

Oxygen-induced frictional evolution and saturation mechanisms in hydrogenated a-C/PEEK interfaces

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Abstract: Reactive molecular dynamics simulations were performed to investigate the tribological behavior of hydrogenated a-C/PEEK interfaces under different oxygen concentrations. The results show that the friction force increases with oxygen concentration and saturates beyond ~300 O₂ molecules. This behavior arises from two coupled mechanisms. First, sliding shear drives oxygen diffusion into the PEEK structure. At high concentrations, oxygen penetration and subsequent saturation diminish the intrinsic lubricity of PEEK. Second, excess oxygen accumulates at the interface as an oxygen-rich layer, which interacts with surface hydrogen on a-C and further enhances interfacial adhesion. In addition, dissociated O atoms preferentially bond with aromatic carbons, ether oxygens, and surface hydrogens of PEEK, disrupting π -conjugation and introducing polar functional groups that increase adhesion. Surface hydrogen, instead of acting as an inert barrier, reduces lubricity through chemical interactions at both low and high oxygen concentrations. These findings provide mechanistic insights into the oxygen-induced increase and eventual stabilization of friction force in a-C/PEEK systems.

Keywords: polyether ether ketone; amorphous carbon; oxygen concentration; tribological mechanism; reactive molecular dynamics

1. Introduction

Polyether ether ketone (PEEK) is a high-performance thermoplastic polymer that has found widespread application in aerospace, biomedical, and precision mechanical engineering due to its outstanding mechanical strength, thermal stability, chemical resistance, and intrinsic self-lubricating properties [1, 2]. In particular, PEEK has emerged as a promising candidate for solid lubrication systems, where its low friction coefficient and excellent wear resistance render it an ideal engineering plastic [3, 4]. However, the structural stability of PEEK becomes a significant concern under long-term sliding conditions. Exposure to elevated temperatures and sustained shear forces during friction can induce the scission, crosslinking, or structural rearrangement of molecular chain, ultimately leading to a decline in lubrication efficiency and tribological performance [5, 6].

To enhance the tribological performance of PEEK under extreme operating conditions, amorphous carbon (a-C) films have been widely employed as protective counterface coatings [7-13]. Owing to their high hardness, chemical inertness, and excellent wear resistance, a-C films can effectively mitigate the wear of polymeric counterparts during sliding [14]. However, the a-C surface typically contains a significant number of unsaturated dangling bonds, which are highly reactive toward

environmental species and may compromise the interfacial stability during the friction process ^[15, 16]. Surface hydrogenation has been proposed as an effective strategy to partially passivate these dangling bonds ^[17, 18]. This surface modification not only reduces the chemical reactivity of the a-C surface but also preserves its intrinsic mechanical properties.

Although hydrogenated a-C/PEEK systems demonstrate excellent tribological performance under inert atmospheric conditions, their tribological behavior and the underlying mechanistic insights in oxygen-rich environments remain insufficiently elucidated ^[19]. For instance, Zhou et al.^[20] conducted a systematic investigation into the tribological properties of a-C/PEEK systems under oxygen, air, and vacuum environments. Their findings revealed that the optimal tribological performance was achieved under vacuum conditions, whereas both the friction coefficient and wear rate increased significantly in the presence of oxygen. This observed degradation in tribological performance was primarily ascribed to oxygen-induced cleavage of PEEK molecular chains, coupled with the potential interfacial interaction between O₂ molecules and the a-C surface under high oxygen concentration conditions. These factors collectively impede stable transfer film formation, exacerbating friction and wear. Similarly, Johansson et al.^[21] reported that CF-PEEK exhibited substantially higher wear rates and friction coefficients when subjected to tribological tests under high oxygen concentrations and laboratory air environments. As a highly reactive species, oxygen not only dissociates at the sliding interface to form new chemical bonds but also modulates the conformational flexibility and self-lubricating characteristics of

PEEK molecular chains through intermolecular interactions [20, 22]. These synergistic effects ultimately give rise to complex physicochemical responses at the a-C/PEEK interface. However, the oxygen concentration-dependent mechanisms governing the tribological behavior of PEEK/a-C interfaces remain insufficiently understood at the atomic scale, limiting controllable lubrication in oxygen-containing or extreme service environments.

In this study, reactive molecular dynamics simulations were employed to investigate the tribological behavior of hydrogenated a-C/PEEK interfaces under varying oxygen concentrations. The simulations systematically characterized the evolution of interfacial structures, frictional responses, oxygen diffusion pathways, and molecular-scale interactions. The results reveal the critical role of oxygen in regulating interfacial friction through both physical and chemical mechanisms, thereby providing theoretical guidance for the design and optimization of polymer-coating systems operating in reactive gaseous environments.

2. Computational details

All reactive molecular dynamics simulations were performed using LAMMPS [23]. The friction model (**Fig. 1**) consisted of a hydrogenated a-C film as the lower counterpart and PEEK as the upper sliding pair. A hydrogen-free a-C (6874 C atoms) was first generated by atom-by-atom deposition [24], followed by H₂ exposure and annealing at 600 K to obtain hydrogen-terminated surfaces [17, 25]. The PEEK structure contained 200 chains of C₃₈H₂₆O₆ with a density of 1.3 g/cm³.

To investigate the effect of oxygen concentration, 0~800 O₂ molecules were

introduced into the interfacial layer, corresponding to simulation cells of $42.88 \times 40.358 \times 147.777\text{--}174.561 \text{ \AA}^3$. Each system was divided into a fixed layer (bulk constraint), a thermostat layer (300 K, NVE with Berendsen thermostat), and a free layer (a-C, O₂, PEEK) for capturing interfacial evolution (**Supporting Information Fig. S1**). Simulations were carried out with a timestep of 0.25 fs under periodic boundary conditions in the x – y directions. The ReaxFF potential developed by Tavazza et al. [26] has been extensively validated in our previous studies for simulating complex interfacial reactions involving amorphous carbon, hydrogenated surfaces, polymers, and oxygen-containing species [27–29]. In particular, it has demonstrated good capability in capturing bond breaking and formation processes, structural evolution under shear, and tribochemical responses at carbon-based interfaces.

