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To cite this article: Scott S. Bair, Ove Andersson, Farrukh S. Qureshi & Michele M. Schirru (2017): New EHL Modeling Data for the Reference Liquids Squalane and Squalane Plus Polyisoprene, Tribology Transactions, DOI: 10.1080/10402004.2017.1310339

To link to this article: http://dx.doi.org/10.1080/10402004.2017.1310339

Accepted author version posted online: 27 Mar 2017.
Published online: 27 Mar 2017.

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New EHL Modeling Data for the Reference Liquids Squalane and Squalane Plus Polyisoprene

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ABSTRACT
An important part of the new quantitative approach to elastohydrodynamic lubrication (EHL) is the use of reference liquids with well-characterized thermophysical properties. New measurements are reported for the thermal and rheological properties of squalane to high pressure and of high shear rate and high-frequency viscosity of squalane thickened with polyisoprene (SQL + PIP) at ambient pressure. The glass transition viscosity of squalane at ambient pressure was found from published viscosity measurements and new glass transition measurements by transient hot wire. The glass transition viscosity so determined was incorporated into the improved Yasutomi model and the calculated glass transition temperatures as a function of pressure are comparable to those directly measured, although the hybrid model yields better agreement. The glass transition viscosity of squalane by any definition must be substantially lower than the “universal value” of $10^{12}$ Pa·s. The second Newtonian inflection cannot be characterized in steady shear at ambient pressure for SQL + PIP due to cavitation; however, acoustic viscometry with matching layer does characterize the second Newtonian inflection. To form the analogy between steady and oscillatory shear requires that the steady shear rate be compared with the ordinary frequency rather than the angular frequency for SQL + PIP.

Introduction

When liquid lubricants are entrained in the contact between nonconformal solids of high yield strength and elastic modulus, the liquid film must necessarily be compressed to high pressure. The liquid responds to the pressure with greatly increased viscosity. These elastohydrodynamically lubricated contacts, in contrast to hydrodynamically lubricated contacts, are small and easily isolated to study film thickness and friction. It should therefore be expected that, over time, the mechanisms of film formation and friction would be thoroughly revealed through experiment and analysis. This has not occurred.

The field of elastohydrodynamic lubrication (EHL) has an unusual history. It is one of the few fields that requires a knowledge of the thermophysical properties of liquids at high pressures, above 0.5 GPa. Despite significant progress in measurement techniques at high pressures (Holzapfel and Isaacs (1)) over the last 40 years, EHL has resisted the use of accurate properties in analysis, although the situation has improved significantly since the mid-1990s when viscosity measurements at high pressure were effectively banned by the peer review process. As an example, in EHL, liquid compressibility is given by the Hayward (2) equation (known in EHL as Dowson and Higginson) with a compression limit and parameters that do not vary with temperature or the type of liquid; Hayward (2) found that this expression was accurate to only 0.1 GPa and then with the appropriate parameterization. By far the most egregiously misrepresented property has been viscosity. Comparisons of viscometer measurements with the viscosity employed in EHL analyses began more than 40 years ago with the significant work of Hutton and Phillips (3). They found orders of magnitude error in the viscosity used in an analysis of transient EHL entrapment. It has been an accepted technique within EHL to adjust viscosity to reach agreement with experimental results, and this procedure continues today (Bair (4); Bair, et al. (5), (6)).

As a result of the acceptance and use of adjusted viscosities, this field has been unable to demonstrate that false assumptions are, in fact, false. One of these false assumptions has been the Newtonian inlet zone. Only recently have methods been developed to account for film thickness with shear-dependent viscosity (Habchi, et al. (7)), and one of the reference liquids used to validate the method, squalane plus polyisoprene (SQL + PIP), is the subject of this article.

Another related false assumption is that the logarithmic shape of a friction curve results from the logarithmic dependence of shear stress on shear rate; that is, the Eyring sinh law (Ree, et al. (8)). An excellent example is the work of Johnson and Tevarrwerk (9). Although the pressure dependence of
viscosity is unlike any measured in a viscometer, this article has had a profound influence on EHL and is the basis of the non-Newtonian model most often applied to high-pressure EHL films, although it has not been applied using accurate pressure dependence of viscosity.

