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ORIGINAL PAPER

Resonance Shear Measurement of Confined Alkylphenyl Ether Lubricants

Junichi Watanabe · Masashi Mizukami ·
Kazue Kurihara

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Abstract The tribological properties of four phenyl ether lubricants, monoalkydiphenyl ether (MADE), dialkyldiphenyl ether (DADE), m-phenoxyphenoxy m-biphenyl (m-4P2E), and m-bis(m-phenoxyphenoxy) benzene (m-5P4E), confined between mica surfaces have been investigated using the resonance shear measurement (RSM). The RSM study revealed that the viscous parameter of these lubricants increased when they were confined in a nano-space. The viscous parameter b_2 values of these lubricants confined in a gap smaller than ca. 2–3 nm were in the order of MADE $>$ DADE $>$ m-4P2E $\approx$ m-5P4E, while their bulk viscosities were in the order of m-5P4E $>$ m-4P2E $>$ DADE $>$ MADE. Further, the MADE, which has better hydrodynamic lubrication property because of the lowest bulk viscosity, was relatively easily squeezed out from the gap compared to others. These results have demonstrated that phenyl ether lubricants confined in a nano-space behave quite differently from those of the bulk phase, and the direct characterization of confined lubricants is imperative for designing efficient lubricants, especially for boundary lubrication.

Keywords Resonance shear measurement · Phenyl ether · Lubricants · Confined space · Tribology

1 Introduction

The regulation of the friction/lubrication for moving mechanical devices is important in order to obtain a better performance, reliability, durability, and energy efficiency. In order to achieve such a regulation, the optimized design of the lubricants is necessary. In general, the bulk properties of the lubricants are empirically adjusted by designing the oil's molecular structure as well as by mixing different kinds of base oils and additives to meet the requirements and to achieve a better performance. However, the lubricants function in a confined narrow space between solid surfaces under a high pressure, in regions called elastohydrodynamic and boundary lubrication regions of the Stribeck curve. In particular, in the boundary lubrication region, the thickness of the lubricant is considered to be on a nanometer scale or less. Recently developed fine measurements [1–12] and computer simulation [13, 14] have revealed that the nano-confined liquids have properties quite different from those of the bulk liquids due to the restriction of motion as well as interactions with the solid surfaces [13]. Therefore, it is imperative to understand the properties of confined lubricants with a nanometer thickness in addition to the bulk properties and the performance in the mechanical machines. However, only few studies have been reported about properties of confined lubricants.

One of the most useful tools to study the tribological properties of a nano-confined lubricant is the shear/friction

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J. Watanabe · M. Mizukami · K. Kurihara (✉)
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
e-mail: kurihara@tagen.tohoku.ac.jp

J. Watanabe
e-mail: jun.watanabe.1123@gmail.com

M. Mizukami
e-mail: mizukami@tagen.tohoku.ac.jp

K. Kurihara
WPI-Advanced Institute for Material Research, Tohoku University, Sendai 980-8577, Japan

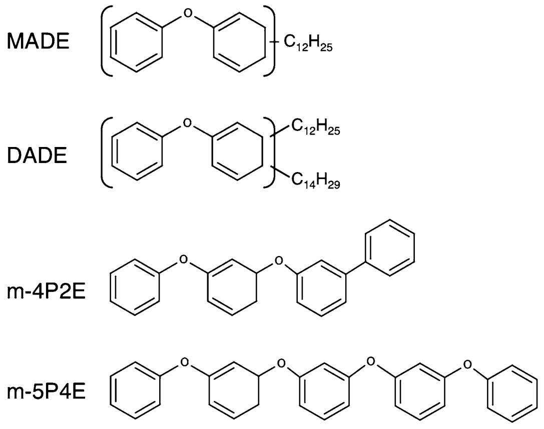

Fig. 1 Chemical structures of phenyl ether lubricants used in this study [15]

forces measurement using a surface forces apparatus (SFA), in which a thin liquid film is formed between two solid surfaces (typically mica) with the crossed cylinder geometry allowing for highly accurate measurements of the surface separation distance (*D*) (ca. 0.1 nm) using an interferometric method [1–12]. SFA-based methods have advantages, i.e., the tribology can be investigated under the well-defined conditions of the surface separation, effective surface area, and normal load. The resonance shear measurement (RSM), which we developed [9–12], is one of the SFA-based shear/friction forces measurements that measures the resonance signal of the upper oscillating mechanical unit. Based on the RSM, the properties of confined liquids can be evaluated via the sensitive changes in the amplitude and frequency of the resonance peak due to changes in the properties of the liquid confined between the upper and lower surfaces. This resonance method has the advantages of a high sensitivity and stability and can continuously monitor the rheological and tribological properties of confined liquids at surface separation distances (*D*) from μm (practically bulk liquid region) to nm thicknesses (nano-confined liquid region).

