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基于界面超分子主客体识别作用的仿生自修复水润滑研究

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摘　要: 通过界面超分子主客体识别作用，成功地将端金刚烷基聚甲基丙烯酸3-磺酸丙酯钾分子组装到接枝环糊精分子的硅片表面；通过原子力显微镜，表面元素分析，膜厚变化，表面润湿特性等手段证实该聚合物的成功组装. 通过摩擦试验证实：表面组装端金刚烷基聚甲基丙烯酸3-磺酸丙酯钾分子后，在轻载条件下，具有极低的摩擦系数，呈现流体润滑状态；而在高载荷条件下，可能是由于表面组装的聚合物被部分剪切掉而呈现较高的摩擦系数. 更重要的是，基于这种超分子作用间的可逆的非共价相互作用，该表面可呈现一种自修复的润滑效果，即在部分端金刚烷基聚甲基丙烯酸3-磺酸丙酯钾分子被剪切掉后，在客体大分子稀溶液中自组装后可再次获得低摩擦系数状态。

关键词: 水润滑; 超分子; 主客体识别; 低摩擦系数; 自修复
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Bionic Self-Healing Aqueous Lubrication Based on Interfacial Supramolecular Host-guest Interaction

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Abstract: In this study, the adamantyl poly 3-sulfopropyl methacrylate potassium was successfully assembled onto the surface of cyclodextrin through the supramolecular host-guest recognition. The micro-topography, chemical composition, thickness and wettability of surface were detected to confirm the successful recognition and assembly. The frictional experiment of hydrophilic supramolecular substrate was implemented by reciprocating friction testing machine. The friction results showed an ultralow friction coefficient after assembling hydrophilic polymer ended with guest molecule under low load condition, but the friction coefficient became high under high load condition because the hydrophilic polymer may be sheared off from the supramolecular interface. More importantly, the surface not only owned ultralow friction coefficient but showed recoverability when friction failed under high load because of the non-

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covalent interaction between the guest and host groups.

Key words: aqueous lubrication; supramolecular; host-guest interaction; low friction coefficient; recoverability

Due to the special modulus of articular cartilage and the bottle-brush like protein macromolecules in synovial fluid, human joints tend to exhibit an ultra-low coefficient of friction (COF 0.001~0.03)[1, 2]. Bioinspired from the lubrication of articular cartilage, researchers have development a series of aqueous lubrication materials such as hydrogels[3-5], surfaces grafted with polymers brushes[6-8], hydrophilic biomacromolecules [9-10], micro-hydrogel[11-12]and so on. Among them, the hydrophilic polymer brush surface grafted from a solid substrate is an effective method to constructing aqueous lubrication materials. Professor Klein have assembled the polymethyl methacrylate-poly(methyl methacrylate epoxide sulfonate) (pMMA-SGMA) brush onto mica surface by molecular hydrophobic interaction and studied the friction behaviors of assembled surface by surface force apparatus. The lubrication mechanism of grafted polymer brush surface was the first to reveal that the hydrophilic polymer brush surface produces osmotic pressure repulsion in the water environment and prevents the intertwining and shearing of the polymer chains to reduce the viscous dissipations during friction process[13]. Prof. Spencer and his cooperators also have modified the positively charged polylysine-polyethylene glycol onto the silicon surface by electrostatic interaction, and the tribological behavior of the surface polymer brush in different solvent environments were studied by atomic force microscopy technique. The relationship between the swelling degree of polymer brushes and the friction coefficient was revealed, namely, in a good solvent (water), water molecules strongly bind with PEG chains through hydrogen bonding and polar interactions. The hydrated PEG chains exhibit low friction, and the combined solvent molecules are not easily squeezed out under compression. However, in a poor solvent, the PEG chains experience progressively collapsed conformation change and exclusion of solvent molecules because of weak hydrogen bonding and polar interactions, which lead to a less fluid interface and thus more energy is dissipated during sliding motion[14]. Our group also studied the aqueous lubrication of polymer brush surface systematically and revealed the relationship between surface wettability and its lubrication characteristic that provides new ideas for designing and preparing controllable surface lubrication materials[15-16]. The ionic polymer brush was grafted from solid surface by surface-initiated atom transfer radical polymerization (SI-ATRP), and the counterions of polymer brushes were exchanged by others bulky ions for changing the surface hydrophobicity and the surface friction coefficient[17-19]. The swelling degree of the ion brush is adjusted under different concentrations of salt solution by ionic charge shielding effect to realize friction coefficient regulation[20].