The assumption that a logarithmic friction response results from a logarithmic constitutive response can be tested with one of the reference liquids that are the subject of this article. Squalane (SQL) was employed for a full thermal EHL simulation of the reference liquids that are the subject of this article. Squa-lane (SQL) was employed for a full thermal EHL simulation of

$\alpha_0 = \text{Initial pressure-viscosity coefficient (Pa}^{-1})$

$\eta = \text{Rate-dependent steady shear viscosity (Pa}\cdot\text{s})$

$\kappa = \text{Thermal dependent oscillatory shear viscosity (Pa}\cdot\text{s})$

$\lambda_{\text{die}} = \text{Dielectric relaxation time (s)}$

$\lambda_{Cp} = \text{Heat capacity relaxation time (s)}$

$\mu = \text{Limiting low-shear viscosity (Pa}\cdot\text{s})$

$\mu_0 = \text{Low-shear viscosity at } p = 0 (\text{Pa}\cdot\text{s})$

$\mu_\infty = \text{Low-shear viscosity for zero argument of the exponential (Pa}\cdot\text{s})$

$\rho = \text{Mass density (kg/m}^3\text{)}$

$\tau = \text{Shear stress (Pa)}$

$\omega = \text{Angular frequency (rad/s)}$

indicates a slope; that is, an “Eyring stress,” of 9.3 MPa. However, the shear dependence of viscosity for the calculation was power law (Björling, et al. (10)), not sinh law. The logarithmic friction disappears when the stress limit is removed, as shown in Fig. 1. Therefore, the logarithmic friction response of squalane results from super-Arrhenius piezoviscosity and a pressure-proportional stress limit (Bair, et al. (11)), not a logarithmic constitutive response.

An alternative to the classical approach of EHL appeared about 10 years ago. Quantitative EHL (Bair, et al. (12)) employs real, measureable thermophysical properties of the liquid, in contrast to classical EHL, which employs fictional narratives concerning the works of Barus, Roelands, and Eyring to adjust these properties to suit the purpose at hand. Reference liquids with well-characterized thermophysical properties at the pressures of EHL have been an important part of the new quantitative elastohydrodynamics.

One such reference liquid is squalane, 2,6,10,15,19,23-hexamethyldocosane, which has pressure-dependent viscosity similar to a 4 cSt polyalphaolefin (Bair (13)). It was obtained from a chemical supply house with stated purity of 99%. This liquid was used by Liu and coworkers (14) in the first numerical solution for EHL film thickness to employ real viscosity and the agreement with experimental film thickness by colorimeter interferometry was striking. The description of the pressure dependence employed by Liu and coworkers (14) was in sharp contrast to the pressure–viscosity coefficient of squalane required to explain the thickness of thin films by classical EHL (Johnston, et al. (15)), which bears no relation to primary measurements. New discoveries followed rapidly once it was demonstrated that both film thickness and friction could be accurately explained and predicted (Björging, et al. (10); Liu, et al. (16); Krupka, et al. (17), (18); Habchi, et al. (19)) without adjusting the properties of the liquid. SQL has been an important subject for these EHL investigations and it was first suggested as a reference standard (Sax and Stross (20)) six decades ago.
Another reference liquid (SQL + PIP) is a solution of 15% by weight cis-polyisoprene (PIP) in squalane, intended to be representative of the polymer-blended multigrade gear oils and engine oils (Bair (21)). The PIP has molecular mass of $4 \times 10^4$ kg/kmol and one of the authors has stored 0.5 kg. Notably, this reference liquid was employed to validate an EHL film thickness formula for liquids displaying a second Newtonian viscosity inflection (Habchi, et al. (7)).

This article adds to the considerable existing literature (Bair (4), (13), (21); Habchi, et al. (7); Björling, et al. (10); Sax and Stross (20); Harris (22); Pensado, et al. (23); Fandino, et al. (24); Comuñas, et al. (25)) some new additional high-pressure thermophysical property measurements on SQL along with correlations for SQL and for SQL + PIP from four different laboratories. For SQL, the thermal conductivity and heat capacity were measured to high pressure at Umeå University and the viscosity was measured to very high pressure at Georgia Tech. For SQL + PIP at ambient pressure, the viscosity at high shear rate was measured at Lubrizol and the viscosity at high frequency was measured at the University of Sheffield.

