

Synergistic interfacial strengthening and ordered transfer film enable ultralow friction of PEEK in ethylene glycol

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ABSTRACT: Achieving ultralow friction in polymer-ceramic contacts typically requires complex material modifications or interface engineering. This study demonstrates that exceptional tribological performance can be unlocked through rational lubricant-polymer pairing, without altering the polymer. Specifically, polyetheretherketone (PEEK) lubricated by ethylene glycol (EG) against Si₃N₄ achieves an ultralow, stable coefficient of friction (COF = 0.0087) and exceptional wear resistance (specific wear rate = $0.99 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$), outperforming polymers like

PTFE and UHMWPE. A comparative investigation of five polymers reveals that PEEK's superiority originates from a unique interfacial synergy with EG, manifesting as concurrent surface strengthening ($\approx 34\%$ increase in nanohardness) and in-situ formation of a continuous, highly ordered graphitic carbon transfer film on the counterface (lowest $I_D/I_G = 0.48$). Density functional theory calculations attribute this synergy to a geometrically matched, dual-site chemisorption between the diols of EG and the carbonyl/ether oxygens on the PEEK backbone (binding energy = -0.01157 Ha), in contrast to the weak physisorption or suboptimal polar interactions observed for other polymers. This work establishes a clear structure-affinity-interface-performance relationship and proposes a paradigm-shifting design strategy for polymer tribosystems based on molecularly synergistic lubricant selection, paving the way for green, sustainable lubrication in precision engineering and biomedical applications.

KEYWORDS: Ultralow friction; ethylene glycol lubrication; PEEK; polymer tribology; density functional theory

1 Introduction

Friction and wear account for a significant portion of global energy consumption and material failure [1]. Superlubricity, defined as a coefficient of friction (COF) below 0.01, offers a promising route to dramatically reduce these losses [2]. Among liquid lubricants, polyols (e.g., ethylene glycol, EG) have demonstrated significant potential as green lubricants due to their unique hydrogen-bonding networks and tunable polarity [3, 4]. EG, the simplest diol, has been studied not only as a hydrodynamic lubricant but also for its complex interfacial tribochemistry. However, a critical and underexplored scientific question remains: when one sliding surface is a chemically inert ceramic (e.g., Si_3N_4) and the other is an engineering polymer, how do the multiple hydroxyl groups of EG interact with the polymer surface and govern its tribological behavior?

To achieve ultralow friction for polyetheretherketone (PEEK), existing strategies follow three main routes. The first involves external interface engineering, such as adding nanoparticles to oil to catalytically form carbon films, using ionic liquids, exploiting physicochemical effects of specific environments [5, 6], or applying hard

coatings (e.g., DLC). The second route is bulk chemical modification, notably sulfonation, which introduces SO_3^- groups to enable hydration lubrication in aqueous solutions [7, 8]. The third route employs multi-component composite (e.g., carbon fibers, graphite, nano- SiO_2) to synergistically reinforce the matrix and stabilize transfer films [9, 10].

In hard material pairs (ceramics, steels), EG has been shown to achieve efficient lubrication—even superlubricity—through multiple mechanisms: boundary adsorption [11, 12], acid-enhanced lubrication [13], synergy with nano-additives [14, 15], tribochemical reactions generating carbonaceous films [16], in-situ formation of ionic liquids [17], and chemical modification of EG itself [18]. These studies demonstrate that EG can be a highly effective lubricant on high-hardness, catalytically active surfaces. However, nearly all of them focus on hard materials; the lubrication behavior and mechanism of EG in engineering polymer/ceramic contacts—where the counterface is chemically inert and the polymer is soft—remain essentially unexplored.

Other recent advances have further expanded the scope of hydration lubrication for polymer composites. For example, embedding hydrogel microcapsules in PEEK enables a “rupture-grow” lubricating film under water lubrication [19]. Incorporating sulfonated polyaryl ether ketone (SPAEEK) with carbon fibers enhances both hydrophilicity and mechanical strength, leading to ultralow friction in aqueous environments [20]. Hydration lubrication theory has also been successfully applied to other engineering polymers, such as UHMWPE, through surface charge engineering [21, 22]. The fundamental mechanisms of hydration lubrication have been comprehensively reviewed [2]. Despite these successes, all existing strategies require modifying the polymer itself or elaborate interface engineering. A more fundamental yet overlooked question emerges: can the intrinsic low-friction potential of a polymer be unlocked without altering the material, simply by selecting a lubricating medium that matches its chemical structure?

It is worth noting that, unlike many previous EG-based superlubricity systems that rely on water, acidic conditions, or chemical modification of the polymer or lubricant, our system achieves ultralow friction with pure EG and unmodified PEEK sliding

against Si_3N_4 . Our preliminary experiments revealed a counterintuitive phenomenon: under identical conditions, PEEK lubricated by EG achieved an ultralow and stable COF of 0.0087 against Si_3N_4 , significantly outperforming traditional low-friction polymers such as polytetrafluoroethylene (PTFE) and ultra-high-molecular-weight polyethylene (UHMWPE). Notably, PEEK is widely recognized as a high-performance engineering polymer with outstanding mechanical strength, thermal stability, and chemical resistance [23, 24]. In contrast, such ultralow friction was not observed with other alcohols: unmodified PEEK in mono-alcohol (ethanol) exhibits a COF of 0.026 [25], and in triol (glycerol) it exhibits a COF of 0.015 [26], both significantly higher than the 0.0087 achieved with EG (diol). These findings suggest a specific molecular compatibility between EG's diol structure and PEEK's aromatic-ether-ketone backbone. We hypothesize that this compatibility leads to a unique interfacial synergy: concurrent surface strengthening and in-situ formation of a highly ordered graphitic transfer film on the counterface.

To test this hypothesis, we selected five representative engineering polymers: PTFE (ultra-low surface energy) [27], UHMWPE (high toughness) [28], polyamide 6 (PA6, strong polarity) [29], polyetherimide (PEI, high rigidity) [30], and PEEK (high-performance crystalline polymer). Through integrated macro-scale tribological tests, nanomechanical characterization, surface chemical analysis (Raman, XPS), and DFT calculations, we aim to (1) elucidate the mechanistic origin of ultralow friction (COF = 0.0087) and wear in the PEEK/EG/ Si_3N_4 system, (2) distinguish the dominant mechanisms of EG at different polymer interfaces, and (3) establish a structure-affinity-interface-performance relationship. A systematic comparison with reported PEEK-based tribological systems is provided in Fig. S1 (Supplementary Information).

2 Experimental

2.1 Description of materials

Materials: In this work, five distinct types of high-performance polymers were investigated as the tribological pairs. PTFE was sourced in sheet form from Zhejiang Guotai Sealing Material Co., Ltd. (China). PA6 sheets were acquired from Mitsubishi

Chemical Corporation (Japan). Blocks of UHMWPE were furnished by Henan Wosen Superhigh Chemical Technology Co., Ltd. (China). PEEK rods were obtained commercially from Wolf Kunststoff-Gleitlager GmbH (Germany). Sheets of PEI, specifically the ULTEM 1000 grade, were procured from Ensinger GmbH (Germany). Ethylene glycol (EG) with Analytical Reagent grade purity, employed as the primary lubricant in this study, was sourced from Sinopharm Chemical Reagent Co., Ltd. (China). Anhydrous ethanol (Analytical Reagent grade, Sinopharm Chemical Reagent Co., Ltd., China) was used as the cleaning solvent. A commercially available Si₃N₄ ceramic ball (Keyuanqi Hardware, China) with a standard diameter of 6.35 mm served as the stationary counterface in the ball-on-disk configuration.

2.2 Specimen preparation

Sample preparation: Prior to testing, the five polymers were fabricated into rectangular blocks measuring 18-21 mm (length) × 10 mm (width) × 5 mm (height). To prepare the contact surface, each block underwent a standardized grinding procedure: the friction surface was progressively polished with #1000, #1200, #1500, and finally #2000 grit silicon carbide sandpaper (Global Eagle brand, Ruidesen Hardware) under a stream of water. This process ensured a consistent and well-defined surface finish. Following grinding, the polymer samples and the Si₃N₄ balls were separately subjected to ultrasonic cleaning in anhydrous ethanol for 15 minutes. Finally, to achieve thorough and consistent drying, all samples were transferred to a forced-air convection oven and maintained at 25 °C for an extended period exceeding 12 hours (overnight).

2.3 Characterization and testing techniques

Surface Roughness: To ensure the comparability of initial surface conditions, the surface roughness of all polished polymer specimens was measured using a non-contact confocal white light interferometer (S neox, Sensofar, Spain). Three independent measurements were conducted on each sample, and the root-mean-square roughness (R_q) values are: PEEK = $0.237 \pm 0.001 \mu\text{m}$, PEI = $0.253 \pm 0.002 \mu\text{m}$, PA6 = $0.260 \pm 0.001 \mu\text{m}$, UHMWPE = $0.264 \pm 0.001 \mu\text{m}$, PTFE = $0.268 \pm 0.002 \mu\text{m}$. The maximum difference in roughness is only approximately 0.03 μm , which is negligible and does

not affect the reliability of the tribological comparison under the applied load.

