Electronic Supplementary Material

Physicochemical and tribological properties of gemini-type halogen-free dicationic ionic liquids

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NP-14-2-14 according to previously reported method, a simple synthesis process is introduced [1]: N, N, N′, N′-tetraethylethylenediamine(0.05 mol), bromotetraadecane (0.1 mol) was mixed in acetonitrile and refluxed at 82 ℃ for 24 h and left for complete white precipitation after cool. The white precipitation recrystallized three times from acetone. Then the solution of sodium phosphate (0.1 mol) was added and stirred at 80 ℃ for 24 h. Washed with water and extracted to obtain organic phase. A bright yellow liquid product was obtained by distillation under reduced pressure in a yield of 85%. The structure of NP-14-2-14 was confirmed by ^{1}H NMR (Bruker 400 MHz), ^{13}C NMR (100 MHz), ^{31}P NMR (162 MHz) and HRMS (Bruker micro-TOF Q II).

The detail data are as following:**NP-14-2-14: ^{1}H NMR (400 MHz, CDCl$_3$)** δ: 4.46 (s, 4H), 3.71-3.65 (m, 8H), 3.59 (t, *J* = 8.0 Hz 4H), 3.33 (s, 12H), 1.81–1.69 (m, 4H), 1.49–1.24 (m, 80H), 0.88–0.83 (m, 30H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 67.98, 67.92, 66.02, 57.19, 50.87, 40.51, 40.43, 32.04, 30.22, 29.82, 29.77, 29.70, 29.61, 29.52, 29.48, 29.17, 26.32, 23.45, 23.25, 23.06, 22.80, 14.24, 11.07. **^{31}P NMR (162 MHz, CDCl$_3$)** δ: 30.06 (s). **m/z (ESI, positive ion)** calc.510.58, found 255.2921[$C_{34}H_{74}N_2$]$^{2+}$, **m/z (ESI, negative ion)** calc. 321.2200, found 321.2190. Purity is 95%.

NP-16-2-16 according to previously reported method, a simple synthesis process is introduced [1]: N, N, N′, N′-tetraethylethylenediamine (0.05 mol), bromohexadecane (0.1 mol) was mixed in acetonitrile and refluxed at 82 ℃ for 24 h and left for complete white precipitation after cool. The white precipitation recrystallized three times from acetone. Then the solution of sodium phosphate (0.1 mol) was added and stirred at 80 ℃ for 24 h. Washed with water and extracted to obtain organic phase. A bright yellow liquid product was obtained by distillation under reduced pressure in a yield of 83%. The structure of NP-16-2-16 was confirmed by ^{1}H NMR (Bruker 400 MHz), ^{13}C NMR (100 MHz), ^{31}P NMR (162 MHz) and HRMS (Bruker micro-TOF Q II).

The detail data are as following:**NP-16-2-16: ^{1}H NMR (400 MHz, CDCl$_3$)** δ: 4.42 (s, 4H), 3.81-3.77 (m, 8H), 3.57 (t, *J* = 8.0 Hz, 4H), 3.30 (s, 12H), 1.79–1.69 (m, 4H), 1.53–1.19 (m, 88H), 0.89–0.85 (m, 30H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 68.72, 68.66, 65.78, 57.19, 50.61, 40.34, 40.26, 32.07, 30.09, 29.86, 29.81, 29.76, 29.62, 29.51, 29.11, 26.41, 23.35, 23.20, 22.83, 14.22, 11.04. **^{31}P NMR (162 MHz, CDCl$_3$)** δ: 30.06 (s). **m/z (ESI, positive ion)** calc. 566.65, found 283.3234 [$C_{38}H_{82}N_2$]$^{2+}$, **m/z (ESI, negative ion)** calc. 321.2208, found 321.2200 [$C_{16}H_{34}O_4P$]$^{-}$. Purity is 93%.

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NP-18-2-18 according to previously reported method, a simple synthesis process is introduced [1]: N, N, N′, N′-tetraethylethylenediamine (0.05 mol), bromooctadecane (0.1 mol) was mixed in acetonitrile and refluxed at 82 ℃ for 24 h and left for complete white precipitation after cool. The white precipitation recrystallized three times from acetone. Then the solution of sodium phosphate (0.1 mol) was added and stirred at 80 ℃ for 24 h. Washed with water and extracted to obtain organic phase. A bright yellow liquid product was obtained by distillation under reduced pressure in a yield of 88%. The structure of NP-18-2-18 was confirmed by ^{1}H NMR (Bruker 400 MHz), ^{13}C NMR (100 MHz), ^{31}P NMR (162 MHz) and HRMS (Bruker micro-TOF Q II).