During the friction process, the friction system was first equilibrated at 300 K for 2.5 ps. Subsequently, the system established contact by loading the PEEK upper layer against the a-C film until reaching 5 GPa contact pressure (25 ps duration). Sliding was then initiated by imposing a constant velocity of 100 m/s along the x -direction on the fixed layer of the upper PEEK counterpart, and the process was simulated for 1250 ps. The contact pressure of 5 GPa was selected, as it is an established value for atomic-scale investigations of friction in a-C films [30, 31]. A high sliding velocity (100 m/s) was used to achieve sufficient sliding distance, sample interfacial configurations, and observe oxygen-related saturation within the practical simulation timeframe. Effective thermostat control (**Fig. S4**) maintained the system temperature near 300 K, mitigating non-physical heating concerns. Given that the key mechanisms identified—such as

shear-activated oxygen diffusion and interfacial chemical bonding—are governed by local chemical environments and reach a steady state, the qualitative trends revealed here are anticipated to hold under slower, experimentally relevant sliding conditions.

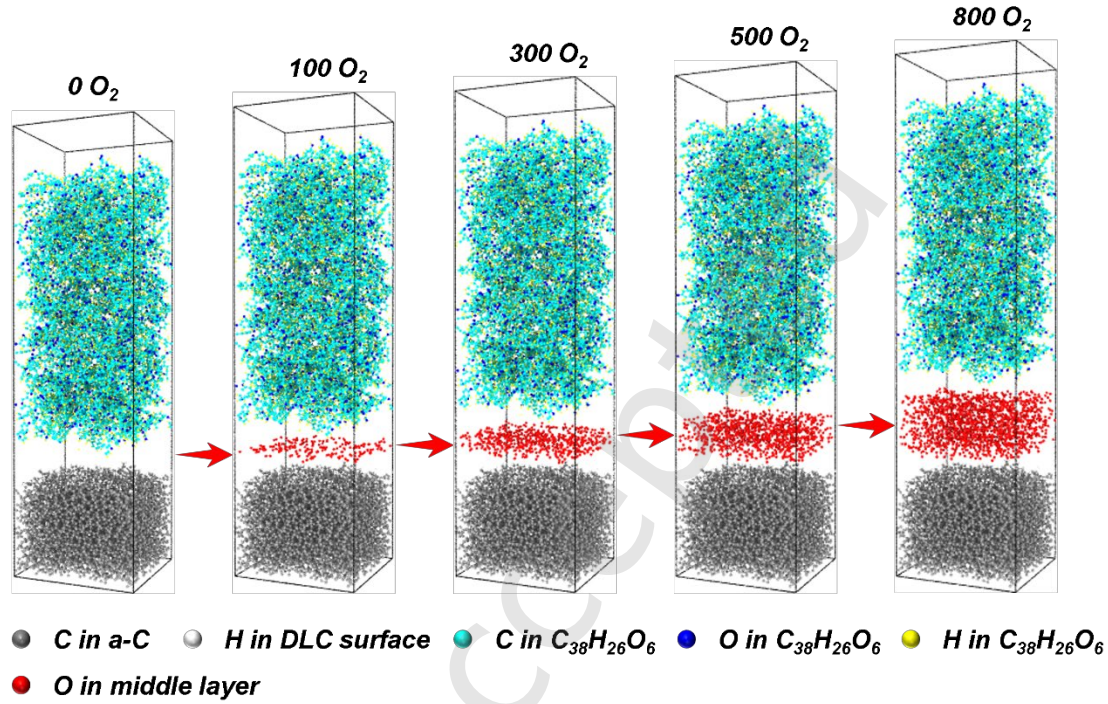


Fig. 1. Friction simulation model of surface-hydrogenated a-C and PEEK with varying oxygen concentrations at the interface.

3. Results and discussion

The friction force of the system was defined by calculating the total force exerted on the fixed-layer atoms along the sliding direction. The temporal evolution of the friction force in the a-C/O₂/PEEK systems under different oxygen concentrations is shown in **Fig. 2a**. Note that the friction force curves of all systems show a relatively stable behavior with only minor fluctuations. These slight oscillations can be attributed to dynamic structural evolution events within PEEK molecules during the friction process, such as intermolecular cross-linking and chain scission ^[32]. Furthermore, no obvious running-in stage was observed, which is primarily ascribed to the low applied contact

pressure (5 GPa). This observation is consistent with the results reported in previous studies under similar load conditions ^[33, 34], further validating the reliability of the current simulation setup.

To quantify the effect of oxygen concentration, friction forces from the final 300 ps of steady-state sliding were averaged. **Fig. 2b** gives the variation of the average friction force with oxygen concentration. The friction force generally increases with oxygen concentration. However, when the number of O₂ molecules exceeds 300, the growth rate slows down and eventually shows a saturation effect. This threshold is specific to the present simulation cell and corresponds to an areal oxygen density of approximately 17.3 O₂ molecules nm⁻². This saturation suggests a transition in the interfacial state, driven by the combined effects of reactive site occupancy on the PEEK surface and the dynamic equilibrium of an interfacial oxygen-rich layer, which will be analyzed in detail in the following sections. This observed correlation between oxygen concentration and friction force aligns with the experimental findings of Johansson et al. ^[16], reporting that the presence of oxygen and moisture significantly alters the tribological response of PEEK-based composites by modifying the interfacial chemistry. This nonlinear behavior indicates that oxygen incorporation does not merely induce interfacial passivation, particularly when the a-C surface is already partially hydrogenated ^[18]. Instead, the changes in tribological performance mainly originate from the complex interfacial interaction mechanisms between oxygen species and PEEK molecules, which warrants further in-depth investigation into the underlying atomic-scale processes. Importantly, the “saturation” discussed here refers specifically

to the frictional response, rather than to oxygen uptake, oxygen diffusion, or the overall interfacial chemical state. Operationally, it denotes the regime in which further increasing the O_2 concentration produces only a limited additional increase in the steady-state friction force. This occurs because the dominant friction-controlling reactive sites on PEEK and near the sliding interface become largely occupied, so additional oxygen species contribute less efficiently to new friction-relevant bond formation. Therefore, although the diffusion coefficient and the fraction of intact O_2 molecules continue to increase with oxygen concentration (**Figs. 3b and 6b**), the interfacial contributions governing friction approach saturation.

