ORIGINAL PAPER

Aqueous Lubrication of SiC and Si$_3$N$_4$ Ceramics Aided by a Brush-like Copolymer Additive, Poly(L-lysine)-*graft*-poly(ethylene glycol)

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Abstract We have examined the adsorption properties of poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG)— a brush-like polymer—on Si$_3$N$_4$ and SiC surfaces and determined its impact on the aqueous lubrication of Si$_3$N$_4$ and SiC at various speeds and applied loads. The addition of PLL-*g*-PEG in aqueous solution reduces the interfacial friction forces significantly for self-mated sliding contacts of these two ceramics, as compared to lubrication with water or buffer solution alone. For SiC, the improved lubricating performance by addition of PLL-*g*-PEG was apparent for all tested speeds (from 1.4 to 185 mm/s under 2 N load). For Si$_3$N$_4$, the effect was more apparent in the slow-speed regime ($\leq$20 mm/s under 2 N load) than in the high-speed regime (>100 mm/s), where extremely low coefficients of friction ($\mu \leq 0.006$) are readily achieved by aqueous buffer solution alone. It was further observed that the optimal lubricating effect with Si$_3$N$_4$ is achieved when the tribopairs are first run-in in polymer-free aqueous buffer to render the sliding surfaces smooth, after which the PLL-*g*-PEG copolymer is added to the buffer solution.

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1 Introduction

Si$_3$N$_4$ and SiC ceramics display excellent tribological properties, such as high abrasive wear resistance and high critical loads to seizure [1], and are used in applications such as abrasives, mechanical seals, and various types of bearings. In particular, their resistance to corrosion [2] and the extremely low friction forces observed at high speeds in an aqueous environment [1–13], even lower than some metal–oil systems [2], have led to an interest in tribological applications of Si$_3$N$_4$ and SiC in water, such as in water pumps without separate oil lubrication.

The aqueous lubrication properties of Si$_3$N$_4$ are particularly interesting because very low coefficients of friction ($\mu < 0.001$ [2, 3, 11, 12]) can be achieved in water alone. These low μ values can only be achieved at high speeds (>40 mm/s) [3, 12] with an estimated water film thickness of 5–70 nm [3, 10]. However, if these conditions are not met, water does not act as a good base lubricant and μ can become as high as 0.7 [3, 14]. The unique self-lubricating properties of Si$_3$N$_4$ in water have been attributed to the tribochemically activated hydrolysis of SiO$_2$ present on the Si$_3$N$_4$ surface [13], but the precise cause of the low friction has been the subject of debate. One argument is that the dissolution of asperities, via SiO$_2$ hydrolysis, leads to extremely smooth surfaces that are conducive to hydrodynamic lubrication [3, 5–9, 12, 13]. Alternatively, it has also been argued that the readily sheared products of the tribochemical reaction remain on the surface, acting as a boundary lubricant [1, 4, 10].

SiC, which is generally harder, more brittle, more wear resistant, and chemically more inert than Si$_3$N$_4$ [9], has shown more consistent μ values (around 0.01) in water over a broad range of speeds and loads [2, 3, 11]. This higher degree of chemical inertness of SiC can be attributed to the difference in electronic properties of Si$_3$N$_4$ and SiC. Water

has a band gap of 8.0 eV, and Si_3N_4 and SiC have band gaps of 5.0 and 2.8 eV, leading to differences compared to the band gap of water of 3.0 and 5.2 eV, respectively [11]. Consistent with the theory of Klopman, who proposed that a smaller band gap difference among reagents leads to a higher reaction rate [15], SiC requires a much longer running-in time and much higher sliding speeds (500 mm/s) [12] to yield μ values that are as low as those of Si_3N_4.

Despite the extremely favorable tribological properties of SiC and Si_3N_4 under high-speed conditions, a reduction of the coefficients of friction under low-speed conditions would be highly advantageous for further applications of the materials in water-lubricated bearings. Past approaches have included modifying the surface charge by adjusting the pH of the lubricant [16] or using additives such as ionic liquids [17]. An alternative, promising approach for aqueous lubrication of ceramics is to use water-soluble brush-like copolymers, which have recently been applied to several oxide-based tribosystems [18–30]. Poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG) has a polycationic backbone that adsorbs onto negatively charged surfaces, such as SiO_2 under neutral pH conditions. Upon adsorption, the hydrated PEG side chains stretch out into the water, due to steric effects at high grafting densities, forming a brush-like layer over the entire surface. Under certain types of abrasive tribocontact, such as sliding contact in the presence of macroscopic asperities, PLL-*g*-PEG performs best when an excess amount of copolymer is present in the base aqueous lubricant. Although the copolymer layer is easily rubbed away during tribocontact, due to its relatively weak but reversible electrostatic attachment, the excess copolymer in the vicinity of the surface can rapidly readsorb onto the surface due to fast surface adsorption kinetics, reforming, or "self-healing" the lubricating brush film [18–20, 22–29].

