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RESEARCH ARTICLE

Adjustable superlubricity system using polyalkylene glycol with various acid aqueous solutions

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Abstract: Polyalkylene glycol (PAG) aqueous solutions have recently been demonstrated to exhibit an ultralow friction coefficient (COF, $\mu < 0.01$). However, the prolonged running-in period and low bearing capacity have limited its widespread application. In this study, we determined that the running-in period can be decreased by more than 75% when the pH value of the lubricant is controlled at 3 by introducing various acid solutions. Additionally, less time was required to realize stable superlubricity with inorganic acid at lower pH values. This was mainly attributed to the acceleration effect of hydrogen ions around the contact region. In case of PAG aqueous solution with organic acid, the wear loss between sliding solid surfaces was reduced, and thus the bearing pressure during the superlubricity period was significantly improved from approximately 30 to 160 MPa. Furthermore, the organic acid molecules were considered to form strong hydrogen bonds with PAG macromolecules and solid surfaces. This in turn strengthened the structure of the adsorption layers. The unique effect of different acids in aqueous polymer lubrication can potentially significantly aid in advancing the study of polymer tribology and broadening industrial applications.

Keywords: superlubricity; running-in time; bearing pressure; organic acid; hydrogen bond

1 Introduction

Harmful friction and wear are ubiquitous and affect our daily life. Specifically, friction can lead to poor surface quality and enormous loss of material and energy. Although many types of traditional lubricants have been used to mitigate friction and wear in mechanical systems, their lubricating performance cannot satisfy the smooth functioning requirements given the development of ultra-precision manufacturing technology and nanoscience [1–3]. In the 1990s, superlubricity was proposed by Hirano and Shinjo to describe an ideal condition in which friction was minimized [4]. Since this concept was proposed, it has attracted significant attention. Furthermore, many studies have been conducted to realize ultralow friction during the sliding process [5–10]. In the last decades, in addition to solid super-lubricants [11–13], breakthroughs have been made in extant studies to realize liquid superlubricity because water has been proven to be an environmentally friendly solvent for generating particular physicochemical reactions with surfaces [14–17]. Ceramic materials [18–20], polymer brushes [21–23], and hydrogels [24–26] exhibit negligible friction when used as frictional pairs in aqueous environments. Meanwhile, some liquids, such as phosphoric acid solutions [27], alkali salt solutions [28, 29], and biological mucus [30–32], have also been proven to reduce friction to near zero levels when selected as lubricants between sliding solid surfaces. It is important to note that water-soluble polymers are able to firmly adsorb on

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surfaces with chains stretching freely in an aqueous environment. This is favorable for forming boundary lubrication layers to lower shear strength and realize superlubricity [33–35].

Polyalkylene glycols (PAGs) are a class of synthetic copolymers polymerized by ethylene oxides and propylene oxides, and they are widely used as important industrial lubricants. Additionally, owing to their excellent film-forming ability and high levels of oxyethylene groups, PAGs are soluble in water at any proportion and adsorb on contact surfaces [36]. Recently, owing to their superior hydration ability and adsorption characteristics, PAGs were observed to exhibit a superlow coefficient of friction (COF) in an aqueous environment when used to lubricate sliding ceramic surfaces [33]. Aqueous solutions of PAGs with various molecular weights can lead to stable superlubricity with a minimum COF value of approximately 0.002 over a wide range of concentrations [35, 37]. By adjusting the applied contact pressure, viscosity of lubricant, and relative sliding speed between sliding surfaces, a controllable superlubricity system of PAG aqueous solutions was established. This provides a comprehensive guide for controlling the superlubricity state and selecting appropriate water-based polymer lubricants [38]. However, for most PAG aqueous solutions, an extremely long running-in period is usually required before ultralow friction is realized. This in turn leads to severe wear on the solid surfaces and weak load-carrying capacity at superlubricity. Thus, a reduction in the running-in time while improving the load-carrying capacity at superlubricity can significantly facilitate and expand the application of PAG aqueous solutions. In this study, we determined that moderate addition of acid aid in reducing the running-in time of PAG aqueous solutions. When selecting PAG aqueous solution with inorganic acid as a lubricant, hydrogen ions in the solution enhance the tribological reaction during the sliding process. This in turn accelerates the wear rate, and thereby reduces the running-in time. With respect to the selection of PAG aqueous solution with organic acid as a lubricant, the addition of organic acid contributes to reducing the area of worn region and improving the bearing pressure at superlubricity. Hence, it is inferred that organic acid molecules in solution form hydrogel bonds with PAG macromolecules and solid surfaces. This enhances the adhesion strength of the adsorbed polymers and thereby improves the load-carrying capacity during the superlubricity process.

2 Materials and methods

2.1 Materials

In the tests, PAGs of HB-400 in the UCON 50-HB series, which were synthesized using equal amounts of ethylene oxide and propylene oxide, were used. These PAGs are comedies from the Dow Chemical Company with a high purity of over 99%. Formic acid (analytical reagent, 99%), acetic acid (analytical reagent, 99%), butyric acid (analytical reagent, 99%), nitric acid (analytical reagent, 99%), sulfuric acid (analytical reagent, 99%) were procured from Shanghai Aladdin Bio-Chem Technology Co., Ltd. They were selected to prepare acid solutions with different pH values.