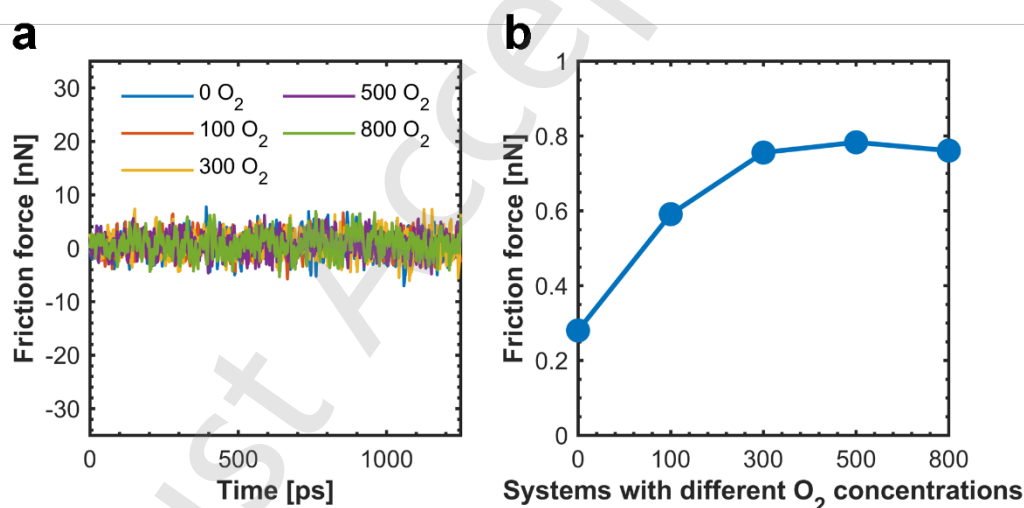


Fig. 2. (a) Temporal evolution of the friction force as a function of simulation time. (b) Dependence of the steady-state friction force on the oxygen concentration.

To elucidate interfacial interactions among a-C, O_2 , and PEEK and the associated friction mechanisms, **Fig. 3a** shows a comparative analysis of the morphology before and after sliding. The system containing 300 O_2 molecules is used as a representative case. Oxygen have already begun to diffuse into the PEEK matrix during the relaxation stage ^[35]. After sliding of 1250 ps, oxygen further permeates into the polymer interior. This diffusion is primarily attributed to the loosely packed morphology of PEEK, which

provides free volume and transient voids that serve as effective diffusion channels for oxygen. Additionally, local thermal effects and shear stresses generated during sliding further promote oxygen diffusion, facilitating penetration of the polymer network. Another notable structural evolution is the spontaneous cross-linking of PEEK chain segments, which appears as early as the relaxation stage (**Supporting Information Fig. S2**). Initially, PEEK exists as discrete chains ($C_{38}H_{26}O_6$). Interchain cross-linking gradually produces a denser, network-like macromolecular structure during relaxation. This phenomenon reflects the intrinsic reactivity of PEEK and can play a crucial role in its subsequent frictional response.

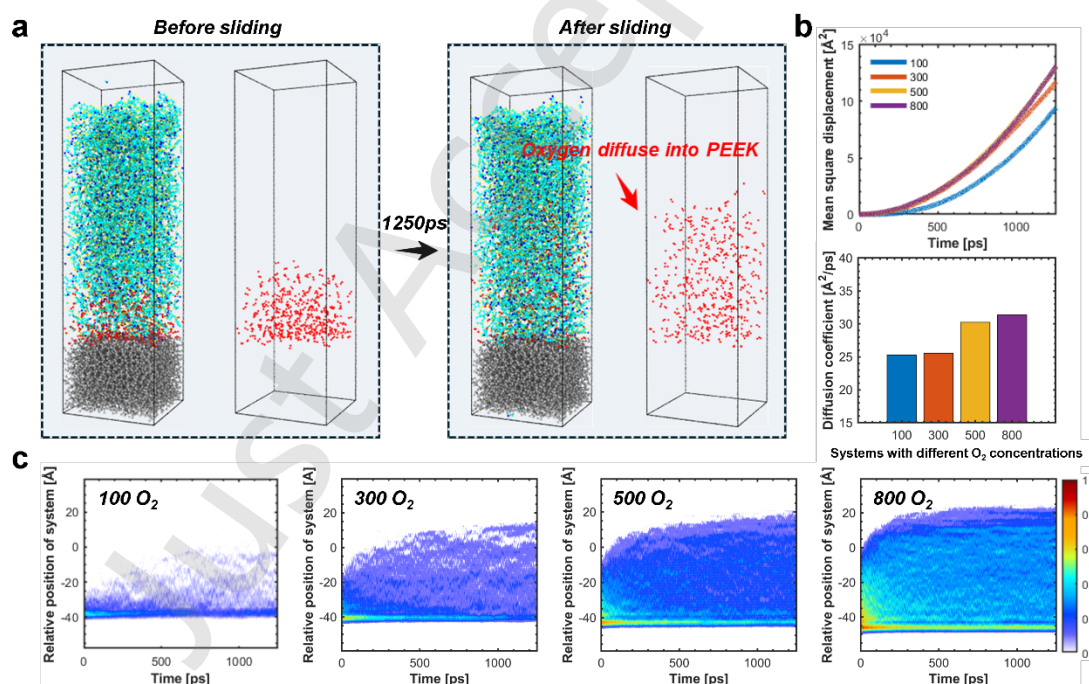


Fig. 3. (a) Structural morphology of the system before and after sliding at an oxygen concentration of 300 molecules. (b) Mean square displacement and corresponding diffusion coefficient of O_2 molecules. (c) Density distribution of O_2 molecules during the sliding process for different systems.