It is known that the polyphenyl ether lubricants of m-phenoxyphenoxy m-biphenyl (m-4P2E) and m-bis(m-phenoxyphenoxy) benzene (m-5P4E) have unique properties such as high thermal and radiation resistance, and chemical stability (Fig. 1) [15, 16]. These properties are suitable for use under severe conditions such as in gas turbine engines and high vacuum pump oils. However, their viscosities are high at low temperature, which is not desirable for hydrodynamic lubrication. To decrease the viscosity of the polyphenyl ether lubricants at low temperature, their alkyl derivatives, monoalkydiphenyl ether (MADE), dialkyldiphenyl ether (DADE), have been developed and used. The magnitude of the bulk viscosity is known to be in the following order: m-5P4E > m-4P2E > DADE > MADE (Table 1). However, the properties of these lubricants in a confined nano-space, which are important for the boundary lubrication, have not been evaluated and could be quite different from those of bulk.

In this study, we applied the RSM for evaluating four phenyl ether-based lubricants (MADE, DADE, m-4P2E, and m-5P4E) confined in nanometer space gap. The properties of four phenyl ether lubricants in a confined space as well as their bulk properties are discussed in terms of their chemical structures. Our RSM study revealed that all of these lubricants showed a significant increase in viscosity when they were confined in a nano-space. However, the lubricant exhibiting the highest viscosity in the confined space was MADE, which was different from the one exhibiting the highest value in the bulk, m-5P4E.

2 Experimental

2.1 Samples

The lubricants used in this study were monoalkydiphenyl ether (MADE), dialkyldiphenyl ether (DADE), m-phenoxyphenoxy m-biphenyl (m-4P2E), m-bis(m-phenoxyphenoxy) benzene (m-5P4E) and obtained from the Matsumura Oil Research Corporation (MORESCO) (Fig. 1). Properties of these lubricants are shown in Table 1. The sizes of the lubricants used were estimated by using "MarbinSketch" program from ChemAxon Ltd, (see Figure S1 in Supplementary Material). These lubricants were used for the measurements after filtration through a PTFE filter with 0.2 μm pores. Muscovite mica was purchased from M.Watanabe & Co., Ltd.

2.2 Resonance Shear Measurement (RSM)

A schematic illustration of the resonance shear apparatus is shown in Fig. 2. This system was used in combination with

Table 1 Properties of four phenyl ether lubricants used in this study [15]

	Bulk viscosity (mPa s)	Pour point (°C)	Viscosity index	Density (g/cm^3)
MADE	12	−55	74	0.946
DADE	125	−40	26 ± 3	0.908
m-4P2E	436	2.5	18 ± 12	1.167
m-5P4E	1,196	2.5	14 ± 1	1.200

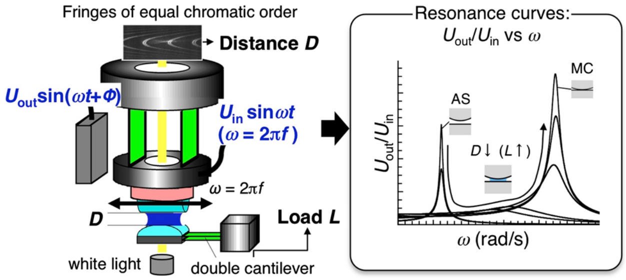

Fig. 2 Schematic illustration of resonance shear apparatus

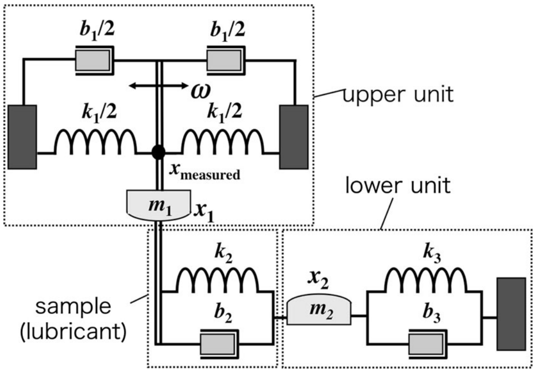

Fig. 3 Schematic illustration of physical model used for analyzing the resonance curves. The parameters of b_1, b_2, and b_3 (Ns/m) are the viscous parameter of the upper unit, the sample, and the lower unit; k_1, k_2, and k_3 (N/m) are the elastic parameter (spring constant) of the upper unit, the sample (lubricant in this study), and the lower unit, respectively. The parameters of m_1 and m_2 are the effective masses of the upper and lower units, and x_1 and x_2 are the position of the upper and lower surfaces, respectively. The $x_{measured}$ value is the deflection of the upper spring (k_1) measured by a capacitance probe and is related to x_1 using the parameter α ($x_1 = \alpha x_{measured}$)

