J Therm Anal Calorim (2011) 106:213–220
DOI 10.1007/s10973-011-1529-2

Decomposition of perfluoropolyether lubricants

A study using TGG–MS in the presence of alumina powder

Mimi Y. Keating · Jon L. Howell

NATAS2010 Conference Special Issue

Abstract Decomposition has been studied in the chemistry of perfluoropolyethers (PFPE), thus far no molecular structure information is reported. TG-MS is a tool to follow the off gassing of decomposition for clues. We selected two PFPEs that have different properties: Krytox® XHT-1000 and Fomblin Z60 heating to normal decomposition and catalytic decomposition in the presence of alumina powder. Comparing the decomposition fragment intensities, the molecular structure of the branched Krytox® XHT-1000 oil is more stable than the blocky Fomblin Z60. We see aluminum-containing fluorine fragments in the rapid decomposition of oils in contact with alumina powder. It has been suggested the formation of $Al(O_{6-n}F_n)$, where $n = 1$, 2, and 3, in which the fluorine atoms are selectively associated with aluminum atom. The major decomposition products are small and large fragments of fluorocarbons and perfluoroalkoxy. In the absence of alumina powder, Krytox XHT-1000 shows only a loss of 13 mass/% after several hours at 330 °C, whereas in the presence of 1 mass/% alumina powder the oil has rapidly decomposed to 67 mass/% of its original mass within 15 min. Fomblin Z60, a product might not be designed for high temperature, exposing to the same conditions at 330 °C for several hours and shows a loss of 98 mass/% alone, but in the presence of 1 mass/% alumina powder shows a loss of 98 mass/% in 3.6 min. When 3 mass/% of two new developmental additives were added to the both oils, the catalytic decomposition in the presence of 1 mass/% alumina powder was significantly reduced in Krytox® XHT-1000, showing only a loss of 23 mass/% in 4 h, but nearly all weight for Z60 in 60 min. In the oil grades that contain the new additives, we see the fragments of Al–O–S, and F–Al–O–S. The sulfur-containing compound has been reported ionically bonded to oxide in a tripod configuration of alumina surface, which shields the formation of Al–F.

Keywords Polypluoropolyethers · Lubricants · High-temperature · TG-MS · Alumina powder

M. Y. Keating (✉)
DuPont Central Research and Development, Experimental Station, Wilmington, DE 19880, USA
e-mail: mimi.y.keating@usa.dupont.com

J. L. Howell
Dupont DCSE, Experimental Station, Wilmington, DE 19880, USA

Introduction

The Krytox® greases and oils are a line of perfluoropolyether (PFPE) lubricants from DuPont Chemical Solutions Enterprise in extreme high temperature applications. The Krytox® PFPEs have been used since its invention just over 50 years for oxidative and thermal stability and chemical inertness 200–400 °C. It is the oxidation stable and heat stable lubricants intended for high temperature usage for removal of combustion deposits on interior surfaces and downstream surfaces of boilers and burners, e.g., in bearings, gears, chains, seals, and shafts [1]. In the lines of PFPE lubricant, there are differences in thermal stability, viscosity, and end-use applications due to structural differences. Two families of PFPE oils are studied in detail in this article—Krytox® XHT-1000, the branched polyether and Solvay's blocky Fomblin Z60. The sulfur additives in these oils have shown the increase of the stabilities significantly of Krytox® oils at the testing temperatures. The decomposition of oils, challenged by mixing with alumina powder, is either catastrophically or resistively to an extent.

Materials

Structures of PFPE lubricant and additives:

The Kaytox® XHT-1000 is $F[CF(CF_3)CF_2O]_nCF_2CF_3$, where $n = 10–60$.

The Fomblin Z60, a product of Solvay, is $CF_3O[CF_2CF_2O]_m[CF_2O]_pCF_2CF_3$.

The additives-1 and -2 are sulfur-containing compounds.

The PFPEs with or without sulfur additive are studied in the presence of ~1 mass/% alumina powder. In most cases, the controls in the absence of alumina are compared.

Krytox® XHT-1000 + 1 mass/% alumina powder
Krytox® XHT-1000
Krytox® XHT-1000/3 mass/% additive-1 + 1 mass/% alumina powder
Krytox® XHT-1000/3 mass/% additive-1
Krytox® XHT-1000/3 mass/% additive-2 + 1 mass/% alumina powder
Solvay Z60 + 1 mass/% alumina powder
Solvay Z60
Solvay Z60/3 mass/% additive-1 + 1 mass/% alumina powder
Solvay Z60/3 mass/% additive-1
Solvay Z60/3 mass/% additive-2 + 1 mass/% alumina powder.

Experimental

The ~25 mg of Krytox® oil, with or without 1 wt% Al_2O_3 powder, was placed in a platinum pan in the helium purged TG in skimmer coupling to QMS. The instrument is commercially available from Netzsch Instruments in two-step pressure reductions by three pumps from 10^3 to 10^{-1} to 10^{-5} mbar through orifice coupling. The MS ion currents were detected in trigger mode at the start of TG scan. The minor air leak to the system was monitored to ensure it was at low levels of fragments from air before starting the experiment. An empty platinum pan was subjected to the same experiment separately, thus the subtracted fragment intensities can be realized as non-noise. Please note that the coupled MS is not heated, therefore *x*-axis in many graphs is in cycle or time in the case of isothermally hold.

