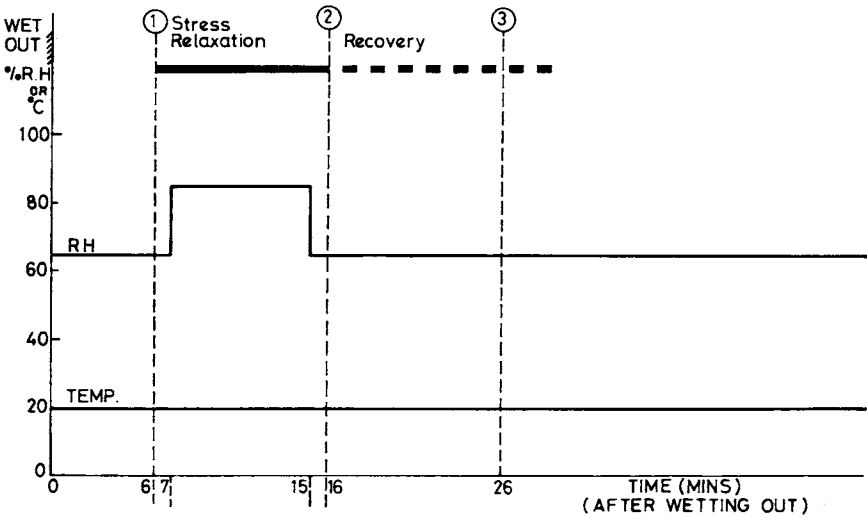
Calculations of G_e from J_e or vice versa are conveniently carried out numerically.⁸

Thus, the behavior of a material which obeys eqs. (7) and (8) is completely determined for any given environmental sequence by a knowledge of $\phi_e(t)$ or $\eta_e(t)$ together with $G_e(t_A, T)$ or $J_e(t_A, T)$ for that particular sequence.

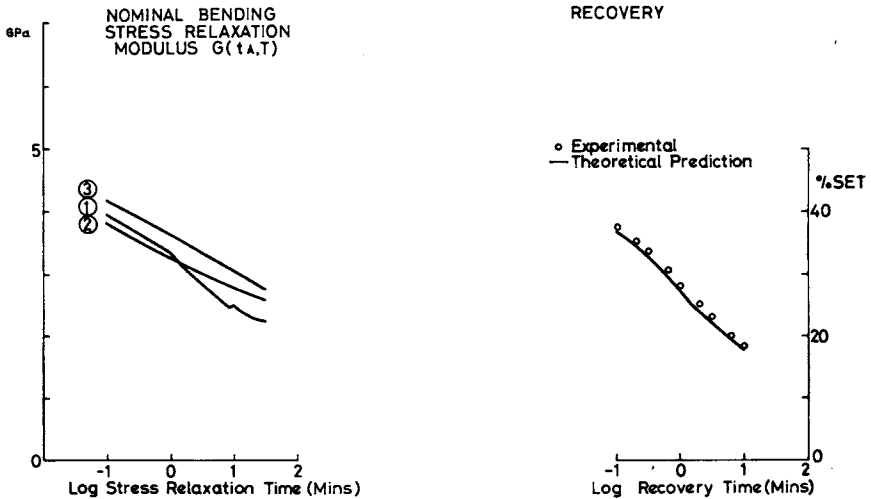
In general, an environmental sequence is understood to mean a given set of histories of the external constraints on the system (apart from stress or strain). Such constraints would include temperature, relative humidity, hydrostatic pressure, etc. It should be emphasized that, while we have used the respective terms "stress relaxation modulus" and "creep com-

pliance" to refer to $G_e(t_A, T)$ and $J_e(t_A, T)$, these functions of t_A and T will be unique only for the given environmental sequence. The subscript e is used here to denote functions which are dependent in this way on a particular environmental history.

