JOURNAL OF APPLIED POLYMER SCIENCE VOL. II, ISSUE NO. 4, PAGES 32-38 (1959)

The Effect of the Sorption Process on the Dynamic Rigidity Modulus of the Wool Fiber

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INTRODUCTION

The paper describes measurements made of the dynamic rigidity modulus of wool fibers during the period when the fibers are sorbing or desorbing water (from the vapor phase). Anomalous behavior is observed including reduced values of rigidity modulus. The behavior appears to provide direct evidence of stresses being induced during the sorption process.

EXPERIMENTS AND DISCUSSION OF RESULTS

The dynamic rigidity modulus of wool fibers was measured by the well-known method (see, e.g., Speakman[1]) of using the fiber as the suspension of a torsion pendulum. The modulus n is related to the period of oscillation T, the length l and radius R of the fiber, and the moment of inertia I of the bob (all of which quantities can be determined) by the expression

$$n = 8\pi(Il/T^2R^4) \quad (1)$$

The method is well established[1,2] for determination of the equilibrium value of rigidity modulus of fibers under given conditions of regain, temperature, etc.

In the present series of experiments cleaned Merino wool fibers were used, of mean diameter 25 μ and length 3.50 cm. The bob was a brass disk of mass 0.68 g. and moment of inertia 0.059 g. cm.^{2} rotating in its own (horizontal) plane; the weight of the bob was just sufficient to remove the fiber crimp. The period of the oscillations observed was in the range 17 to 33 sec.

If the period of oscillation is measured while the suspension fiber is sorbing or desorbing water vapor, the effect of the sorption process on the rigidity modulus can be observed. Curve I of Figure 1 shows the result of such an experiment, in which a fiber which had been dried (0% relative humidity (R. H.) at 20°C. for 20 hr.) was suddenly introduced into an atmosphere of 61% R. H. For convenience relative rigidity rather than rigidity modulus has been plotted. The term rigidity is here taken to mean the restoring torque per unit angular displacement of the bob. Denoting this by N we have

$$N = (\pi/2)(nR^4/l) \quad (2)$$

$$= 4\pi^2(I/T^2) \quad (3)$$

Relative rigidity is defined

$$N/N_0 = (T_0/T)^2 \quad (4)$$

where N_0 is the rigidity of the dry fiber and T_0 the period of oscillation with the dry fiber as suspension. As abscissa (time$^{1/2}$) is used, chiefly for convenience in presenting the time range involved. The striking feature of the curve (Curve I) is the pronounced "undershoot" followed by a gradual recovery toward the equilibrium value. The latter value agrees closely with published data. Figure 1 also shows the regain vs. time$^{1/2}$ curve (curve II) obtained simultaneously during the experiment by the automatic vibroscope[3] method.

The pronounced dip in the curve of relative rigidity requires explanation. If relative rigidity is calculated for a series of values of regain, using eq. (2) and published equilibrium values for rigidity modulus[1] and fiber radius,[4] no dip is observed. This curve is plotted in Figure 1 as Curve III. (The slight rise in N/N_0 at the beginning is due to increasing diameter outweighing the falling rigidity modulus in this regain range.)

It is not strictly correct to take equilibrium values of swelling vs. regain to calculate rigidity during the sorption process since the water is then not uniformly distributed through the fiber. The outer part of the fiber has nearly attained its equilibrium