Surface Wettability: The wettability of the pristine polymer surfaces by the lubricant was assessed through static contact angle measurements at a controlled ambient temperature of 25 ± 1 °C. These measurements were carried out using an optical contact angle goniometer (CA200, Beidou Instrument, China) with ethylene glycol (EG) as the test liquid. For statistical reliability, five measurements were performed on each material, and the mean value was utilized for further analysis.

Macro-mechanical Property: The bulk mechanical property, in terms of Shore D hardness, was evaluated for all polymers using a calibrated digital durometer (ZBLX-D, Zhenggruitaibang, China) following the ISO 868 standard protocol. Ten independent measurements were taken across the surface of each sample to obtain a representative average hardness value.

Nano-mechanical Property: To probe the near-surface mechanical properties before and after tribological exposure, nanoindentation tests were conducted. A custom-built nanoindenter (Wuhan Research Institute of Materials Protection, China) with a Berkovich diamond tip was employed in a standard quasi-static load-unload mode. Tests were performed on both the virgin polymer surfaces and within the wear tracks generated under ethylene glycol lubrication. A minimum of ten indentations per condition yielded averaged values for nanohardness (H) and reduced Young's modulus (E_r).

Tribological Tests: The friction and wear behaviors were evaluated using a commercial reciprocating ball-on-disk tribometer (MFT-5000, Rtec Instruments, USA). All tests were performed at room temperature with the contact fully immersed in 40 mL of ethylene glycol (Analytical Reagent grade). A silicon nitride (Si_3N_4) ball (6.35 mm diameter) served as the stationary counter-body against the polymer disk. A constant normal load of 60 N was applied throughout the 30-minute test, with a reciprocating frequency of 7 Hz and a stroke length of 8 mm (linear speed: 112 mm/s). The coefficient of friction was monitored continuously. To confirm the repeatability of the results, each experiment was triplicated.

Wear Quantification: Post-test analysis involved a comprehensive characterization of the wear tracks. A non-contact confocal white light interferometer (S neox, Sensofar, Spain) was used to acquire high-resolution three-dimensional topographical maps of the wear scars. From these maps, critical wear dimensions—including maximum width, maximum depth, and cross-sectional profiles—were extracted. The wear volume (V) was directly computed by the instrument's dedicated software. The specific wear rate (W) was subsequently derived from the standard equation: $W = V / (F \times L)$, where F is the applied load (60 N) and L is the total sliding distance.

Surface Chemical and Morphological Analysis: A multi-technique surface analysis strategy was adopted. The intrinsic chemical signatures of the virgin polymers were verified by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet IS 10, Thermo Fisher Scientific, USA) in ATR mode. Potential chemical modifications or transfer film formation on the worn surfaces were investigated using micro-Raman spectroscopy (DXR Raman microscope, Thermo Fisher Scientific, USA) with a 532 nm excitation source. The topography of the worn polymer surfaces and the corresponding Si₃N₄ ball scars, along with their elemental compositions, were examined using a scanning electron microscope (SEM, JSM-6510LV, JEOL, Japan) integrated with an energy dispersive X-ray spectrometer (EDS, X-ACT, Oxford Instruments, UK).

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha spectrometer with monochromatic Al K α radiation ($h\nu = 1486.6$ eV). The binding energy scale was calibrated with the C 1s peak of adventitious carbon at 284.8 eV. XPS was used to analyze the surface chemical composition of pristine PEEK, EG-soaked PEEK, and the worn PEEK surface after sliding in EG.

2.4 Modeling framework and simulation approach

Simulation model and methodology: In this work, DFT-based simulations were carried out to explore the interfacial behavior of ethylene glycol molecules on five polymeric surfaces: PTFE, UHMWPE, PA6, PEEK, and PEI. All computations were executed in the DMol3 environment of Materials Studio 2024 employing the GGA-BLYP functional and DNP basis set [31]. Initial structural optimizations of individual

polymers and ethylene glycol were conducted under strict convergence thresholds (energy: 2×10^{-6} eV/atom; force: 0.02 eV/Å). The binding energy for each polymer–glycol complex was determined via: $E_{bind} = E_{complex} - (E_{polymer} + E_{glycol})$. These energies quantitatively reflect the adsorption strength of ethylene glycol on different polymers. To probe electronic interactions, spatial distributions of electrostatic potential were visualized, and frontier molecular orbital (HOMO–LUMO) analyses were performed to assess charge transfer feasibility. Additionally, density of states (DOS) profiles were generated to characterize the hybridized electronic structures, thereby revealing the underlying adsorption mechanisms and the influence of polymer electronic characteristics [32].

3 Results and discussion

3.1 Molecular architecture and vibrational spectroscopy of polymers

Figure 1 delineates the molecular structures and FTIR spectra of PTFE, UHMWPE, PA6, PEEK, and PEI, with a focus on their potential for specific molecular interactions with the ethylene glycol lubricant. The fully fluorinated linear backbone of PTFE ($-\text{CF}_2-\text{CF}_2-$) (Fig. 1a) results in a non-polar surface, as evidenced by its dominant FTIR absorptions: C–F stretching vibrations ($\nu_{\text{as}} \text{CF}_2$ and $\nu_{\text{s}} \text{CF}_2$) in the $1150\text{--}1250\text{ cm}^{-1}$ region, and CF_2 wagging (ωCF_2) and bending (δCF_2) modes at 635 and 553 cm^{-1} [23, 27]. This spectral profile indicates minimal capacity for polar interactions with EG. In contrast, polymers capable of polar interactions present distinct spectral features. UHMWPE's extended alkane chain ($-\text{CH}_2-\text{CH}_2-$) (Fig. 1b) shows characteristic methylene vibrations at 2917 ($\nu_{\text{as}} \text{CH}_2$), 2850 ($\nu_{\text{s}} \text{CH}_2$), 1465 (δCH_2), and a doublet at $730/720\text{ cm}^{-1}$ (ρCH_2), indicative of its crystalline, albeit non-polar, nature [28]. Consequently, its interaction with EG is expected to be weak and dominated by van der Waals forces.

PA6 (Fig. 1c), containing amide linkages, exhibits a broad hydrogen-bonded N–H stretch (νNH) at 3300 cm^{-1} , alongside amide I ($\nu \text{C=O}$, 1635 cm^{-1}) and amide II ($\delta \text{NH} + \nu \text{C-N}$, 1540 cm^{-1}) bands [29]. These features highlight its strong potential for hydrogen-bonding with the hydroxyl groups of EG, suggesting a fundamentally different interfacial chemistry compared to non-polar polymers. The spectra of the aromatic polymers further reveal their interactive potential. PEEK (Fig. 1d) demonstrates a sharp ketone carbonyl stretch ($\nu \text{C=O}$) at 1650 cm^{-1} and a strong aromatic ether stretch ($\nu_{\text{as}} \text{Ar-O-Ar}$) at 1245 cm^{-1} [7, 10]. PEI (Fig. 1e) displays the imide carbonyl doublet ($\nu_{\text{as}} \text{C=O}$ at 1778 cm^{-1} , $\nu_{\text{s}} \text{C=O}$ at 1723 cm^{-1}) and the C–N stretch at 1355 cm^{-1} [30]. The presence of these polar carbonyl and ether/imide groups in PEEK and PEI establishes a clear potential for strong dipole-dipole and hydrogen-bonding interactions with the polar ethylene glycol molecules. This spectroscopic characterization confirms a spectrum of chemical functionalities—from the inert, non-polar PTFE to the highly interactive PA6 and polar aromatics. These intrinsic molecular-level properties are decisive for interpreting the subsequent divergence in

tribological performance, including friction stability, wear resistance, and interfacial film formation within the ethylene glycol environment.

