

Wear Evaluation of Poly(vinyl alcohol) Hydrogel by UV Spectrometry and TOC Measurement of Lubricant

Haruna Takefuji

Kyushu University Faculty of Sciences Graduate School of Sciences: Kyushu Daigaku Rigaku Kenkyuin
Rigakufu Rigakubu

Masahiko Annaka

Kyushu University Faculty of Sciences Graduate School of Sciences: Kyushu Daigaku Rigaku Kenkyuin
Rigakufu Rigakubu

Shintaro Yashima (✉ yashima@chem.kyushu-univ.jp)

Kyushu University Faculty of Sciences Graduate School of Sciences: Kyushu Daigaku Rigaku Kenkyuin
Rigakufu Rigakubu <https://orcid.org/0000-0002-6677-0660>

Research Article

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Abstract

We report the wear evaluation of poly(vinyl alcohol) (PVA) hydrogel by measuring the polymer concentration in the lubricant after the sliding test. Hydrogels are expected as biomaterials, and wear evaluation is required for their application. However, the swelling and drying behavior of hydrogels makes accurate wear evaluation difficult by applying the same method for solid materials. In this work, sliding tests were conducted, then the microscopic observation of the worn gel sample and the quantitative wear evaluation using the lubricant were performed. To understand the relationship between wear and surface geometry, glass substrates with various surface roughness and hydrogels with different surface geometries were used. UV spectrometry and total organic carbon measurements of the lubricant revealed that the wear amount increases with sliding time or surface roughness of the substrate, and it is possible to quantitatively evaluate the wear of the PVA gel. The effect of surface dimples on the hydrogel was different depending on the counter substance; friction and wear decreased against the glass, but low friction and high wear appeared against the gel. Because there were a few wear scars on the gel with dimples, it was suggested that dimples scrape and trap the generated wear particles, reducing the transfer of wear particles and surface damage. Measuring the concentration of PVA polymers in the lubricant made it possible to separately and quantitatively evaluate whether the wear of the gel was due to surface deformation and transfer, or loss due to surface damage.

1. Introduction

Hydrogel is a substance that has a three-dimensional polymer network structure swollen with water. It has many features, such as high water content, softness, permeability, and stimuli-responsiveness. Moreover, among artificial materials, it is the most similar to biological tissues. Therefore, hydrogels are applicable in biomaterials, and there are many studies on the application of hydrogels as artificial joint cartilages[1–5]. Biocompatibility, mechanical properties, and durability are issues and evaluation points that must be considered in order to apply hydrogels as biomaterials[6, 7]. For artificial cartilage, hydrogels must have the same level of low friction and wear resistance as biological joints.

In the tribological studies of hydrogels, although there are many reports on the friction of gels, there are few reports on the wear of gels. One of the reasons for this is that the evaluation methods used for other solids, such as metals, are difficult to apply to hydrogels. The gel, which is in the equilibrium swollen state, is worn by friction, then it reaches a new equilibrium state by swelling when it is stored in water, or drying when it is stored in air. Therefore, it is hard to maintain the worn state of the gel. The measurement of weight change of the sample before and after the test, observation by microscope, and surface roughness meter are used as the evaluation methods for the wear of gels[8–10], however, each method cannot avoid the influences of swelling and drying. In addition, there is a possibility that a new scuff, which is different from the wear scar, is generated by surface scratches from roughness measurements, and irreversible change is caused to the gel.

As stated earlier, wear is often evaluated by observing its surface morphology; however, this method cannot distinguish whether the wear scars on the gel are generated by releasing the wear particles into the lubricant or by changing its surface shape. The wear particles in the lubricant obviously reflects the loss amount of the materials, and they are the effective target for the wear evaluation particularly in low wear conditions.

