

The Force-Temperature Behavior of Swollen Cellulose Model Filaments

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1. INTRODUCTION

The study of force as a function of temperature has proved to be a useful tool in the elucidation of the elastic mechanisms in rubber and rubberlike polymers. Its usefulness stems from the well-known thermodynamic relations

$$f = \left(\frac{\partial H}{\partial l} \right)_{P,T} - T \left(\frac{\partial S}{\partial l} \right)_{P,T} \quad (1)$$

and

$$- \left(\frac{\partial S}{\partial l} \right)_{P,T} = \left(\frac{\partial f}{\partial T} \right)_{P,l} \quad (2)$$

where the symbols have their usual meaning. On the basis of two equations, the force f may be written

$$f = \left(\frac{\partial H}{\partial l} \right)_{P,T} + T \left(\frac{\partial f}{\partial T} \right)_{l,P} \quad (3)$$

Thus, a measurement of force at constant length l as a function of temperature gives the change in entropy with elongation from the slope of the resulting curve, eq. (2), and the change in enthalpy with elongation, eq. (3). The results of experiments^{1,2} of this kind led to the well-known theories of rubber elasticity of Guth and James³ and Flory.⁴

However, rubber and rubberlike polymers are not the only substances to be studied by this technique. Proteins have received and, at present, are undergoing extensive study.⁵

Fibers have also been studied extensively.⁶⁻⁸ Rayon fibers were studied by Roseveare and Poore,⁶ and Bryant and Wakeham.⁷ In the dry state, cellulose does not lead to very interesting results. The force-temperature curves are monotonically and, in fact, linearly decreasing with increasing temperatures,⁶ which is the normal behavior of a crystalline or glassy elastic substance with a positive coefficient of expansion. (It is worthwhile to note that no change in slope occurs at 62°C., where Uberreiter⁹ reported a "glass transition"

for cellulose.) However, when cellulose is swollen with a solvent, a considerably more complicated behavior occurs. Such behavior is best exemplified by the results of Roseveare and Poore, who reported curves with a minimum when the rayon was swollen with water. The temperature of the minimum was a function of the orientation, increasing from about 0°C. for "isotropic" rayon to about 50°C. for tire yarn type and to over 100°C. for very highly oriented rayon.

The thermodynamic analysis in this case is not quite as straightforward as in the case of rubber. Here, account must be taken of the fact that the system contains two components and two phases, and the thermodynamics must be modified accordingly. Katz¹⁰ has shown that the force-temperature coefficient in this case is given instead of by eq. (2), by

$$\left(\frac{\partial f}{\partial T} \right)_{P,l} = \left(\frac{\partial f}{\partial T} \right)_{P,l,n} + \left(\frac{\partial f}{\partial n} \right)_{P,l,l} \left(\frac{\partial n}{\partial T} \right)_{P,l} \quad (4)$$

and

$$\left(\frac{\partial f}{\partial T} \right)_{P,l,n} = - \left(\frac{\partial S}{\partial l} \right)_{T,P,n} \quad (5)$$

where n is the amount of swelling agent in the polymer. Thus the observed force-temperature coefficient (left-hand side of eq. (4)) is not related directly to an entropy change on elongation as in eq. (3), but has a term involving the water content of the polymer. If the degree of swelling is not independent of temperature ($\partial n / \partial T \neq 0$), this term may account for a significant fraction of the total observed force-temperature coefficient.

Bryant and Wakeham⁷ attempted to evaluate this term and decided that the literature data were not precise enough. The present paper is concerned with work on model filaments swollen in water. The aim of the work was to evaluate the effect of orientation on the force-temperature behavior, and to evaluate the importance of the swelling terms.

II. EXPERIMENTAL

A. Materials

The filaments used were prepared by the method of Hermans and de Leeuw.¹¹ Viscose solution containing 7.4% cellulose and 6.6% NaOH was spun from a buret into 2 *N* ammonium sulfate solution where it was coagulated. The cellulose was regenerated in a 3% sulfuric acid, 12% ammonium sulfate solution for 1½ hours and washed with distilled water.

Six series of filaments, differing in orientation, were prepared. Series A consisted of isotropic filaments. They were not stretched and were allowed to dry without tension. The filaments in series B through F were stretched 20, 40, 60, 80, and 100% while in the freshly regenerated stage and allowed to dry at constant length. Table I gives a summary of the pertinent characteristics of all the filaments. The density was measured in a density gradient column, and is very similar to the densities found by Hermans.¹² The densities correspond to crystallinities between 18 and 30%.

