

Modification of POSS and their tribological properties and resistant to space atomic oxygen irradiation as lubricant additive of multialkylated cyclopentanes

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Abstract: Developing functional additive resistant to space atomic oxygen (AO) irradiation through simple molecular design and chemical synthesis to enhance the lubricating performance of multialkylated cyclopentanes (MACs) oil is a significant challenge. Herein, sulfur-containing polyhedral oligomere silsesquioxane (POSS) were synthesized via a click-chemistry reaction of octavinyl polyhedral oligomeric with alkyl sulfide. The reduce-friction (RF), anti-wear (AW) properties and anti-AO irradiation of POSS-S-R as MACs base oil additives in atmospheric and simulated space environments were systematically investigated for the first time. Results demonstrate that POSS-S-R not only possesses outstanding anti-AO irradiation capacity but also effectively improves the RF and AW of MACs in atmospheric or simulated space surroundings. This improvement is due to the excellent anti-AO irradiation properties of the POSS structure itself and the high load-carrying ability of silicon-containing and sulfur-containing compounds generated by tribo-chemical reactions, which effectively separates the direct contact of the friction interface. We believe that this synthesized POSS-S-R is a promising additive for space lubricants.

Keywords: polyhedral oligomere silsesquioxane (POSS), additive, reduce-friction, anti-wear, multialkylated cyclopentanes (MACs), resistant atomic irradiation

1 Introduction

Spacecraft operating in orbit environment are exposed to various types of space erosion, including high vacuum, extreme temperatures, solar electromagnetic radiation, charged particle radiation, neutral atmosphere, space debris and micrometeoroids, plasma, micro-vibration, microgravity, artificial radiation, humidity and others [1–4]. These harsh environmental factors, especially high vacuum, atomic oxygen (AO), charged particles, neutral particles, and electromagnetic radiation, can severely damage spacecraft stability and lifespan [5–6]. Consequently, material and lubrication

technology must meet new challenges, especially for developing high-performance lubricants that can ensure long-term normal operation of spacecraft. Currently, common lubricants used in space environments include multialkylated cyclopentanes (MACs), silicone hydrocarbon oil, perfluoropolyether oil, silicone oil containing fluorochlorophenyl, ionic liquid and its corresponding grease [7–11]. However, these lubricants are difficult in maintaining stable molecular structures in harsh space environments, especially in the low Earth orbit between 200–700 km [12–13]. In this environment, AO poses the most significant threat to spacecraft [14–15], causing chemical bond cleavage,

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decomposition, oxidation and polymerization, which degrades the physical and chemical properties of space lubricants and seriously endangers the operational safety of spacecraft [16–17].

The shortened life of space lubricants will seriously affect the operational safety of space equipment. In recent years, polyhedral oligomere silsesquioxane (POSS) and its derivatives have been extensively studied for their high thermal stability, oxidation resistance, high toughness, flame resistance, absence of volatile substances, no odor and environmental friendliness [18–20]. The numerous benefits of POSS have led to its use as an additive for space polymer composites to reduce materials damage caused by radiation [18, 21–23]. A lot of research proves that incorporating POSS groups into polymer matrices or copolymerization them with polymer monomers can significantly improve the mechanical properties (strength, modulus, rigidity) and anti-AO radiation properties of polymer materials [6, 13, 24, 25]. Verker R et al. [25] studied the stability of a diphenyl ether-terminated polyimide film doped with a phenyl-substituted POSS compound under the co-bombardment of ultra-high-speed chips and AO. The polyimide film, when doped with 15 wt% POSS compound, exhibited excellent anti-AO and high-speed debris bombardment performance and complete surface. Prof. Yan prepared an amino acid-substituted POSS cross-linked phospholipid-functional polyimide film with anti-AO radiation properties. AO was absorbed by the POSS cage structure in the film during AO irradiation, after which the ring structure was destroyed and the partial $-\text{Si}-\text{O}-\text{Si}-$ structure was transformed into a complex $\text{Si}-\text{O}$ structure such as SiO_2 and $\text{O}=\text{Si}-\text{O}-$ [26]. Prof. Kong and others used a reasonable molecular design to copolymerize aromatic polymerizable precursors with POSS-based monomers to obtain a class of aromatic polymers with excellent anti-AO radiation properties [27]. All of the above studies have shown that modifying the bulk phase of the material with POSS structure can greatly improve its anti-AO irradiation performance. However, to date, no additives with anti-AO irradiation performance have been reported for improving space lubricants. We hope to develop a new class of POSS-based lubrication additives that exhibit anti-AO irradiation performance through molecular design.

As is widely recognized, sulfur-containing organic compounds are a promising class of lubricant additives [28]. Previous studies have shown that organic sulfur lubricant additives possess excellent anti-wear properties [29–31], such as ZDDP [32, 33]. In this article, we successfully synthesized a series of organic–inorganic hybrid additives with anti-wear and anti-AO radiation properties by grafting long-chain thioethers onto the POSS ring through a click-chemistry reaction. Besides, they were added into multialkylated cyclopentanes (MACs) to investigate their prominent tribological and anti-AO performance.