Fig. 3b shows the temporal evolution of the mean square displacement (MSD) of O_2 molecules at different concentrations. The data values from the final 300 ps are fitted from the MSD curves to extract the corresponding diffusion coefficients. It can be

observed that as the oxygen concentration increases, the rising rate of the MSD curves accelerates. The diffusion coefficient also increases accordingly, indicating that O₂ molecules exhibit higher mobility and fluidity under oxygen-rich conditions. Furthermore, **Fig. 3c** depicts the density distribution of O₂ molecules during the sliding process. The results show that O₂ molecules at different concentrations can diffuse into the deeper regions of PEEK. Their distribution is mainly concentrated in the central region of the PEEK structure. The absence of a pronounced gradient along the *z*-direction, despite a slight concentration increase near the interface, demonstrates that oxygen permeation extends beyond the immediate friction interface into the PEEK matrix.

To further investigate the diffusion behavior of O₂ molecules during sliding, **Fig. 4** displays the displacements of O atoms in systems with different oxygen concentrations (100, 300, 500, and 800 O₂) during the final 300 ps of the simulation. The displacement magnitudes are color-coded from blue (low displacement) to red (high displacement), directly illustrating the mobility range of oxygen species. To better understand the directional characteristics of oxygen diffusion, the atomic displacements are decomposed into the *x*, *y*, and *z* components (**Supporting Information Fig. S3**). The results reveal that the displacement contribution along the *x*-direction is dominant, highlighting the crucial role of the applied shear force in driving oxygen diffusion. By contrast, the distributions in the *y*- and *z*-directions approximate normal distributions centered near zero, suggesting that O₂ molecules in these directions remain largely localized without significant migration. This indicates that part of the oxygen

population becomes trapped within the PEEK matrix during sliding, likely due to chemical bonding or local physical confinement, while others primarily migrate along the sliding direction. Notably, the displacements of O₂ molecules in the interfacial region approach zero under high oxygen concentrations, particularly in the 500 and 800 oxygen systems. This suggests the formation of an interfacial “oxygen-rich layer”, supported by the elevated oxygen concentration observed at the interface in **Fig. 3**. In this scenario, a fraction of O₂ molecules fails to fully diffuse into the polymer interior and instead accumulates near the sliding interface, forming a high-density oxygen distribution zone. Such an oxygen-rich layer may result from molecular adsorption or atomic bonding, which enhances interfacial polarity and strengthens intermolecular interactions, thereby increasing the adhesion between the two sliding counterparts. The emergence of this structural feature helps explain the continuous increase and subsequent saturation of the friction force in systems with high oxygen concentrations.

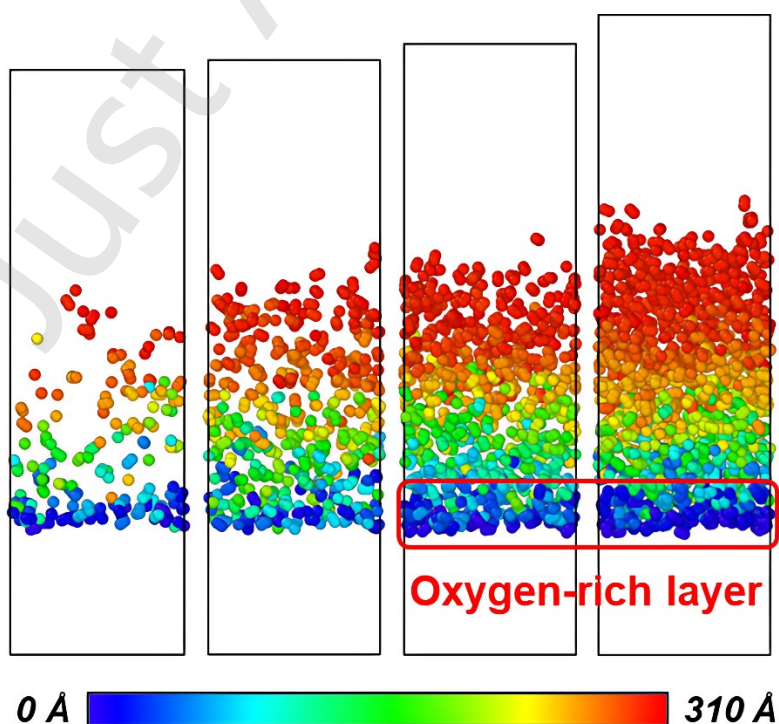


Fig. 4. Displacement of O atoms during the final 300 ps of the sliding process.

Before analyzing the specific role of oxygen in interfacial chemical reactions, it is essential to clarify the intrinsic cross-linking behavior of PEEK molecules during friction. After a brief relaxation stage, initially discrete molecular chains spontaneously cross-link to form a macromolecular structure. The PEEK counterpart is mainly composed of these cross-linked macromolecules, accompanied by a smaller fraction of oligomers generated through chain scission or secondary cross-linking reactions during sliding. As shown in **Fig. 5a**, the total number of $C_{38}H_{26}O_6$ PEEK molecules gradually decreases with sliding time in all systems, reflecting the continuous incorporation of small molecules into the growing cross-linked network. This phenomenon highlights the internal reactions of PEEK under shear loading, where friction-induced activation further facilitates chain recombination and growth. Moreover, unsaturated molecular structures produced by chain scission can chemically react with diffusing O atoms at the interface, generating new cross-linking sites and promoting further network evolution.