In this work, the hydrophilic macromolecules were anchored to the solid surface by the interfacial supramolecular host-guest interaction, and the macroscopic tribological behavior of the surface in aqueous environment was studied by reciprocating friction tester. Because of the hydrophilic guest polymer infusion, the lubrication properties of surface improved tremendously under low applying load in aqueous surrounding. But with the increasing of apply load, the interfacial friction coefficient also raised because the hydrophilic guest polymer may be sheared off from host surface. But it is because of its non-covalent bond supramolecular interaction, the surface has self-healing lubricating property, namely, the worn host-guest surface will recognize and assembly the guest hydrophilic polymer to achieve ultralow friction coefficient.

1 Experiment

1.1 Materials and Chemicals

Monocrystalline silicon wafer (p-type, Suzhou Ruicai Semiconductor Co, Ltd), 3-glycidyloxypropyl-trimethoxysilane (97%, Beijing J&K Technology Co, Ltd), aminocyclodextrin (97% Binzhou Zhiyuan Bio Technology Co, Ltd), Potassium 3-sulfonate propyl-methacrylate (97%, Beijing J&K Technology Co, Ltd), 2-bromoisobutyryl bromide (97%, Energy Chemical Technology), adamantane methanol (98%, Beijing J&K Technology Co, Ltd), bipyridyl (Shanghai Kefeng Industrial Co, Ltd), cuprous bromide (Tianjin Komio Chemical Reagent Co, Ltd), methanol, ethanol and acetic acid are supplied by Tianjin Komio Chemical Reagent Co, Ltd. Except that cuprous bromide was refluxed with acetic acid for 4 h, the other reagents were used without any treatment.

1.2 Preparation of Guest Macromolecules

Adamantyl 2-bromoisobutyrate is obtained by reacting 2-bromoisobutyryl bromide with adamantane methanol in dichloromethane. The terminal adamantyl polymethyl methacrylate propyl sulfonate (PSPMA-AD) is prepared by the ATRP method using amantadine 2-bromoisobutyrate as an initiator and methanol/water as a solvent.

1.3 Preparation of hydrophilic supramolecular surface

Silicon wafer was treated by oxygen plasma for 3 min to remove surface organic pollutants, and the 3-glycidoxypropyltrimethoxysilane (0.5%) in methanol was spin-coated to the surface. The surface of the silicon wafer was heated in an oven at 80 ℃ for 2 h to obtain the substrate covered with epoxy groups. The epoxy-modified silicon wafer was immersed in DMF solution of aminocyclodextrin (1 mg/ml). After standing at room temperature for 24 h, it was taken out and rinsed with ethanol to obtain a surface of a silicon substrate modified with cyclodextrin molecules. The cyclodextrin modified silicon wafer was placed in an aqueous solution of PSPMA-AD (1 mg/ml) overnight, and rinsed with purified water, and blown dry with nitrogen to obtain a guest macromolecular modified surface. The preparation process is shown in Fig.1.