TGA-MS: Netzsch STA 409/QMS 403, skimmer coupling
MS: cathode 70 eV, SEM 1600 V, MS 30-512 amu, 0.1 s cycle speed
TGA: 20 °C/min in helium to 330 °C, isothermally hold for 4 h in Pt pan.

Results and discussions

The PFPE lubricants provide both high temperature and chemical inertness that are important to users in a diversity of industries. In this study, we used a hyphenated technique TG-MS to track the extent of decomposition and decomposition products. This testing was carried out in helium and without the confounding effect of oxygen, although previous studies have not shown significant differences. All ion currents detected from off gassing that went into the MS are *m*/*z* (mass/charge). For simplification, they are discussed as masses of ions with charges being 1.

TG monitors the isothermal stability of Krytox® XHT-1000

As compared in Fig. 1, the decomposition of XHT-1000 itself at 330 °C does not occur easily in the lubricant, neither in the versions of additives with 3 mass/% additive-1. This confirms the high temperature stability of Krytox® lubricants. In fact, the control formulations show that they retain most its original masses (loss of 13–15%) in 4 h holding at 330 °C. However, in the presence of 1 mass/%

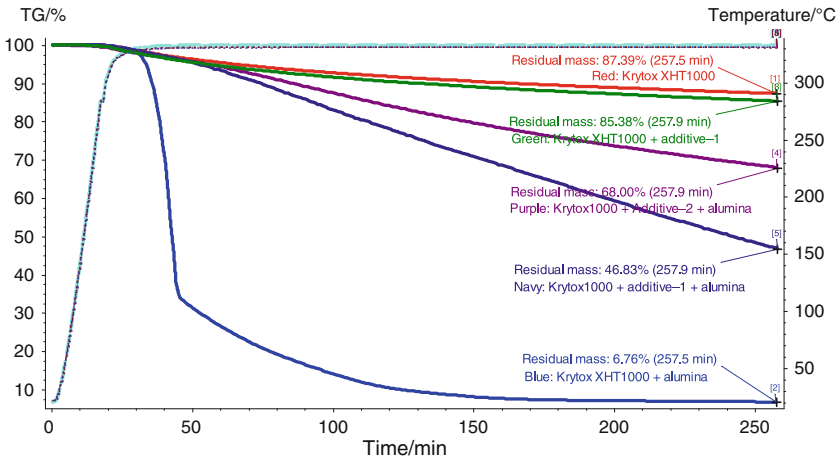


Fig. 1 Mass losses by isothermal hold at 330 °C in helium for 4 h of Krytox XHT-1000 alone, Krytox XHT-1000 + alumina, Krytox XHT-1000/additive-1, Krytox XHT-1000/additive-1 + alumina, and XHT-1000/additive-2 + alumina

alumina powder, the rapid decomposition of the XHT-1000 grade lubricant retains only 7 mass/% (a loss of 93 mass/%) in 4 h. The catalytic decomposition occurs within 15 min at 330 °C to 67 mass/% of its original mass in the presence of alumina; whereas Krytox® XHT-1000 alone 3 mass/% in 15 min. The catalytic decomposition of PFPE in contact with alumina powder (aluminum oxide-ignited powder) is well known.

MS monitors the fragments of isothermally hold Kryton® XHT-1000

The detected major decomposition products are small and large fragments of fluorocarbons and perfluoroalkoxy: CF_2, CF_3, $(CF_2)_2$, CF_2CF_3, $FCF(CF_3)CF_2$, CF_2CFCF_2, OCF, OCF_2CF, and OCF_2CFCF_2, (mass 50, 69, 100, 119, 169, 131, 47, 97, and 147). The intensities of XHT-1000 fluorocarbons in the presence of alumina powder, shown in Fig. 2, and that in its absence of alumina powder, shown in Fig. 3, are drastically different. The two figures are intentionally plotted in the same scales.

Similarly, the intensities of perfluoroalkoxy fragments $OCFCF_2$, $OCFCF_2CF_2$ (mass 97, 147) of XHT-1000 in the presence/absence of alumina powder are compared in Fig. 4. The question is how does Al_2O_3 decompose catalytically the Krytox® XHT-1000? Is there additional molecular information of this PFPE? The aluminum-containing fluorine fragments are found in the rapid decomposition of Krytox® XHT-1000 in contact with alumina powder: mass 46, 62, 65, and 78, suggesting the formation of AlF, AlF_2, OAlF, and AlO_2F. It was reported by Denkenberger, Bowers, Jones, and Mueller's NMR study [2]

