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Oxygen-related interfacial tribo-chemical reaction and wear mechanism between a-C coating and PEEK

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ABSTRACT

Amorphous carbon (a-C) coating can effectively reduce wear of the counterpart PEEK components in engineering equipment. While, the tribological performance of both a-C and PEEK demonstrates pronounced sensitivity to ambient atmosphere. Here, tribological behaviors of a-C/PEEK were compared under various environments including atmosphere, vacuum, and O₂, the interfacial tribo-chemical reaction was discussed from experimental investigation and atomic-level simulations. Results show that, oxygen content is one key factor to influence interfacial tribo-chemical reaction and wear mechanism for a-C/PEEK pair. Under ambient atmosphere and O₂, oxygen molecules break molecular chains of PEEK, even bond or absorb on the a-C under higher oxygen content, which can hinder the formation of the transfer film and result in elevated COF and worse wear of PEEK.

1. Introduction

Due to its excellent mechanical properties, thermo-plasticity, electrical insulation and self-lubrication, polyether ether ketone (PEEK) is widely used in marine equipment, aerospace, biomedical fields and other engineering equipment [1,2]. Essentially, the excellent self-lubricating property of PEEK derives from the formation of a transfer film on the hard pair surface during sliding [3,4], but the continuous and accelerated material consumption may causes the failure of some core PEEK components under the long-term friction heating and large mechanical load [5,6].

Applying a protective coating on the counterpart may change and retard the interfacial interaction with PEEK and the following formation and consumption of the transfer film, providing an effective and promising solution for above-mentioned issue, especially under some extreme operating conditions. Interestingly, amorphous carbon (a-C) coating is a famous solid lubricating material formed by sp³ and sp² carbon bonds [7,8], the graphitization characteristic of this coating during friction can not only reduce the coefficient of friction (COF), but also effectively protect the counterpart materials against wear. For example, Dong et al.[9] compared tribological properties of a-C, TiN, TiAlN and WC-Co coatings against carbon fiber reinforced PEEK (CF-PEEK), and found that PEEK paired with a-C coating showed extremely low wear.

It is worth noting that the tribological properties of both PEEK and a-C are largely dependent on the environment. For example, Johansson P. et al.[10] found that CF-PEEK exhibited higher wear rates and COF values under high oxygen (1000 ppm) and laboratory gas environments. Geraldine et al.[11] compared the tribological properties of PEEK composites under air, H2 and vacuum conditions, and found a lower COF value in vacuum and H₂, but a higher wear rate and COF in air, since the hydrogen bond in PEEK molecules hindered the formation of transfer films. Similarly, Li et al.[12] pointed out that compared with dry nitrogen, the COF and wear rate of a-C increased significantly in oxygen-containing environments, and they proposed that oxygen molecules might induce interfacial chemical reactions. Chen et al.[13] found that oxygen molecules would trigger the break of C-C bond, and erode the a-C shallow layer region, resulting in increased surface wear in O2 environment. For practical applications, a-C/PEEK components are often exposed to atmospheric environments, the existing oxygen

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Table 1

Deposition parameters of the Cr/a-C nano-composited coating.

Procedure	Ar flow	Power	Substrate DC bias	Time
	(sccm)	(W)	(V)	(min)
Etching Cr transition a-C interlayer	100 40 40	1500 1075 2000	600 600 600	30 30 420
Cr interlayer	40	340	600	420
a-C top layer	40	2000	600	225

molecules are closely related to the formation of transfer films and wear characteristics, deciding their durability and service performance. However, lack of in-situ analysis under different atmospheric environments and experimental analysis from the molecular or atomic scale, it is challenging to understand the underlying interfacial tribo-chemical reaction and wear mechanism of PEEK/a-C friction system, limiting their service life in practice.

In this work, nano-composited design was used for a-C coatings, due to their improved tribological properties [14,15]. To figure out the role of oxygen molecules, the tribological behavior and tribo-chemical reaction of the a-C/PEEK pair were investigated in ambient atmosphere (~ 21 vol% O₂), vacuum and O₂ environments. Most importantly, reactive molecular dynamics (RMD) simulation was conducted to simulate the in-situ friction process of PEEK/O₂/a-C system from atomic/molecular scale. This study reveals the interface tribological behavior of a-C/PEEK with various oxygen concentration, offering insightful implications for PEEK components used in high-tech engineering equipment.