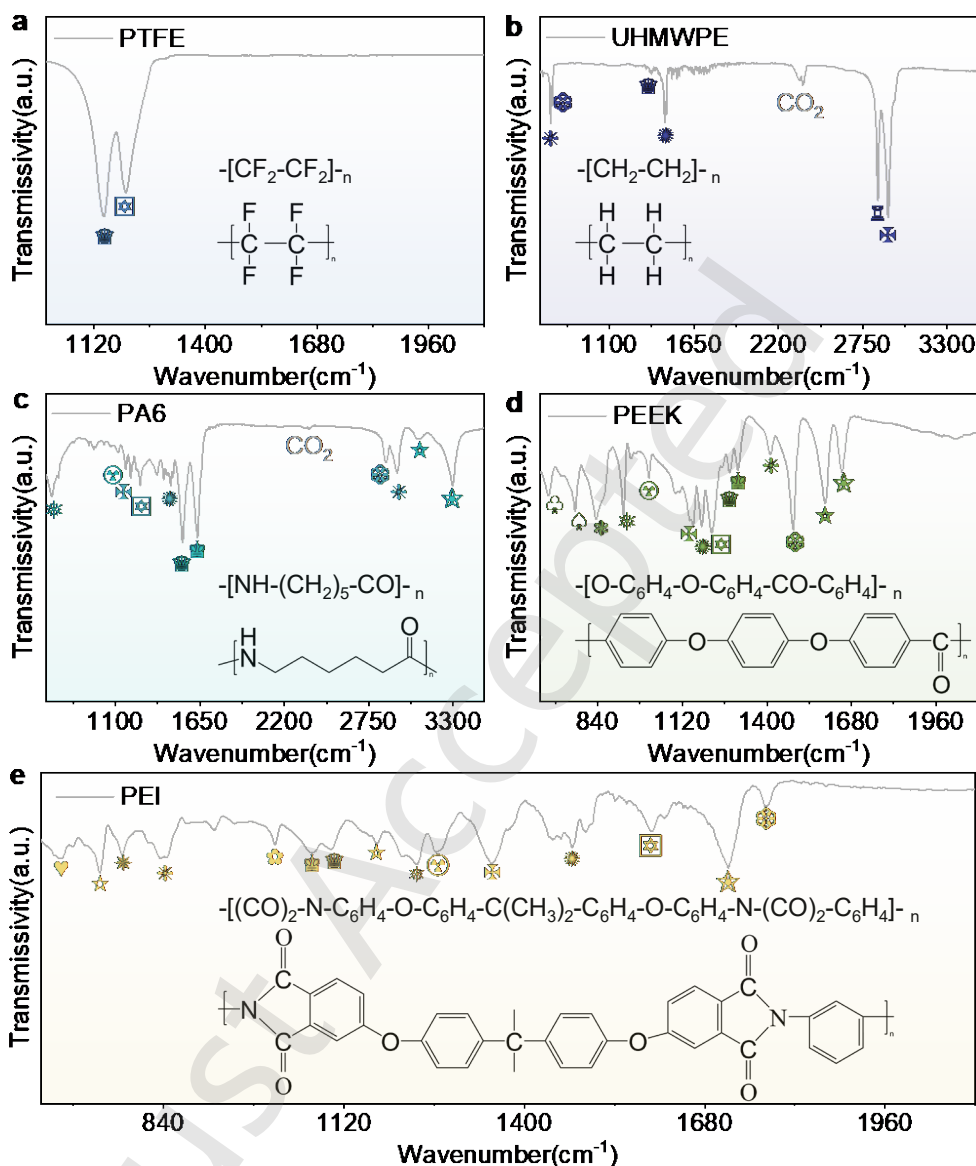


Fig. 1 Molecular structures and FTIR spectral characterization of the five polymers: (a) PTFE, (b) UHMWPE, (c) PA6, (d) PEEK, and (e) PEI.

3.2 Frictional evolution and resultant wear morphology

The temporal evolution of the COF under EG lubrication is presented in Figure 2a. A striking contrast emerges in the run-in behavior and steady-state stability among the five polymers, directly correlating with their molecular structures described in Section 3.1. PEEK demonstrates unparalleled frictional stability, attaining a steady state within a remarkably brief period of approximately 8 s. This instantaneous stabilization

suggests the rapid formation of a coherent and protective interfacial layer upon sliding initiation. UHMWPE follows, stabilizing after about 20 s, indicating a moderately effective but slower interfacial adjustment process. In marked contrast, PTFE and PA6 undergo extended and gradual run-in processes, requiring roughly 130 and 350 s, respectively, to reach equilibrium. The prolonged run-in of PTFE, despite its low surface energy, implies inefficient lubricant adsorption or film formation, while PA6's slow stabilization may reflect a complex balance between hydrogen-bonding and plasticization effects. PEI displays the most anomalous response, characterized by a tri-phasic evolution: an initial ultra-low friction state (COF 0.009) lasting until 60 s, a gradual ascent to a second plateau (0.013) by 380 s, and a final, abrupt transition into severe instability culminating in a high COF (>0.06) after 1770 s. This complex behavior hints at a progressive, time-dependent degradation of the interfacial integrity, likely related to environmental stress cracking as will be discussed later.

The amplitude of COF fluctuations during the nominal steady state ranks as: $PEI > PA6 > PTFE > UHMWPE > PEEK$, with PEEK exhibiting near-negligible variance. This hierarchy directly reflects the stability and effectiveness of the formed interfacial layers. The mean COF values, averaged over the entire test duration, are quantified in Fig. 2b. PEEK registers the lowest friction coefficient at 0.0087. The subsequent order is UHMWPE (0.0231), PEI (0.0210), PA6 (0.0329), and PTFE (0.0640). Notably, while PEI shows a moderately low average COF, its large error bar and erratic friction profile (Fig. 2a) indicate unreliable performance, contrasting sharply with PEEK's exceptional consistency. Wear assessment via scar dimensions reveals further material-specific disparities (Figs. 2c and d). PTFE sustains the most severe volumetric loss, evidenced by the greatest scar depth (345.39 μm) and width (3.1324 mm). PEI ranks second in depth (251.67 μm), though its scar width (1.6458 mm) is comparable to that of UHMWPE (1.6926 mm). The large error margins for PEI's dimensional measurements signal substantial inhomogeneity across its wear surface—a finding consistent with its erratic friction profile and indicative of localized, severe damage. PEEK, conversely, exhibits outstanding wear resistance, manifesting the shallowest depth (3.64 μm) and

narrowest scar width (0.6890 mm) among all materials. These minimal wear dimensions visually corroborate the effectiveness of the protective interface formed in the PEEK/EG system.

The three-dimensional topography of the wear scars (Figs. 2e-i) provides direct visual evidence of these divergent wear mechanisms. The wear track on PEEK (Fig. 2h) is exceptionally shallow, smooth, and uniform, characteristic of a gentle, polishing-like wear regime enabled by a stable interfacial film. In stark contrast, the scar on PEI (Fig. 2i) presents a deep, irregular, and debris-littered morphology. This severely damaged topography, coupled with the delayed friction transition observed in Fig. 2a, suggests a progressive loss of interfacial integrity that precludes the formation of any coherent protective tribolayer—a fate diametrically opposed to that of PEEK. The specific wear rates, calculated from volumetric loss, are summarized in Fig. 2j. The ranking mirrors the geometric data: PEEK possesses superlative wear resistance with a rate of only $0.99 \times 10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$. This value is two orders of magnitude lower than that of PTFE ($437.54 \times 10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$) and significantly lower than PEI ($80.36 \times 10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$), confirming that low friction does not necessarily correlate with low wear unless a durable interfacial architecture is established.

In summary, the tribological response to ethylene glycol lubrication varies profoundly across the polymer series. PEEK delivers optimal performance with rapid interface formation, an ultralow COF of 0.0087, and minimal wear ($0.99 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$). UHMWPE and PA6 offer moderate performance, while PTFE exhibits severe wear despite its low friction, and PEI suffers from progressive interfacial degradation.

To ensure these performance differences reflect genuine material properties rather than hydrodynamic artifacts, the lubrication regime for each tribopair was determined using the Hamrock-Dowson point contact model [2]. The calculated film thickness ratios (λ) for PEEK, PEI, PA6, UHMWPE, and PTFE are 0.26, 0.22, 0.17, 0.04, and 0.006, respectively (detailed parameters in Table S2). All λ values are far below 1, confirming that every tribopair operated within the boundary lubrication regime. The low viscosity of ethylene glycol (21 mPa·s) precludes the formation of a separating

hydrodynamic film. The stark performance contrasts in Fig. 2 therefore originate from intrinsic differences in interfacial interactions with EG.

The robustness of PEEK's superlubricity was further verified by a Stribeck-style analysis across varying loads (20–120 N) and speeds (16–256 mm/s). PEEK maintains a COF near or below 0.01 over nearly two orders of magnitude of the Hersey parameter ($\eta \cdot v/P$), as shown in Fig. S2 [2]. The monotonic reduction in COF with increasing $\eta \cdot v/P$ reflects the progressive ordering and maturation of the boundary tribofilm, rather than a transition to mixed or elastohydrodynamic lubrication.

Dry friction tests conducted under identical conditions (60 N, 112 mm/s) confirm that the liquid medium is essential for the observed tribological performance. Without EG, PEEK exhibits a high, fluctuating COF of 0.308, a specific wear rate of $9.33 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, and no graphitic transfer film on the Si_3N_4 counterface (see Fig. S3). The introduction of EG therefore serves as the decisive factor enabling ultralow friction and wear. These findings, especially the counter-intuitive failure of the initially hardest polymer (PEI), point to EG-induced changes in surface mechanical properties, which we examine next.