1.4 Characterization

The chemical composition of the sample was characterized by X-ray photoelectron spectroscopy (XPS), and the measurement was carried out on an ESCALAB 250xi spectrometer (Thermon Scientific, USA) by using Al Kα radiation. The binding energy of C1s (284.8 eV) was used as the reference. Static and dynamic contact angles (CAs) were measured using a DSA-100 optical contact angle meter (Krüss Company, Germany) at ambient temperature (25 ℃). A droplet of 5 μL of deionized water was used as the probe liquid to obtain the static contact angle, and the average CAs were measured at three different positions on the sample. The thickness of the polymer layer was measured using a spectroscopic ellipsometer (Gaertner model L116E) equipped with a He-Ne laser source (*λ* = 632.8 nm) at a fixed angle of incidence of 50°. The refractive index of polymer film was 1.5. Surface topography images were obtained using an atomic force microscope (AFM) (Agilent 5 500) in tapping mode with a commercially available type-II MAC lever, of which the nominal force constant was 2.8 N/m. The friction test during aqueous-

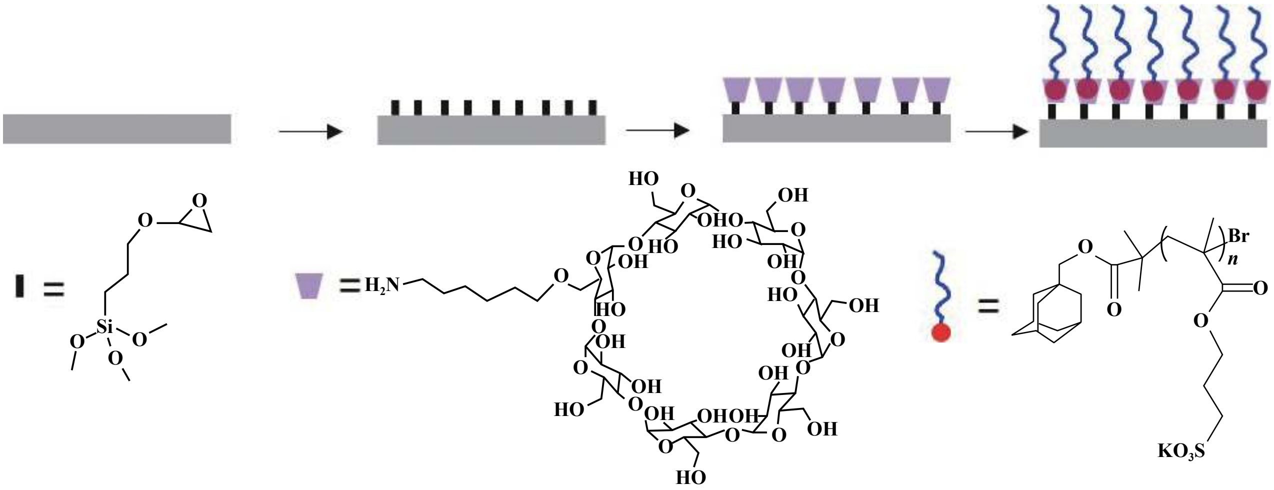
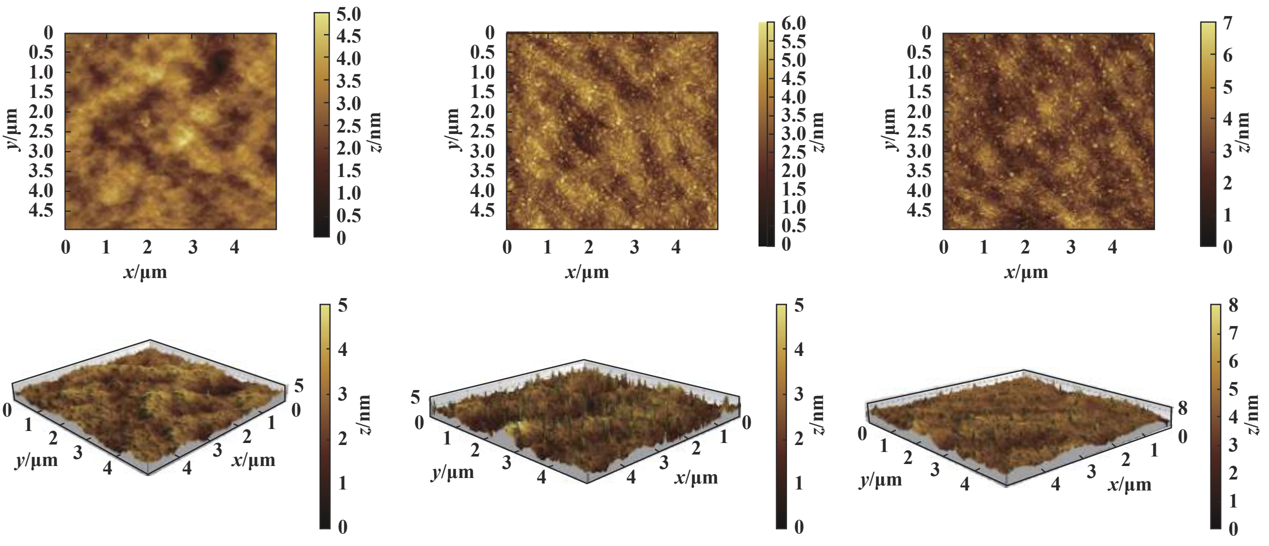


