Diffusion-Controlled Mechanical Properties of Polyvinyl Alcohol and Polyvinyl Formals

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INTRODUCTION

When water vapor diffuses into a polymeric solid such as polyvinyl alcohol, the solid is softened, due either to the breaking of water-sensitive bonds such as hydrogen bonds, or to the plasticizing effect of the penetrant. The softening process effected by diffusion of water molecules may be traced quantitatively by observation of its accompanying mechanical effects. Hence, various studies[1] of the mechanical process have lately been carried out elsewhere in an effort to clarify the action of water molecules upon the structure of solids.

Meanwhile, recent researches on the diffusion of water into polymeric solids have revealed two types of diffusion behavior: (1) diffusion in which the diffusion coefficient depends only on concentrations in a system such as Amilan–water, (2) diffusion in which the diffusion coefficient depends both on concentration and on time, in a system such as polyvinyl alcohol–water.[2]

In the former case, the research by A. Kishimoto and H. Fujita[1] on the mechanical process occurring in the adsorption of water has successfully revealed some useful information on the action of water on the structure of polymer. For the latter case, however, their theory did not provide satisfactory explanations.

The present authors have tried to elucidate the diffusion mechanism of water molecules into PVA film at temperatures below the glass transition by observing a mechanical effect: the creep phenomenon attendant on adsorption of water. In analyzing the creep curves according to a simple Voigt model, the following assumptions are made. (1) As in the case of other elastomers, the crystal parts of the film perform the role of the network junctions, while the amorphous parts act as the network chains. (2) It is only the hydrogen bonds in the network chains that participate in the resistance against the elongation of PVA film, and thus the breaking of the hydrogen bonds by absorption of water molecules contributes to the elongation of the film. (3) The diffusion of water molecules proceeds in a manner usually denoted as time-dependent, non-Fickian behavior. Thus, as described in the previous paper,[3] the theoretical formulation for the creep curves at different temperatures and relative humidities is approximately derived, and the activation energy and entropy for the diffusion process is calculated accordingly.

To confirm the hypothesis that such creep phenomena can be described quantitatively by the theoretical treatment proposed here, suitable experiments have been carried out on polyvinyl alcohol and a family of polyvinyl formals (PVF) of different degrees of "formalization," i.e. polyvinyl alcohols in which some of the hydroxyl groups have reacted to acetals with formalin, and crystallinity.

EXPERIMENTAL

Materials

The polyvinyl alcohol used in the present study was furnished by Kurashiki Rayon K.K., and the degree of polymerization was about 2,000. Polyvinyl formals (PVF) of varying degrees of formalization were prepared by stirring a mixture of about 1 g. PVA and the desired equivalent amount of formalin in 20 ml. of $3N$ HCl for 5–6 hr. at 40–50°C. Then, the PVF was purified by washing and reprecipitation with methyl alcohol.

Films of these polymers were prepared by slow evaporation (at room temperature for about a week) of about 2% aqueous solution (or pyridine–water solution) of polymer cast on a mercury surface. The films thus obtained were dried in a vacuum desiccator for 3–4 days.

The degrees of formalization of the sample films, measured by the usual acetylation method with pyridine–anhydride acetic acid (3:1) mixture, were 6, 15.4, and 42.5%. Each film, when finally ex-

amined, was about 0.0015 cm. in thickness, 10 cm. in length, and 0.5 cm. in width.

Experimental Apparatus and Procedure

An improved Morey's apparatus[5] (Fig. 1) was used to put the sample film under a constant stress during the measurement. The apparatus was placed in an air thermostat controllable to an accuracy of ±0.2°C.

First, the sample film was set between clips s_1 and s_2 in vessel v_1 in which the relative humidity was kept constant at a given value by the concentration of the aqueous H_2SO_4 solution poured into the vessel v_2. The elongation of the film was read as proportional to the angle rotated through by a needle (shown at the top of the diagram). Elongations up to 0.003 cm. could be read. In the present experiment, the stress applied to each film by a 20-g. weight loaded on dish w was kept constant at nearly 2×10^7 dynes/cm.[2]

EXPERIMENTAL RESULTS

Figures 2–5 show, respectively, creep behavior for PVA, PVF, (6%), PVF (15.4%), and PVF (42.5%). Each figure shows creep curves at relative humidities of 60, 67, 74, and 81% at a constant temperature of 30°C.

Figures 6, 7, and 8 show respectively, creep curves for PVA, PVF (6%), and PVF (42.5%). In each figure are given creep curves at temperatures of 20, 30, 40, and 50°C. at a constant relative humidity of 60%.

Each creep curve attains a constant equilibrium value in about 100 minutes, and each has its characteristic inflection point. It is also found that, the higher the temperature and relative humidity, the earlier the inflection point occurs. In order to study the creep phenomena of the films and to make the subsequent theoretical treatment easier, the values of equilibrium elongation under each measuring condition are given in Table I.

Table II shows the time required for the inflection point to appear in each curve under different conditions.

