

A Rheological Model of Viscose Rayon

STANISŁAWA AKSAN and WITOLD ŻUREK, *Instytut Włókiennictwa, Łódź, Poland*

Synopsis

In viscose rayon samples subjected to cyclic loading the phenomenon of supertension was observed as a variation of the linear elasticity limit in the consecutive cycles. To enable a mathematical description of this phenomenon a rheological model with an inertional-frictional element was devised. The curves calculated on the basis of the model well approximated the experimental results.

INTRODUCTION

For interpretation of the phenomena which occur in yarn during fatigue stretching, it is necessary to determine the relationship between the fundamental parameters: stress, strain, and time. The relationship can be determined using a rheological model.

The use of an idealized model to represent the strain mechanism in macromolecular polymers dates back to 1924 when Shorter devised a three-element system to describe the creep phenomenon in wool. None of the heretofore proposed systems—neither the standard system devised by Shorter nor any of the later, more sophisticated systems including the seven-element system proposed by Vreedenburg—gives a satisfactory concurrence between the theoretical and experimental curves.⁵ So far, the greatest interest was evoked by the nonlinear model proposed by Eyring,^{3,5,6} and it seemed that at last a universal model had been devised. However, thorough testing revealed that the suitability of this model was limited to only a few types of fiber, and the fiber for which the thereby obtained mechanical characteristics was closest to the real characteristics was acetate rayon.³

The difficulty of devising a suitable model for fiber at large lies in the complexity of fiber inner structure. In the cyclic loading graphs, this complexity shows itself in the shape of the stress-strain curves which are characteristically different for different types of fibers. Analysis of viscose rayon fatigue stretching curves reveals certain properties of the fiber which, as has been asserted from the relevant literature,³⁻⁷ have been so far overlooked in model evolution. This was felt to be a sufficient justification for attempting the construction of a new model including elements that would enable representation of the phenomena involved with the cyclic loading of viscose fiber.

Selection of the present model was based on an analysis of the load-extension curves of the viscose rayon manufactured by Wrocławskie Zakłady Włókien Sztucznych, Wrocław, of which the linear density and protective twist were, respectively: linear density = 133/30/dtex and $t = 82$ twists/m; linear

density = 333/60/dtex and $t = 101$ twists/m. The curves were obtained on a Zwick stress-strain tester operating on the principle of constant elongation rate.

The distance between clamps (net sample length) was 500 mm. This length was chosen to eliminate the influence of errors caused by unavoidable strain of yarn in clamps.

The rate of elongation was constant and equal to 0.2 mm/sec, except one comparative investigation, when the rate of elongation was 3.3 mm/sec. All experiments were performed at 20–22°C temperature and 62–67% humidity.

ANALYSIS OF THE STRESS-STRAIN CURVES

Figure 1 shows two superimposed curves representing the stretching: curve 1 represents continuous loading to break (monocyclic stretching), and curve 2 is a strain-relaxation curve representing repeated loading at constant extension rate (multicyclic stretching). When comparing the two curves the following phenomenon is observed:

In the first loading cycle, the two curves are ideally superimposed, but already in the second cycle, curve 2 shows a "supertension" in relation to curve 1, and this supertension is more and more pronounced as more cycles are added. It appears that in multicyclic loading, a greater force must be applied at the beginning of each consecutive cycle to obtain the same amount of ex-

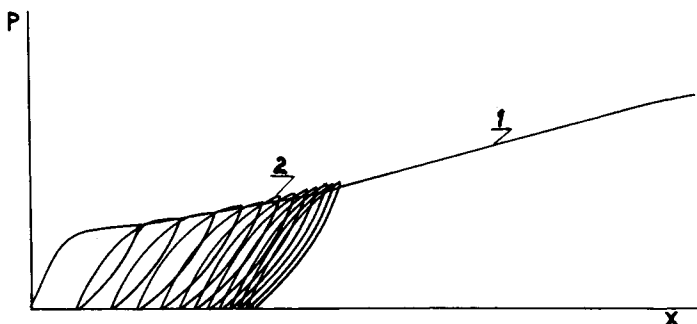


Fig. 1. Mono- and multicycle stretching graphs.