**Squalane glass transition**

Oddly, there is little mention of the glassy state in EHL literature, although many numerical simulations have treated the lubricant as if the liquid were at temperatures well below the glass transition temperature at the Hertzian pressure. Liquid lubricants readily supercool. That is, they avoid crystallization on cooling or compression and become solid only by vitrification. The viscosity becomes so large that no liquid-like response is possible and by most means of observation the material is solid. In contrast to crystallization, the glass transition occurs over a range of temperature or pressure, and for a given means of detecting the transition it occurs at a specific viscosity, $\mu_g$, that is independent of temperature and pressure. Therefore, the glass transition point can be used as a marker for viscosity in EHL studies.

The Williams, Landel, and Ferry (WLF; Williams, et al. (26)) equation,

$$\mu = \mu_\infty \exp \left[ \frac{-2.303C_1(T - T_g)}{C_2 + (T - T_g)} \right],$$  

is equivalent to the Vogel, Tamann, and Fulcher (VTF) equation (Angell (27)),

$$\mu = \mu_\infty \exp \left[ \frac{D_p T_\infty}{T - T_\infty} \right].$$

The WLF and VTF equations are related by $D_p T_\infty = C_2 \ln(\mu_\infty/\mu_0)$, $\mu_\infty = \mu_\infty \exp(2.303C_1)$, and $T_\infty = T_g - C_2$. The WLF equation employs the glass transition as an isoviscous reference state and can be derived from the concept of free volume.

Yasutomi and coworkers (28) applied the WLF equation to both the temperature and the pressure dependence of viscosity by making the glass transition temperature, $T_g$, and the relative thermal expansivity of the free volume, $F$, functions of pressure:

$$\mu = \mu_0 \exp \left[ \frac{-2.303C_1(T - T_g(p)) F(p)}{C_2 + (T - T_g(p)) F(p)} \right]$$

using the Oels and Rehage (29) equation for the glass transition pressure.

$$T_g(p) = T_g(0) + A_1 \ln(1 + A_2 p).$$

There is an advantage in a correlation that employs the glass transition. The measurement of $T_g$ as a function of pressure by dilatometry is relatively easy (Weitz and Wunderlich (30)) compared to viscometry at high pressures and the empirical function (4) is accurate for elevated pressure. Recently, an improved function for the pressure dependence of the relative thermal expansivity of the free volume, $F(p)$, was introduced (Bair, et al. (31)) to correct nonphysical behavior at high pressure:

$$F = (1 + b_1 p)^{b_2}.$$  

The fit at low pressure also improves with Eq. [5].

The thermal properties for elevated pressure of squalane; thermal conductivity, $\kappa$; and volumetric heat capacity, $\rho C_p$, were required in a previous numerical simulation predicting friction in the thermoviscous regime of EHL traction (Björling, et al. (10)); empirical relations for the temperature and pressure dependence of the thermal conductivity and volumetric heat capacity may be found in Björling, et al. (10). These properties were measured by the transient hot-wire method (Håkansson, et al. (32)). The glass transition was revealed in these measurements as shown in Figs. 2 and 3 for thermal conductivity and volumetric heat capacity, respectively. In particular, the heat capacity goes from a large liquid-like value to a relatively smaller solid-like value as the temperature is reduced. A peak in conductivity marks the transition. The glass transition temperatures are listed as a function of pressure in Table 1 and for ambient pressure, $T_g = 174.4$ K. Combining the uncertainties

![Figure 2. Temperature dependence of the thermal conductivity of squalane at pressures of 30 and 800 MPa.](image)
in temperature and pressure gives an estimated uncertainty in \( T_g \) of 1 K. Fitting the Oels and Rehage (29) equation gives \( A_1 = 200 \text{ K} \) and \( A_2 = 0.650 \text{ GPa}^{-1} \). The measurement of a glass transition temperature is associated with a characteristic time of the experiment. Because of the short characteristic time of the hot-wire experiment, the heat capacity relaxation time is only about \( 0.3 \text{ s} \) (Andersson (33)) at the glass transition temperature in Figs. 2 and 3.

