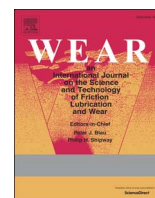




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Reduction in friction and wear of alumina surfaces as assisted with surface-adsorbing polymers in aqueous solutions

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ABSTRACT

We have investigated the aqueous lubricating effects of various polymers for the sliding contacts of self-mated alumina surfaces in neutral aqueous environment. Given that isoelectric point (IEP) of alumina is ca. pH 9, polyanions can readily adsorb onto alumina surface at neutral pH via electrostatic attraction and form a protective layer. For example, polyacrylic acid (PAA) showed a reduction in coefficient of friction by ca. 28% and wear rate by 50% at a concentration of 10 mg/mL in PBS solution compared to polymer-free buffer solution. This effect was comparable to reported lubricating effects at moderately acidic and or alkaline pH conditions via electrostatic repulsion between opposing bare alumina surfaces. Interestingly, polycations, such as (polyallylamine hydrochloride) (PAH) or branched poly(ethylene imine) (b-PEI) have also shown effective surface adsorption and lubrication at neutral pH, when phosphates (HPO_4^{2-}) are present to mediate the bonding between polycations and positively charged alumina. The present study thus provides various routes to lubricate alumina surfaces in aqueous environment by means of surface adsorbing polymeric additives without shifting from neutral pH.

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1. Introduction

Ceramics have many favorable properties for tribological applications, such as high thermal stability, high abrasion resistance, low deformability, and corrosion resistance [1–4]. In particular, corrosion immunity of ceramics allows them to be applicable as bearing materials under circumstances where exposure of tribosystems to water is unavoidable, such as in marine applications [5–8], high humidity [9,10], or biomedical applications [11,12]. Moreover, water can be employed as base lubricant for ceramic materials in engineering bearing systems [13–21]. An outstanding example is the lubrication of silicon nitride with distilled water; the coefficient of friction, μ , can be reduced from $\mu \approx 0.7$ to $\mu \leq 0.002$ with the increase of sliding speed from 2 mm/s to ca. 65 mm/s [13–15], which was attributed to favorable tribochemical reactions to generate extremely smooth surfaces and onset of hydrodynamic lubrication. However, this approach is applicable only for a few ceramic materials and under limited conditions, namely high speeds and high loads [16,17]. More broadly applicable methods to improve the aqueous lubrication properties of ceramics are highly desirable. For example, dispersion of surface-active additives in base stock is a universal approach to reduce friction and wear for oil-based lubricants, and it can be applied to

aqueous lubricants as well. Previous studies of employing ionic liquids [22,23] or polycationic-polyethylene glycol copolymer, poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG) [24], as additives have shown improved boundary lubrication properties for silicon nitrides in neutral pH aqueous solutions.

In this study, we are particularly interested in aqueous lubrication of alumina. In general, the friction forces of alumina-based tribosystems are known to be reduced as lubricated with water, but its efficacy is not significant, especially in low speed regime [17,25]. This is because, unlike the case of silicon nitride mentioned above, favorable tribochemical reaction to initiate surface smoothing does not readily occur because of the high mechanical and chemical stability of alumina. Novak and Kalin have reported that self-mated sliding of alumina displays particularly low wear rates due to electrostatic repulsion between either positively ($\text{pH} < 8$) or negatively (at $\text{pH} > 9$) charged surfaces [26], given the IEP of alumina is at ca. pH 8.8 [27]. Thus, superior tribological performance, i.e. lower friction and wear, is expected at either at acidic or alkaline conditions. At too high or low pH conditions ($\text{pH} \leq 1$ or ≥ 13), however, wear and surface smoothing via tribochemical reactions can be activated [26,28,29]. Electrostatic repulsion between opposing alumina surfaces at moderately acidic and alkaline condition can contribute to lower the interfacial friction forces too. Nevertheless, non-neutral pH is not a favorable means of aqueous lubrication. We conjecture that surface-adsorbing polymeric additives, which have shown to be effective in reducing friction and wear for many other tribological

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Table 1
Mechanical and surface properties of alumina-alumina tribological interface.

Material	Young's modulus (GPa)	Poisson's Ratio	Hardness (GPa)	Roughness, R_q (nm)		Pressure (MPa) at 10 N load
				Disk	Ball	
Alumina	370	0.22	13.4	1780 Worn: 144	14.3 Worn: 29.1	1340 ^a (Hertzian) 342 ^b , 17.1 ^c (Rough/worn at injection)

^a Minimum pressure assuming smooth sphere on smooth plane contact. Real contact pressure is probably higher due to roughness.

^b Calculated as flat-flat contact and assuming only contact at the top 25% of asperity height distribution, i.e. real area is 5% of apparent contact area. Pressures at local asperity contacts may be much higher. See also footnote and Greenwood and Williamson [38].

