Exploration on Aqueous Lubrication of Polymeric Microgels between Titanium Alloy Contacts

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ABSTRACT: Since titanium alloys have been widely used as joint replacement biomaterials, their superficial lubrication has evolved to be a critical factor for normal use. For this purpose, one kind of typical microgel, poly(NIPAAm-co-AA), was synthesized by emulsifier-free emulsion polymerization and used as an aqueous lubricating additive between titanium alloy contacts. The results show that the as-synthesized microgels reduced the coefficient of friction by 46% and the wear volume by 45%, compared with pure water. Meanwhile, due to their thermosensitive property, the microgels were employed as smart additives to modulate the interfacial friction, which was attributed to the transition of the hydrated state and the elastic deformation of microgel particles. To further dissect the lubrication mechanism, it was found that the lubricating property of microgels was substantially associated with the formation of a hydrated layer surrounding microgels, microbearing effect, interfacial adsorption, and the colloidal stability. Looking beyond, as one kind of soft colloidal lubricant, the microgels may play an important role in the biomedical metal lubrication.

INTRODUCTION

In human joints, the lubrication failure will cause pain and joint disease, which have troubled millions of people in the world.1−3 In severe cases, the joint replacement surgery has to be performed. Because of high strength, good biocompatibility, and anticorrosion, titanium alloy has been widely used as a joint replacement material.4−6 Based on this, how to reduce friction and enable good lubrication between titanium alloy contacts is always a challenge in the biomedical field. In recent years, aqueous lubrication has attracted much attention because it is closely related to the development of green environment-friendly lubricants for biomedical lubrication.7−10 It is known from the literature that water is a naturally harmless lubricant because of good fluidity and cooling performance.11 However, it cannot maintain boundary lubrication under overly high normal load, unlike lubricating oil or grease. To circumvent this problem, various lubricant additives have been developed to enhance the lubrication in aqueous medium. Especially, the famous tribologist Jacob Klein systematically studied the phenomenon of aqueous lubrication and demonstrated the therapy of hydration lubrication.12,13 The formation of the hydration layer between sliding interfaces is the core of hydration lubrication. Based on this mechanism, the addition of hydratable molecules into water can effectively improve the interfacial lubrication in aqueous medium,16−18 which is the basic principle for synthesizing and developing water-based lubricating additives.

Here, one kind of soft matter, microgel, was introduced to lubricate titanium alloy contacts in aqueous medium. Microgels are intramolecularly cross-linked micro/nanoscale poly...
meric colloids, whose network structure can be filled with free-flowing water. Based on the advantage of colloidal stability, convenient preparation, facile functionalization, and good biocompatibility, microgels have evolved to be a good candidate as lubricating additives for hydration lubrication. In particular, stimuli-responsive microgels can be employed as smart lubricants for modulating the interfacial friction under the environmental stimuli (e.g., temperature, light, and pH). As a representative, thermosensitive poly(N-isopropylacrylamide) (PNIPAAm) based microgels have been widely studied for aqueous lubrication. In 2013, Liu et al. investigated the tribological behavior of poly(N-isopropylacrylamide)-graft-poly(ethylene glycol) (PNIPAAm-g-PEG) microgels and stated that these microgels exhibited a good lubricating effect between steel/steel contacts. In 2019, Xu et al. further confirmed the aqueous lubricating performance of PNIPAAm microgels between steel and ultrahigh-molecular-weight polyethylene (UHMWPE). In 2020, Zhang et al. prepared poly(N-isopropylacrylamide-2-methacryloyloxyethyl phosphorylcholine) (PNIPAAm-PMPC) microgels by introducing hydrophilic MPC into the microgels. Compared with pure PNIPAAm microgels, the addition of hydrophilic component improved the hydration lubrication between polytetrafluoroethylene (PTFE) ball and silicon wafer. However, previous research focused on the verification of the lubricating performance of microgels and lacked the exploration on the tribological behavior of microgels between biomedical metal surfaces, especially titanium alloy.