SFA (NL-SF001, Nippon Laser & Electronics Lab.) [17]. The backside of the mica sheets (2.7–3.5 μm thickness in this study) used as the substrates were coated by a vacuum deposited silver layer of 50 nm in thickness to produce interference fringes, then glued onto cylindrical quartz disks [a radius of curvature (R) = 20 mm] using epoxy resin (Shell, Epikote 1004). The surface separation distance between the mica surfaces (D) was determined using the fringes of equal chromatic order (FECO) with a resolution of 0.1 nm [18]. The lower surface was supported by a double cantilever spring (spring constant k_N = ca. 200 N/m) and driven by a pulse motor. The interaction force F [normal load (L)] was obtained with a resolution of 10 nN by measuring the deflection of a spring (Δd) using Hook's law ($F = k_N \cdot \Delta d$). When the surfaces were pressed together under the normal load (L) roughly >0.1 mN, the surfaces were elastically flattened due to the elastic deformation of the epoxy resin and mica sheet on it. The temperature inside the apparatus measured by a platinum resistance thermometer was equilibrated ca. 24 °C due to the irradiation by a white light used for FECO.

As shown in Fig. 2, the resonance shear measurement system was composed of an upper unit (an upper surface connected to the four-sectored piezo tube and hung by a pair of vertical leaf springs) and a lower unit (a lower surface mounted on the horizontal leaf spring). The upper unit was laterally moved by applying a sinusoidal voltage of the amplitude (U_{in} = 1.0 V), and the frequency (f) to one sector of the piezo tube as well as an opposite phase voltage to the opposing sector. The deflection of the vertical spring was measured by a capacitance probe (Mircosense 4830, Japan ADE) as an output voltage (U_{out}) with the sensitivity of 5 μm/V. By scanning the frequency of the input voltage, the resonance curve [U_{out}/U_{in} vs. ω (=2πf)] was obtained. It showed the maximum intensity U_{out}/U_{in_res} at a resonant frequency ω_{res} of the oscillating unit. The property of the liquids confined between the upper and lower surfaces could be evaluated with a high sensitivity based on the peak intensity (U_{out}/U_{in_res}) and frequency (ω_{res}) which were perturbed by the confined liquid between the surfaces.

2.3 Analysis of RSM Data

The viscous parameter of sample b_2 could be quantitatively evaluated by analyzing the resonance curve using Eq. 1 derived from the physical model (Fig. 3) [11].

$$\frac{U_{out}}{U_{in}} = \frac{C}{\alpha}\sqrt{\frac{\left(K_2 - m_2\omega^2\right)^2 + \omega^2 B_2^2}{\left[(K_1 - m_1\omega^2)(K_2 - m_2\omega^2) - \omega^2 B_1 B_2 - k_2^2 + b_2^2\omega^2\right]^2 + \omega^2\left[(K_1 - m_1\omega^2)B_2 + (K_2 - m_2\omega^2)B_1 - 2k_2 b_2\right]^2}} \tag{1}$$

where the $B_1 = b_1 + b_2$, $B_2 = b_2 + b_3$, $K_1 = k_1 + k_2$, $K_2 = k_2 + k_3$, and C is an intensity parameter including the sensitivity of the capacitance probe and piezoelectric constant of piezo tube. The details of the resonance shear measurement were previously described [9–12, 19–22].