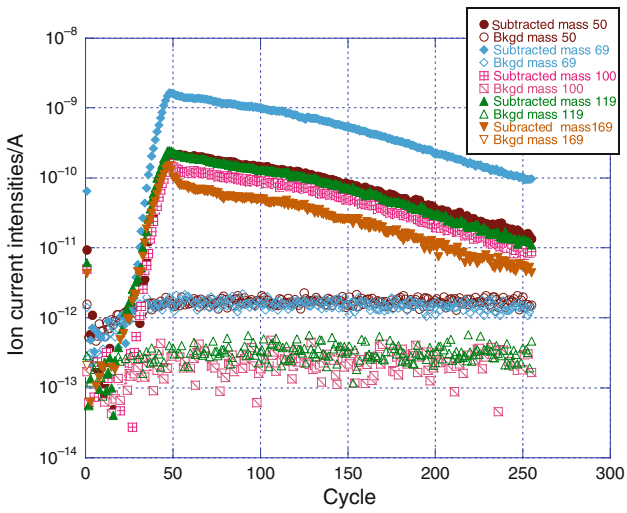


Fig. 2 XHT-1000 + alumina—ion current intensities versus MS cycle of fluorocarbons CF_2, CF_3, $(CF_2)_2$, CF_2CF_3, $FCF(CF_3)CF_2$, and CF_2CFCF_2 (mass 50, 69, 100, 119, and 169)

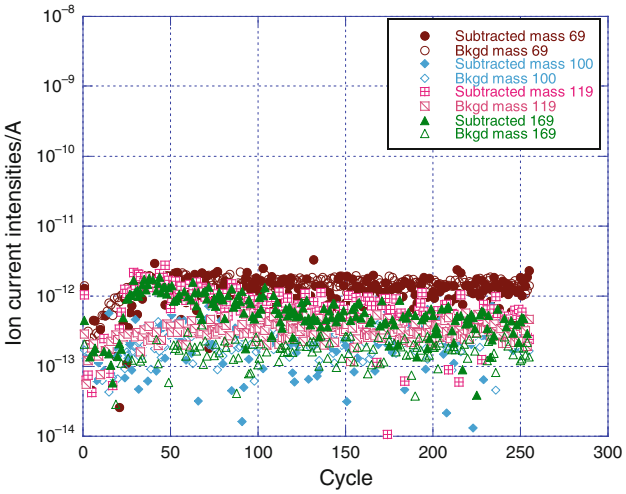


Fig. 3 Ion current intensities of XHT-1000 without alumina versus MS cycle—low intensities of CF_3, CF_2CF_2, CF_2CF_3, and $FCF(CF_3)CF_2$ (mass 69, 100, 119, and 169)

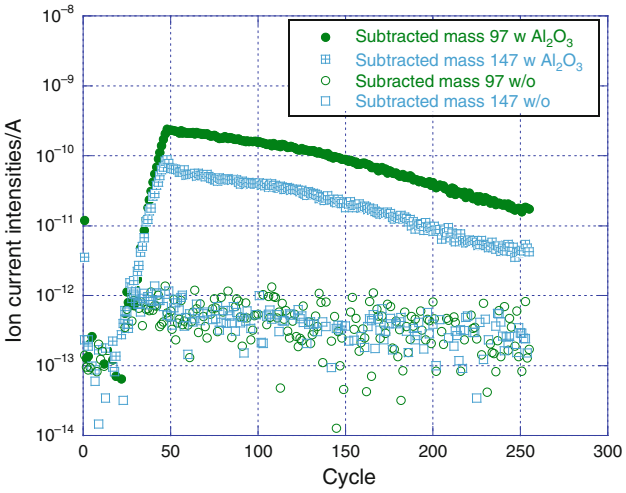
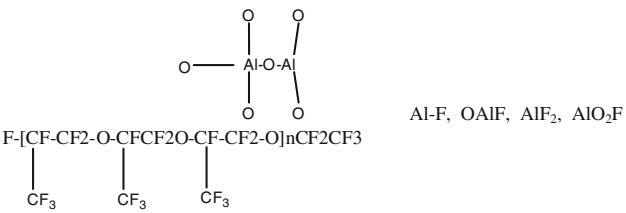


Fig. 4 XHT-1000 w/wo alumina—ion current intensities versus MS cycle: fluoroalkoxy OCF_2CF, OCF_2CFCF_2 (mass 97, 147)

suggests the formation of $Al(O_{6-n}F_n)$, where $n = 1$, 2, and 3, in which the fluorine atoms are selectively associated with aluminum atom.



The rapid decomposition of lubricant Krytox® XHT-1000 in the presence of alumina powder occurs at 330 °C to 67 mass/% of its original mass within 15 min—this is estimated from the ion intensities are taken in MS cycle 45.

The XHT-1000 itself comparatively shows only a 13 mass/% loss after several hours holding at 330 °C at the end of the experiment of cycle 255. For simplification of discussing the catalytic decomposition, only a few representative ions mass/charge (*m*/*z*) are selected: OCF (mass 47), CF_3 (mass 69), OCF_2CF (mass 97), $OCFCF_2CF_2$ (mass 147), $F_2C(CF_3)CF_2$ (mass 169), AlF (mass 46), AlF_2 (mass 65), AlOF (mass 62), AlO_2F (mass 78), and $AlOF_2$ (mass 84).