Table I also shows the relation between the degree of equilibrium elongation and the degree of formalization at different relative humidities and constant temperature of 30°C. From this table, it is seen that the equilibrium elongation shows a maximum in the range of formalization between 10 and 20%. This may be explained by reference to
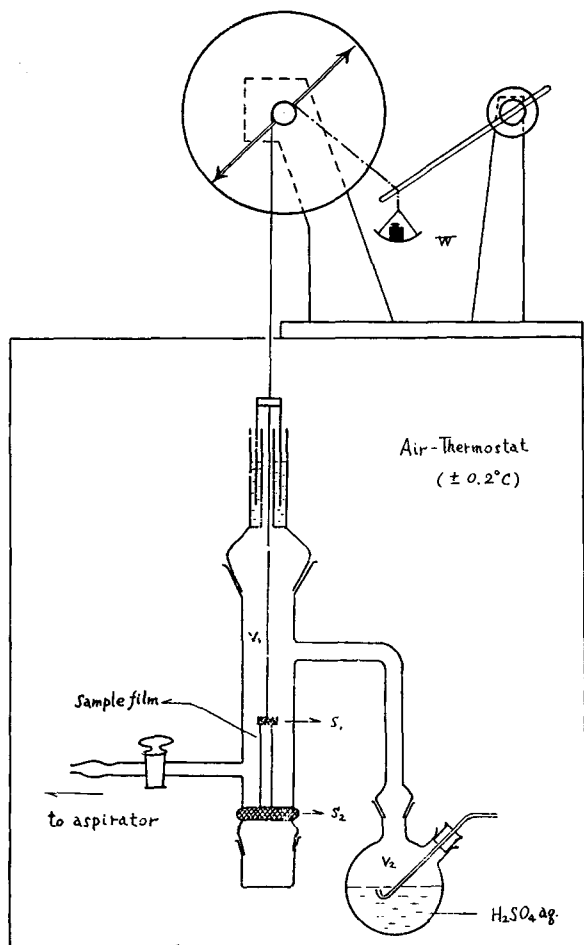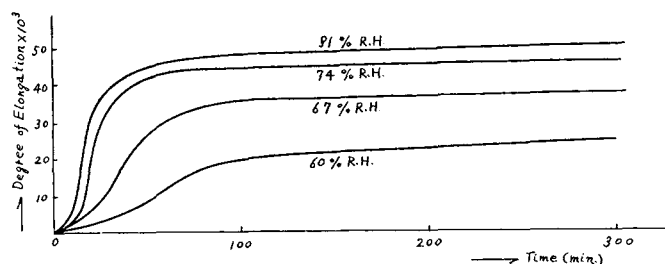

Fig. 1. Experimental apparatus.

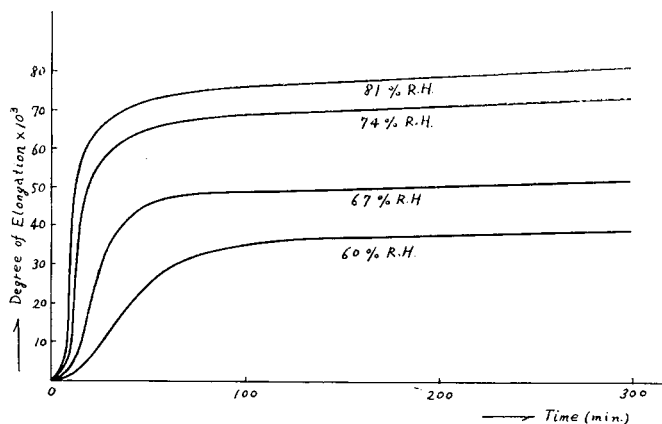Fig. 2. Creep curves for PVA film at various relative humidities, 30°C.

Fig. 3. Creep curves for PVF (6%) film at various relative humidities, 30°C.
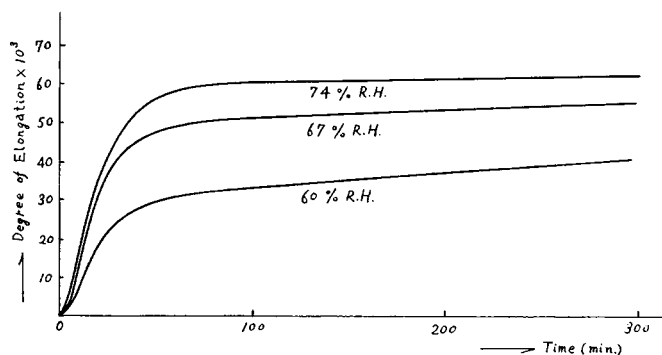

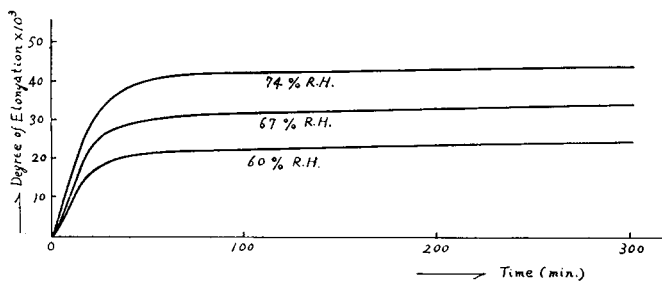Fig. 4. Creep curves for PVF (15.4%) film at various relative humidities, 30°C.