The surfaces of SiC and Si_3N_4 tend to spontaneously form an oxide layer in air [8, 31]. Past work on the adsorption [18–20, 24, 32–35] and tribological properties [18–20, 22–29] of PLL-*g*-PEG on oxide surfaces, especially SiO_2, suggest that PLL-*g*-PEG is a promising candidate as an aqueous lubricant additive. To investigate the possible benefits of PLL-*g*-PEG as an aqueous lubricant additive, adsorption tests using ellipsometry (ELM) and X-ray photoelectron spectroscopy, as well as tribological tests at a variety of speeds, using a pin-on-disc tribometer, have been carried out.

2 Experimental

2.1 Materials

2.1.1 Polymer Synthesis

For the experiments in this study, PLL(20)-*g*[2.9]-PEG(5) and PLL(20)-*g*[3.6]-PEG(5), indicating a poly(L-lysine)

backbone polymer of 20 kDa (including Br^- counterions) and poly(ethylene glycol) side chains of 5 kDa grafted onto every 2.9th or 3.6th lysine unit, were employed. Little difference in the adsorption and tribological performance is expected in these two polymers [34]. Complete details of the synthesis of PLL-*g*-PEG can be found in previous publications [32, 36, 37]. Briefly, 20 kDa poly(L-lysine) hydrobromide (Fluka, Switzerland) was dissolved at a concentration of 100 mM in a 50 mM sodium borate buffer solution adjusted to pH 8.5. The solution was filtered through a 0.22 μm filter. To graft PEG onto PLL, the *N*-hydroxysuccinimidyl ester of methoxypoly(ethylene glycol) propionic acid (mPEGSPA, Nektar, Huntsville, AL) was added to the PLL–HBr solution. The reaction was allowed to proceed for 6 h at room temperature, after which the reaction mixture was dialyzed (Spectra-Por, molecular weight cutoff size 6–8 kDa, Spectrum, Houston, TX) for 48 h against deionized water. The product was freeze dried and stored in powder form at −20 °C.

For all tribometry and adsorption experiments described in this article, PLL-*g*-PEG was dissolved at a concentration of 0.25 mg/mL in an aqueous buffer solution consisting of 1 mM 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (abbreviated HEPES 0, Fluka, Switzerland), adjusted to pH 7. For the adsorption measurements described in Sects. 2.2.1 and 2.2.2, samples were allowed to incubate for 30 min in the PLL-*g*-PEG solution to allow for polymer adsorption.

2.1.2 Preparation of Tribopairs

Discs of SiC (Hexaloy SA, Saint-Gobain, Northboro, MA) and Si_3N_4 (approximately 25 mm in diameter) were polished to a 1 μm finish with diamond paste. Along with 6-mm ball bearings of the same materials (polished by the manufacturer Saphirwerk AG, Brügg, Switzerland, and used as received), they were ultrasonicated in a series of solvents (heptane or pentane, acetone, ethanol, water, and ethanol again) for 10 min each to remove all possible contaminants from the polishing process. They were subsequently plasma cleaned in air plasma (Harrick Scientific, Ithaca, NY) for 2 min before use in the tribometer or the adsorption experiments with ELM.

2.2 Experimental Procedures

2.2.1 Polymer Adsorption Measurements with Ellipsometry (ELM)

ELM was performed with an M200-F Variable Angle Spectroscopic Ellipsometer (J. A. Woollam Co. Inc., Lincoln, NE) with a spectral range of 245–995 nm. Measurements were performed in air at angles of 65°,

70°, and 75° from the surface normal. Optical constants of clean, bare surfaces of Si_3N_4, SiC, and SiO_2 (silicon wafers with thermal oxide) were measured first, after which samples were incubated in a PLL-*g*-PEG solution (described in Sect. 2.1.1) for 30 min and rinsed with HEPES 0 and water, and dried in a stream of N_2. WVASE 32 analysis software was used to fit the data to multilayer models, using a Cauchy model ($A = 1.45$, $B = 0.01$, $C = 0$) [38].

2.2.2 Adsorption Measurements with XPS

The surface chemistry of the samples before and after polymer adsorption was investigated with X-ray photoelectron spectroscopy (XPS). The X-ray source of the PHI Quantera SXM (ULVAC-PHI, Chanhassen, MN) is a focused and scanned monochromatic AlKα beam with a diameter that can be chosen between 9 and 200 μm. The emitted electrons are collected and retarded with a lens system similar to the Omega lens available from Physical Electronics Inc. After passing a spherical capacitor energy analyzer, the electrons are detected by a 32-channel detector. The system is also equipped with a high-performance, floating-column ion gun and an electron neutralizer for charge compensation.

Small-area XPS spectra were collected with a beam size of 100 μm diameter with a power of 24.5 W in the constant analyzer energy mode using a pass energy of 26 eV and a step size of 0.05 eV. Under these conditions, the full-width-at-half-maximum (fwhm) for $Ag3d_{5/2}$ is 0.55 eV. Survey spectra were acquired with 280 eV pass energy and a step size of 1 eV. The whole set of spectra (detailed and survey spectra) was acquired within 30 min/area.

The residual pressure was always below 5×10^{-7} Pa. The system was calibrated according to ISO 15472:2001 with an accuracy of ±0.05 eV.