If the sample is sufficiently thin and the temperature and humidity changes relatively slow such that appreciable gradients of temperature and moisture are not set up within the sample, then the functions G_e and J_e will represent true material properties for that particular environmental sequence. For larger samples under rapid environmental changes, the func-

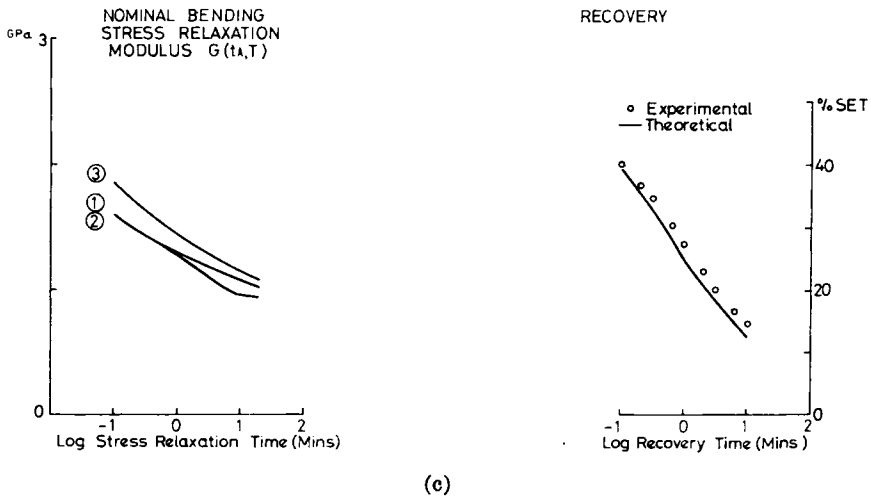


(a)



(b)

Fig. 1 (continued)



(c)
 Fig. 1. (a) Graphic representations of the mechanical and environmental sequences of experiment 1. Temperature and R.H. are plotted vs. the time after wetting out: (1) onset of stress relaxation; (2) recovery; (3) auxiliary stress relaxation experiment; (■■■■) duration of the step strain; (■■■■) duration of recovery. (b) Result of experiment 1 for Lincoln wool. The averaged nominal bending relaxation moduli functions $G_e(t_1, T)$, $G_e(t_2, T)$, and $G_e(t_3, T)$, marked (1), (2), and (3), are plotted in GPa against relaxation time on the left of the figures. On the right-hand side of the figures are shown the averaged experimental recovery points and the averaged theoretically predicted recovery from eq. (7) (solid lines). (c) The same as (b) using nylon fibers.

tions G_e and J_e obtained will in addition depend on the thermal and moisture transfer characteristics of the material and will therefore depend on the size and shape of the specimen chosen. For the 50- μm textile fiber investigated below, these secondary effects are probably negligible.

APPLICATION OF THE THEORY

A dummy run may be performed on a sample held at zero strain to determine $\phi_e(t)$ for the particular environmental sequence of interest. A series of stress relaxation experiments is then performed on fresh samples (or the same sample brought back to its original state) by imposing a step strain ϵ_0 at different times (t_A) during the course of the sequence. The stress relaxation modulus can thus be determined from

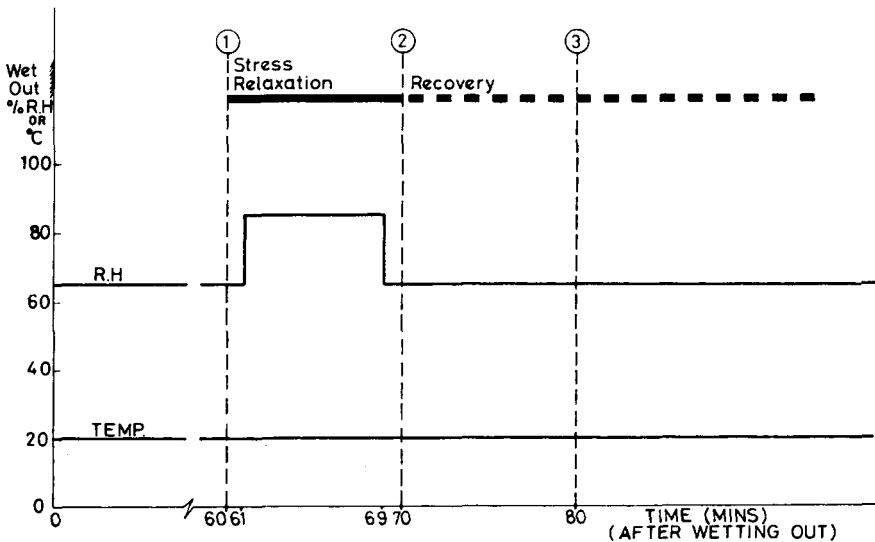
$$f(t) = \phi_e(t) + \epsilon_0 G_e(t_A, t - t_A).$$