Fig. 5. Creep curves for PVF (42.5%) film at various relative humidities, 30°C.

the fact that the proportion of amorphous polymer in the PVF film becomes maximum when the degree of formalization reaches 10–20%; and to the fact that the penetration of the water molecules into the crystalline polymer on the other hand, is much restricted, as was reported previously.[6]

THEORETICAL

As was reported in the previous paper,[3] it is assumed that the elongation of films is due to the breaking of hydrogen bonds in the amorphous parts of the film, through adsorption of water molecules at the OH-radical sites. Of all the water molecules adsorbed on the polymer film, the portion adsorbed at the OH-radical sites is to be considered in this paper.

Let us assume N to be the number of OH-radical absorbing sites, N' to be the number of other adsorbing sites on the film, n_1 to be the number of the water molecules adsorbed on OH-radicals, and likewise n_2 the number adsorbed on the other sites, the total regain of adsorbed water molecules being n.

Since the differentials of free energy $\partial F/\partial n_1$ and $\partial F/\partial n_2$, must be zero when the equilibrium adsorption is attained, n_1 and n_2 may be calculated ap-
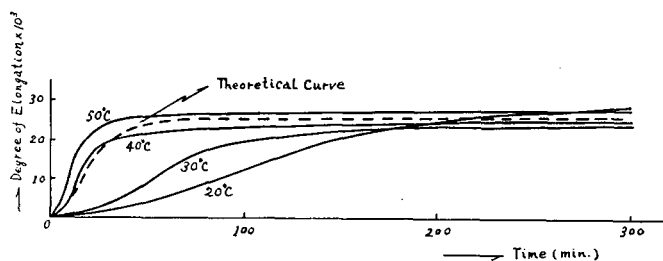
Fig. 6. Creep curves for PVA film at various temperatures, 60% R.H. (——); theoretical curve at 40°C., 60% R.H. (———).
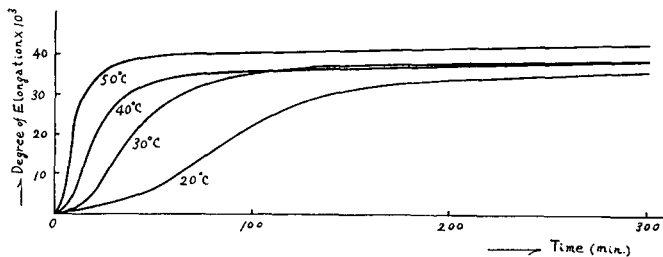

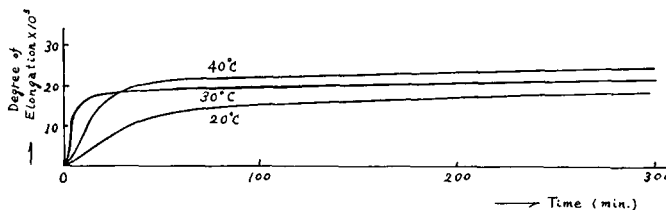Fig. 7. Creep curves for PVF (6%) film at various temperatures, 60% R.H.

Fig. 8. Creep curves for PVF (42.5%) film at various temperatures, 60% relative humidity.

proximately as below, assuming $E_1 - E_2 \gg kT$, where E_1 is the heat of adsorption of water on the OH radical and E_2, that on the other sites, thus:

$$n_1 = Nn/(N + i)$$
$$n_2 = n^2/(N + n)$$
(1)

As described in detail in the previous paper, and assuming that no bonds between the network chains other than the hydrogen bonds in the amorphous parts (which are weak and easily broken) contribute to elongation, the equilibrium elongation is represented as follows:

$$\gamma_\infty \sim Nn/(N + n)$$
(2)

Because the crystalline parts of the film perform a role similar to that performed by the network in other elastomers,[7] a final and constant elongation is eventually attainable (though not immediately, owing to the potential between the chains). Thus,

the situation can be represented by a simple Voigt model[4] in which ϵ is the elasticity factor and η is the viscosity factor in the "dashpot" analogy; the following equation is then obtained for equilibrium adsorption:

$$\gamma = \gamma_\infty(1 - e^{\kappa t})$$
(3)

where $\kappa \equiv \epsilon/\eta$.

Elongation attending adsorption of water is computed by summing each elongation $\Delta\gamma_t$ in each successive period $\Delta t;$ each elongation is calculated by setting γ_∞ equal to $\gamma_{\infty 1}, \gamma_{\infty 2}, \gamma_{\infty 3} \ldots \gamma_{\infty i}$ in eq. (3). Here, $\gamma_{\infty 1}, \gamma_{\infty 2}, \ldots \gamma_{\infty i}$ are successive equilibrium elongations for each period Δt. Figure 9 illustrates schematically the accumulation of $\Delta\gamma_t$ in each period Δt, while each curve is represented by eq. (3). For the first period Δt in which the film regains water at a constant rate, the elongation is expressed by eq. (3), thus:

$$\Delta\gamma_1 = \gamma_{\infty 1} \kappa_1 \Delta t$$

TABLE I
Degrees of Elongation at Equilibrium Elongation

Films	$\gamma_\infty \times 10^3$ at 30°C. and various relative humidities				$\gamma_\infty \times 10^3$ at 60% R.H. and various temperatures			
	60%	67%	74%	81%	20°C.	30°C.	40°C.	50°C.
PVA	27.0	39.2	46.8	51.5	30.5	27.0	25.8	29.4
PVF (6%)	40.3	53.8	74.5	84.0	38.1	40.3	39.2	44.2
PVF (15.4%)	42.6	55.7	62.4	—	—	42.6	—	—
PVF (42.5%)	25.7	34.3	44.2	78.1	18.0	25.7	21.6	—