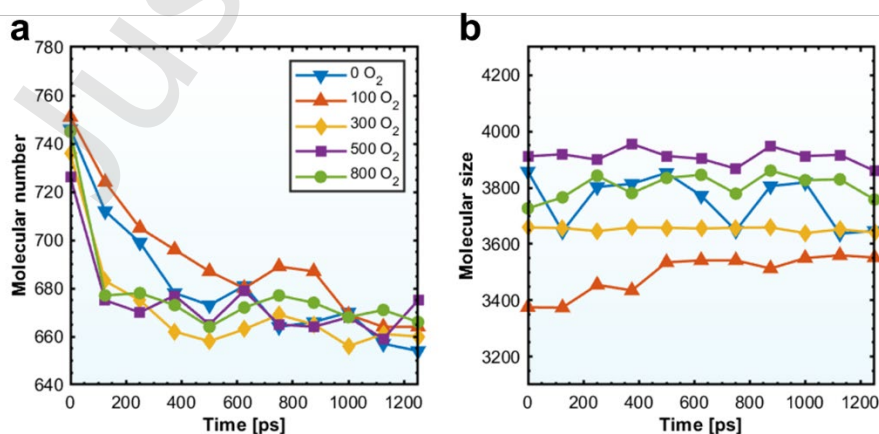


Fig. 5. (a) Evolution of the number of PEEK molecular species in different systems as a function of sliding time. (b) Number of atoms incorporated into spontaneously formed cross-linked PEEK chains.

Fig. 5b compares the variation in the number of atoms contained within the largest cross-linked chain across different oxygen concentrations. The results reveal that when the number of O₂ molecules exceeds ~300, the atomic count of the largest cross-linked chain remains essentially stable throughout sliding. This finding indicates that oxygen diffusion at higher concentrations provides effective terminal passivation and suppresses further chain scission. In contrast, in systems with lower oxygen concentrations, this stabilization trend only emerges in the later stages of sliding, suggesting that insufficient oxygen limits its passivating and protective effects. Notably, in oxygen-free system, pronounced fluctuations are observed, characterized by repeated decreases and recoveries in the atomic count of the largest cross-linked chain. This behavior can be attributed to alternating shear-induced scission and re-cross-linking events, while the absence of oxygen passivation renders the chain structures more susceptible to cyclic rupture and reorganization.

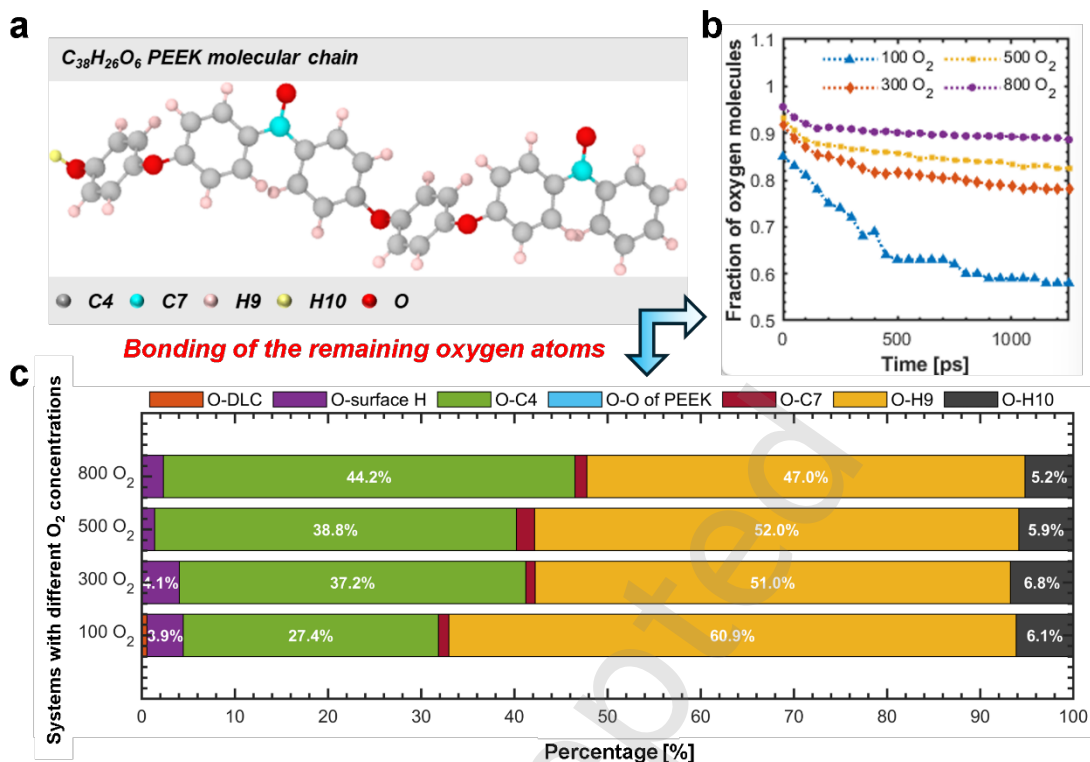


Fig. 6. (a) C₃₈H₂₆O₆ PEEK molecular chain with specific atomic sites labeled by color: grey (C4) for aromatic carbons, cyan (C7) for carbons bonded to ether oxygen, pink (H9) for hydrogen atoms on the phenyl rings, and yellow (H10) for terminal hydrogen atoms bonded to oxygen. (b) Fraction of intact O₂ molecules at the sliding interface. (c) Fraction of O atoms contributing to the coordination with other atomic species.