2 Experimental

2.1 Chemicals and synthesis of the POSS-S-12 and POSS-S-18

Multialkylated cyclopentanes (MACs) was generously provided by prof. Feng, a researcher at the State Key Laboratory of Solid Lubrication. Octavinyl polyhedral oligomeric silsesquioxane (octavinyl-POSS) was provided by the Nanohybrid Plastics. Azobisisobutyronitrile (AIBN) was purchased from Shanghai National Medicine Group Chemical Reagent Co., Ltd. 1-dodecanethiol and 1-octadecanethiol were acquired from Aladdin Industrial Corporation (Shanghai, China). All chemicals were used as received without further purification. POSS-S-12 (polyhedral oligomere silsesquioxane ethyl dodecyl thioether) and POSS-S-18 (polyhedral oligomere silsesquioxane ethyl octadecyl thioether) were synthesized according to the literature reported procedure [34]. Different amounts of POSS-S-12 and POSS-2-18 were accurately weighed and added to the MACs to achieve mass concentrations of 0.5%, 1%, 2%, and 3% for subsequent testing.

2.2 Spectroscopic characterization

The structures of the POSS-S-12 and POSS-S-18 were characterized by proton nuclear magnetic resonance spectroscopy (^1H NMR, 400 MHz, Bruker, USA), Fourier transform infrared (FT-IR) spectra recorded on a spectrometer (Nicolet Nexus 670, Thermo Fisher, USA) with wave numbers ranging from $4,000\text{ cm}^{-1}$ to 600 cm^{-1} .

2.3 Thermal stability

The thermal stability of pure MACs and MACs with different concentrations of POSS-S-12 and POSS-S-18 was evaluated using a synchronous thermal analyzer system (STA 449 F3, Netzsch, Germany) under a nitrogen atmosphere with an alumina crucible. The temperature was increased from room temperature (RT) to 600 °C at a heating rate of 10 °C/min during the temperature ramp-up thermogravimetric (TG) analysis. The nitrogen flow rate was maintained at 50 mL/min during the analysis.

2.4 Atomic oxygen space irradiation experiment

Pure MACs and MACs blends containing 3 wt% POSS-S-12 and POSS-S-18 were placed on a 25 mm diameter steel block with each thickness being no more than 4 mm to subject to AO irradiation. The AO beam flowed from top to bottom perpendicular to effective contact surface of pure MACs or MACs blends. The flux density of the AO beam was 5.6×10^{15} atoms/(cm²·s), with an average kinetic energy of 5 eV. The vacuum degree of the irradiation environment was maintained at 3.0×10^{-2} Pa, and the AO irradiation duration was 4 h.

2.5 Friction and wear test

2.5.1 Friction and wear test under atmospheric conditions

The tribological properties of pure MACs and MACs blends were investigated using an Optimal SRV-IV oscillating reciprocating friction and wear tester at RT on steel/steel contacts. An AISI 52100 bearing steel ball was chosen and used for a ball-on-flat geometry. The test conditions for SRV are presented in Table 1. Prior to each test, all contact areas were cleaned. 0.2 mL of lubricant was applied to the contact site, and the friction data was automatically recorded by the software under the given test conditions. The wear volume of the lower disk was measured using a Bruker NPFLEX surface mapping microscope profile meter. The worn surfaces were analyzed using scanning electron microscopy (SEM, FEI Quanta FEG 250) and Energy-dispersive X-ray spectroscopy (EDS) test accessories are assembled. The X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI-5702 multifunctional X-ray photoelectron spectroscopy system using Al-K α radiation as the

exciting source. The binding energies of the target elements were determined at a pass energy of 29.35 eV and with a resolution of ± 0.3 eV, using the binding energy of carbon (C 1s: 284.8 eV) as the reference.

2.5.2 Friction and wear under the condition of space atomic oxygen irradiation

After AO irradiation, the tribological behaviors of pure MACs and MACs blends were evaluated using a self-developed ball-on-disc tribometer under vacuum conditions at RT (10^{-4} Pa, relative humidity 30%) [7]. 1 mL of AO-irradiated MACs and MACs blends were evenly smeared on the GCr15 bearing steel round block as the lower sample, which had a surface roughness (R_a) of 0.02 μ m and a hardness of 800–900 HV. The upper sample was a GCr18 bearing steel ball with a diameter of 6 mm. The test conditions for the space friction are shown in Table 1.

Table 1 Tribological parameters and AO irradiation parameters in atmospheric and space environments.

	Atmospheric	Space
	SRV	Ball-on-disk
Load (N)	150	2
Frequency (Hz)	25	/
Temperature (°C)	25	25
Amplitude (mm)	1	/
AISI 52100 ball (HV)	700–800	700–800
Steel block (HV)	700–800	800–900
Rotation speed (r·min ⁻¹)	/	300
AISI 52100 ball (mm)	10	6
Steel block (mm)	$\varnothing = 24, {}^1h = 7.9$	$\varnothing = 25, h = 8.0$
Surface roughness (μ m)	30–50	30–50
Duration (min)	30	30
Irradiation time (min)	0	240
Density of irradiation (atoms·(cm ² ·s) ⁻¹)	0	5.6×10^{15}
Atmospheric pressure (Pa)	87.5×10^3	3.0×10^{-2}

¹ h means height.