TABLE II
Time t_0 of Inflection of Creep Curves

Films	t_0 at 30°C. and various relative humidities, min.				t_0 at 60% R.H. and various temperatures, min.			
	60%	67%	74%	81%	20°C.	30°C.	40°C.	50°C.
PVA	58	30	19	14	112	58	13	9
PVF (6%)	30	19	14	9	82	30	16	7
PVF (15.4%)	14	12	11	—	—	14	—	—
PVF (42.5%)	8	7	6	—	18	8	4	—

Similarly, for the 2nd and ith Δt periods, the following equations are obtained:

$$\Delta\gamma_2 = \gamma_{\infty_2}K_2 \exp\left\{-K_2(\Delta t - \Delta t_1)\right\}\Delta t$$

$$\Delta\gamma_i = \gamma_{\infty_i}\kappa_i \exp\left\{-\kappa_i[(i-1)\Delta t - \Sigma\Delta t_1]\right\}\Delta t$$

Generalizing each relation, omitting suffixes, we have:

$$\Delta\gamma = \gamma_\infty\kappa \exp\left\{-\kappa(t - \Sigma\Delta t_1)\right\}\Delta t \qquad (4)$$

where the terms $\kappa_1, \kappa_2, \ldots \kappa_i$ are conveniently substituted for by the given mean value κ for the entire duration of the process, although κ_i may have different values corresponding to each γ vs. t curve. Furthermore, as reported in our previous paper,[3] a series of equations is obtained:

$$\Delta\gamma_1 = \gamma_{\infty_2}[1 - \exp\left\{-\kappa_2(\Delta t - \Delta t_1)\right\}]$$

$$\Delta\gamma_1 + \Delta\gamma_2$$
$$= \gamma_{\infty_3}[1 - \exp\left\{-\kappa_3(2\Delta t - \Delta t_1 - \Delta t_2)\right\}]\ldots$$

$$\Delta\gamma_1 + \Delta\gamma_2 + \ldots + \Delta\gamma_{i-1}$$
$$= \gamma_{\infty_i}[1 - \exp\left\{-\kappa_i[(i-1)\Delta t - \Sigma\Delta t_1]\right\}]$$

Simplifying likewise and summing the equations, the elongation γ is expressed thus in eq. (5), since $\Delta\gamma_1 + \Delta\gamma_2 + \ldots = \Delta\gamma$:

$$\dot\gamma = \gamma_\infty\left\{1 - e^{-\kappa t}e^{\kappa\Sigma\Delta t_1}\right\} \qquad (5)$$

Eliminating $\exp\left\{\kappa\Sigma\Delta t_1\right\}$ through eqs. (4) and (5), we have:

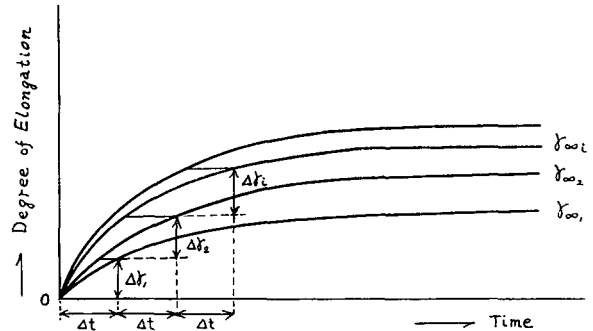$$d\gamma/dt + \kappa\gamma = \kappa\gamma_\infty \qquad (6)$$

Fig. 9. Schematic illustration for the accumulation of $\Delta\gamma_i$ in each Δt period when elongation vs. time curve is represented by successive Voigt models.

where, needless to say, γ_∞ depends upon time t.

If the time-dependence of γ_∞ is known, eq. (6) can be solved with respect to t. It is also revealed that γ_∞ depends upon the number of water molecules adsorbed on OH radicals in the amorphous parts of the film. The number of water molecules is computed approximately from the total regain of water molecules in the film, as given in eq. (2). Therefore, if the total regain of water molecules could be obtained as a function of time, the dependence of γ_∞ upon time t would also be known. Consequently, in order to know the total regain of water molecules in the progress of adsorption, the diffusion process of water molecules into the film has to be investigated in some detail.

