SHORT COMMUNICATION

The viscosity at the glass transition of a liquid lubricant

Scott BAIR

Center for High-Pressure Rheology, George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta GA 30332-0405, USA

Abstract: In the classical study of elastohydrodynamic lubrication (EHL) which does not employ real, measurable viscosity in analysis, the possibility of a glass transition has not been considered in many years. Indeed, the two rheological assumptions of classical EHL, the Newtonian inlet and the equivalence of a traction curve to a flow curve, would not have persisted so long had the pressure dependence of the viscosity been accurately stated. With the recent appearance of viscosity obtained from viscometers in EHL analysis, the possibility of a glass transition in the contact should be reexamined, especially for the fragile traction fluids. This article employs published data for a synthetic cycloaliphatic hydrocarbon to estimate the glass transition viscosity so that, when using real viscosities in EHL simulations, the state of the liquid may be assessed. Far into the glassy state the liquid should be treated as an elastic solid with a yield stress.

Keywords: elastohydrodynamic lubrication; glass transition; high pressure viscosity; EHL friction

1 Introduction

The glass transition in elastohydrodynamic lubrication (EHL) liquids under pressure has been the subject of discussion and speculation for more than forty years [1, 2]. The glass transition has not been a recent topic of classical EHL as the viscosity there is described by simple pressure relations based on fictional accounts [3] of viscometer measurements in which the viscosity does not usually reach to the large values for which the transition occurs. With the recent move towards quantitative EHL [4], which employs real thermophysical properties, the glass transition in EHL liquids should be reexamined.

The limiting low shear viscosity at the glass transition is most often given by a "rule-of-thumb" as $\mu_g = 1 \times 10^{12}$ Pa·s [5] which seems to be more appropriate for molten minerals [6] than organic liquids. Experimental measurements of the glass transition and the viscosity of liquid lubricants over a range of temperature and pressure more than thirty years ago

[7] indicated that the glass viscosity must be much smaller, 10^7 Pa·s to 10^9 Pa·s. Schweyer [8] found $\mu_g = 10^8$ Pa·s for asphalts under pressure. Measurements at ambient pressure of viscosity up to 3.7×10^8 Pa·s from the University of Chicago [9] compared with glass transition measurements by transient hot-wire at Umea University [10] give the viscosity at the transition to be $\mu_g = 1.23 \times 10^7$ Pa·s for squalane when the observation time is 0.3 seconds.

2 Glass transition temperature and pressure

Glass transition temperatures and pressures [11] and precise viscosity [12] data exist for a liquid lubricant, MCS 460, a cycloaliphatic synthetic hydrocarbon produced by Monsanto. It is one of the model lubricants for which the properties have been tabulated by Hamrock et al. [13], although the pressure-viscosity plots in Ref. [13] are extrapolations not representative of the measured viscosity for this oil. MCS 460 displays a dynamic crossover in both the temperature-viscosity

* Corresponding author: Scott BAIR, E-mail: scott.bair@me.gatech.edu

and the pressure-viscosity response at a viscosity of the order of 100 Pa·s [12]. A dynamic crossover is not unusual in fragile liquids.

The relative volumes in isobaric cooling and isothermal compression experiments are plotted in Figs. 1 and 2, respectively. These measurements were performed in dilatometers described in [14]. For characterization of the temperature and pressure of the glass transition, it is not necessary to precisely determine volumes (or densities), only the relative changes in volume. The relative volumes reported in Figs. 1 and 2 represent the positions of a piston that applies the pressure and is not corrected for the elastic deformation of the containment and is, therefore, only a representation of the liquid volume through an unknown linear relationship.

All measured glass temperatures for pressures from 400 to 700 MPa are shown in Fig. 3 and listed in Table 1.
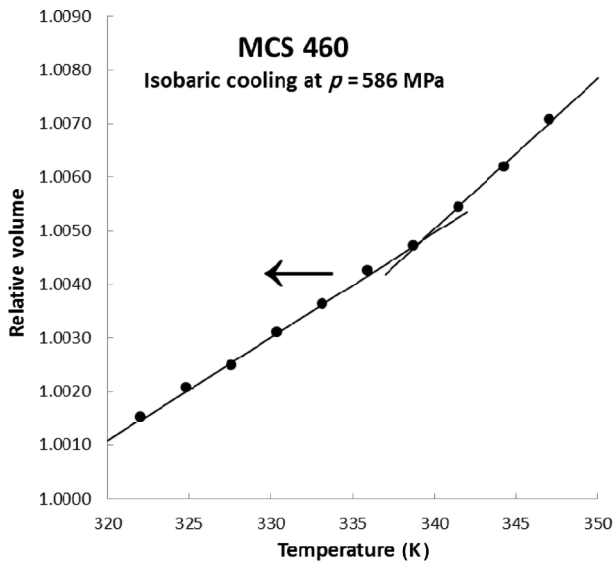

Fig. 2   The glass transition detected in isothermal compression at 322 K. The arrow indicates the time sequence in which the measurements were made.