2. Methods

2.1. Deposition of Cr/a-C nano-composited coating

The Cr/a-C nanocomposite coating was prepared by a home-made DC magnetron sputtering (DCMS) technique, utilizing equally dimensioned rectangular targets of high-purity graphite (99.99 wt%) and chromium (99.999 wt%), each sized at 380 mm× 100 mm× 7 mm. 17–4 stainless steel was selected as the substrate, since it was widely used in some offshore equipment. Before deposition, the substrates were ultrasonically cleaned in acetone and anhydrous ethanol for 10 min each, then mounted on a rotating holder positioned 12 cm from each target. After evacuating the chamber to 4×10^{-5} Torr, the substrates were

subjected to Ar^* ion etching via glow discharge at a DC pulsed bias of 300 V for 30 min to remove surface contaminants.

Thereafter, the buffer layer of 300 nm-thick Cr was deposited for 30 min to improve the adhesion strength of coating. Then, 200 V and 900 V voltages were applied to Cr and C targets respectively, and Cr/a-C nano-composited layers were prepared by slow rotation (0.15 rpm) of the holder under a DC pulsed substrate bias of 600 V for 7 h. In this process, the Ar gas flow rate was 40 sccm. Finally, the a-C top layer with a thickness of 150 nm was specially fabricated for 225 min to yield the excellent load bearing capacity. The total thickness of coating was 2.1 μ m approximately. Table 1 illustrates the specific parameters for cleaning process and coating deposition.

2.2. Characterization methods

A transmission electron microscope (TEM, Talos F200X, USA) was employed to examine coating cross-sections microstructures, with specimens prepared via FIB (Carl Zeiss Auriga, Germany). Surface morphologies of the wear track were observed using a scanning electron microscope (SEM, FEI Quanta FEG 250, USA). The wear scar of PEEK was characterized by a Zeiss optical microscope (Axio Imager 2, Germany). Chemical composition analysis and atomic bonding states of the coatings were characterized using an Axis UltraDLD X-ray photoelectron spectrometer (XPS, Kratos Analytical, Japan). When conducting depth profiling on PEEK, a total of 11 etches were performed, each lasting 100 s, with each etching depth being 10 nm.

The microstructure and atomic bond of the coatings before and after tribological tests were investigated by a confocal micro-Raman spectroscopy (Renishaw inVia Reflex, UK, 532 nm). The debris on the wear track was qualitatively analyzed by Microscopic Fourier transform infrared spectrometer (Micro-FTIR, Agilent Cary660 +620, USA). The coating's hardness and elastic modulus were measured using a G200 nanoindentation tester (MTS, USA) in continuous stiffness mode (CSM) with a Berkovich diamond indenter, applying a maximum indentation depth of 1800 nm. The adhesion strength between Cr/a-C nanocomposited coating and substrate were measured by the Revetest scratch test system (CSM) accompanied with an optical microscope and acoustic detector. The thermal failure process of PEEK in N₂ and O₂ environments was tested by thermogravimetric and infrared combined instrument(TG-IR, TGA 8000, USA).

The tribological tests were performed by a ball-on-disk vacuum tribometer (Anton Paar TRB3, Switzerland). The cavity pressure was pumped below 3×10^{-5} mbar for vacuum friction test. On this basis,



Fig. 1. Simulated models of a-C coating and PEEK.



Fig. 2. Cross-sectional TEM images of Cr/a-C coating at low magnification (a) and high magnification (b), the corresponding HRTEM (c) and SAED of cr layer (d).

oxygen was injected to keep the cavity pressure at 7 mbar to create an oxygen atmosphere. Under the rough assumption that the residual gas composition within the vacuum chamber mirrors atmospheric constituents (i.e., oxygen constitutes 21 % by volume), the partial pressure of oxygen under the specified vacuum condition is calculated to be approximately 6.3×10^{-6} mbar. This derivation adheres to Dalton's law of partial pressures, wherein the oxygen fraction scales linearly with the total system pressure.