TABLE I
Physical Properties of the Model Filaments Used

Type fiber	Pre-stretch, %	Denier (0% R.H.)	ρ	$N\gamma - N\alpha^a$
A	0	1026	1.512	0.002
B	20	439	1.514	0.016
C	40	383	1.517	0.020
D	60	349	1.520	0.024
E	80	328	1.522	0.026
F	100	321	1.525	0.032

^a Difference in refractive index along and transverse to the fiber axis.

B. Apparatus

The force temperature apparatus was of standard design. A strain gauge was used to measure the force and a thermocouple to measure the temperature. An X-Y recorder then gave a plot of force as a function of temperature directly. The sensitivity of the apparatus was such that forces of 3 mg. could be determined. The temperature could be measured with a precision within $\pm 0.30^\circ\text{C}$. The apparatus was so constructed that thermal expansion effects in the apparatus were negligible. The sample was mounted in water in essentially the inner chamber of a condenser. The water in the condenser jacket was then pumped from a heated or cooled reservoir and the temperature of the fiber bath thus changed.

C. Method

The fibers themselves were allowed to equilibrate at room temperature for 15 hours before a run was started. The filament was then heated to 95°C . stretched the desired amount, and allowed to relax for at least one hour. The temperature was then lowered to 5°C . and raised again to 95°C ., the whole cycle taking about three hours. Hysteresis was found to be negligible, except at the very end points where temperature changes were somewhat abrupt. However, one fiber was run over a period of 24 hours, and no difference between this and the normal runs was found, so that the normal runs were probably at equilibrium.

III. RESULTS AND DISCUSSION

A. Force-Temperature Results

The results of runs on Filament A are given in Figure 1. Several points are of interest. First, these curves show a maximum, which is entirely unlike the "normal" behavior of rayon fibers. However, the behavior was not entirely new and has been reported elsewhere.^{6,7} Another point of interest is that, at the lowest strain, the force falls to zero at a finite temperature. This implies

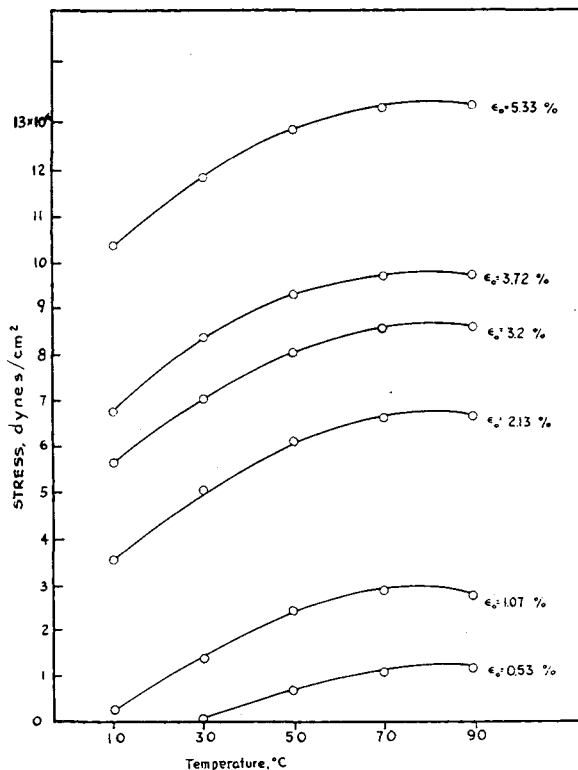


Fig. 1. Force-temperature behavior of isotropic model filament. The force is calculated on the basis of the dry dimensions.

that there is no thermoelastic inversion in this material and that the linear coefficient of expansion is negative, which strongly suggests that the degree of swelling is changing considerably with temperature.

The results for the whole series of filaments are given in Figure 2. These are at 2.5% strain. It will be seen that these filaments show a maximum whose temperature decreases with orientation, instead of a minimum whose temperature increases with orientation, which was the previous observation.⁶ These observations, however, are not contradictory. As will be seen below, the force-

maximum "rubbery" and the behavior above the maximum "glassy," for this implies that the elasticity is caused by certain definite molecular mechanisms, whereas the force-temperature behavior of this gel could be caused simply by changes in the degree of swelling.