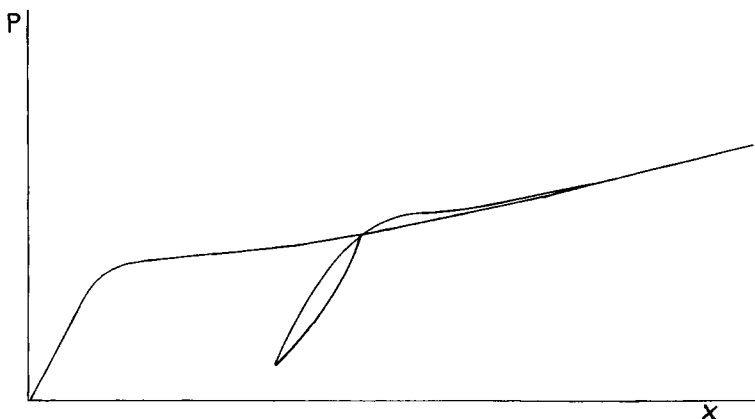


Fig. 2. Disappearance of supertension.

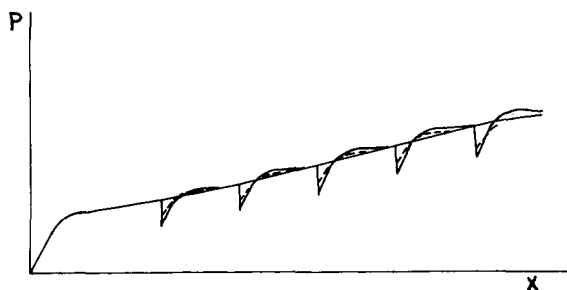


Fig. 3. Stretching with on-load relaxation. Broken line: relaxation time 40 sec; solid line: relaxation time 300 sec.

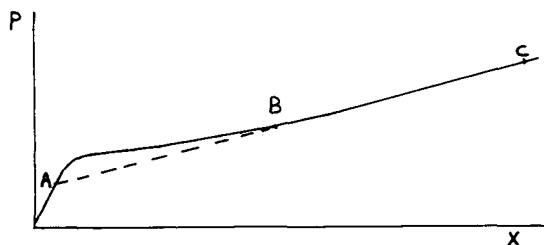


Fig. 4. Supertension in monocyclic stretching.

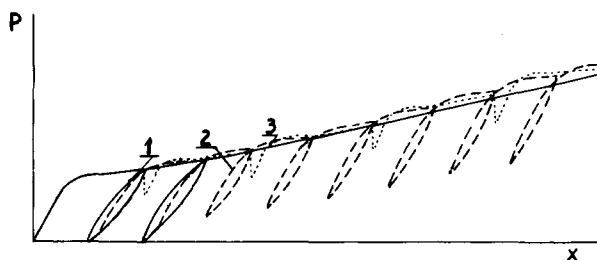


Fig. 5. Cyclic stretching graphs: (1) loading with release till complete relaxation; (2) stretching with releasing by constant extension length; (3) stretching with on-load relaxation (300 sec).

tension as in monocyclic loading. As follows from Figure 2 the supertension disappears when loading is further continued.

The supertension phenomenon in viscose rayon can be observed not only in the "load-relaxation" procedure; it is even more pronounced in the "stress-on-load relaxation" curves (Fig. 3). In the latter case, the effect of time on supertension is observed. Figure 3 shows that the supertension level is higher following a longer relaxation time.

The phenomenon of supertension is also observed in monocyclic loading (Fig. 4). In the extension zone marked B-C, there is a linear relation between extension and load. When the B-C zone is extended to A, supertension is clearly indicated by that A-B part of the curve which is above the straight line A-C.