Measurements were taken on one clean, polished (not tribostressed) sample each of Si_3N_4 and SiC and one of each incubated for 30 min in a PLL-*g*-PEG solution (described in Sect. 2.1.1) for 30 min and rinsed with HEPES 0 and water, and dried in a stream of N_2. Three measurements were taken for the SiC coated with PLL-*g*-PEG.

Detailed spectral analyses were processed using Casa-XPS software (V2.3.12, Casa Software Ltd., UK). An iterated Shirley–Sherwood background subtraction was applied before peak fitting using a linear-least-squares algorithm. Minor charging was observed and corrected by referencing, for SiC, to the carbide component of the Si 2p 3/2 peak 100.8, as per Contarini et al. [39] and for Si_3N_4, to the hydrocarbon component of the C1s peak at 284.6, as per Bertoti et al. [40].

2.2.3 Pin-on-Disc Tribometry

All pin-on-disc experiments were performed on a CSM tribometer (Peseux, Switzerland) with self-mated tribopairs of either SiC or Si_3N_4.

2.2.3.1 Change of Lubricant A series of experiments was performed on Si_3N_4 by changing the lubricant during the test to examine the effects of tribological contact history on the value of μ. To change the lubricant from PLL(20)-*g*[2.9]-PEG(5) solution (see Sect. 2.1.1) to HEPES 0, the PLL-*g*-PEG solution was removed from the tribological testing cup, the sample and cup were dried with hot air, and HEPES 0 was added to the cup. As indicated in a previous study [24], an excess of PLL-*g*-PEG should be present in the lubricant to insure the self-healing of the PLL-*g*-PEG coating and thus effective lubrication. Therefore, a superficial layer remaining on the surface, if present, should be removed within a few rotations and have no persistent lubricating effect. To change from HEPES 0 to PLL-*g*-PEG solution, the HEPES 0 was removed from the cup and the PLL-*g*-PEG solution was added. These experiments were performed at 120 mm/s under 5 N applied load with no running-in procedure.

2.2.3.2 Speed Dependence A series of measurements was performed in which the speed dependence of the friction of self-mated pairs of Si_3N_4 and SiC was tested in solutions of HEPES 0 and PLL(20)-*g*[2.9]-PEG(5), as further described in Sect. 3.1. For Si_3N_4, experiments were performed under an applied load 2 N and a speed of 10 mm/s on different tracks with no running-in procedure. Another series of experiments was performed on samples of both Si_3N_4 and SiC. First, a running-in procedure of 100 rotations at a speed of 2 mm/s was performed, and the same ball position was used for all experiments on the same sample to insure a consistent pin geometry. Experiments on each sample were first performed in HEPES 0, then in PLL-*g*-PEG solution, at speeds of 185, 17, and 1.4 mm/s, with a different track for each speed and lubricant. Each pair of HEPES 0 and PLL-*g*-PEG experiments was performed on tracks of similar radii (±0.5 mm) to maintain similar rotational speeds and linear speeds among the different lubricants. These experiments were performed under an applied load of 2 N, and each group of experiments was repeated three to four times.

2.2.3.3 Wear Track Morphology The final series of experiments was performed to compare the surface topographies of SiC and Si_3N_4 after tribological contact in HEPES 0 buffer solution and in PLL-*g*-PEG solution. With a fresh area of the pin and fresh track for each test, 30,000 rotations were performed at 185 mm/s under 2 N applied

load in either HEPES 0 or PLL(20)-g[3.6]-PEG(5) solution. The resulting surface topography was examined by AFM (Dimension II, Digital Instruments, Santa Barbara, CA) using a sharp Si_3N_4 tip with a triangular cantilever of spring constant 0.12 N/m. Wear tracks on the pins and discs were measured with an Axioskop 2 plus optical microscope and AxioVision software (Carl Zeiss Inc., Jena, Germany).