To the best of our knowledge, research on the evaluation of gel wear using lubricants has not been reported, and a new method for evaluating the concentration of wear particles in lubricants is required. Herein, we attempt to evaluate the wear of gels using a *lubricant* that may contain wear particles instead of a worn gel sample. As the evaluation methods for the lubricant, spectrometric oil analysis program (SOAP) method, ferrography and particle counter method are known to detect the metal wear[11–15]. In addition, spectroanalysis such as UV-vis spectrometry and total organic carbon (TOC) measurement may be useful. The advantages of the latter two methods are the following: the relatively short measurement time, recoverability, and the ability to measure with a small amount of lubricant make it possible to detect even a small amount of the gel wear. Note that, we focused on the wear particles to measure merely the wear degree of the gels here. However, because the wear particles are the cause of inflammation for the surrounding tissues of artificial joint[1], it can be said that the measurement of the concentration of the wear particles is advantageous for the applications of the gels.

In this study, we evaluated the wear of poly(vinyl alcohol) (PVA) gels. Because PVA gel is biocompatible and has superior mechanical properties, it has been widely studied as a candidate for artificial cartilage[1, 3, 16]. PVA is fabricated industrially by saponification of poly(vinyl acetate); however, the saponification process is not perfect, and hence, un-saponified parts remain[17] (Scheme 1). It has been reported that the carbonyl group contained in these un-saponified parts has an absorbance band around the wavelength of 280 nm[18, 19]. Therefore, it is possible to detect PVA and quantitatively evaluate its concentration or wear amount. Moreover, TOC measurement may be a key method because the PVA polymer itself is composed of organic carbons. Here, we adopted two methods to evaluate the wear of PVA gels, UV-vis spectrometry and TOC measurement.

We confirmed that the friction property of the PVA gel is drastically changed by its surface geometry[20]. In particular, the gel with hemispherical surface dimples, showed lower friction compared with the gel with a flat surface. The relationship between the friction of the gel and wear, however, is still unclear, and the effects of the gel surface geometry on the wear properties are not well known.

In this work, PVA gels were prepared and sliding tests were performed. Then, we studied whether it was possible to evaluate the wear of gels by evaluating the lubricant that was obtained after the sliding tests using UV-vis spectrometry and TOC measurement. First, the glass substrates with surface roughness were used as a counter substrate for the sliding test of the gel to examine whether these methods could evaluate the wear of gels. The rough substrate is considered to be suitable for the first try because it is predicted that the hard glass surface projection will cause abrasive wear that cuts the soft gel surface and a large amount of wear particle will be surely generated and released into the lubricant. Then, the

hydrophobically treated flat glass was also used as a counter substrate and it is examined these wear evaluation methods are appropriate even in the system that adhesive wear is predicted to predominantly occur. Adhesive wear is considered to be classified as mild wear and the wear amount is relatively low compared with the case that the rough glass is used, and it is investigated whether these proposed methods can be useful as evaluation methods in low wear cases or not. In addition, the relationship between the surface geometry of gels and friction or wear properties was studied using PVA gels that were given hemispherical dimples on their surfaces. Furthermore, in bio-system such as our articular joints, soft tissues which resemble gel slide against the other soft tissue, so the sliding test was conducted in the configuration of gel-on-gel and performed its wear evaluation.

2. Materials And Methods

2.1 Materials

Poly(vinyl alcohol) (PVA) (Degree of Polymerization: 2000; Degree of Saponification: min. 98.5 mol%) was purchased from Nacalai Tesque, Inc. Dimethyl sulfoxide (DMSO), hexamethyldisilazane (HMDS) and *1H, 1H, 2H, 2H*-perfluorodecyltrichlorosilane (FDTS) was purchased from Wako Pure Chemical Industries, Ltd. Polydimethylsiloxane (PDMS) (SILPOT 184) was purchased from Dow Corning Toray Co. All chemicals were used without further purification.

2.2 Droplet replication

To impart the surface dimples on the PVA gel, PDMS template were prepared by replicating the condensed droplets on a HMDS-treated hydrophobic glass surface[21, 22]. To obtain hemispherical water droplets, float glasses were modified with HMDS. In order to clean the glass surface, glass was soaked in the solution of 10 wt% NaOH in ethanol for 1 hour, then 10 wt% HCl aqueous solution for at least 1 day. For further cleaning, vacuum UV light with wavelength of 172 nm was irradiated to the glass surface for 3 minutes using Excimer irradiation unit (UER 20-172, USHIO Inc.). The cleaned float glass pieces were exposed to HMDS vapor under 20 kPa for 16 hours in a desiccator. The contact angle to water θ of the HMDS-coated glass was $71.8 \pm 1.5^\circ$.