^c If the contact is perfect smooth flat-on-flat.

systems [30–32], can be employed to lubricate alumina surfaces at neutral pH condition too. As alumina is known to display exceptionally high isoelectric point (IEP) of $\text{pH} > 8$ among oxide ceramics [28], its surface is positively charged in neutral aqueous solution. Thus, polyanions or copolymers with anionic anchoring units can adsorb onto alumina surfaces via electrostatic attraction and potentially act as boundary lubricant additive [33–35] and can further modify the surface potential and tribological properties [36]. In this study, we demonstrate that negatively charged polyacrylic acid (PAA) or PAA-based copolymers indeed adsorb and lubricate alumina surfaces in neutral aqueous environment. Moreover, not only polyanionic macromolecules, but also polycationic macromolecules can lubricate alumina surfaces in neutral pH aqueous solutions when divalent phosphate salts are further employed to mediate the linking polycationic macromolecules to alumina surfaces.

2. Materials and methods

2.1. Alumina balls and disks

6 mm diameter alumina balls (1365 Vickers Hardness (13.4 GPa), Young Modulus of 370 GPa, Ultimate tensile strength 300 MPa, Poisson's ratio 0.22) were obtained from Boca Bearings (Boynton Beach, FL). 42 mm diameter alumina (> 99.6%) disks of 1440 Vickers hardness (14.1 GPa) were purchased from Graphitstore.com, Inc. (Lexington, IL). Roughness measurements were performed with tapping mode AFM, Bruker Dimension Edge (NanoScope v. 8.02 control software) and analyzed with NanoScope Analysis v. 1.40.

2.2. Polymers and formulation of aqueous lubricants

Poly(acrylic acid) (PAA(5.1 kDa)), PAA(250 kDa), poly(allylamine hydrochloride) (PAH(17 kDa)), branched poly(ethyleneimine) (b-PEI (800 Da)), poly(vinyl alcohol) (PVA(9 kDa)), poly(ethylene glycol) (PEG(5 kDa)), poly(sodium 4-styrenesulfonate) (PSS 70 kDa), and bovine submaxillary mucin (BSM) were all purchased from Sigma-Aldrich (Brøndby, Denmark) and used without further purification. The numbers in the brackets after the acronyms of the polymers represent the molecular weights. BSM is an amphiphilic biomacromolecule with reported molecular of 5–20 MDa [37]. BSM was purchased from Sigma Aldrich (Type I-S) too and used without further purification. Poly(acrylic acid)-graft-poly(ethylene glycol) (10 grafted PEG (1.8 kDa) side chains on a PAA (8.0 kDa) backbone and PDI 1.8) was purchased from Polymer Sources Inc. (Montreal, Canada). Phosphate buffered saline (PBS) was prepared as buffer (pH 7.4) by dissolving PBS tabs from VWR (BDH Prolabo) in MilliQ water (18 M Ω cm). Polymers or protein were initially dissolved at higher concentration in PBS and pH was adjusted by

HCl (aq.) or NaOH(aq.) to achieve pH 7.4 or 2.0. Then the targeted concentrate of polymer or protein was obtained by addition of PBS.

2.3. X-ray photoelectron spectroscopy (XPS)

A K-Alpha XPS with included flood gun from Thermo Scientific (Al K α radiation source) was used for the surface chemical analysis of the alumina samples before and after exposing to polymer or protein solutions. Thermo Avantage software v. 5.932 was used for the elemental data analysis. Two spots were measured for mean and standard deviation calculations. Alumina disks were polished with silicon carbide sand paper (Grit 1000) and cleaned by ultrasonication in Hellmanex (1 vol%) surfactant aqueous solution for 15 min, then in PBS for 15 min, and finally in MilliQ water for 15 min. After drying with nitrogen, the alumina disks were submerged or covered with buffer or 10 mg/mL polymer or protein solutions for 30 s. Then, the alumina disk was dipped in MilliQ water to gently remove non-adsorbed species, and finally blow-dried with nitrogen before XPS measurements commenced.

2.4. Friction and wear measurements

Aqueous lubricating properties of polymers for alumina-alumina interfaces were examined with a pin-on-disk tribometer, by employing 6 mm diameter alumina sphere sliding on a 3 mm thick alumina disk with 10 N load (dead weight) if not stated otherwise. The mechanical and surface properties of the tribosystems are presented in Table 1.

A standard procedure to assess the lubricating properties of a polymer is as follows: firstly, a sliding contact between alumina-alumina pair was allowed on a fixed track for 5000 laps at 50 mm/s in polymer-free buffer solution. Then, a concentrate additive solution (30 mg/mL) was added to the buffer solution to afford a final concentration of 10 mg/mL, and the sliding contact was continued for another 5000 laps. The decrease in the friction coefficient ($\mu = \text{friction force}/\text{load}$) was quantified by taking the difference in μ values before and after addition of the polymers, i.e. % reduction = $\{(\mu_{\text{buffer}} - \mu_{\text{polymer}})/\mu_{\text{buffer}}\} \times 100\%$, where μ_{buffer} is the average value over the first 5000 laps and μ_{polymer} is the average value over 5200–6200 laps. A friction drop of 2.5% was observed to occur on average for 5200–6200 laps when omitting addition of the polymers, thus this decrease in friction was subtracted in the calculation of % reduction in μ values. The initial 200 laps after the injection of polymer solution was excluded as μ values were generally not stabilized in that range. The results of average % reduction in μ values and standard deviations are shown in the legends of friction data plots (Figs. 2–4). Control experiments include the sliding contacts at lower sliding speeds (1 mm/s and 10 mm/s), where the alumina-alumina pair was slid for 30 min before injection and continued for another 30 min after injection. In this case, μ_{polymer} values were obtained from the range of