The supertension phenomenon, which is involved with the beginning of each loading cycle irrespective of whether the fiber has been previously stretched or not, points to the presence, in the fiber, of some "inhibitors"

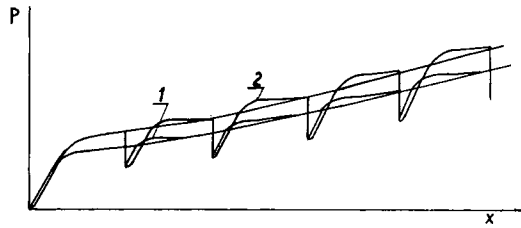


Fig. 6. Stretching with on-load relaxation at the following rates: (1) 0.2 mm/sec; (2) 3.3 mm/sec.

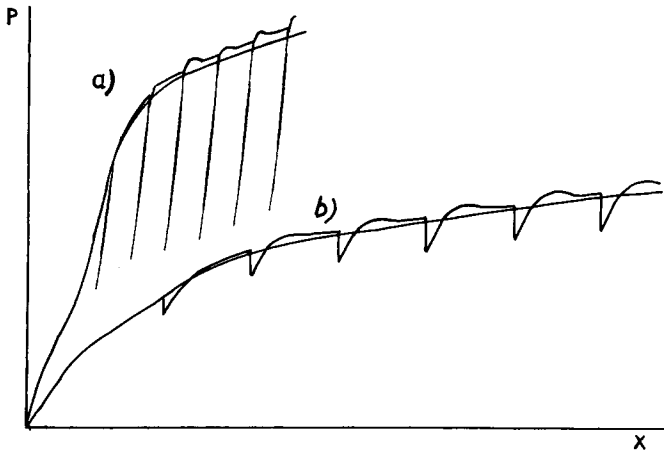


Fig. 7. Mono- and multicycle stretching graphs for: (a) polyamide filament; (b) polyester filament.

which resist extension and gain in magnitude with added number of cycles. This is not a place to attempt determining the nature of the inhibitors, however, on comparing the curves in Figure 5, which represent (1) loading with release till complete relaxation, (2) loading to constant extension and release, and (3) stretching with on-load relaxations, it is observed that supertension is greater following longer on-load relaxations (curve 3), while it is very small in the initial cycles of curve 1.

On the other hand, in stretching at a higher extension rate (Fig. 6), it was observed that the proportionality limit tended to ascend to a higher level and supertensions were registered in the consecutive load-relaxation cycles. Above the proportionality limit, fragments of the two curves are displaced in relation to each other, but they do not point to a relationship between the magnitude of supertension and extension rate. It seems, therefore, that the two phenomena—the strengthening accompanying higher extension rate and the supertension involved in cyclic loading—are each of a different nature.

It has been noticed that supertension appears not only in viscose fiber. Mono- and multicycle loading of polyamide filament (Stilon 44.5/44/dtex) and polyester filament (Torlen 165/32/dtex) show a gradually ascending level of the proportionality limit with added number of cycles (Fig. 7).

Freudenthal⁴ has described the phenomenon of raised plasticity limit in a polycrystal metal stretched with on-load relaxations at constant rate and to constant extension, wherein he has remarked the effect of the on-load relaxa-

tion time on the strengthening level. Displacement of the plasticity limit is observed here directly upon interruption of the on-load relaxation, and the continued stretching results in a curve which corresponds to that of monocyclic loading.

However, the following differences have been observed between the phenomenon in polycrystal metal and in viscose fiber: In fiber, the supertension persists for some time, whereas in metal it disappears almost instantaneously. In metal, the strengthening level depends on stretching rate, whereas no such dependence has been observed in fiber. In metal, the strengthening effect is observed to disappear prior to termination of the stretching (i.e., before rupture), while in fiber, rupture occurs at continuing supertension (i.e., while the sample strength is still increasing).