In this work, we explored the tribological behavior of poly(NIPAAm-co-AA) microgels between titanium alloy contacts and revealed the mechanism of aqueous lubrication when using polymeric microgels as additives (Figure 1). The components of this microgel were well defined by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (1H NMR), and simultaneous thermal analysis (STA). The morphology was observed by scanning electron microscopy (SEM). The hydrated ability and thermosensitive property were investigated by dynamic light scattering (DLS) and UV–vis spectroscopy. Furthermore, the tribological property was studied by a universal mechanical tester (UMT-3) and 3D optical profilometer. More importantly, the lubrication mechanism of microgels was revealed from the viewpoint of hydration effect, colloidal viscosity, and interfacial adsorption. This exploration on the tribological mechanism of microgels may provide an efficient idea for studying and designing soft colloidal lubricants in the field of biomedical lubrication.

FIG RESULTS AND DISCUSSION

Analysis of the Chemical Component and Morphology. The resultant poly(NIPAAm-co-AA) microgels were characterized by FTIR, STA, and 1H NMR to analyze the chemical component and thermostability. From the FTIR spectrum in Figure 2a, the appearance of the following characteristic peaks indicated the successful synthesis of poly(NIPAAm-co-AA). The stretching vibration peaks of N–H groups appeared at 3600–3200 cm⁻¹, and the absorption peaks of C=H in –CH₃ and –CH₂= appeared at 2975–2935 cm⁻¹. The characteristic peaks of C=O in –COOH and –CONH– appeared at 1745 and 1648 cm⁻¹, respectively. The double peaks at 1388 and 1368 cm⁻¹ were assigned to the vibration absorption of the two –CH₃ in –CH(CH₃)₂. As shown in Figure 2b, the molecular structure of these microgels was further investigated by 1H NMR spectroscopy. The peaks at 7.2 ppm (1H, –NH–), 3.83 ppm (1H, –CH(CH₃)₃), and 1.04 ppm (6H, –CH(CH₃)₂) all originated from the NIPAAm moiety. The peaks at 2.01 ppm (2H, –CH–C=O) and 1.42 ppm (4H, –CH₂–CH–) were assigned to the same groups in NIPAAm and AA moieties. In addition, the peak at 2.50 ppm came from the reagent DMSO-d₆. The thermal decomposition curve in Figure 2c demonstrated that the microgel showed a good thermodynamic stability with the thermal decomposition temperature of ∼346 °C, which was much higher than the boiling point of water, indicating that this microgel could remain stable in aqueous lubrication without being thermally decomposed. Further, the morphology of microgels was observed by SEM. As shown in Figure 2d, the microgels showed perfect spherical structures with a uniform particle size, suggesting that these microspheres could be considered as “microrolling balls” to reduce interfacial friction by rolling lubrication. From the enlarged view (Figure 2e), the diameter was measured to be ∼426 nm.

Thermosensitive Property in Aqueous Medium. The thermosensitive property of microgels was analyzed by UV–vis spectroscopy and DLS. As shown in Figure 3a, the transmittance of the microgel suspension decreased gradually with the increase in temperature, and the lower critical solution temperature (LCST) was measured to be ∼34.3 °C. Below LCST, the hydrogen bond was formed between the NIPAAm moiety and water molecules, resulting in a clear and transparent colloidal suspension. When the temperature rose to above LCST, the hydrogen bond was destroyed and the suspension became milky white. In addition to the light transmittance, the temperature also affects the hydrated diameter of thermosensitive microgels. Similar to the change trend of transmittance, the D₄₅ of microgels decreased gradually with the increase in temperature (Figure 3b). At 25 °C, the microgels were fully swollen with a hydrated diameter of 1466 nm, which was much greater than that of dry microgels in SEM images. At 50 °C, the D₄₅ was reduced to ∼441 nm due to the dehydration and collapse of microgels. During the whole process, the PDI remained relatively small, suggesting that the microgels were dispersed homogeneously in aqueous media.
These results demonstrated that the microgels possessed an excellent hydration ability at room temperature and could undergo a significant swelling/collapse thermosensitive transmission around LCST. These characteristics provide a possibility for modulating the interfacial friction using polymeric microgels as lubricating additives.

**Investigation of Lubricating Performance.** One kind of titanium alloy, Ti6Al4V, was chosen as the friction pair for evaluating the lubricating performance of as-synthesized microgels. All experiments were performed in the reciprocating mode on a UMT-3. From the friction curves in Figure 4a, the microgel suspension reduced the interfacial friction obviously (COF: ∼0.2332) in comparison with pure water (COF: ∼0.4322), indicating that this microgel could be used as an additive for lubricating Ti6Al4V interfaces in aqueous medium.