Fig. 1 The preparation process of host-guest supramolecular interfacial material

lubricated sliding was carried out on the conventional pin-on-desk reciprocating tribometry apparatus (MFT-R4000, HuaHui, Lanzhou) by acquiring the friction coefficient (μ) at different loads and frequencies. These pins are elastomeric poly(dimethylsiloxane) (PDMS) hemispheres with a diameter of 6 mm, and they were prepared by a commercial silicone elastomer kit (SYLGARD 184 silicone elastomer, base and curing agents, Dow Corning, Midland, MI); the weight ratio of the base and curing agents was 10:1. A polystyrene cell culture plate with a round-shaped well (Siqi Biotechnology, Beijing) was used to prepare the hemisphere PDMS pins as a mold. The mixtures were put into the mold after removing bubbles and then incubated in a 70 ℃ oven for 4 h. Each sample was measured at least three times at different positions to get the mean value.

2 Results and discussion

Different chemical composition of the solid surface usually has different microstructure, and it is generally characterized by atomic force microscopy. Fig.2 shows the AFM image of a silicon surface at various steps of the hydrophilic supramolecular surface preparation process. Fig.2(a) is the AFM image of clean silicon wafer surface. It can be seen that the surface of the silicon wafer has obvious undulating gully and the roughness is 0.67 nm. Fig.2(b) is the surface of the modified cyclodextrin molecule. Compared to the Fig.2(a), the dense spots in Fig.2(b) appears which can be attributed to the cyclodextrin aggregate. Due to the large amount of hydroxyl groups on the outside of the cyclodextrin, a large number of hydrogen bonds can be formed between the cyclodextrin molecules to aggregate, and the surface roughness is also increased to 0.95 nm. Fig.2(c) shows the surface AFM image after assembly of the hydrophilic guest macro- molecule. Compared with Fig.2(b), the surface bright spot density is significantly reduced, indicating that the number of surface cyclodextrin aggregates is reduced. The terminal adamantane poly(methyl methacrylate) 3-sulfonate bound to the cyclodextrin and destroyed the hydrogen bond between the cyclodextrin molecules. The long polymer chain of poly(methyl methacrylate) 3-sulfonate covered most of the cyclodextrin molecules, and the surface roughness was also reduced to 0.73 nm. The AFM morphology and roughness confirmed the successful modification of cyclodextrin and adamantyl macromolecules. To further demonstrate the successful modification of cyclodextrin and adamantyl macromolecules, the surface chemical composition was characterized by XPS technique. As shown in Fig.3, the surface of the silicon wafer after modification of the cyclodextrin molecule has a characteristic peak at 400.1 eV,