Putting stress relaxation time $T = t - t_A$, we obtain:

$$G_e(t_A, T) = \frac{f(t_A + T) - \phi_e(t_A + T)}{\epsilon_0}. \tag{13}$$

The behavior of the material is therefore completely determined for this sequence.

Single straight fibers, provided they are structurally symmetrical in cross section, will remain straight in spite of temperature and relative humidity changes. Thus, bending experiments on straight fibers provide a particularly convenient technique for studying the viscoelastic properties since $\phi_e(t)$ (the bending stress¹¹ at zero bending strain) and $\eta_e(t)$ (the bending strain at zero bending stress) will remain zero throughout any environmental sequence.¹² However, a fiber with an initial natural curvature (defined as zero bending strain) or a straight fiber with a bilateral structure will exhibit curvature changes giving rise to nonzero background functions. Fortunately, fairly straight sections of Lincoln wool and nylon fibers are available over the short lengths required for bending studies (~ 1 mm), and thus the effects of the background functions may be neglected.



(a)



(b)

Fig. 2 (continued)

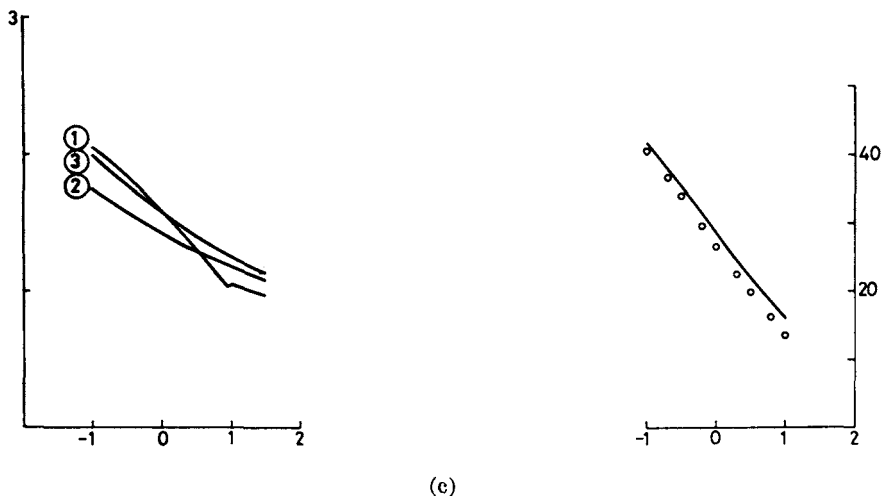


Fig. 2. (a)–(c) Graphic representations of mechanical and environmental sequences of experiment 2. Other data as in Fig. 1.

EXPERIMENTAL

A lock of Lincoln wool fibers had been washed thoroughly in petroleum ether and then in distilled water and allowed to dry in air at 65% R.H. and 20°C. Three Lincoln fiber specimens were mounted as previously described¹⁴ for testing in the single-fiber bending apparatus. Nylon 66 fibers from an I.C.I. multifilament yarn approximately 53 μm in diameter were boiled off¹⁵ in distilled water for 1/2 hr and allowed to condition in air at 65% R.H. and 20°C, and three fiber specimens were mounted. The dimensions of the wool and nylon specimens were measured in air at 65% R.H. and 20°C, and these dimensions were used to calculate nominal^{6,11} bending stress and strain values in subsequent tests which involved different environmental conditions.