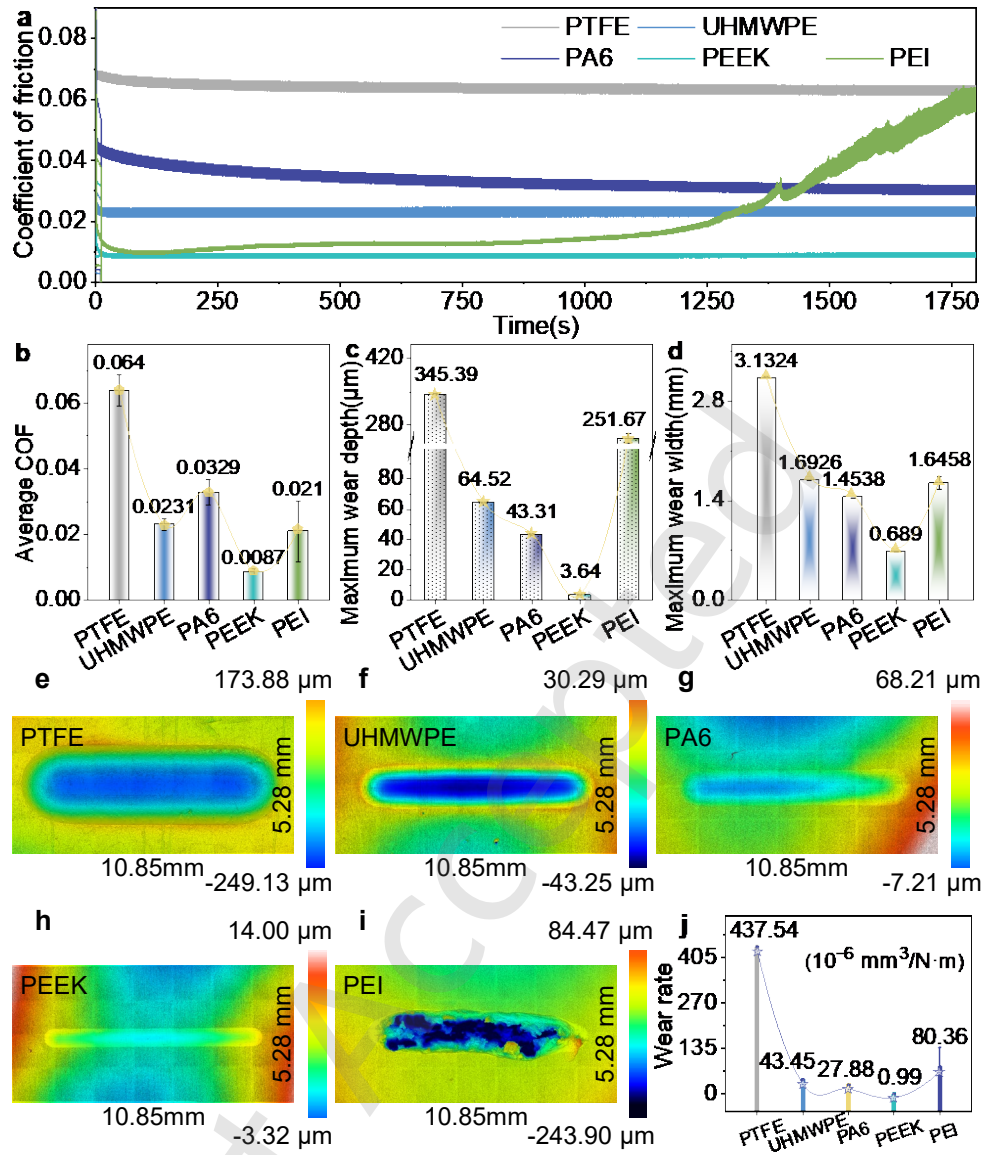


Fig. 2 Friction and wear in ethylene glycol. (a) COF evolution during sliding. (b) Average friction coefficient with standard deviation. (c) Maximum wear depth and (d) maximum wear width. (e)-(i) Three-dimensional wear scar profiles for each polymer: (e) PTFE, (f) UHMWPE, (g) PA6, (h) PEEK, and (i) PEI. (j) Resulting specific wear rates.

3.3 Evolution of interfacial mechanical properties and wettability

The starkly divergent friction and wear behaviors presented in Section 3.2, especially the catastrophic failure of the initially hardest polymer (PEI), prompt an investigation into the stability of surface properties within the polyol medium. We systematically evaluated the polymers' inherent and tribologically altered interfacial mechanical

characteristics, along with their affinity for EG [33, 34], to establish a comprehensive understanding of the surface-level transformations governing performance. The Shore D hardness (Figure 3a) ranks as follows: PEI (89.8) > PEEK (85.7) > PA6 (74.1) > UHMWPE (67.4) > PTFE (54.7). Notably, this sequence shows little correlation with the actual wear resistance (Fig. 2j), where the hardest (PEI) and softest (PTFE) materials suffered the most severe damage, while PEEK exhibited outstanding durability. This discrepancy underscores that bulk hardness alone is an insufficient predictor of performance in chemically active media like EG; interfacial stability under combined mechanical-chemical exposure becomes the decisive factor. Nanoindentation data [35] from pristine surfaces and wear tracks (Figs. 3b-f) reveal crucial surface transformations induced by sliding. Most strikingly, PEEK demonstrates a consistent and notable interfacial strengthening effect (Fig. 3e). Its nanohardness and Young's modulus increased by approximately 34% and 14%, respectively, post-sliding. The minimal data scatter in both states points to a homogeneous and stable surface modification. This enhancement indicates that shear stress combined with the EG environment facilitates molecular ordering or densification in PEEK's surface region, creating a robust load-bearing interface — a phenomenon we term "interfacial consolidation [36, 37]." This consolidation is the fundamental basis for its ultralow, stable friction and exceptional wear resistance.

Conversely, PEI (Fig. 3f) undergoes a severe deterioration of its surface mechanical properties. Despite high initial values, the nanohardness and modulus within the wear scar decreased by about 31% and 23%, respectively. Critically, the worn-state nanohardness data exhibits exceptionally high variability. This extreme scatter is direct evidence of heterogeneous surface damage, consistent with micro-crack and craze formation driven by environmental stress cracking (ESC) [38]. The macroscopic whitening on the PEI wear scar (Fig. 2i) visually corroborates this subsurface damage network. This mechanically compromised zone is the direct cause of the multi-stage friction instability (Fig. 2a), irregular scar morphology, and high, scattered wear rate [39]. PTFE, UHMWPE, and PA6 exhibit intermediate responses. PTFE (Fig. 3b) shows

moderate surface softening (a 33% reduction in hardness), which originates from shear-induced molecular chain reorientation and alignment, as directly evidenced by in-situ surface vibrational spectroscopy on shear-aligned PTFE films [27]. UHMWPE (Fig. 3c) displays significant surface hardening, with increases of 13% in hardness and 30% in modulus, resulting from strain-induced crystallization and the formation of shish-kebab structures under shear/compressive stress [28], contributing to its stable frictional behavior. PA6 (Fig. 3d) presents a slight decrease in surface mechanical properties caused by mild plasticization via hydrogen bonding between EG's hydroxyl groups and PA6's amide groups, without leading to catastrophic failure [29]. Contact angle measurements with EG (Figs. 3g-l) provide complementary insight into the interfacial affinity and potential lubricant-polymer interactions [40]. The values span a broad spectrum: PTFE (90.75°) > UHMWPE (65.28°) > PEEK (54.09°) > PEI (44.76°) > PA6 (25.67°). This wettability gradient reveals a critical trade-off: sufficient lubricant adsorption versus detrimental fluid penetration.

For PEEK, its moderate wettability strikes an optimal balance. It enables sufficient EG adsorption to form a lubricating film, while the concurrent surface strengthening mechanism prevents deleterious fluid ingress into the bulk [41]. This synergy between controlled wetting and interfacial consolidation is central to PEEK's superior performance. For PEI, however, its high wettability becomes a critical weakness. The strong affinity between polar EG molecules and PEI's rigid, polar imide structure ensures efficient fluid penetration to the tips of stress-concentrated regions, drastically accelerating ESC [42, 43]. Thus, PEI's failure exemplifies how excellent wettability, in the absence of a stabilizing surface response, can lead to catastrophic environmental degradation. PA6's near-zero contact angle indicates complete wetting, which may aid lubrication but also suggests pronounced fluid-polymer interaction, potentially contributing to its extended run-in period. PTFE's high contact angle (indicating low surface energy towards EG) likely restricts lubricant adsorption, contributing to its elevated friction and poor wear protection. Collectively, these results demonstrate that

the friction and wear outcomes in an ethylene glycol environment are dictated by a complex interplay of interfacial processes, rather than being predetermined by bulk hardness. A dynamic competition between surface consolidation (beneficial) and environmental degradation (detrimental) under combined chemical-mechanical exposure governs performance. PEEK's superior behavior stems from a unique synergy where EG interaction promotes surface strengthening without triggering degradation. PEI's failure, despite its high nominal hardness, reveals that resistance to environmental stress cracking is a more critical attribute than absolute mechanical strength in such systems. This insight provides a vital criterion for selecting polymers for applications involving polyol lubricants. While surface mechanical reinforcement explains PEEK's wear resistance, it does not fully account for the ultralow friction. The key to that likely lies in the interfacial architecture, specifically the transfer film formed on the counterface, which we examine in the following section.