2.2 Preparation of the acidic PAG aqueous solutions

First, pure PAG was dissolved in deionized water to prepare a 60 wt% PAG aqueous solution, where the weight fraction of the PAG in the solution was 60 wt%. The mixed solution was placed in an ultrasonic bath for 20 min to increase its stability. Then, the formic acid solution, acetic acid solution, butyric acid solution, nitric acid solution, and sulfuric acid solution were added to the 60 wt% PAG aqueous solution to prepare acidic PAG solutions at pH values of 2, 3, 4, and 5, respectively. A pH meter (FiveEasy™, Mettler Toledo), with an accuracy of ±0.01, was used to measure the pH variation of the solution during the dripping process and ensure the final pH value.

2.3 Tribological tests

Reciprocating tribological tests were performed on a universal micro-tribometer (UMT-3) procured from Bruker (USA) by using a ball-on-disk mode. A Si_3N_4 ball with a diameter of 4 mm and an Al_2O_3 substrate were selected as the solid sliding surfaces. The roughness of the surfaces was less than 10 nm. A constant normal load of 3 N was applied during the frictional process, which was controlled by a 2D sensor with a precision of 0.25 mN. The instantaneous normal force and friction force were recorded every 0.04 s. The reciprocating stroke was set to 3 mm with an average linear speed of 24 mm·s^{-1}. Meanwhile, the temperature was maintained at approximately 25 °C throughout the duration of the experiments with a relative humidity of approximately 30%.

2.4 Characterizations of the worn region

After the tribological evaluation, the Si_3N_4 ball and sapphire were cleaned with acetone, ethanol, and deionized water in an ultrasonic bath for 15 min to remove the residual liquid. The morphology of the contact regions on ball and sapphire was observed using an optical microscope (Olympus BX60) and a white light interferometer (ZYGO Nexview). The changes in the chemical components in the contact region of the ball were analyzed via X-ray photoelectron spectroscopy (XPS).

3 Results and discussion

In the study, three types of PAG-related samples, including the original PAG aqueous solution (≈ 55 mPa·s), PAG aqueous solution with sulfuric acid at pH of 3 (≈ 59 mPa·s), and PAG aqueous solution with acetic acid at pH of 3 (≈ 56 mPa·s), were selected as lubricants for tribological tests. The evolution of the friction coefficient with time between the ball-on-disk surfaces is shown in Fig. 1(a), and the relationships between the stable COF and time before the stabilized COF (running-in period) are shown in Fig. 1(b). For the original PAG aqueous solution, approximately 7,000 s were required for the running-in period to slowly decrease the COF to a value of approximately 0.0025. This is in accordance with our earlier research on neutral PAG aqueous solutions [35]. However, the PAG aqueous solution displayed distinct frictional behavior after the introduction of acids. Specifically, only 700 s were required for the PAG aqueous solution with sulfuric acid to finish the running-in process, which was followed by a sharp decrease in COF until it decreased to a superlow value of approximately 0.0028. The PAG aqueous solution with acetic acid was observed to enter the superlubricity regime in less time with the stabilized COF at approximately 0.0034. The images of the worn region on Si_3N_4 ball and the final contact pressures for these lubricants at superlubricity are shown in Fig. 2. For the original PAG aqueous solution, the diameter of the worn region was approximately 390 μm, corresponding to an average contact pressure of approximately 27 MPa, and the diameter of the PAG aqueous solution with sulfuric acid was approximately 318 μm, corresponding to an average contact pressure of approximately 37 MPa. It is evident that the diameter of the worn region, lubricated by the PAG aqueous solution with acetic acid, was measured as approximately 166 μm, and the corresponding average contact pressure was approximately 140 MPa. This was significantly increased by more than three times when compared with that of the other solutions. Moreover, 3D morphology of the ball with a white light interferometer revealed certain cracks in the worn region. They were observed owing to the severe wear during the running-in time. When compared to the worn region lubricated by the original PAG aqueous

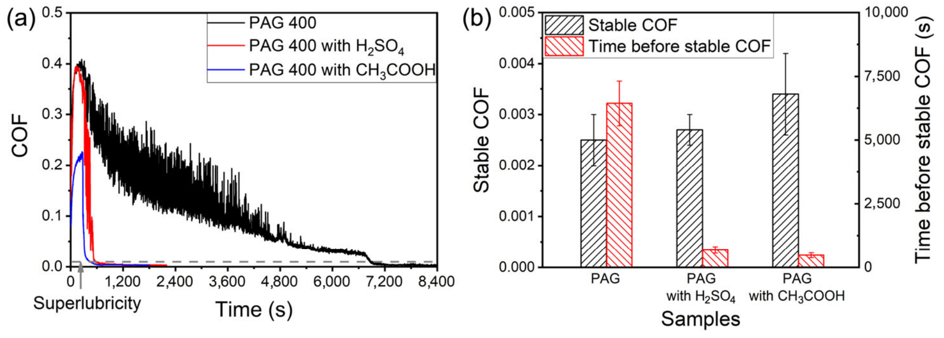

Fig. 1 (a) Evaluation of friction coefficient with time, and (b) time for realizing stable COF and final diameters of the worn region when lubricated by original PAG aqueous solutions and PAG aqueous solutions with acids at pH of 3.