The applied normal load was 5 N. According to the formula [16], the maximum contact stress was calculated to be 72.3 MPa. The linear speed and track's length were 2 cm/s and 5 mm, respectively, and the sliding time and distance were 120 min and 160 m. The counterpart was a 6 mm diameter PEEK ball. The ambient humidity of the laboratory atmosphere was ~52 %RH, and the ambient temperature was 25°C. After vacuuming, the humidity inside the cavity was less than 5 %RH. Furthermore, in order to explore the influence of humidity on the tribological performance of the a-C/PEEK pair, continuously dry air (10 sccm) was introduced into the cavity to stabilize the humidity of the cavity at 8 %RH.

After the tribological tests, a three-dimensional optical profiler (UP-Lambda, USA) was used to observe the morphology of wear track. The wear volume of PEEK balls V is approximated as the volume of the crown, and the formula is as follows [17]:

$$V = \frac{\pi}{3} \left(R - \sqrt{R^2 - r^2} \right)^2 (2R + \sqrt{R^2 + r^2})$$
(1)

Where R and r are the ball and wear scar radius.

2.3. Computational details

All RMD calculations in this study were performed using a large-scale atomic/molecular massive parallel simulator [18]. Fig. 1 illustrates the molecular dynamics model of the a-C/O₂/PEEK friction system. The

system consisted of a lower a-C coating, a middle O2 molecules, and an upper PEEK as frictional pairs. The initial a-C structure was created via an atom-by-atom deposition simulation [19]. The molecular formula of a single PEEK chain is C38H26O6, with 200 molecules used in the simulation. The material density was set to 1.3 g/cm^3 . The molecular structure of PEEK was constructed by implementing a random-filling algorithm within a predefined rectangular simulation box. Geometric optimization was performed iteratively throughout the filling process to minimize local energy barriers and ensure structural stability. For investigating the dependence of the friction on the oxygen concentration, the middle layer was composed of different numbers of oxygen molecules, i.e., 0, 100, 300, 500 and 800, which resulted in system sizes of $42.88 \times 40.358 \times 147.777$ Å³, $42.88 \times 40.358 \times 153.864$ Å³, $42.88 \times 40.358 \times 158.992$ ų, $42.88 \times 40.358 \times 163.579$ ų, and $42.88\times40.358\times170.908$ Å 3 respectively. In addition, each friction system shown in Fig. 1 had three layers, including fixed layer, thermostat layer, and free layer. The fixed layer was utilized to simulate an infinite system, while the NVE setting with the Berendsen thermostat maintained the thermostat layer at 300 K [20]. The free layer comprised the remaining a-C, O₂ and PEEK materials, which was incorporated to simulate the friction-induced structural evolution at the interface. The timestep was 0.25 fs, and periodic boundary conditions were applied in the x- and y-directions. The interactions among C-C, C-H, and H-H in the system were modeled using the ReaxFF potential developed by Tavazza et al.[18], a potential whose validity has been confirmed in prior investigations [21,22].

The simulation protocol consisted of three stages: First, a 2.5 ps geometry optimization at 300 K was performed. Following this, the system established contact by loading the PEEK upper layer against the a-C coating until reaching 5 GPa contact pressure (25 ps duration). The final stage involved sliding the PEEK's fixed layer at 100 m/s along the x-axis for 1250 ps. Notably, following previous studies [23–25], the applied



Fig. 3. TG and infrared curves of PEEK in N2 (a, c) and O2 (b, d) environments.

contact pressures significantly exceeded experimental values to enable atomic-scale investigation of interfacial friction behavior under different contact conditions.