(a) Si

(b) Si-CD

(c) Si-CD-PSPMA-AD

Fig. 2 The AFM images of (a) Si, (b) Si-CD and (c) Si-CD-PSPMA-AD substrates

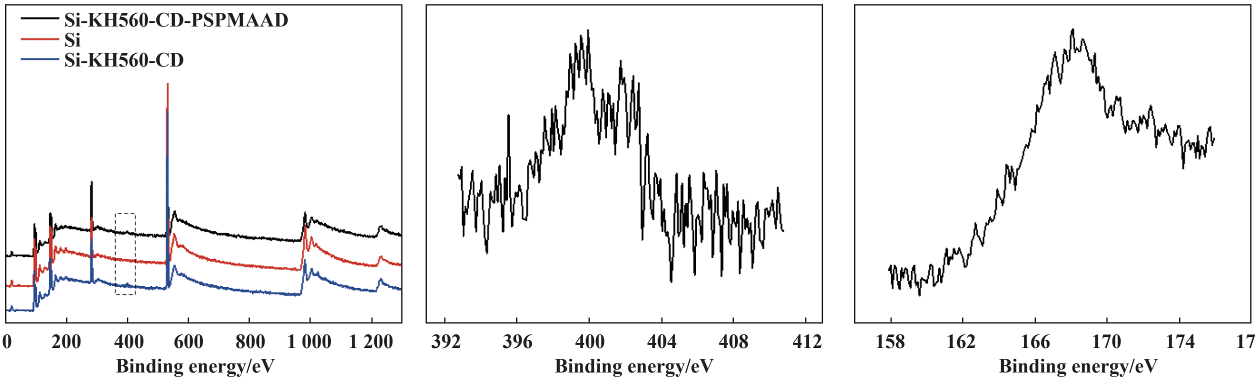


Fig. 3 The XPS (a) full spectrum and (b) N, (c) S fine spectrum of various substrates

which can be attributed to the signal peak of the nitrogen element of aminocyclodextrin. A distinct peak at 168.0 eV also appeared after assembling PSPMA-AD, which can be attributed to the sulfur element signal peak in the terminal adamantyl polymethyl methacrylate 3-sulfonate potassium. Each surface XPS analysis also have confirmed the successful modification of the cyclodextrin and guest macromolecules on the surface.

Molecular modification also affects the surface thickness. As shown in Fig.4(a), the change in thickness of the substrate at different preparation process were measured by an ellipsometer. The thickness of the clean silicon wafer is 20.5 nm, which is mainly the thickness of the silicon oxide layer of wafer. After the spin-coating of the dilute solution of 3-glycidyloxypropyltrimethoxysilane, the thickness of the silicon wafer increases 4 nm to 24.5 nm. It is may be mainly caused by 3-glycidyloxypropyl trimethoxysilane multilayer cross-linking during the spin coating process. After modifying the cyclodextrin, the surface thickness of the silicon wafer is increased by 1.6 nm that matches the size of the cyclodextrin. The result indicates that the cyclodextrin molecule is grafted on the surface with monolayer modification. Further modification of the terminal adamantyl poly(methyl methacrylate) propyl sulfonate molecule, the surface thickness increases 5.1 nm to 31.2 nm, which indicates this hydrophilic guest polymer molecule assembly successfully. Surface wettability is closely related to surface chemistry, and also can be used to demonstrate successful modification. As shown in Fig.4, the contact angle of the silicon wafer after the oxygen plasma treatment is less than 10°, and the superhydrophilic state is exhibited because of abundant silicon hydroxyl on wafer surface after the oxygen plasma treatment. After the modification of the 3-glycidoxypropyltrimethoxysilane molecule, the surface contact angle is increased to 49.8°. It is mainly because the epoxy is a hydrophobic group. After modifying the cyclodextrin molecule, the surface contact angle is reduced to 36.4°, which is mainly because the large