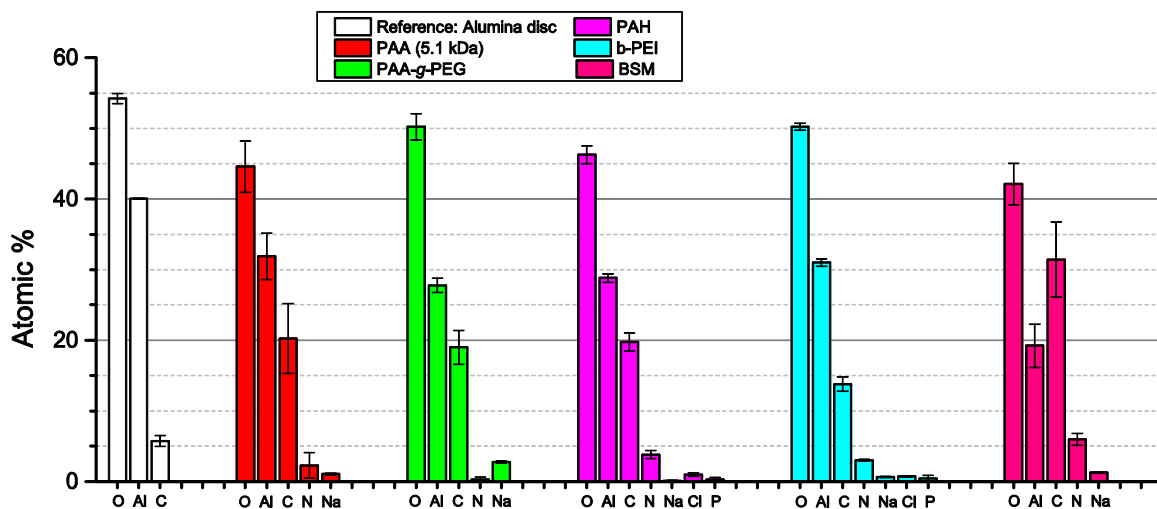


Fig. 1. XPS surface elemental analysis of alumina disk after dipping in polymer or protein solution (10 mg/mL) for 30 s.

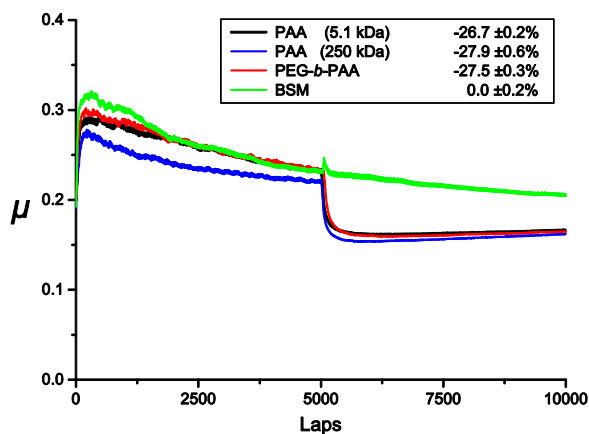


Fig. 2. Pin-on-disk tribometry of alumina-alumina interface in PBS (pH 7.4) with injection of polyanions or protein lubricant additives after 5000 laps. In legend, the percentage decrease designates the changes in average μ values (laps 5200–6200) relative to those before injection. Final concentration of PAA(5.1 kDa), PAA (250 kDa) PAA-g-PEG, and BSM was 10 mg/mL.

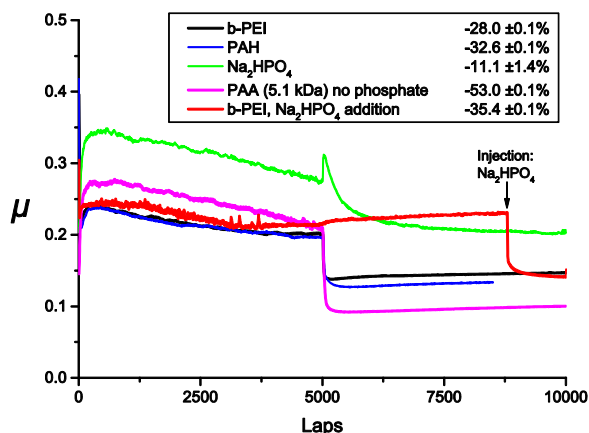


Fig. 3. Pin-on-disk tribometry of alumina-alumina contact with injection of polyelectrolyte or salt lubricant additives after 5000 laps if not stated otherwise. 10 mM Na_2HPO_4 was added to aqueous 150 mM NaCl pH 7.4 for samples ' Na_2HPO_4 ' and 'b-PEI, Na_2HPO_4 addition'. The average μ values of laps 9200–10,000 were used to assess friction drop for 'b-PEI, Na_2HPO_4 addition'. In sample 'PAA (5.1 kDa) no phosphate' the aqueous solution condition was 150 mM NaCl at pH 7.4. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).

