Supplementary Information

Molecular design of advanced lubricant base fluid: Hydrocarbon-mimicking ionic liquids

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This file includes:

1. Lubricant data

Five P-SiSO[α-β][χ-δ] samples have been synthesized by Nisshinbo Holdings Inc. (Tokyo). The chemical structures are given by the formula $[(n\text{-}C_{\alpha}H_{2\alpha+1})_3(n\text{-}C_{\beta}H_{2\beta+1})P][(C_{\chi}H_{2\chi+1})_3SiC_{\delta}H_{2\delta}SO_3]$, where the variables α, β, χ, and δ determine the number of carbon atoms in the alkyl groups. Reported properties can be seen in Table 1. The bulkier cations, [4-16], and [6-14], have lower viscosities than the smaller [4-12] cation, as expected due to the weaker ion bonds in bulkier ions. The PFPE samples were supplied by Aldrich and used as received, the properties are shown in Table 2, with the full names of PFPE-L and PFPE-H being Fomblin Y 317926, and Fomblin Y 317950 respectively. The linear formula of these PFPEs are $CF_3O[-CF(CF_3)CF_2O-]_x(-CF_2O-)_yCF_3$ and the molecular weight of Fomblin Y 317950 is reported as 3300 g/mol. The [BMIM][TFSA] properties are shown in Table 3, supplied by Kanto Chemical Co., Inc. (Tokyo).

Table 1. Properties of P-SiSO.

Code	Density, g cm^{-3}	Viscosity, mPa·s		Melting point, °C	10% weight loss at, °C	Water content, ppm	Chemical formula
	25 °C	25 °C	60 °C				
P-SiSO[4-12][1-2]	0.90	2570	208	-6	311	68	$[(n\text{-}C_4H_9)_3(n\text{-}C_{12}H_{25})P][(CH_3)_3SiC_2H_4SO_3]$
P-SiSO[4-12][1-3]	0.93	2429	104	2	291	93	$[(n\text{-}C_4H_9)_3(n\text{-}C_{12}H_{25})P][(CH_3)_3SiC_3H_6SO_3]$
P-SiSO[4-16][1-2]	0.91	1932	269	5	316	137	$[(n\text{-}C_4H_9)_3(n\text{-}C_{16}H_{33})P][(CH_3)_3SiC_2H_4SO_3]$
P-SiSO[4-16][1-3]	0.90	1735	142	-5	299	68	$[(n\text{-}C_4H_9)_3(n\text{-}C_{16}H_{33})P][(CH_3)_3SiC_3H_6SO_3]$
P-SiSO[6-14][1-2]	0.92	1879	200	-19	310	83	$[(n\text{-}C_6H_{13})_3(n\text{-}C_{14}H_{29})P][(CH_3)_3SiC_2H_4SO_3]$

Table 2. Properties of PFPE.

Code	Density, g cm^{-3}	Viscosity, mPa·s		Flash Point, °C
	25 °C	20 °C	60 °C	
PFPE-L	1.9	113	x	>113
PFPE-H	1.9	513	x	>113

Table 3. Properties of [BMIM][TFSA].

Code	Density, g cm^{-3}	Viscosity, mPa·s		Flash Point, °C
	25 °C	20 °C	40 °C	
[BMIM][TFSA]	1.44	56.8	28.4	>200

2. Calculation of wear volume

Hertz theory of normal contact between elastic solids states that for circular point contacts, the radius of contact circle, denoted below as *HzR*, is determined by the following relation [1].

$$HzR = \left(\frac{3PR'}{E'}\right)^{1/3} \tag{S1}$$

P represents the load, R' represents the effective radius defined in equations S2-S4, and E' represents the effective modulus of elasticity, defined in equation S5.

$$R' = \left(\frac{1}{R'_x} + \frac{1}{R'_y}\right)^{-1} \tag{S2}$$

$$R'_x = \left(\frac{1}{r_{1,x}} + \frac{1}{r_{2,x}}\right)^{-1} \tag{S3}$$

$$R'_y = \left(\frac{1}{r_{1,y}} + \frac{1}{r_{2,y}}\right)^{-1} \tag{S4}$$

$$E' = \frac{1-\nu_1^2}{2E_1} + \frac{1-\nu_2^2}{2E_2} \tag{S5}$$

The volume of a spherical cap, V_{sc}, is given by equation S6, using notation according to Figure 1.