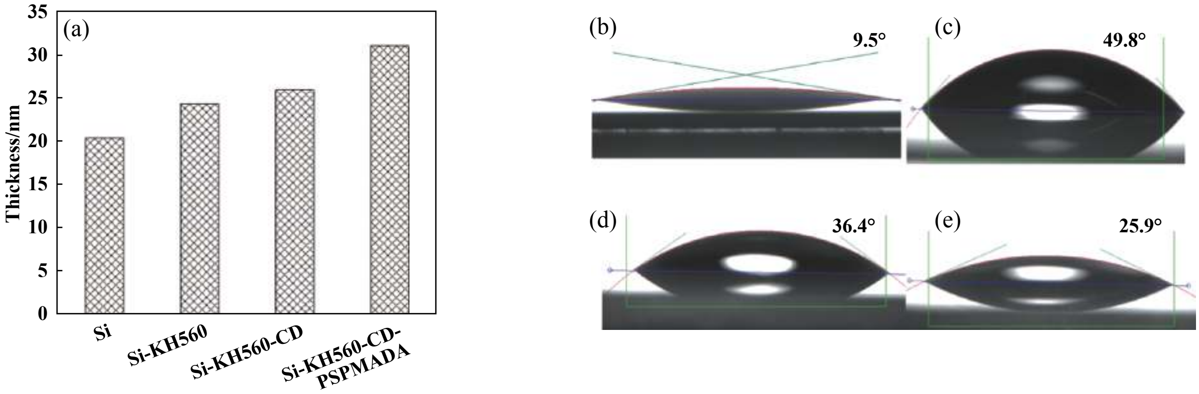


Fig. 4 The (a) thickness and wettability of various substrates, (b) Si, (b)Si-KH560, (c) Si-KH560-CD, (d) Si-KH560-CD, (e) Si-KH560-CD-PSPMADA

amount of hydroxyl groups on the outer side of the cyclodextrin lead to the cyclodextrin hydrophilic characteristic of outer wall. After assembly of the guest macromolecule, the surface contact angle is further reduced to 25.9°, mainly because the guest macromolecule is a water-soluble polymer, and the sulfonic acid group can be combined with a plurality of water molecules to achieve a high degree of hydration. It is also the main reason for the low friction coefficient of the surface after the subsequent assembly of guest macromolecules.

The tribological properties of the surface were completed by a MFT-R4000 high-speed reciprocating friction tester. The silicone rubber hemisphere with diameter of 6 mm was selected as frictional pair. The friction experiment was carried out in the dilute adamantyl polymethyl methacrylate 3-sulfonate potassium aqueous solution. The friction curve of the modified hydrophilic guest macromolecule surface is shown in Fig.5(a). The friction coefficient is about 0.05 under 0.2 N load. While for the Si-KH560 surface without cyclodextrin molecules, the friction coefficient is above 0.6 under the same friction test conditions. The difference of friction coefficient between the two substrates is more than 10 times. The change of surface friction coefficient before and after modification of cyclodextrin fully reflects the role of cyclodextrin molecules in surface recognition and assembly. Cyclodextrin molecules acted as anchors to bond the hydrophilic guest macromolecules on the silicon surface and highly hydrated in the water environment to form a lubricating film, which greatly reduces the surface friction coefficient. But the surface without modifying the cyclodextrin molecule can not effectively anchored the hydrophilic macromolecule, which leads to a large friction coefficient.

The friction coefficient of the supramolecular surface also have related to the friction time. Fig.5(b) shows the dependence of friction coefficient on time under the load condition of 0.8 N. It can be seen that the surface friction coefficient is only 0.05 during the initial 45 s, and then the surface friction coefficient increases sharply to about 0.1. At last, the friction coefficient increase to about 0.2 slowly with time extends. This phenomenon could be because by the continuously shear off of the PSMMA-AD molecules from host surface during the rubbing process. When the amount of the polymer being sheared reaches a certain level, the surface friction coefficient has increased dramatically. Since the supramolecular host-guest interaction is a non-covalent bond interaction, the strength of the interaction is lower than the covalent bond, which results in weak binding strength of the guest macromolecule on the host surface. Under high load and long-term friction conditions, the guest molecule adamantane is easily extracted from the cyclodextrin molecule and destroyed the hydrophilic polymer layer.