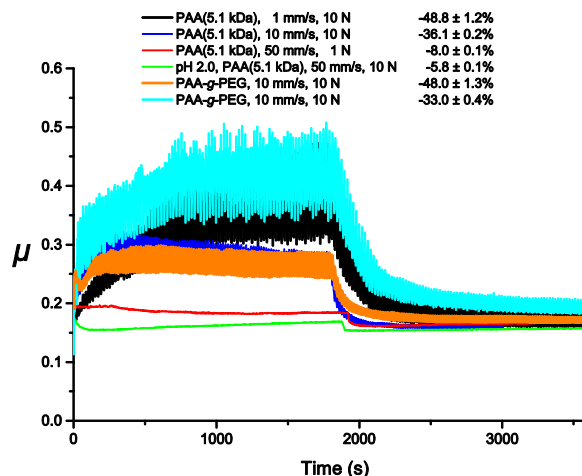


Fig. 4. Pin-on-disk tribometry of alumina contact polymer at non-standard conditions for μ vs. time. Due to different speed for each measurement, the x-axis was plotted in time (s) than laps for better relative comparison. 1900 s is equal to 5000 laps at 50 mm/s as plotted in Fig. 3. The average μ values of time 2200–3000 s was used to assess friction drop. Final concentration of polymer was 10 mg/mL.

time=2200–3000 s. Wear tests were carried out by performing sliding contacts under the respective conditions or lubricant (10 mg/mL) from the beginning of the experiment. The volume loss was characterized by examining the wear spot of alumina sphere from optical microscopic images. The base buffer was PBS at pH 7.4 if not stated otherwise.

3. Results and discussions

3.1. Adsorption of polymeric additives onto alumina surface

In this study, we have employed XPS to characterize the adsorption properties of various polymers onto alumina surfaces. Due to unexpected lubricating performance of polycations, such as b-PEI (800 Da) and PAH (17 kDa), to be addressed below (Section 3.4), their adsorption properties onto alumina surface was also studied by XPS. Dipping time of alumina disk into the polymer solutions was limited to 30 s because the friction experiments (see sections below) indicated that adsorption of the additives onto alumina disk surfaces progressed very rapidly, namely on the level of a few seconds. More importantly, in the present study, the

adsorption properties of the additives in a short time scale are more relevant to their lubricating properties; cyclic tribological stress applied in the pin-on-disk tribometry experiments enforces the initially adsorbed polymeric additives to desorb and the surface desorption/adsorption is continuously re-established in a very short time scale. Fig. 1 displays the elemental surface analysis of the alumina disks after dipping in 10 mg/mL solutions of the polymeric additives, then washing and blown-drying with nitrogen.

The reference “bare” alumina disk, immersed in buffer solution, showed $5.7 \pm 0.8\%$ carbon content, originated presumably from airborne carbon species [39,40]. In all cases of immersion into polymeric additive solutions, the carbon contents were observed to be higher than the reference. For instance, PAA(5.1 kDa), PAA-g-PEG, and PAH (17 kDa) showed the carbon content of ca. 20% and were not statistically distinguishable from each other. In contrast, b-PEI (800 Da) and BSM showed somewhat lower (ca. 15%) or higher (ca. 31%) carbon contents. PAA(5.1 kDa) and PAA-g-PEG showed a trace amount of nitrogen ($2.3 \pm 1.8\%$ and $0.3 \pm 0.3\%$, respectively), for which the origin is not clear. Nitrogen was also observed from PAH (17 kDa) and b-PEI (800 Da) of $3.8 \pm 0.6\%$ and $3.0 \pm 0.1\%$, respectively, which most probably originate from their nitrogen-containing repeating units, $(-\text{CH}_2\text{CH}-\text{CH}_2\text{NH}_2)_n$ and $(-\text{CH}_2\text{CH}_2\text{NH}-)_n$. However, the carbon-to-nitrogen % ratios were 5.2 and 4.6 for PAH (17 kDa) and b-PEI (800 Da), respectively, thus were higher than their net formulas. This discrepancy is ascribed to the additional adsorbing airborne carbon species as mentioned above. The nitrogen content was highest for BSM ($6.0 \pm 0.8\%$) among the additives, originating from its proteinaceous structure. Lastly, sodium was present in PAA (5.1 kDa) and PAA-g-PEG seemingly as counter ion (Na^+) to carboxylate groups. Likewise, chlorine was observed from PAH (17 kDa) and b-PEI (800 Da), probably as counter ion (Cl^-) for the positively charged $-\text{NH}_3^+$ and $-\text{NH}_2^+$ groups. Phosphorus was also observed from PAH (17 kDa) and b-PEI (800 Da). While it is not certain if phosphates (H_2PO_4^- , HPO_4^{2-}) in PBS act as counter ions for the polycations, divalent HPO_4^{2-} may act as chelating salt-bridge between amine groups and the positively charged alumina. See more discussion on this subject in Section 3.4. Presence of PO_4^{3-} is not realistic given the pK_a of HPO_4^{2-} is 12.3 [41].