B. Equilibrium Stress-Strain Curves

If the coefficient of expansion at zero force were known for the filaments, stress-strain curves at any temperature could be calculated from the force-temperature curves. These curves would

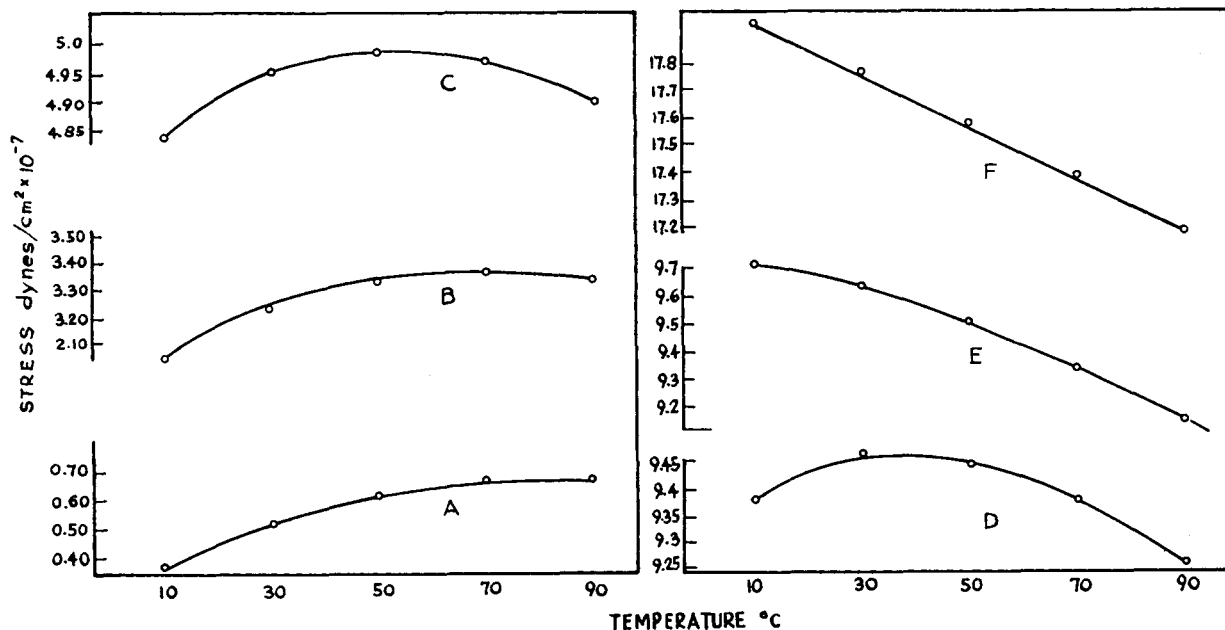


Fig. 2. Force-temperature behavior of model filaments as a function of orientation. The elongation at 95°C. in each case is 2.5%.

temperature behavior of cellulose is dependent upon its microstructure, and a change in this can invert the force-temperature curves. At an orientation achieved for the F filament the maximum has disappeared and a behavior reminiscent of dry rayon is left.

Although these elongations were generally taken to only about 5%, filament D was stretched up to 20%. At that time its behavior corresponded to the behavior of the E filament. This makes us believe that this set of curves is part of a family of curves which could be obtained from the A filament.

Without an evaluation of the magnitude of the swelling correction terms no analysis of the force and its temperature coefficient in terms of enthalpy and entropy of elongation can be made. It would not do to call the behavior below the

be equilibrium stress-strain curves,² in the sense that they are curves which would be obtained in an extremely slow stress-strain experiment.

The coefficient of linear expansion was measured at zero force for the various fibers. This was done by measuring the lengths of a filament with a measuring microscope, changing the temperature, and keeping the force zero by means of the strain gauge and extension apparatus. The results of this experiment are shown in Figure 3, which gives the change in length per unit length as a function of temperature. Since 95°C. was chosen as the relaxation temperature, the length at this temperature was chosen as the reference length.

It will be noted that the coefficient of expansion of the isotropic A filament is negative—a fact which could have been predicted from the force-temperature behavior. The coefficient of ex-