3 Results and discussion

3.1 Physicochemical properties of POSS-based compounds as MACs additives in atmospheric environment

The molecular structure of the POSS-based compound

is illustrated in Fig. 1(a). Figure 1(b) displays the nuclear magnetic resonance (NMR) spectra of vinyl-POSS and thioether-modified POSS compounds (POSS-S-12 and POSS-S-18). As can be observed from Fig. 1(b), the chemical shift of the double bond (5.88–6.16 ppm) in vinyl-POSS completely vanished after successful grafting of thioether onto the POSS ring using a click chemical reaction. Additionally, in the NMR spectra of POSS-S-12 and POSS-S-18, a distinct alkyl chain peak appeared at about 1.5 ppm, providing further evidence of the complete grafting of thioether onto the POSS ring. The FT-IR spectra of POSS before and after modification are shown in Fig. 1(c). In the FT-IR spectra of POSS, the wide peak at $3,400\text{ cm}^{-1}$ represents O–H stretch of the hydroxyl group from water, while the broad multiple peaks between $3,000\text{ cm}^{-1}$ and $3,300\text{ cm}^{-1}$ correspond to the stretching vibration of POSS. Absorbing peaks at $1,004\text{ cm}^{-1}$ and $1,110\text{ cm}^{-1}$ can be attributed to the Si–O–Si structure in the POSS cage. For the FT-IR curves of POSS-S-12 and

POSS-S-18, the adsorbing peaks at $2,852\text{ cm}^{-1}$ and $2,930\text{ cm}^{-1}$ are related to the stretching modes of $-\text{CH}_3$ and $-\text{CH}_2-$. The above results confirm the successful modification of thioether to the POSS ring structure.

The dispersion stability of POSS-S-12 and POSS-S-18 in MACs was evaluated, as shown in Figs. 1(d) and 1(e). Initially, it was observed that different concentrations of POSS-S-12 and POSS-S-18 could be stably dispersed in MACs. After aging for 30 days, low concentrations of POSS-S-12 and POSS-S-18 did not show significant sedimentation, while high concentration of POSS-S-12 exhibited partial sedimentation, whereas POSS-S-18 was still dispersed and stable. These results demonstrate that both POSS-S-12 and POSS-S-18 can be stably dispersed in MACs within an appropriate concentration range, and the increase in alkyl chain contributes to higher dispersion stability of such compounds at high concentrations because a longer alkyl chain leads to a lower molecular polarity.

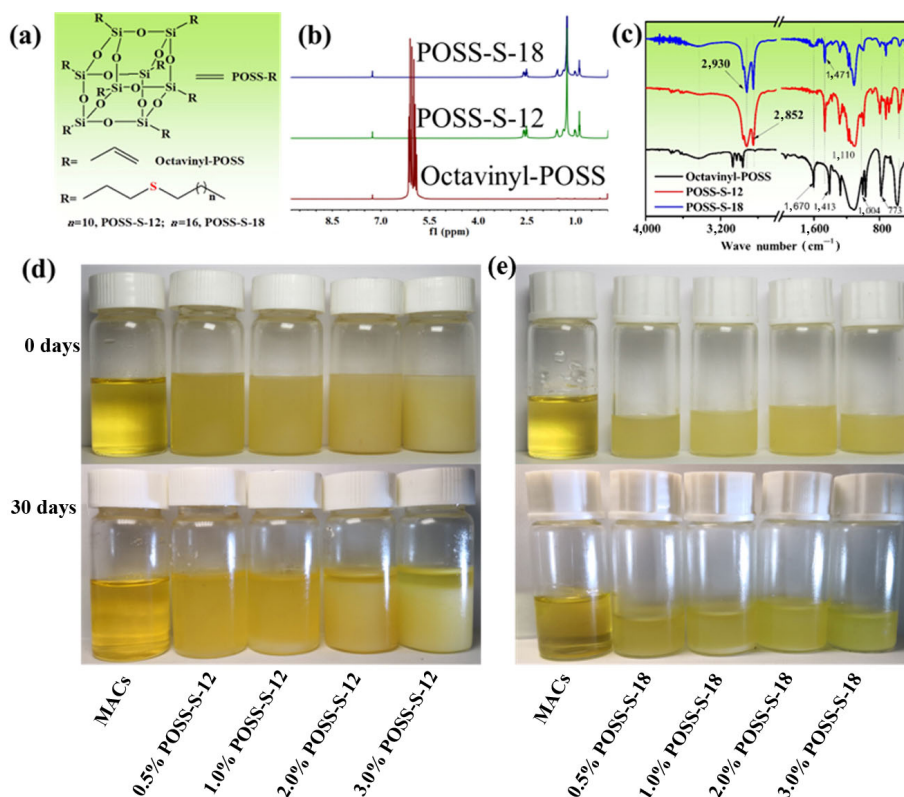


Fig. 1 (a) Structures of POSS-S-12 and POSS-S-18. (b) ^1H NMR (CDCl_3) spectra and (c) FT-IR spectra of octavinyl-POSS, POSS-S-12 and POSS-S-18. (d) Dispersion stability test of different concentrations of POSS-S-12 and POSS-S-18 as MACs additives. (d) Optical images of MACs blends with different concentrations of POSS-S-12 (From left to right: MACs, MACs + 0.5%, MACs + 1%, MACs + 2%, MACs + 3%) after 0 days and 30 days. (e) Optical images of MACs blends with different concentrations of POSS-S-18. (From left to right: MACs, MACs + 0.5%, MACs + 1%, MACs + 2%, MACs + 3%) after 0 days and 30 days.