Adsorption of PAA onto alumina surfaces is known to be achieved predominantly via hydrogen bonding at $\text{pH} < 4$ and electrostatic attraction at $\text{pH} = 5.0\text{--}9.2$ [35]. Several previous studies have reported facile adsorption of PAA onto alumina surface, within the range of $0.04\text{--}0.3 \text{ mg m}^{-2}$, depending on solution pH, molecular weight, and bulk concentration [33–35,42]. Nevertheless, nearly all of these studies were performed on alumina colloidal suspension whereas the information on the adsorbed amount of PAA on planar alumina surface is very rare to date due to a number of technical problems. In this study too, adsorption properties onto alumina disk by XPS (Fig. 1) were focused on the comparison of relative adsorbed amount among the polymeric additives. As carbon and oxygen signals have multiple origins, we judged that it would be most straightforward to determine the relative adsorbed mass from the reduction in aluminum element signal upon exposure to polymer solutions. The results show that BSM adsorbed to the largest extent onto alumina in that the atomic % signal reduction is the largest with respect to bare alumina disk, namely a drop from $40.1 \pm 0.03\%$ to $19.2 \pm 3.0\%$. In the same context, the relative adsorbed amounts were estimated to be in the order $\text{BSM} > \text{PAA-g-PEG} \geq \text{PAH (17 kDa)} \geq \text{b-PEI (800 Da)} \geq \text{PAA(5.1 kDa)}$. However, considering the overlapped standard deviations among the aluminum signals for the polymers as shown in Fig. 1, the magnitude of reduction in aluminum element is statistically comparable to each other. Moreover, the fact that aluminum element signal is reduced only to a half in all cases upon exposure to polymeric additives and it still comprises ca. 20% of the total signals indicates that a thick polymer layer was not

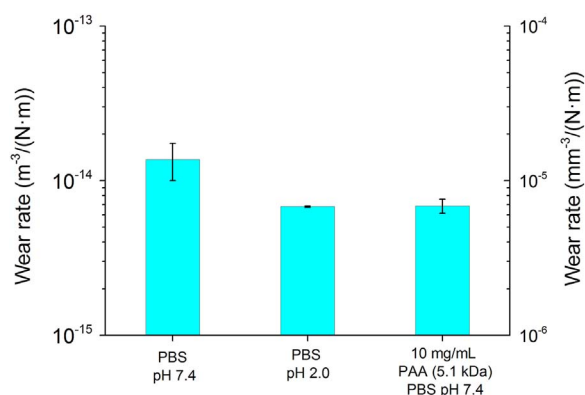


Fig. 5. Wear rates of alumina pin caused by sliding against alumina disk at 50 mm/s for 94.2 m (5000 laps).

formed on the alumina disk surface. Instead, the polymeric layers were either very thin or bare alumina surface was still exposed to a certain extent.

3.2. Lubrication by PAA

Fig. 2 shows the frictional responses of the sliding contacts of alumina-alumina interface in aqueous buffer to addition of various polyanions.

In these experiments, the lubricating effect was quantified by calculating % reduction in μ values after adding concentrated additive solution to the tribological contacts in buffer for individual measurement (Section 2.4). This was mainly because the sliding contacts of alumina-alumina interface in buffer did not provide the identical μ values and thus raw data may mislead the lubricating efficacy when μ values are directly compared in absolute values.

Addition of PAA led to immediate (less than 10 s after addition) decrease in μ values, reflecting fast adsorption kinetics of PAA onto alumina surface. PAA(5.1 kDa) clearly showed an ability to lower the friction of the sliding alumina-alumina contact by showing $26.7 \pm 0.2\%$ reduction in the μ values. PAA(250 kDa) was also tested in order to investigate the influence of molecular weight, but the relative decrease in μ values was comparable to that for PAA (5.1 kDa), namely $27.9 \pm 0.6\%$ (Fig. 2). One could expect that the polymers with higher molecular weight would provide higher adsorption stability, and thus more effective lubricity, as long as the chain conformation on surface of both PAAs remain ideally flat-lying [34,43]. As a control experiment, sodium acetate (10 mg/mL in the final concentration), corresponding to the monomeric units of PAA, was injected, but it did not induce any friction lowering effect on the sliding alumina-alumina interface (data not shown). This means that the lubricating effect of PAA (5.1 kDa) was not achieved simply via the adsorption of monomeric acrylic acid units to alumina surface, but some degree of polymerization was needed to enhance the anchoring strength of the adsorbate. On the other hand, linear homopolymers show increasing tendency to form loop conformation with increasing molecular weight on adsorbing solid surfaces. In turn, this can lead to bridging between the two opposing surfaces, and may contribute to increased adhesion and friction [44]. Nearly identical lubricating effects observed from the two PAAs in this study may be explained by that the difference in the molecular weight of the two PAA is not large enough to induce significant conformational changes or improved adsorption stability. Alternatively, it is also likely that extremely high contact pressure exerted on alumina-alumina interface may have suppressed any possible changes arising from the molecular weight (chain length) of PAA. If electrostatic repulsion between alumina surfaces with the same

charges at moderate acid or alkaline condition provides an effective lubrication as proposed by Novak and Kalin [26,28,29], adsorption of PAA onto positively charged alumina may reduce the electrostatic repulsion effect by charge compensation. The clear reduction in μ values by adsorption of PAAs onto alumina surface thus implies that suppression of direct contact between bare alumina surfaces by an organic layer overwhelms the reduced electrostatic repulsion, and eventually more beneficial for aqueous lubrication of alumina-alumina interface.