Fig. 1   The glass transition detected in isobaric cooling at pressure of 586 MPa. The arrow indicates the time sequence in which the measurements were made.
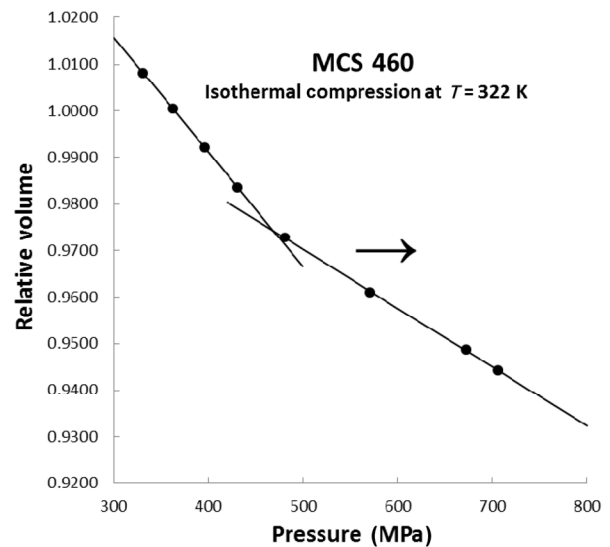

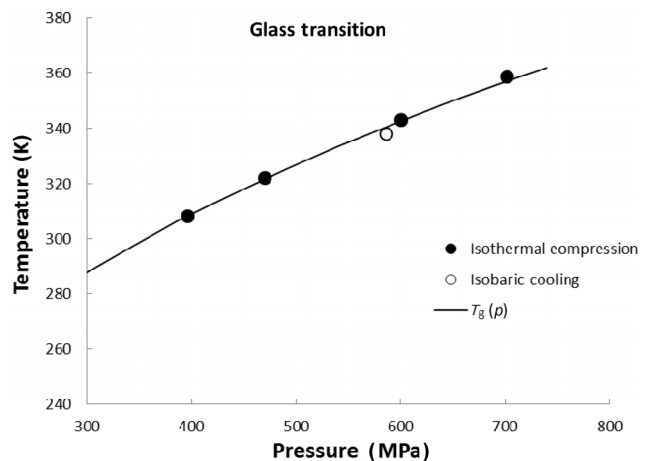**Fig. 3**   The glass transition temperature as a function of pressure and the correlation of Oelsand Rehage.

Table 1 The glass transition state (pressure and temperature) from experiment.

Path	p/MPa	T/K
Isobaric cooling	586	338
Isothermal compression	397	308
Isothermal compression	470	322
Isothermal compression	601	343
Isothermal compression	701	358

The curve fitted to these data represents the equation of Oels et al. [15]:

$$T_g(p) = T_{g0} + A_1 \ln(1 + A_2 p) \tag{1}$$

with $T_{g0} = 196.1$ K (–81.55 ℃), $A_1 = 130.16$ K, and $A_2 = 3.652$ GPa^{-1}. The fit is good with average absolute deviation of 0.9 K.

3 Temperature and pressure dependence of viscosity

Extrapolations of viscosity to the glass transition may be bedeviled by a dynamic crossover as shown in Fig. 4 for the temperature dependence of the viscosity [12] of MCS 460 at 300 MPa. A crossover occurs at slightly higher temperature or slightly lower pressure than the glass transition and represents a change from one
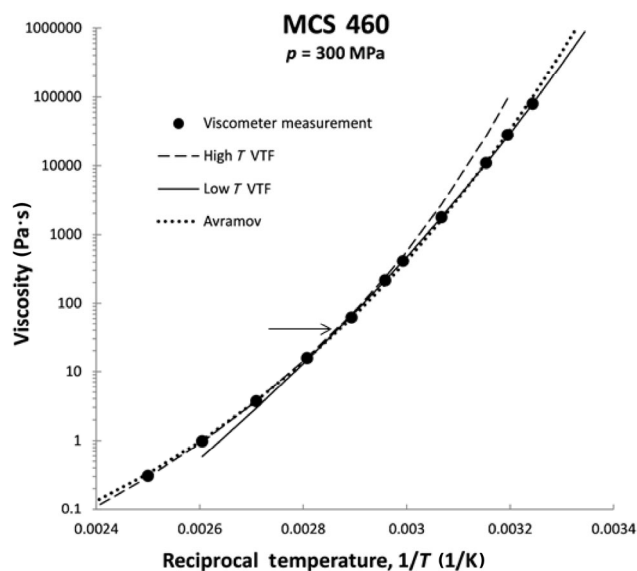