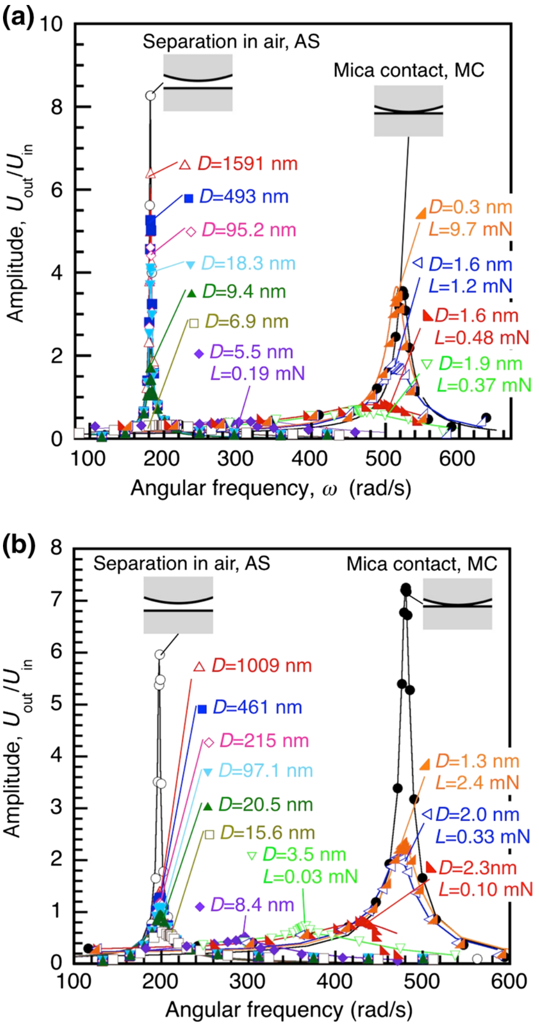

Fig. 4 **a** Resonance shear curves measured for monoalkydiphenyl ether (MADE) between mica surfaces. **b** Resonance shear curves measured for dialkyldiphenyl ether (DADE) between mica surfaces. *Symbols* and *solid lines* are the experimental data and fitting curves drawn by Eq. 1, respectively. The parameters used for fitting of the MADE data are as follows: $k_1 = 786$ N/m, $b_1 = 0.034$ Ns/m, $m_1 = 0.025$ kg, $k_3 = 7{,}000$ N/m, $b_3 = 0.50$ Ns/m, $m_2 = 0.015$ kg, and those for the DADE data are $k_1 = 786$ N/m, $b_1 = 0.05$ Ns/m, $m_1 = 0.025$ kg, $k_3 = 6{,}000$ N/m, $b_3 = 0.18$ Ns/m, $m_2 = 0.015$ kg

3 Results and Discussion

3.1 Resonance Shear Measurement for Alkyldiphenyl Ether Lubricants: MADE and DADE

To study the properties of phenyl ether lubricants as a function of the surface separation distance (D), we performed the resonance shear measurement at various D's. Figure 4a shows the resonance curves obtained for the monoalkydiphenyl ether (MADE) between the mica surfaces at various surface separation distances (D) and normal loads (L). Before injection of the lubricant between the mica surfaces, two reference resonance curves were measured. When the mica surfaces were separated in air (AS), which corresponded to the condition of free oscillation of the upper unit, a resonance peak appeared at a frequency $\omega_{\mathrm{res}} = 182$ rad/s with an intensity $U_{\mathrm{out}}/U_{\mathrm{in\_res}} = 8.3$. When the mica surfaces were in contact in air (MC), the upper and the lower surfaces moved together with a strong adhesion contact. Thus, the resonance frequency of the MC curve shifted to a higher frequency of 522 rad/s due to the contribution of the mass and spring constant of the lower surface units, and the peak intensity $U_{\mathrm{out}}/U_{\mathrm{in\_res}}$ was 3.6. When the MADE thickness D was 1,591 nm, the ω_{res} remained same as that of AS and the $U_{\mathrm{out}}/U_{\mathrm{in\_res}}$ decreased to 6.4 (77 % of AS) due to the bulk viscosity of MADE. With the distance decreasing to 9.4 nm, the $U_{\mathrm{out}}/U_{\mathrm{in\_res}}$ decreased to 1.7 which demonstrated that the viscosity of MADE gradually increased. At $D = 6.9$ nm, the resonance peak became low and broad ($U_{\mathrm{out}}/U_{\mathrm{in\_res}} = 0.3$, $\omega_{\mathrm{res}} = 206$ rad/s), indicating that a ca. one order of magnitude increase in the viscosity when compared to the bulk value due to the confinement. At $D = 5.5$ nm, the peak was small and broad ($U_{\mathrm{out}}/U_{\mathrm{in\_res}} =$ ca. 0.4) and its frequency shifted to $\omega_{\mathrm{res}} =$ ca. 300 rad/s. The higher frequency shift of the ω_{res} indicated the transmission of the shear force to the lower surface due to the further increase in the viscosity of the confined MADE. With a further decrease in the distance to 0.3 nm, the ω_{res} further shifted to the higher frequency of 516 rad/s and the $U_{\mathrm{out}}/U_{\mathrm{in\_res}}$ increased to 3.4 (94 % of MC peak). Upon further increase in the normal load, the thickness of the MADE layer could not be lower than 0.3 nm. The smallest thickness of the confined liquids is the so-called hard wall thickness. The observed changes in the resonance curve indicated that the viscosity of the confined MADE significantly increased at distances below ca. 10 nm. In particular, the high peak intensity at the hard wall thickness of $D = 0.4 \pm 0.2$ nm, which was smaller than the smallest dimension of MADE molecule (0.68 nm, see Figure S1 in Supplementary Material), indicated that MADE layer was less than one and lost its lubricity under high normal load of 3.5 mN. The hard wall thicknesses were obtained from the distance between mica surfaces at high normal loads as shown in Figure S2 in Supplementary Material.