We have evidenced the formation of Al–F bond (mass 46) as well as F–O–Al, O–Al–F (mass 62), and F–O–Al–O (mass 78) that accelerate the breakage of C–F bonds in the lubricant. The intensities of mass 46, 62, and 78 shown in Figs. 5 and 6 are definitely larger than the intensities of the background (noise).

In the oil grades that contain additives-1 or -2 sulfur-containing additives, we see the fragments of Al–O–S, and F–Al–O–S (mass 75, 94), but no SO, SO_2, Al–OSO, and Al–OSO_2 (mass 48, 64, 91, and 107). The F–Al–O–S (94) fragment is just slightly larger than that of the background and almost not distinguishable from it in Fig. 6. The question is what is the function of additives-containing sulfur? We suggest that the additive-1 role in protecting the decomposition of XHT-1000 in the presence of alumina powder is quite positive, because the TG mass losses have been improved (Fig. 1) and also the formation of Al–O–S (mass 75) as shown in Fig. 7. The sulfur-containing material has been reported [3] ionically bonded to oxide in a tripod configuration of alumina surface, which shields the formation of Al–F. Also the fluorocarbonsulfonic acid polymer is used for synthesizing fluoroproducts, e.g., Nafion®s, and it being coated onto an alumina support [4] improves its efficiency as catalyst itself.

The effectiveness of additive-1 better than additive-2 in Krytox® XHT-1000 are compared side-by-side in Fig. 8a and b in the same logarithmic scale of the selected ion

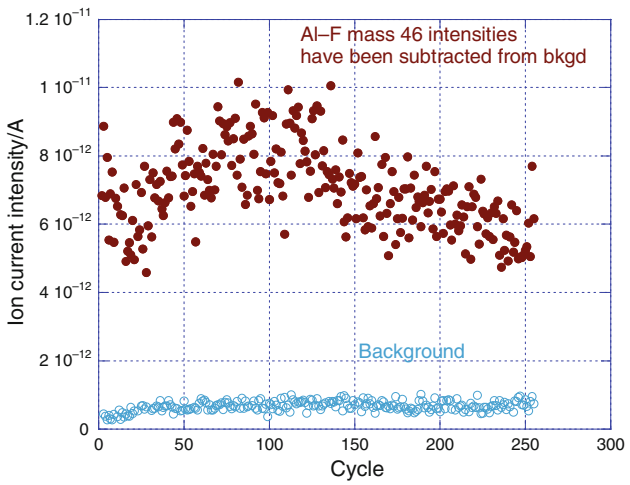


Fig. 5 XHT-1000/alumina isothermally hold at 330 °C for 4 h—the detectable Al–F (mass 46)

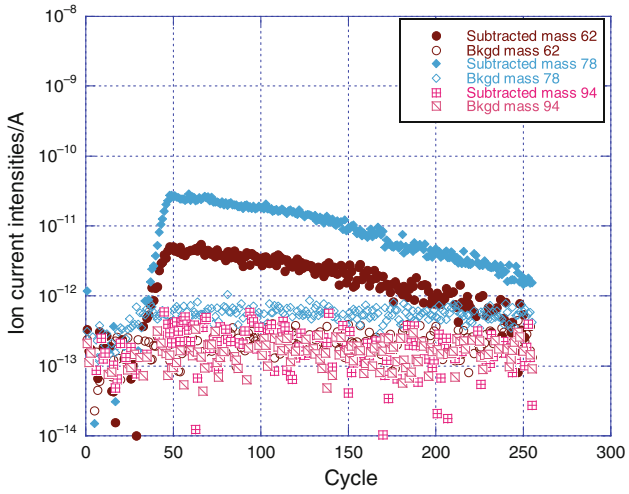


Fig. 6 XHT-1000/alumina—ion current versus time/cycle, suggesting Al–F bond formation OAlF, OAlOF (mass 62, 78) and in the XHT-1000/3% additive-1/alumina. The presence of ion current of sulfur-containing FAl–O–S (mass 94)

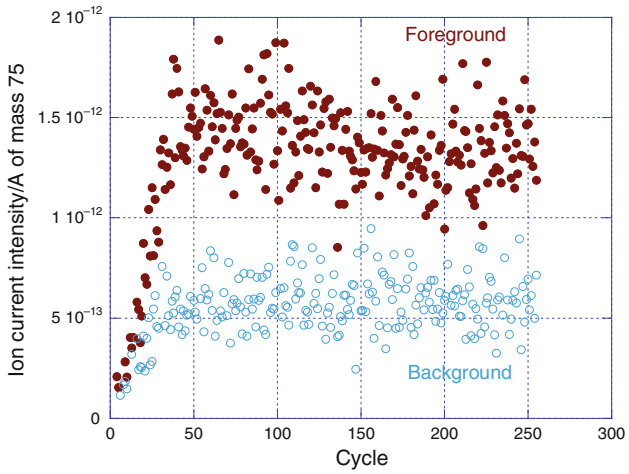


Fig. 7 Krytox® XHT-1000/3% additive-1 + alumina—ion current of Al–O–S (mass 75) versus MS cycle. Isothermally hold at 331 °C/4 h in helium

intensities of CF3 (69), OCF (47), AlOF (62), AlO_2F (78), AlOS (75), and AlOSF (94). The selected ion intensities versus MS cycles in Fig. 8 are taken from all cycles of the entire experiments. An example of MS bargraph of Krytox® XHT-1000, cycle 50/330 °C, is shown in Fig. 9.