Figure 2 depicts the thermogravimetric analysis (TGA) curves of pure MACs and MACs blends with varying amounts of POSS-S-12 and POSS-S-18 additives, and corresponding experimental results are listed in Table 2. The thermal decomposition temperature of MACs was determined to be 296.338 °C at 10% weight loss. As shown in Table 2 and Fig. 2, the addition of POSS-S-12 and POSS-S-18 significantly improved the thermal stability of MACs. For instance, the MACs blends exhibited higher thermal decomposition temperatures after incorporating 0.5%, 1%, 2%, and 3% of POSS-S-12, which were 297.338 °C, 301.838 °C, 308.438 °C, and 312.138 °C, respectively. In addition, the MACs blends displayed higher thermal decomposition temperatures at the same mass loss when POSS-S-18 was added in the same concentration. This is because the longer alkyl chain length resulting in stronger intermolecular force, consequently the thermal decomposition temperature increased. Specifically, the thermal decomposition temperatures of the MACs blends after incorporating 0.5%, 1%, 2%, and 3% of

Table 2 Thermal decomposition temperature of MACs and MACs blends with different concentrations of POSS-S-12 or POSS-S-18.

Lubricant	TG temperature (°C) per weight loss		
	10%	20%	50%
MACs	296.338	316.538	343.638
0.5% POSS-S-12	297.338	319.538	349.338
1% POSS-S-12	301.838	322.238	351.238
2% POSS-S-12	308.438	330.938	363.238
3% POSS-S-12	312.138	333.038	363.538
0.5% POSS-S-18	311.675	333.375	364.675
1% POSS-S-18	312.575	335.075	370.875
2% POSS-S-18	312.675	336.475	373.375
3% POSS-S-18	313.175	339.475	379.375

POSS-S-18 were 311.675 °C, 312.575 °C, 312.675 °C, and 313.175 °C, respectively.

3.2 Tribological properties of POSS-based compounds as MACs additives in atmospheric environment

The friction coefficient and the wear volumes of neat MACs and MACs blends with 0.5%, 1%, 2%, 3% POSS-S-12 and POSS-S-18 are presented in Fig. 3. The addition of POSS-S-12 and POSS-S-18 to MACs significantly improves the lubrication performance of the base oil. As depicted in Fig. 3(a), the friction coefficient for neat MACs is initially around 0.6, probably owing to the rupture of the oil film and severe scuffing of the contact surface. With the addition of only 0.5% POSS-S-12, the friction coefficient decreases, and with the addition of 1% POSS-S-12, a significant reduction in friction coefficient is observed. Meanwhile, the friction coefficient keeps relatively stable throughout the entire testing process. Increasing the concentration of POSS-S-12 from 1% to 2% leads to a continuous reduction in the friction coefficients. Nevertheless, further increasing the content of POSS-S-12 from 2% to 3% does not significantly affect the friction coefficient. The friction coefficients become more stable when more POSS-S-12 is added, indicating a more stable interface is generated and a stable lubricating film is formed. Being similar to the tendency of the friction coefficient, the wear volumes follow a similar trend to the friction coefficient and are significantly reduced with the addition of POSS-S-12 (Fig. 3(a1)). By considering both friction coefficient and wear volume,

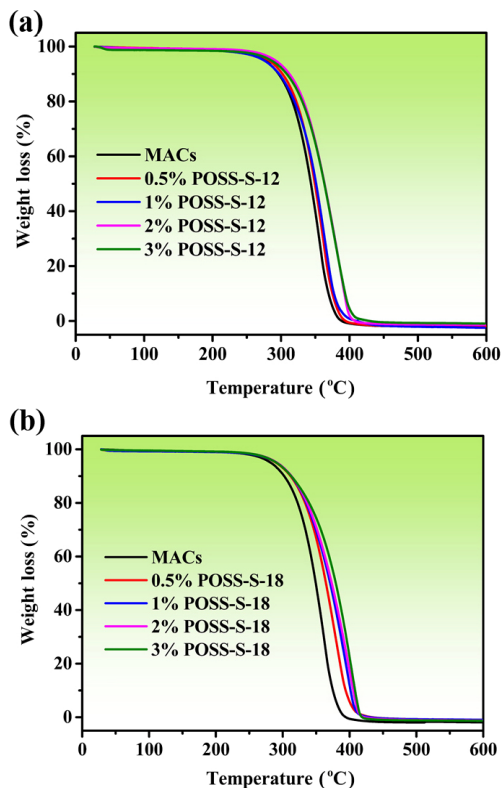


Fig. 2 (a) TGA curves of pure MACs and its blends with 0.5% POSS-S-12, 1% POSS-S-12, 2% POSS-S-12 and 3% POSS-S-12. (b) TGA curves of pure MACs and its blends with 0.5% POSS-S-18, 1% POSS-S-18, 2% POSS-S-18, 3% POSS-S-18.