Fig.6(a) is the change of the friction coefficient of the host-guest surface under different loads. It can be seen that the surface friction coefficient increases gradually from the lowest 0.05 to 0.22 with the applying load increases. The assembled hydrophilic macro-

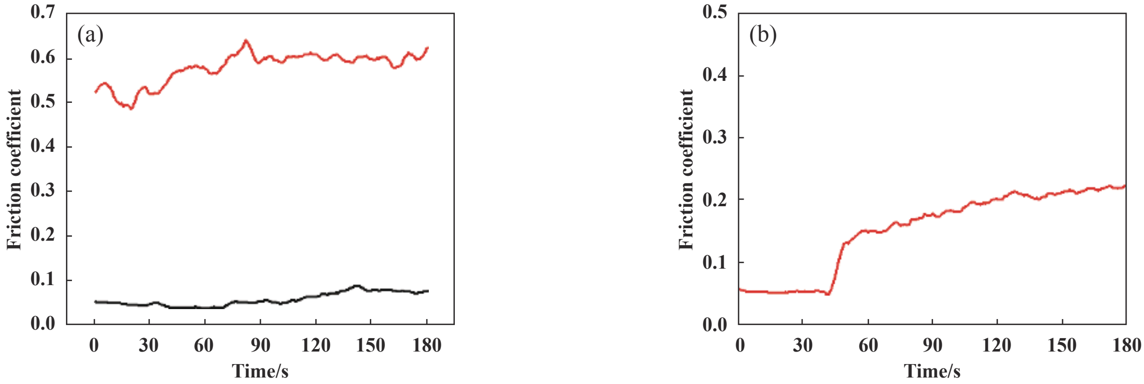


Fig. 5 (a) The friction coefficient of Si substrates before and after modifying with CD molecules under 0.2 N load, (b) the variation trend of friction coefficient during long time friction under 0.8 N load

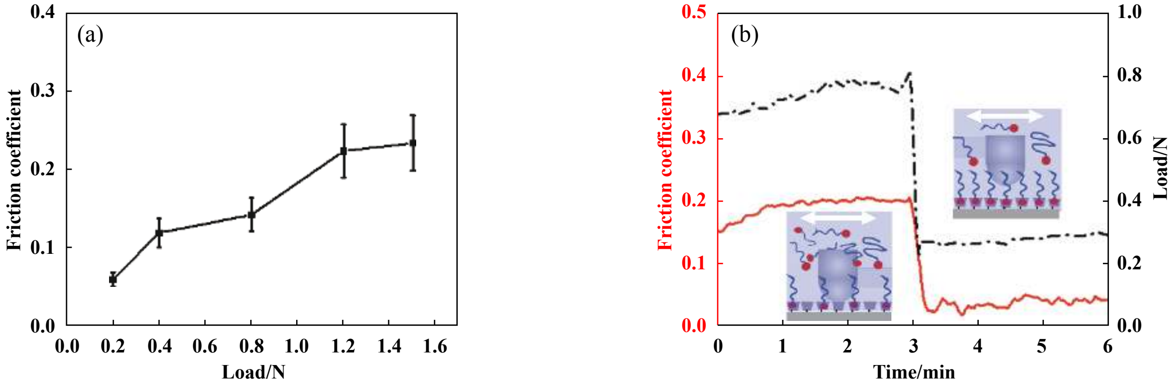


Fig. 6 The variation trend of friction coefficient under (a) different loads and (b) continuous variable load

