

Original Paper

# Estimation of the Glass Transition Pressure of Liquids under Very High Pressure by Viscoelastic Analysis

Ikuya FUJISHIRO, Yuichi NAKAMURA  
(Department of Mechanical and Materials Engineering)

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The method of estimating the glass transition pressure is proposed. A constitutive equation of viscoelastic solid mechanics such as a 3-parameter model is employed for analyzing pressure relaxation behavior of liquids at constant strains. In generating high pressures up to 15 GPa, a diamond-anvil high-pressure device and the ruby fluorescence pressure sensing method were employed. The glass transition pressures at room temperature of 4Methanol-1Ethanol and 16Methanol-3Ethanol-1Water obtained by this method are 10.6 GPa and 12.3 GPa respectively. These values show good agreement with the existed values which obtained from the ruby fluorescence line broadening method.

## 1. Introduction

In a cooling process, some liquids do not crystallize but remain in liquid state. Whether crystallization or glass transition occurs depends on their molecular structure and cooling conditions (super cooling). Glass transition temperature is detected by the discontinuity of the thermal expansion coefficient, and its viscosity goes to  $10^{12}$  Pa·s or more. The glass transition also occurs by pressing, and glass-like liquids show viscoelastic behavior as non-Newtonian, and pressure relaxation can be observed at the constant strain condition. In this paper, the method of estimating the glass transition pressure is shown for such a behavior of liquids by applying constitutive equation of viscoelastic solid mechanics such as a 3-parameter model.

For the generation of high pressures up to 15 GPa, a diamond-anvil high-pressure device and the ruby fluorescence pressure sensing method were employed. The experimental data of the pressure relaxation for some alcohol mixtures are analyzed by this method.

## 2. Viscoelastic model

The general form of the viscoelastic constitutive equation is expressed as follows,<sup>1)</sup>

$$A\sigma = B\varepsilon \quad (1)$$

where  $\sigma$  and  $\varepsilon$  are the stress and strain respectively. A and B are differential operators expressed as

$$A = \sum_{k=0}^m a_k \frac{d^k}{dt^k}, \quad B = \sum_{k=0}^n b_k \frac{d^k}{dt^k}$$

This equation is derived from the combination of some springs and dashpots. The following two assumptions are employed for the application of this model to the viscoelastic behavior of liquids under high pressure.

- (1) Only hydrostatic stress (pressure  $p$ ) and strain (volumetric compression  $\varepsilon_V$ ) components are considered in this analysis.
- (2) While loading, mechanical moduli such as viscosity or elasticity depend on the pressure, but in the present analysis, mean values during the loading process are employed. Thus,

$$\bar{\varepsilon} = \frac{\int_{p_0}^{p_1} C(p) dp}{p_1 - p_0} \quad (2)$$

where  $C(p)$  is a mechanical modulus as a function of pressure,  $\bar{\varepsilon}$  is its mean value and  $p_0, p_1$  are the pressure before and after loading respectively. In the case of a 3-parameter solid shown in Fig. 1, differential operators are as follows.

$$A = 1 + \frac{\bar{\eta}}{\bar{K}_1 + \bar{K}_2} \frac{d}{dt}, \quad B = \frac{\bar{K}_1}{\bar{K}_1 + \bar{K}_2} (\bar{K}_2 + \bar{\eta} \frac{d}{dt}) \quad (3)$$

where  $\bar{K}_1, \bar{K}_2$  are mean values of bulk modulus of each spring, and  $\bar{\eta}$  is that of volume viscosity. As for the boundary condition, volumetric strain  $\varepsilon_V$  is loaded by Heaviside unit step function  $H(t)$ ,

$$\varepsilon_V = \varepsilon_0 H(t) \quad (4)$$

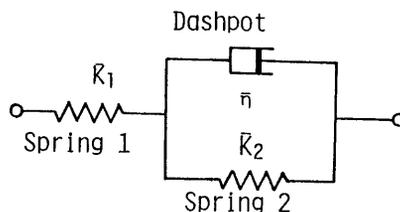


Fig. 1 3-element viscoelastic model

Taking Laplace transformation of equations (2), (3) and (4) then operating inverse Laplace transformation, we have the following relaxation equation.

$$p(t) = \varepsilon_0 \left( \frac{\bar{K}_1^2}{\bar{K}_1 + \bar{K}_2} e^{-\frac{t}{\tau}} + \bar{K} \right) \quad (5)$$

$$\tau = \frac{\bar{\eta}}{\bar{K}_1 + \bar{K}_2}, \quad \bar{K} = \frac{\bar{K}_1 \cdot \bar{K}_2}{\bar{K}_1 + \bar{K}_2}$$

where  $\tau$  is the relaxation time,  $\bar{K}$  is the mean value of a bulk modulus when  $t$  tend to infinity. Experimental results,  $p$ - $t$  relations, are fitted by the equation (5) in order to yield the viscosity  $\eta$ . The glass transition pressure is obtained by interpolating (or extrapolating)  $p$ - $\eta$  relation to  $10^{12}$  Pa.s.