Considering that the strong interaction between the network chains is due to the hydrogen bonds.

it may be expected that the relaxational movement of the segments in the chains would cause non-Fickian diffusion, as reported by Crank and Park;[2] hence, the dependence of the diffusion coefficient both on concentration and on time is expressed as:

$$dD/dt = \alpha(D_c - D) \qquad (7)$$

where D_c is the equilibrium diffusion coefficient, c is the concentration of water in the film, and α is the rate constant at which diffusion coefficient D attains the equilibrium value D_c. Integrating eq. (7) with respect to time, we have:

$$D = D_c(1 - e^{-\alpha t}) \qquad (8)$$

Now, let c_0 be the concentration of water at the surface of the film and c, the concentration in the layer a distance λ from the surface, and α' the rate of diffusion of the water molecules. Then, dc/dt can be assumed to be expressed by the first-order relation:

$$dc/dt = \alpha'(c_0 - c) \qquad (9)$$

Integrating eq. (9), we have:

$$c = c_0(1 - e^{-\alpha' t}) \qquad (10)$$

For the gradient of concentration, the following equation is obtained:

$$(c_0 - c)/\lambda = c_0 e^{-\alpha' t}/\lambda \qquad (11)$$

If D_c is taken as an integrating diffusion coefficient and Q as the quantity of adsorbed water, the following equation, assuming that α in eq. (8) and α' in eq. (9) are equal, is obtained:

$$dQ/dt = (c_0 D_c/\lambda)(1 - e^{-\alpha t})e^{-\alpha t} \qquad (12)$$

Letting l represent the thickness of the film, and substituting $c = Q/\lambda$ in eq. (10), we have the following equation:

$$dc/dt = F(l)(c_0 D_c/\lambda)(1 - e^{-\alpha t})e^{-\alpha t} \qquad (13)$$

where $F(l)$ is a form factor. Since the term $F(l)c_0 D_c/\lambda$ in eq. (13) designates a constant under the present experimental conditions, we have the following equation:

$$dc/dt = A(1 - e^{-\alpha t})e^{-\alpha t} \qquad (14)$$

where A is a constant. Integrating eq. (14), we have,

$$c = (A/2\alpha)(1 - e^{-\alpha t})^2 \qquad (15)$$

Finally, since $A/2\alpha$ corresponds to the concentration of adsorbed water at time $t = \infty$, eq. (15) may be rewritten as follows:

$$n = n_s(1 - e^{-\alpha t})^2 \qquad (16)$$

where n_s is the water regain in the film at the point of equilibrium adsorption.

By use of eqs. (2) and (16), eq. (6) can be integrated with respect to t. Since the rate of deformation of the film and the rate constant of diffusion, (i.e., the rate of formation of holes through which the penetrant diffuses into the film), depend mainly upon the rate at which hydrogen bonds break, it is not altogether improbable to consider that $\alpha = \kappa$. Thus, from eqs. (2), (6), and (16), the following equation is obtained:

$$d\gamma/dt + \kappa\gamma$$
$$= A\,[Nn_s(1 - e^{-\kappa t})^2]/[N + n_s(1 - e^{-\kappa t})^2] \qquad (17)$$

Integrating eq. (17) by introducing the boundary conditions that $\gamma = 0$ at $t = 0$, and $\gamma = \gamma_\infty$ at $t = \infty$, and setting n_s/N equal to s, we obtain the following equation in the first approximation:

$$\gamma = \gamma_\infty/(1 + s)\{(s + 1)(1 - e^{-\kappa t})$$
$$- 2\kappa t e^{-\kappa t} - e^{-\kappa t} \ln\,[1 + s(1 - e^{-\kappa t})^2]$$
$$+ (1 - s/s^{1/2})e^{-\kappa t}\tan^{-1} s^{1/2}(1 - e^{-\kappa t})\} \qquad (18)$$

where the final equilibrium elongation γ_∞ differs from γ_∞ in eq. (4) in that it is no longer dependent on time. Finally, by series expansion of the arctangent term, the following equation is derived:

$$\gamma = (\gamma_\infty/1 + s)[(s + 1)(1 - e^{-\kappa t}) - 2\kappa t e^{-\kappa t}$$
$$- se^{-\kappa t}(1 - e^{-\kappa t})^2 + (1 - s)e^{-\kappa t}(1 - e^{-\kappa t})] \qquad (19)$$

DISCUSSION

The theoretical creep curves at constant temperature and relative humidity are obtained from eq. (19), once s and κ have been determined. The ratio s of the equilibrium adsorbed water regain to the number of OH radicals in the amorphous parts is computed from the adsorption data for these films. By use of the results obtained by H. Tadokoro, S. Seki, and I. Nitta,[8] on assuming that the degree of crystallization of the PVA film is 30%, s

for the PVA film can be calculated. The values obtained are shown in Table III.

TABLE III
Values of s in PVA Film

R.H., %	Total adsorbed water at equilibrium g./g. polymer	s
60	0.083	0.3
67	0.114	0.4
74	0.139	0.5
81	0.171	0.6

As regards the adsorbed water regain of the PVF films, no corresponding data seem available at this data. The authors assumed that s for PVF films is nearly equal to s for PVA films at the same temperature and relative humidity. This follows from the assumption that, with an increase in the degree of formalization, the degree of crystallization decreases, while the number of available OH-radical sites for adsorption of water remains nearly unchanged.

Furthermore, to determine n_s, (i.e., the equilibrium adsorbed water regain for the PVF films), the relation $\gamma_\infty \backsim n_s/(1 + s)$ given by eq. (2) is adopted. Thus n_s values for PVF are determined by comparing γ_∞ for the PVA films with γ_∞ for the PVF films. To facilitate further theoretical treatments, $n_s/(1 + s)$ is tabulated in Tables IV–IX for both PVA and PVF films under different conditions. The value of s for each film is assumed to be almost constant over the range 30 to 50°C., at constant relative humidity.