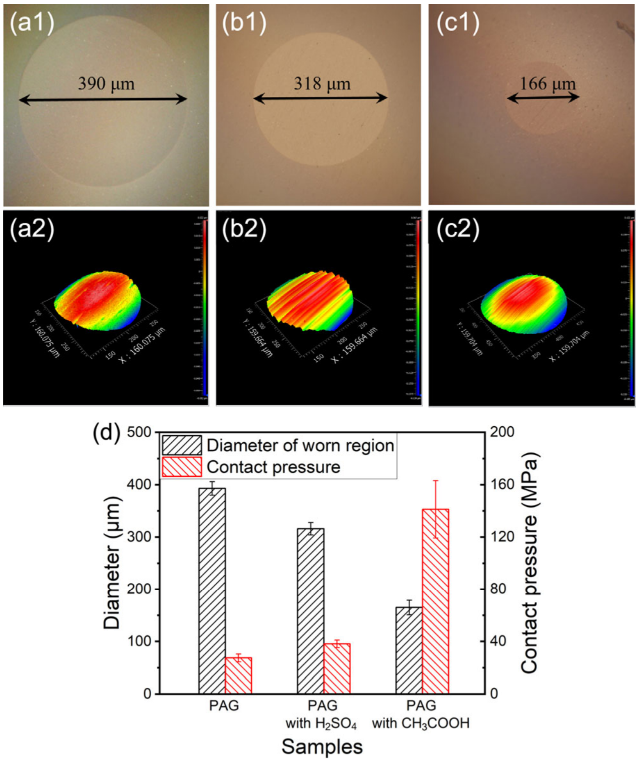

Fig. 2 Optical images (a1, b1, c1) and 3D morphology (a2, b2, c2) of the worn region on ball lubricated by (a1, a2) the PAG aqueous solution, (b1, b2) PAG aqueous solution with sulfuric acid, and (c1, c2) PAG aqueous solution with acetic acid. (d) Diameter of worn regions and the corresponding contact pressures.

solution, more grooves were formed in the worn region lubricated by PAG aqueous solutions with acids. The grooves can potentially originate from the chemical erosive effect enhanced by hydrogen ions in the solution. Thus, it can be inferred that although the concentration and viscosity are controlled, the addition of acid probably significantly impacted the tribological processes of PAG aqueous solutions, including reducing the running-in time for realizing superlow COF, influencing the surface quality of the worn regions, and improving the final contact pressure at superlubricity.

To further study the effect of acids, the minimum film thickness $h_{\min}$ can be calculated based on the Hamrock–Dowson theory, and it is evaluated by the following formula:

$$h_{\min} = 3.63\frac{U^{0.68}G^{0.49}R}{W^{0.073}}(1-\mathrm{e}^{-0.68k}) \tag{1}$$

where $U=\eta_0 u/ER$, $G=\alpha E$, and $W=F/ER^2$. Furthermore, η_0 and u donote the shear viscosity of the liquid lubricant and the average relative viscosity between the sliding surfaces, respectively. α is the pressure–viscosity coefficient of the liquid lubricant, and it corresponds to 7×10^{-9} Pa^{-1} for the fluids. F is the normal load, and k (≈ 1) is the ellipticity of the ball. To satisfy the application requirement of Hamrock–Dowson equation, the measured contact area shuold be transferred to the Hertz contact area with the equivalent radius R [33, 39], which can be calculated by Eq. (2) as

$$R=\frac{ED^3}{6F} \tag{2}$$

where D denotes the diameter of the worn region on ball, and E is the effective modulus of elasticity of the friction pairs, which can be described by Eq. (3) as

$$E=1\bigg/\left(\frac{1-v_1^2}{E_1}+\frac{1-v_2^2}{E_2}\right) \tag{3}$$

where ν_1 (≈ 0.25) and ν_2 (≈ 0.22) are the Poisson's ratios of the Si_3N_4 ball and Al_2O_3 surface, respectively. E_1 (≈ 300 GPa) and E_2 (≈ 350 GPa) are the elasticity moduli of the Si_3N_4 ball and Al_2O_3 surface, respectively. Then the ratio of the theoretical film thickness to the combined surface roughness can be obtained to determine the dominant lubrication regime when superlubricity is achieved. The ratio can be calculated using Eq. (4) as

$$\lambda=\frac{h_{\min}}{\sigma}=\frac{h_{\min}}{\sqrt{\sigma_1^2+\sigma_2^2}} \tag{4}$$

where σ denotes the composite surface roughness, and σ_1, σ_2 denote the surface roughness of the worn region on Si_3N_4 ball and Al_2O_3 disk, respectively. Thus, the sliding solid surfaces can be lubricated in elastohydrodynamic lubrication if λ is higher than 3, mixed lubrication if λ is between 1 and 3, and boundary lubrication if λ is less than 1.