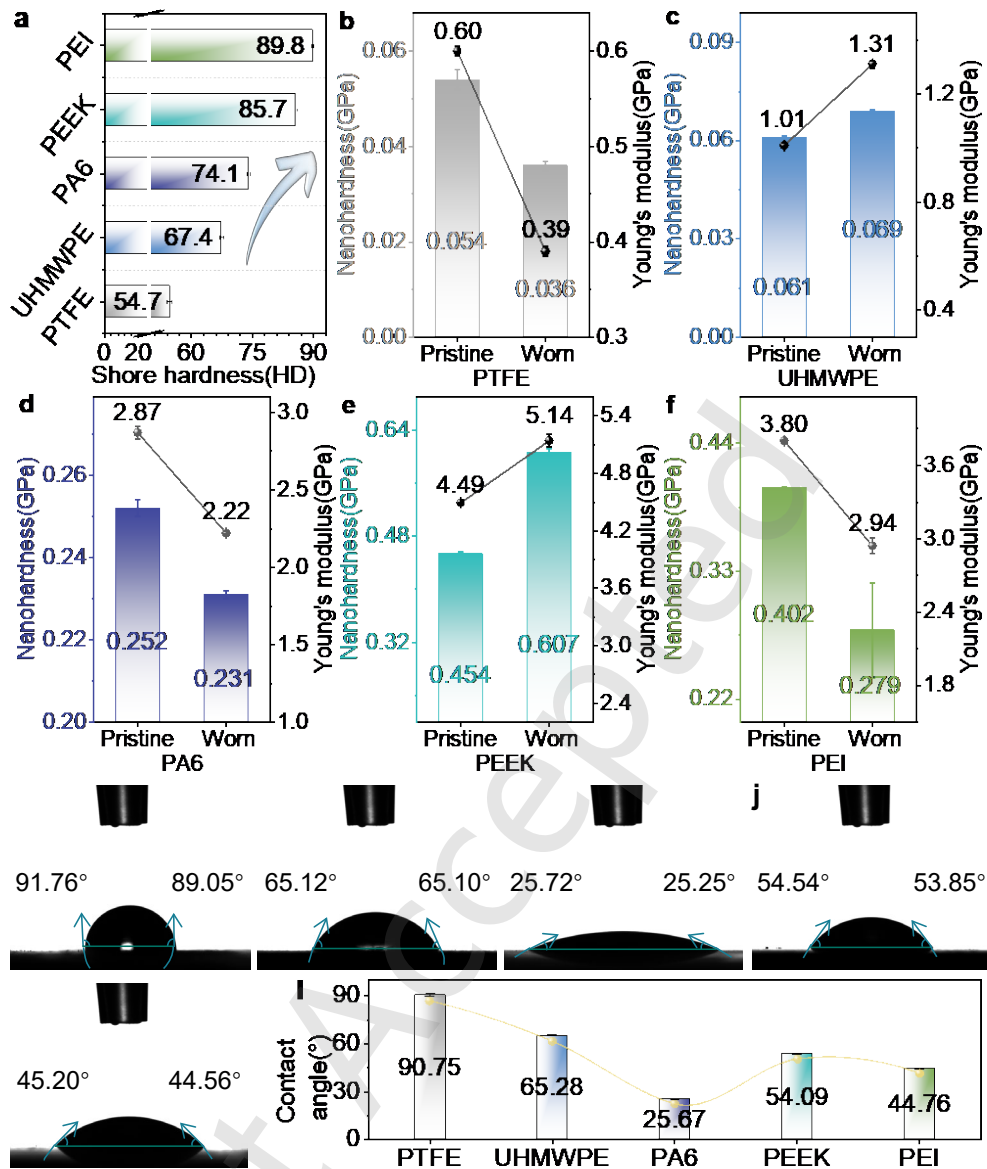


Fig. 3 Evolution of surface mechanics and ethylene glycol wettability. (a) Shore D hardness. (b-f) Nanoindentation and Young's modulus measured on pristine surfaces and inside wear tracks under ethylene glycol lubrication for (b) PTFE, (c) UHMWPE, (d) PA6, (e) PEEK, and (f) PEI. (g-k) Representative sessile-drop images of ethylene glycol on (g) PTFE, (h) UHMWPE, (i) PA6, (j) PEEK, and (k) PEI. (l) Mean contact angles of ethylene glycol.

3.4 Wear mechanisms and the pivotal role of transfer films

3.4.1 Wear mechanisms of polymer surfaces

To decipher the fundamental reasons behind the divergent tribological performance presented in Section 3.2, a comprehensive mechanistic investigation was conducted,

spanning from microscopic surface morphology to the molecular structure of interfacial transfer films. We begin with an analysis of the worn polymer surfaces, which provide direct evidence of the operative wear mechanisms. A comparative SEM analysis (Figure 4) reveals fundamentally distinct modes of material response and degradation in the EG environment, directly corresponding to the mechanical and wetting properties discussed in Section 3.3. PTFE displays extensive surface damage, dominated by scuffing (Fig. 4a). Higher magnification images reveal a network of micro-cracks, spalling pits, and the formation of fibrillar structures bridging these defects (Fig. 4, Area 1 & 2). This morphology is characteristic of PTFE's low shear strength and high ductility [44]. The shear stress, combined with limited lubricant adsorption due to poor EG wettability, leads to severe plastic deformation and fibril formation. These fibrils subsequently detach as debris, directly accounting for PTFE's catastrophic wear rate in Fig. 2j. For UHMWPE and PA6, abrasive and adhesive mechanisms prevail. UHMWPE's wear scar is covered with debris and scuffing marks (Fig. 4b), with severe scuffing and spalling pits visible at higher magnification (Fig. 4, Area 3 & 4). PA6 displays distinct ploughing grooves (Fig. 4c), accompanied by adhesive lifting-up and interfacial cracking along the groove edges (Fig. 4, Area 5 & 6). While EG provides some lubrication, it is insufficient to prevent direct mechanical penetration and micro-cutting by the hard Si_3N_4 counterpart or entrapped debris in these polymers, resulting in their moderate wear rates.

In stark contrast, PEEK's wear scar is exceptionally smooth and narrow, as delineated by the dashed boundary in Fig. 4d. Low magnification reveals minimal surface disruption. Higher magnification confirms an ultra-smooth topography with only faint, mild scuffing marks (Fig. 4, Area 7 & 8). This morphology is a direct manifestation of a benign, polishing-like wear regime, which is commonly observed for high-performance PEEK under effective liquid lubrication [7]. Crucially, the absence of severe ploughing, cracking, or adhesive failure indicates the establishment of an effective protective interface. This aligns perfectly with the nanoindentation results

showing surface strengthening (Fig. 3e) and suggests that EG facilitates a unique process in PEEK: the synergistic action of shear and the polar medium promotes molecular alignment and densification at the surface, forming a consolidated, low-shear superficial layer that acts as a robust physical barrier. PEI's failure presents a completely different scenario. The surface is characterized by massive brittle fracture and plate-like protrusions (Fig. 4e). At higher magnification, these features are resolved into cracked spalling regions and fractured, plate-like fragments (Fig. 4, Area 9 & 10). This morphology is the microstructural signature of ESC. The rigid, polar structure of PEI, coupled with its excellent EG wettability, allows the polyol to penetrate and plasticize the highly stressed subsurface region, accelerating craze initiation and brittle fracture [45]. This fluid-assisted embrittlement leads to craze initiation, crack propagation, and eventual brittle spallation of large fragments, explaining its severe, inhomogeneous wear and frictional instability. Taken together, the SEM analysis reveals a clear mechanistic dichotomy: PTFE, UHMWPE, and PA6 undergo conventional wear (fibrillation or abrasion), PEI succumbs to fluid-accelerated environmental stress cracking, while PEEK alone benefits from a synergistic interaction with EG that produces a strengthened, smooth interfacial layer. This protective polymer surface, however, represents only one component of the engineered interface—the transfer film formed on the counterface is equally decisive, as examined below.