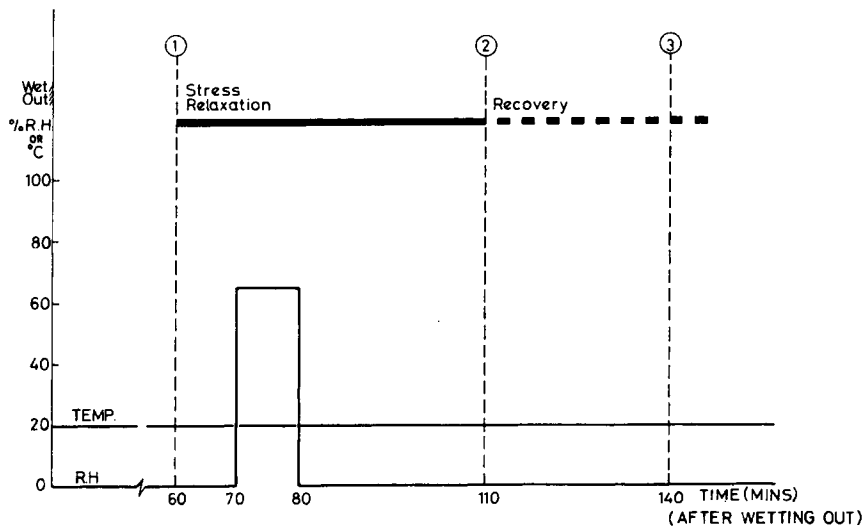
It has previously been found⁸ that following bending experiments performed in air on wool and nylon fibers, the fibers could be brought back to a standard state by wetting out (unstrained) and conditioning for a given time in air at specified conditions. The specimens are wet out by dripping water continuously onto them for 5 min, after which surplus liquid is removed. This procedure enables one fiber specimen to be used for many tests with more direct and accurate comparison possible than if many separate specimens had been used.

A series of five bending stress relaxation and recovery experiments was designed to test the validity of eqs. (7) and (8) when the relative humidity and temperature were allowed to vary during the course of the experiment. Figures 1a, 2a, 3a, 4a, and 5a are graphic representations of the mechanical and corresponding environmental sequences used. Relative humidity and temperature are plotted as a function of time after wetting out, and the periods of stress relaxation (from time 1) and recovery under

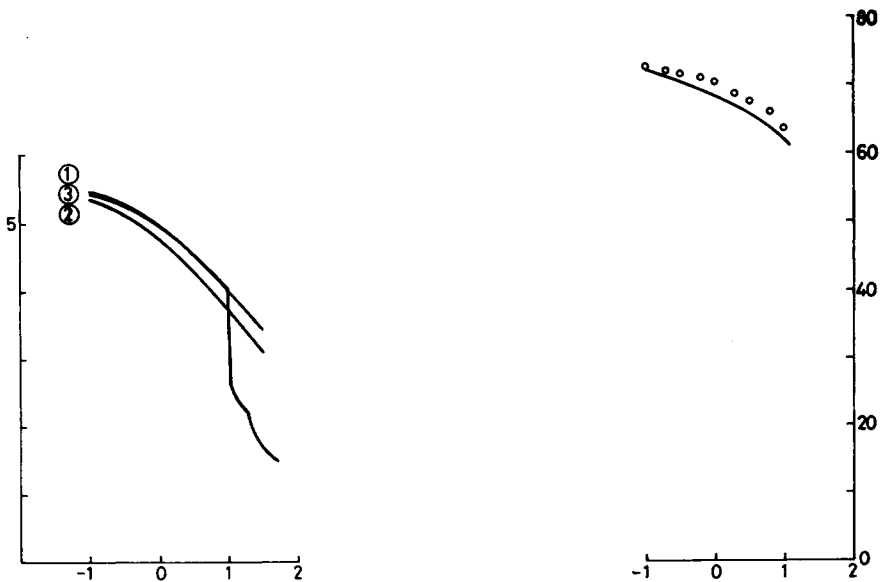
zero load (from time 2) are marked. All stress relaxation was done at 1% bending strain.

The experiments (labeled 1 to 5) are briefly summarized below. After wetting out,

1. Fiber conditioned 6 min at 65% R.H., 20°C; strained to 1% for 10 min during which time a burst of air at 85% R.H. was admitted for 8 min; then the R.H. was returned to 65% 1 min before recovery.