TG monitors the mass loss of isothermally hold Fomblin Z60 from Solvay

The Fomblin grade Z60 oil from Solvay is a commercial PFPE Fomblin fluid which has the least thermal stability but best viscosity profile. It might not be designed for high temperature usage, but comparatively Z60 alone decomposes as temperature reaches 330 °C to 2% of its original mass in 4 h. In the presence of alumina powder, the

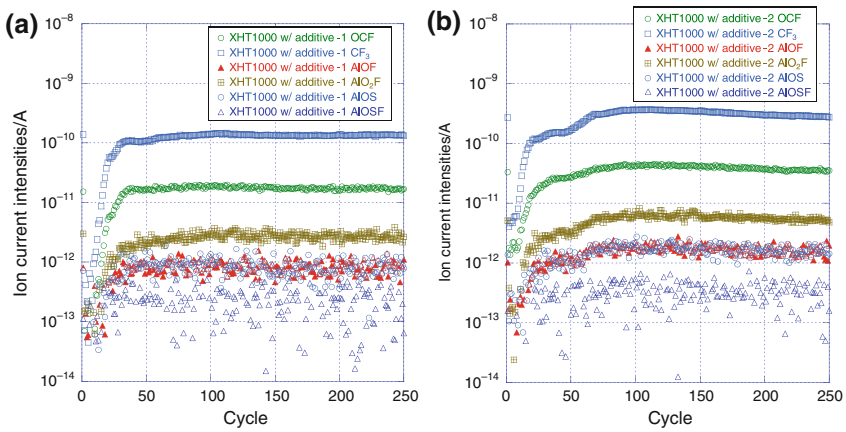


Fig. 8 The selected ion current intensities of Krytox® XHT-1000 with additive-1 (**a**), with additive-2 (**b**). Additive-1 is more effective than additive-2. Note: the intensities have been subtracted from backgrounds

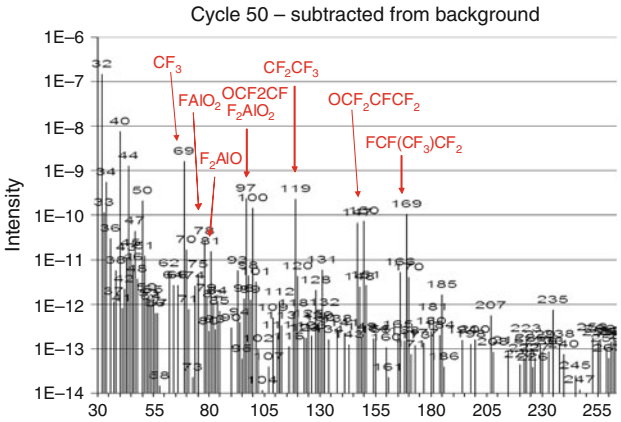
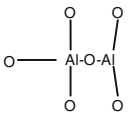


Fig. 9 The MS bargraph of XHT-1000 + alumina versus cycle at 333 °C, cycle 50, 15 min from the starting the isothermally hold. We see fluorocarbons CF_3, CF_2CF_3, $FCF(CF_3)CF_2$, fluoroxy OCF_2CF, OCF_2CFCF_2 and small ions Al–F (46), Al–O–F (62), and AlO_2F (78)

decomposition of Z60 starts 260 °C and in another 3.6 min it lost almost all the original mass. See the TG weight loss summary in Fig. 10. The Z60 with 3 mass/% additive-1 lost all its original mass in 1 h in the presence of 1 mass/% alumina. The Z60 with 3 mass/% additive-2 in the presence of alumina lost all its original mass in 35 min. The linear blocky structure of polyether has more sites for the formation of Al–F and Al–O–F bonds.

MS monitors the fragments of isothermally hold Z60

The block structure of Z60, alumina and its anticipated reaction products between this PFPE and alumina are given below. Again, we are trying to find the clues of catalytical decomposition from the



A-F Al-O-F Al-F-O OAlOF

CF3-O-[CF2CF2-O]m[CF2-O]pCF2CF3

molecular structure of Z60. Why it is different from Krytox® XHT-1000, a branched PFPE lubricant? Comparing