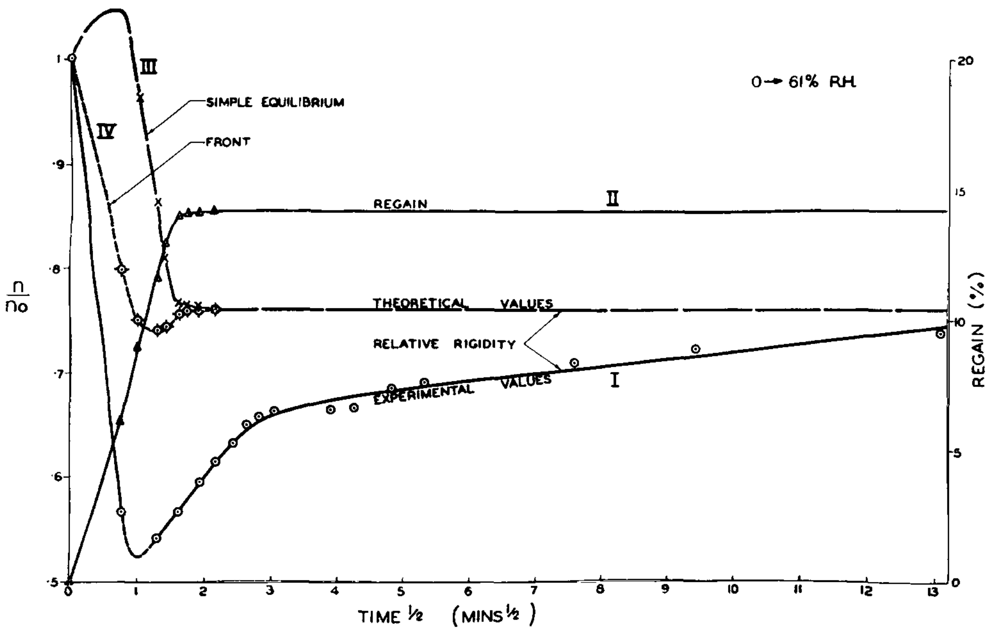

Figure 1.

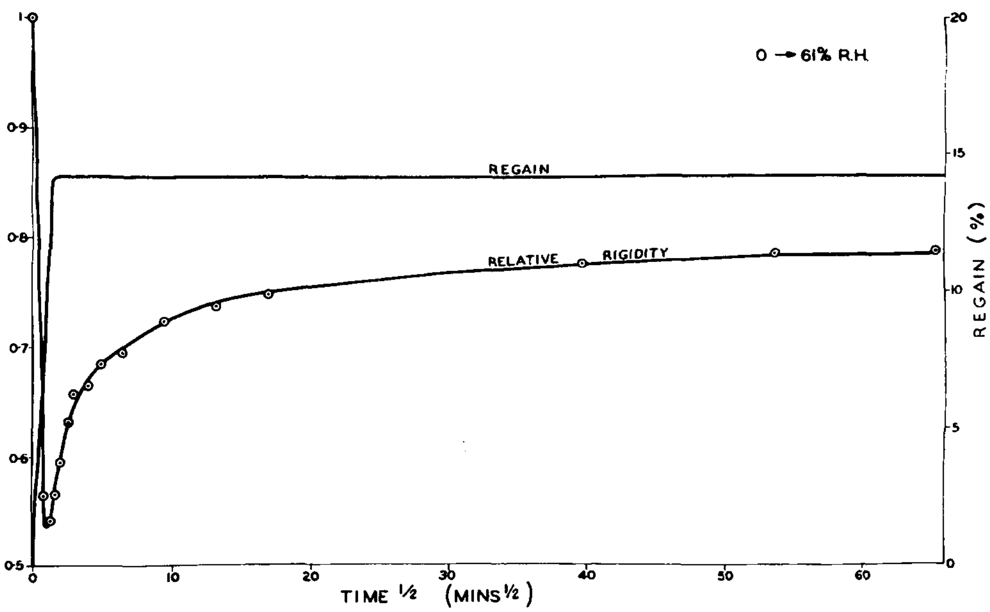

Figure 2.