The detail data are as following:***NP-18-2-18*: ^{1}H NMR (400 MHz, $CDCl_3$)** δ: 4.49 (s, 4H), 3.72–3.69 (m, 8H), 3.59 (t, *J* = 8.0 Hz, 4H), 3.31 (s, 12H), 1.81–1.65 (m, 4H), 1.48–1.11 (m, 96H), 0.84 (t, *J* = 8.0 Hz, 30H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 68.10, 68.05, 65.92, 57.27, 50.69, 40.47, 40.39, 32.04, 30.16, 29.82, 29.77, 29.71, 29.62, 29.55, 29.47, 29.15, 26.31, 23.38, 23.24, 22.80, 14.23, 11.18, 11.04. **^{31}P NMR (162 MHz, $CDCl_3$)** δ: 30.06 (s). **m/z (ESI, positive ion)** calc. 622.7100, found 311.3500 $[C_{42}H_{90}N_2]^{2+}$, **m/z (ESI, negative ion)** calc. 321.2208, found 321.2200 $[C_{16}H_{34}O_4P]^-$. Purity: 95%.

Table S1 Conductivity of the ionic liquid lubricants.

Lubricants	Conductivity (uS/cm)
L-P 104	1451
NP-14-2-14	7.31
NP-16-2-16	6.98
NP-18-2-18	6.33