Next, the tribological tests under varied parameters were systematically performed. First, the effect of suspension concentration on the tribological performance of microgels was investigated (Figure 4b). It was found that the COFs gradually decreased with the increase in concentration, which was attributed to the viscosity increase of the microgel suspension, resulting in a tighter adsorption layer. Then, the effect of normal load on the tribological property was investigated to explore the load-bearing capability of microgels (Figure 4c). With the increase in applied load, the COF increased slightly, which originated from the deformation of microgels under increased force. From the viewpoint of a microspherical structure, the microgels played a microbearing role in the friction interfaces. When increasing the normal load, the soft microgels deformed, resulting in the reduction of the microbearing role. Thus, the COF increased slightly with the increase in applied load. Finally, the tribological test was performed by changing the frequency to study the effect of sliding speed on the lubricating performance of microgels (Figure 4d). The result showed that the COFs decreased gradually with the increase in sliding frequency. During the friction, the increase in sliding frequency shortened the run-in period, which was beneficial to decrease the COFs. In a word, the change trend of COFs was consistent with the boundary lubrication from the Strubeck curve.

In addition to the lubricating performance, the antiwear ability of microgels was evaluated intuitively by observing the 3D topographies of wear scars on the Ti6Al4V plates. As shown in Figure 5a,b, it is clear that the addition of microgels into water significantly reduced the surficial wear of the Ti6Al4V plate. From Figure 5c, the width and depth of wear scars both became smaller. Compared with pure water, the wear volume was reduced by 45% (Figure 5d). Also, the wear of Ti6Al4V balls was obviously reduced when using the microgel suspension as a lubricant (Figure S3). These results proved that the polymeric microgels had the antiwear property while reducing the COF.

**Analysis of Lubrication Mechanism.** To see through the appearance to perceive the essence, we would like to analyze

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Figure 2. Characterization of chemical components and morphology of as-synthesized microgels. (a) FTIR spectrum. (b) 1H NMR spectrum. (c) STA curve. (d, e) SEM images, where panel (e) is the enlarged view.
the lubrication mechanism in terms of hydration lubrication, microbearing effect, rheological behavior, and interfacial adsorption. Based on the DLS result in Figure 2b, the poly(NIPAAm-co-AA) microgels were highly hydrated, and the water molecules were bound onto the polymeric networks, endowing the microgel with good water retention capacity. Thus, during the friction process, the hydration lubrication could be achieved when using microgels as the aqueous lubricating additives. More interestingly, the microgels showed a good spherical structure, which has been proved by the SEM image in Figure 2d. During the friction process, microgels could act as lots of microbearing balls and be rolled freely in the sliding interface, avoiding the direct contact between the friction pair. Importantly, the relative motion was changed from the sliding friction state to the rolling friction state, which brought about a positive effect on interfacial lubrication.16 Meanwhile, the good colloidal dispersibility enabled the microgels to effectively avoid aggregation during the friction process.28

Viscosity was deemed to be another important factor affecting the lubrication performance of the liquid lubricant. As mentioned above, water cannot be used as a good lubricating additive mainly due to very low viscosity. At room temperature, the viscosity of pure water was about 0.001 Pa·s.27 As shown in Figure 6a, at a low shear rate, there was a typical shear-thinning phenomenon for the microgel suspension, which exhibited the characteristic of a non-Newtonian fluid. It was noteworthy that the viscosity of the microgel suspension at a high shear rate was increased very slightly with shear rate, indicating that the microgel suspension showed a shear-thickening phenomenon instead of a shear-thinning

Figure 3. Study on the thermosensitive tribological behavior of as-synthesized microgels. (a) Transmittance of the microgel suspension as a function of temperature at the wavelength of 500 nm; the inset is the digital picture of the microgel suspension at 25 and 50 °C. (b) $D_h$ and corresponding PDI of the microgels as a function of temperature.