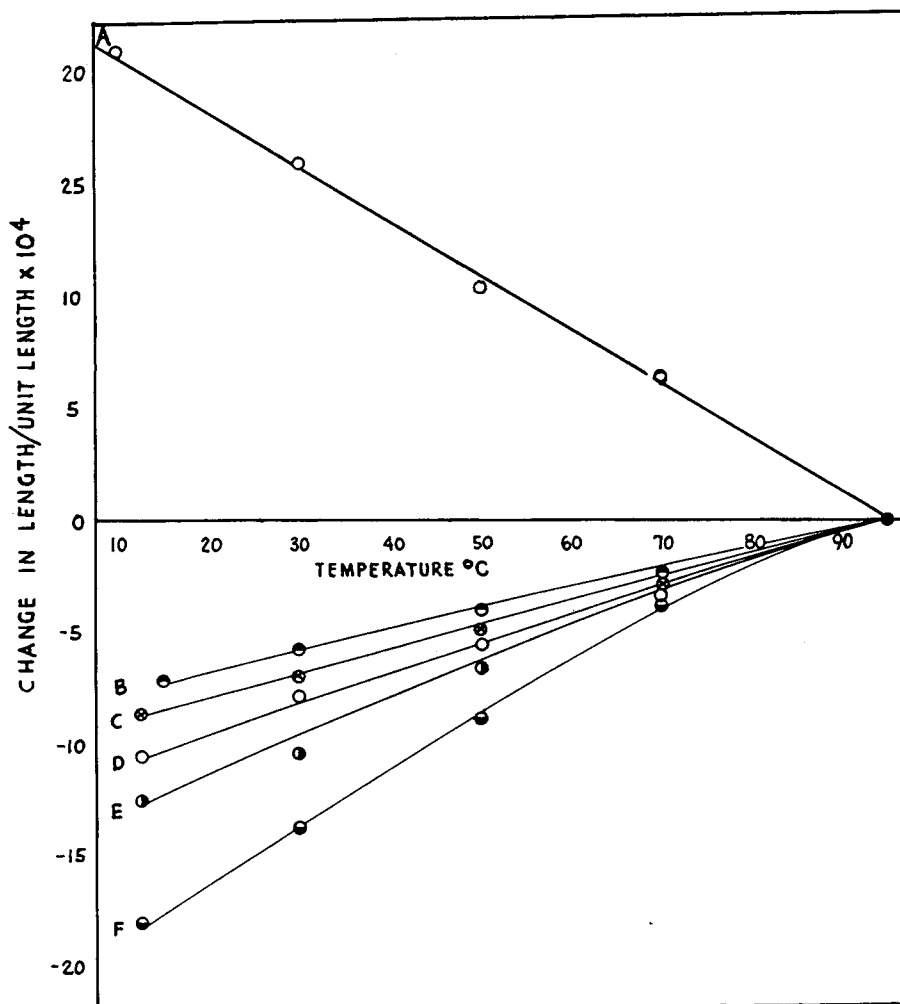


Fig. 3. Length as a function of temperature for model filaments of various orientations. The A filament is an "isotropic" filament.

pansion increases with orientation. The observed values are given below.

Filament	Linear expansion coefficient
A	-2.4×10^{-5}
B	0.9×10^{-5}
C	1.1×10^{-5}
D	1.2×10^{-5}
E	1.5×10^{-5}
F	2.1×10^{-5}

On the basis of these values, the correct strain can be computed at any temperature and the force-temperature data cross-plotted to yield stress-strain curves.

Such curves are shown in Figure 4 for the isotropic filament. The stress-strain behavior is essentially linear up to 5%. The small curvature is probably due to inaccuracies in measurement of the expansion coefficient. The curves at 50°C. and above are practically the same, since, as can

be seen from the force-temperature curves, the force is not a strong function of the temperature in this temperature range.

Theoretical analysis of these curves is difficult. None of the present theories of elastic mechanisms in polymer gels has yet taken into account all the factors necessary for an understanding of the elasticity of cellulose gels. The most important missing factors in the present theories are chain stiffness, crosslinking by crystallites, and possibly change of crystallinity with temperature, although the last topic has been adequately treated recently by Flory.⁵ These certainly play a significant role in determining the elastic behavior in cellulose materials. However, even though it is inapplicable, it is interesting to see what results are obtained when the kinetic theory of rubber elasticity is applied. Using the well-known equation⁴:

$$\sigma = \frac{\rho RT}{M_c q^{-1/3}} [\alpha - 1/\alpha^2] \quad (6)$$

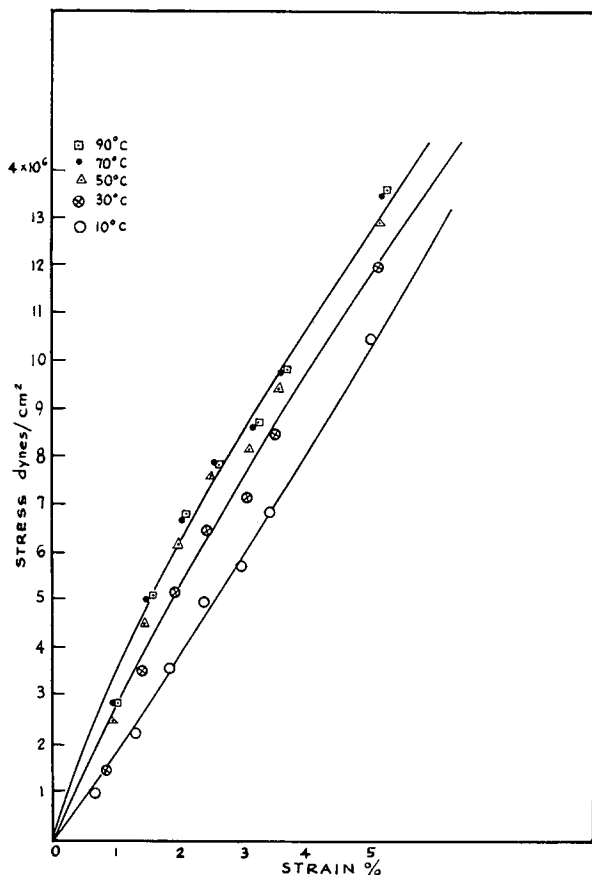


Fig. 4. Equilibrium stress-strain curves for the isotropic model filament. The curvature is probably due to experimental error.