By observing the 3D morphology of the worn regions on solid surfaces, the composite surface roughness after lubrication by the original PAG aqueous solution, the PAG aqueous solution with sulfuric acid, and the PAG aqueous solution with acetic acid was approximately measured as 9.28, 13.29, and 15.02 nm, respectively. The calculated theoretical film thicknesses and λ values of these samples are listed in Table 1. At a sliding speed of 24 mm·s^{-1}, the theoretical film thickness of the PAG aqueous solution was approximately 54 nm, and the corresponding λ value was 5.8. This indicates that the original PAG aqueous solution lubricates in the elastohydrodynamic lubrication regime, where fluid lubrication plays a major role. When sulfuric acid was added to the PAG aqueous solution, the theoretical film thickness decreased to approximately 43 nm, corresponding to a λ value of 3.3, which is also in the regime of elastohydrodynamic lubrication. When acetic acid was introduced, the theoretical film thickness significantly decreased to a value of approximately 16 nm and the corresponding λ value was 1.1. This implies that the main lubrication regime is transferred to mixed lubrication, which is considered as a combination of boundary lubrication and elastohydrodynamic lubrication. Given that the value of λ value is rather low, approaching the boundary lubrication regime, non-fluid lubrication is expected to exhibit an inescapable effect during the sliding process. Moreover, given that the sliding speed is a critical factor that affects the stability of the superlubricity state, it is necessary to observe the minimal sliding speed that can maintain the superlubricity. This is termed as the minimal superlubricity speed. Table 2 lists the theoretical film thicknesses of different PAG aqueous solutions at a minimal superlubricity speed. For the original PAG aqueous solution, a superlow COF was maintained until the relative sliding speed decreased to 6 mm·s^{-1} and then increased sharply. The theoretical film thickness at 6 mm·s^{-1} was calculated as approximately 21 nm with a corresponding λ value of 2.3. Similarly, for the PAG aqueous solution with sulfuric acid, the minimal superlubricity sliding speed was measured as 9 mm·s^{-1} with a theoretical film thickness of approximately 22 nm and λ value of 1.7. This indicates that mixed lubrication invariably affects the maintenance of superlubricity for these two samples, where non-fluid lubrication begins to play a role in avoiding the contact of asperities due to decreases in lubrication film thickness. For the PAG aqueous solution with acetic acid, the COF value did not correspond to superlubricity when the sliding speed decreased to less than 12 mm·s^{-1}. The theoretical film thickness at this speed was calculated to be approximately 10 nm, which was lower than the composite roughness of the worn region, and the corresponding λ value was 0.7, which was in the regime of boundary lubrication. Thus, the addition of acid to PAG aqueous solutions improved non-fluid lubrication, which exhibited an indispensable and prominent effect on maintaining superlubricity. Specifically, organic acids appeared to play a more powerful role in enhancing tribological properties at superlubricity, such as improvements in the running-in time and load-carrying property, as shown in Figs. 1 and 2.

To further examine the effect of different acids, two types of inorganic acids (sulfuric acid and nitric acid) and three types of organic acids (formic acid, acetic acid, and butyric acid) were introduced into the PAG aqueous solution (pH of 6), to realize samples with pH of 2, 3, 4, and 5. The preparation of the PAG aqueous solution with butyric acid at pH below 4 requires a large volume of butyric acid liquid. This changes the concentration of PAG, and thus butyric acid is only used to prepare PAG aqueous solutions with pH of 5 and 4. The results of the frictional tests are shown in Fig. 3. Generally, decreases in the pH value increases the concentration of hydrogen ions in the solution and significantly decreases time

Table 1 Calculated theoretical film thickness and λ values of different PAG aqueous solutions.

Sample	PAG aqueous solution	PAG aqueous solution with sulfuric acid	PAG aqueous solution with acetic acid
v (mm·s^{-1})	24	24	24
$h_{\min}$ (nm)	54	43	16
λ	5.8	3.3	1.1

Table 2 Calculated theoretical film thickness and λ values of different PAG aqueous solutions at minimal superlubricity speed.

Sample	PAG aqueous solution	PAG aqueous solution with sulfuric acid	PAG aqueous solution with acetic acid
$v_{\min}$ (mm·s^{-1})	6	9	12
$h_{v\min}$ (nm)	21	22	10
λ_v	2.3	1.7	0.7

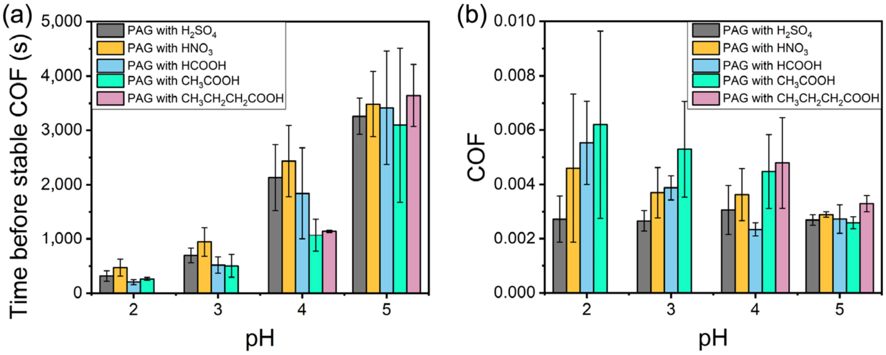

Fig. 3 (a) Time before stable COF and (b) stable COF of PAG aqueous solutions with different acids at different pH values.