Figure 4. Evaluation of the lubrication performance of as-synthesized microgels. (a) Friction curves of the microgel suspension between Ti6Al4V ball/Ti6Al4V plate contacts (suspension concentration: 1.0 wt %; normal load: 1 N; frequency: 1 Hz; amplitude: 2 mm). (b) COFs of the microgel suspension with different concentrations (normal load: 3 N; frequency: 1 Hz; amplitude: 2 mm). (c) COFs of the microgel suspension under different normal loads (frequency: 1 Hz; amplitude: 2 mm; concentration: 1.0 wt %). (d) COFs of the microgel suspension with different reciprocating frequencies (normal load: 3 N; amplitude: 2 mm; concentration: 1.0 wt %).
process. This result demonstrated that this type of microgel displayed good colloidal and mechanical stability in aqueous medium during the high-speed sliding process, which provided a promotion effect on aqueous lubrication.22 Beyond above factors, the interfacial adsorption was another key factor affecting the friction. As shown in Figure 6b, the adsorption layers on Ti6Al4V plates were investigated by X-ray photoelectron spectroscopy (XPS) before and after friction test when using microgels as lubricating additives. Before friction, the signals of Ti 2p3 and N 1s appeared from the Ti6Al4V plate. After friction, the signal of N 1s was slightly enhanced, which was attributed to the PNIAAam components of microgels. Meanwhile, the strength of the Ti 2p3 peak was significantly reduced, which was caused by the covering effect of the microgel adsorption layer. The change of these two signals proved the adsorption of microgels on the frictional surfaces. The adsorption microgel layer could be considered as a boundary lubricating layer to reduce the interfacial friction. More importantly, this adsorption layer could fix water molecules through hydrogen bond interactions onto the sliding interface, thereby enhancing the effect of hydration lubrication. Meanwhile, the adsorbed microgels could act as microsized additives to fill and repair the worn position. In a word, the aqueous lubricating ability of microgels depended on the synergistic effect of these multiple factors.

**Study on Thermosensitive Tribological Behavior.** Since the PNIPAAm segment of microgels could respond to environmental temperature, the effect of temperature change on the tribological behavior of poly(NIPAAm-co-AA) microgels was systematically investigated. It can be observed that the COFs were slightly decreased with the increase in temperature (Figure 7a,b), which was analyzed from two aspects: hydrated lubrication and microbearing effect. From the viewpoint of hydration lubrication, the increase in temperature enabled the microgels to dehydrate and become hydrophobic, resulting in the failure of hydration lubrication. This factor tended to increase the COF. From the viewpoint of a microbearing ball, as the temperature rose, the internal network of the microgels tended to collapse and become tight, which was beneficial for
realizing the function of rolling lubrication. This factor tended to reduce the COF. That is to say, the final COF was dependent on the balance of these two opposite factors. As far as this lubricating system went, the COF decreased slightly with the increase in temperature. Briefly, the increase in temperature did not cause the increase in COFs, which was beneficial for microgels to lubricate Ti6Al4V interfaces in the physiological enticement of the human body.

**CONCLUSIONS**

In summary, one kind of typical microgel, poly(NIPAAm-co-AA), was developed and used as an aqueous lubricating additive, which showed a good lubricating ability between the Ti6Al4V friction pair. Based on the thermosensitive performance, the as-synthesized microgels were employed as smart additives to modulate the interfacial friction, which was enslaved to hydration lubrication and collapse/swelling switch. Furthermore, the lubrication mechanism of microgels was dissected from various viewpoints. First, the hydrated layer surrounding microgels enabled the hydration lubrication in aqueous medium. Second, the spherical structure of microgels introduced the rolling lubrication mechanism of the microbearing. Third, the colloidal stability in the shear process played a positive effect for aqueous lubrication. Finally, the adsorption of microgels on the sliding surfaces produced a boundary lubricating layer to reduce the interfacial friction. In a word, the synergistic effect of these four factors contributed to the aqueous lubrication property of polymeric microgels. Looking beyond, the exploration on the aqueous lubrication of microgels between biomedical metal interfaces will provide a valuable theoretical basis for expanding the applications of soft colloidal lubricating additives.