where σ is the stress based on the dry cross-sectional area, ρ is the density, q is the degree of swelling, α is the ratio of stretched length to unstretched length, and M_c is the molecular weight between crosslinks, we obtain approximately five glucose residues for M_c .

Curves for other degrees of orientation are given in Figure 5. Again, the curves are linear. The modulus increases from 2.66×10^8 dynes/cm.² for the isotropic filament to 78.5×10^8 dynes/cm.² for the oriented filament.

C. Determination of Swelling Correction Terms

In order to evaluate the magnitude of the swelling correction terms, we must measure such quantities as $(\partial n / \partial T)_{P,l}$ and $(\partial f / \partial n)_{P,T,l}$. To measure these over the whole range of temperature, forces, and length is obviously too large a job to be performed profitably. However, it is possible to measure the size of the terms under one set of conditions to get an estimate of the size of the correction.

Before explaining how these terms were evaluated

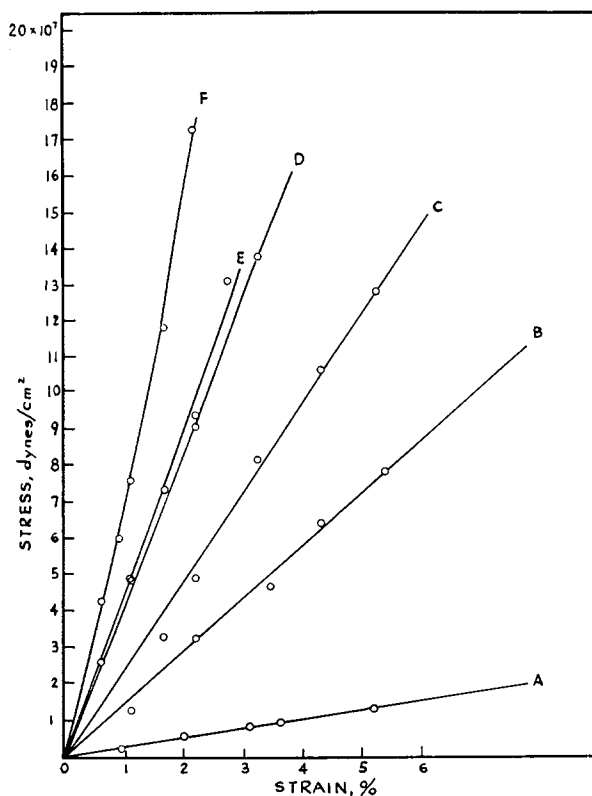


Fig. 5. Equilibrium stress-strain curves for filaments of various orientations. The modulus varies from 2.66×10^8 dynes/cm.² to 78.5×10^8 dynes/cm.².

it is convenient to transform the term $(\partial f / \partial n)_{P,T,l}$ to:

$$\left(\frac{\partial f}{\partial n}\right)_{P,T,l} = - \left(\frac{\partial l}{\partial n}\right)_{P,T,f} \left(\frac{\partial f}{\partial l}\right)_{P,T,n} \quad (7)$$

so that Eq. 4 becomes

$$\left(\frac{\partial f}{\partial T}\right)_{P,l} = \left(\frac{\partial f}{\partial T}\right)_{P,l,n} - \left(\frac{\partial n}{\partial T}\right)_{P,l} \left(\frac{\partial l}{\partial n}\right)_{P,T,f} \left(\frac{\partial f}{\partial l}\right)_{P,T,n} \quad (8)$$

Thus, the evaluation of the magnitude of these swelling terms requires the measurement of the quantities $(\partial n / \partial T)_{P,l}$, $(\partial l / \partial n)_{P,T,f}$, and $(\partial f / \partial l)_{P,T,n}$. These measurements are all possible, provided certain reasonable approximations are permitted. The method of measuring each of these quantities will be discussed in turn.