before COF stabilizes, as shown in Fig. 3(a). For the PAG aqueous solution with sulfuric acid, time to realize superlubricity at pH of 5, 4, 3, and 2 corresponded to 3,400, 2,000, 700, and 300 s, respectively, and thereby indicating that the running-in time decreased by 30%–60% when the concentration of hydrogen ions increased by an order of magnitude. However, the final superlow COF value appears almost pH-independent with increasing concentration of sulfuric acid, as shown in Fig. 3(b). Furthermore, similar results were obtained during the frictional tests using the PAG aqueous solution with nitric acid, and it was inferred that inorganic acids could exhibit similar effect on the frictional behaviors of PAG aqueous solutions. The decreasing pH of the PAG aqueous solutions with inorganic acid significantly affects the running-in process without significantly affecting the stability of PAG aqueous solutions. In contrast to PAG aqueous solutions with inorganic acids, approximately 3,100, 1,100, 500, and 250 s were required for the PAG aqueous solution with acetic acid to realize a stable superlow COF at pH of 5, 4, 3, and 2, respectively. The running-in time decreased by over 50% when the concentration of hydrogen ions increased by an order of magnitude. The COF value was observed to increase gradually as pH decreased, and the fluctuating range of COF increased at lower pH values. This indicates that a large volume of acetic acid in solution can affect the stability of superlubricity. Furthermore, similar trends concerning the stable COF and time before stable COF were observed when other organic acids were selected as the lubricating additives including formic acid and butyric acid. Thus, when compared to inorganic acids, organic acids were observed to exhibit an improved effect on decreasing the running-in time albeit a slightly negative effect on maintaining a low COF.

The diameters of the worn regions on ball and the corresponding contact pressures after lubrication with PAG aqueous solutions with different acids as a function of pH are shown in Fig. 4. For PAG aqueous solutions with inorganic acids, the diameters of the worn regions after lubrication were measured as approximately 360, 350, 310, and 270 μm at pH of 5, 4, 3, and 2, respectively, as shown in Fig. 4(a). The corresponding contact pressures, as shown in Fig. 4(b), were calculated as approximately 29, 32, 40, and 50 MPa, respectively, which fluctuated within a narrow range. For PAG aqueous solutions with organic acids, the diameters of PAG aqueous solutions with formic acid were measured as approximately 350, 310, 170, and 160 μm at pH of 5, 4, 3, and 2, corresponding to contact pressures of approximately 31, 40, 131, and 142 MPa, respectively. The load-carrying capacity of the PAG aqueous solution at superlubricity was observed to increase significantly as the pH was decreased by introducing a formic acid solution. Specifically, the contact pressure at a pH of 2 was over five times higher than that of the original PAG aqueous solution (27 MPa, shown in Fig. 2). Additionally, when acetic acid was introduced in the PAG aqueous solution, the contact pressure at superlubricity was also observed to increase by more than 25% with each descending level of the pH value. Specifically, a maximum contact pressure of approximately 160 MPa was obtained at a pH of 2. When butyric acid was selected as the acid additive, the contact pressure of the PAG aqueous solution at superlubricity increased to approximately 140 MPa at a pH of 4. This was five times higher than that of the

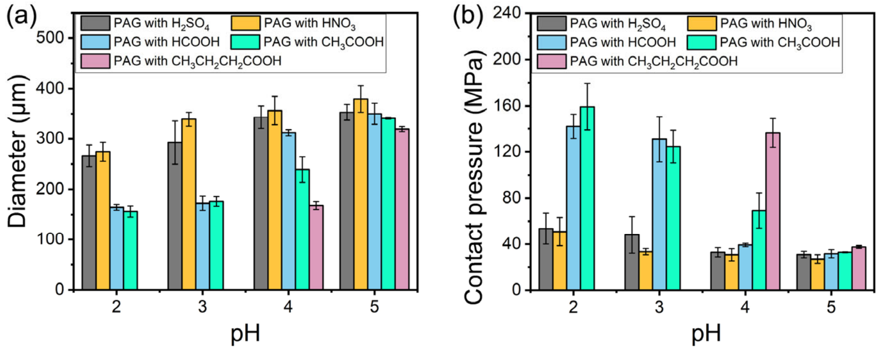

Fig. 4 (a) Diameters of worn regions on the ball and (b) the corresponding contact pressures lubricated by PAG aqueous solutions with different acids at different pH values.

original PAG aqueous solution. Thus, when compared with the inorganic acid, the addition of organic acid was more effective in decreasing the weight loss between solid surfaces and significantly improved the load-carrying capacity of the PAG aqueous solution at superlubricity. Hence, lower wear loss and higher bearing pressure can be obtained in the superlubricity system by using PAG aqueous solutions with higher concentrations of organic acids with longer carbon chains.