3 Results

3.1 Adsorption Measurements

3.1.1 XPS

The data collected for Si_3N_4 can be seen in Fig. 1 and Table 1, with the C–C component of the C1s peak at 284.6 eV used as an internal reference. The Si 2p3/2 peaks at 101.6 and 103.5 eV closely match the analysis of Bertoti, who measured a Si–N component at 101.8 eV and a Si–O component at 103.5 eV [40]. This differs from the analysis of Hah, who reports Si–O around 101 eV, a SiO_xN_y at 102 eV, and a SiO_aN_b/SiO_2 species at 103 eV [40]. The O1s signal consisted of a major contribution at 532.1 eV, corresponding to an O–Si bond, measured at 532.3 eV by Bertoti. An additional minor contribution at 530.9 eV, too low to be an SiO_xN_y species [41], which can be attributed to hydroxide or carbonate bonded to a NH_3 species, corresponds to the value of 530.8 eV measured by Bertoti. A final contribution to the O1s spectrum at 533.1 eV can be ascribed to adsorbed water or ethanol remaining from the cleaning process or possibly the Na Auger contribution, which was present in the full spectra as a minor contaminant. The N1s spectrum contained a NSi_3 contribution at 397.5 eV, but a shoulder corresponding to
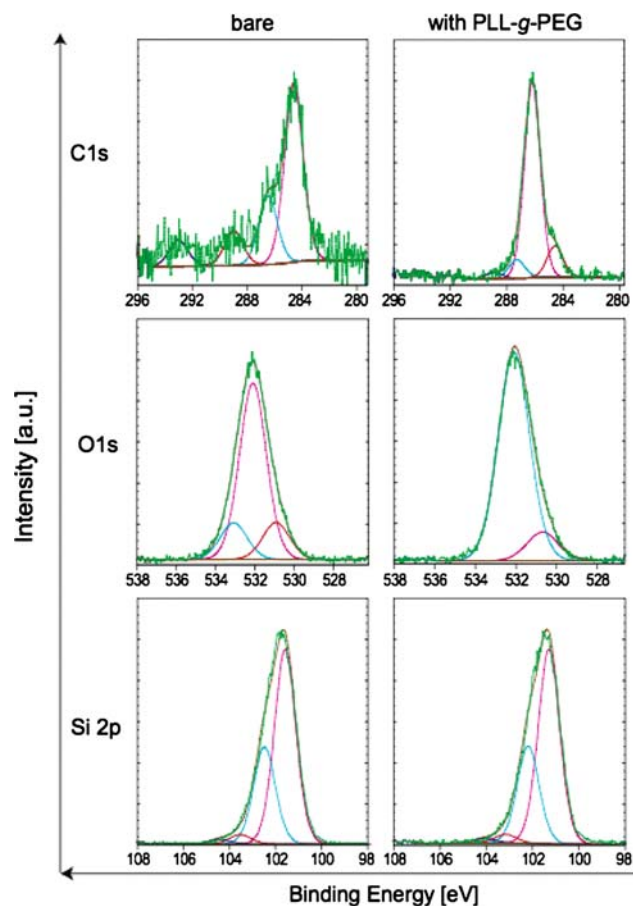

Fig. 1 XPS measurements of Si_3N_4 before and after adsorption of PLL-g-PEG

the NH_2 contribution at 399.3 eV, as reported by Bertoti, was not found.

After PLL-g-PEG adsorption there is good agreement with the values of Huang et al. [33] (referred to C1s at 284.6 eV). The O1s-Si peak overlaps with the NHC=O,

Table 1 XPS analysis of PLL-g-PEG adsorbed onto Si_3N_4 with 0.4 eV subtracted from the values of Huang et al. [33] to be consistent with a binding energy of 284.6 eV for hydrocarbon C1s

Element	Bond	Bare Si_3N_4, measured	Si_3N_4 with PLL-g-PEG, measured	Si_3N_4 by Bertoti et al. [40]	PLL-g-PEG referred to Cls at 284.6 eV [33]
C1s	C–C/C–H	284.6	284.6	284.6	284.6
	C–O/C–N		286.2		286.1/285.8
	NHC=O		287.3		287.7
O1s	O–Si and NHC=O	532.1	532.2	532.3	531
	OH/CO_3 to NH_4 and C–O	530.9	530.8	530.8	532.4
	Contamination (H_2O, ethanol, or Na Auger)	533.1			
Si 2p 3/2	Si–N	101.6	101.4	101.8	
	Si–O	103.5	103.2	103.5	

Fig. 2 XPS measurements of SiC before and after adsorption of PLL-*g*-PEG

shifts in the Si 2p 3/2 of 0.4 eV for the SiN$_4$ component and 0.3 eV for the SiO$_4$ component.

The results of the SiC analysis are provided in Fig. 2 and Table 2. In the case of SiC, the Si–C component of the Si 2p 3/2 at 100.8 eV was used for internal calibration, yielding the Si–O component of the Si 2p 3/2 at 103.3 eV, correlating well with the results of Contarini et al. [39]. However, slight discrepancies exist between the present analysis with those of Contarini, including a slightly higher value (285.6 eV) for the C–C/C–H components of the C1s signal than Contarini (285 eV), as well as a slightly higher O1s signal corresponding to the O–Si bond (533 eV compared to 532.3 eV). Both of these discrepancies can probably be attributed to the different forms of SiC used in the analysis—sintered discs in this study and powders by Contarini.

Following adsorption of PLL-*g*-PEG, the value of the Si–O component of the Si 3p 2/3 peak remains within 0.1 eV of the previously measured value of the bare SiC as well as the value of Contarini. The C–Si component of the C1s peak shows a slight shift to 283.2 ± 0.03 eV. The C–C/C–H component is found at 285.6 ± 0.05 eV, which is 0.6 eV higher than the bare SiC value reported by Contarini et al. [39] or the theoretical PLL-*g*-PEG value reported by Huang et al. [33], and is shifted by about 1.6 eV from the value measured on bare SiC. Additionally, a C–O/C–N component at 287.2 ± 0.05 eV is shifted 1.4 eV from the measurement on bare SiC, and is around 0.7 eV higher than the theoretical value of the C–O component for PLL-*g*-PEG. Small N1s peaks are measured at 400.7 and 402.4 eV.