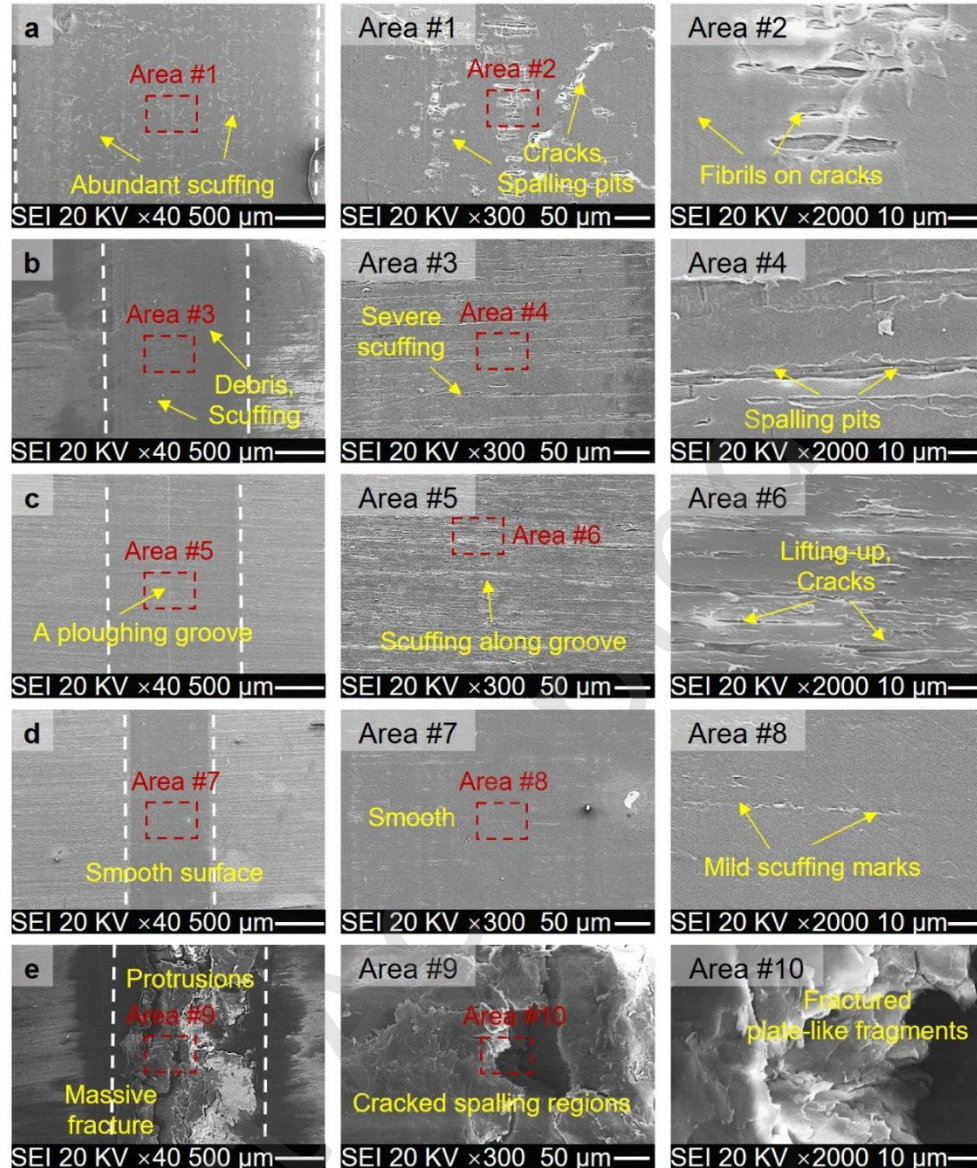


Fig. 4 Post-sliding surface morphology under ethylene glycol lubrication. SEM overview ($\times 40$) of wear scars (a-e) with boundaries outlined. Representative regions are imaged at increasing magnifications of $\times 300$ and $\times 2000$, corresponding to Areas 1-10. Samples shown: (a) PTFE, (b) UHMWPE, (c) PA6, (d) PEEK, (e) PEI.

3.4.2 The pivotal role of transfer films on the counterface

This protective layer, however, represents only one component of the engineered interface. To achieve ultralow friction, material must also be transferred to the counterface in a controlled manner. We therefore directly interrogate the material transferred to the Si_3N_4 counterface (Figures 5 & 6). The quality, structure, and

chemistry of this transfer film are posited as the definitive performance differentiator [46], providing a direct link between molecular synergy and macroscopic tribological supremacy. PTFE, UHMWPE, and PA6: Ineffective Interfacial Engineering. These polymers generate transfer films that are non-coherent and structurally under-developed. PTFE's counterpart shows grooves and patches (Figs. 5a, 6a, b), with Raman indicating disorder ($I_D/I_G=1.02$, Fig. 5b). The high disorder suggests a mechanically degraded, amorphous carbon structure that provides poor lubrication. UHMWPE and PA6 counterparts exhibit adherent debris and grooves (Figs. 5d, g; 6d, e, g, h). Their Raman signatures ($I_D/I_G=0.56-0.62$, Figs. 5e, h) suggest limited ordering, but the films appear discontinuous. EDS confirms transfer but with modest carbon levels (Figs. 6c, f, i). These films are ineffective as continuous protective barriers, leading to the moderate wear observed.

PEEK–The Engineered Interface: The PEEK counterpart reveals the hallmark of successful interfacial engineering: a small, regular scar entirely covered by a uniform, continuous film (Figs. 5j, 6j, k). This film is not merely present; it is highly structured. Raman spectroscopy provides conclusive evidence: it exhibits the highest degree of structural order (lowest $I_D/I_G=0.48$) and an exceptionally strong 2D-band (Figs. 5k, l), characteristics approaching those of a well-sheared, graphitic carbon structure. The low I_D/I_G ratio indicates a low density of defects, consistent with a crystalline, lubricious carbon phase. EDS corroborates a substantial, carbon-rich layer (Fig. 6l). The formation of this coherent, graphitized carbonaceous film is the direct product of a unique, multi-step synergy between EG and PEEK under shear, defined as follows: (i) Molecular Anchoring: DFT calculations and XPS analysis (Section 3.5, Fig. S4, Table S3) verify that EG's diol groups engage in a geometrically matched, dual-site weak chemisorption (specific interfacial interaction) with PEEK's carbonyl and ether oxygen groups, leading to stable interfacial adhesion between EG and the PEEK surface. (ii) Surface Consolidation: The oriented interfacial interaction drives shear-induced molecular ordering and densification of the PEEK subsurface, confirmed by a 34% increase in surface nanohardness (Fig. 3e), forming a robust consolidated surface that resists

uncontrolled material loss. (iii) Ordered Tribofilm Formation: Under contact stress and shear, tribochemical reactions occur at the consolidated EG-PEEK interface. The diol structure of EG is crucial here; glycols are known to facilitate tribochemical reactions and stabilize ordered carbonaceous species at sliding interfaces through the activity of their hydroxyl groups [11]. On the PEEK side, shear stress induces the scission of carbonyl and ether bonds and the ring-opening of aromatic structures, directly generating carbon-rich precursors that evolve into a graphitic transfer film, as previously established for PEEK sliding contacts [46]. In our system, these two mechanisms converge, yielding the highly ordered graphitic carbon film on the Si₃N₄ counterface (verified by the low Raman I_D/I_G ratio of 0.48, Fig. 5k). This synergistic process, in which a specifically adsorbed lubricant orchestrates both surface strengthening and the formation of an ordered protective film, constitutes the core of this highly effective lubrication mechanism.

PEI: Destructive Interfacial Degradation. The PEI counterpart underscores the absence of such synergy. It is covered with large, irregular debris plates (Figs. 5m, 6m, n), matching the brittle spallation observed on the polymer surface (Fig. 4e). Raman demonstrates significant disorder (I_D/I_G=0.71, Fig. 5n), and EDS indicates oxidation (Fig. 6o), suggesting that the transferred material is chemically degraded. The transfer layer is discontinuous and unstable, reflecting EG's role in accelerating brittle fracture rather than fostering protective film formation. Therefore, the analysis establishes a clear hierarchy of interfacial engineering in EG. The ultralow friction and wear state is not accidental but is correlated with the in-situ construction of a high-quality transfer film. PTFE, UHMWPE, and PA6 fail to construct such a film, resulting in direct contact and moderate-to-high wear. PEI's interface degenerates into fractured debris. Solely the PEEK/EG pair achieves the synergistic conditions necessary to catalyze the formation of a continuous, dense, and highly ordered graphitic carbon film [11]. This engineered interfacial architecture—comprising a consolidated polymer surface and an ordered transfer film—is the fundamental mechanism that defines and enables the ultralow friction and wear in the PEEK/EG/ Si₃N₄ system.