To confirm the relationships between wear condition and acids, the wear rate w_{v}, which is defined as the volume loss of the ball in unit running-in time, is provided in Eq. (5) as

$$w_{\mathrm{v}} = \frac{W_{\mathrm{v}}}{T} \tag{5}$$

where T denotes the running-in time and W_{v} denotes the total volume loss of the ball, which is calculated in Eq. (6) as

$$W_{\mathrm{v}} = \pi\left(R_0 - \frac{H}{3}\right)H^2 \tag{6}$$

where R_0 denotes the radius of the upper ball and H denotes the height of the segment, which is obtained using Eq. (7) as

$$H = R_0 - \sqrt{{R_0}^2 - \frac{D^2}{4}} \tag{7}$$

The wear rate as a function of the pH values of PAG aqueous solutions with different acids is shown in Fig. 5. All the points at a pH of 6 denote the wear rate of the original PAG aqueous solution. For PAG aqueous solutions with inorganic acids, the wear rate immediately increased after the introduction of the inorganic acid and then continuously increased with a further decrease in the pH value. This indicates that increases in the amount of inorganic acids in the PAG aqueous solution can increase the wear rate between the solid surfaces. With respect to PAG aqueous solutions with organic acids, there was a significant decrease in the wear rate with a decrease in the pH value. Specifically, at a pH of 3, the wear rate of the solution decreased with the addition of organic acid to approximately a third of that of the solution with inorganic acid and half that of the original PAG aqueous solution. Thus, the results shown in Figs. 3 and 4 indicate that the addition of acids significantly affects the sliding process lubricated by the PAG aqueous solution, and the effects are dependent on the type of acid. When inorganic acid is introduced in the PAG aqueous solution, the running period

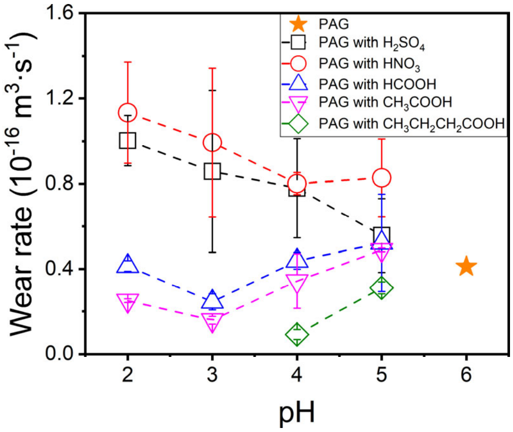

Fig. 5 Wear rate on the ball lubricated by PAG aqueous solutions with different acids at different pH values. The orange star denotes the wear rate of the original PAG aqueous solution.

effectively shortens with decreases in the pH value while the final area of the worn region is expected to remain approximately constant. Furthermore, the addition of inorganic acid can aid in increasing the wear rate between the sliding surfaces and accelerating the formation of the worn region as opposed to improving the bearing pressure of the PAG aqueous solution in the superlubricity state. When organic acid is introduced in the PAG aqueous solution, the wear rate between sliding surfaces significantly decreases and the running-in process is accelerated leading to less wear. Thus, the superlubricity of the PAG aqueous solution can be maintained at a higher bearing pressure by increasing in the volume of organic acid. Hence, the addition of organic acid decreases running-in time, significantly decreases weight loss between sliding surfaces, and improves the load-carrying capacity of PAG aqueous solutions at superlubricity.

To explore the nature of the different effects between inorganic acid and organic acid, XPS spectra were utilized to analyze the chemical elements present on the worn region of the Si_3N_4 ball after lubrication with the PAG aqueous solution and that with various acids. When selecting the original PAG aqueous solution as a lubricant, as shown in Fig. 6(a), the C 1s peaks detected at 284.8 and 285.9 eV deconvoluted into C–C bond or C–H bond and C–O bond, respectively. These bonds are potentially derived from the molecules of the liquid lubricant. Si 2p peaks detected at 101.3 and 102.0 eV, as shown in Fig. 6(b), prove the existence of Si-N bond and Si–O bond on the worn region. These bonds are potentially generated via reactions between Si_3N_4 and water as $Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3$ [18, 40, 41]. A silica layer is expected to form on the worn region of the Si_3N_4 ball. Thus, hydrated PAG macromolecules should form hydrogel bonds with the hydroxyl groups (Si–OH) on the surfaces. This in turn forms a stable adsorption layer during the sliding process, and thereby decreases the shear force between solid surfaces. When selecting the PAG aqueous solution with an inorganic solution as the lubricant, C–O bond, C–C bond, Si–N bond and Si–O bond are still observed in the worn region, thereby indicating that the reaction type during the sliding process should not be changed, as shown in Figs. 6(c) and 6(d). The change in the binding energy of C–O bond and Si–N bond is potentially due to the existence of abundant number of hydrogen ions near the contact region. With respect to selecting the PAG aqueous solution with organic acid as a lubricant, in addition to C–O bond, C–C bond, Si–N bond and Si–O bond, a new peak at 288.2 eV corresponding to the C=O bond is observed, as shown in Figs. 6(e) and 6(f).