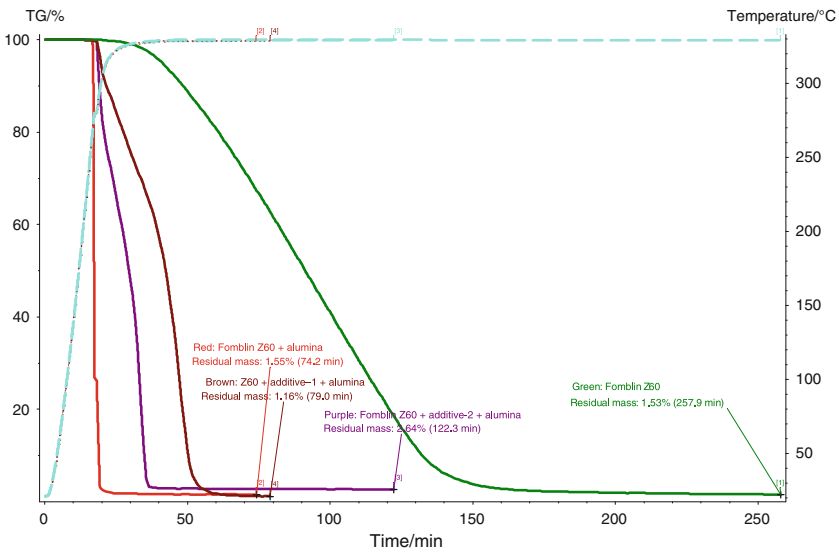


Fig. 10 The summary plot of TG mass losses of Z60, Z60 + alumina, Z60/additive-1 + alumina, and Z60/additive-2 + alumina at 330 °C hold

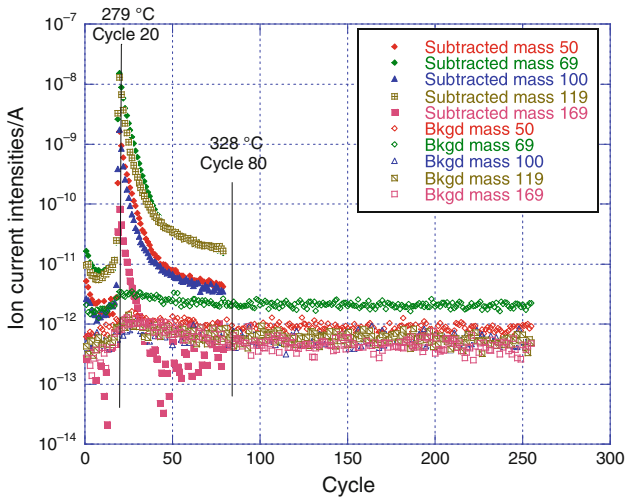


Fig. 11 Ion current intensities of CF_2, CF_3, $(CF_2)_2$, CF_2CF_3, $FCF(CF_3)CF_2$, and CF_2CFCF_2 (mass 50, 69, 100, 119, 150, and 169). Isothermally hold of Z60 + alumina—backgrounds are tested with no sample

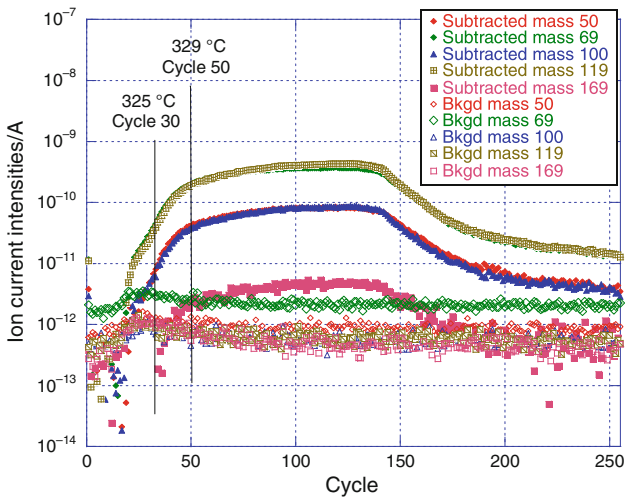


Fig. 12 Ion current intensities of CF_2, CF_3, $(CF_2)_2$, CF_2CF_3, $FCF(CF_3)CF_2$, and CF_2CFCF_2 (mass 50, 69, 100, 119, 150, and 169). Isothermally hold of Z60 alone in 4 h

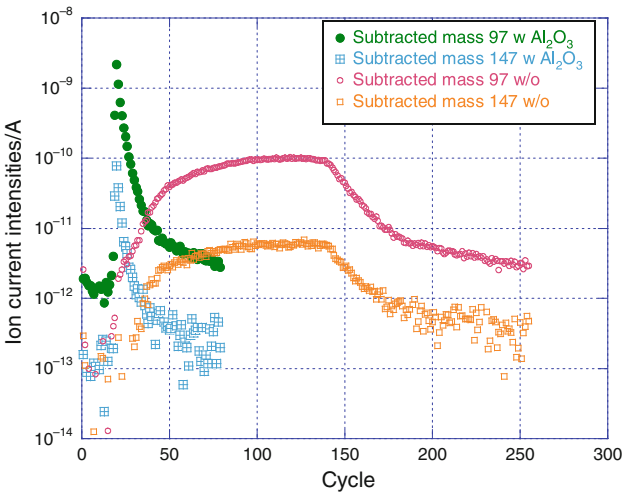


Fig. 13 Ion current intensities the fluoroalkoxy CF–CF_2O, CF–O–CF_2CF_2 (mass 97, 147) of isothermal hold of Z60 in the presence or absence of alumina