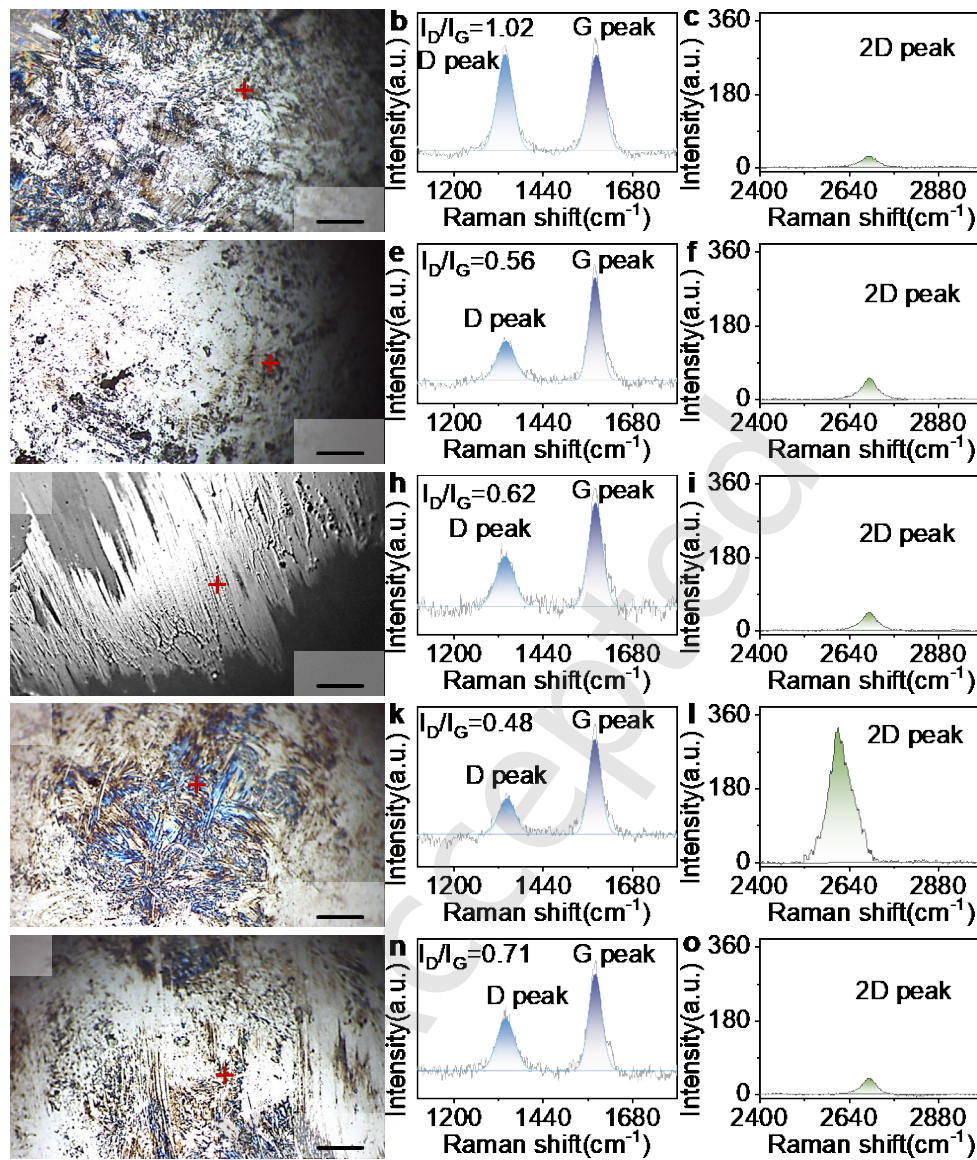


Fig. 5 Wear scar characterization of Si_3N_4 counterfaces tested under ethylene glycol lubrication with various polymers. For each polymer, the left image is an optical micrograph of the wear scar; the middle and right plots are Raman spectra from the cross-marked region over the 1100-1800 cm^{-1} and 2400-3000 cm^{-1} ranges, respectively. The corresponding I_D/I_G ratio is displayed on the middle spectrum for (a) PTFE, (d) UHMWPE, (g) PA6, (j) PEEK, and (m) PEI.

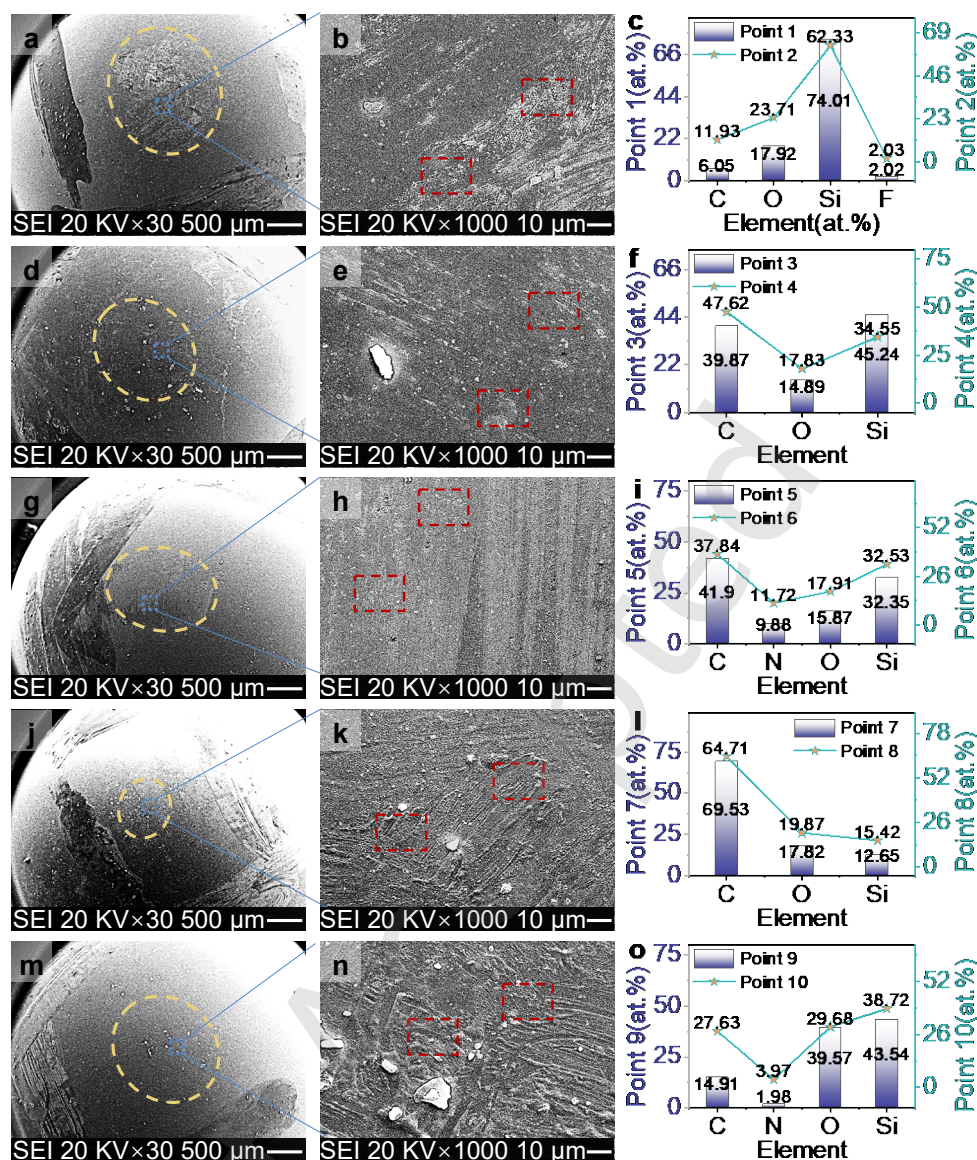


Fig. 6 Wear scar morphology and elemental composition on Si_3N_4 balls tested with various polymers. For each material pair: a wide-field SEM image (×30) of the scar (left), a magnified SEM image (×1000) of the selected area (middle), and EDS point analysis results (at. %) collected from the labeled positions (right). Rows correspond to (a) PTFE, (d) UHMWPE, (g) PA6, (j) PEEK, and (m) PEI.

3.5 Molecular-scale origins of tribological selectivity

To decode the molecular origins of this tribological selectivity, density functional theory (DFT) calculations were performed to probe the electronic structure [47], binding affinity, and interaction mechanisms at the polymer-EG interface. The electronic stability of each polymer-EG interface was first assessed by the

HOMO-LUMO energy gap (ΔE) [48, 49]. As shown in Figure 7a, the gaps follow the order: UHMWPE (0.2269 Ha) > PTFE (0.1402 Ha) > PEI (0.1196 Ha) > PA6 (0.1174 Ha) > PEEK (0.0878 Ha). A wider gap signifies greater electronic inertness and resistance to charge transfer. PEEK exhibits the narrowest gap, indicating its frontier orbitals are most susceptible to interaction with EG, a prerequisite for strong interfacial chemical activity [50, 51]. This electronic "softness" facilitates the charge redistribution necessary for stable adsorption and potential interfacial reaction under shear. ESP analysis reveals the critical role of specific molecular complementarity (Fig. 7b). The diol structure of EG, featuring two hydroxyl groups, enables complex, multi-point binding modes. For PEEK, a clear "bridging" configuration is observed. The two positively charged hydrogen atoms (blue) of EG's hydroxyl groups are simultaneously attracted to two distinct, strongly negative sites (red) on the PEEK segment—namely, the carbonyl oxygen (C=O) and an ether-linkage oxygen (Ar-O-Ar). This geometrically matched, dual-site anchoring provides a stable and robust adsorption motif [52], effectively locking the EG molecule onto the PEEK surface.

For PEI, EG's diols also engage with multiple polar sites (carbonyl and imide groups) on the rigid polymer structure. However, the geometric match and electrostatic complementarity appear less optimal than for PEEK, potentially leading to a less stable or more strained adsorption geometry. PA6 shows strong potential for hydrogen-bonding via its amide groups, but in the modeled conformation, it does not facilitate an equally clear and effective dual-anchorage with EG. In stark contrast, the ESP surfaces of PTFE (uniformly weak negative) and UHMWPE (uniformly weak positive) are essentially featureless. They offer no specific, high-affinity sites for the polar EG molecule, precluding strong, oriented adsorption. This hierarchy of electrostatic and geometric compatibility is quantitatively confirmed by the calculated binding energies (BE, Fig. 7c). The BE trend is: PEEK (-0.01157 Ha) > PEI (-0.00088 Ha) > PA6 (-0.00058 Ha) > UHMWPE (-0.00011 Ha) > PTFE (-2.00×10^{-6} Ha). PEEK's binding energy is an order of magnitude stronger than its closest polar competitor (PEI) and several orders of magnitude stronger than the non-polar polymers. This uniquely

strong chemisorption is the molecular foundation for forming a stable, load-bearing interfacial layer with EG. It explains the rapid run-in and stable friction of PEEK, as EG molecules quickly and tenaciously populate the interface.