The strengthening effect in polycrystal metals, which is outwardly observed as increased plasticity limit, is a result of progressive granular comminution due to stretching.⁴ In the macromolecular polymers, among which the fiber material belongs, the strengthening in stretching is an effect of the changes which occur in their supermolecular structures, viz., improved orientation and ordering of the molecules, a changed crystallite size distribution, etc.^{6,7}

THE ADOPTED MODEL

On the basis of analysis of the cyclic stretching curves for viscose rayon, from which it can be detected* that some resistance is present in fiber at the beginning of each stretching cycle, a model can be adopted in which the mechanism of the resistance will be replaced by an inertional-frictional system of mass M and friction force Tx_2 proportional to the strain. The frictional element is constructed so that it gives increasing resistance in one direction, while in the opposite direction the resistance has a constant value equal to the maximum resistance in a loading cycle. The inertional-frictional system is incorporated in a parallel system composed of a Hook's spring with a constant k_2 and a Newton damper of viscosity η_2 . The whole is connected in a row to a Hook's spring of a constant k_1 .

The discussed system is mathematically described by this modified Kelvin-Voigt equation:

$$\frac{dx_2}{dt} = \frac{P - k_2x_2 - M \frac{d^2x_2}{dt^2} - Tx_2}{\eta_2} \quad (1)$$

where x_2 is the deformation of the parallel system at deformation of the whole system by a magnitude x ; P is the force generated in the constant k_1 spring as a result of the system deformation by the magnitude x ; and t is the loading time.

Hence;

$$P = k_1x_1 \quad (2)$$

where x_1 is deformation of the spring of constant k_1 .

* The phenomenon was first disclosed in an unpublished paper by J. Choraży² prepared under the guidance of W. Zurek.

In accordance with Boltzmann's superposition theory,

$$x = x_1 + x_2 \tag{3}$$

A schematic drawing of the model is presented in Figure 8.

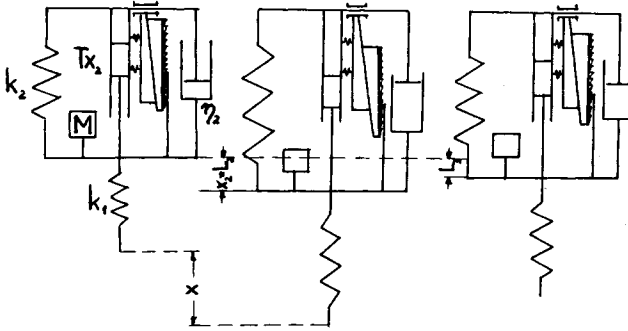


Fig. 8. Inertial—frictional model and its operation.

Below, a complete stretching cycle is mathematically described, based on eq. (1):

When stretching at a constant rate c ,

$$x = ct \tag{4}$$

and eqs. (2) and (3) give

$$P = k_1(x - x_2). \tag{5}$$

By substituting (4) into (5) and then (5) into (1), we obtain

$$M \frac{d^2x_2}{dt^2} + \eta_2 \cdot \frac{dx_2}{dt} + (k_1 + k_2 + T) \cdot x_2 = k_1ct \tag{6}$$

And if

$$\frac{\eta_2}{M} = H; \frac{k_1}{M} = K_1; \frac{k_2}{M} = K_2; \frac{T}{M} = T_1; \tag{7}$$

eq. (6) will assume the form

$$\frac{d^2x_2}{dt^2} + H \frac{dx_2}{dt} + (K_1 + K_2 + T_1) \cdot x_2 = K_1ct; \tag{8}$$

For the initial conditions $t = 0, dx_2/dt = u_0$; and, if $H^2 - 4(K_1 + K_2 + T_1) = 0$, the equation is solved as follows:

$$x_2 = \frac{k_1}{k_1 + k_2 + T} \left[ct - \frac{\eta_2 c}{k_1 + k_2 + T} + \frac{\eta_2 c}{k_1 + k_2 + T} \times \left(1 + \frac{\eta_2}{2M} t \right) e^{-\frac{\eta_2}{2M} t} - \left(c - \frac{k_1 + k_2 + T}{k_1} u_0 \right) t e^{-\frac{\eta_2}{2M} t} \right]. \tag{9}$$