The initiation of changes in friction forces upon addition of the concentrated PAA solution occurred usually in less than 10 s. However, it should be noted that this fast frictional responses is largely indebted from the relatively high concentration of the added PAA solution (final concentration, 10 mg/mL). We propose that the concentration gradient is an important parameter to determine the efficacy of lubrication by PAA in this study; as the adsorption of PAA on alumina surface is primarily based on physisorption (electrostatic attraction), the films are easily removed by tribostress encountered in tribometry experiment. Thus, PAA layers on alumina surface can be sustained only when ample amount of PAA is available in bulk solution and thus continuous fast re-adsorption (“self-healing”) can take place [45]. A control experiment with a lower concentration (1 mg/mL) of PAA(5.1 kDa), for example, showed only a 4.5% reduction in μ values (Fig. S1, Supplementary Material).

While all the experiments with PAA discussed above were conducted under 10 N load, a control experiment with PAA (5.1 kDa) as shown in Fig. 2, yet under a higher load (25 N) was carried out. Even though the μ values, both before and after injecting PAA(5.1 kDa) solution (30 mg/mL) into buffer solution, were somewhat higher, the % reduction (28.2%) was comparable to that of the 10 N case. This observation suggests that the lubricating performance by PAA(5.1 kDa) might be effective even for a higher load range and deserves further investigation in the future. The results are presented in Fig. S2, Supplementary Material.

PSS has previously shown to adsorb onto alumina, thus it was conjectured that such a strong polyelectrolyte would provide lubricity to the sliding alumina contact as well [46]. However, when 10 mg/mL PSS (70 kDa) in PBS pH 7.4 was injected only a marginally drop ($4.2 \pm 0.4\%$) in friction was observed (Fig. S3, Supplementary Material). Thus, the interaction strength between the alumina and negative benzene-sulfonate groups are not as strong as to the PAA, indicating that PAA-alumina have characteristic electrostatic static bonding.

3.3. Lubrication by PAA-g-PEG and BSM

Following the effective performance of PAA as polymeric additive to lubricate the sliding interface of alumina-alumina, a graft copolymer, namely PAA-g-PEG, was employed for comparison. Two or more constituent polymers in a copolymer may display selective solubility to solvent and/or affinity to the substrates. In the case of PAA-g-PEG, while both PEG and PAA show excellent solubility in water, PAA only shows effective affinity to alumina surface at neutral pH via electrostatic attraction. Thus, PAA backbone in PAA-g-PEG copolymer is expected to act as anchor onto alumina surface, whereas grafted PEG side chains stretch out to bulk water to attract solvent (water) and can possibly improve the lubricating capabilities compared to PAA alone [47,48]. The results showed that the reduction in the μ values by PAA-g-PEG was $27.5 \pm 0.3\%$ (Fig. 3), which is comparable to that by PAA(5.1 kDa) and no particular improvement was observed in the lubricating properties.

For the particular PAA-g-PEG in this study, a low grafting density of PEG chains along the PAA(8 kDa) backbone (one per every eleven acrylic acid monomer units) may hinder extensive

stretching of PEG side chains (1.8 kDa) to form “brush-like” conformation. Nevertheless, nearly identical lubricating effect of the PAA-g-PEG with PAA(5.1 kDa) cannot be ascribed to low grafting density of PEG chains only, as some extent of improvement was reported from steel-glass interface under a similar condition [47]. We propose that extremely high contact pressure of alumina-alumina interface (estimated to be ca. 342 MPa, Table 1) may have overwhelmed their pressure-opposing effects expected from the osmotic pressure. The contact pressure exerted on the contact area is more than one order of magnitude larger than the maximum osmotic pressure achievable by polymer brushes that are commonly available, i.e. ca. 15–25 MPa as reported in literature [49–51].

BSM has previously shown facile adsorption and lubrication of non-polar surfaces [52,53], but corresponding studies on ionic surfaces are scarce to date. While the XPS data in the previous section confirmed the facile adsorption of BSM onto alumina surface, addition of BSM did not give any lubricating effect. Inefficient and inferior lubricating properties of BSM to PAA or PAA-g-PEG could be due to lower charge density on BSM, which may lead to relatively weaker adsorption strength on alumina surface and lower hydration.

3.4. Lubrication by polycationic additives

It was most interesting to observe that the two polycations in this study, namely PAH (17 kDa) and b-PEI (800 Da), have also provided significant reductions in the μ values, $28.0 \pm 0.1\%$ and $32.6 \pm 0.1\%$, respectively, upon addition to the sliding contacts of alumina-alumina interface, similarly with the polyanions (Fig. 3).