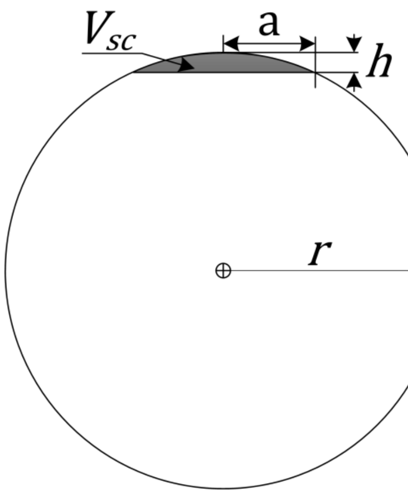


Figure 1. Parameters required to determine volume of spherical cap. Not to scale, $r \gg h$ should be assumed.

$$V_{sc} = \frac{\pi}{3} h^2 (3r - h) \tag{S6}$$

Assuming $r \gg h$, equation S7 relates the depth to the diameter of the spherical cap.

$$h = \frac{a^2}{2r}, \qquad \text{if } r \gg h \tag{S7}$$

Inserting (S7) in (S6) gives an expression for the spherical cap volume:

$$V_{sc} = \mathrm{a}^4 \pi \cdot \frac{12r^2 + a^2}{48r^3} \tag{S8}$$

Inserting $a = \left(\frac{WSD}{2}\right)$, and $r = R_{ball}$ in equation S8 gives the apparent wear volume V_{WSD}, corresponding to the material in the spherical cap defined by the *WSD* as base.

$$V_{WSD} = \left(\frac{WSD}{2}\right)^4 \pi \cdot \frac{12{R_{ball}}^2 + \left(\frac{WSD}{2}\right)^2}{48{R_{ball}}^3} \tag{S9}$$

As the test is lubricated and low wear volumes are expected, the elastic deformation is expected to be significant in relation to the wear depth [2]. Therefore, the volume of the elastically displaced material, V_{HzD} is calculated by inserting $a = HzR$ and $r = R_{ball}$ into equation S8:

$$V_{HzD} = HzR^4 \pi \cdot \frac{12{R_{ball}}^2 + HzR^2}{48{R_{ball}}^3} \tag{S10}$$

Finally, the wear volume is given by equation S11.

$$W = V_{WSD} - V_{HzD} \tag{S11}$$

3. Copper strip corrosion test results

The results of the ASTM D130-12 copper strip corrosion test can be seen in Figure 2 and Table 4.

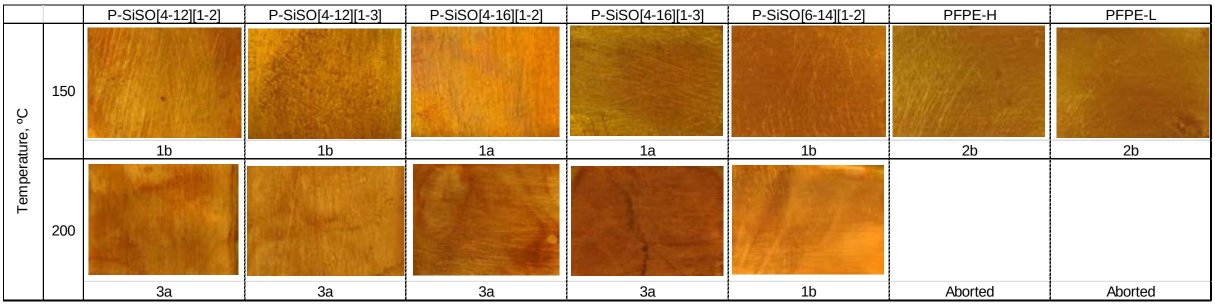


Figure 2. Photographed copper strip samples from ASTM D130-12 corrosion test.

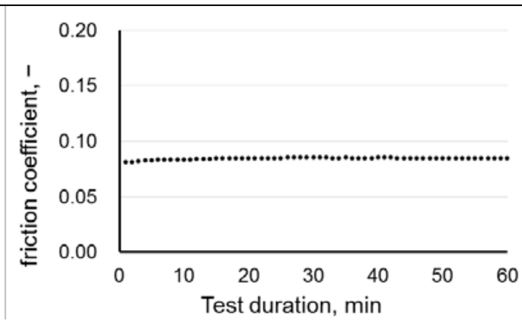
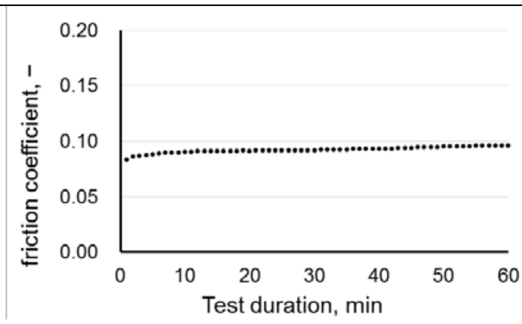
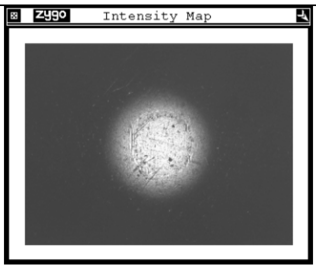
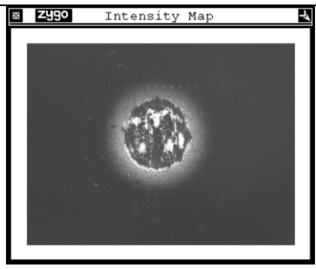
P-SiSO[6-14][1-2] was received at a later stage in the evaluation, and was therefore not part of the 10 repeated tests seen in Table 4. It has been tested once at a later occasion with similar results, as seen in Figure 2. In all the tests performed, at no time did P-SiSO indicate corrosion to the copper strip.