3.1.2 ELM

ELM results, in general, show that dry film thicknesses of adsorbed PLL-*g*-PEG on Si$_3$N$_4$ and SiC are similar to the amounts seen on silicon wafers. Si$_3$N$_4$ and SiC have adsorption amounts of 15.7 ± 1.6 and 16.8 ± 0.7 nm,

which, at 532.2 eV, still matches well with that of the bare Si$_3$N$_4$ (532.1 eV) and the measurements of Bertoti (532.3 eV), but is higher than that of the theoretical value of 531.0 eV of Huang. In Fig. 1, a clear C–O peak appears upon adsorption of PLL-*g*-PEG. Notable shifts include a shift to lower binding energies in the C1s contribution from the NHC=O, from 287.3 to 287.7 eV, and small chemical

Table 2 XPS analysis of PLL-*g*-PEG adsorbed onto SiC (using an internal calibration of Si 2p 3/2 to 100.8 eV binding energy)

Element	Bond	Bare SiC, measured	SiC with PLL-*g*-PEG, measured (average of three measurements)	SiC, bare by Contarini et al. [39]	Theoretical PLL-*g*-PEG by Huang et al. [33]
C1s	C–Si	283	283.2 ± 0.03	282.8	
	C–C/C–H	284	285.6 ± 0.05	285	285
	C–O/C–N	285.8	287.2 ± 0.05		286.5(/286.2)
	NHC=O		288.3 ± 0.06		288.1
O1s	O–Si	533	533.2 ± 0.02	532.3	
	C/NHC=O		531.8 ± 0.02		531.4/532.8
Si 3p 3/2	Si–C	100.8	100.8	100.8	
	Si–O	103.3	103.2 ± 0.02	103.3	

respectively, which is within the same range of adsorption as for PLL-g-PEG on SiO$_2$ (17.5 ± 0.7 nm).

3.2 Pin-on-Disc

3.2.1 Change of Lubricant

Figure 3 details an example of the evolution of the coefficient of friction (μ) on a self-mated sliding tribopair of Si$_3$N$_4$ at 120 mm/s under an applied load of 5 N. After an initial running-in period in HEPES 0 (<10,000 rotations), μ stabilized at around 0.02. After the addition of PLL-g-PEG solution, μ immediately decreased to about 0.003. Upon subsequent removal of the PLL-g-PEG, μ increased to around 0.009. In short, low μ obtained in buffer solution can be further lowered with the addition of PLL-g-PEG. However, when the experiments were performed with the changing of the lubricants in reverse order, the results are somewhat different. Figure 4 shows an initial μ value of a self-mated sliding contact of Si$_3$N$_4$ tribopair in PLL-g-PEG solution at 5 N applied load and 120 mm/s of around 0.03 (from ca. 5,000 to 20,000 rotation). Upon removal of the PLL-g-PEG solution and addition of HEPES 0 (at ca. 21,000 rotations), the μ is reduced to 0.01. After changing back to PLL-g-PEG solution (ca. at 40,000 rotations), μ is slightly reduced to 0.008.

3.2.2 Speed Dependence

Figure 5 details μ of Si$_3$N$_4$ at a slower speed of 10 mm/s with and without PLL-g-PEG in the aqueous lubricant at

Fig. 4 Pin-on-disc experiment of a Si$_3$N$_4$ pin against a Si$_3$N$_4$ disc at 185 mm/s under 5 N applied load. The experiment began with PLL-g-PEG as the lubricant. When the PLL-g-PEG was replaced with HEPES 0, after an initial period of running-in, μ decreased. After the HEPES 0 was then replaced with PLL-g-PEG solution, μ decreased further
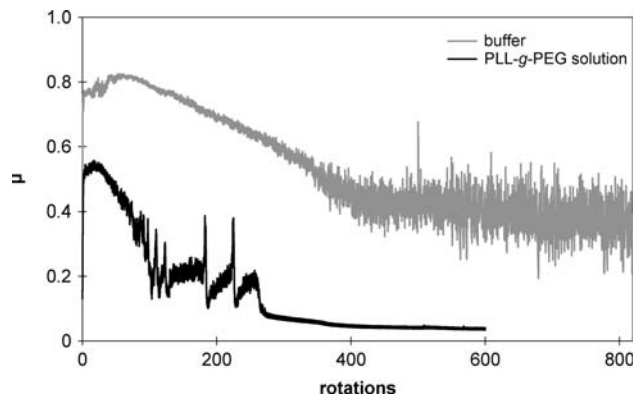
Fig. 5 Coefficient of friction (μ) of self-mated Si$_3$N$_4$ at a speed of 10 mm/s and applied force of 2 N lubricated with buffer and with PLL-g-PEG solution

2 N, with no running-in procedure performed. At this slow speed, μ was reduced tenfold from 0.4 with buffer alone to 0.04 with PLL-g-PEG solution. As shown in Fig. 6, the series of Si$_3$N$_4$ measurements conducted after running in reveals a clear reduction in μ in PLL-g-PEG solution under loads of 2 N at lower speeds. The dramatic reduction of μ is observed at speeds of 1.4 mm/s (0.91–0.20) and 17 mm/s (0.87–0.17). However, Si$_3$N$_4$ lubricated with buffer solution at high speed yielded a slightly lower μ value (0.02) than that of Si$_3$N$_4$ in PLL-g-PEG (0.04); this observation is consistent with Fig. 4, in which the μ values are slightly higher in PLL-g-PEG solution if the tribological contact occurs first in PLL-g-PEG solution, followed by contact in HEPES solution. PLL-g-PEG is thus most effective at low-to-medium speeds, which occur during start-up and in reciprocal motion.
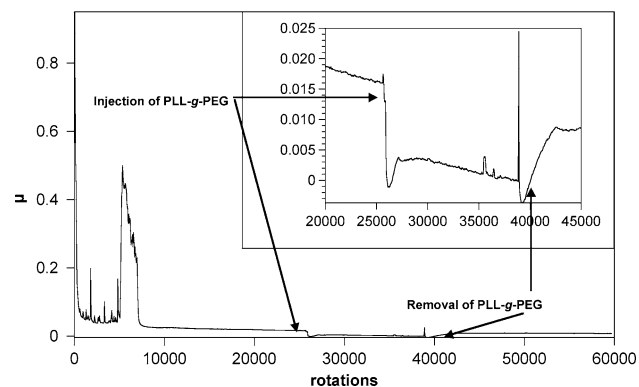