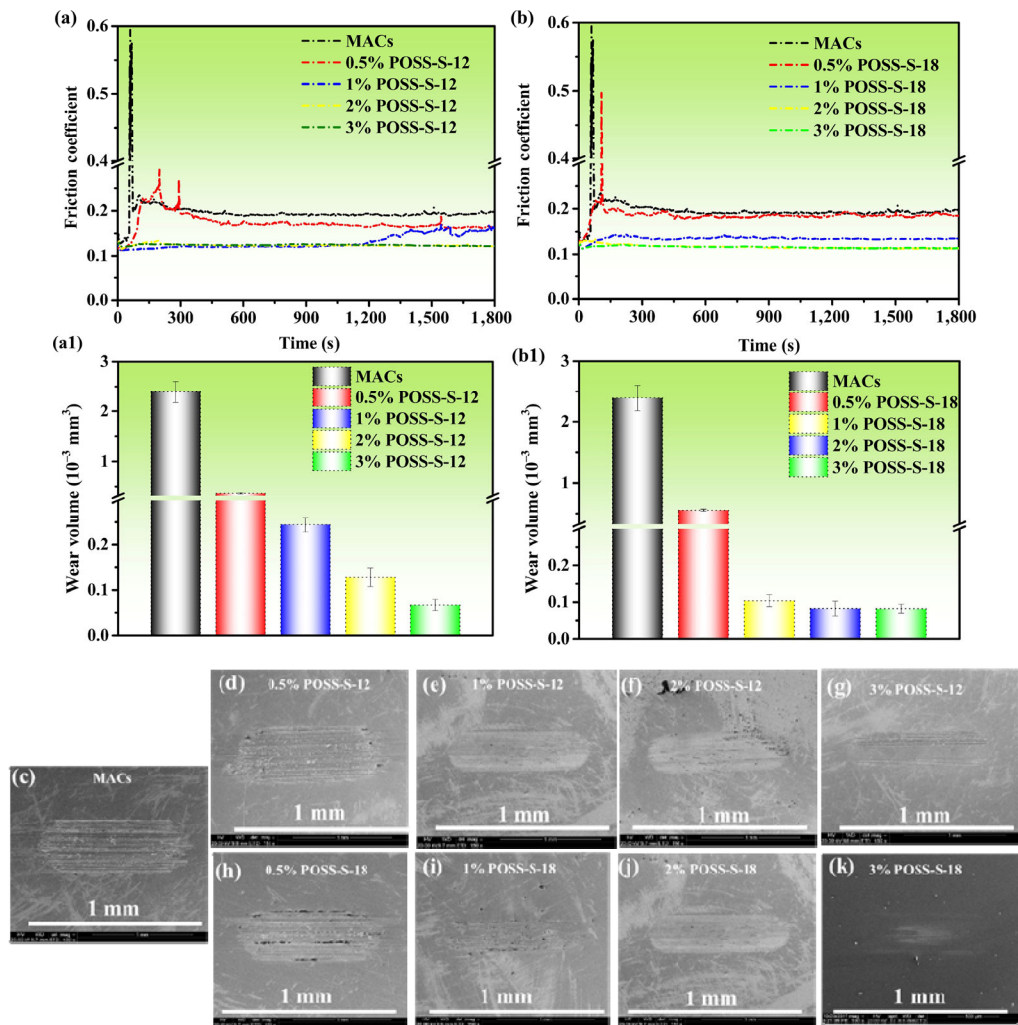


Fig. 3 Evolution of the friction coefficient of MACs added with (a) POSS-S-12 and (b) POSS-S-18; wear volume losses of MACs added with (a1) POSS-S-12 and (b1) POSS-S-18. (c–k) Corresponding wear surface SEM morphologies.

when the content of POSS-S-12 is 2%, the lubricant blend exhibits an optimal wear-reduction effects, resulting in a wear volume reduction of up to 90% compared with that of the rubbing surface lubricated with neat MACs.

Figures 3(b) and 3(b1) illustrate the friction coefficient and wear volume of MACs blends with different concentrations of POSS-S-18. As observed from the figure, the addition of POSS-S-18 results in a similar reduction in friction coefficient and wear volume as POSS-S-12. With an increase in the amount of POSS-S-18, the friction coefficient and wear volume of MACs blends decrease significantly. Notably, the addition of 1% and 2% POSS-S-18 to the MACs results in a remarkably smooth friction coefficient and low wear volume. These findings suggest that POSS-S-18

exhibits superior anti-friction and anti-wear properties compared with POSS-S-12 in the same concentration range. These results further support the notion that an increase in the length of the alkyl chain can improve the reduce-friction and anti-wear properties of such compounds at low concentrations.

The surface morphology of the wear spot lubricated with pure MACs and MACs blends is shown in Figs. 3(c)–3(k). As shown in Figs. 3(d)–3(g), as the concentration of POSS-S-12 gradually increases, the diameter of the wear spot and the scratch on the surface of the friction track is significantly reduced. Compared with POSS-S-12, a similar trend in wear spot diameter and wear scar depth is observed from Figs. 3(h)–3(k), for the addition of POSS-S-18. Moreover, at the same concentration, the POSS-S-18

results in a smaller wear spot and a shallower scratch. Notably, when 3% POSS-S-18 is added, the wear spot becomes almost imperceptible.

To provide a concise demonstration of the reduce-friction and anti-wear mechanism of POSS-based compounds, EDS and XPS analyses were performed on the surface of the wear spot lubricated with pure MACs and MACs blends with 3% POSS-S-18, as shown in Fig. 4, whose corresponding SEM images are Figs. 3(c) and 3(k). The elemental analysis in Fig. 4(a) shows only the intrinsic elements of steel, such as C, O, Fe, Cr, on the surface of the wear spot after lubrication with MACs. In contrast, a large number of S and Si elements, originating from the molecular structure of the POSS compound, were detected on the surface of the wear spot lubricated with MACs containing POSS. In addition, further XPS analysis revealed weak S 2p peaks at approximately 168.8 eV, indicating the formation of sulfur-containing compounds [35]. The peaks at 102.4 eV in the Si 2p spectra are assigned to SiO₂ and other decomposition products of the POSS-S-18, respectively. These decomposition products play an important role in reducing friction and wear in steel/steel contacts, attaching to the worn surface, lubricating the friction pair, and producing effective protective films to prevent

steel/steel contact. Based on the aforementioned EDS and XPS results, a complex tribo-chemical reaction occurred during the rubbing process.