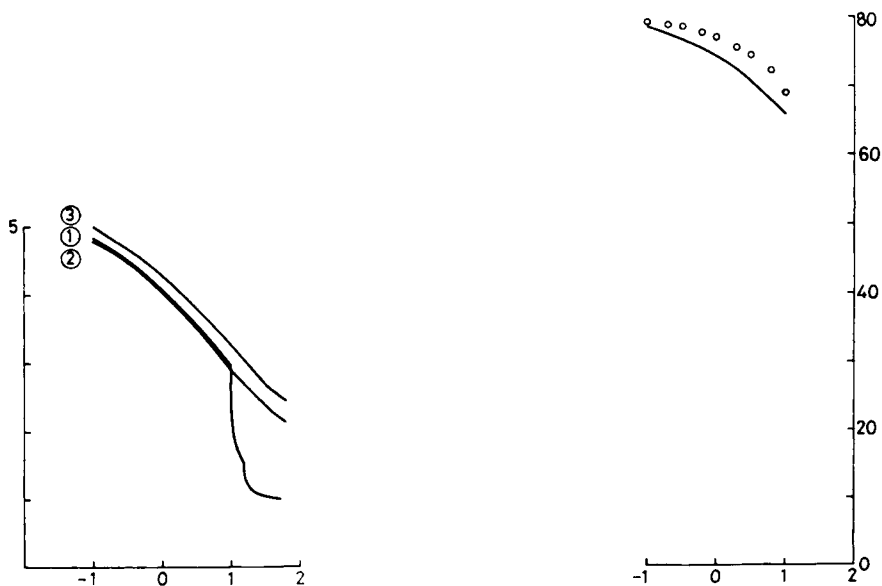


(a)



(b)

Fig. 3 (continued)



(c)

Fig. 3. (a)–(c) Graphic representations of mechanical and environmental sequences of experiment 3. Other data as in Fig. 1.

2. As in 1, except that the fiber was conditioned 60 min.
3. Fiber conditioned 60 min at 0% R.H., 20°C; strained to 1% for 50 min, but during stress relaxation the R.H. was changed abruptly to 65% after 10 min stress relaxation. After 10 min at 65% R.H., the air was changed back to 0% R.H. 30 min before recovery.
4. Fiber conditioned for 30 min at 65% R.H., 20°C after which time the R.H. dropped continuously for remainder of experiment to 33% 1 hr later. At time of commencement of the drop in R.H., the fiber was strained to 1% for 15 min before recovery.
5. Fiber conditioned for 30 min at 65% R.H., 20°C. Temperature then rose and R.H. simultaneously fell, gradually over the remainder of the experiment until a condition of 46°C and 15.5% R.H. was reached after 1 hr. At the time of commencement of drop in R.H. and rise in temperature, the fiber was strained to 1% for 30 min before being recovered.

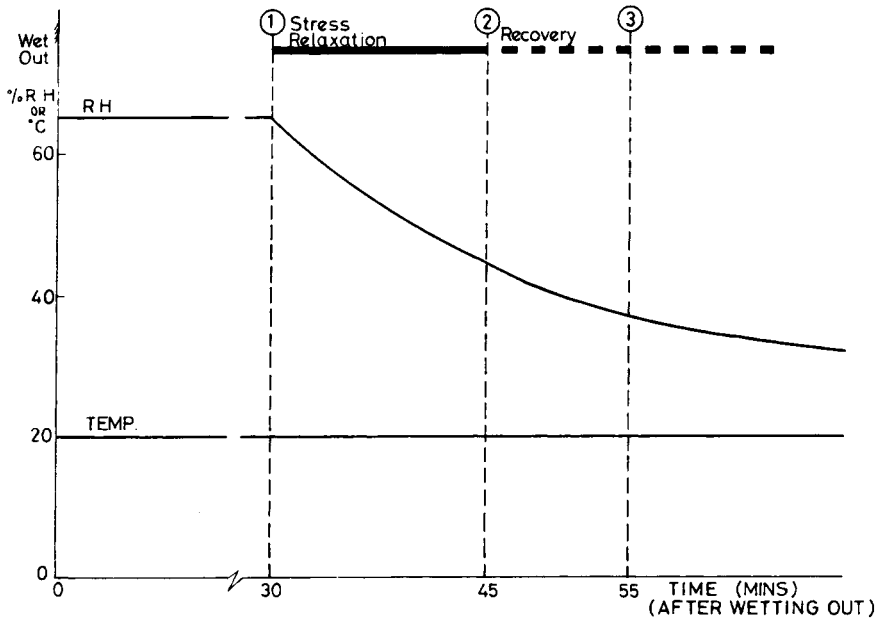
Each of the six fiber specimens was subjected to tests 1 to 5 in sequence. However, after each main stress relaxation and recovery test, the specimen was subjected to two additional stress relaxation tests. It was wet out and subjected, unstrained, to the same environmental sequence as for the main test. However, when the original recovery time (marked 2 in Fig. 1a) was reached, a stress relaxation step strain was imposed and maintained until the end of the environmental sequence. The fiber was then wet out again and the procedure repeated with the step strain now being imposed at time 3. If we let the times associated with points 1, 2, and 3 be given by