3. Results and discussion

3.1. Mechanical and thermal failure performance

Fig. 2 shows the cross-sectional TEM images of Cr/a-C nanocomposited coating and the selected area electron diffraction (SAED) patterns of the Cr layer. The total thickness of the coating is about 2.1 μ m, of which the Cr transition layer is 300 nm, the modulation period of the Cr/a-C nano-composited intermediate layer is about 27 nm, and the top layer a-C is about 150 nm. The surface scanning energy spectrum shows that Cr and C were deposited alternately in the intermediate layer, as shown in Fig. 2(b, b-1, b-2). Through high-resolution TEM, it can be seen that the C layer is a typical amorphous structure, and the Cr layer is a nanocrystalline structure. The (110), (200) and (211) crystal faces of Cr are observed by SAED in the Cr layer, as shown in Fig. 2(d).

Nanoindentation was used to test the hardness and modulus values of Cr/a-C nano-composited coating, as shown in Fig. S1. With the increase of the pressing depth, its values approximate to the hardness and modulus of 17–4 stainless steel. The hardness and modulus at 1/10 of the coating thickness are 17.2 GPa and 264.8 GPa, respectively.



Fig. 4. COF-time curves (a) and wear volume of PEEK (b) under different conditions.



Fig. 5. The morphology of wear tracks on Cr/a-C coatings and wear scars on PEEK under different conditions (a) and the cross-sectional profile of the wear tracks (b).

According to the scratch track and acoustic signal curves, the adhesion strength of the coating on substrate is determined to be 12.1 N, as shown in Fig. S2.

The thermal failure process of PEEK in a high-oxygen environment was analyzed by TG-IR, as shown in Fig. 3. In an inert gas (N₂) environment, PEEK begins to lose weight at 542.8°C. At around 600°C, PEEK decomposes rapidly, and by 800°C, the weight loss is less than 50 %. The IR results show that at 608°C, PEEK still retains ether bonds and benzene ring (Fig. 3c). In O₂ environment, the PEEK begins to lose weight at 520.2°C. It decomposes rapidly at ~600°C, and the weight loss of PEEK reaches 100 % after reaching 700°C. After 600°C, PEEK has completely decomposed, as shown in Fig. 3(d). Obviously, in a high-oxygen environment, PEEK is more prone to thermal decomposition.

3.2. Tribological performance

Fig. 4 shows the tribological properties of Cr/a-C nano-composited coating against PEEK under different conditions. In the ambient atmosphere and vacuum environment, the COF values remain stable at 0.38 and 0.10 respectively. In oxygen environment, COF values is floated in 0.25–0.35. Fig. 3(b) shows the wear volume of PEEK under different conditions. The wear volumes in atmospheric, Vacuum and O₂ environment are 9.67, 6.10 and 10.20×10^{-3} mm³, respectively. Obviously, it had a more unstable COF value and higher wear of PEEK in O₂ and atmosphere, which indicates that oxygen plays an adverse effect on the friction process between PEEK and Cr/a-C coating. In addition, the wear volume difference of PEEK in the atmosphere and O₂ environment is not significant.

Fig. S3 shows the COF curves of the a-C/PEEK pair and the morphology of wear scar under the environments of 8 %RH and 52 % RH. Under the condition of lower humidity, the COF value rises to 0.40, and the average wear volume of PEEK reaches 11.20×10^{-3} mm³. This indicates that although oxygen in the atmosphere is not conducive to the

friction performance of the a-C/PEEK pair, a certain level of humidity can reduce friction and wear. The tribological behavior of a-C/PEEK pairs in the atmospheric environment is synergistically influenced by water molecules and oxygen molecules.

3.3. Investigation on the wear surface

Fig. 5(a) shows the morphology of wear tracks and wear scars under different conditions. Compared with vacuum, the wear of PEEK is more serious in ambient atmosphere and oxygen environment, which corresponds to Fig. 4(b). After 2 h test in vacuum, a large number of transfer materials appear on the wear track (as shown in Figs. S4 and S5). IR analysis from the transfer material exhibits the characteristic peaks of PEEK, such as ether bond and diphenyl ether, as shown in Fig. S5. It is indicated that PEEK transfer film is formed on the surface of the coating after sliding. Notably, all characteristic absorption peaks in the transfer film exhibit systematic redshifts compared to pristine PEEK. Specifically, the carbonyl group peak shifts from 1654.6 cm^{-1} to 1650.7 cm^{-1} , while the ketone peak demonstrates a redshift from 1311.3 cm^{-1} to 1305.5 cm^{-1} . The ether absorption undergoes a more pronounced displacement from 1245.7 cm^{-1} to 1220.7 cm^{-1} , and the diphenyl ether bond peak similarly shifts downward from 933.4 cm^{-1} to 927.6 cm^{-1} . This coordinated wavenumber migration pattern suggests significant molecular-level structural modifications within the transfer film. The peak intensities of carbonyl and ketone groups weaken, while those of ether and diphenyl ether bonds increase. These results indicate the occurrence of chemical reactions during the friction process [26].