Fig. 3 Pin-on-disc experiment of Si$_3$N$_4$ pin against a Si$_3$N$_4$ disc at 185 mm/s under 5 N applied load. The experiment began with HEPES 0 buffer as the lubricant. The buffer was then replaced with PLL-g-PEG solution, after which an immediate reduction in friction can be seen. After the PLL-g-PEG is replaced with HEPES 0, the friction increases slightly
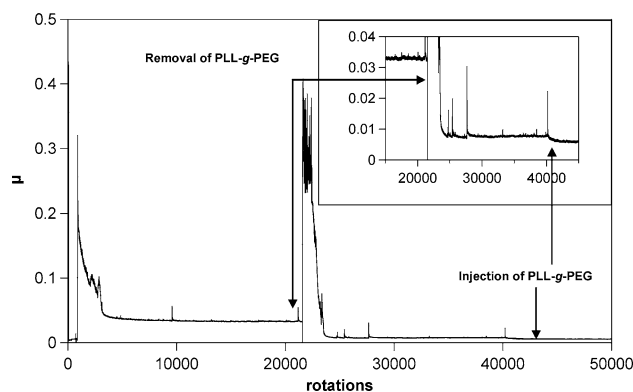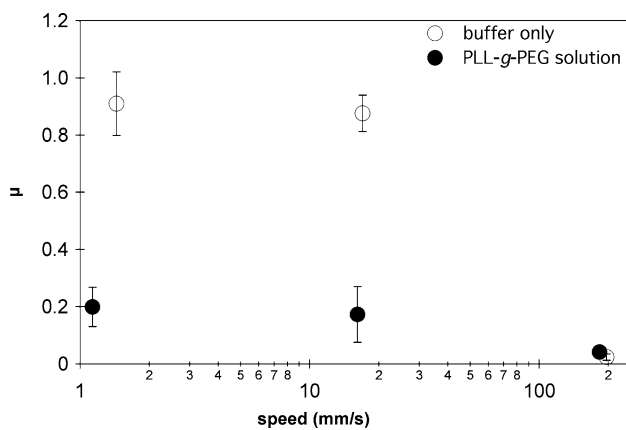
Fig. 6 Average coefficient of friction (μ) of self-mated Si_3N_4 under 2 N applied load at various speeds in buffer and in PLL-g-PEG solution
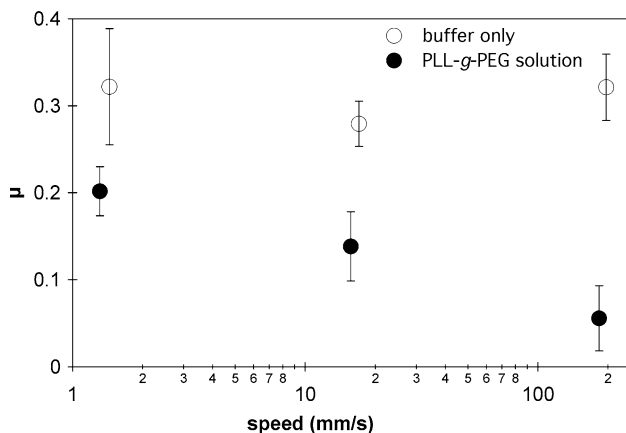

Fig. 7 Average coefficient of friction (μ) of SiC against SiC under 2 N applied load at various speeds in buffer and in PLL-g-PEG solution

PLL-g-PEG reduces μ in each of the studied speed regimes on SiC, as can be observed in Fig. 7. Although the μ values for SiC in buffer show no apparent speed dependence, a clearly decreasing trend of μ (from 0.20 to 0.06) with increasing speed (from 1.4 to 185 mm/s) is observed for the samples lubricated with PLL-g-PEG solution.