t_1 , t_2 , and t_3 , the stress relaxation functions we have obtained are $G_e(t_1, T)$, $G_e(t_2, T)$, and $G_e(t_3, T)$.

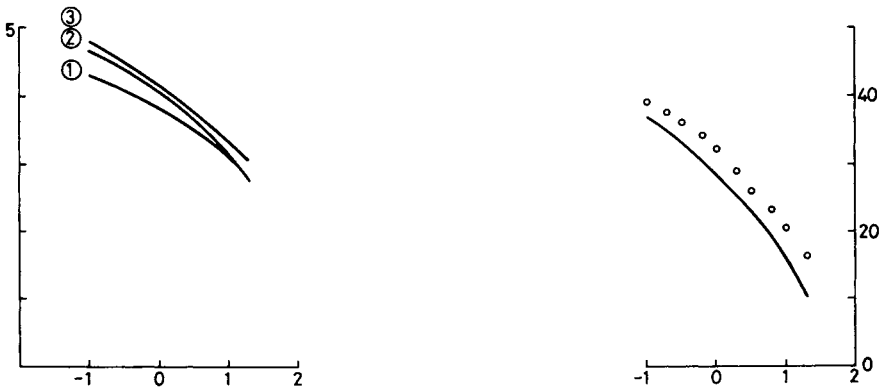
CALCULATIONS

For recovery following stress relaxation at strain ϵ_0 , since $\phi(t) = 0$ for all t , eq. (7) becomes

$$0 = \epsilon_0 G_e(t_1, t - t_1) + \int_{t_2}^t G_e(\tau, t - \tau) d\epsilon(\tau).$$



(a)



(b)

Fig. 4 (continued)

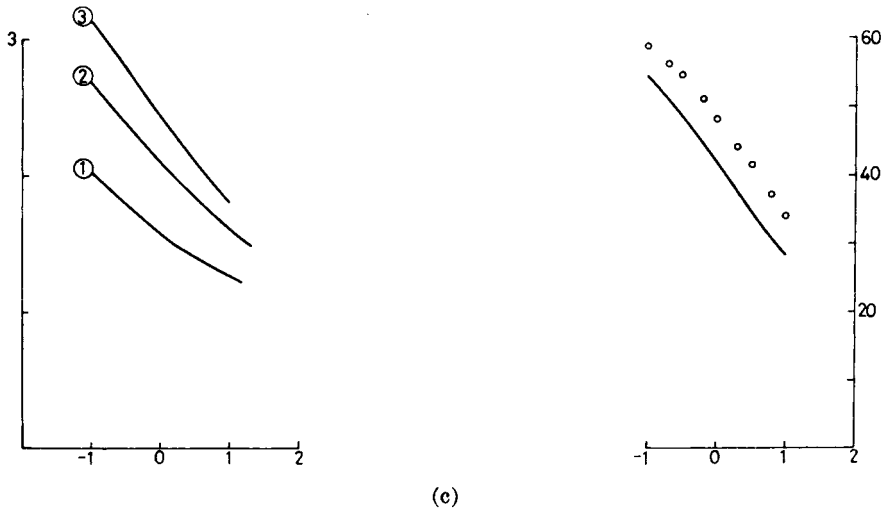


Fig. 4. (a)–(c) Graphic representations of mechanical and environmental sequences of experiment 4. Other data as in Fig. 1.