Fig. 5(b) exhibits the cross-sectional profile of wear tracks by a threedimensional optical profiler. Under vacuum condition, a transfer film with uneven thickness is formed inside the wear track, approximately 300–800 nm. In the atmospheric and oxygen environment, the transfer film is almost not formed, but more abrasive debris is formed on both sides of the wear tracks. Under vacuum conditions, due to the



Fig. 6. Raman spectra (a) and fitted results (b) of the Cr/a-C nano-composited coating after sliding under different conditions.



Fig. 7. XPS spectra of c 1 s of Cr/a-C nano-composited coating after sliding in different environment.

lubricating effect of the transfer film, the a-C/PEEK pair has a relatively low COF value and wear volume of PEEK. However, under atmosphere and O_2 conditions, the wear resistance of PEEK mainly depends on the mechanical properties of the material itself, resulting in similar wear volumes of PEEK. In addition, Shallow furrows appeared on the surface of the coating, with a maximum depth of approximately 30 nm, indicating that the coating had undergone slight wear.

Raman spectroscopy was used to characterize the carbon bond structure of the Cr/a-C coatings before and after sliding, the results are shown in Fig. 6. The ratio of the area of G peak and D peak (I_D/I_G) and

the G peak position of the coating are significantly increased after sliding under different conditions, which indicates that the sp² cluster size and content in the wear tacks are increased [27,28]. The I_D/I_G and G peak position change more significantly after sliding in O_2 , increasing from 1.57 and 1541.69 cm⁻¹ to 2.92 and 1567.14 cm⁻¹, respectively. It is indicated that the graphitization degree of the coating is more significant in the O_2 environment. The full width at half maximum of the G peak (G_{FWHM}) is decreased after friction, which indicates that the distortion of C bond [29,30]. In addition, the Raman curve is obviously inclined after friction test in vacuum environment, which may be caused

Table 2

The area of C1s peaks after sliding in different environment.

Conditions	Concentration(%Area)				
	sp ²	sp ³	C-O	0-C=0	
As-deposited	38.83	43.76	17.41	-	
Vacuum	37.56	46.45	9.64	6.36	
Atmosphere	45.49	34.90	13.33	6.27	
O ₂	50.05	32.68	16.74	0.53	

by the fluorescence effect from the polymer, as shown in Fig. 6(a) [31].

The wear tacks were characterized by XPS, and the fine spectrum and peak areas of C 1 s are shown in Fig. 7 and Table 2. The sp²-C,sp³-C, C-O and O-C=O can be fitted with binding energies of 284.4, 285.3, 286.5 and 288.6 eV, respectively [32,33]. Compared with the deposited coating, the sp² content on wear tracks increase. In the O₂ environment, the sp² content of the coating increases most significantly, from 38.83 % to 50.05 %, which is corresponding to the Raman result. It is worth noting that O-C=O bonds are detected on the wear tacks after sliding 2 h in all environment, which may attribute to the adhesion of PEEK and oxidation reaction of coating surface. In addition, due to the formation of a large number of transfer films on the surface of the coating in

vacuum, the C 1 s may almost reflect the information of PEEK, resulting in an abnormal increase of sp³ content after sliding. A depth profiling of PEEK after sliding in O₂ was conducted using XPS, as shown in Fig. S6. With the increase of etching depth, the intensity of O 1 s decreases significantly, and the O content on the wear scar decreases from 14.32 % to 3.92 %. The XPS peaks of C 1 s at different depths almost overlap.