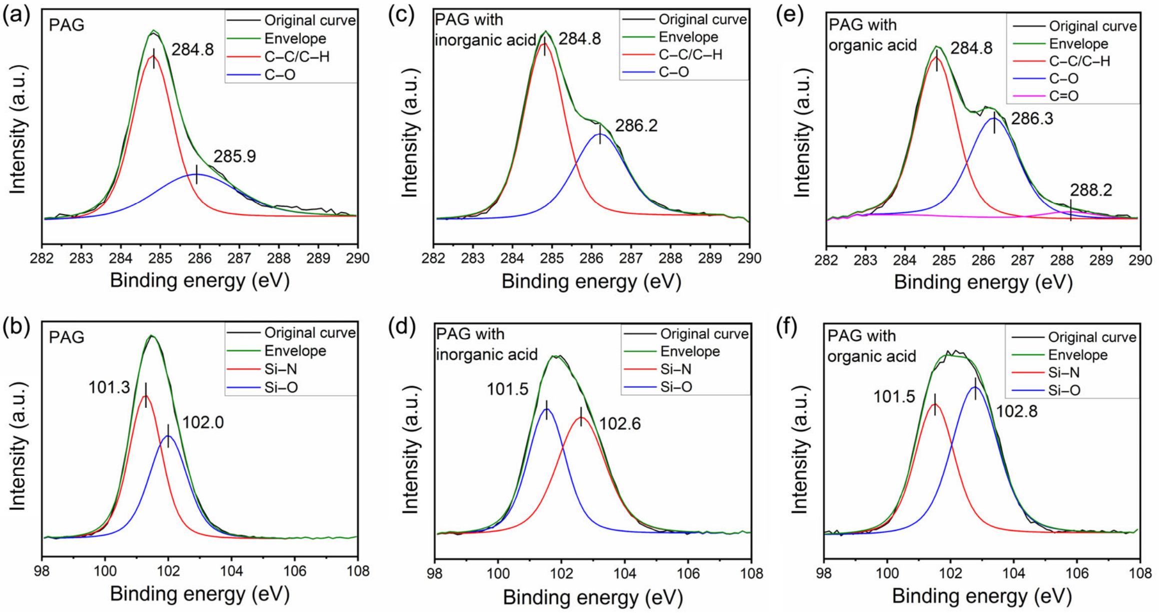

Fig. 6 XPS spectra of (a, c, e) C 1s and (b, d, e) Si 2p in the worn region on the Si_3N_4 ball after lubrication with (a, b) original PAG aqueous solution, (c, d) PAG aqueous solution with inorganic acid, and (e, f) PAG aqueous solution with organic acid.

This indicates that molecules of organic acid combine with the solid surfaces and become a part of the adsorption layer on the solid surface during the sliding process. Simultaneously, the binding energy of C–O bond, Si–N bond and Si–O bond also shifted to a higher energy region with a value of 286.3, 101.5, and 102.8 eV, respectively. This is potentially due to the existence of hydrogen ions and structural change in the adsorption layer.

To investigate the composition content in the contact region, the estimated relative concentrations of C–O bond and Si–O bond were evaluated as $c_{\mathrm{re}}(\mathrm{C{-}O}) = c(\mathrm{C{-}O})/[c(\mathrm{C{-}O})+c(\mathrm{C{-}C})]$ and $c_{\mathrm{re}}(\mathrm{Si{-}O}) = c(\mathrm{Si{-}O})/[c(\mathrm{Si{-}O})+c(\mathrm{Si{-}N})]$, where $c(\mathrm{C{-}O})$, $c(\mathrm{C{-}C})$, $c(\mathrm{Si{-}O})$, $c(\mathrm{Si{-}N})$ denote the concentration of C–O bond, C–C bond, Si–O bond, and Si–N bond (which are based on the corresponding fitted peak areas in the XPS spectra), respectively. The relative concentration of C–O bond on the worn region after lubrication with PAG aqueous solution, PAG aqueous solution with inorganic acid, and PAG aqueous solution with organic acid was calculated as 34.9%, 37.4%, and 43.1%, respectively. Simultaneously, the relative concentration of Si–O bond after lubrication with PAG aqueous solution, PAG aqueous solution with inorganic acid, and PAG aqueous solution with organic acid corresponded to 45.4%, 45.7%, and 57.1%, respectively. More silica is expected to form on the solid surface with the addition of acid, thereby indicating that the reaction is enhanced by the hydrogen ions during the sliding process. Specifically, the increased concentration of C–O bond in the worn region lubricated by the PAG aqueous solution with organic acid suggests that the introduction of organic acid can promote more lubricant molecules to form a strong combination with the solid surface.