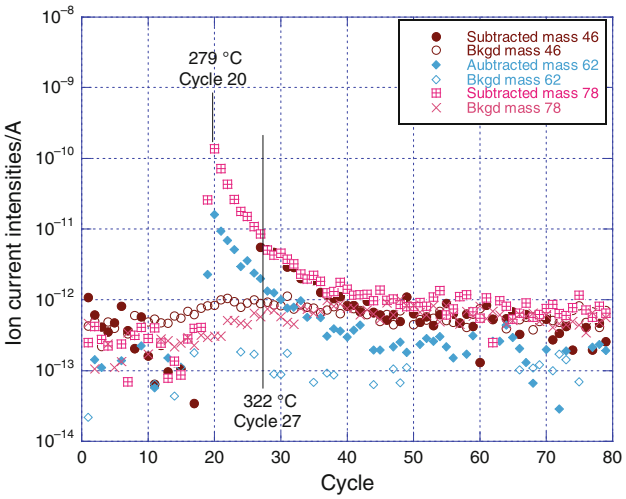


Fig. 14 Z60 + 1% alumina isothermally hold 330 °C/4 h—the formation of aluminum–fluorine bond AlF, Al–O–F, and O–Al–OF (mass 46, 62, and 78)

in Figs. 11, 12, the ion current intensities are very different of Z60 from rapid decomposition of the oil in the presence of alumina powder and not so rapid decomposition of Z60 alone. As for all PFPE oils, the major decomposition products are small and large fluorocarbons fragments: CF_2, CF_3, $(CF_2)_2$, CF_2CF_3, $FCF(CF_3)CF_2$, and CF_2CFCF_2, (mass 50, 69, 100, 119, 169, and 131). In Fig. 11, the case of alumina powder accelerated decomposition of Z60, the detectable fragments reach to its maxima at 280 °C/cycle 20. In Fig. 12, the fragmentation of Z60 itself becomes significant at 325 °C/cycle 30 and 329 °C/cycle 50. The perfluoroalkoxy OCF_2CF, $CFOCF_2CF_2$ (mass 97, 147) fragments from Z60 in the presence/absence of alumina are compared in Fig. 13. The rapid decomposition was so fast; it is hardly to have the 1 wt% alumina weighed preciously at the start of experiment. The intensities of fluorocarbons are nearly 80–100 holds larger in catalytically accelerated by alumina powder than those without. Higher ion intensities at lower temperature/time/cycle of Z60 can be explained that molecular structural difference of being blocky $[CF_2CF_2O]_m[CF_2O]_p$ rather than being branchy $[CF(CF_3)CF_2O]_n$ as XHT-1000 is compared in Figs. 14 and 9.

The cause of the rapid decomposition of Z60 in contact with 1 mass/% alumina is seen in the formation of AlF, OAlF, and OAlOF (mass 46, 62, and 78) isothermally hold 330 °C/4 h. The next question is that does the sulfur-

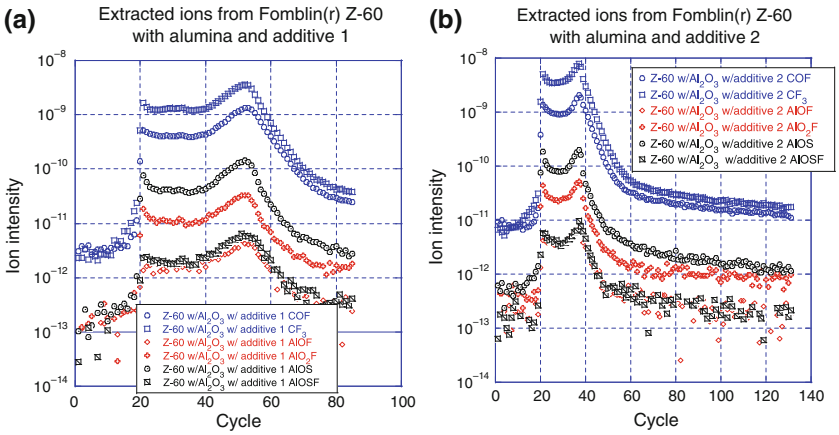


Fig. 15 The fragment intensities of ions from Z60 series with additive-1 (**a**) and with additive-2 (**b**): FCO (47), CF_3 (69), AlOF (62), AlO_2F (78), AlOS (75), and AlOSF (94). The intensities have been subtracted from background