**Squalane viscosity**

The viscosity at the glass transition, \( \mu_g \), has been the subject of speculation, and given the extreme difficulty in measuring this property it is ordinary assigned an estimated “universal” value of \( 10^{12} \text{ Pa} \cdot \text{s} \). Matusita and coworkers (34) found that for three fluoride glasses in isobaric cooling, \( \mu_g \) increases with decreasing cooling rate and that \( 10^{12} \text{ Pa} \cdot \text{s} \) was the value for all glasses studied in the limit of zero rate. Giordano, et al. (35) found \( \mu_g = 10^{11.06} \text{ Pa} \cdot \text{s} \) for volcanic minerals. Schweyer (36) found \( \mu_g = 10^{9} \text{ Pa} \cdot \text{s} \) for asphalts under pressure. Bair (37) required \( \mu_g = 10^{9.1} \text{ Pa} \cdot \text{s} \) to fit the original Yasutomi model to viscosity and glass transition measurements on a naphthenic mineral oil. In the original formulation of the Yasutomi model, it was sometimes necessary to assume \( \mu_g \) to be as low as \( 10^{7} \text{ Pa} \cdot \text{s} \) to be consistent with dilatometer measurements of \( T_g(p) \) (Yasutomi, et al. (28)). In tribology, the glass transition of oils has traditionally been studied by dilatometry or light scattering (Alsaad, et al. (38)).

Deegan and coworkers (39) have presented viscosity measurements of squalane at ambient pressure down to 169 K that cross the glass transition. Their data were successfully fitted to a single VTF equation (Eq. [2]; Deegan, et al. (39)), thus precluding a dynamic crossover. Solving for \( T \sim 174.4 \text{ K} \) gives the glass viscosity as \( \mu_g = 1.23 \times 10^{7} \text{ Pa} \cdot \text{s} \) (10.69 Pa·s) for squalane. This value for the glass viscosity can be incorporated into the improved Yasutomi model (Hutton and Phillips (3)). For this purpose, viscosities are available from Bair (21) for pressure up to 1.0 GPa at 20°C and to 1.2 GPa at 40 and 65°C. The estimated uncertainty is 4%. To generate viscosity data closer to the glass pressure at more usual EHL temperatures, additional viscosity measurements were performed in a falling cylinder viscometer.

The viscometer is an improved version of the instrument described in Bair (40). The intensifier pressure relation is now determined by the resistance of a manganin wire that was calibrated with a dead-weight tester to 1.4 GPa. The hollow sinker was fabricated with an iridium core. The large mass density of iridium reduces the error in the buoyancy correction resulting from error in the sample density estimate. Density was estimated from the Tait equation (Bair (21)). Measurements were made at 21.5 and 40°C. It was not possible to repeat the previous results at 20°C because of the high laboratory ambient temperature of an Atlanta summer. The new measurements are reported in Table 2. Because of the rather long fall times, lasting up to 4 h, the estimated uncertainty in viscosity is 12% here. Uncertainties for pressure and temperature are 5 MPa and 0.3°C, respectively.

These viscosities and those of Bair (21) were fitted to the improved Yasutomi model (Eqs. [3]–[5]) with \( \mu_g = 1.23 \times 10^{7} \text{ Pa} \cdot \text{s} \). The resulting parameters are listed in Table 3 and \( T_g \) extrapolated to ambient pressure is found to be 184.5 K, 10 K greater than that from the hot-wire measurement. The viscosities are compared with the model in Fig. 4. The standard devia-

### Table 1. Glass transition temperature at elevated pressures from transient hot-wire. \( T_g \) corresponds to a heat capacity relaxation time of about 0.3 s.

<table>
<thead>
<tr>
<th>( p ) (GPa)</th>
<th>( T_g ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>174.4</td>
</tr>
<tr>
<td>0.025</td>
<td>178</td>
</tr>
<tr>
<td>0.075</td>
<td>185</td>
</tr>
<tr>
<td>0.15</td>
<td>194</td>
</tr>
<tr>
<td>0.25</td>
<td>206</td>
</tr>
<tr>
<td>0.35</td>
<td>217</td>
</tr>
<tr>
<td>0.45</td>
<td>227</td>
</tr>
<tr>
<td>0.6</td>
<td>238</td>
</tr>
<tr>
<td>0.8</td>
<td>256.2</td>
</tr>
</tbody>
</table>