3.3 Tribology properties of POSS-based compounds as MACs additives after AO irradiation

In order to prove the excellent anti-AO irradiation properties of POSS-based compounds, a 4 h-AO irradiation experiment was performed on a MACs composition containing 3% of POSS-S-18. As shown in Fig. 5(a), after 4 hours of AO irradiation, the color of the MACs changed to white and showed slight contraction (see 1 and 2 in Fig. 5(a)), suggesting that AO affected the structural stability of MACs. However, after AO irradiation, the color of the MACs blends containing POSS changed slightly (see 3 and 4 in Fig. 5(a)), demonstrating that the addition of POSS compound had a certain inhibitory effect on the erosion of AO. To demonstrate the effect of AO irradiation on tribological properties, the tribological properties of the samples before and after AO irradiation were tested. From Fig. 5(b), compared with intact MACs, the friction coefficient of MACs irradiated by AO was significantly increased and fluctuating, and the reduce-friction property was also significantly reduced. However, when 3% POSS-S-18 was used as an additive

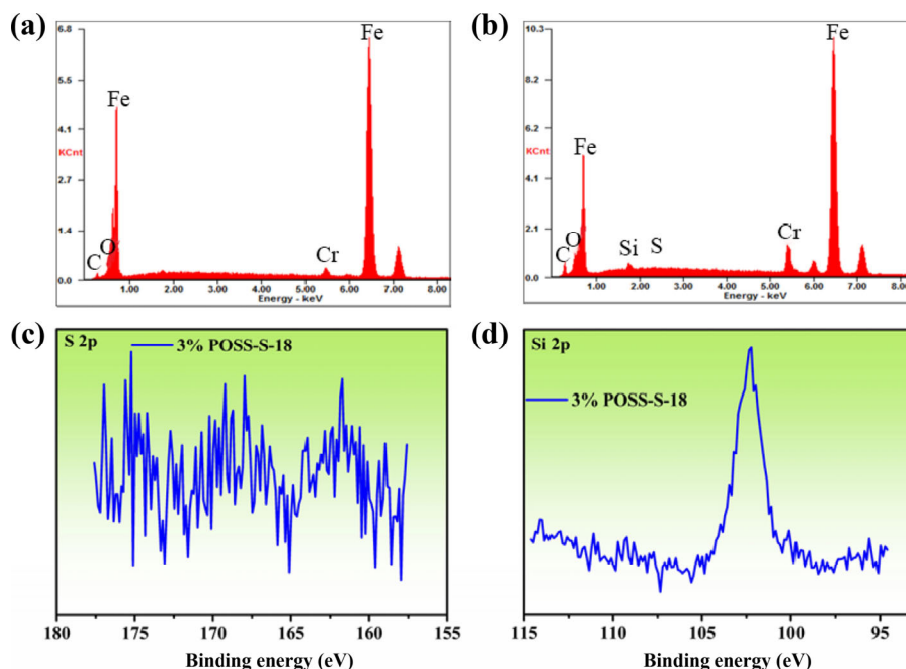


Fig. 4 EDS of the wear spot surface lubricated with MACs (a) and MACs blends with 3%POSS-S-18 (b). XPS spectra of S 2p (c) and Si 2p (d) lubricated by MACs blends with 3% POSS-S-18 for steel/steel contacts at RT.

for MACs, the anti-AO irradiation performance of the composition was significantly improved. The MACs blends containing 3% POSS-S-18 remained almost stable at the same level before and after irradiation.

Figures 5(c)–5(e) and 5(c1)–5(f1) show 3D optical microscopic and SEM images of wear tracks lubricated by MACs, AO-irradiated MACs, MACs blends with 3% POSS-S-18 and AO-irradiated MACs blends with 3% POSS-S-18, respectively. It can be seen that the friction track after MACs lubrication is narrow, and the furrows of the wear spots are shallow. In contrast, the friction track of the wear spot lubricated by AO-irradiated MACs is rough, indicating significant scratching and adhesive wear has occurred. These results further confirm that the structure of MACs significantly changes after exposure to AO, leading to the loss of its lubricity. Figures 5(e) and 5(e1) shows that the friction track of MACs blends before irradiation. It can be seen that the addition of POSS

can significantly improve the tribological performance of MACs in a vacuum environment. Compared to pure MACs the frictional track becomes smaller, and the wear becomes lighter. The results indicate that MACs has poor resistance to AO, causing the loss of lubrication performance and significant fluctuation of the friction coefficient. In contrast, the addition of POSS-S-18 exhibits excellent anti-AO irradiation performance, and even after nearly 240 minutes of AO irradiation, the sample still has a very stable, very low coefficient of friction. This further suggests that POSS-S-18 is a promising space lubrication additive.