Fig. 4 The temperature dependence showing a crossover (at the horizontal arrow) which can be best represented by two VTF equations or with less accuracy by a single Avramov equation.

temperature-viscosity relation (or pressure-viscosity relation) to another. The crossover occurs at approximately the same viscosity regardless of the pressure or temperature. When a crossover occurs, the Eq. (2) as described by Vogel, Tammann and Fulcher (VTF) [16] must be applied over two adjacent temperature intervals for an accurate fit to the data in Fig. 4.

$$\mu = \mu_\infty \exp\left[\frac{D_F T_\infty}{T - T_\infty}\right] \tag{2}$$

For temperatures above the crossover, greater than 345 K, $\mu_\infty = 8.20 \times 10^{-6}$ Pa·s, $D_F = 6.92$ and $T_\infty = 241$ K with average absolute deviation of the relative viscosity (AARD) of 2.0%. For temperatures below the crossover, less than 345 K, $\mu_\infty = 2.40 \times 10^{-10}$ Pa·s, $D_F = 27.2$ and $T_\infty = 170$ K with AARD= 2.5%. The crossover viscosity is about 47 Pa·s [12].

Another correlation is plotted in Fig. 4, the Avramov & Milchev equation [17]

$$\mu = \mu_\infty \exp\left[\frac{A}{T}\right]^q \tag{3}$$

which sometimes provides the temperature-viscosity response across an ostensible crossover with a single expression [18] and accuracy similar to the two VTF equations. The fitted Avramov equation in Fig. 4 represents $\mu_\infty = 1.639 \times 10^{-3}$ Pa·s, $q = 4.675$ and $A = 571.6$ K with AARD= 7.3% and is less accurate than the double VTF form.

Crossovers were seen for the pressure dependence of MCS 460 as well as shown for example in Fig. 5 for $T = 313$ K where the crossover occurs for $\mu = 56$ Pa·s [12]. The curves in the figure are the pressure analog of the VTF equation, the Johari and Whalley (J&W) equation [19]

$$\mu = \mu_{JW} \exp\left[\frac{C_F p_\infty}{p_\infty - p}\right] \tag{4}$$

for pressures less than 200 MPa, $\mu_{JW} = 1.194 \times 10^{-14}$ Pa·s, $C_F = 28.4$ and $p_\infty = 0.88$ GPa with AARD=0.9%. For pressures greater than 200 MPa, to fit the data with AARD=0.7%, C_F and p_∞ must both be very large with $C_F/p_\infty = 55.11$ GPa^{-1}. This is Arrhenius response with $\mu_{JW} \exp(C_F) = 1.859 \times 10^{-3}$ Pa·s.
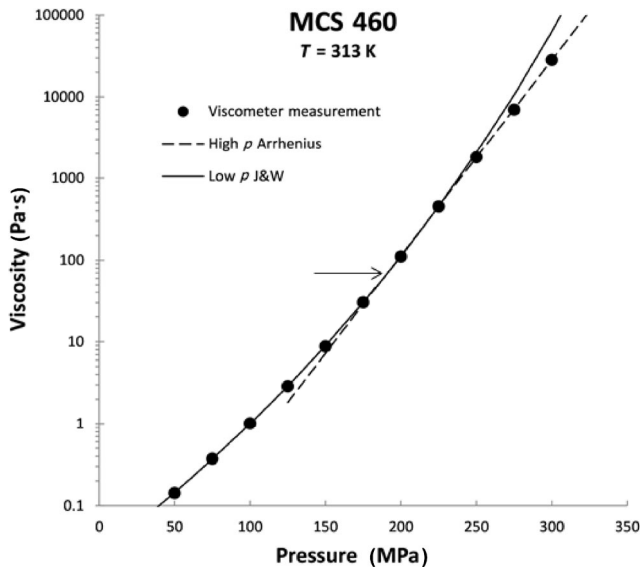
Fig. 5 The pressure dependence at 313 K showing a crossover (at the horizontal arrow) which can be best represented by two J&W equations (4).

$$\mu = \mu_{JW} \exp(C_F) \exp\left(\frac{C_F}{p_\infty} p\right) \qquad (5)$$

The equation above is plotted in Fig. 5 marked as Arrhenius. The parameters of the J&W equation are tabulated in Ref. [12] for the other measured isotherms.