### 3. Experimental Results

The mixtures of 4Methanol-1Ethanol (4M1E)<sup>2)</sup> and 16Methanol-3Ethanol-1Water (16M3E1W)<sup>3)</sup> in volume are employed as the samples. These mixtures show the hydrostatic behavior up to 10 GPa and thus they are often used as pressure transmitting media in the research of high pressure. A diamond-anvil high-pressure device was used for the pressure generation. The pressure (i.e. a hydrostatic stress component) relaxation was observed under constant strain at room temperature. The pressure is determined by the ruby fluorescence method within the error range of 0.03 GPa<sup>4)</sup>. The pressure in the sample was loaded, and kept constant volume (stroke) at room temperature. The pressure decreased gradually as shown in Fig. 2. The best fitting curves of equation (5)

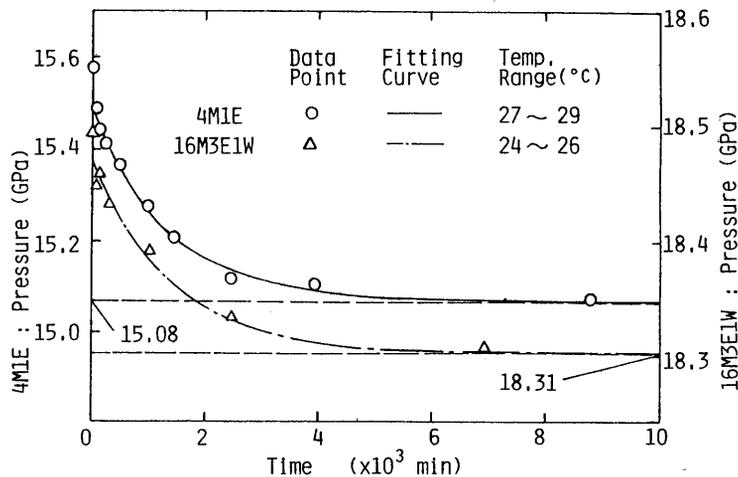


Fig. 2 Pressure relaxation and viscoelastic fitting curves

in this figure provide the mean value of volume viscosity described above. The volume viscosity after loading is derived from equation (2). The shear viscosity (generally called viscosity) is estimated from the volume viscosity using the relation analogous to that of elastic moduli.

$$G = \frac{3K(1-2\nu)}{2(1+\nu)} \quad (6)$$

$$\mu = \frac{3\eta(1-2\nu)}{2(1+\nu)} \quad (7)$$

where  $G$  is shear modulus,  $\mu$  is viscosity and  $\nu$  is Poisson's ratio. The Poisson's ratio  $\nu$  of the glassy state solid is assumed to be about 0.3, then obtained

Sample Liquid	Volume Viscosity $\eta$ (Pa·s)	(Shear) Viscosity $\mu$ (Pa·s)
4M1E	$5.06 \times 10^{18}$	$2.34 \times 10^{18}$
16M3E1W	$2.10 \times 10^{19}$	$9.68 \times 10^{18}$

Table 1 Volume viscosity and (shear) viscosity

viscosities are shown in Table 1. The glass transition pressures are shown in Fig. 3. These pressures are estimated from the interpolation of the viscosity to  $10^{12}$  Pa·s. In this figure,  $\mu = \mu_0 e^{\beta P}$  as a pressure-viscosity relation is employed, where  $\mu_0$  is the viscosity at the atmospheric pressure,  $\beta$  is the materials constant. This relation is common in the viscosity of lubricants under high pressure.<sup>5)</sup> In Fig. 3, the glass transition pressures obtained from the ruby fluorescence line broadening method are also inserted. The glass transition pressures of 4M1E and 16M3E1W in this work are 10.6 GPa and 12.3 GPa, respectively, on the other hand in using the fluorescence line broadening method, 10.4 GPa and 14.4 GPa, respectively. These values show that as for 4M1E, there is a good agreement between the glass transition pressures of both methods, but not for 16M3E1W. In the case of 16M3E1W, the pressures were obtained by four rubies in the same cell. The optical alignment was readjusted to each ruby, so the reproducibility of this process might yields less accuracy.

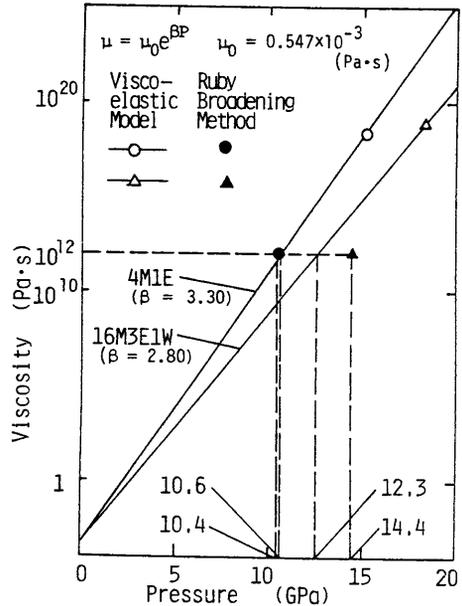


Fig. 3 Glass transition pressure and viscosity-pressure relation

#### 4. Concluding Remarks

In spite of several coarse assumptions, the glass transition pressures are estimated successfully from the pressure relaxation analysis by applying the simple viscoelastic model. Moreover this method may serve to estimate the viscosity of very high viscous materials under high pressure. But in order to establish this method, more discussions and improvements are required.

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