In accordance with eqs. (4) and (5), $P = k_1 (ct - x_2)$. Hence, the tension P is

$$P = \frac{k_1^2}{k_1 + k_2 + T} \left[\frac{k_2 + T}{k_1} ct + \frac{\eta_2 c}{k_1 + k_2 + T} - \frac{\eta_2 c}{k_1 + k_2 + T} \times \left(1 + \frac{\eta_2}{2M} t \right) e^{-\frac{\eta_2}{2M} t} + \left(c - \frac{k_1 + k_2 + T}{k_1} u_0 \right) t e^{-\frac{\eta_2}{2M} t} \right]. \quad (10)$$

Equation (1) for releasing load is solved in a similar way. As $H^2 - 4(K_1 + K_2) > 0$, the solution of this equation is changed.

Generally, for the loading cycle it can be assumed that

$$P = Ax + B + (Cx - B)e^{-ax} \quad (11)$$

and for the cycle of releasing,

$$P = R - A_1 x' - W_2 - e^{-ax'} [W_1 \sin h(a\beta x') - W_2 \cos h(a\beta x')] \quad (12)$$

where $x' = L_m - x$, and L_m is elongation of sample at the very beginning of releasing.

TESTING OPERATION OF THE MODEL

The following values from eq. (11) can be found:

and
$$P = 0 \quad \text{for } x = 0;$$

$$P \rightarrow \infty \quad \text{for } x \rightarrow \infty$$

according to the equation, $P_\infty = Ax + B$, which represents the linear part B - C of the dependence of load versus elongation (Fig. 4). Extrapolation of this equation to the ordinate axis gives $P_\infty = B$ for $x = 0$. This value can be found directly as a point of intersection of the straight line with the ordinate axis.

The value of A is determined as the slope of the straight $P_\infty = Ax + B$ versus x axis. At point A of curve (Fig. 4) $Cx_A - B = 0$, hence $C = B/X_A$.

TABLE I
Constants of Equations (11) and (12)

| dtx | 133 | | | | 333 | | | |
|----------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| | 1st Cycle | | 2nd Cycle | | 1st Cycle | | 2nd Cycle | |
| | Loading | Releasing | Loading | Releasing | Loading | Releasing | Loading | Releasing |
| $a[m^{-1}]$ | 222 | 222 | 222 | 222 | 143 | 143 | 143 | 143 |
| $A \left[\frac{N}{m} \right]$ | 25,38 | | 25,38 | | 52,2 | | 52,2 | |
| $A_1 \left[\frac{N}{m} \right]$ | 24,13 | | 24 13 | | 40,00 | | 40,0 | |
| $B[N]$ | 0.46 | | 0.76 | | 0.91 | | 1.31 | |
| $C \left[\frac{N}{m} \right]$ | 199 | | 100 | | 350 | | 264 | |
| $W_1[N]$ | 3.62 | | 1.86 | | 4.86 | | 4.18 | |
| $W_2[N]$ | 0.76 | | 0.96 | | 1.50 | | 1.80 | |
| β | 0.15 | | 0.15 | | 0.37 | | 0.37 | |
| $R[N]$ | 0.95 | | 1.14 | | 1.90 | | 2.12 | |

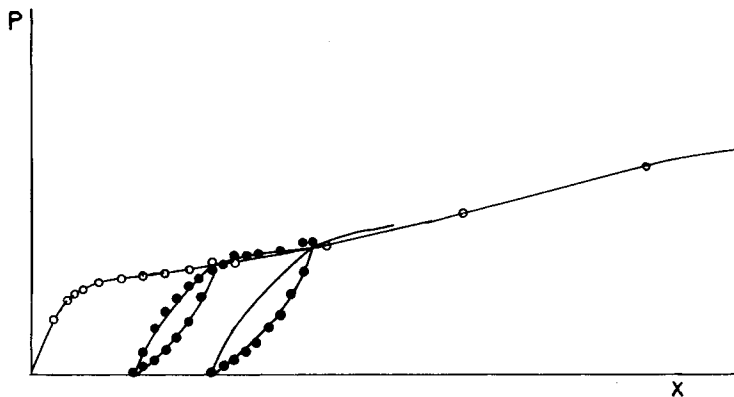


Fig. 9. Mono- and multicycle stretching of viscose rayon 133 dtex; white points represent values calculated from eq. (11); dark points represent values calculated from eqs. (11) and (12).