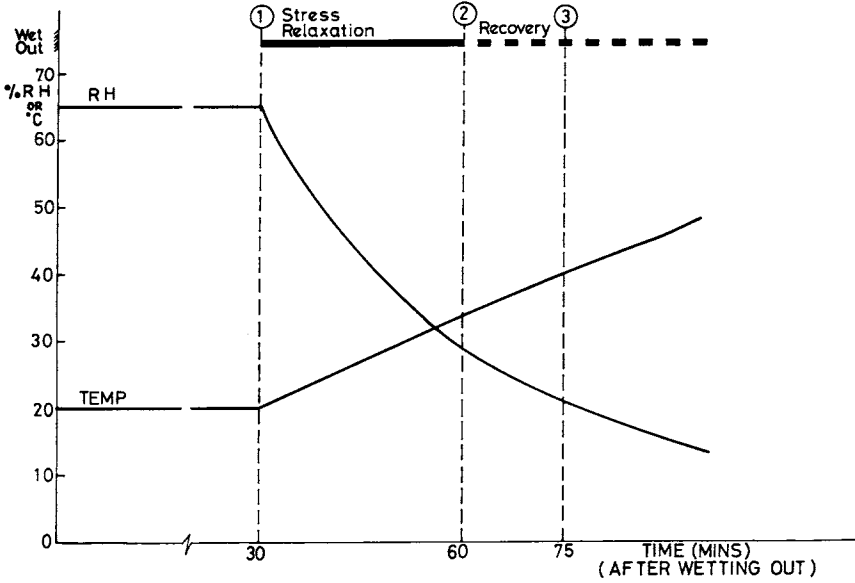
Thus, it is evident that in order to calculate recovery strain^{6,8} $\epsilon(t)$ it is necessary to know the function $G_e(t_1, T)$ and all functions $G_e(t_i, T)$ where $t_2 < t_i < t$. By using a linear interpolation technique between the known functions $G_e(t_2, T)$ and $G_e(t_3, T)$, we may estimate intermediate functions. This interpolation is reasonable since there are no discontinuities in R.H. or temperature in any of the tests (1 to 5) which might give rise to discontinuities or sharp changes in the value of G_e between t_2 and t_3 .

It should be noted that it is necessary to know function $G_e(t_1, T)$ for $t_2 < t_1 + T < t$, i.e., a small extrapolation of the originally determined function at time t_1 is necessary. However, in the case of tests 1 and 2, extrapolation was not possible, and a subsidiary stress relaxation was done by imposing a step strain at time t_1 and maintaining it until the end of the environmental sequence.

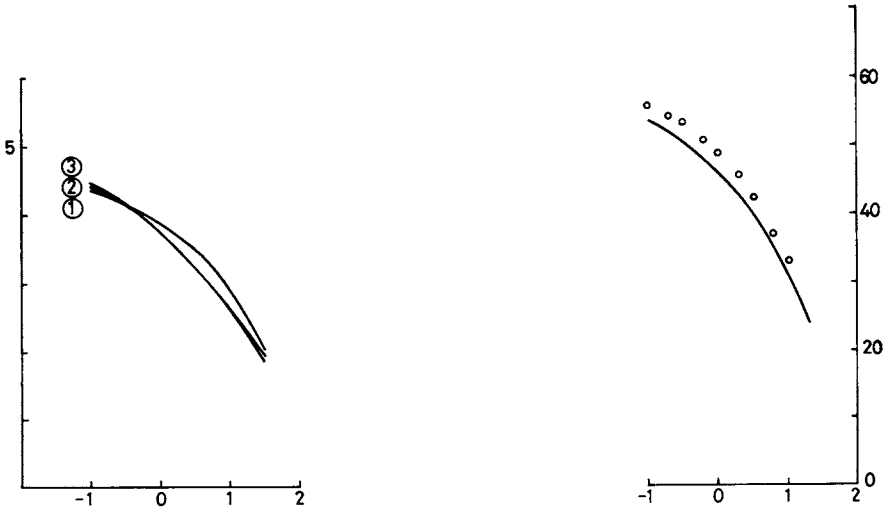
For each test on each fiber specimen, the three G functions $G_e(t_1, T)$, and $G_e(t_3, T)$ were used to calculate recovery using the methods of references 6 and 8. For each test, each of these G functions was averaged over the three wool fibers used. The corresponding experimental recovery points and the predicted recovery curves were similarly averaged. These results are shown in Figures 1b, 2b, 3b, 4b, and 5b where the averaged G functions (expressed in GPa) are labeled (1), (2), and (3), respectively and have been plotted against the logarithm of time on the left of each figure. The averaged experimental recovery points and averaged theoretical recovery curves have been plotted against log of recovery time on the right-hand side of each graph. Recovery is expressed as percentage set,⁶ i.e., the percentage of the original strain remaining after any recovery time. The results for the nylon fibers are similarly shown in Figures 1c, 2c, 3c, 4c, and 5c.