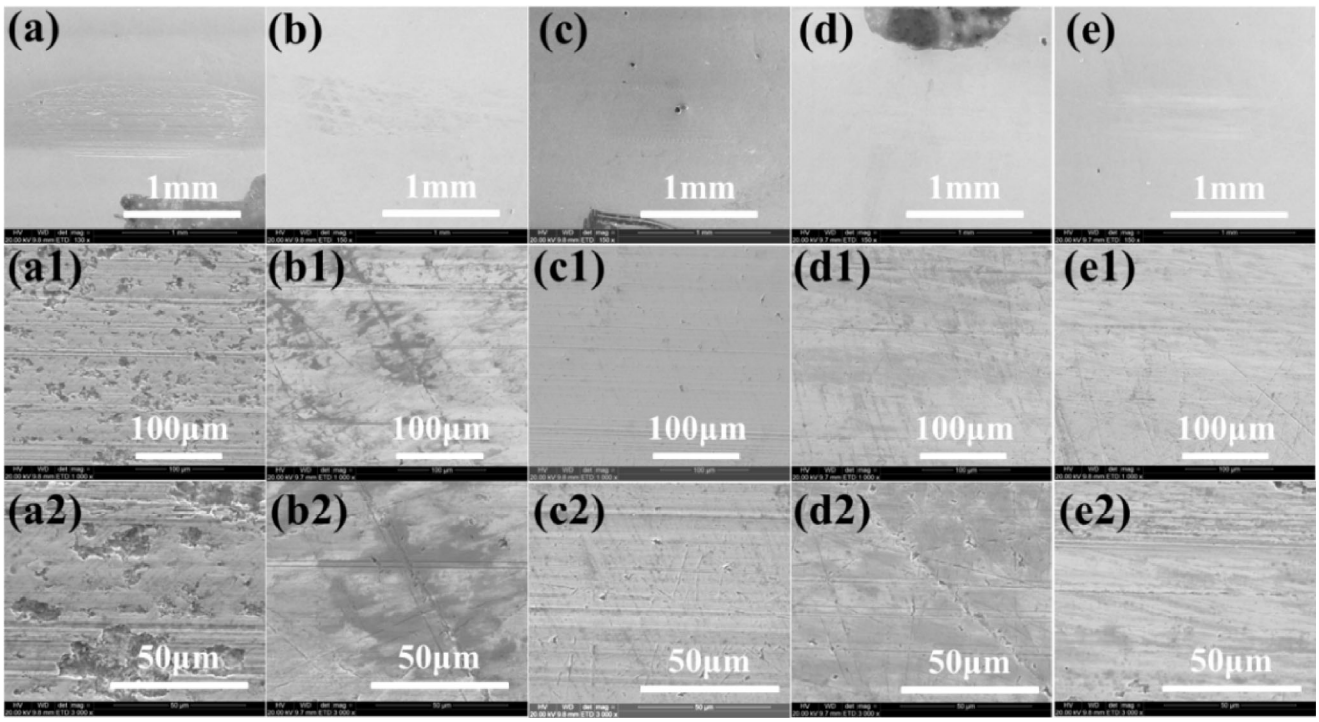

Fig. S1 SEM morphologies of worn surfaces lubricated by (a, a1, a2) PAO 10, (b, b1, b2) L-P104, (c, c1, c2) NP-14-2-14, (d, d1, d2) NP-16-2-16, and (e, e1, e2) NP-18-2-18 (the magnification of the (a)–(e) is 150× and that of the middle (a1)–(e1) is 1,000×, the magnification of the (a2)–(e2) is 3,000×, SRV: load = 300 N; frequency = 25 Hz; stroke = 1 mm; duration = 30 min; RT).

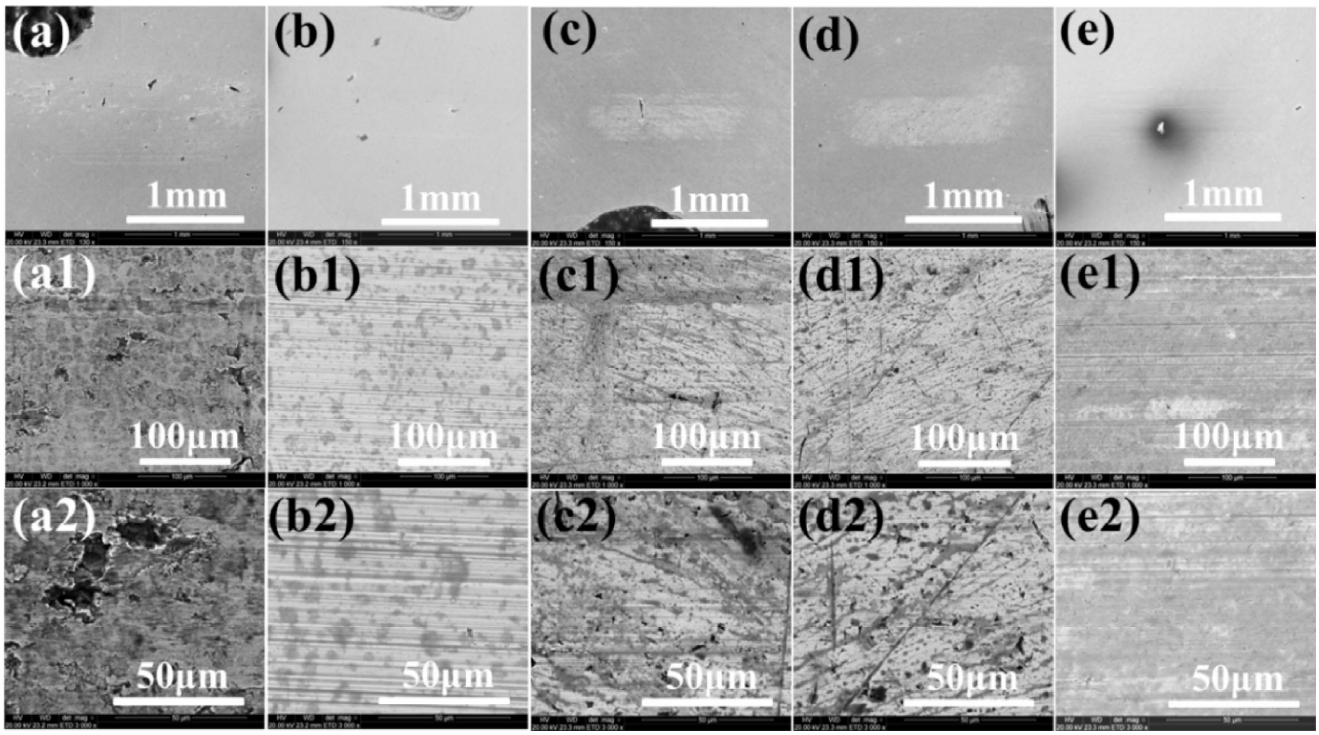

Fig. S2 SEM morphologies of worn surfaces lubricated by (a, a1, a2) PAO 10, (b, b1, b2) L-P104, (c, c1, c2) NP-14-2-14, (d, d1, d2) NP-16-2-16, and (e, e1, e2) NP-18-2-18 (the magnification of the (a)–(e) is 150× and that of the middle (a1)–(e1) is 1,000×, the magnification of the (a2)–(e2) is 3,000×, SRV: load = 300 N; frequency = 25 Hz; stroke = 1 mm; duration = 30 min; RT).