### Table 2. New viscosity measurements (Pa·s) for squalane at indicated temperatures and pressures.

<table>
<thead>
<tr>
<th>( p ) (MPa)</th>
<th>( T ) (°C)</th>
<th>( \nu ) (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000</td>
<td>21.5</td>
<td>20,000</td>
</tr>
<tr>
<td>1,100</td>
<td>25.0</td>
<td>75,000</td>
</tr>
<tr>
<td>1,200</td>
<td>28.4</td>
<td>350,000</td>
</tr>
<tr>
<td>1,300</td>
<td>33.4</td>
<td>13,000</td>
</tr>
<tr>
<td>1,350</td>
<td>36.0</td>
<td>44,000</td>
</tr>
<tr>
<td>1,400</td>
<td>34.8</td>
<td>91,000</td>
</tr>
</tbody>
</table>

### Table 3. Parameters of the improved Yasutomi model.

<table>
<thead>
<tr>
<th>( \mu_g ) (Pa·s)</th>
<th>( T_g ) (°C)</th>
<th>( A_1 ) (°C)</th>
<th>( A_2 ) (GPa)</th>
<th>( b_1 ) (GPa)</th>
<th>( b_2 ) (GPa)</th>
<th>( C_1 )</th>
<th>( C_2 ) (°C)</th>
<th>SD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.23 \times 10^7 )</td>
<td>( -88.69 )</td>
<td>( 263.8 )</td>
<td>( 0.3257 )</td>
<td>( 13.73 )</td>
<td>( -0.3426 )</td>
<td>( 11.66 )</td>
<td>( 39.17 )</td>
<td>( 9.2 )</td>
</tr>
</tbody>
</table>

```latex
\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|}
\hline
\( p \) (MPa) & \( T \) (°C) & \( \nu \) (Pa·s) \\
\hline
1,000 & 21.5 & 20,000 \\
1,100 & 25.0 & 75,000 \\
1,200 & 28.4 & 350,000 \\
1,300 & 33.4 & 13,000 \\
1,350 & 36.0 & 44,000 \\
1,400 & 34.8 & 91,000 \\
\hline
\end{tabular}
\end{table}
```
A correlation is required in an EHL simulation to describe, at the least, the pressure dependence of the viscosity of the liquid and, often, the temperature dependence as well. After choosing a property relation that, hopefully, is capable of reproducing all of the trends in the data, a regression analysis is used to find the parameters of the correlation that reduces some measure of the deviations. This approach is helpful in some applications; however, in EHL the sensitivity of the viscosity to pressure, \( \partial \ln \mu / \partial p \), is important, too. The pressure–viscosity slope near \( p = 0 \) influences the film thickness and the pressure–viscosity slope at the maximum contact pressure influences the slope of the logarithmic portion of the friction curve (Bair, et al. (6)). Unfortunately, the \( \partial \ln \mu / \partial p \) that exists in the data is not weighted in the usual regression analysis. This can be shown in Fig. 6, which is a pressure–Stickel plot (Casalini, et al. (42)) of \( [\partial \ln \mu / \partial p]^{-1/2} \) versus pressure for squalane at 40°C. In this presentation, the Paluch equation (Paluch, et al. (43)),

\[
\mu = \mu_0 \exp \left( -\frac{C_D p}{p - p_n} \right),
\]

plots as a descending straight line.
The various curves in Fig. 6 represent correlations that have been applied to the data of Bair (21) at 40°C that extend to only 1.2 GPa. The points are calculated from those data and the two highest pressure entries represent the new viscosities at 1.3 and 1.35 GPa. The correlations are the improved Yasutomi (Bair, et al. (31)), the Murnaghan-Doolittle free volume (Bair (21)), the Vogel-like thermodynamic scaling (Björling, et al. (10)), and the hybrid model (Bair (44)),

$$
\mu = \mu_0 \left( 1 + \frac{\alpha_0}{q} \frac{p}{\mu_0} \right)^q \exp \left( \frac{C_T p}{\mu_0} \right),
$$

which combines the faster-than-exponential response of the Paluch equation (Eq. [6]) at high pressure with the slower-than-exponential behavior of the McEwen equation (McEwen (45)). The Roelands model has also been fitted to the data to 1.2 GPa. This is the most widely used expression in classical EHL, although it is inappropriate for the task. Clearly, the hybrid model is best for extrapolation, and in Fig. 5 the pressure at the glass viscosity is a better fit to the measured glass temperatures. Adding the new data to those already available for squalane at 40°C, the parameters of the hybrid model have been newly regressed and are listed in Table 4 for pressures to 1.2 GPa and again for 1.35 GPa. The hybrid model is plotted in Fig. 4 with the new parameters.

