We have compared the experimental results on solvent squeeze from cylindrical poly(vinyl alcohol) (PVA) gels with
the model presented in this paper. The model says that a characteristic time for solvent squeeze, which is also a retardation
time of the creep of gels, is proportional to the diameter squared. A simplified version of the model, which is valid when
the creep strain is small enough, indicates that retardation time is independent of the applied stress and the height of gels
approaches to a constant value in a single-exponential manner. Experiments on PVA gels say that the change in height oc-
curs almost in a single-exponential manner. The retardation time was independent of the applied stress at small stresses but
became longer in the high stress region, as in the case of the presented model. The diameter dependence of the retardation
time for the PVA gels was weaker than the model prediction. As a whole, the simplified version of the model is useful to
explain the squeezing behavior of the PVA gels.

Key Words: Solvent squeeze / Polymer gel / Mechanical model / Creep

1. INTRODUCTION

Nakamura et al.\textsuperscript{1)} have reported very unique deformation
for cylindrical gellan hydrogels: They carried out the
uniaxial compression at very slow deformation rates in the air
by using a conventional tensile tester and found that the sol-
vent is squeezed out by the compression but the diameter of
the gel specimen is kept constant during compression.
Furthermore, they found that the compressed gel absorbs wa-
ter to recover almost the original dimension, when the com-
pressed gel is immersed into water. Similar compressional
behavior has been observed for agarose gels\textsuperscript{2–4)}. To describe
the detailed compressional behavior of these gellan and aga-
rose gels, the use of the Poisson ratio (\(\mu\)) is helpful. An ex-
tended definition of \(\mu\) to large deformation is given by\textsuperscript{5)}
\[
\mu = \frac{\ln \lambda_\parallel}{\ln \lambda_\perp}
\]
where \(\lambda_\parallel\) and \(\lambda_\perp\) are the stretch ratios parallel and perpendicu-
lar to stretch, respectively. The compression at a constant di-
ameter corresponds to the process at \(\mu = 0\).

Swelling and deformation of polymer gels are affected
by several factors. Among them, the network structure be-
comes essential in some case. Usually, the polymer gel is
implicitly assumed to have a jungle gym-like structure, with
each side being composed of a single polymer strand. The
equation of motion of polymer gels by Tanaka et al.\textsuperscript{6)} and the
stress-diffusion coupling in polymer gels\textsuperscript{7)}, which are typical
of the theoretical approaches to the swelling and deformation
of polymer gels, are built up in a phenomenological frame in
principle, but the origins of forces are now interpreted based
on the jungle gym-like molecular model. On the other hand,
we know that a kitchen sponge is quite different from the
jungle gym in structure but can apparently keep a large
amount of water (liquid) inside. Cellar materials such as the
kitchen sponge can be categorized into the polymer gel al-
though the objection to this classification might exist. The
gellan hydrogels used by Nakamura et al.\textsuperscript{1)} are transparent,
but the network structure of the gels appears to be different
from the single-strand jungle gym structure; the jungle gym
is composed of thicker fibrils\textsuperscript{8)}. For the agarose gels showing
the similar compressional behavior the sponge-like structure
has actually been observed\textsuperscript{9)}. These structures must enable
the unique compression at \(\mu \sim 0\) by the conventional tensile
tester. We prepared poly(vinyl alcohol) (PVA) hydrogels by
using a modified freezing and thawing cycles\textsuperscript{9,10)}. The PVA
gels thus obtained were opaque probably due to the cellar
structure, and thus were successfully compressed at \(\mu \sim 0\) in
the creep mode\textsuperscript{10)}.

If the structure of polymer gels is quite far from the sin-
gle strand jungle gym (\textit{i.e.}, a cellar structure, for example),
the polymer-solvent interaction is much reduced. In this case, the unique compressional behavior at $\mu \sim 0$ is easily realized and the solvent squeezing kinetics becomes quite different from that based on the jungle gym structure; only phenomenological approach becomes useful. The aim of this paper is to present the phenomenological model describing the solvent squeezing kinetics for the gels. The model is applied to actual polymer gel systems to analyze the solvent squeezing kinetics.