To systematically elucidate the interfacial interaction mechanisms among O₂ molecules, the PEEK structure, and a-C, key sites of a single C₃₈H₂₆O₆ PEEK chain are first labeled, as shown in **Fig. 6a**. These include the C4 and C7 carbon atoms in the aromatic ring, the oxygen atom in the ether linkage (O of PEEK), and hydrogen atoms located at different site (H9, H10). Some O₂ molecules that diffuse into the interface dissociate, and the resulting O atoms could form chemical bonds with the reactive sites of PEEK chains during sliding.

Fig. 6b illustrates the temporal evolution of the fraction of intact O₂ molecules in systems with different oxygen concentrations. The results show that this fraction increases with rising oxygen concentration, indicating that bonding sites at the interface

become saturated under oxygen-rich conditions. Consequently, the excess O₂ molecules preferentially exist in a physically adsorbed state inside the PEEK structure or at the PEEK surface instead of undergoing dissociation. This interpretation also reconciles the apparent difference between the continued evolution of intact O₂ molecules and the saturation of friction force. The increasing fraction of intact O₂ molecules at high concentration indicates that not all added O₂ molecules dissociate or form new friction-relevant bonds. Once the dominant reactive sites on PEEK are occupied, additional oxygen species are more likely to remain molecular, become physically trapped, or participate in secondary interactions.

Fig. 6c further analyzes the bonding types and site distributions of dissociated O atoms. O atoms primarily bond with C4 in the aromatic ring, with H9, and with the ether linkage along the PEEK chain. The formation of O–C4, O–H9, and O–O(PEEK) bonds disrupts the π -conjugated system of the aromatic ring, weakening the intrinsic lubricity of PEEK. At the same time, these reactions introduce polar functional groups at the interface (e.g., C–O, C=O, O–H), thus strengthening interfacial adhesion and increasing the friction force [20, 36, 37]. This trend becomes more pronounced at high oxygen concentrations, where the higher availability of oxygen promotes their increased participation in bonding. Similarly, Zhang et al. [27] demonstrated that tribochemistry facilitated by functional fillers can significantly modulate the friction performance of PEEK composites, suggesting that managing interfacial reactive sites is key to controlling the friction of polymer-based systems. In addition, these reactions can enhance the physical interactions between the PEEK structure and the penetrating

O₂ molecules, thereby restricting the flexibility of the PEEK chains, with this flexibility being beneficial for lubrication, as in aromatic rings. In low-oxygen systems (<300 O₂), the chemical reactivity of O₂ molecules is more evident. On one hand, dissociated O atoms bind to active sites on aromatic rings and ether linkages of PEEK chains. On the other hand, they react with hydrogen atoms used to passivate the a-C surface. These reactions can lead to the re-exposure of previously passivated a-C sites or, conversely, to the passivation of the a-C surface by O atoms. In the 100 O₂ system, direct bonding between oxygen and the a-C surface is even observed, further confirming the potential passivating effect of oxygen. Therefore, there exists a competitive effect between oxygen bonds and interface passivation at the frictional interface under low oxygen concentration.

The atomic-scale insights obtained from our RMD simulations provide a mechanistic foundation for interpreting experimental observations, particularly those from X-ray photoelectron spectroscopy (XPS) analyses of tribo-oxidized PEEK and a-C interfaces. The formation of O–C4, O–O(PEEK), and O–H bonds, as identified in our simulations (Fig. 6c), corresponds directly to the emergence of C–O, C=O, and O–H functional groups commonly detected in XPS studies of worn PEEK surfaces and transfer films [38, 39]. More specifically, O–C4 bonding indicates oxidation of aromatic carbon sites in PEEK and would contribute to enhanced C–O/C=O components in the C 1s spectrum, whereas O–O(PEEK) and O–H motifs are consistent with oxygenated-carbon and hydroxyl-related contributions in the C 1s and O 1s spectra. Thus, the simulations suggest an increase in the relative intensity of oxygen-containing XPS components with

oxygen concentration. For instance, experimental work by Zhou et al. [38] reported increased intensities of C–O and C=O peaks in XPS spectra after sliding tests of a-C/PEEK pairs under oxygen-rich conditions, attributing these changes to interfacial oxidation. Our simulations confirm that such oxidation is driven by shear-activated oxygen dissociation and subsequent bonding with specific reactive sites on PEEK chains, notably aromatic carbons and ether linkages. The introduction of these polar groups disrupts the π -conjugation of PEEK's aromatic rings and enhances interfacial polarity, thereby rationalizing the experimentally observed increase in friction and adhesion. In addition, the stable temperature profile (**Supporting Information Fig. S4**) further supports that the observed oxygen diffusion and chemical bonding are shear-driven rather than thermally activated.

To verify the influence of oxygen–PEEK physical interactions on the overall structural response under different oxygen concentrations, **Fig. 7** presents the stress distributions of PEEK and oxygen during sliding. With increasing oxygen concentration, the stress distribution in PEEK shifts from an initial weak compressive stress to tensile stress, whereas the stress distribution of O atoms consistently remains compressive stress. At low oxygen concentrations, only a limited number of O atoms diffuse into the interface (**Fig. 4**). In this case, the PEEK chains can buffer the external shear load through local orientation and compressive deformation, resulting in a slightly compressive overall stress state. However, as the oxygen concentration increases, many O₂ molecules gradually dissociate and chemically bond with reactive carbon and hydrogen sites in the PEEK chains, forming oxygen-containing bonds such as C–O,

C=O, and O–C–O (**Fig. 6**). These newly formed bonds increase the crystallinity and rigidity of the PEEK segments. More importantly, the excess non-dissociated O₂ molecules establish physical interactions with the PEEK structure, significantly reducing its flexibility. The polymer chains can no longer effectively dissipate energy through conformational adjustments, leading to a transition of the overall PEEK stress distribution from compression to tension during the sliding process.