3.4 Mechanism analysis of anti-atomic oxygen irradiation properties of POSS based compounds

To demonstrate the anti-AO irradiation property of POSS-based compounds, infrared spectra of MACs and MACs blends with POSS-based compounds as additives before and after AO irradiation were

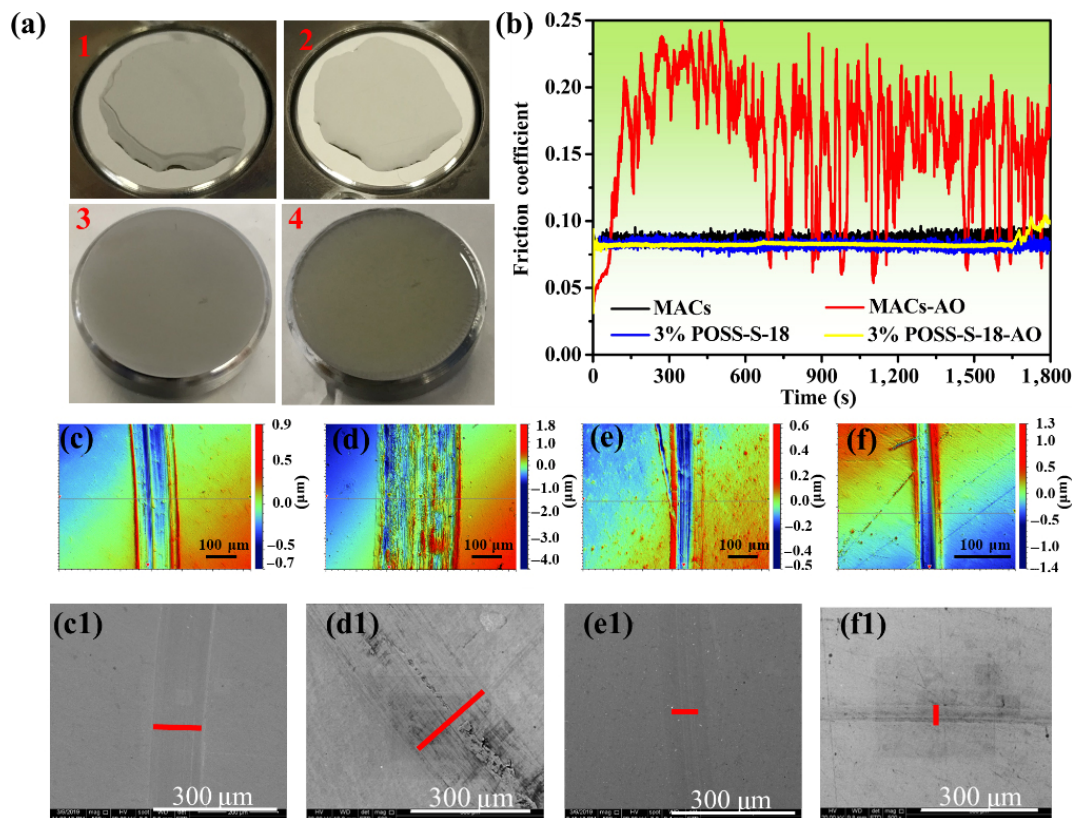


Fig. 5 (a) Photos of MACs and MACs containing 3% POSS-S-18 before irradiation are marked with 1 and 3, respectively. Photos of MACs and MACs containing 3% POSS-S-18 after irradiation are marked with 2 and 4, respectively. (b) Friction coefficients of oil sample before and after atomic oxygen irradiation in simulated space environment. (c, d, e, f) 3D optical microscopic images and (c1, d1, e1, f1) SEM morphologies of the wear tracks lubricated by MACs, AO irradiated MACs, MACs with 3% POSS-S-18 and AO irradiated MACs with 3% POSS-S-18.

analyzed. As shown in Fig. 6(a), the original infrared absorption peaks were significantly weakened after exposure to AO, indicating a change in the sample's structure. Further observation, the -O-Si stretching vibration peak at $1,155\text{ cm}^{-1}$ for POSS-S-18 disappeared after AO irradiation, indicating a significant change in the Si-O bond in the POSS structure. In contrast, AO-irradiated MACs blends did not show the $1,048\text{ cm}^{-1}$ peak, which is the peak of oxidation product and appears for MACs-AO. This result suggests that the addition of POSS-S-18 improves the anti-AO irradiation performance of MACs. The C-H bond peak at 726 cm^{-1} was significantly weakened for both MACs and MACs blends, indicating partially oxidation of the C-H bond.

In Fig. 6(b), it is obvious in the ^{29}Si NMR spectrum that the chemical shift of silicon changes significantly. The chemical shift of the -O-Si-O- bonded silicon in POSS-S-18 before AO irradiation is -68.19 ppm . After AO irradiation, due to the high reactivity of AO, bombardment of POSS-S-18 produces a silicon-containing compound with a chemical shift of -80.19 ppm , indicating that the main ring is broken. POSS-S-18 acts as a sacrificial anti-AO irradiation

agent, thereby improving the anti-AO irradiation performance of the lubricating oil. This suggests that irradiation causes partial destruction of the molecules structure.

Figure 6(c) shows the TGA curves of pure MACs and MACs blend with 3% POSS-S-18 before and after AO irradiation. The MACs after irradiation exhibits a significant decrease in temperature of decomposition (T_d) from 302 to $291\text{ }^\circ\text{C}$, indicating that the molecular structure of MACs has suffered serious damage during the irradiation process. The T_d of $340\text{ }^\circ\text{C}$ for the MACs blend indicates its excellent thermal stability and high heat capacity, making it almost unaffected by irradiation. Overall, the TGA curves demonstrate that AO irradiation has a significant impact on the thermal stability of MACs due to the destruction of the molecular structure. Notably, the addition of POSS-S-18 to MACs enhances the thermal stability and anti-AO irradiation properties of the blend, as evidenced by its higher decomposition temperature compared to neat MACs before and after irradiation.