regain and is separated from the inner part by a region of steep concentration gradient, so that the water penetrates with a pronounced "front."[5,6] Qualitatively this behavior can explain a dip in the rigidity vs. time curve since early in the sorption process the outer part of the fiber, which is principally responsible for the torsional rigidity, will have sorbed water and have a lowered modulus, but the fiber diameter will not have increased much owing to the constraint of the inner unswollen region. For both these reasons the rigidity of the fiber will fall. Subsequently the inner part of the fiber will swell and the overall diameter of the fiber increase, so that the fiber rigidity will increase somewhat (see eq. (2)). The rigidity can therefore be expected to pass through a minimum value. However, an estimate of the magnitude of this effect has been made (see Appendix) and plotted as Curve IV, Figure 1 from which the effect may be seen to be by no means sufficient to account for the observed behavior of Curve I. In fact, even if the extreme and obviously unattainable case is assumed in which the fiber has the equilibrium value of rigidity modulus for 61% R. H. but a diameter corresponding to 0% R. H., the predicted value of N/N_0 would not fall below 0.59 whereas the experimental value at the dip is 0.52.

It seems impossible therefore to account for the observed behavior of Curve I in terms of equilibrium values of rigidity modulus. The indication is that there is during the sorption process a transient reduction in value of the modulus to well below the final equilibrium value to which it finally recovers. The cause of this reduction is probably the transient stress arising from the differential swelling during water penetration. Stresses due to differential swelling have been observed by Hermans[7] in isotropic cellulose filaments and have been estimated by Crank[8] in a study of anomalous diffusion in polymers. In wool fibers also there is evidence,[5,9] e.g., from kinetic studies of sorption, for a tensile radial stress in the vicinity of the penetrating front, the stress being greater the more abrupt is the front. If this stress causes temporary rupture of some of the radial bonds in the structure, it is likely that the torsional rigidity will be lowered. After the passage of the front, the stress will fall and reformation of bonds can be expected. The observed rate of recovery of the rigidity (Curve I, Figure 1) is comparable with the rate of the second stage of interval desorption in wool, where a mechanism of bond reformation has also been postulated.[9] Figure 2 shows the recovery on an extended time scale. An interesting feature is the considerable change in rigidity which occurs long after equilibrium regain has been attained.

A series of experiments has been conducted in which the relative humidity around the fiber has been increased from 0 to 61% at different rates, with a corresponding variation in the rate of regain change (Fig. 3a). As the rate is reduced the steepness of the concentration gradient in the fiber and the magnitude of the stresses associated with it also fall. The corresponding behavior of the dynamic rigidity modulus is shown in Figure 3b. The anomalous dip in modulus becomes less marked and eventually disappears as the rate of regain change is reduced, behavior which is consistent with the idea that the temporary reduction in modulus is brought about by the transient sorption-induced stress associated with the front.

The effect of a very large and sudden increase in regain is seen in Figure 4, where relative rigidity is plotted against time$^{1/2}$ for the case of a step in R. H. from 0 to 94% approximately. In this case the transient reduction in rigidity is so pronounced that no oscillation of the pendulum is obtainable initially. Apparently the stress is so great as to bring the material temporarily close to a state of torsional plasticity.

Interesting behavior is also observed during the desorption process and is illustrated in Figure 5. A fiber was subjected to an abrupt fall in surrounding humidity from 94% approximately to 61% R. H. In these circumstances a very sharp initial fall in regain occurs.[9] Observation of the relative torsional rigidity over this period and subsequently showed it to increase much more slowly than would be predicted from the observed rate of regain change using equilibrium values[1] of dynamic modulus. For example, 80% of the regain change plotted in Figure 5 occurs in 0.41 min., but 80% of the change in relative rigidity occupies 13.6 min. Again the explanation of this anomaly is believed to lie in stresses associated with a concentration gradient. During desorption there is no advancing front corresponding to that in sorption, but there is nevertheless a steep concentration gradient at the fiber surface early in the desorption process.[6] The fiber may be thought of as having a skin of low regain stretched over a core of high regain, with high tensile tangential stress in the surface layer. As before the stress can be expected to break some bonds and reduce the rigidity modulus in this region. After the stress has dropped back to its final value the bonds will gradually reform and the modulus will rise toward its equilibrium value. The rate of approach to equilibrium is seen to be almost identical with the rate at which rigidity recovers in the sorption process, as would be expected on the present theory.