**EXPERIMENTAL SECTION**

**Materials.** N-Isopropylacrylamide (NIPAAm, 99%) was obtained from TCI Co., Ltd. Acrylic acid (AA, 99%) was obtained from Aladdin Co., Ltd. N,N'-Methylene bis(acrylamide) (MBA, 98%) was obtained from Sigma-Aldrich Co., Ltd. Potassium persulfate (KPS, 99%) was obtained from Acros Co., Ltd. The titanium alloy (Ti6Al4V; modulus: 110 GPa) balls (diameter: 5.0 mm) and plates were obtained from Baoji Dingding Titanium Products Co., Ltd., China. The deionized water used in the experiment was produced by a ULUPURE pure water machine.

**Synthesis of Poly(NIPAAm-co-AA) Microgels.** The microgels were prepared via emulsifier-free emulsion polymerization according to previous methods. 29,30 The synthetic process was described in detail: 0.8 g of NIPAAm, 0.2 g of AA, and 0.03 g of MBA were added to 50 mL of pure water and stirred evenly, and then the mixture was put into a 100 mL three-necked flask with a magnetic stirrer and condenser. At room temperature, the mixture was ventilated with nitrogen for 30 min to remove oxygen. Then, the temperature was increased to 75 °C, and 0.03 g of KPS was added after stabilization. After 4 h of reaction, the resultant microgel suspension was put into a dialysis tube with a molecular weight cutoff of 8–14 kDa (Solarbio) and dialyzed in 1000 mL of deionized water for 72 h to remove the unreacted or incomplete monomers. The water was changed every 12 h to ensure the dialysis effect.

**Characterization.** FTIR spectrum was obtained on a Fourier transform infrared spectrometer (Bruker, Germany). The 1H NMR spectrum was obtained on a Bruker 400 M spectrometer (USA) using DMSO-d6 as a solvent. The thermal property of the microgels was evaluated by an STA 449F3 (Netzsch, Germany) instrument. The dynamic viscosity of microgels (ca. 1.0 wt %) was tested using an RS6000 rheometer (Germany). The morphology of microgels was observed by SEM (FEI Helios G4 CX, USA).

**Study on Thermosensitive Behavior.** To study the thermosensitive behavior of microgels, the nanoparticle size and transmittance at different temperatures were measured. The hydrodynamic diameters (Dh) and particle dispersion index (PDI) of microgels were measured by a particle size analyzer (Zetasizer Nano ZS, Malvern Instruments, UK) from 20 to 50 °C. The amount of microgel suspension was 1.5 mL for each test. The transmittance of the colloidal solution at 500 nm was obtained by a Lambda 365 UV−vis spectrophotometer (PerkinElmer, USA) from 20 to 50 °C. The amount of microgel suspension was 3.5 mL for each test.

**Tribological Test.** The tribological behavior of the microgel suspension was investigated on a universal mechanical tester (UMT-3, Bruker, USA) in the reciprocating mode (amplitude: 2 mm). The Ti6Al4V ball and polished Ti6Al4V plate were employed as the upper and lower friction contacts, respectively. The roughness of the Ti6Al4V plate was measured to be ∼48 nm by a 3D optical profiler (Figure S2). Before the thermosensitive study, the temperature was controlled at 25 °C. During the thermosensitive study, the temperature was adjusted to 25, 35, 45, and 55 °C. The amount of microgel suspension was 2.0 mL for each test. The experimental parameters in the tribological experiment are listed in Table 1.

After friction, the Ti6Al4V plate was fully cleaned to remove wear debris. Then, the morphology and volume of wear were
Table 1. Experimental Parameters in the Tribological Experiment

| Experimental Parameter | Normal Load (N) | Reciprocating Frequency (Hz) | Microgel Concentration (wt %) |
|------------------------|-----------------|-------------------------------|-------------------------------|
| Value                  | 1, 2, 3, 4, 5   | 1, 2, 3, 4, 5                 | 0.5, 1, 2, 4                  |

“The different concentrations were obtained by concentrating and diluting the microgel suspension.

obtained using a 3D optical profiler (Bruker NPFLEX, USA). The elemental compositions of the adsorption layer on the Ti6Al4V plate were measured by an X-ray photoelectron spectrometer (PHI 5000 VersaProbe III, Al Kα radiation).

■ ASSOCIATED CONTENT

1. Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04988.

Optical image of the tribotester, 3D topography of the surface of the Ti6Al4V plate, and optical images of the wear tracks of Ti6Al4V ball in pure water and microgel suspension (PDF)

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Notes
The authors declare no competing financial interest.

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