Table 4. Classification of P-SiSO in ASTM D130-12 corrosion test.

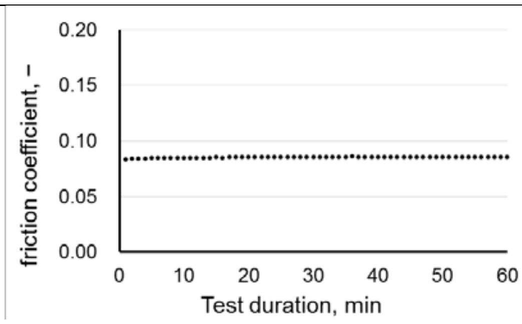
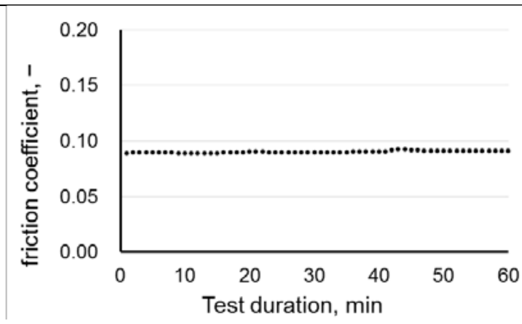
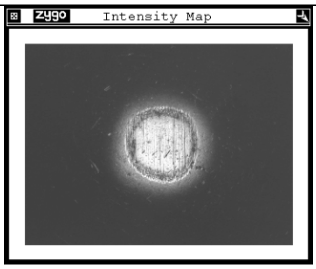
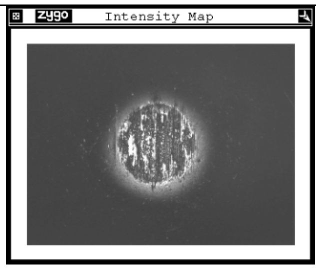
P-SiSO[4-12][1-2]		P-SiSO[4-12][1-3]		P-SiSO[4-16][1-2]		P-SiSO[4-16][1-3]	
150 °C	200 °C	150 °C	200 °C	150 °C	200 °C	150 °C	200 °C
1b	3a	1a	3a	1b	3a	1a	3a
1b	3a	1a	3a	1b	3a	1a	3a
1b	3a	1a	3a	1b	3a	1a	3a
1b	3a	1a	3a	1b	3a	1a	3a
1b	3a	1a	3a	1b	3a	1a	3a
1b	3a	1a	3a	1b	3a	1a	3a
1b	3a	1a	3a	1b	3a	1a	3a
1b	3a	1a	3a	1b	3a	1a	3a
No data	3a	1a	3a	1a	3a	1a	3a
No data	3a	1a	3a	2b	3a	1a	3a

4. Additional tribotest results

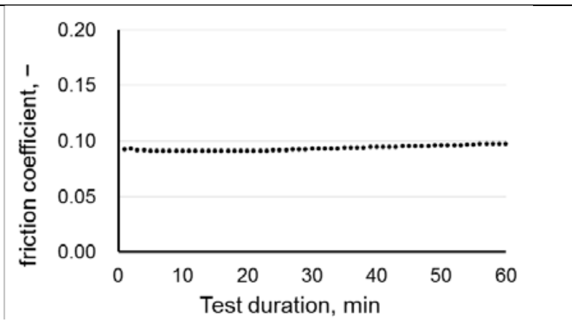
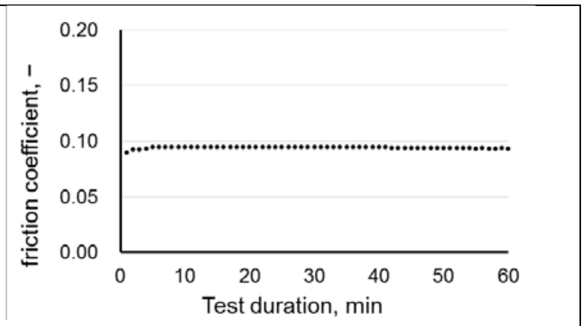
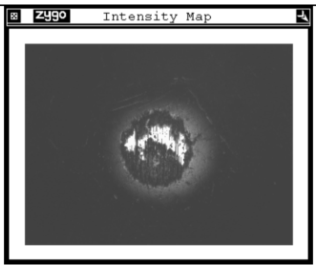
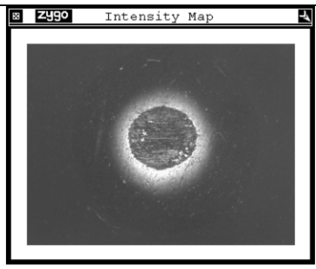
P-SiSO [4-12] [1-2] evaluated at C{100 N/25 °C/60 min}