The lubricating capabilities of polycationic b-PEI (800 Da) and PAH (17 kDa) are consistent with their adsorption properties shown in XPS data (Fig. 1) and further support the strong interaction with the positively charged alumina. This is surprising and counter-intuitive from a Coulombic interaction viewpoint as mentioned above. Two possible interaction mechanisms can be proposed for the alumina-polycation interaction. Firstly, hydrogen bonding between the polycations and alumina surface can be strong enough to overcome the electrostatic repulsion between them. pK_a values of 8.8 and ca. 8.18–9.94 have been reported for PAH and b-PEI, respectively, thus some of the amine repeating units are expected to be non-charged at pH 7.4 and can participate as either hydrogen bonding donor or acceptor [54]. As an indirect way to test this hypothesis, PVA (9–10 kDa) or PEG(5 kDa), representing strong hydrogen bonding donor and receptor, respectively, were added to the sliding alumina-alumina contacts (10 mg/mL final concentration). Nevertheless, no friction decrease was observed for neither PVA nor PEG (data not shown), which suggests that hydrogen bonding is probably not a major contributing factor. Secondly, phosphate ions from Na_2HPO_4 in PBS may act as a mediator between two positively charged substances (polycations and alumina surface). To test this hypothesis, a control experiment was conducted by employing an aqueous solution containing 150 mM NaCl at pH 7.4, yet excluding phosphates, as base lubricant. Upon addition of b-PEI (800 Da) to the buffer where alumina-alumina sliding contact is taking place, virtually no change in the friction was observed (data in red lines in Fig. 3). However, when Na_2HPO_4 (10 mM) was further added in the same solution, a clear and immediate decrease in the μ value by $35.4 \pm 0.1\%$ was observed. In fact, addition of Na_2HPO_4 (10 mM) alone into 150 mM NaCl water pH 7.4 also resulted in $11.1 \pm 1.4\%$ reduction in μ values. Even though the reduction in μ is not large by Na_2HPO_4 alone, this observation confirms a strong affinity of phosphate ions on alumina surface. Moreover, by employing 10 mM HEPES buffer salt with 150 mM NaCl buffer solution, another common neutral buffer without phosphate as base lubricant,

only a minor decrease of $10.0 \pm 2.3\%$ in μ value was observed (data not shown) by b-PEI (800 Da) injection. Both control experiments support the critical importance of phosphate ions to induce lubricating effects by the polycations for alumina-alumina interface in neutral buffer solutions.

Based on all the experimental results in this section, we propose that phosphate-mediate adsorption of polycations can occur as follows. Most inorganic aluminum phosphates have very low solubility in water, implying strong electrostatic forces between the ions [55,56], hence increasing the stability of the alumina-phosphate salt bridge to polycations even under strong tribostress. Furthermore, both PAH and b-PEI have in other studies were observed to bind to phosphates and form aggregates [57,58]. As shown in Fig. 3, removing phosphates from the PAA (5.1 kDa) solution increased the friction reduction to $53.0 \pm 0.1\%$ from $26.7 \pm 0.2\%$ in the buffer, despite the presence of 150 mM NaCl. This suggests adsorption competition between PAA and phosphates, i.e. PAA seemingly can adsorb more strongly – thus affording lower friction – when omitting phosphates in solution.

Inspired from the interesting mediator role by phosphate ions, a similar experiment with those shown in Fig. 3 was conducted by employing SO_4^{2-} as another divalent salt mediator (Na_2SO_4). Addition of b-PEI (800 Da) (10 mg/mL) into the tribocup where alumina-alumina sliding contact is taking place in an aqueous solution (10 mM Na_2SO_4 + 150 mM NaCl), however, did not lead to any reduction in μ values (data not shown). Thus, presently, the unique function as a mediator between polycations and alumina surfaces in neutral aqueous solution should be limited to Na_2HPO_4 .

3.5. Lubrication by PAA: at lower speeds, lower loads, and acidic pH

Fig. 4 shows additional experiments to investigate the lubricating properties of PAA (5.1 kDa) at alumina-alumina interface by varying parameters, such as sliding speed, load, and pH of aqueous solution, from the standard conditions (Section 3.3).

For instance, sliding contacts between alumina surfaces at linear sliding speeds of 1 mm/s or 10 mm/s resulted in greater reduction in the μ values with decreasing speed, namely $48.8 \pm 1.2\%$ and $38.1 \pm 0.2\%$, respectively, compared to the case of 50 mm/s (Fig. 2). This is, however, because the μ values of alumina-alumina interface in buffer solution was gradually increasing with decreasing speed, reaching $\mu=0.35$ – 0.4 at 1 mm/s, whereas the μ values for PAA-lubricated contacts were rather similar at all speeds. The sliding contact of alumina-alumina interface under much lower load, namely 1 N, showed lower friction coefficients in buffer solution. In an ideally elastic contact, the coefficient of friction is expected to be inversely proportional to load with a power of $-1/3$ [59]. Thus, increasing μ values with increasing load in the sliding contacts between alumina surfaces imply that some other energy dissipation modes than interfacial friction, such as plastic wear from ploughing/abrasion, are active. The assessment of wear properties is discussed below (see Section 3.6). Meanwhile, nearly identical μ values observed from the alumina-alumina interface as lubricated by PAA (5.1 kDa) solution at both 1 and 10 N load suggest that the friction lowering effect by PAA (5.1 kDa) is more pronounced under higher contact pressure. Moreover, nearly constant μ value of ca. 0.17 for the alumina-alumina interface over the speed range of 1 mm/s to 50 mm/s as lubricated by PAA(5.1 kDa) is another indication of the prevalence of boundary lubrication.

