Thermal Expansion of a Viscoelastic Gel

GEORGE W. SCHERER

DuPont Co., Experimental Station 356/384, Wilmington, DE 19880 USA

scherer@esvax.dnet.dupont.com

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Abstract. It was previously shown [J. Non-Cryst. Solids, 130, 157 (1991)] that the permeability of a saturated gel can be determined from a measurement of its rate of expansion during a change in temperature. The existing analysis assumes that the solid network of the gel behaves elastically, but in many cases the gel is likely to be viscoelastic, especially when the gel exhibits syneresis. In this paper, the expansion kinetics are determined for a gel with a viscoelastic (VE) network. Sample calculations for a silica gel containing ethanol indicate that a naive application of the elastic analysis could result in errors exceeding a factor of two in the estimate of the permeability of a VE gel. However, in such cases, there are qualitative features in the experimental data that alert the experimenter to the existence of significant VE relaxation. Therefore, it is possible to avoid errors by careful examination of the data.

Keywords: permeability, relaxation, viscoelasticity, thermal expansion, strain

1 Introduction

A gel can be regarded as a composite material consisting of a continuous solid network incorporated in a continuous liquid phase. When the gel is heated, the thermal expansion of the liquid is typically very much larger (at least an order of magnitude larger, in the case of silica gel) than that of the solid phase. Ideally, the expanding liquid would prefer to flow out of the gel, leaving the unexpanded network behind. However, unless the heating rate is extremely slow, the low permeability of the gel inhibits the liquid from escaping as the temperature rises. Consequently the liquid expands inside the gel and stretches the network like a spring. If the temperature is raised and then held constant, the liquid gradually drains from the network and allows it to contract to its original dimensions. Indeed, by subjecting a gel to a gentle thermal cycle and measuring its dilatation, it is possible to determine the permeability of the network [1]. Some gels exhibit syneresis (spontaneous contraction driven by condensation reactions or interparticle attraction [2]), and the thermal expansion measurement has been used to obtain simultaneous measurements of the permeability and the kinetics of syneresis [3, 4]. However, it has recently been recognized [5] that the chemical environment that permits syneresis may also allow viscoelastic relaxation of the gel network. Therefore it is necessary to examine the influence of viscoelasticity on the thermal expansion behaviour of a gel. In particular, it is important to quantify the error in the calculated permeability, if the elastic analysis is applied to a gel that is actually viscoelastic. The purpose of this paper is twofold: to determine the rate of viscoelastic relaxation that causes significant errors in the calculation of permeability, and to seek qualitative evidence that reveals to the experimenter that important relaxation effects are present.

In the next section, an analysis is presented of the thermal expansion kinetics of a viscoelastic gel. Sample calculations are presented in section 3 that examine the range of relaxation parameters that lead to erroneous estimates of permeability, if viscoelasticity is ignored in the calculation.

2 Theory

2.1 Viscoelastic Analysis

The starting point for the viscoelastic (VE) analysis is the elastic analysis presented in ref. 1. The constitutive equations describing the mechanical behaviour of the gel were derived by Biot [6], and he showed that the viscoelastic analogy [7] could be applied to predict the behaviour of VE gels. The analogy states that the elastic equations are identical to the Laplace transform of the viscoelastic equations. Therefore, we simply have to interpret the elastic solution as the transform of the VE solution and invert the transform to obtain the result we seek. This procedure was applied in ref. 5 to find
the relaxation behaviour of a gel in a beam-bending experiment, and the constitutive equations are discussed in some detail in that paper.

We assume that the movement of liquid within the gel obeys Darcy’s law \[8\]:

\[
J = \frac{D}{\eta_L} \nabla P
\]

(1)

where \(J\) is the flux, \(D\) is the permeability of the network, \(\eta_L\) is the viscosity of the liquid, and \(P\) is the stress in the liquid (which differs from the pressure only in sign; \(P\) is positive when the liquid is in tension). Regardless of the constitutive behaviour of the gel, the continuity equation was shown in ref. 1 to be

\[
\frac{\partial \varepsilon}{\partial t} = 3 \frac{\partial \varepsilon_T}{\partial t} - \nabla \cdot \left( \frac{D}{\eta_L} \nabla P \right)
\]