Test run 1	Test run 2
	
 WSD = 332 µm	 WSD = 342 µm

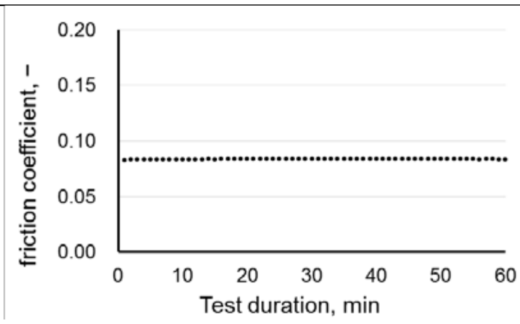
P-SiSO [4-12] [1-2] evaluated at C{150 N/25 °C/60 min}

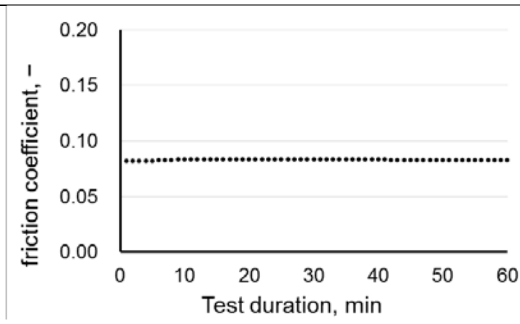
	
 WSD = 380 µm	 WSD = 394 µm

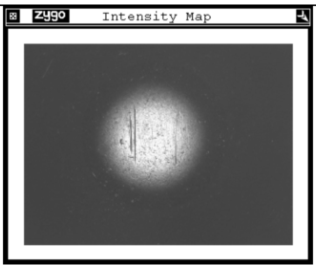
P-SiSO [4-12] [1-3] evaluated at C{100 N/25 °C/60 min}

	
 WSD = 376 µm	 WSD = 329 µm

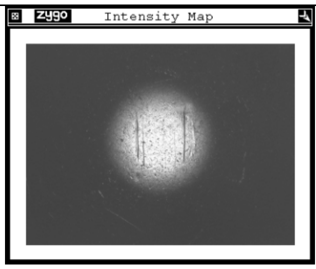
P-SiSO [4-16] [1-2] evaluated at C{100 N/25 °C/60 min}