Figure 4b shows the resonance curves obtained for dialkyldiphenyl ether (DADE) between the mica surfaces.[1] At $D = 1{,}009$ nm after the injection of DADE, the $U_{\mathrm{out}}/U_{\mathrm{in\_res}}$ value decreased to 1.39 (23 % of AS) due to the

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[1] The intensity and frequency of the AS and MC peaks for DADE were different from those observed for MADE (Fig. 4a). This was caused by the change in the effective spring constants and viscous parameters of the upper and lower units due to the disassembly and assembly of the apparatus. Thus, we always measured the AS and MC resonance curves for the each set of measurements as the references for the physical model analysis.

bulk viscosity. The decrease in the U_{out}/U_{in_res} was more significant compared to that observed for MADE, indicating the higher viscosity of DADE. This was consistent with the literature values of MADE and DADE in their bulk states (MADE: 12 mPa s, DADE: 125 mPa s). With the decreasing distance to 15.6 nm, the peak intensity U_{out}/U_{in_res} decreased to 0.60. At $D = 8.3$ nm, the ω_{res} shifted to the higher frequency of 295 rad/s, indicating that the viscosity further increased and the shear force was transmitted to the lower unit through the confined DADE layers. At $D = 4.6$ nm, the U_{out}/U_{in_res} increased to 1.63 and the ω_{res} shifted to 468 rad/s. With the further decreasing of the distance to 1.3 nm (hard wall thickness), the ω_{res} further shifted to a higher frequency close to that of the MC peak, then the U_{out}/U_{in_res} increased to 2.3 (32 % of MC peak). These changes in the resonance curve revealed the viscosity of the confined DADE at distances below ca. 16 nm. The average hard wall thickness of DADE was 1.6 ± 0.4 nm, and the smallest dimension of DADE was 0.70 nm (see Figure S1 in Supplementary Material). This indicated that two layers of DADE remained at the hard wall thickness, while the MADE was squeezed out from the gap. This could be related to the larger size and branched shape of DADE molecule.

The resonance peak intensity at long distances normalized by the AS peak intensity $(U_{out}/U_{in\_res})/(U_{out}/U_{in\_res\_}AS)$ reflects the bulk viscosity. The higher value of $(U_{out}/U_{in\_res})/(U_{out}/U_{in\_res\_}AS)$ for MADE (77 %) than that for DADE (23 %) is well correlated with the smaller bulk viscosity of MADE [15]. The distance at which the significant increase in the viscosity started was greater for DADE (ca. 16 nm) when compared to that of MADE (ca. 10 nm). On the other hand, at the hard wall thickness, MADE showed the high peak intensity of 94 % of the MC peak while that of DADE was 32 % of the MC peak. This indicated the higher friction (less lubricity) of MADE under confinement. The viscosity and lubricity of the confined MADE and DADE will be discussed later based on the viscous parameter b_2 obtained by analyzing the resonance curves together with those of the polyphenyl ethers (m-4P2E and m-5P4E).