2. MODEL

We try to build up a model of the solvent squeeze at $\mu = 0$ by using a spring-linked cylinder shown in Fig. 1. This is based on the model for consolidation in geomechanics\(^{11}\) but is much simpler the original one. The upper moving disk and bottom plate of the cylinder cannot be penetrated by the solvent, but the lateral wall of the cylinder is made of a membrane, through which solvent can move. The upper disk is linked to the bottom by a spring whose volume can be neglected and the inside of the cylinder is filled by the solvent. Let diameter of the cylinder be $d$, and the gap between the moving disk and the bottom plate be $h$. The polymer gel intrinsically possesses the function of membrane but this original function is here substituted by the outside membrane because a gel is now replaced by the spring and the solvent. The thickness of the membrane $l$ in this model corresponds to an effective flow path in the actual polymer gels, and thus we assume that $l \ll d$. Finally, the actual gel showing solvent squeezing is modeled by using the three components: a single spring, the solvent in the cylinder, and the lateral membrane.

When a weight is applied to the upper disk, the solvent is expelled, and thus $h$ decreases with time ($t$) while $d$ remains constant. Here, we designate the initial value of $h$ as $h_{\text{ini}}$. The compressional force applied ($\sigma_{\text{ext}}$ in stress) is balanced by the effective stress supported by the spring ($\sigma$) and the solvent pressure ($p$)\(^{11}\):

$$\sigma + p = \sigma_{\text{ext}} \tag{2}$$

The spring corresponds to the polymer phase (or the polymer network) showing elasticity in actual gels. Because the pressure outside the cylinder is taken to be zero, $p$ corresponds to the pressure difference between the outside and inside regions of the cylinder. In this model, $\sigma_{\text{ext}}$ is supported only by the spring at $t \to \infty$, while $p = \sigma_{\text{ext}}$ at $t = 0$. Thus, this works similarly to the Voigt model in rheology. For $\sigma$ we assume the following linear equation:

$$\sigma = E\varepsilon \tag{3a}$$

where $E$ is the elastic constant of the spring and $\varepsilon$ is the strain defined by

$$\varepsilon = \frac{h_{\text{ini}} - h}{h_{\text{ini}}} \tag{3b}$$

For $p$, Darcy’s law\(^{7,11}\) is assumed between the pressure gradient and the flux density of solvent at the lateral surface ($v$):

$$v = k \left( \frac{P}{l} \right) \tag{3c}$$

where $k$ is a constant called the permeability and includes the viscosity of solvent. The solvent volume conservation law gives

$$\frac{d}{dt} \frac{dh}{4h} \tag{4}$$

By combining Equations (2), (3) and (4), we have for $t \geq 0$

$$\frac{E(h_{\text{ini}} - h)}{h_{\text{ini}}} - \frac{dl}{4kh} = \sigma_{\text{ext}} \tag{5}$$

The solution of this equation is given by

$$h(t) = \frac{h_{\text{ini}} - h_{\text{eq}}}{h_{\text{ini}} - (h_{\text{ini}} - h_{\text{eq}}) \exp \left(-\frac{t}{\tau} \right)} = h_{\text{ini}} \left(1 - \varepsilon_{eq} \right) \exp \left(-\frac{t}{\tau} \right) \tag{6}$$

where $\varepsilon_{eq}$ is the equilibrium strain (i.e., the strain at $t \to \infty$) written by $\varepsilon_{eq} = (h_{\text{ini}} - h_{\text{eq}})/h_{\text{ini}}$ with $h_{\text{eq}}$ being the equilibrium value of $h$, and $\tau$ is a kind of retardation time. If we write the initial value of $v$ as $v_{\text{ini}}$, $\sigma_{\text{ext}} = E\varepsilon_{eq} = v_{\text{ini}}(l/k)$ holds in our model, as in the case of the Voigt model showing retarded elasticity. Therefore, $\tau$ can be written as
It is clear that $\tau$ depends on $\sigma_{\text{ext}}$. This suggests that $\tau$ increases with increasing $\sigma_{\text{ext}}$. We also know that $\tau \propto d^2$ because $l \propto d$.