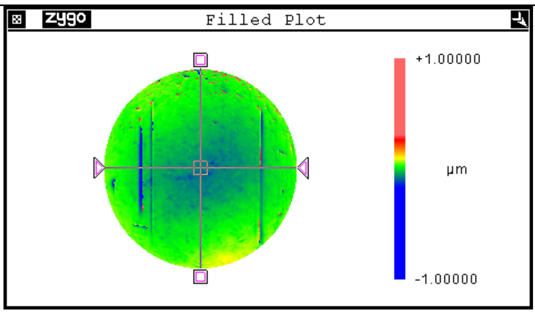


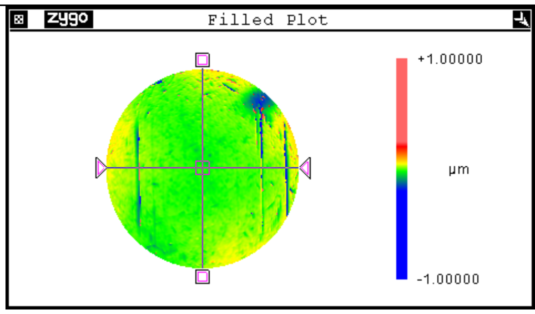


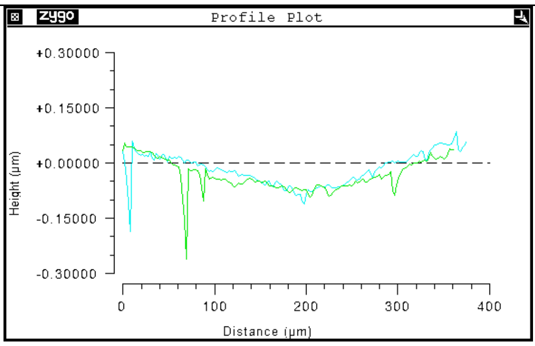
WSD = 333 µm

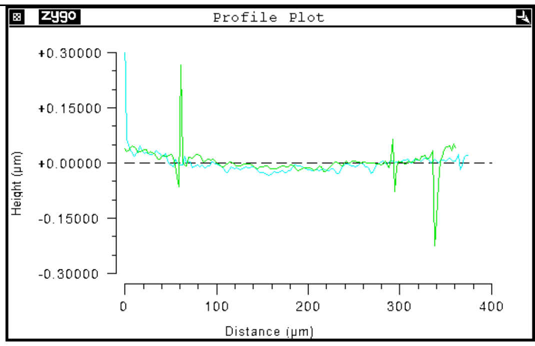


WSD = 332 µm

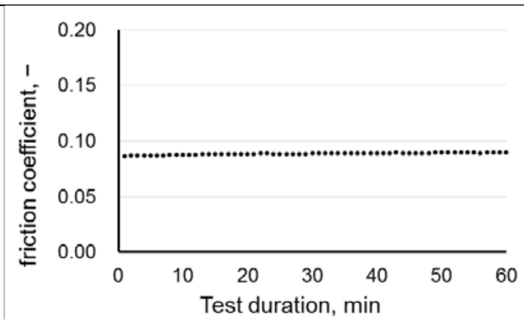


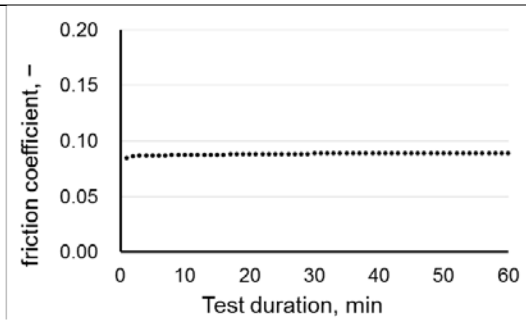


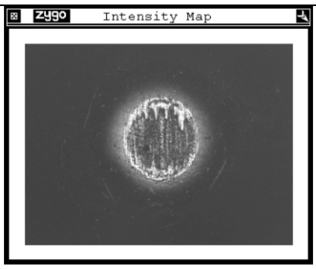




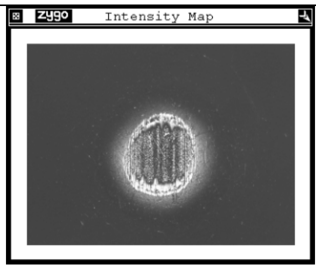
P-SiSO [4-16] [1-2] evaluated at C{150 N/25 °C/60 min}