Based on the aforementioned analysis, the introduction of an acid can significantly affect the superlubricity behavior of PAG aqueous solutions, which in turn affects the tribochemical reaction during the sliding process, combination of the lubricant molecules and solid surfaces, and formation of an adsorption layer near the contact region. Therefore, potential lubrication models between the sliding surfaces of the PAG aqueous solution and PAG aqueous solutions with various acids are shown in Fig. 7. When using the original PAG aqueous solution as a lubricant, the mechanical wear smooths out the solid surfaces and meantime decreases the contact pressure. Then, a silica layer is formed on the solid surfaces because of the narrow energy gap [42]. This in turn leads to the formation of hydrogen bonds with hydrated PAG macromolecules for establishing the adsorption layer, as shown in Fig. 7(a). The slow generation and weak structure of the silica layer and adsorption layer lead to the long running-in period, the low bearing pressure, and the superlow COF value, which has already given detailed discussions in the previous work [35]. When using the PAG aqueous solution with inorganic acid as a lubricant, the tribochemical reaction is enhanced by hydrogen ions during the sliding process, and a stronger silica layer can be formed considerably quickly in the worn region, as shown in Fig. 7(b). The hydrogen ions near the contact region improve the interactions between PAG macromolecules and hydroxyl groups ([Al–OH] and [Si–OH]) on the silica layer, which increases the adsorption rate. Given that molecules of inorganic acid are ionized completely in aqueous solution, which is

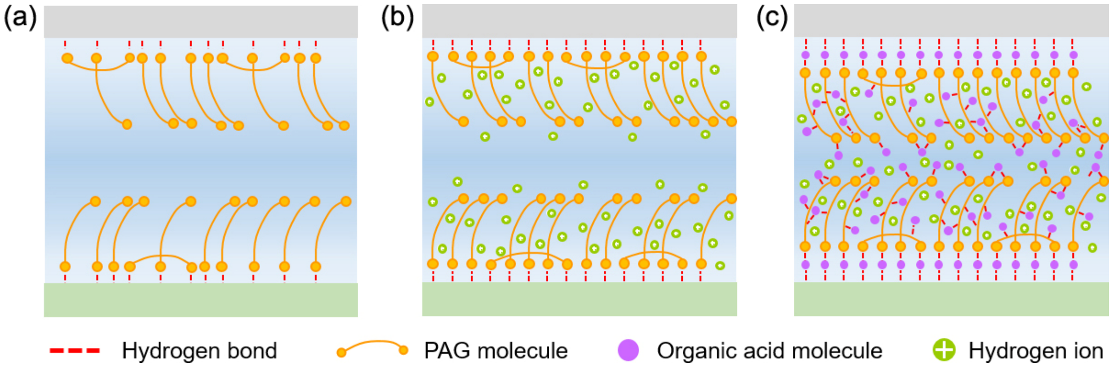

Fig. 7 Schematic illustration of the proposed lubrication models between two sliding solid surfaces for (a) original PAG aqueous solutions, (b) PAG aqueous solutions with inorganic acid, and (c) PAG aqueous solutions with organic acid.

hardly combined with the groups on the surfaces, the binding energy between polymer molecules and final structure of the adsorption layer should not be enhanced. Thus, the load-carrying capacity and frictional properties of PAG aqueous solutions with inorganic acid in the superlubricity state are similar to those of the original PAG aqueous solution. It is concluded that moderate addition of inorganic acid potentially accelerates the running-in process of the PAG lubricants but barely affects their final superlubricity behavior. Specifically, excessive addition of inorganic acid can lead to the presence of a large number of hydrogen ions in solution and contribute to the formation of enhanced electric double layers near the contact region, thereby leading to an increase in the bearing pressure. When using the PAG aqueous solution with organic acid as a lubricant, the effect significantly differs from that of inorganic acids. In addition to the formation of more silica on the surfaces due to the presence of hydrogen ions, unionized organic acid molecules are expected to form hydrogen bonds with PAG macromolecules and hydroxyl groups on the silica layer. The introduction of organic acid molecules enhances the binding strength between the polymer molecules and solid surfaces. This improves the overall structural strength of the adsorption layer, as shown in Fig. 7(c). Thus, it is concluded that the introduction of organic acids can contribute to the formation of strong hydrogen bonds with the polymers and silica layer. This significantly improves the strength of the surface structure near the contact region, and thereby increases bearing pressure during the superlubricity process.

4 Conclusions

In this study, different acids were selected as additives to prepare acidic PAG aqueous solutions at various pH values. The results of tribological experiments indicate that the addition of acids can effectively reduce the running-in time without breaking the superlubricity state of the PAG aqueous solution. The morphology of the worn region suggests that the addition of organic acid reduces wear loss on sliding surfaces and thereby improves bearing pressure in the superlubricity process, while the addition of inorganic acid merely accelerates the running-in process. Based on the analysis of elements in the worn region, in the case of PAG aqueous solution with inorganic acid, hydrogen ions promote the rate of the tribochemical reaction and physical absorption of PAG molecules during the sliding process. However, the binding force between the polymer molecules and the final structure of the adsorption layer on the surface is not enhanced, and thus the bearing pressure does not improve. With respect to the PAG aqueous solution with organic acid, the wear condition and the bearing pressure during the sliding process are significantly improved in unison. The unionized organic acid molecules in the solution are assumed to form hydrogen bonds with adsorbed PAG macromolecules and hydroxyl groups on the solid surfaces. This significantly increases the adhesion strength of the adsorption layer, and thereby enhances tribological properties during the superlubricity process. Therefore, unique effects of different acids are expected to hold great potential in terms of broadening applications of polymer lubricants.

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