When $\varepsilon_\infty << 1$, Equation (6) can be simplified to

$$h(t) = (h_\infty - h_0) \exp\left(-\frac{t}{\tau}\right) + h_0 = h_\infty \exp\left(-\frac{t}{\tau}\right) + (1 - \varepsilon_\infty)$$

and $\tau$ is also simplified to

$$\tau = \frac{dl}{4kE}$$

In this case, $\tau$ becomes independent of $\sigma_{\text{ext}}$.

For $\varepsilon$ Equation (6) gives

$$\varepsilon(t) = \varepsilon_\infty \left[1 - \exp\left(-\frac{t}{\tau}\right)\right]$$

and this can also be simplified to the following form if $\varepsilon_\infty << 1$.

$$\varepsilon(t) = \varepsilon_\infty \left[1 - \exp\left(-\frac{t}{\tau}\right)\right]$$

This equation is the same expression as the creep strain of the Voigt element\textsuperscript{5, 12}, which indicates that the cylinder unit can be simply replaced by an equivalent Voigt element. The viscosity of the dashpot ($\eta$) is assigned to $\eta = dl/4k$ if the spring constant in the equivalent Voigt element is $E$. Figure 2 shows two $\varepsilon(t)$ curves calculated by Equations (8) (solid) and Equation (8\textsuperscriptprime}) (dashed) for $\varepsilon_\infty = 0.5$. At this value of $\varepsilon_\infty$, Equation (8\textsuperscriptprime}) does not work as an approximation of Equation (8) in principle, but the difference between two curves, which becomes largest around $t/\tau = 1$, is not still so large.

Because a single cylinder unit in Fig. 1 gives a single retardation time, we can introduce plural retardation times by a series connection of the cylinder units, as is the case of the generalized Voigt model\textsuperscript{5, 12}. If $h$ shows an very fast change around $t = 0$, we have only to set $\eta \rightarrow 0$ (i.e., $k \rightarrow \infty$ in the original cylinder model), which corresponds to a degenerated state of the element where only the spring exists.

3. EXPERIMENTAL

Commercial PVA (VM-17, Japan Vam & Poval Co.) was used in this study. The average degree of polymerization was 1700 and the degree of saponification ranged from 95 to 97 mol%. The solvent used was distilled water (Wako). PVA hydrogels were prepared by modified freezing and thawing cycles, and potassium carbonate was added to the pre-gel solutions to trigger off the salting-out at low temperatures: Details on the preparation method were described elsewhere\textsuperscript{10}. The PVA concentration and the salt concentration in the pre-gel solutions were fixed to be 10 wt% and 3 wt%, respectively.

The shape of the gel specimens used for creep (i.e., solvent squeezing) was cylindrical (height $h$; diameter $d$): the initial value of $h$ ($h_\text{ini}$) and the initial value of $d$ ($d_\text{ini}$) were mostly fixed to be 10 mm. One cylindrical sample with $h_\text{ini} = 10$ mm and $d_\text{ini} = 26$ mm was also employed to examine the $d_\text{ini}$ dependence of $\tau$. Applied weight ranged from 49 g to 264 g. Experimental setup for the solvent squeeze was basically the same as that used to estimate the sol-gel transition entropy\textsuperscript{13}: In this study the apparatus was set in a saturated water vapor. The squeezing (creep) process was recorded by a combination of video camera and DVD recorder, and then analyzed based on the recorded data. The PVA gels used are sample-coded as PVA\text{xxxyyy}, where the two digits $xx$ stands for $d_\text{ini}$ in mm and the three digits $yyy$ stands for the applied force (weight) in g.

4. COMPARISON WITH EXPERIMENT AND CONCLUDING REMARKS

In Fig. 3, $t$-dependence curves of $h$ (filled symbols) and $d$ (open symbols) for PVA10049 are shown. Just after loading, $h$ instantaneously drops to a certain value (we hereafter write this as $h_0$, which corresponds to $h$ at $t \rightarrow +0$), and $d$ instantaneously increases to $d_0$ (a value of $d$ at $t \rightarrow +0$) by loading. This change in $h$ and $d$ is due to the elastic deformation of the gel by the compressional stress, and this occurs at $\mu \neq 0$ although we could not estimate $\mu$ in the compression with enough accuracy. The fast solvent squeezing may also
be involved in the instantaneous change in $h$, but the contribution of the fast squeezing seems to be not so large. A gradual decrease in $h$ after the instantaneous drop continues until a constant value ($h_\infty$), while $d$ throughout remains at $d_0$. This creep, of course, corresponds to the solvent squeezing process of the PVA gel. It is noticed that the gel keeps the constant diameter ($d_0$) during solvent squeezing. The similar behavior was observed for all gel samples examined.