1. Measurement of $(\partial n / \partial T)_{P,l}$

This is the measurement of the change in degree of swelling with temperature at constant length. One way of determining this is to assume additivity of volumes in the gel and to compute this quantity from the measured coefficient of expansion of the

gel, the coefficient of expansion of the polymer in the gel, and the coefficient of expansion of water. The quantity desired, in terms of grams of water per gram of cellulose per degree is given by

$$\left(\frac{\partial n}{\partial T}\right)_{P,l} = \frac{q}{\rho} \beta_g - \frac{\beta_c}{\rho} - \frac{q-1}{\rho} \beta_w \quad (9)$$

where ρ is the density of cellulose, q is the degree of swelling, and β_g , β_c , and β_w are the coefficients of volume expansion of the gel, cellulose, and water, respectively.

The assumption of additivity of volumes will certainly not make a large error at these swelling ratios.¹³ The coefficient of expansion of the cellulose is the coefficient of expansion as measured in a water dilatometer. The coefficient of volume expansion of the gel can be determined by measuring the change in diameter with temperature and calculating from this the change in volume at constant length. Discussion of results will be postponed until after a description of measurement of the other two terms.

2. Measurement of $(\partial f/\partial l)_{P,T,n}$

This is the slope of the equilibrium stress-strain curve. The only assumption is that n remains constant during a curve. As will be seen below, the degree of swelling is not a strong function of the orientation, so that this assumption is undoubtedly a good one.

3. Measurement of $(\partial l/\partial n)_{P,T,f}$

This represents the change in length with change in water content of the gel. This was measured by measuring the length and weight of a dry sample, and remeasuring and reweighing after the sample was wet.

This, of course, gives an integral determination for a differential quantity, but the value determined in this way is just what would have been calculated on the basis of isotropy for the A filament, so that this may not be too serious an objection. Also, the measurements were done at zero force. It is difficult to see how this can influence the results markedly.

D. Results

Considering the approximations made in measuring these terms, the final results are undoubtedly somewhat in error. However, they probably are a fair estimate of the magnitude of the solvent effects. The results of these measurements are shown in Table II. The first column gives q , the degree of swelling. The second column gives the coef-

ficient of volume expansion of the gel. Note that in all cases this is negative. This means that the degree of swelling decreases as temperature increases, which also follows from the negative heat of swelling of cellulose. Its magnitude is approximately 0.1% of the degree of swelling per degree. This is in contrast with the positive coefficient of linear expansion expressed by Figure 3. The magnitude of the volume coefficient is also about two orders of magnitude greater than the magnitude of the linear coefficient. This indicates that, while the chains are quite mobile in the transverse direction, they change their extension only slightly on swelling, even with the added freedom permitted by expansion of the total volume. Even the "isotropic" filament apparently has considerable anisotropy, for the transverse coefficient of expansion (essentially β) is about 10 times as great in magnitude as the linear coefficient. Also of interest is the fact that this coefficient is of the same magnitude for all the filaments, regardless of orientation, and actually seems to increase (in magnitude) with orientation.

The third column gives the change in water content as computed by the method described above: the necessary coefficient of volume expansion of cellulose was measured in a water dilatometer and was 2.69×10^{-4} . The fourth column gives the modulus as read from the equilibrium stress-strain curves, expressed as grams per denier for a 1% elongation.

The next column gives the change in length with water content as determined by the method described. It is interesting to note here that the value measured for the isotropic filament is just what would be calculated on the basis of isotropy of swelling. For the oriented filaments, obviously most of the swelling takes place in the transverse direction, and the change in length is only of the order of a few per cent.

The next column gives the product of the preceding three columns and is just the swelling correction term that was sought. In all cases this is negative. When compared to the measured force-temperature coefficient evaluated at 25°C., (column 7), it is seen that the swelling term is in all cases larger in magnitude and, up to filament D, of opposite sign. The algebraic sum of these two quantities is the force-temperature coefficient at constant swelling, which is related to the change in entropy on extension at constant water content. This is given in the last column and in all cases is negative, as is the force-temperature coefficient for dry rayon. Thus it is clear that the positive slope of some of the curves at some temperature cannot

TABLE II
Comparison of the Term $W = (\partial n/\partial T)_{P,l} (\partial f/\partial l)_{P,T,n} (\partial l/\partial n)_{P,T,l}$ with the Measured Force-Temperature Coefficient at 25°C.