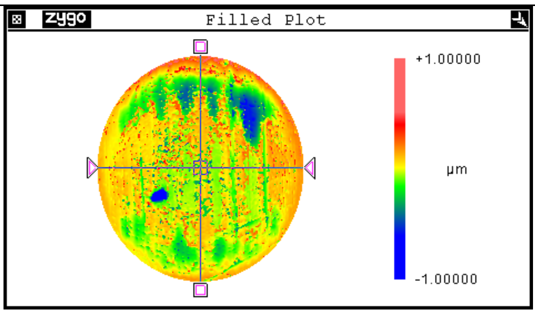


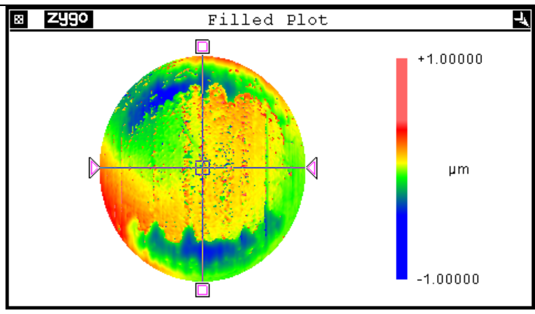


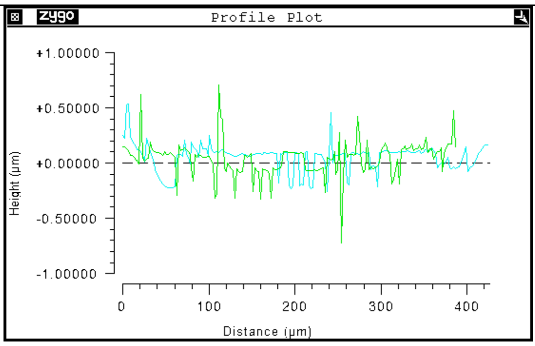
WSD = 392 µm

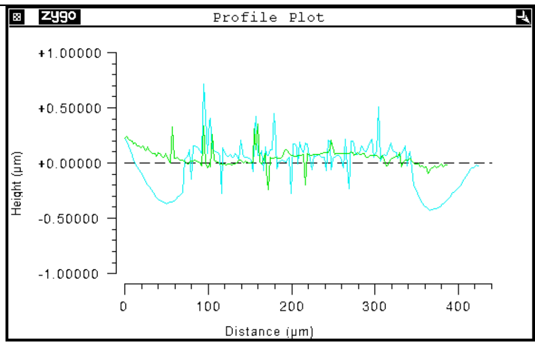


WSD = 392 µm

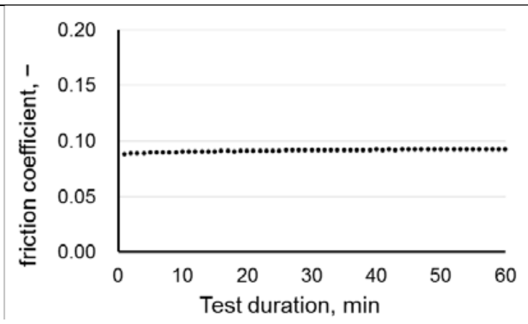


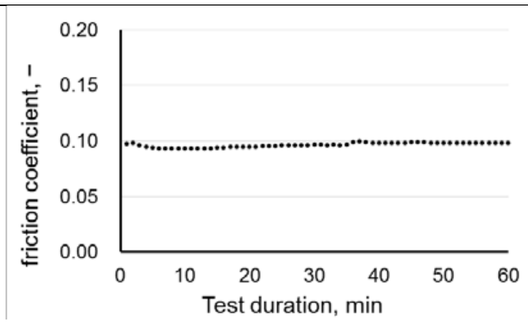


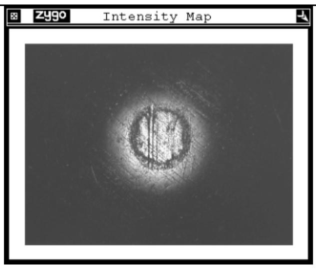




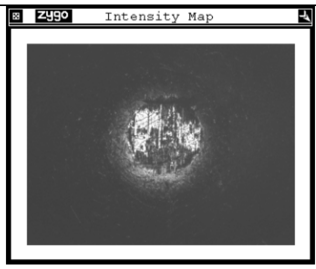
P-SiSO [4-16] [1-3] evaluated at C{100 N/25 °C/60 min}





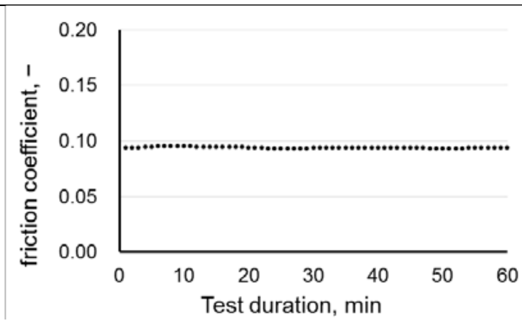


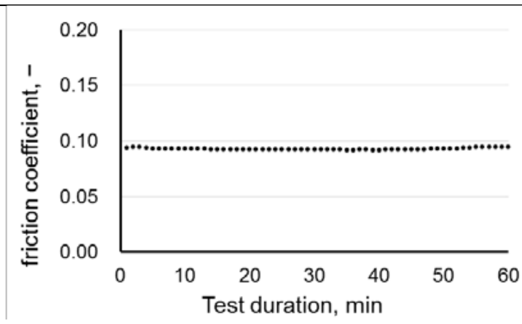
WSD = 324 µm

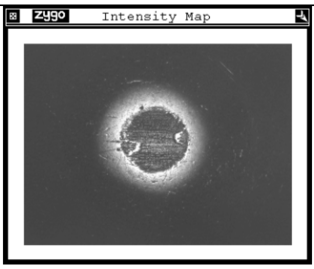


WSD = 382 µm

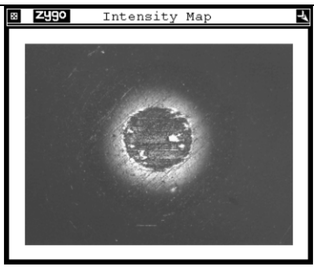
P-SiSO [6-14] [1-2] evaluated at C{100 N/25 °C/60 min}