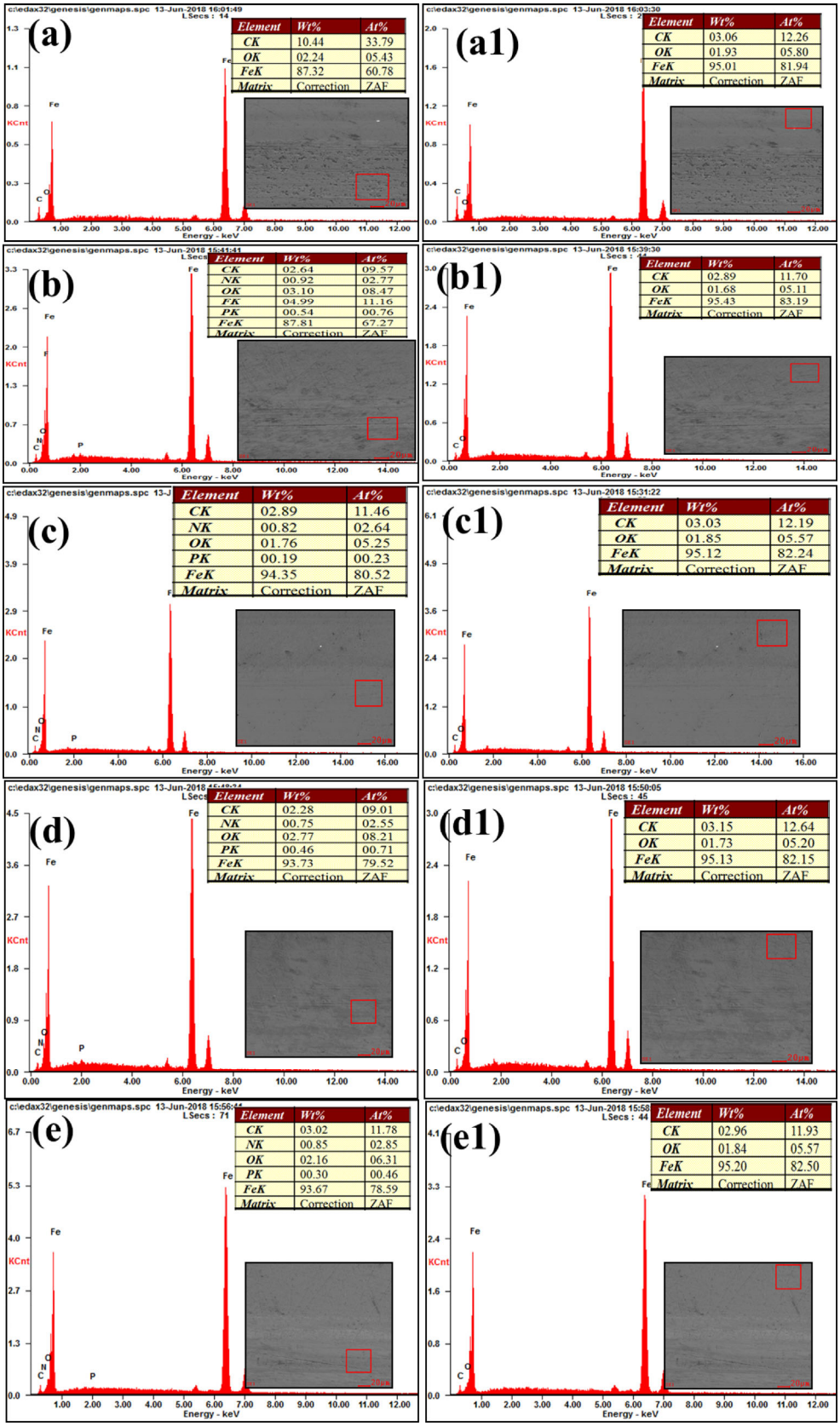

Fig. S3 EDS analysis of the central part (a–e) and external part (a1–e1) of the wear surfaces under RT test conditions (a, a1: PAO 10, b, b1: L-P104, c, c1: NP-14-2-14, d, d1: NP-16-2-16, e, e1: NP-18-2-18).