DISCUSSION

The recovery curves of Figures 2 and 3 indicate good agreement between the theoretical predictions and the experimentally determined values. Thus, for the environmental sequences investigated, wool and nylon

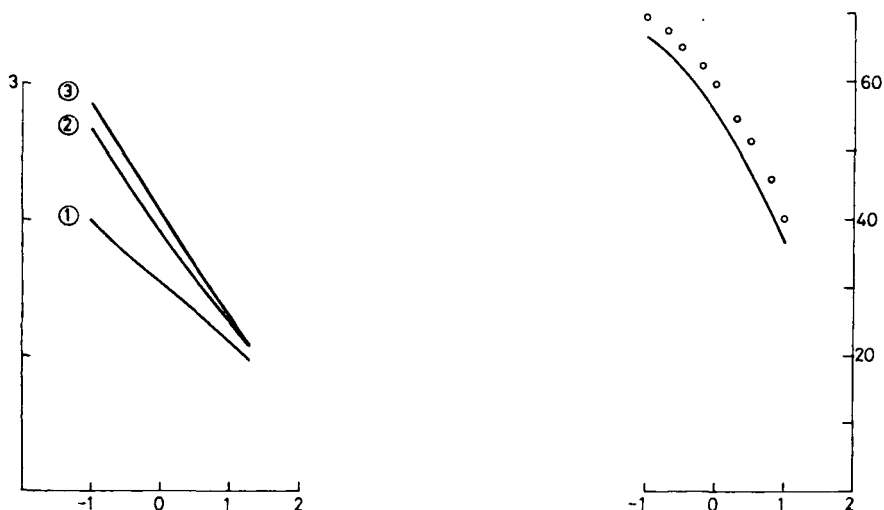


(a)



(b)

Fig. 5 (continued)



(c)

Fig. 5. (a)-(c) Graphic representations of mechanical and environmental sequences of experiment 5. Other data as in Fig. 1.

fibers exhibit responses which, although not time invariant, are linearly superposable. It should be noted that the first three experiments 1 to 3, which involve step changes in R.H., show better agreement than 4 and 5. Except in one case, the deviation was always such that the observed recovery was less complete than what was predicted. A similar phenomenon has previously been noted for "aged" wool⁸ and nylon¹⁶ fibers which had been stress relaxed at 1% bending strain and recovered under constant conditions. The greater the time of stress relaxation, the greater the deviation. Moreover, for strains above 1%⁶ this discrepancy becomes much more marked. It is possible that at 1% strain, we are slightly out of the linear viscoelastic strain region, and this suggests that if the present experiments were performed at 0.5% strain, the small discrepancies observed would be much less. Yannas et al.¹⁷ have found for polycarbonate that longer times of stress relaxation and higher temperatures effectively reduce the region of linearity.

Equation (7) has been found to hold for the situations investigated here when the background function $\phi(t) = 0$, and the converse eq. (8) should also be valid under the same conditions since Stuart¹⁸ has shown that one equation implies the other. Experiments in tension, where $\phi_e(t) \neq 0$ and $\eta_e(t) \neq 0$, could be used to test these equations more completely.

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