molecules by supramolecular host-guest interaction are sheared off under high load and reciprocating friction conditions, and the hydrated boundary lubrication film is partial destructed which cause the increase of friction coefficient. However, based on the non-covalent bond-based supramolecular recognition, after the adamantyl hydrophilic macromolecule is sheared off, the surface of the cyclodextrin can be recognized and assembled in the adamantyl hydrophilic macromolecular solution. Therefore, the aqueous lubrication performance of the host-guest surface has a certain self-healing property. The self-healing properties of cyclodextrin-adamantyl surface water lubrication can be seen from the continuous variable load friction test. The applied load is automatically controlled by the friction tester indenter. As shown in Fig.6(b), the surface friction coefficient is about 0.16 under a high load (0.8 N) state, showing relatively large friction coefficient; but when the applied load is reduced to 0.3 N, the surface friction coefficient is only about 0.05, showing ultra-slippery state. This phenomenon can be attributed to the fact that some of the guest hydrophilic macromolecules are sheared off under high load conditions, and the guest macromolecules can be assembled again to the surface to exhibit an ultra-low friction coefficient when the applied load reduces.

Fig.7(a) shows the friction coefficient of the modified guest macromolecular surface under 0.2 N at different friction frequencies. The surface friction coefficient decreases sharply from 0.25 to 0.05 with the increase of frequency, and then slowly decreases to 0.02. This trend is consistent with the trend of the famous Stribeck curve [Fig.7(b)], namely, as the shear rate increases, the state of surface lubrication changes from boundary mixing lubrication to fluid lubrication, and the friction coefficient also reduces with the state of lubrication. For the host-guest supramolecular surface, much more guest macromolecules may be sheared off, which results in loss of lubricating performance and an increase of friction coefficient at low friction frequency

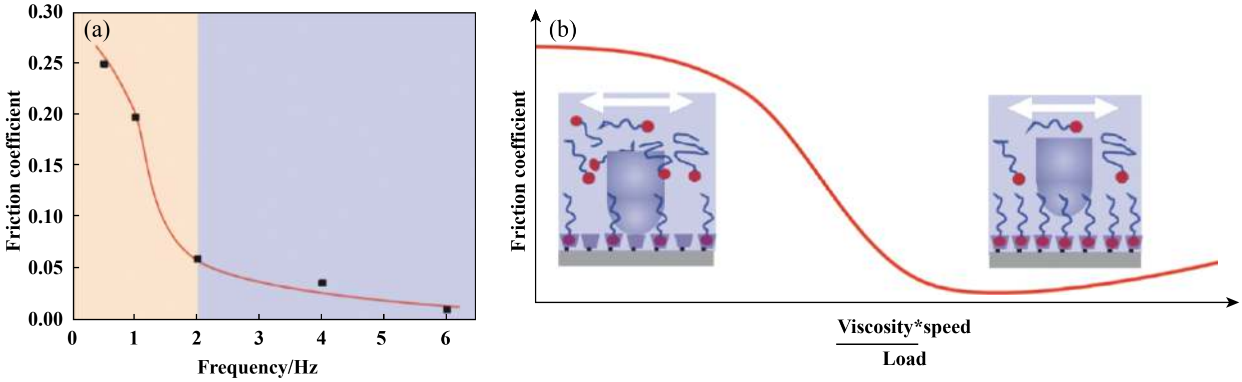


Fig. 7 (a) The variation trend of friction coefficient under different frequencies, (b) the possible friction mechanism of the supramolecular interfacial material and high load condition. But at high friction frequency and low load condition, the fluid lubrication appears, and shows low friction coefficient.

3 Conclusion

In this work, the terminal adamantyl polymethyl methacrylate 3-sulfonate was prepared, and assembled on cyclodextrin surface by host-guest supramolecular recognition. After assembly the guest polymer molecules, the friction coefficient of surface in aqueous surrounding can be effectively reduced due to the hydrophilic characteristic. Because of the weak non-covalent bond between the cyclodextrin-adamantan, the host-guest supramolecular surface shows a poor bearing capacity and wear resistance. The guest polymer molecules are easily to be sheared off from host surface under high load and low friction frequency, which causes the rise of friction coefficient. And also because of the reversible non-covalent bond between the cyclodextrin-adamantan, the lubrication behavior of host-guest surface showed a self-healing characteristic. An ultralow friction coefficient obtained again when the host surface immersing in dilute guest polymer solution.

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