3.4. Dynamic analysis during friction process in O₂

The results above indicate that oxygen molecules play a crucial role in the tribo-chemical reactions occurring between the a-C coating and PEEK, leading to fluctuations in the COF value and contributing to the accelerated wear of PEEK. To investigate the underlying mechanisms at the atomic scale and gain a deeper understanding of oxygen's role at the interface, RMD simulations were further performed. The friction morphologies reveal that oxygen molecules progressively diffuse into the PEEK substrate as the sliding process continues, as shown in Fig. 8(a) and (b). Concurrently, the molecular chains of PEEK begin to break and interact with the incoming oxygen atoms. At the same time, under the simulated conditions, PEEK molecular chains experience simultaneous chain scission and extensive crosslinking reactions upon interaction. The



Fig. 8. Morphologies of PEEK/O₂/a-C system during friction in 100 O_2 molecules (a) and 800 O_2 molecules (b) separately; distribution of oxygen molecules along the z direction during friction process under different number of O_2 molecules (c).



Fig. 9. Structure and hybridization sites of PEEK molecular chain (a); coordination number contribution of oxygen molecules to different bonding sites of PEEK molecules (b).

fixed layer of upper PEEK maintains intact $C_{38}H_{26}O_6$ molecular structures post-loading. However, in the active region (encompassing both thermostatic and free layers), the original molecular architecture undergoes substantial modification through chain fragmentation and crosslinking processes, leading to the disruption of the pristine $C_{38}H_{26}O_6$ molecular configuration, which attributes to the characteristic cross-linking behavior of PEEK long-chain molecules.

The intrusion of oxygen atoms into the PEEK triggers the breaking of PEEK's molecular chains, a key factor in the material's reduced tribological performance. PEEK, a polymer known for its high structural integrity and excellent wear resistance, relies heavily on the stability and length of its molecular chains to maintain these properties. When oxygen molecules penetrate the PEEK inside, they initiate oxidative reactions that cleave the polymer chains. This chain scission weakens the overall material structure, resulting in a reduction of mechanical strength and an increased susceptibility to wear. As the molecular chains break, PEEK's abilities to resist deformation and abrasive wear are significantly diminished, making its more prone to material loss during sliding, which in turn leads to an increase in the COF.

The vertical distribution mappings of oxygen molecules during sliding are depicted in Fig. 8(c), where different colors reflect the difference in O_2 concentration, which further support the above observation. The increased oxygen concentration at the interface enhances the diffusion behavior of oxygen atoms, which in turn accelerates the degradation of PEEK's molecular structure. This accelerated diffusion and subsequent degradation explain the observed decline in PEEK's tribological performance under these conditions. This result corresponds to the results in Figs. 3 and S6. Unlike oxygen molecules, water molecules can hardly be adsorbed on the a-C surface or diffuse into the interior of PEEK, as shown in Fig. S7. This indicates that in a humid atmospheric environment, the frictional chemical reactions of oxygen on the interface may dominate.



Fig. 10. Morphologies of PEEK transfer film on a-C surfaces under different O2 contents.



Fig. 11. Coordination number contribution of oxygen molecules to a-C(a) and the number of bonds between oxygen atoms and intrinsic a-C (b).

Further investigation was conducted to examine the behavior of transfer film observed in macroscopic experiments, as illustrated in Fig. 9, where C3, C6, H8, and H9 represent different hybridization sites in PEEK molecules. With the increase of oxygen molecules, the contribution of various elements in PEEK molecules to the a-C coordination gradually decrease, indicating that the degree of bonding between PEEK and a-C reduces. Fig. 10 shows the formation process of PEEK transfer film on a-C coating, where the lower row shows the single atom morphology that only bonds with the surface a-C, and the upper row shows the result of iterative search for bonding. Under vacuum and low oxygen conditions, a substantial transfer film forms on the a-C surface.