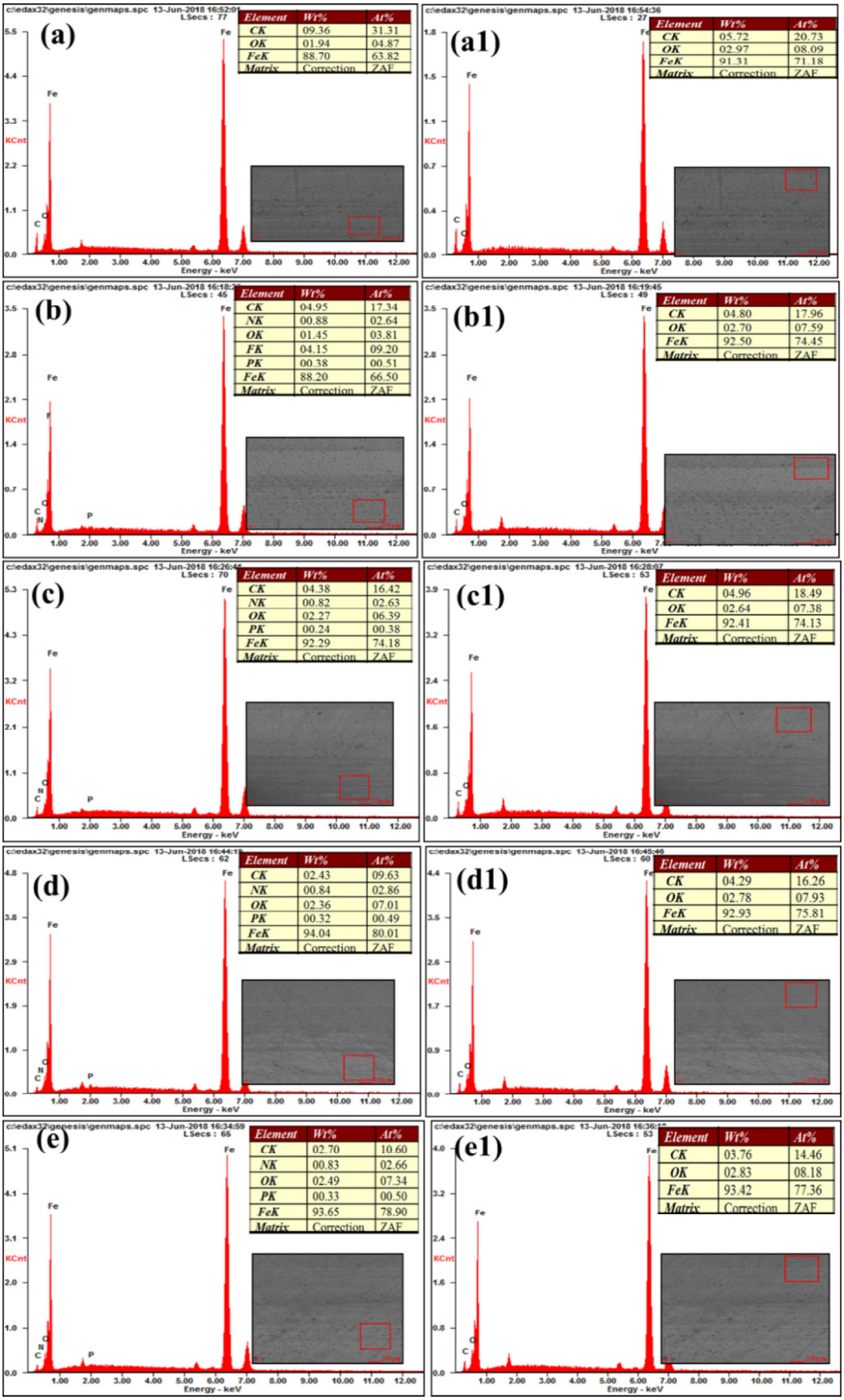

Fig. S4 EDS analysis of the central part (a–e) and external part (a1–e1) of the wear surfaces under 100 °C test conditions (a, a1: PAO 10; b, b1: L-P104; c, c1: NP-14-2-14; d, d1: NP-16-2-16; e, e1: NP-18-2-18).

References

[1] Yu Q L, Zhang C Y, Dong R, Shi Y J, Wang Y R, Bai Y Y, Zhang J Y, Cai M R, Zhou F. Novel N-, P-containing oil-soluble ionic liquids with excellent tribological and anticorrosion performance. *Tribol Int* **132**: 118–129 (2019)