Some measurements made of damping of the oscillations in the torsion pendulum experiments show that the changes in internal friction of the fiber during sorption are correlated with the anomalous behavior of the rigidity modulus. For example, in a change from 0 to 65% in ambient R. H. the equilibrium value of internal friction was found to increase by a factor of 3, but during the sorption process the internal friction reached a transient value more than six times its initial value.

Summarizing the results presented, we may say:

(*1*) When a large increase is made in the relative humidity surrounding a wool fiber, its dynamic torsional rigidity is found to pass through a minimum value considerably less than the final equilib-

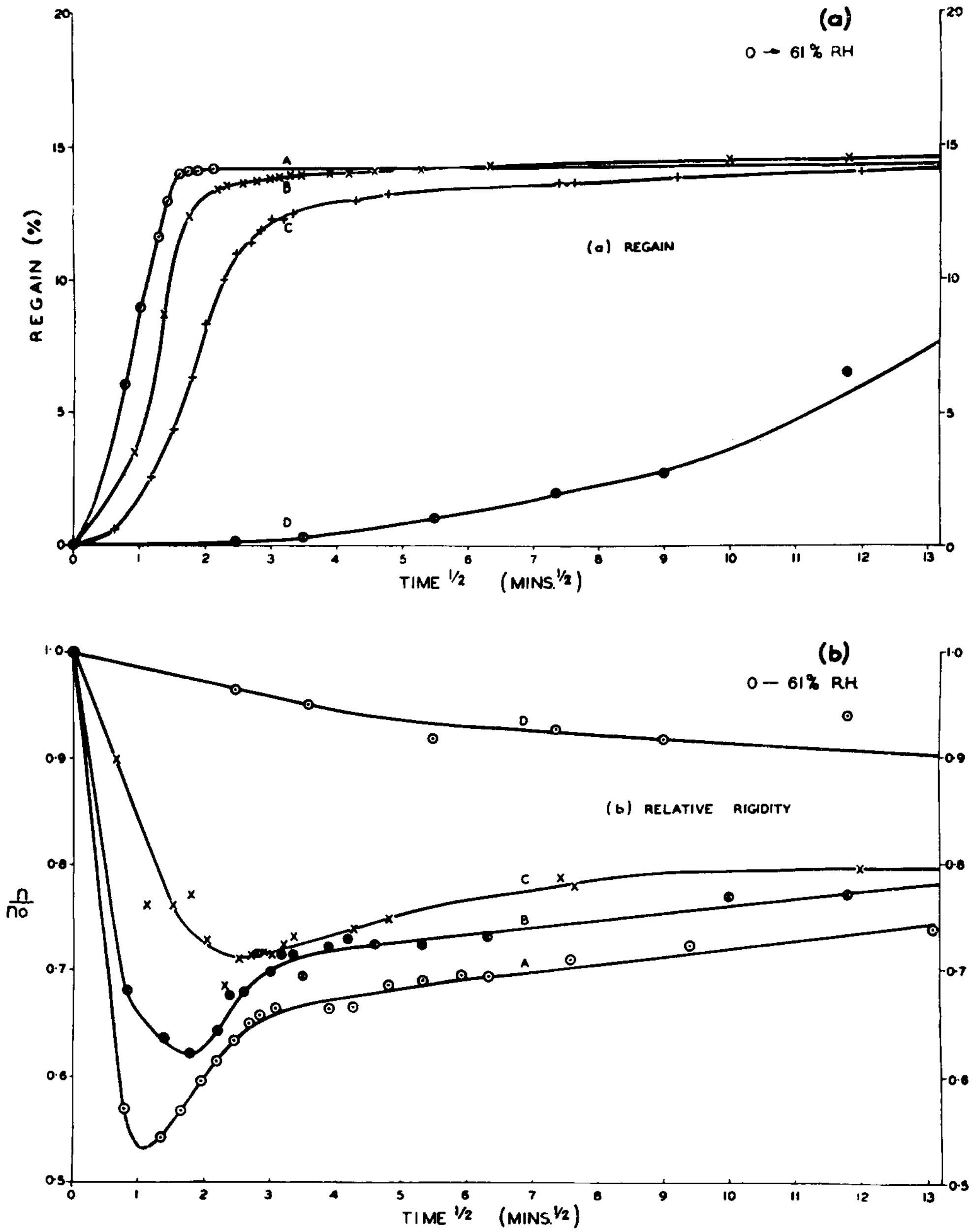

Figure 3.

rium value (Figure 1). This is true for all except very gradual increases in humidity.