The coefficient a can be found basing on the value of intersection point $-x_s$ of the straight $P_\infty = Ax + B$ with the tangent to the curve (11) at the point $x = 0$. Its value is

$$a = \frac{B - Cx_s}{Bx_s}$$

To obtain the value

$$\beta = \sqrt{1 - \left(\frac{2M}{\eta_2}\right)^2 \frac{k_1 + k_2}{M}}$$

it is necessary to calculate the rheological constants k_1 , k_2 , η_2 , and M . These constants can be determined from the following five equations:

$$\left. \begin{aligned} \frac{k_1(k_2 + T)}{k_1 + k_2 + T} &= A \\ \frac{k_1^2 \eta_2 c}{(k_1 + k_2 + T)^2} &= B \\ \frac{\eta_2}{2M} &= ac \end{aligned} \right\} \begin{array}{l} \text{from analysis of equation (10)} \\ \text{where } A, B, \text{ and } a \text{ are constants} \\ \text{determined from the loading} \\ \text{diagram } c \text{ is the stretching rate} \end{array}$$

$$\left(\frac{\eta_2}{2M} \right)^2 - \frac{k_1 + k_2 + T}{M} = 0 \left\} \begin{array}{l} \text{by assumption} \\ \\ \text{from analysis of the equation for} \\ \text{releasing load, where } A_1 \text{ is a constant} \\ \text{determined by trial and error} \end{array}$$

$$\frac{k_1 k_2}{k_1 + k_2} = A_1$$

The constants determined for eqs. (11) and (12) of viscose rayon of 133 dtex and 333 dtex are given in Table I. The calculated tensions are plotted as points on the experimental curves (Figs. 9 and 10). As can be seen from

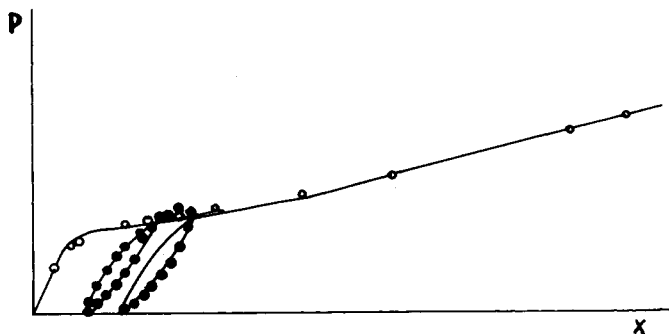


Fig. 10. Mono- and multicycle stretching of viscose rayon 333 dtex; open circles represent values calculated from eq. (11), dark circles represent values calculated from eqs. (11) and (12).

the presented results, there is a good correspondence with the experimental curves.

CONCLUSIONS

1. The cyclic stretching of viscose rayon entails the phenomenon of supertension in that a greater force is required to extend the sample by a constant length in each consecutive cycle. This phenomenon can be observed when the loading of a sample is followed by complete or partial relaxation or by on-load relaxation. It disappears upon longer, uninterrupted stretching.

2. The supertension level is dependent on the time of relaxation or on-load relaxation. No effect of the stretching rate on the supertension level was observed.

3. The supertension level is a function of the number of cycles and therefore the loading frequency. At higher frequencies, supertension results in a considerable increase of the sample tension. This may have a substantial effect on the durability of viscose rayon in technological processes. This durability, as follows from the eq. (1), depends *inter alia* on the magnitude of the tension amplitude.

4. The adopted inertional-frictional model satisfactorily represents the supertension phenomenon observed in a viscose rayon sample subjected to cyclic stretching. The formulae evolved on the basis of the model state equation give a good approximation between the calculated and experimental results.

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