TABLE IV
κ and Data Required for its Evaluation, PVA Film at 30°C.

R.H., %	s	κt	t_0, min.	κ	$n/(1 + s)$, g./cm.³
60	0.3	1.423	58	0.0245	0.0923
67	0.4	1.388	30	0.0463	0.1051
74	0.5	1.358	19	0.0715	0.1195
81	0.6	1.334	14	0.0953	0.1379

TABLE V
κ and Data Required for its Evaluation, PVA Film at 60% R.H.

Temp., °C.	s	κt	t_0, min.	κ	$n/(1 + s)$, g./cm.³
20	0.3	1.423	112	0.0127	0.0923
30	0.3	1.423	58	0.0245	0.0923
40	0.3	1.423	13	0.1095	0.0923
50	0.3	1.423	9	0.1581	0.0923

TABLE VI
κ and Data Required for its Evaluation, PVF (6%) Film at 30°C.

R.H., %	s	κt	t_0, min.	κ	$n/(1 + s)$, g./cm.³
60	0.3	1.423	30	0.0474	0.1211
67	0.4	1.388	19	0.0731	0.1426
74	0.5	1.358	14	0.0970	0.1885
81	0.6	1.334	9	0.1482	0.2232

TABLE VII
κ and Data Required for its Evaluation, PVF (6%) Film at 60% R.H.

Temp., °C.	s	κt	t_0, min.	κ	$n/(1 + s)$, g./cm.³
20	0.3	1.423	82	0.0174	0.1211
30	0.3	1.423	30	0.0474	0.1211
40	0.3	1.423	16	0.0889	0.1211
50	0.3	1.423	7	0.2033	0.1211

TABLE VIII
κ and Data Required for its Evaluation, PVF (42.5%) Film at 30° C.

R. H., %	s	κt	t_0, min.	κ	$n/(1 + s)$, g./cm.³
60	0.3	1.423	8	0.1779	0.0760
67	0.4	1.388	7	0.1983	0.0884
74	0.5	1.358	6	0.2263	0.1019

TABLE IX
κ and Data Required for its Evaluation, PVF (42.5%) Film at 60% R.H.

Temp., °C.	s	κt	t_0, min.	κ	$n/(1 + s)$, g./cm.³
20	0.3	1.423	18	0.0791	0.0760
30	0.3	1.423	8	0.1779	0.0760
40	0.3	1.423	4	0.3558	0.0760

Then, for the calculation of κ, the parameter for the diffusion process, (i.e., the parameter for the accompanying mechanical effect), we must recall that each of the creep curves given by eq. (19) has an inflection point as shown in the experimental results, and that at each inflection point the following equation must be satisfied:

$$d^2\gamma/dt^2 = \gamma_\infty \kappa^2 \frac{e^{-\kappa t}}{s + 1} [9se^{-2\kappa t} - 4(3s - 1)e^{-\kappa t}$$

$$+ 2\kappa t + 3s - 4] \quad (20)$$

$$= 0$$

Hence,

$$9se^{-2\kappa t_0} - 4(3s - 1)e^{-\kappa t_0} + 2\kappa t_0 + 3s - 4 = 0$$

$$(21)$$

where t_0 represents the time the inflection point appears. Thus κ can be computed easily by adopting t_0 estimated from each curve and s in eq. (21). Values for κ and t_0 under different conditions are tabulated in Tables IV–IX.

Upon calculation of the theoretical creep curves through substitution of s and κ into eq. (19) as illustrated in Figure 6 by the dashed line, the coincidence of the theoretical curves with the experimental curves becomes evident. This coincidence lends validity to our procedure adopted in deriving eq. (19). By computing from κ the activation energy for the diffusion of water into such polymers and by comparing it with the activation energy obtained from the adsorption data, one may also confirm the validity of the present theoretical treatment and its applicability to experimental data for a series of PVF films.

To compute the activation energy for the diffusion process, κ is expressed by the following equation as the rate of reaction, thus:

$$\kappa = Ae^{-E/RT} \qquad (22)$$

where A is the frequency factor and E is the activation energy.

Now let us have E_1 and E_2 represent, respectively, the energy in the hydrogen bond between OH radicals and that between the other adsorbing sites; let us assume, firstly, that the hydrogen bonds are broken only by the adsorption of water molecules, and secondly, that the OH radicals, having adsorbed water molecules, behave as effectively as the other adsorbing sites, and finally, that the energy between the other sites remains constant when each site has adsorbed water molecules; then we may express E, using eq. (1), thus:

$$E = \frac{N^2/(N + n)}{N + N'} E_1 + \frac{N' + Nn/(N + n)}{N + N'} E_2$$

$$(23)$$

Since the activation energy E seems to decrease as the number of the adsorbed water molecules increases the following equation is obtained:

$$E_0 - E = (E_1 - E_2)/(N + N') \cdot (Nn/N + n)$$

$$(24)$$

where E_0 is the activation energy extrapolated to zero concentration of adsorbed water molecules. Substituting ξ for $(E_1 - E_2)/(N + N')$ into eq. (24), we have:

$$\kappa = Ae^{-E_0/RT}e(\xi/RT) \cdot (n/1 + s)$$

and

$$\ln \kappa = \ln A - (E_0/RT) + (\xi/RT) \cdot (n/1 + s)$$

$$(25)$$

From the plots, shown in Figures 10 and 11, of $\ln \kappa$ against $1/T$ for different temperatures at constant relative humidity, and $\ln \kappa$ likewise against $n/(1 + s)$, for different relative humidities at a
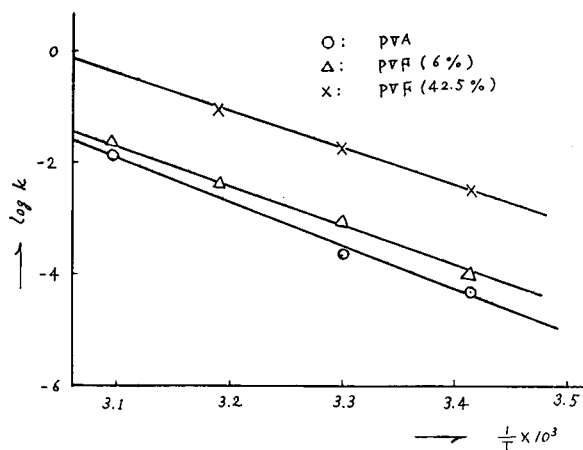

Fig. 10. Relations between log κ and $1/T$ for various films at constant relative humidity.

constant temperature, $\ln A$ and $\ln (A - E_0/RT)$ can be calculated, and E_0 can subsequently be computed from the difference between the two quantities.

Next, the activation entropy ΔS is calculated in the usual manner from the following equation:

$$\ln A = \ln kT/h + \Delta S/R \qquad (26)$$

where A is constant within the temperature range over which the observations were made. Thus, the activation energy and the entropy for the diffusion process of water molecules into PVA and PVF films are obtained, and values thus calculated are shown in Table X.

The results stand in fairly reasonable agreement with those reported by Hauser and McLaren.[9] Table VII shows that the PVF film formalized to 6%, i.e., in which 6% of the hydroxyl groups have reacted with formalin, has the largest activation energy and the smallest entropy change. This
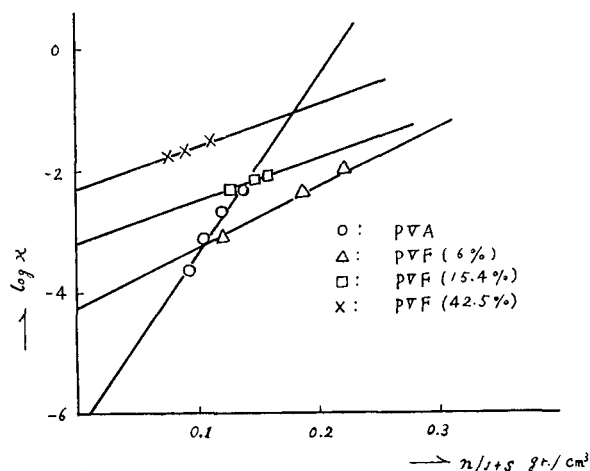
Fig. 11. Relations between log κ and the amount of water adsorbed on OH radicals in the amorphous polymer in various films at a constant temperature.

fact is explicable in the light of the fact that the PVF film becomes richest in amorphous polymer when the degree of formalization ranges from 10 to 20%, as described above. For the same reason, the equilibrium elongation γ_∞ becomes larger when the degree of formalization is between 10 and 20%.

TABLE X

Activation Energy and Entropy for Diffusion Process, Computed from Elongation Process Factors

Samples	E_0, kcal./mole	ln A	ΔS, cal./deg.-mole
PVA	17.3	22.33	−14.3
PVF (6%)	14.3	19.33	−20.3
PVF (42.5%)	13.8	20.53	−17.9

It is very interesting that a perspective of the transport phenomena of water molecules in polymers with many water-sensitive bonds can be obtained through measurement of a mechanical process such as deformation. The authors intend to continue similar researches on different types of polymers.

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Synopsis

The elongation of polyvinyl alcohol and of formalized polyvinyl alcohol films under constant load for a wide range of conditions of temperature and humidity seems to be affected predominantly by the diffusion of water molecules into these polymeric films, as these films have many water-sensitive bonds. In order to obtain a perspective of the diffusion mechanism of water molecules into these polymer films, the theoretical analysis of creep curves is here worked out. Since the diffusion is a time-dependent, non-Fickian process, the time dependence of the diffusion coefficient is considered into our theoretical treatment. It is also assumed that the elongation is caused only by the breaking of hydrogen bonds due to the absorption of water molecules in amorphous regions of the polymer film.

To evaluate theoretical equations for the creep curves in accordance with a simple Voigt model, the parameter α for the rate of diffusion is conveniently substituted for by κ, the parameter for the rate of elongation. Experiments were performed at temperatures from 20 to 50°C. at 60% R.H., and also at different relative humidities ranging from 40 to 80% at a constant temperature of 30°C. A series of creep curves for PVA and PVF, the latter having a degree of formal substitution ranging from 6% to 42.5% were obtained.