(*2*) The more abrupt the increase in R. H., and the larger the step, the more pronounced is the effect (Fig. 3).

(*3*) The recovery from the minimum to the equilibrium value of rigidity takes much longer than the time to regain equilibrium.

(*4*) The effect cannot be accounted for in terms of fiber geometry during sorption, assuming equilibrium values of rigidity modulus for the regains concerned.

(*5*) The probable explanation of the temporary reduction in rigidity modulus is that it is due to the transient stresses produced as a result of differential swelling during the penetration of the water "front" into the fiber and that these stresses cause temporary rupture of bonds which contribute to the rigidity.

(*6*) During desorption also values of dynamic rigidity modulus are observed to be lower than the equilibrium values. Stresses due to differential swelling again offer the probable explanation.

(*7*) Simultaneously with the behavior in rigidity

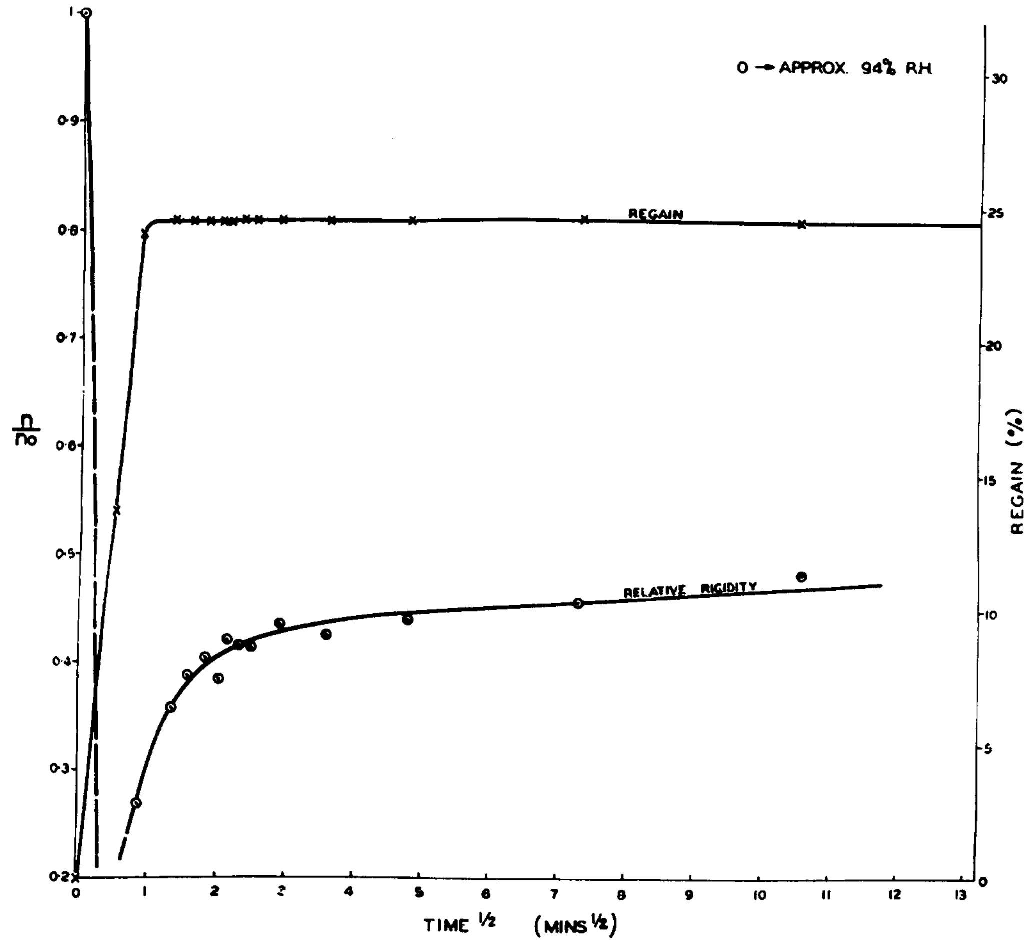

Figure 4.

during sorption, anomalous effects are observed in the internal friction, which increases to a transient value much greater than the final value at equilibrium.