Of course, thermal EHL analysis requires a temperature as well as pressure correlation such as the free volume models. The free volume approach cannot reproduce the crossover [12]. Thermodynamic scaling [20] is promising; however, it also requires the equation of state.

The underlying mechanism of the crossover remains the subject of intense speculation and research. An excellent and detailed discourse on possible mechanisms has been contributed by Roland and coworkers [21].

4 Viscosity at the glass transition

The viscosities at the glass transition condition may now be calculated at the pressure (300 MPa) for which a viscosity isobar was obtained and the five temperatures (293 K to 388 K) for which viscosity isotherms were measured in Ref. [12]. See Table 2. The transition viscosity varies from 2.30×10^7 Pa·s to 15.6 ×

10^7 Pa·s with the arithmetic average being 6.2×10^7 Pa·s and the geometric mean being 4.7×10^7 Pa·s. This is in the same range as for the EHL reference liquid squalane [10]. The glass transition viscosity is much less than the "universal value" of 10^{12} Pa·s. Using the "universal" glass transition viscosity and the extrapolations of Barus and Roelands pressure-viscosity equations given by Hamrock [13] for this oil at 311 K, the glass transition pressure would be 955 MPa and 855 MPa for Barus and Roelands, respectively. In fact, the glass transition pressure should be about 410 MPa as shown in Fig. 6 and this oil will be in the glassy condition for a portion of an EHL contact at this temperature.

Table 2 The glass transition state (pressure and temperature) from the Oels and Rehage equation (1) and the viscosity calculated by the given correlation.

p/MPa	T_g/K	μ_g /Pa·s	Viscosity correlation
300	288	8.69×10^7	Avramov&Milchev
300	288	2.70×10^7	Low TVTF*
323	293	3.08×10^7	High p J&W (Arrhenius)
422	313	2.35×10^7	High p J&W (Arrhenius)
569	338	2.30×10^7	High p J&W (Arrhenius)
829	373	8.64×10^7	High p J&W (Arrhenius)
964	388	1.56×10^8	High p J&W (Arrhenius)

*The high temperature VTF relation gives $\mu_g = 2.3 \times 10^{10}$ Pa·s for this state.
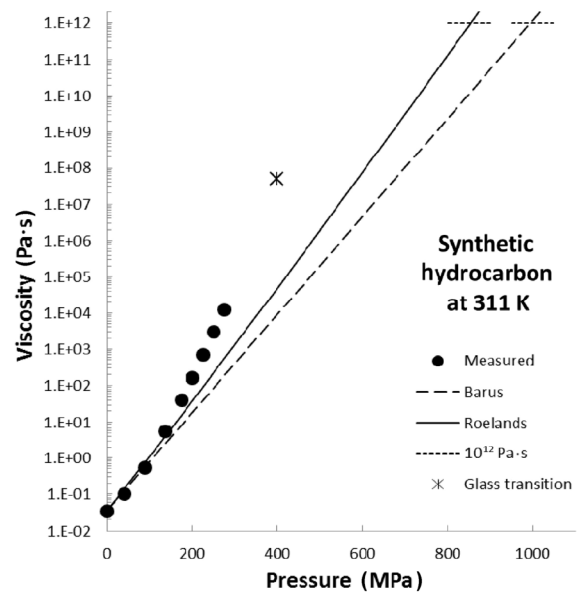

Fig. 6 The Barus and Roelands extrapolations of Hamrock et al. [13] compared with the measurements and showing the glass transition pressure.

5   Conclusion

For much of the last forty years, the temperature and pressure dependence of viscosity in EHL has been specified by simple models which prevent the viscosity from reaching realistic values. With the recent trend toward the use of real viscosity in analyses, the possibility of a glass transition in the lubricant film cannot be overlooked. This event is more likely for the liquids designed for high friction, traction fluids, which are also susceptible to a dynamic crossover. The glass transition is a phenomenon occurring at a specific value of viscosity for a given liquid. It seems well-established that for the much studied inorganic liquids (mineral melts) the glass transition viscosity is of the order of 10^{12} Pa·s, as in Ref. [22] for example. However, the situation for organic liquids is less clear [7, 8]. Here, for one liquid lubricant, the glass transition by dilatometry combined with falling cylinder viscometry places the viscosity at the transition at between 10^7 Pa·s and 10^8 Pa·s, in the same range as squalane [10].

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Scott BAIR. He received the B.S., M.S. and Ph.D degrees in mechanical engineering from Georgia Institute of Technology where he is Regents' Researcher in the George W. Woodruff School of Mechanical Engineering. He has been performing experimental research in high pressure rheology for 44 years and has eleven U.S. patents and has published more than 180 journal articles.