The characteristic time of an EHL contact might be regarded as the transit time through the high-pressure region. For example, if the contact width is 2 × 10⁻⁴ m and the speed is 0.01 to 5 m/s, then the characteristic time is 2 × 10⁻² to 4 × 10⁻⁵ s or 15 to 7,500 times less than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment. This would make the glass transition viscosity 15 to 7,500 times lower than that of the hot-wire experiment.

### Squalane + Polysoprene shear-dependent viscosity

Before exploring the shear thinning of SQL + PIP, the existing low-shear viscosity data to 1.0 GPa from Bair (21) were fitted to the improved Yasutomi model (Eqs. [3]–[5]) and the parameters are entered in Table 3. The universal value of $\mu_g = 10^{12}$ Pa·s was retained here.

Existing shear-dependent data (Bair (21), (46)) are plotted in Fig. 7 for 200, 300, and 450 MPa, the three upper flow curves. New high-shear rate data at ambient pressure were generated with an ultrasonic viscometer. These are the three lower flow curves for 50, 100, and 150°C. The high-temperature, high-shear at 150°C condition (HTHS150) is indicated by a circle on the plots where the shear rate is $10^6$ s⁻¹. The shear stress for the HTHS150 condition is 5 kPa for which the viscosity is 5.11 mPa·s compared to the limiting low-shear value of 6.09 mPa·s. The HTHS150 condition is not sufficiently severe to greatly shear-thin this oil.

Shear thinning occurs when the product of shear rate (or frequency) and the rotational relaxation time of a molecule approaches unity. This relaxation time is approximately proportional to the low-shear viscosity. Hence, the product of shear rate and viscosity, the shear stress, is approximately constant at the Newtonian limit. The presentation of Fig. 7, viscosity as a function of shear stress, illustrates this superposition property of shear-thinning liquids. Flow curves can be superimposed by a vertical shift long a path of nearly constant shear stress. The exception is the data at ambient pressure and 50°C.

The failure of the measurement to superimpose at ambient pressure and 50°C is due to shear cavitation in which a tensile stress appears in one of the principal shear stress directions (Kottke, et al. (47)). The principal normal

---

**Table 4. Parameters of the hybrid model for data to $p = 1,350$ and to 1,200 MPa.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Squalane</th>
<th>Squalane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>0.1 to 1,350</td>
<td>0.1 to 1,200</td>
</tr>
<tr>
<td>$\mu_0$ (MPa·s⁻¹)</td>
<td>0.0158</td>
<td>0.01566</td>
</tr>
<tr>
<td>$\alpha_0$ (GPa⁻²)</td>
<td>18.03</td>
<td>17.836</td>
</tr>
<tr>
<td>$q$</td>
<td>5.324</td>
<td>4.412</td>
</tr>
<tr>
<td>$C_T$</td>
<td>5.515</td>
<td>8.923</td>
</tr>
<tr>
<td>$p_H$ (GPa)</td>
<td>2.517</td>
<td>3.030</td>
</tr>
<tr>
<td>SD (%)</td>
<td>2.0</td>
<td>0.7</td>
</tr>
</tbody>
</table>
stress cavitation criterion predicts that the first cavitation bubbles appear when (Kottke, et al. (47)),

$$\frac{N_1 + \sqrt{N_1^2 + 4r^2}}{2} > \rho, \quad [8]$$

where $N_1$ is the primary normal stress difference, the tensile stress in the flow direction less the tensile stress in the cross-flow direction. For polymer-thickened oils, $N_1$ may be estimated from (Bair (48)):

$$N_1 = \frac{2\tau^2}{G}, \quad [9]$$

where $G$ is the Newtonian limit shear stress obtained from a measurement of shear thinning.

The curves in Fig. 7 are the modified Carreau equation (Habchi, et al. (7)).

$$\eta = \mu_2 + (\mu - \mu_2) \left[1 + \left(\frac{\tau}{\mu} \right)^2 \right]^{\frac{n-1}{4}}, \quad [10]$$

The shifting rule is

$$G = G_R \left(\frac{\mu_R}{\mu_R} \right)^m, \quad [11]$$

with $n = 0.65$, $\mu_2/\mu = 0.28$, $G_R = 19$ kPa, $\mu_R = 10$ Pa·s, and $m = 0.1$ obtained by fitting the flow curves. The value of $m$ is typical. The principal normal stress cavitation criterion predicts cavitation bubbles at ambient pressure for shear stress greater than 23 kPa.