Although the observations reported have been confined to the dynamic rigidity modulus of the wool fiber, the pronounced transient disturbance to the structure which apparently occurs during sorption may be expected to influence other mechanical behavior, e.g., the "static" torque in a twisted fiber. Furthermore, the results presented here are likely to be observed qualitatively in other natural and synthetic fibers. They emphasize the need to distinguish between transient and equilibrium values in determinations of dynamic modulus of rigidity.

APPENDIX

Torsional Rigidity of a Fiber with Nonuniform Regain Distribution

A number of assumptions will be made to simplify the solution. The case here considered is that of a dry fiber suddenly transferred into a humid atmosphere. We assume that water penetrates with an abrupt front; i.e., that from the center to a radius r the fiber is dry and for radii from r to R

TABLE I[a]

Time (min.$^{1/2}$)	0	0.765	1.000	1.29	1.41	1.61	1.73	1.93	2.17
Regain (%)	0	6.16	9.00	11.68	12.95	14.00	14.07	14.11	14.20
Relative radius, R/R_0	1.000	1.023	1.036	1.047	1.053	1.058	1.0585	1.0587	1.059
Relative rigidity, N/N_0	1.000	0.789	0.741	0.724	0.729	0.739	0.740	0.742	0.742

[a] The results for N/N_0 vs. time$^{1/2}$ are plotted in Curve IV of Figure 1.

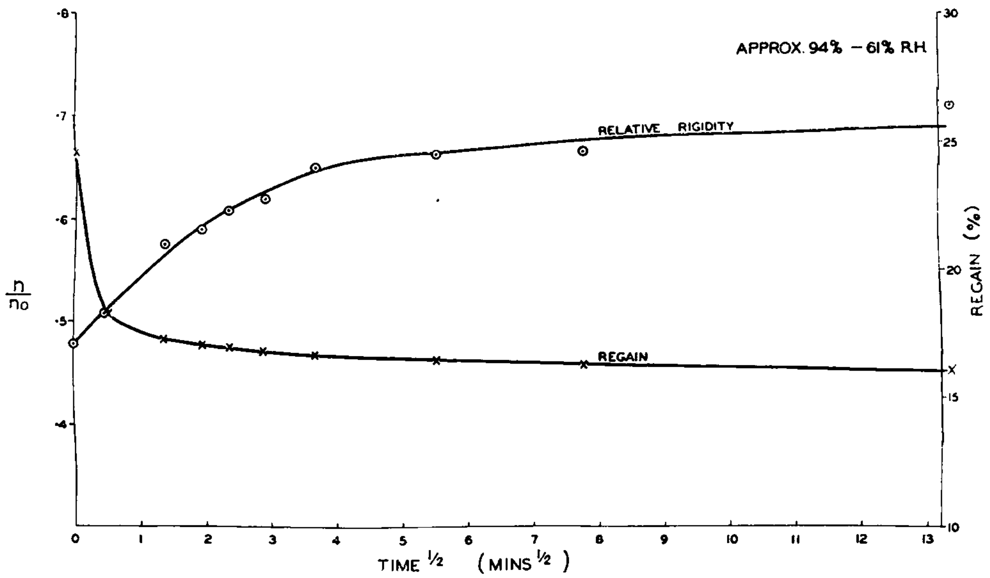

Figure 5.