Sample	q	β , deg. $^{-1} \times 10^4$	$\partial n/\partial T$ g./g. deg. $\times 10^4$	$\partial f/\partial l$ g./den. % $\times 10^3$	$\partial l/\partial n$, %/g./g.	W , g./den. deg. $\times 10^4$	$(\partial f/\partial T)_{P,l}$ g./den. deg. $\times 10^4$	$(-\partial S/\partial l)_{P,T,l}$ g./den. deg. $\times 10^{4a}$
A	2.3	-6.7	-13.7	2.0	38	-1.14	0.47	-0.67
C	2.3	-9.3	-18.0	20	5.2	-1.84	0.18	-1.6
D	2.5	-13.3	-26.2	38	4.0	-4.1	0.13	-4.0
E	2.5	-12.7	-25.0	39	4.2	-3.9	-0.47	-4.4
F	2.5	-12.3	-24.3	59	4.1	-5.9	-0.74	-6.6

^a This column is the sum of the preceding two columns and is equal to $(\partial f/\partial T)_{P,l,n}$.

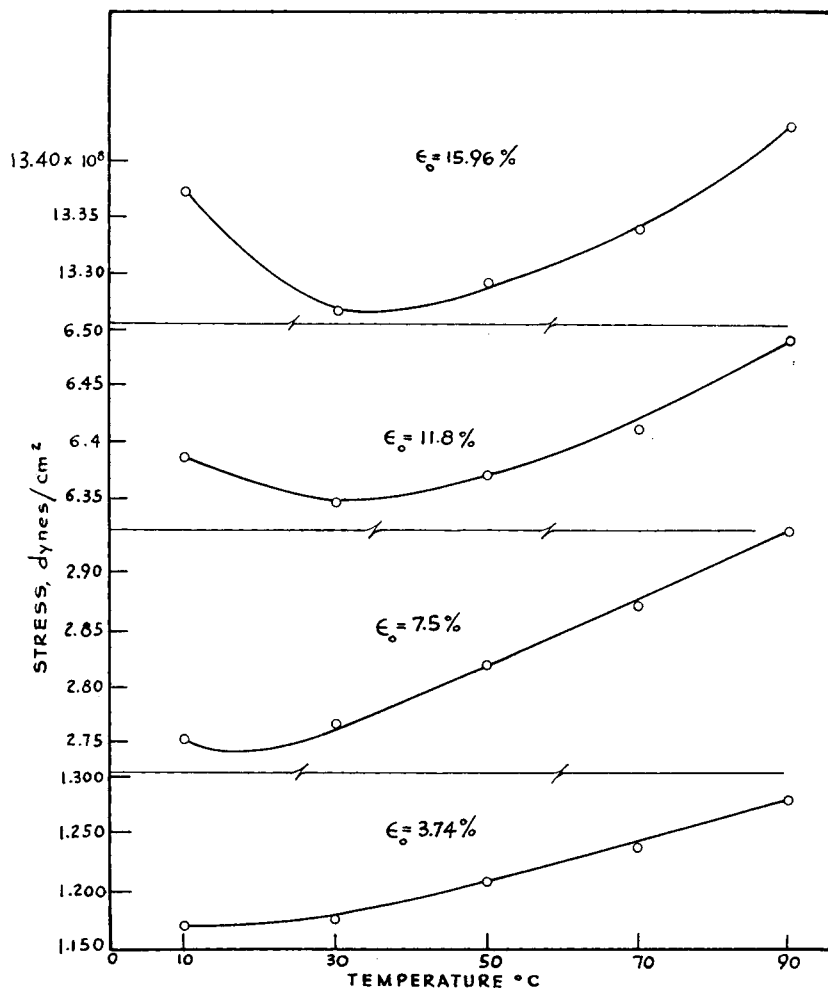


Fig. 6. Force-temperature behavior of a model filament with approximately 50% skin structure at various initial elongations.

be interpreted as a decrease in entropy of the polymer chains with extension, but is, rather, an expression of the manner in which the water content of the gel changes with temperature.

Unfortunately we cannot explain the maximum in the force-temperature curves. Unquestionably, these various correction terms are temperature sensitive, so that their effect at high temperatures

might be considerably less than at low temperatures. In that case, the measured force-temperature coefficient could change sign, and would be zero at the point where

$$-\left(\frac{\partial S}{\partial l}\right)_{T,P} = \left(\frac{\partial n}{\partial T}\right)_{P,l} \left(\frac{\partial f}{\partial l}\right)_{P,T,n} \left(\frac{\partial l}{\partial n}\right)_{P,T,l}$$

The accuracy of determination of these quantities

was not high enough to allow their precise evaluation over the whole temperature range. The measurement of $(\partial n/\partial T)_{P,l}$ is particularly bad since the filaments are quite small (diameter = 0.2 mm.), and all that could be obtained was an average value, with a precision within, perhaps, $\pm 30\%$. In order to investigate the detailed behavior of the force-temperature coefficient over the whole temperature, all the quantities would have to be determined over the whole range of forces and temperatures.