3.2 Resonance Shear Measurement on Polyphenyl Ether Lubricants: m-4P2E and m-5P4E

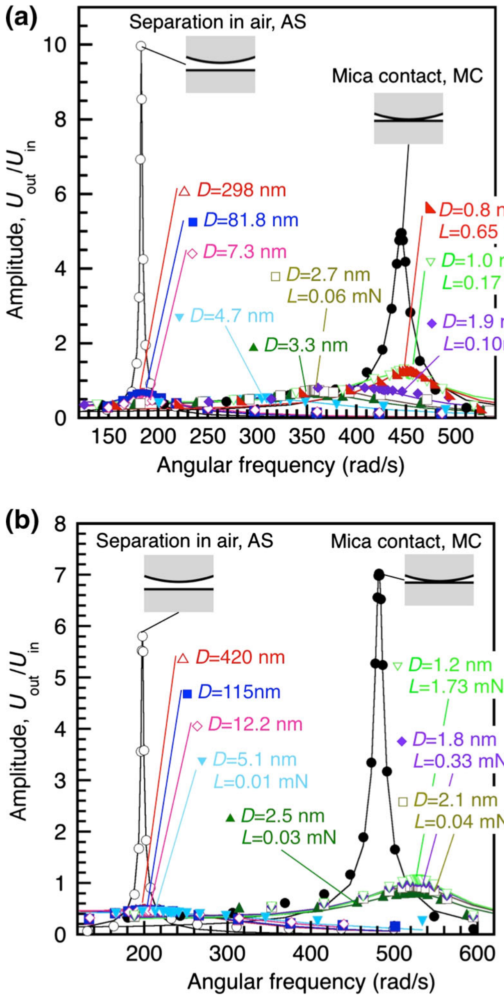

Fig. 5 **a** Resonance shear curves measured for m-phenoxyphenoxy m-biphenyl (m-4P2E) between mica surfaces. **b** Resonance shear curves measured for m-bis(m-phenoxyphenoxy) benzene (m-5P4E) between mica surfaces. *Symbols* and *solid lines* are the experimental data and fitting curves drawn by Eq. 1. The parameters used for fitting of the m-4P2E data are $k_1 = 786$ N/m, $b_1 = 0.037$ Ns/m, $m_1 = 0.026$ kg, $k_3 = 4{,}200$ N/m (MC), $k_3 = 5{,}600$ N/m ($D \leq 1.0$ nm), $b_3 = 0.40$ Ns/m, $m_2 = 0.015$ kg, and those for the m-5P4E data are $k_1 = 786$ N/m, $b_1 = 0.057$ Ns/m, $m_1 = 0.026$ kg, $k_3 = 6{,}000$ N/m (MC), $k_3 = 8{,}000$ N/m ($D \leq 2.5$ nm), $b_3 = 0.14$ Ns/m, $m_2 = 0.015$ kg

The resonance curves of 4P2E and 5P4E confined between mica surfaces are shown in Fig. 5a, b. The resonance peaks at long distances were quite small (<10 % of AS peak) due to the high viscosity values of m-4P2E (436 mPa s) and m-5P4E (1,196 mPa s). At the distances below ca. 5 nm, the resonance peak shifted to the higher frequencies due to the increase in the viscosity of the confined m-4P2E or m-5P4E. At the hard wall thicknesses (0.8 nm for m-4P2E, 1.2 nm for m-5P4E), the peak intensity U_{out}/U_{in_res} increased to 1.3 (26 % of MC peak) for m-4P2E and to 1.1 (15 % of MC peak) for m-5P4E. The lower U_{out}/U_{in_res} value at the hard wall thicknesses compared to those of MADE and DADE indicated that the viscosity of the confined m-4P2E and m-5P4E were lower than those of MADE and DADE and contributed to their better lubricity. The average hard wall thicknesses of m-4P2E and m-5P4E were 0.6 ± 0.2 nm and 1.3 ± 0.2 nm, respectively. These values agreed with the smallest dimensions of m-4P2E (0.68 nm) and twice the m-5P4E (0.73 nm). This indicated that one layer of m-4P2E and two layers of m-5P4E remained in the hard wall thicknesses.