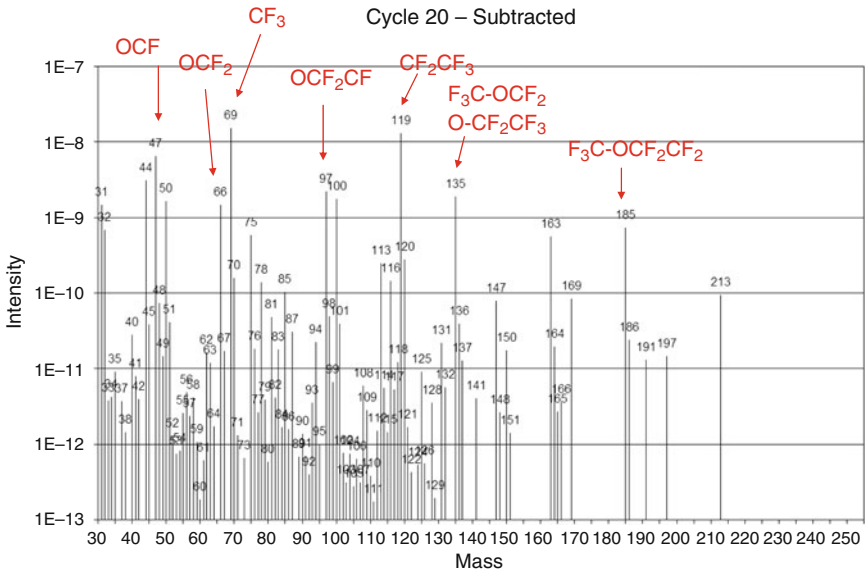


Fig. 16 Z60/alumina—bargraph at 279 °C, cycle 20 (peak of the ion intensity) OCF, OCF_2, CF_3, OCF_2CF, CF_2CF_3, OCF_2CF_3, $F_3C\text{-}OCF_2CF_2$ the fluorocarbons and fluoroxy ions. Smaller ions AlOF, AlO_2F (mass 62, 78)

containing additives-1 and -2 shield the catalytic decomposition of Z60 oil? In grades that contain additive-1, it is not stable at 330 °C with weight loss to 94% of its original mass; additive-2 with mass loss to 97%. Additive-2 in Z60 shows less effective than additive-1 in slowing the decomposition in the presence of alumina powder. TG weight loss as a function of time in Fig. 10 is evident.

In addition to the formation of A–F, Al–O–F, and O–Al–OF (mass 46, 62, and 78), the Z60/additive-1 shows the fragments of Al–O–S, F–Al–O–S (mass 75, 94), but no Al–OSO, Al–OSO_2 (mass 91, 107). The reason is the same as being eluted in earlier in the case of with Krytox® XHT section; the formation of aluminum–fluorine (Al–F) in decomposition hinders by the formation of Al–O–S shields the catalytic decomposition of the contact of Al_2O_3 with Z60. Because of the blocky structure, not as shield by CF3 branching in Krytox®, Z60 decomposition rapidly regardless of the presence of additives. A pair of the summarized graphs of Z60/additive-1 and Z60/additive-2 in selected ions of OCF, CF_3, AlOF, AlO_2F, AlOS, and AlOSF (mass 47, 69, 62, 78, 75, and 94) is compared in Fig. 15. Again, the additive-1 is more effective than additive-2 in reducing the decomposition of Z60.

The MS high ion intensities from decomposition of PFPE of Z60/alumina (Fig. 16) at 279 °C/cycle 20 are very different from that of previous XHT-1000/alumina (Fig. 9) at 330 °C/cycle 50. The intensities from decomposition of Z60 with additives are not only at lower temperature (279 °C, not yet reach the 330 °C testing temperature) and earlier cycle, but also high in ion currents. The higher temperature utility of XHT-1000 from its branchy molecular structure is confirmed. Z60 might not be good for high temperature applications.

Conclusions

- The use of high temperature isothermal TG to study the weight loss of PFPE Krytox® XHT-1000 was confirmed.

- The coupling of a mass sensitive detector with the TG equipment provides molecular information on the effect of alumina and additives on Krylox® XHT as well as on Fomblin Z60. The branch structure is more protected the catalytic decomposition of alumina.
- For the first time aluminum fluorides (A–F) and oxy-fluorides (O–CF, Al–OF, and AlO_2F) have been observed among the decomposition products of PFPE's.
- The thermal stability of PFPE's is Krytox® $\gg$ Fomblin® Z60 at the testing temperature and time duration.
- Two new additives provide protection from alumina catalytic decomposition of Krytox® XHT-1000, but much less so for Fomblin® Z-60 at 1 mass/% alumina loading.
- Aluminum oxy-sulfur and aluminum oxy-sulfur fluorides (AlO–S, AlO–SF) were observed among the decomposition products in Krytox® XHT-1000/additive-1, Krytox® XHT-1000/additive-2, and Fomblin® Z60/additive-1 and Z60/additive-2.

References

1. Band TM, Walther HC, Howell JL. PCT Int Appl. US patent 20070295287-A1 (20071227), US 2005-241567 (20050930), US 7544646-B2 (20090609). 2006. p. 21.
2. Denkenberger KA, Bowers RA, Jones AD, Mueller KT. NMR studies of the thermal degradation of a perfluoropolyether on the surfaces of gamma-alumina and kaolinite. Langmuir. 2007;23:8855–60.
3. Hall JT, Hansma PK. Adsorption and orientation of sulfonic acids on aluminum oxide: a tunneling spectroscopy study. Surf Sci. 1978;71:1–14.
4. Weaver JD, Tasset EL, Fry WE. Supported fluorocarbonsulfonic acid catalysts. Catal Today. 1992;14:195–210.