E. Behavior of Skin Filaments

It is instructive to ask why these filaments have such a different behavior from that more commonly observed for cellulose fibers, namely that which shows a minimum in the force-temperature curve. The type of yarns which best demonstrate this more "normal" behavior are tire yarns. The main structural difference between a tire yarn and a model filament is that the tire yarns have a "skin" structure while the model filaments have a "core" structure. The primary difference between these two types of structure¹⁴ is that the skin structure, relative to the core structure, is less crystalline, or at least has smaller and more imperfectly formed crystallites. Thus it becomes interesting to determine what type of force-temperature behavior would be exhibited by filaments with a skin structure. Several filaments of size comparable to the normal model filaments but with a structure which was about 50% skin were prepared and oriented in a manner similar to our D fiber. The force-temperature behavior of these filaments is shown in Figure 6. This behavior is very similar to that observed by Roseveare and Poore, *viz.*, the force shows a minimum, at which temperature the force increases with increasing orientation. Thus, it can be concluded that the force-temperature behavior is not dependent on orientation alone, but also on the type of microstructure of the rayon. Whether the difference in behavior can be ascribed to an actual difference in elastic mechanisms of the cellulose chains (which seems highly unlikely) or a difference in swelling characteristics brought about by a different morphological structure (which seems very likely) cannot at present be ascertained. What would be necessary is a detailed analysis of the swelling characteristics of the "skin" filaments. This was not done, and, because of their irregular crenulated cross section, would be rather hard to do.

IV. CONCLUSIONS

It can be concluded that changes in swelling with temperature are of primary importance in deter-

mining the force-temperature behavior of cellulose fibers, and any conclusions about the elastic mechanisms drawn without taking this into account are apt to be in error. It can also be concluded that changes in the microstructure of the cellulose, as exemplified by a change from a core structure to a skin structure, have a profound influence on the force-temperature behavior, for such a change in structure can even reverse it.

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Synopsis

The force as a function of temperature at constant length for cellulose model filaments swollen in water shows a maximum the temperature of which decreases with increasing orientation. At an orientation achieved by a prestretch of 80%, no more maximum exists, and the force decreases monotonically with increasing temperature. This behavior cannot be attributed to changes in the entropy and enthalpy of elongation with temperature, but is due rather to changes in the degree of swelling. When corrections are made for this, the positive force-temperature coefficient observed for some of the curves becomes negative. The equilibrium stress-strain curves are linear up to elongations of 5%. Theoretical evaluation of these curves is not possible with the present state of theory. Filaments with predominantly a skin structure show a minimum in the force-temperature curves; this is the more common behavior.

Résumé

Lorsqu'on considère la force de filaments de cellulose gonflés dans l'eau en fonction de la température et à longueur constante, on constate un maximum; la température de celui-ci décroît avec une augmentation d'orientation. À

une orientation de 80% obtenue par un étirement préalable il n'existe plus de maximum, et la force décroît monotoniquement avec une augmentation de température. Ce comportement ne peut pas être attribué à des variations d'entropie et d'enthalpie d'élongation avec la température, mais est dû à des variations du taux de gonflement. Lorsque des corrections sont faites pour cela, le coefficient positif du diagramme force-température observé dans certains cas devient négatif. Les courbes tension-élongation à l'équilibre sont linéaires jusqu'à des élongations de 5%. Une évaluation théorique de ces courbes n'est guère possible dans l'état actuel de la théorie. Les filaments avec une structure superficielle développée manifestent des courbes force-température à minimum, ce qui est le comportement le plus habituel.

Zusammenfassung

Für in Wasser gequollene Modell-Cellulosefasern zeigt die Kraft als Funktion der Temperatur, bei konstanter

Länge, ein Maximum; die Temperatur dieses Maximums nimmt mit zunehmender Orientierung ab. Bei einer Orientierung, die durch eine Vorstreckung um 80% erreicht wird, tritt kein Maximum mehr auf; es nimmt dann die Kraft monoton mit steigender Temperatur ab. Dieses Verhalten kann nicht den Veränderungen der Dehnungsentropie und -enthalpie mit der Temperatur zugeschrieben werden, sondern ist eher auf Veränderungen des Quellungsgrades zurückzuführen. Wenn die dafür erforderlichen Korrekturen angebracht werden, wird der bei einigen Kurven beobachtete positive Temperaturkoeffizient für die Kraft negativ. Die Gleichgewichts-Zug-Spannungskurven sind bis zu Dehnungen von 5% linear. Beim gegenwärtigen Stand der Theorie ist eine theoretische Auswertung dieser Kurven nicht möglich. Fässern mit einer vorherrschenden Hautstruktur zeigen in der Kraft-Temperaturkurve ein Minimum, was dem allgemeineren Verhalten entspricht.

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