The solvent, in this case squalane, begins to shear-thin as the shear stress approaches 6 MPa (Bair (13)), at the termination of the curves plotted in Fig. 7. Shear thinning of the base oil usually precedes a second Newtonian plateau in gear oils as it would here.

Generally, steady shear viscosity measurements at ambient pressure cannot sustain sufficient shear stress due to cavitation to observe the second Newtonian inflection in modern lubricants, much less reach any second Newtonian plateau. However, oscillatory shear measurements can produce shear thinning without generating high shear stress (Bair, et al. (49)), as demonstrated in the following.

### Squalane + Polysoprene viscosity at high frequency

The viscosity of SQL + PIP was measured at atmospheric pressure using a calibrated acoustic viscometer based on matching layer theory (Schirru, et al. (50)). Ultrasonic viscometers shear the fluid by exciting the vibration of the solid–fluid boundary, using polarized acoustic shear waves. A shear ultrasonic wave that is incident to a liquid is partly transmitted (and quickly dissipated) in the liquid and partly reflected. The amount of energy that is reflected is a function of viscosity. Ordinarily, the acoustic impedance of the solid is much higher than the liquid impedance, giving a reflection coefficient close to unity and, therefore, insensitive to the viscosity. The use of an interposed matching material, a 40-μm-thick polyimide layer, between the solid and the oil overcomes the acoustic mismatch and increases the sensitivity to viscosity (Schirru and Dwyer-Joyce (51)).

The ultrasonic reflection from the sample was converted to viscosity using a viscoelastic semi-empirical Maxwell model (Schirru, et al. (50); Schirru and Dwyer-Joyce (51)). It was possible to excite fluid resonance at 1, 5, and 15 MHz, resulting in the viscosities listed in Table 5. The 1 MHz viscosity at 23°C, 84.0 mPa·s, can be used to estimate the 1 MHz viscosity, 75.7 mPa·s, at 25°C using the temperature dependence from the improved Yasutomi correlation. These viscosities at 25°C are plotted in Fig. 8 as a function of frequency. Two definitions for frequency are used. Normal frequency, $f$ (Hz), is the reciprocal of the period of the oscillation and angular frequency is $\omega = 2\pi f$ (rad/s).

The Cox-Merz rule provides an analogy between the viscosities in steady and oscillatory shear (Bair, et al. (49)):

$$\eta(\dot{\gamma}) = \tilde{\eta}(\omega), \quad \dot{\gamma} = \omega. \quad [12]$$

This rule may be tested with the shifted modified Carreau equation [10], which is the curve plotted in Fig. 8. Clearly the steady and oscillatory analogy for this viscometer comes with equating ordinary frequency with shear rate:

$$\eta(\dot{\gamma}) = \tilde{\eta}(f), \quad \dot{\gamma} = f \quad [13]$$

and the agreement is good. Notably, the viscosity generated by the acoustic technique with matching layer does define the second Newtonian inflection for ambient pressure in SQL + PIP, whereas steady shear cannot.
Conclusions

1. The glass transition viscosity of squalane at ambient pressure was found from published viscosity measurements and new glass transition measurements by transient hot-wire for a characteristic time of 0.3 s.

2. The glass transition viscosity was incorporated into the improved Yasutomi model and the calculated glass temperatures as a function of pressure are comparable to those directly measured, although the hybrid model yields better agreement.

3. The hybrid model is superior to many others for pressure extrapolation.

4. The glass transition viscosity of squalane by any definition must be substantially lower than the universal value of 10^{12} Pa·s.

5. The second Newtonian invar can be characterized in steady shear at ambient pressure for SQL + PIP due to cavitation.

6. The shear stress at the HTHS150 condition is insufficient to characterize the shear dependence of SQL + PIP.

7. Acoustic viscometry with a matching layer does characterize the second Newtonian for SQL + PIP.

8. To form the analogy between steady and oscillatory shear requires that the steady shear rate be compared with the ordinary frequency rather than the angular frequency for SQL + PIP.

Acknowledgement

Bair thanks Mark Robbins of Johns Hopkins for suggesting the additional viscosity measurements of squalane.

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