(where R = fiber radius), the fiber is at a regain ρ_a in equilibrium with the surrounding humidity. For radii 0 to r the rigidity modulus is assumed to have the equilibrium value n_0 of a dry fiber; similarly for radii r to R a value n is assumed which is the equilibrium value for a fibre of regain ρ_a. Furthermore, the radius of the fiber at any instant is assumed to have the same value as it would if the sorbed water were uniformly distributed.

The torsional rigidity of a rod of radius r, length l, and rigidity modulus n_0 is

$$N_0 = (\pi/2)(n_0 r^4/l) \quad (5)$$

Similarly the rigidity of a hollow cylinder of modulus n and of inner and outer radii r and R, respectively, is

$$N_1 = (\pi/2)(n/l)(R^4 - r^4) \quad (6)$$

The fiber will be regarded as compounded of such a rod and cylinder, and will have a rigidity N equal to the sum of N_0 and N_1.

$$N = (\pi/2l)(n_0 r^4 + n(R^4 - r^4)) \quad (7)$$

The relative rigidity N/N_0, where N_0 is the rigidity of the dry fiber, is given by

$$N/N_0 = (r/R_0)^4[1 - (n/n_0)] + (n/n_0)(R/R_0)^4 \quad (8)$$

where R_0 = radius of the dry fiber.

The assumptions made above concerning regain distribution imply that

$$\pi(R^2 - r^2)\ \rho_a = \pi R^2 \rho \quad (9)$$

where ρ is the regain of the fiber as a whole and is that value for which the fiber radius would be R under equilibrium conditions.

From eq. (9) we have

$$r^2 = R^2\ [1 - (\rho/\rho_a)]$$

whence

$$(r/R_0)^4 = (R/R_0)^4\ [1 - (\rho/\rho_a)]^2 \quad (10)$$

Substituting eq. (10) in eq. (8) and simplifying, we get

$$N/N_0 = (R/R_0)^4\ \{[1 - (n/n_0)][1 - (\rho/\rho_a)]^2 + (n/n_0)\} \quad (11)$$

We now evaluate eq. (11) for the case of an increase in ambient humidity from 0 to 61%. The ρ_a has been measured as 14.2%, and from Speakman's equilibrium data[1] on rigidity modulus we find n/n_0 = 0.590. Table I gives the results of calculations for a series of time values and corresponding regains taken from Curve II of Figure 1. The required values of R/R_0 were obtained from published data.[4]

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Synopsis

Using a torsion pendulum, measurements have been made of the dynamic modulus of rigidity of wool fibers during the process of sorbing or desorbing water (from the vapor phase). Anomalous behavior is observed, with low values of rigidity which cannot be accounted for in terms of equilibrium data. It appears that transient stresses occurring during sorption and desorption cause a temporary lowering of the rigidity modulus.

Résumé

En utilisant un pendule de torsion, on a effectué des mesures du module dynamique de rigidité de fibres de laine au cours du processus de sorption et désorption d'eau (venant de la phase vapeur). Un comportement anormal s'observe pour des faibles valeurs de rigidité; il ne peut s'accorder avec les résults obtenus à l'équilibre. Il apparait que des forces transitories formées au cours de la sorption et de la désorption, provoquent un abaissement temporaire du module de rigidité.

Zusammenfassung

Mittels eines Torsionspendels wurden Messungen des dynamischen Moduls der Steifigkeit von Wollfasern während des Prozesses der Sorption und Desorption von Wasser (aus der Dampfphase) ausgeführt. Es wird ein anomales Verhalten mit niedrigen Steifigkeitswerten beobachtet, das mit den Gleichgewichtsdaten unverträglich ist. Es scheint, dass während der Sorption und Desorption vorübergehend Spannungen *auftreten*, die eine *zeitweilige Erniedrigung* des Steifigkeitsmoduls verursachen.

Received December 16, 1958