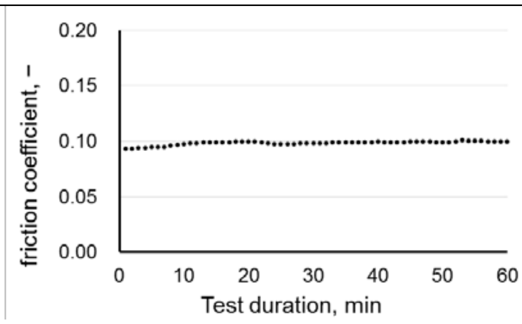


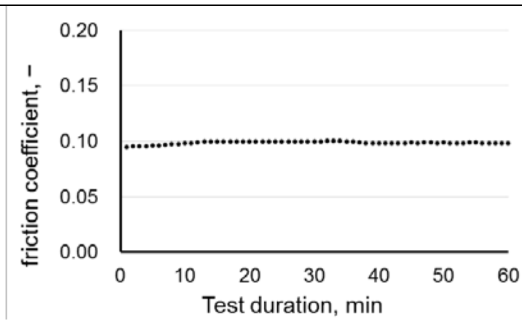
WSD = 336 µm

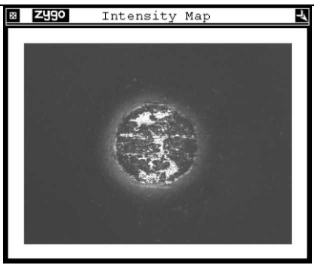


WSD = 334 µm

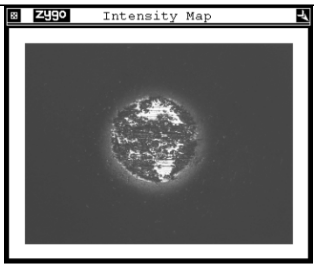
P-SiSO [6-14] [1-2] evaluated at C{150 N/25 °C/60 min}





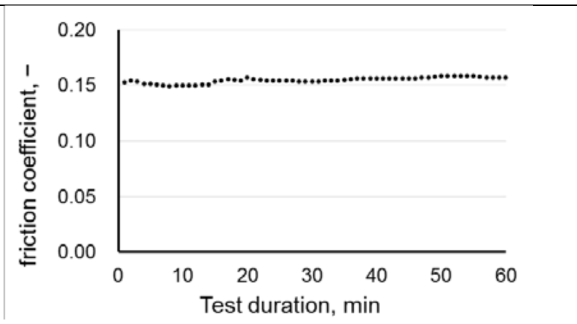


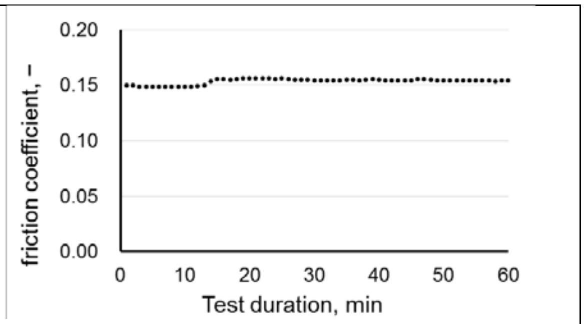
WSD = 404 µm

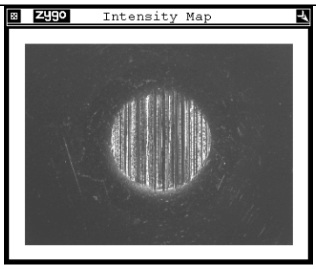


WSD = 430 µm

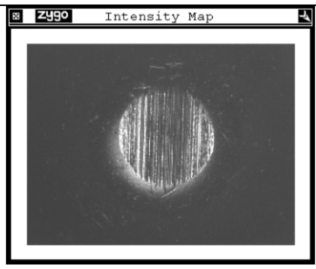
PFPE – L (Fomblin-Y 317926) evaluated at C{100 N/25 °C/60 min}





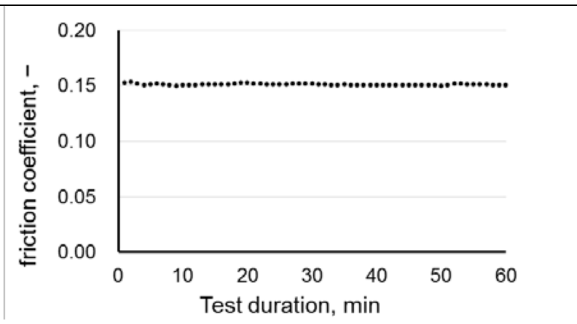


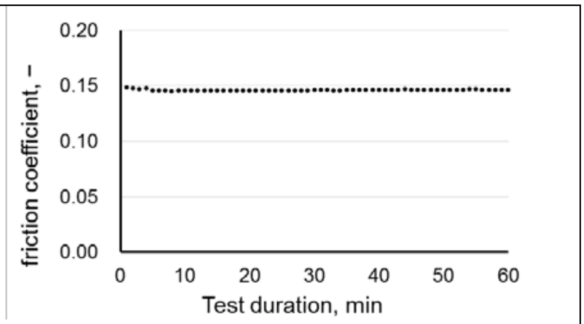
WSD = 503 µm

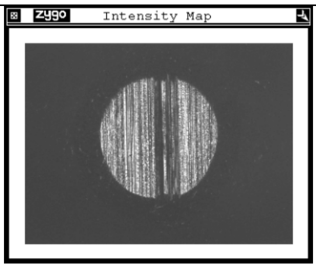


WSD = 481 µm

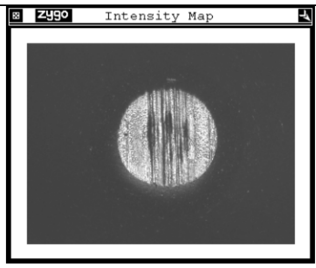
PFPE – L (Fomblin-Y 317926) evaluated at C{150 N/25 °C/60 min}