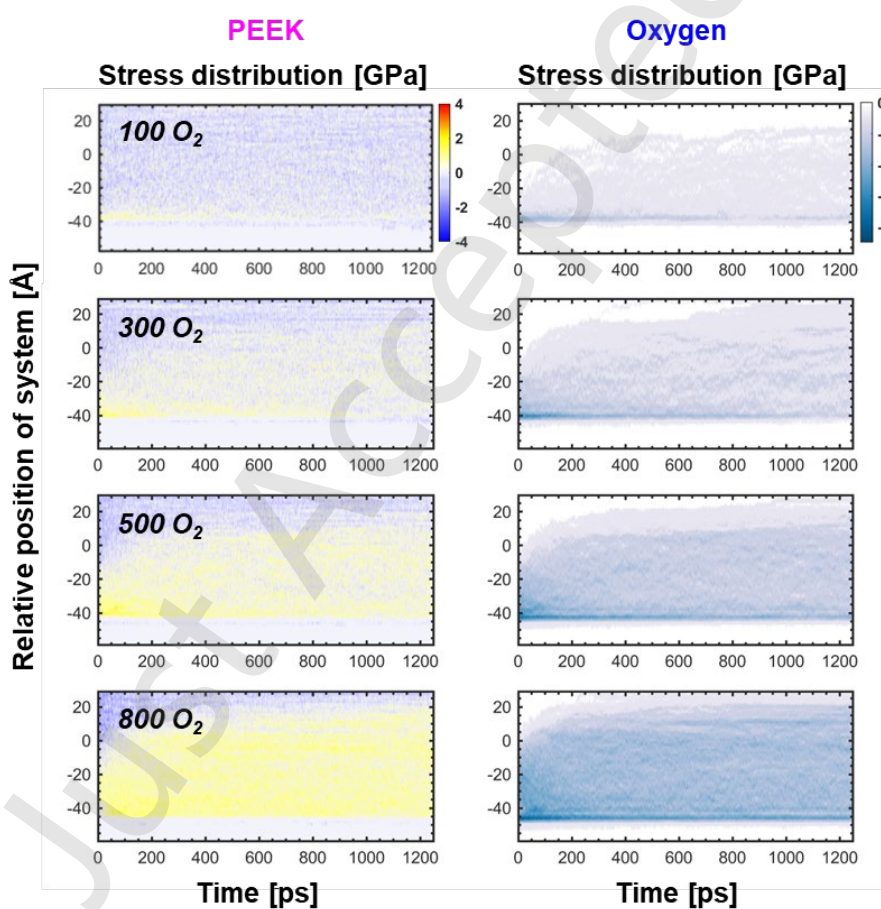


Fig. 7. Stress distribution of PEEK and oxygen during the sliding process.

In contrast, the stress distribution of oxygen consistently exhibits compression throughout the sliding process. This is because oxygen primarily resides in embedded or interstitial configurations, where they are subjected to dual compression from both the a-C surface and the PEEK chains. Even when chemical bonding occurs, most O

atoms remain confined within these compressed local environments (**Fig. 4**), preventing the development of tensile stress.

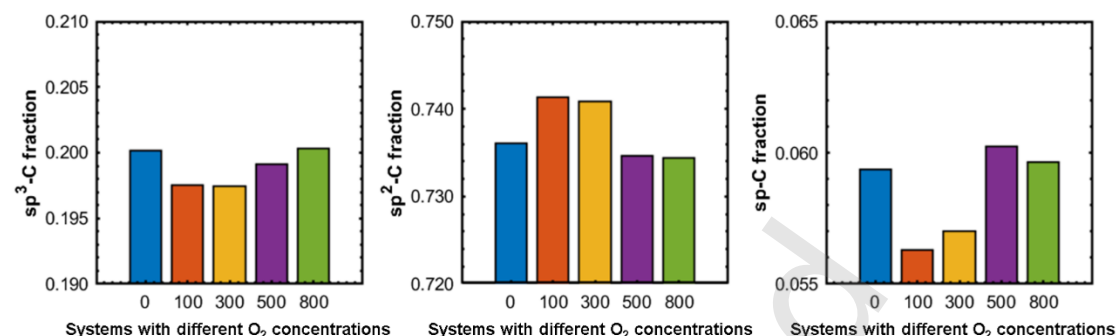


Fig. 8. Hybridized structure of a-C films in systems with different oxygen concentrations.

A detailed analysis of the interactions between oxygen and PEEK and the bonding contributions of oxygen to a-C is presented in the above discussion. These bonding effects are reflected in the hybridization evolution of a-C during sliding, which has a critical influence on its tribological performance. **Fig. 8** shows the final fractions of sp³, sp², and sp carbon atoms at the interface at the end of the sliding process under different oxygen concentrations. Since the friction curves for all cases reached a stable steady-state toward the end of the simulation, these values effectively represent the hybridization structure under the respective oxidative conditions. Combined with the hybridization evolution shown in **Supporting Information Fig. S5**, it can be observed that the sp³-C fraction exhibits only slight variation among the systems. This indicates that the internal skeleton of a-C remains relatively stable under the friction conditions employed in this study. This stability is attributed to the relatively low contact pressure (5 GPa), which avoids deep structural reconstruction, and to the localization of oxygen/PEEK interactions at the interface. These interactions are dominated by

noncovalent intermolecular forces and do not significantly disrupt the subsurface sp^3 -dominated regions.

In contrast, the variations in sp^2 -C and sp -C are more representative. In particular, in the low- and medium-oxygen systems (100 and 300 O_2), the sp -C fraction decreases markedly, while sp^2 -C increases significantly, suggesting an active sp – sp^2 hybridization transition. This process can originate from two mechanisms: (i) unsaturated fragments generated by chain scission in PEEK migrate to the a-C surface and participate in bonding reactions, and (ii) O_2 molecules at low and medium concentrations more readily dissociate and react with unsaturated sp -hybridized carbon atoms at the a-C surface, forming oxygen-containing functional groups such as C–O and C=O. These reactions convert sp -C states into the more stable sp^2 -C configuration, thus passivating interfacial sites. By contrast, in the high-oxygen systems (500 and 800 O_2), the fractions of sp^2 and sp change only slightly. This reflects a state of interfacial chemical equilibrium under oxygen-rich but site-saturated conditions, characterized mainly by irregular sp^2 – sp^3 interconversion at the a-C surface.