When POSS-based compounds are used as MACs additives, they can improve the lubricating properties of MACs both in atmospheric and irradiated

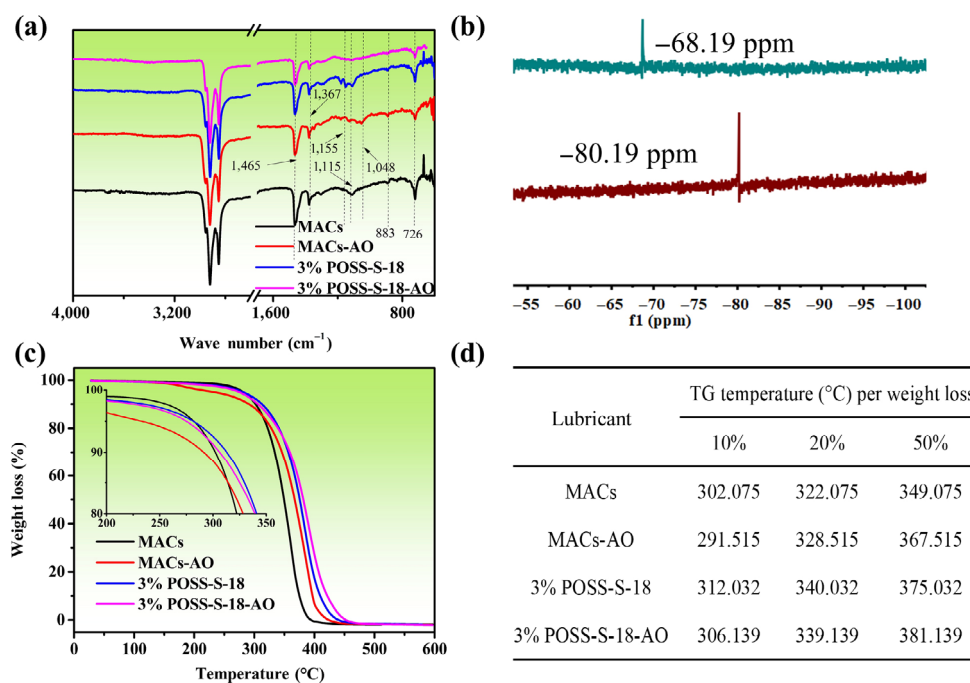


Fig. 6 (a) FT-IR curves for MACs and MACs containing POSS-S-18 additives before and after AO irradiation. (b) ^{29}Si NMR curves for POSS-S-18 additives before and after AO irradiation. (c) The TGA curve of MACs and MACs containing POSS-S-18 additives before and after AO irradiation. (d) T_d of MACs and MACs blends contained 3% POSS-S-18 under corresponding mass loss before and after AO irradiation.

environments. This is inextricably linked to the anti-AO irradiation characteristics of POSS itself. As shown in Fig. 7, the lubrication mechanism and anti-AO irradiation mechanism of POSS-S-18 in atmospheric and irradiation environments are presented based on the previous literature and our experimental results, we present in atmospheric conditions, S and Si in the POSS-based compound react with the metal substrate surface to form a corresponding boundary lubrication film, which hinders the direct contact of the friction pair and reduces friction and wear. This mechanism is applicable to space lubrication conditions. However, in the space environment, POSS-based compounds are decomposed into various structural fragments due to the fracture of the $-\text{Si}-\text{O}-\text{Si}-$ bond of the main POSS. This consumption of AO effectively protects the structural stability of MACs by indirectly reducing AO corrosion, thereby acting as an anti-AO irradiation agent.

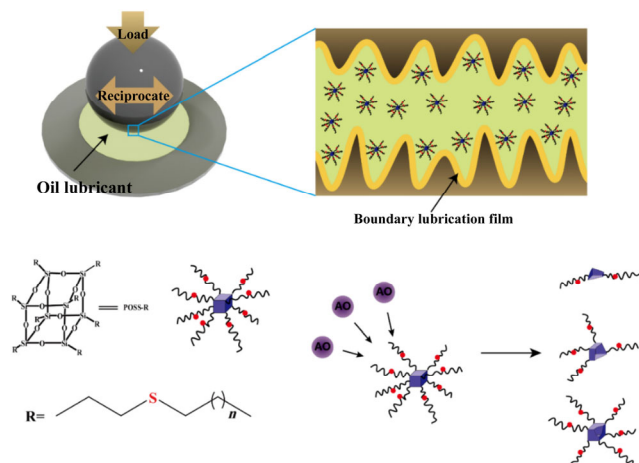


Fig. 7 Schematic diagram of lubrication mechanism against AO radiation.

4 Conclusions

In this study, we successfully synthesized POSS-S-12 and POSS-S-18 and evaluated their potential as lubricant additives for MACs. Adding POSS-S-12 or POSS-S-18 into MACs lubricant showed significant tribological properties such as lower coefficient of friction and smaller wear volume than pure MACs. XPS analysis revealed that a stable protective film containing sulfur and silicon is formed on the contact surface due to complex tribo-chemical reactions. This

protective film effectively prevents direct contact of the sliding pair and plays a key role in lubrication and wear resistance. Furthermore, space anti-irradiation experiments and space friction experiments show that POSS-S-12 and POSS-S-18 have excellent anti-AO irradiation properties. By comparing the apparent morphology, the thermal stability, the infrared spectra and silicon NMR spectra of oil samples before and after irradiation, we further speculate on the structure changes of the POSS-based compound after AO irradiation. Its anti-AO irradiation ability is attributed to the consumption of AO during irradiation through the fracture of its own POSS structure, thereby greatly protecting the structural stability and lubrication stability of MACs.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article. The author Feng ZHOU and Weimin LIU are the Editorial Board Members of this journal.

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