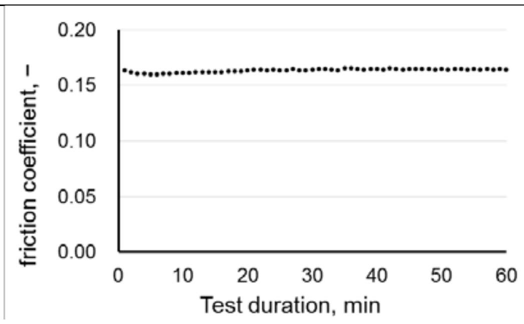
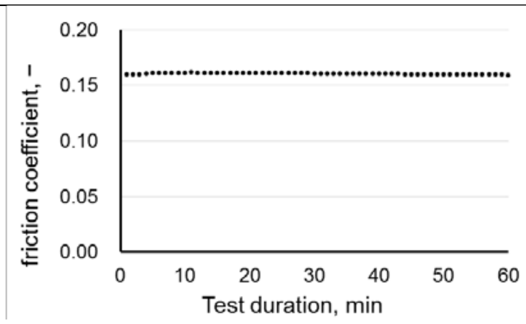
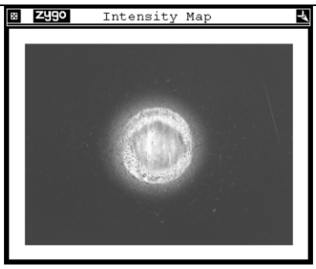
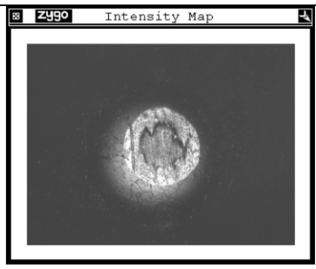


WSD = 599 µm

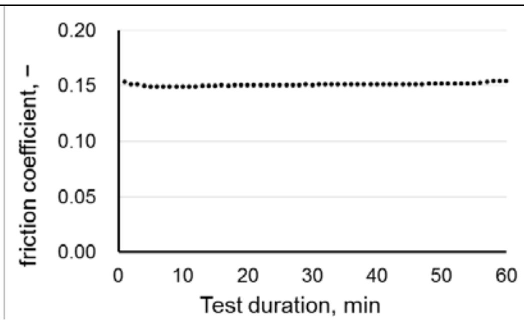
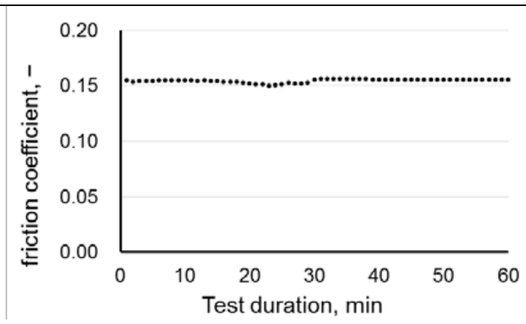
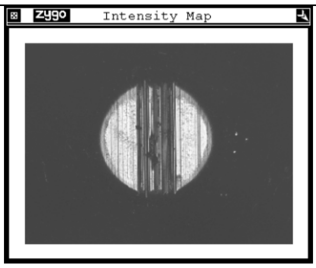
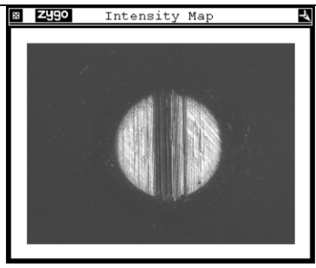


WSD = 492 µm

PFPE –H (Fomblin-Y 317950) evaluated at C{100 N/25 °C/60 min}

	
 WSD = 378 µm	 WSD = 387 µm

PFPE –H (Fomblin-Y 317950) evaluated at C{150 N/25 °C/60 min}

	
 WSD = 573 µm	 WSD = 537 µm

[1] K. L. Johnson, *Contact mechanics*. Cambridge: Cambridge Univ. Press, 1985.

[2] "ASTM Standard G133-05: Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear," *Annu. B. ASTM Stand.*, vol. 5, pp. 1–9, 2010.