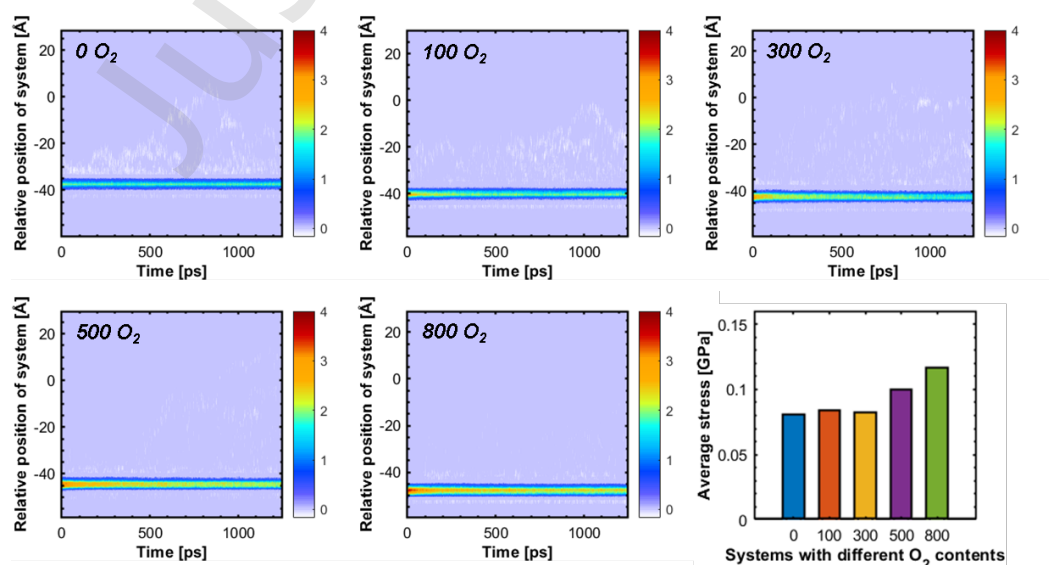


Fig. 9. Stress distribution of hydrogen atoms on a-C surface during the sliding process and average stress of hydrogen atoms at the end of the sliding.

In addition, the passivating effect of surface hydrogen plays a crucial role in regulating the frictional interface, as shown in **Fig. 9**. As the oxygen concentration increases, the tensile stress of surface hydrogen atoms increases markedly, with the 500 O₂ and 800 O₂ systems exhibiting significantly higher local stress peaks compared with the low-oxygen cases. This suggests that some O₂ molecules remain trapped in the interfacial region, where they form an oxygen-rich layer (**Fig. 4**) that strengthens interactions with the PEEK structure. As a result, the tensile stress on surface hydrogen atoms becomes higher under oxygen-rich conditions. At the same time, certain O atoms may directly react with surface hydrogen, weakening the stability of existing C–H bonds and even inducing hydrogen migration or desorption. In contrast to the intrinsic low-friction mechanisms of pure amorphous carbon interfaces reported by Li et al. ^[10], where structural passivation dominates the sliding behavior, our results indicate that the introduction of O atoms disrupts the original steady state, leading to a transition from low-friction sliding to a high-adhesion regime due to the loss of hydrogen passivation. Both mechanisms contribute to the amplification of local stress acting on surface hydrogen atoms. This trend indicates that passivating hydrogen on the a-C surface no longer acts as a purely beneficial barrier for friction reduction at high oxygen concentrations. Instead, it can serve as an active response site in oxygen–PEEK interfacial interactions, thereby reshaping the tribochemical environment of the sliding interface. Overall, surface hydrogen plays a concentration-dependent role under oxidative conditions. At low O₂ concentrations, it mainly acts as a passivating site,

although local reactions with dissociated O atoms weaken this effect. At high O₂ concentrations, it becomes an active response site involved in oxygen-mediated interfacial interactions. This transition explains why surface hydrogenation is not purely friction-reducing in oxygen-containing environments.

4. Conclusion

In this study, reactive molecular dynamics simulations were conducted to explore the tribological mechanisms of hydrogenated a-C/PEEK interfaces under different oxygen concentrations. The key conclusions can be summarized as follows:

- ❖ **Frictional response:** The increase in friction force and subsequent stabilization with oxygen concentration can be attributed to the loss of intrinsic lubricity of PEEK caused by oxygen diffusion and to the enhanced interfacial polarity induced by the formation of an oxygen-rich layer.
- ❖ **Chemical bonding:** Dissociated O atoms form bonds with aromatic carbons, ether oxygens, and hydrogen atoms of PEEK, leading to disruption of π -conjugation, introduction of polar functional groups, and enhanced interfacial adhesion.
- ❖ **Oxygen diffusion and interfacial structure:** Oxygen diffusion is primarily driven by sliding shear, enabling O₂ molecules to penetrate into the PEEK structure. At high oxygen concentrations, oxygen intrusion and saturation suppress the intrinsic lubricity of PEEK, while the oxygen-rich layer retained at the interface further interacts with surface hydrogen on a-C.
- ❖ **Role of surface hydrogen:** Passivating hydrogen on a-C surfaces is no longer purely beneficial for friction reduction. At low oxygen concentrations, hydrogen

atoms participate in chemical bonding with dissociated oxygen species, while at high oxygen concentrations, they interact with the interfacial oxygen-rich layer. Both effects partially offset the intrinsic lubrication of surface hydrogen through additional interfacial adhesion, meaning surface hydrogenation is no longer purely beneficial under oxidative conditions.

Acknowledgments

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