Figure 4 shows semi-logarithmical plots of $(h - h_\infty)/h_\text{ini}$ vs $t$ for the PVA gels at $d_\text{ini} = 10$ mm. After the instantaneous change by the application of weight, the curves appear to have tendency to move upwards with increasing $\sigma_\text{ext}$; at present why the plot for 69 g is located at the bottom is not unclear. The lines in the figure are drawn based on Equation (6′) to estimate the retardation time $\tau$ of the gel samples, and the middle line is the fit to the two curves of 49 g and 89 g. It is clear that the lines well approximate the $t$-dependence curves:

Even a simplified version of the model can be applicable to the squeezing of the PVA gels. The slopes of the lower two lines are almost identical but the upper line has a smaller slope or longer retardation time. In our model, $\tau$ generally increases with increasing $\sigma_\text{ext}$ (Equation (7)), but in the small $\sigma_\text{ext}$ region $\tau$ becomes independent of $\sigma_\text{ext}$ (Equation (7′)). The experimental results that $\tau$ except for 109 g remains constant, which agrees well with the prediction of the simplified version, while $\tau$ at 109 g becomes smaller is consistent with the model prediction, although $\tau$ for 109 g was obtained from Equation (7′).

Figure 5 shows the $\sigma_\text{ext}$-dependence of (a) the strain by the instantaneous deformation ($\varepsilon_0$: $\varepsilon_0 = (h_\text{ini} - h_\text{0})/ h_\text{ini}$) and (b) the equilibrium strain $\varepsilon_\infty$ of the PVA gels at $d_\text{ini} = 10$ mm. Both $\varepsilon_0$ and $\varepsilon_\infty$ are increasing function of $\sigma_\text{ext}$. The former indicates that the instantaneous deformation increases with increasing $\sigma_\text{ext}$ although a saturation may occur at large $\sigma_\text{ext}$. The panel (b) says that the total amount of solvent...
squeezed out also increases with increasing $\sigma_{\text{ext}}$ as the model suggests.

Table I tabulates sample code, $d_{\text{ini}}$, $\sigma_{\text{ext}}$ in Pa, retardation time reduced by $d_{\text{ini}}^{-2}$ ($\tau/d_{\text{ini}}^{-2}$), $\varepsilon_0$ and $\varepsilon_\infty$. In this table we employ a reduced retardation time $\tau/d_{\text{ini}}^{-2}$ to compare $\tau$ of the gels with different $d_{\text{ini}}$ because the present model assumes $l \propto d$.

Of course, for the reduced retardation time, $d_0$ must be used in principle instead of $d_{\text{ini}}$ but we used here $d_{\text{ini}}$ because the difference between $d_0$ and $d_{\text{ini}}$ is too small to be negligible. The value of $\tau/d_{\text{ini}}^{-2}$ at the smallest $\sigma_{\text{ext}}$, which corresponds to the data for the gel at $d_{\text{ini}} = 26$ mm, becomes smaller than others at $d_{\text{ini}} = 10$ mm. This may indicates that the $d$-dependence of the actual gels is weaker than that presented in the model and thus the relation $l \propto d$ may be reconsidered.

In conclusion, we compared the experimental results on solvent squeeze from PVA gels with the model presented in this paper. As a whole, we think that the simplified version of the model is very useful to explain the squeezing behavior of the PVA gels. Concerning $\tau$, a characteristic time for solvent squeeze and also a retardation time for the creep of gels, the model says that $\tau$ depends on the applied stress and is also proportional to $d^2$. When $\varepsilon_\infty << 1$, a simplified version of the model becomes valid. The simplified version says that retardation time for the creep of gels, the $\tau$-dependence of the gels is weaker than that presented in the model. In these gels, multi-exponential nature emerges on the $h$ vs $t$ curve: we think that multi-element analysis as briefly stated in this paper becomes important.

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