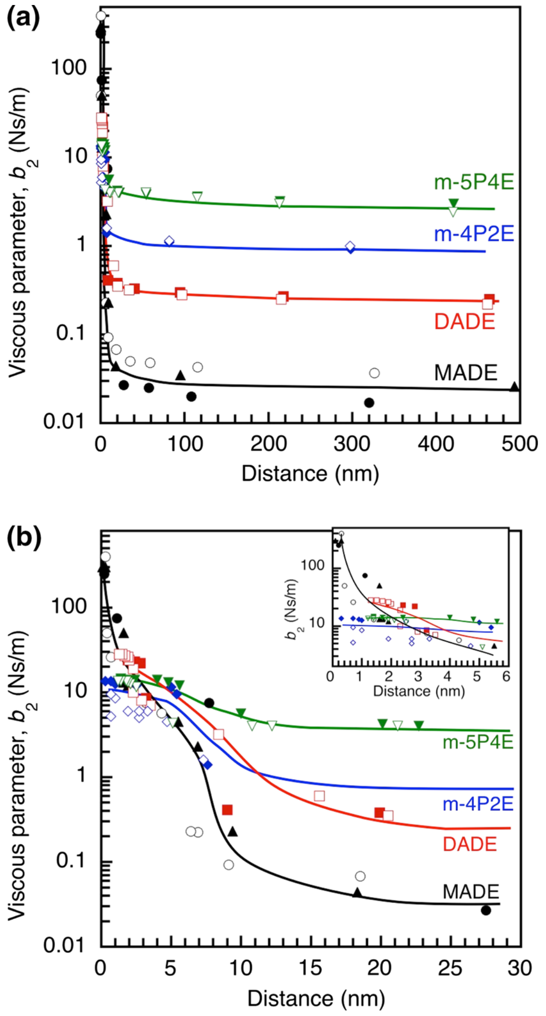

Fig. 6 **a** Viscous parameters (b_2) of phenyl ether lubricants, MADE, DADE, m-4P2E, and m-5P4E confined between mica surfaces plotted as a function of the surface separation distance (D). **b** Viscous parameters (b_2) of phenyl ether lubricants at a short surface separation distance (D) in order to compare the viscosity in a confined space. *Different symbols* represent the data obtained from the separate preparations. *Solid lines* are the guides for eyes. The *inset* shows the magnified plots at shot distance

We note that an unusual resonance response was observed for both m-4P2E and m-5P4E, that is, the peak frequency became higher than that of the MC peak at distances less than ca. 2 nm. In general, the confined liquids exhibit the increase in both b_2 and k_2 parameters. However, the increase in b_2 and/or k_2 could shift the peak frequency only up to the frequency of MC peak. Therefore, to explain this frequency shift beyond MC frequency, the increase in the elastic parameter k_3 should be considered. A possible cause of the increase in the k_3, we could think of, was the increase in the effective contacting area, which was possibly due to the significantly high bulk viscosity and/or due to increase in the elastic parameter (k_2) upon confinement. Although the evidence of the larger contacting area was not obtained, we could observe the peak at the frequency higher than that of MC peak when the two mica surfaces were glued together with large area as shown in Supplementary Material. To take this effect into account, the resonance curves for m-4P2E and m-5P4E were analyzed using the k_3 parameters greater than the value for MC as shown in the caption of Fig. 5.

Table 2 Viscosity of four phenyl ether lubricants: bulk value from the literature, viscous parameter b_2 at long D, and viscous parameter b_2 at hard wall thickness

	Bulk viscosity (mPa s) [15]	b_2 at long D (Ns/m)	b_2 at hard wall (Ns/m)	Hard wall thickness (nm)
MADE	12	0.02 ± 0.1	338 ± 75	0.4 ± 0.2
DADE	125	0.22 ± 0.02	26 ± 3	1.6 ± 0.4
m-4P2E	436	0.95 ± 0.07	18 ± 12	0.6 ± 0.2
m-5P4E	1,196	2.73 ± 0.31	14 ± 1	1.3 ± 0.2

3.3 Viscous Parameters of Phenyl Ether Lubricants as a Function of D

To compare the viscosity of the four phenyl ether lubricants confined between the mica surfaces, the viscous parameter b_2 (Ns/m) was determined by analyzing the resonance curves using the physical model [11] shown in Fig. 3. The obtained b_2 values were plotted versus the surface separation distance (D) in Fig. 6a, b. The b_2 values at high D's as well as at the hard wall thickness are summarized in Table 2.

At distances longer than 100 nm, the b_2 values of the lubricants were almost constant and the ratio of the b_2 values of four lubricants was quantitatively agreed well with the ratio of their bulk viscosities from the literature as shown in Table 2. This indicated that there was no change in the viscosity of the four lubricants at $D >$ ca. 100 nm. At $D <$ ca. 100 nm, the b_2 values of the four lubricants gradually increased. The drastic increase in the b_2 values occurred at $D <$ ca. 20 nm for MADE and DADE and at $D <$ ca. 10 nm for m-4P2E and m-5P4E. The alkyl chain introduced on the diphenyl ether backbone of MADE and DADE might induce longer ranged intermolecular interactions.