Fig. 8 Topography of the as-polished Si_3N_4 disc (*left*) as well as the wear track surface of Si_3N_4 after 30,000 rotations with 5 N applied force and 185 mm/s linear speed in HEPES 0 (*middle*) and PLL-g-PEG solution (*right*); larger fracture pits can be seen in the wear track of the sample lubricated with PLL-g-PEG solution
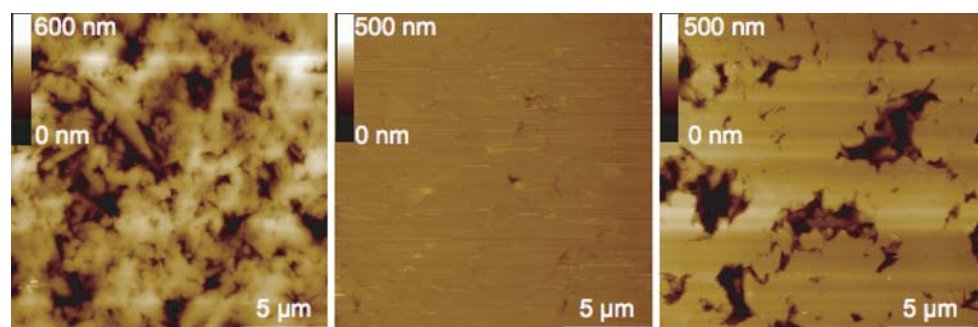
3.2.3 Wear-Track Morphology

A dramatic difference in the appearance of the wear track can be seen in the AFM images in Fig. 8. In comparison to the as-polished surface in Fig. 8 (left), the surface of the sliding track in HEPES 0 buffer is noticeably smoother; the microcracks, presumably created during the polishing process prior to testing, appear to have been significantly polished away, tribochemically. The topography of the Si_3N_4 surface lubricated with PLL-g-PEG shows a number of relatively large pits, larger than those of the as-polished surface, with smooth areas in between, suggesting both tribochemical polishing of the surface as well as micro-fracture induced by the tribocontact. Figure 9 (left) details the values for average roughness (R_a) and root-mean-square roughness (RMS) of the wear scars of the Si_3N_4 discs. In both cases, the roughness values for Si_3N_4 lubricated with PLL-g-PEG are approximately twice as high as the values for Si_3N_4 lubricated in HEPES 0. Finally, in Fig. 9 (middle), Si_3N_4 lubricated with HEPES 0 has wear scars approximately twice the width or diameter of Si_3N_4 lubricated with PLL-g-PEG. For SiC, little difference can be seen in the morphology of the wear tracks lubricated with HEPES 0 solution and with PLL-g-PEG solution, as seen in Fig. 10. No difference was seen in the roughness for Fig. 10 (middle) and (right), in which R_a was approximately 52 nm and RMS was around 65 nm.

4 Discussion

According to the ELM (Sect. 3.1.2) and XPS measurements (Figs. 1, 2; Tables 1, 2), PLL-g-PEG adsorbs onto both Si_3N_4 and SiC surfaces. Film thicknesses on both ceramics are similar to that measured on a Si wafer, and the typical components of PLL-g-PEG are visible within the XPS spectra. Possible chemical shifts of 0.2–0.3 eV in the SiN_4 and SiO_4 components of the Si 2p 3/2 peak may indicate that the adsorption of PLL-g-PEG occurs not only through the interaction with oxygen but with the nitrogen as well, suggesting that PLL-g-PEG could be used on other nonoxide surfaces, not only for lubrication but also for
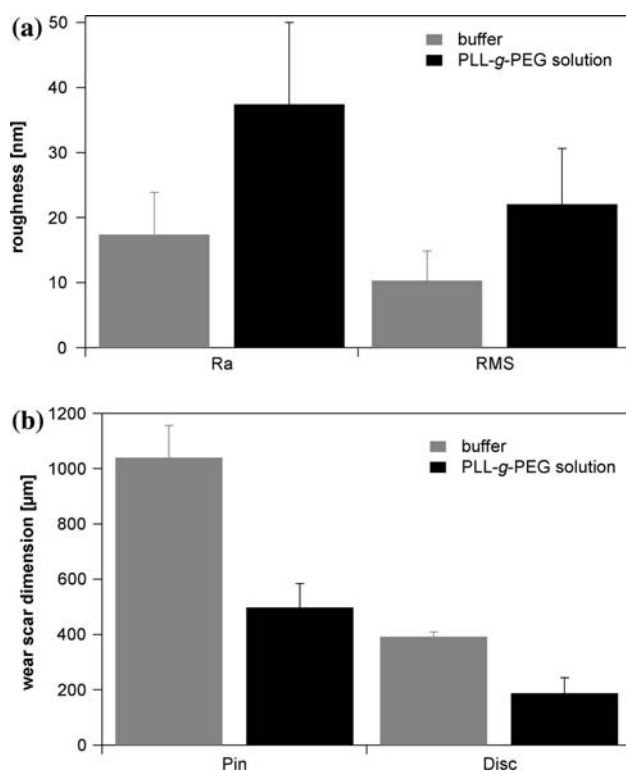
Fig. 9 Comparison of (**a**) R_a and RMS of the wear tracks and (**b**) dimensions of the wear scars (pin diameter and disc scar width) of Si_3N_4 pin-on-disc experiments of 30,000 rotations at speeds of 185 mm/s and 5 N applied load, lubricated with buffer and with PLL-*g*-PEG solution

prevention of nonspecific protein adsorption. However, it was not possible to detect any chemical shifts for SiC with the present analysis.