(2)

where \(\varepsilon\) is the volumetric strain of the gel, \(t\) is the time, and the thermal strain is defined as

\[
\frac{\partial \varepsilon_T}{\partial t} = (1 - \rho)(\alpha_L - \alpha_S) \frac{\partial T}{\partial t}
\]

(3)

where \(\rho\) is the relative density (= volume fraction of solids) in the gel, \(\alpha_L\) and \(\alpha_S\) are the linear thermal expansion coefficients of the liquid and solid phases, respectively, and \(T\) is the temperature. If the experiment under consideration is done properly, the sample experiences small strains and negligible temperature gradients, so it is permissible to remove \(D\) and \(\eta_L\) from the operator in Eq. (2). Then that equation can be written in the form

\[
H \frac{\partial \varepsilon}{\partial \theta} = 3H \frac{\partial \varepsilon_T}{\partial \theta} - \nabla^2 P
\]

(4a)

\[
= 3H \frac{\partial \varepsilon_T}{\partial \theta} - \frac{1}{u} \frac{\partial}{\partial u} \left( u \frac{\partial P}{\partial u} \right)
\]

(4b)

where Eq. (4b) applies for a cylindrical body. In Eq. (4) we have introduced the quantities \(u = r/R\), where \(r\) is the radial coordinate and \(R\) is the radius of the cylinder, and the dimensionless time

\[
\theta \equiv \int_0^l \frac{dr'}{\tau(r')}
\]

(5)

where \(\tau\) is called the hydrodynamic relaxation time, and is defined by

\[
\tau \equiv \frac{\eta_L R^2}{DH}
\]

(6)

The longitudinal elastic modulus, \(H\), is defined by \(H = (1 - \nu)E/[3(1-2\nu)]\), where \(E\) is Young’s modulus and \(\nu\) is Poisson’s ratio for the gel network.

The Laplace transform of the function \(f(u, \theta)\) with respect to \(\theta\) is defined by \[9\]

\[
\mathcal{L}[f(u, \theta)] = \tilde{f}(u, s) = \int_0^\infty \exp(-s\theta)f(u, \theta) d\theta
\]

(7)

An important property of the transform is that

\[
\mathcal{L} \left[ \frac{\partial f}{\partial \theta} \right] = \tilde{f}(u, s) - f(u, 0)
\]

(8)

Applying the transform to Eq. (4b) leads to

\[
sH\tilde{\varepsilon} = 3sH\tilde{\varepsilon}_T - \frac{1}{u} \frac{\partial}{\partial u} \left( u \frac{\partial \tilde{P}}{\partial u} \right)
\]

(9)

since the strains and stresses are initially zero. Equation (9) is the Laplace transform of the continuity equation for either an elastic or viscoelastic gel.

Neglecting the thermal expansion of the solid phase, we find from Eq. (17) of ref. 1 that the volumetric strain of the elastic gel is

\[
\varepsilon = 3\varepsilon_s - \left[ \beta P + (1 - \beta)(P) \right] \frac{K}{\mathcal{M}}
\]

(10)

where \(\varepsilon_s\) is the linear strain caused by syneresis, \(K = E/[3(1-2\nu)]\) = \(\beta H\) is the bulk modulus of the drained network, and the constant \(\beta\) is defined by

\[
\beta = \frac{1 + \nu}{3(1 - \nu)}
\]

(11)

The volume-averaged stress in the liquid is defined as

\[
\langle P \rangle \equiv 2 \int_0^1 P(u, \theta)u \, du
\]

(12)

According to the viscoelastic analogy \[7\], the Laplace transform of the VE volumetric strain can be obtained directly from the elastic equation, Eq. (10), by replacing the strains and the moduli with transformed functions. In the transformed VE equation, Young’s modulus is replaced by \(\mathcal{M}\) and Poisson’s ratio is replaced by \(\mathcal{N}\), where \[5, 7\]

\[
\mathcal{M} = Es\tilde{\psi}(s)
\]

(13)

The relaxation function \(\psi(\theta)\) varies from \(\psi(0) = 1\) toward zero as \(\theta \to \infty\); the functional form of \(\psi\) will be discussed in the next subsection. As explained in ref. 5, Poisson’s ratio is not expected to show significant time dependence in a gel, so we assume

\[
\mathcal{N} = \nu = \text{constant}
\]

(14)