In analyzing the observed creep curves by the present theoretical treatment, we can easily compute the values of κ through application of the condition for the characteristic inflection point of each curve, i.e., $d^2\gamma/dt^2 = 0$. By use of the values of κ thus obtained and by application of the theory of absolute reaction rates, the activation energy and entropy for the diffusion process of water molecules are duly determined. The values thus obtained are also compared with those calculated by Hauser and McLaren. The activation energy and entropy are highest and lowest, respectively for PVF (6%); this is made adequately explicable by the fact that the proportion of amorphous polymer in these films is found to be maximum when the degree of formalization is between 10 and 20%.

Résumé

L'élongation de l'alcool polyvinylique et du formal polyvinylique sous tension constante dans n'importe quelle condition semble être affectée principalement par le processus de diffusion des molécules d'eau dans ces films polymériques; ceux-ci possèdent de nombreuses liaisons sensibles à l'eau. On a effectué l'analyse théorique des courbes de rétraction en vue d'obtenir une image de ce mécanisme de diffusion. La dépendance du coefficient de diffusion par rapport au temps devrait faire l'objet d'une analyse théorique pour autant que le processus de diffusion ne suit pas la loi de Fick pour cette

dépendance. Il est également admis que l'élongation est provoquée uniquement par la rupture de liaisons hydrogène, dues à l'absorption de molécules d'eau dans les parties amorphes du polymère. En évaluant les équations théoriques des courbes de rétraction d'après un modèle de Voigt simple, le paramètre α de la vitesse du processus de diffusion est avantageusement remplacé par le paramètre κ de la vitesse du processus d'élongation. Des expériences ont été effectuées pour 60% d'humidité relative à des températures de 20° à 50°C et également à température constante de 30°C pour des humidités relatives différentes, allant de 40 à 80%. Une série de courbes de rétraction a été obtenue pour le PVA et pour le PVF. (Le degré de formalisation de ce dernier allant de 6 à 42,5%). En analysant les courbes de rétraction observées par l'analyse théorique décrite on peut aisément évaluer les valeurs de κ par l'application de la condition du point d'inflexion caractéristique de chaque courbes c'est-à-dire: $d^2\gamma/dt^2 = 0$. En utilisant les valeurs de κ ainsi obtenues et en appliquant la théorie de la vitesse de réaction absolue, on a pu déterminer l'énergie d'activation et l'entropie du processus de diffusion des molécules d'eau. Les valeurs ainsi obtenues ont été comparées à celles qui ont été calculées par Hauser et McLaren. La variation de l'énergie d'activation et de l'entropie causée par un accroissement du taux de formalisation du PVF est compréhensible en raison du fait que la proportion des parties amorphes dans ces polymères atteint une valeur maximum pour un taux de formalisation de l'ordre de 10 à 20%.

Zusammenfassung

Die Dehnung von Polyvinylalkohol und von formalisiertem Polyvinylalkohol unter einer konstanten Belastung scheint bei gegebenen Bedingungen vorwiegend durch die Diffusion der Wassermoleküle in die Polymerfilmeb eeinflusst zu werden, da diese Filme ja viele gegen Wasser empfindliche Bindungen besitzen. Zur Gewinnung eines Verständnisses dieses Diffusionsmechanismus wird in der vorliegenden Arbeit eine theoretische Analyse der Kriechkurven ausgeführt. Insofern als der Diffusionsprozess eine nicht-Ficksche Zeitabhängigkeit besitzt, muss bei der theoretischen Behandlung die Zeitabhängigkeit des Diffusionskoeffizienten in Betracht gezogen werden. Weiters wird angenommen, dass die Dehnung nur durch die Spaltung von Wasserstoffbindungen durch Adsorption von Wassermolekülen in den amorphen Bereichen des Polymeren hervorgerufen wird. Bei der Auswertung der theoretischen Gleichungen für Kriechkurven nach einem einfachen Voigt-Modell wird der Parameter für die Geschwindigkeit des Diffusionsprozesses, α, zweckmässig durch κ, den Parameter für die Geschwindigkeit des Elongationsprozesses substituiert. Versuche wurden bei Temperaturen von 20 bis 50°C bei 60% relativer Feuchtigkeit und auch bei Variierung der relativen Feuchtigkeit von 40 bis 80% bei einer konstanten Temperatur von 30°C durchgeführt. Eine Reihe von Kriechkurven wurden für PVA and PVF (Formalisierungsgrade im Bereich von 6 bis 42,5%) erhalten. Eine Analyse der beobachteten Kriechkurven an Hand der hier durchgeführten theoretischen Behandlung liefert eine einfache Bestimmung des Wertes von κ aus der Bedingung für den charakteristischen Wendepunkt jeder Kurve, d.h. $d^2\gamma/dt^2 = 0$. Unter Benützung der so erhaltenen Werte von κ und durch Anwendung der Theorie der absoluten Reaktionsgeschwindigkeit werden die Aktivierungsenergie und -entropie für die Diffusion der Wassermoleküle erhalten. Diese Werte werden mit den von Hauser und McLaren berechneten verglichen. Die Abhängigkeit der Aktivierungsenergie und -entropie von der Zunahme der Formalisierung von PVF wird dadurch verständlich, dass der Anteil der amorphen Bereiche in diesen Polymeren, wie festgestellt wird, ein Maximum im Bereiche der Formalisierungsgrade zwischen 10 und 20% erreicht.