The b_2 values of m-4P2E and m-5P4E were 11.0 Ns/m at $D = 2.7$ nm and 12.0 Ns/m at $D = 2.5$ nm, respectively, then only slightly increased with the further decreasing D. They reached 18 ± 12 and 14 ± 1 Ns/m at the hard wall thicknesses of 0.6 ± 0.2 nm for m-4P2E and 1.3 ± 0.2 nm for m-5P4E nm, respectively (Table 2). The b_2 value of DADE exhibited more significant increase, and was 25.0 Ns/m at $D = 2.3$ nm and 26 ± 3 Ns/m at $D = 2.0$ nm, then remained constant at distances down to

1.6 ± 0.4 nm (hard wall thickness). The b_2 values of MADE exhibited a most significant increase and reached 28.0 Ns/m at 1.6 nm and 338 ± 75 Ns/m at 0.4 ± 0.2 nm (hard wall thickness). These results demonstrated that the viscosity of the alkylphenyl ether lubricants (MADE and DADE) became higher than those of the phenyl ether lubricants (m-4P2E and m-5P4E) when they were confined in a gap smaller than ca. 2–3 nm as can be seen in an inset of Fig. 6b.

As summarized in Table 2, the viscous parameter b_2 of the four phenyl ether lubricants confined in the hard wall thickness showed almost the reverse order of magnitude compared to those of the bulk. In particular, the significantly high b_2 value of confined MADE (338 ± 75 Ns/m) should be related to the lowest hard wall thickness of 0.4 ± 0.2 nm where part of MADE molecules could be squeezed out. This could be due to the weaker interaction of MADE with mica surfaces and resulted in almost no sliding condition. The b_2 values both of polyphenyl ether lubricants of m-4P2E (18 ± 12 Ns/m) and m-5P4E (14 ± 1 Ns/m) at the hard wall thickness were smaller than those of MADE and DADE. Due to the steric hindrance between the neighboring phenyl rings, the structure of these lubricants cannot be linear. Thus, the smaller b_2 value of m-4P2E and m-5P4E at the hard wall could be related to the poorer molecular packing of m-4P2E and m-5P4E in the confined space.

The obtained results indicated that the regulation of the bulk properties was not enough to achieve the better lubrication properties when the thickness of the lubrication layer was on a nm level and could result in poorer properties under the boundary lubrication conditions. Therefore, the direct evaluation and the determination of the properties of nano-confined lubricants are imperative for the innovative design of the lubricant system.

4 Conclusions

We have investigated the tribological properties of four phenyl ether lubricants, i.e., monoalkydiphenyl ether (MADE), dialkyldiphenyl ether (DADE), m-phenoxyphenoxy m-biphenyl (m-4P2E), m-bis(m-phenoxyphenoxy) benzene (m-5P4E) confined in a nano-space gap between mica surfaces using surface forces and resonance shear measurements (RSM).

The drastic increase in the viscosity parameter b_2 occurred at $D <$ ca. 20 nm for MADE and DADE and at $D <$ ca. 10 nm for m-4P2E and m-5P4E. The alkyl chain introduced on the diphenyl ether backbone of MADE and DADE might induce the longer ranged intermolecular interactions, thus the drastic increase in their b_2 values occurred at longer distances.

The viscosity of the alkylphenyl ether lubricants (MADE and DADE) increased more than those of the phenyl ether lubricants (m-4P2E and m-5P4E) at $D <$ ca. 3 nm. The viscous parameter b_2 of the four phenyl ether lubricants confined in the hard wall thickness showed an almost reverse order of magnitude, MADE $\gg$ DADE $>$ m-4P2E $\approx$ m-5P4E, compared to those of the bulk. In particular, MADE showed a significantly high b_2 value of 338 ± 75 Ns/m at the hard wall thickness of 0.4 ± 0.2 nm, and the resulting friction was comparable to that of the mica–mica solid contact. The smaller b_2 values of m-4P2E and m-5P4E might be related to the less dense molecular packing of m-4P2E and m-5P4E in the confined space due to the less symmetrical structure.

These results indicated that the regulation of the bulk properties is not sufficient to achieve the better lubrication properties and could result in a higher friction in the case of boundary lubrication. It was also indicated that the high friction in the boundary lubrication, which has been considered to be due to the partial direct contact of the solid surfaces, could be due to the significantly high viscosity of the lubricants confined in a nano-space gap. Thus, to avoid or reduce the frictional wear as well as seizure, the direct evaluation of the properties of the nano-confined lubricants is imperative. The RSM can continuously evaluate the properties of confined liquids as a function of the separation distance between two solid surfaces from the bulk to a nanometer thickness under various the normal loads. Thus, the RSM can be regarded as one of the promising tools for the innovative design of a lubricant system. The combination of the RSM and the twin-path SFA [23], which we developed and is only one SFA applicable for the non-transparent samples, can further extend the target to the lubrication between metal surfaces via confined lubricants.

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