The nature of these electronic interactions is further elucidated by density of states (DOS) analysis (Figs. 7d-h). In systems with strong chemical interaction (PEEK, PA6), the DOS of the complex is not a mere superposition of its components. For the PEEK-EG complex (Fig. 7g), noticeable peak shifts and broadening near the Fermi level indicate significant orbital hybridization and electron redistribution—a hallmark of chemical interaction. The narrow HOMO-LUMO gap is visually evident as the occupied and unoccupied states are in close proximity. Similarly, for the PA6-EG complex (Fig. 7f), peak broadening signifies interaction, albeit weaker than for PEEK. Conversely, the DOS plots for PTFE-EG and UHMWPE-EG complexes (Figs. 7d, e) are essentially additive. No hybridization features are present, confirming the absence of chemical interaction and consistent with weak physisorption. Their wide energy gaps manifest as broad, flat regions with negligible electronic states between the main peaks. The PEI-EG complex (Fig. 7h) demonstrates intermediate characteristics, with subtle indications of interaction but lacking the definitive hybridization signature seen for PEEK.

The DFT simulations converge on a coherent molecular mechanism: PEEK's ultralow friction originates from the geometrically matched, dual-site chemisorption between EG's diols and PEEK's carbonyl/ether oxygens. This binding mode yields the highest adsorption energy (-0.01157 Ha) among all five polymers, facilitating the formation of a stable, chemisorbed interfacial film that serves as the precursor to the ordered graphitic transfer film (Figs. 5 & 6). In contrast, the weaker or geometrically mismatched interactions of PEI, PA6, UHMWPE, and PTFE fail to induce interfacial consolidation, explaining their inferior tribological performance.

This DFT-predicted chemisorption is directly corroborated by XPS analysis of pristine, EG-soaked, and worn PEEK surfaces (Fig. S4 and Table S3). The C–O component (286.3 eV) increases progressively from 12.9% (pristine) to 19.7% (EG-soaked) to 24.8% (worn), while the C=O signal nearly vanishes ($<0.1\%$ on the

worn surface). Concurrently, the O–H component (533.5 eV) rises from 35.4% to 56.9%. These systematic shifts confirm that EG molecules are retained on PEEK even after washing, and that mechanical shear promotes hydrogen-bonded chemisorption between EG's hydroxyl groups and PEEK's carbonyl/ether oxygens—consistent with the DFT-predicted dual-site anchoring mechanism.

A comparison between EG and polyethylene glycol (PEG) further clarifies the superlubricity mechanism of the EG/PEEK system. Both EG and PEG are environmentally friendly polyhydroxy lubricants that reduce friction by forming hydrogen-bonded interfacial adsorption films [53, 54]. As a small-molecule diol with low viscosity, EG can rapidly adsorb onto the PEEK surface to form a dense, compact, and low-shear interfacial layer; quantitative calculations confirm that the film thickness ratio λ is far less than 1 under all test conditions, indicating that the entire operating range belongs to the boundary lubrication regime, and the decreased friction coefficient at higher sliding speeds is attributed to more sufficient and uniform interfacial adsorption of EG molecules under shear, rather than a transition to mixed or elastohydrodynamic lubrication. In contrast, PEG is a polymeric macromolecule with significantly higher viscosity that mainly operates through elastohydrodynamic or mixed lubrication [53], and its large molecular size makes it difficult to form the compact, ordered interfacial structure required for superlubricity, especially under high contact pressures [54]. Thus, EG exhibits clear advantages for achieving boundary superlubricity under high-load conditions, whereas PEG is more suitable for liquid-film lubrication at low or moderate loads.

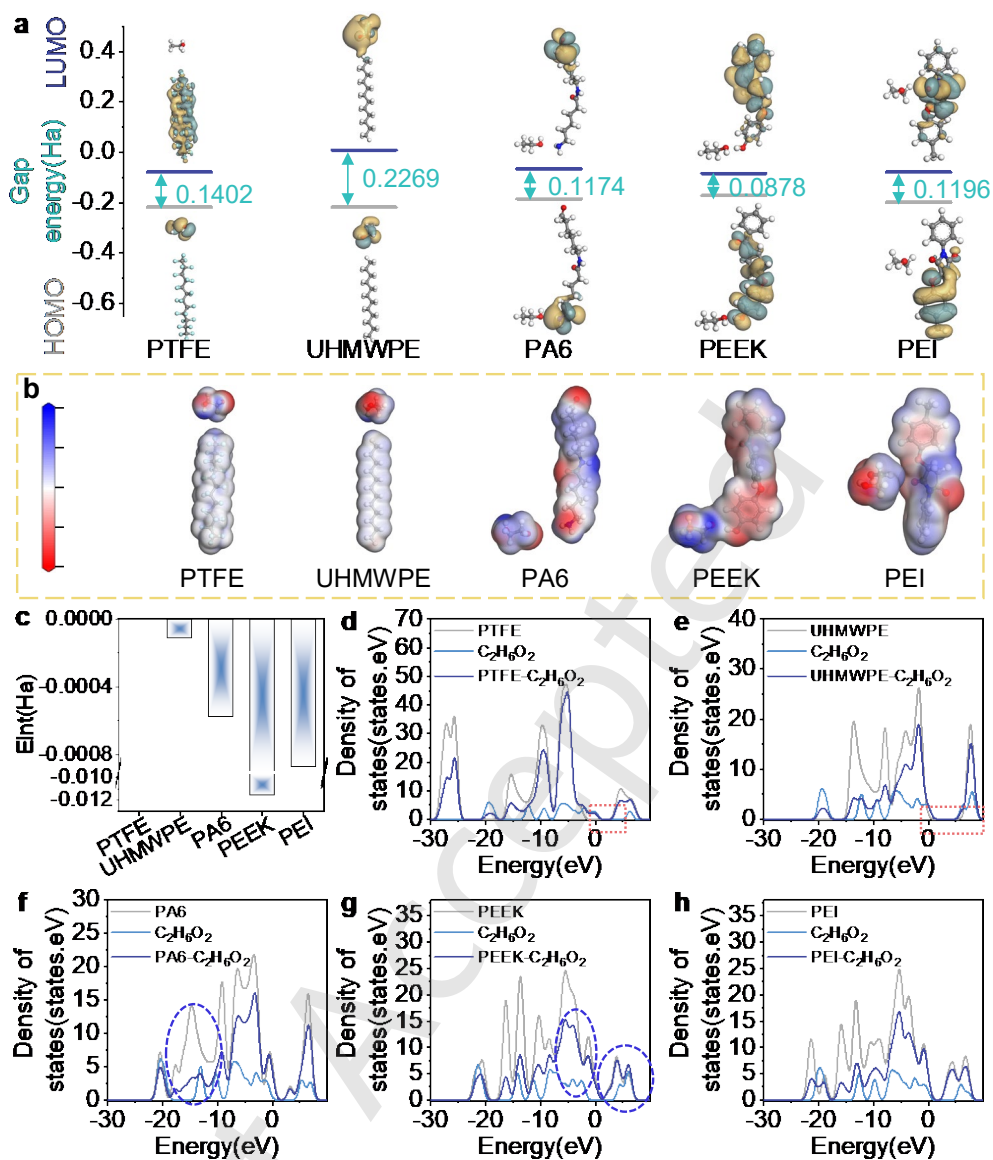


Fig. 7 Molecular-scale analysis of polymer-ethylene glycol interfacial interactions. (a) Calculated HOMO-LUMO energy gaps (ΔE) for the polymer-EG complex systems. (b) ESP maps of isolated polymer segments and an EG molecule. Positive and negative regions are indicated in blue and red, respectively. (c) Calculated BE between a single EG molecule and the respective polymer segment. (d-h) DOS plots for the (d) PTFE-, (e) UHMWPE-, (f) PA6-, (g) PEEK-, and (h) PEI-EG complexes, compared with the DOS of their isolated components.

4. Conclusion

In this study, the molecular origin of ultralow friction in the PEEK/EG/Si₃N₄ system

was systematically elucidated through a comparative tribological investigation integrated with nanomechanical characterization, surface analysis, and DFT simulations. The main conclusions are as follows:

(1) PEEK exhibits exceptional tribological performance in EG, achieving an ultralow COF of 0.0087 and a specific wear rate of $0.99 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, significantly outperforming PTFE, UHMWPE, PA6, and PEI.

(2) The superior performance stems from a unique interfacial synergy: EG molecules form strong, geometrically matched dual-site chemisorption with PEEK's carbonyl and ether groups, leading to surface consolidation ($\approx 34\%$ increase in nanohardness) and the in-situ formation of a continuous, highly ordered graphitic transfer film ($I_D/I_G = 0.48$) on the Si_3N_4 counterface.

(3) In contrast, other polymers fail to establish such a coherent interface due to either weak physisorption (PTFE, UHMWPE), suboptimal polar interactions (PA6), or lubricant-accelerated environmental stress cracking (PEI).

(4) Our findings shift the paradigm for achieving superlubricity in polymer composites: instead of relying solely on material modification, rational “molecular matchmaking” between the polymer and lubricant can activate intrinsic low-friction potential. This strategy provides a theoretical foundation for designing green, high-performance tribosystems for precision engineering and biomedical applications.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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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