However, as the oxygen concentration increases, the transfer film becomes less pronounced and may even disappear. This phenomenon can be attributed to the increased occupation of active sites on the a-C surface by oxygen atoms, which hinders the formation of an effective transfer film. Consequently, wear debris is likely to accumulate around the wear tracks, consistent with the observations shown in Fig. 5.

Different from PEEK, oxygen molecules do not invade the inside of the a-C coating, only chemically bond with the outermost a-C layer, as shown in Fig. 11(a). In addition, the further passivation effect of oxygen molecules on a-C is limited, especially at low oxygen content, as shown in Fig. 11(b). It is corresponded to the XPS result that the C-O bond do



Fig. 12. Wear mechanism diagram of a-C sliding against PEEK in oxygen environment.

not rise significantly after sliding in O_2 , as shown in Table 2.

3.5. Discussion

On the whole, a-C/PEEK exhibits the highly environment-dependent tribological behavior. In essence, different environments lead to different formation processes of transfer film, resulting in their different COF and wear. Specifically, under vacuum condition, a large number of PEEK transfer films attach to the wear tracks (In Fig. 4), because the C atoms of PEEK are easy to bond with C atoms on the a-C coating (In Fig. 9). The formation of transfer film significantly decreases the COF value and the wear of PEEK. In the oxygen environment, oxygen molecules penetrate into the PEEK interior, while the molecular chain of PEEK breaks and bonds with the O atom, as shown in Figs. 7 and 8(a). With the increase of oxygen content, the erosion effect of O₂ on PEEK reaches saturation, and part of O₂ can bond with a-C or adsorb on the coating surface (In Fig. 9), which makes the transfer film almost impossible to form and a large number of wear debris are formed on both sides of the wear tracks (In Fig. 4), resulting in the fluctuating COF values and higher wear volume of PEEK (In Fig. 3). In atmospheric environment, under the combined effect of oxygen promoting the breakage of PEEK molecular chains and the adsorption of water molecules or other gases, a stable PEEK transfer film cannot be formed on the a-C coating surface either, resulting in a higher COF value of the system and the wear of PEEK similar to that in the O₂ environment. In addition, when the oxygen content is relatively low (100 oxygen molecules in Figs. 9 and 10), there are still a large number of transfer films on the a-C surface, which indicates that there is a boundary of oxygen concentration between the breakage of PEEK molecules and hindering the formation of PEEK transfer films. The wear mechanism of a-C sliding against PEEK in oxygen environment as shown in Fig. 12.

4. Conclusions

In this work, interfacial tribological behaviors of a-C/PEEK were compared under vacuum, ambient atmosphere and oxygen environment. Both comprehensive experimental and atomic-scale RMD simulation were carried out to reveal atmosphere-related interfacial tribochemical reaction and wear mechanism, the following conclusions are obtained.

In the ambient atmosphere, the COF values remain stable at 0.38. Under vacuum conditions, the a-C/PEEK pair has the lowest COF. However, in oxygen, the COF value is still unstable after sliding 2 h, and the wear volume of PEEK is the highest.

In the vacuum environment, C-C bonding occurs between a-C and PEEK, which promotes the formation of transfer film from PEEK material, causing the decreased COF value and wear of PEEK to some extent. In an oxygen-containing environment, oxygen molecules diffuse into PEEK and break its molecular chains, hindering the formation of transfer film. The erosion of oxygen molecules and the non-formation of transfer film result in various interfacial tribo-chemical reaction and wear mechanism for a-C/PEEK pair.

CRediT authorship contribution statement

Peiling Ke: Writing – review & editing, Supervision, Funding acquisition. **Aiying Wang:** Writing – review & editing, Funding acquisition. **Naizhou Du:** Methodology, Investigation. **Hao Li:** Methodology, Investigation. **Xiaohui Zhou:** Writing – original draft, Validation, Methodology, Investigation. **Peng Guo:** Writing – review & editing, Supervision, Methodology. **Xiaowei Li:** Writing – review & editing, Supervision, Methodology. **Rende Chen:** Methodology, Investigation, Funding acquisition. **Kwang-Ryeol Lee:** Supervision, Methodology, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.triboint.2025.110840.

Data availability

Data will be made available on request.

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