The morphological features of wear scars examined with AFM (Figs. 8, 9) suggest that tribochemical polishing occurs to a much lesser degree when the ceramic surfaces are lubricated with PLL-*g*-PEG than with HEPES 0; since former studies have observed extremely smooth surfaces when tribochemical polishing occurs [3, 5, 6, 10, 12, 13], it can be assumed that the smoother, lower-friction surfaces must be the result of the tribochemical polishing reactions. Below a certain threshold speed, which is around 40 mm/s

for Si_3N_4 [3, 12], wear occurs predominately via microfracture, whether it is in HEPES or in a PLL-*g*-PEG solution. At high speeds, the essential tribochemical reaction is believed to be partially inhibited by the PLL-*g*-PEG layer, causing wear to occur via both microfracture and tribochemical reaction. This is consistent with a previous study [42], in which the tribochemical reactions of Si_3N_4 with water to produce a smooth morphology are inhibited by the addition of NaCl, due to the strong interaction of Na^+ ions with the surface. The narrower wear scars observed for PLL-*g*-PEG-lubricated Si_3N_4 may further indicate an inhibition of tribochemical wear. Tribochemical wear occurs mostly at asperities; wear scar edges are also more chemically active than other surfaces, allowing the wear scars to propagate laterally. In the case of wear via microfracture, wear would only take place under the contact area vertically, and propagation at the edges would be slower.

In contrast to the distinct topographies of the differently lubricated Si_3N_4 surfaces, little difference in the wear tracks of SiC lubricated with HEPES 0 and PLL-*g*-PEG solution can be seen in the AFM images in Fig. 10. Similarly, both R_a and RMS roughness are around 90 nm for both HEPES 0-lubricated and PLL-*g*-PEG-lubricated samples. Since tribochemical wear is not expected at speeds lower than 500 mm/s [12], no difference is expected in the topography or the wear mechanisms of SiC lubricated with water or with PLL-*g*-PEG solution. Since tribochemical smoothening of SiC is only observed at speeds higher than 500 mm/s, and wear occurs predominantly via microfracture, it is not expected that the behavior of SiC observed is similar to that of Si_3N_4 at low speeds, where PLL-*g*-PEG is most effective as an aqueous lubricant additive.

The adsorption of PLL-*g*-PEG as characterized by XPS (Tables 1, 2), the dry film thickness (Sect. 3.1.2), and the reduction of friction at lower speeds for Si_3N_4 (Fig. 6) and at all tested speeds for SiC (Fig. 7) are all consistent with the view that the lubrication mechanism of PLL-*g*-PEG on these ceramic surfaces is similar to those discussed in previous investigations on oxide surfaces [18, 19, 22–25,

Fig. 10 Topography of the as-polished SiC disc (*left*) as well as the wear track surface of SiC after 30,000 rotations with 5 N applied force and 185 mm/s linear speed in HEPES 0 (*middle*) and PLL-*g*-PEG solution (*right*)
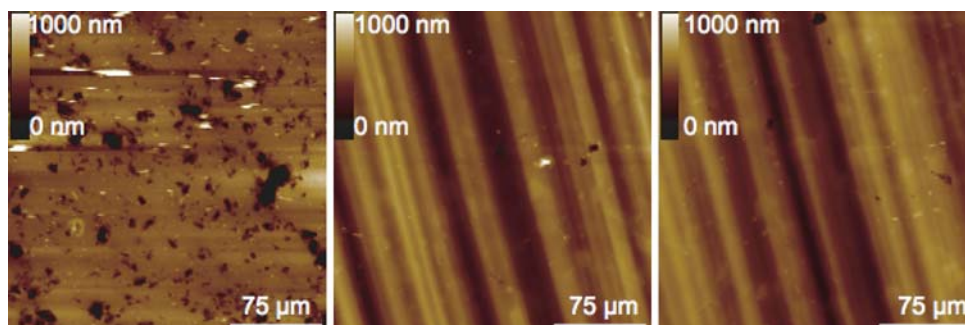
27–29, 43, 44]; PLL-*g*-PEG acts as a boundary lubricant additive via adsorption onto the ceramic surfaces and maintains the lubricating effect through a "self-healing" mechanism [24]. The only exception to this apparent boundary lubrication is in the case of sliding contact at high speed for Si_3N_4, as shown in Fig. 2. The magnitude of reduction in μ values by PLL-*g*-PEG under these conditions is less pronounced, mainly because the extremely low friction forces are already obtained upon lubrication in aqueous buffer solution alone. On the other hand, the fact that PLL-*g*-PEG further lowers the already-low friction achieved with buffer may suggest that a purely hydrodynamic lubrication regime is not reached with water alone under the conditions employed in this study.

5 Conclusions

PLL-*g*-PEG is an effective aqueous lubricant additive that can adsorb onto Si_3N_4 and SiC and lower the coefficient of friction at all speeds with SiC and at moderate-to-low speeds on Si_3N_4. At higher speeds on Si_3N_4, PLL-*g*-PEG partially inhibits the tribochemical reactions that lead to smooth surfaces, resulting in a combination of wear via microfracture and tribochemical polishing, and leading to rougher surfaces. However, coefficients of friction measured on Si_3N_4 in PLL-*g*-PEG solution are nearly as low as those in water alone, and can be further lowered at high speeds with PLL-*g*-PEG after performing a running-in procedure in water.

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