In order to investigate if protonated, non-charged PAA also shows lubricating effects at the sliding alumina-alumina contact, a pin-on-disk tribometry experiment was performed at pH 2. As PAA's pK_a is reported to be 6.12, and alumina increases its positive zeta potential with decreasing pH lower than its isoelectric point, electrostatic attraction between them is nearly impossible at pH

2.0 [60]. PAA(5.1 kDa) was able to decrease the relative friction by $5.8 \pm 0.1\%$ at pH 2.0 only, as compared to $26.7 \pm 0.2\%$ decrease at pH 7.4 in PBS buffer. This suggests that PAA molecules are still able to bind to alumina surface in the sliding interface at pH 2.0 to some extent, most likely via hydrogen bonding, but the adsorbed amount is not significant and/or anchoring is not as strong. It is to note that μ values at pH 2.0 before addition of PAA were already lower than those at pH 7.4 (Fig. 5), which can be explained by the repulsion effect between the alumina surfaces at pH 2.0 as suggested by Novak and Kalin [26,28]. The larger decrease in μ values by PAA at pH 7.4 can thus be interpreted to arise from superior adsorption in amount and/or strength via electrostatic interaction between carboxylate groups and $\text{AlO}-(\text{OH}_2^+)$.

3.6. Wear rates of alumina pin

Lastly, the influence of PAA(5.1 kDa) on the wear properties of alumina-alumina sliding interface was evaluated by comparing the wear rates of alumina pins lubricated with PAA polymer solution (concentration, 10 mg/mL in PBS) and those with polymer-free buffer solution. Optical microscopic images of wear spots of alumina pins and disks are shown in Fig. S4, Supplementary Material (Please also see AFM images of alumina disk before and after wear in Fig. S5, Supplementary Material). In order to compare the reduction in wear rates as assisted by the adsorbed PAA vs. electrostatic repulsion [26], a wear experiment was conducted at in polymer-free, buffer at pH 2.0 as well. The results are shown in Fig. 5.

PAA(5.1 kDa) solution reduced the wear rate of alumina by 50% compared to buffer at pH 7.4. Furthermore, the magnitude of reduction in the wear rate by 10 mg/mL of PAA(5.1 kDa) was comparable to that by acidic aqueous solution at pH 2.0. This is similar to the frictional properties in that alumina-alumina contacts under 10 N reaching $\mu=0.16$ – 0.17 when it is lubricated by either PAA solution (10 mg/mL) or acidic buffer (pH 2.0) (Sections 3.2 vs 3.5). In turn, this means that comparable lubricating performance with moderately acidic or alkaline pH aqueous solutions [26] can be achieved even at pH 7.4 as long as it is assisted by PAA anionic homopolymer. Hence, more complex – and expensive – structures like graft copolymer PEG-g-PAA are not required to afford lubricity and lower wear in self-mated alumina sliding contact.

The impact of alumina wear particles on the subsequent tribological process is debatable; Fischer and Chaiwan reported that wear debris in dry alumina contacts were grinded into fine soft powder, concentrated in surface pits, and did not induce a secondary abrasive wear mechanism. But, it does not necessarily exclude the possible contribution to higher friction and/or if the wear particles bond to injected PAA or PAA-g-PEG, thus influencing both the friction and wear effects in the sliding interface [61,62].

4. Conclusions

In this study, we have shown that the friction and wear properties of alumina-based tribosystems in aqueous environment can be readily improved when polyanionic macromolecules are added as surface-adsorbing additives by employing PAA as a principal example. Negatively charged PAA molecules readily adsorb onto positively charged alumina surface at neutral pH and the high bulk concentration (10 mg/mL) allows for continuous replenishment of the polymers that are sheared off from the surface due to tribological stress. Due to extremely high contact pressure at the self-mated contact between alumina (> 300 MPa under 10 N in this study), however, the sliding contacts of alumina-alumina interface in PAA solution were dominated by boundary lubrication and the %

reduction in friction coefficient was saturated at 25–30% in high-speed regime and ca. 50% in low-speed regime, respectively. In the same context, PAA-g-PEG did not provide any further improvement in the lubrication effect compare to PAA, despite its potential as brush-forming capabilities. It was most interesting to observe that polycationic macromolecules, such as PAH and b-PEI, also lubricated the sliding alumina-alumina interface to a similar extent with PAA. Control experiments have revealed that salt bridging by negatively charged divalent phosphate salt is indispensable for the adsorption of positively charged PAH and b-PEI onto also positively charged alumina surface. However, divalent sulfate salt did not show the same effect on PAH and b-PEI. Bovine submaxillary mucin (BSM) did not show any lubricating effect probably due to too few anchoring sites. The results in this study are significant in practical applications because aqueous lubrication of alumina-alumina interface has been considered most effective at either acidic or alkaline conditions via electrostatic repulsion between the opposing surfaces, whereas the present study provides an alternative and general means to improve the lubricating properties at neutral pH conditions.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.wear.2016.09.025>.

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