Water evaporated from a water bath heated to 70°C was condensed on the glass kept at room temperature ($\sim 25^\circ\text{C}$), resulting in numerous droplets on the surface. The size of the water droplets could be changed by the time the glass was exposed to the vapor, the exposure time was set to 600 seconds in this work. Then, a degassed mixture of cross-linkable liquid silicone, liquid PDMS was poured to the glass surface with droplets and cured at 70°C for 2 hours. When the crosslinked PDMS was peeled off from the HMDS-treated glass, the negative image of condensed water droplets appeared on its surface. To achieve positive replication of droplets, liquid PDMS was poured onto the negative replicated PDMS template and crosslinked.

2.3 Hydrogel preparation

The physically crosslinked PVA hydrogels were prepared by quenching from 10 wt% PVA solution of mixture solvent (DMSO:H₂O=3:1, w/w). PVA solution was prepared by heating and stirring PVA powder in the mixture solvent for 2 hours at 100°C. Then, the degassed PVA solution was poured into a home-made reaction cell, consists of two glass plates separated with a silicone rubber spacer of 3.0 mm thickness, to form a hydrogel sheet. To impart hydrogel surface dimples, one of the glass plate surface of reaction cell was covered by the PDMS template with hemispherical surface bumps. To make the hydrogel with flat surface, the flat PDMS template was also used as a mold. The solution was quenched at -40°C for 16 hours. The hydrogel sheets were then allowed to warm up to room temperature and subsequently immersed in a large amount of deionized water for at least one week to extract the DMSO. The water content of the gel was about 86% regardless of the surface geometry, and the Young's modulus E of the gel prepared was 94.0 ± 1.4 kPa.

In this paper, we name the PVA hydrogel with the flat surface "*Flat*" and that with the surface dimples "*Concave*". The surface morphology of the hydrogels was observed using a geometry measurement laser microscope (KS-1100, Keyence Corp.). In the observation, the diameter and depth of each dimple shape on the surface of Concave was evaluated, and the values were averaged for 30 dimples. The mean dimple size was 820 ± 80 μm in diameter and 390 ± 50 μm in depth. Comparatively, no surface pattern shape was observed for Flat.

2.4 Sliding test

Friction and wear measurements were performed using a strain-controlled rheometer (ARES, TA Instruments, Co.). The disc-shaped hydrogel, which was 15.70 mm in diameter and 2.70 mm in thickness, was glued onto the stage of the rheometer using a cyanoacrylate instant adhesive agent (Toa Gosei Co., Ltd.). The normal pressure, P , was set as an experimental parameter. Prior to the friction and wear measurements, the normal strain was applied and gradually increased until the normal stress reached a prescribed value. Although the normal load changes during the tests, the primary normal stress P_0 was set to 28 kPa. After 10 minutes of preloading, the test was started in step rate test (SRT) mode. For the first 5 seconds, the stage was rotated with angular velocity $\omega=0.13$ rad/s, then ω was increased to $\omega=1.3$ or 5.2 rad/s. The friction force, F , was calculated as $F = 4T/3r$, where T is the friction torque recorded during the measurement and r ($= 7.85$ mm) is the radius of the apparent contact area[23]. The data acquisition rate was set to 350 points per measurement time. The average friction stress, τ , generated at the interface is qualified as the friction force per unit area, $\tau = F/\pi r^2$. Although the sliding velocity varies along the radial direction in the parallel-plate geometry from 0 at the rotational center to ωr at the perimeter, we adopted the sliding velocity v at the perimeter of the disc-shaped samples, $v = \omega r$, when indicating the sliding velocity as a representative value.

In this study, we conducted three types of friction and wear measurements: (1) Flat gel sliding against glass substrates with different surface roughness, (2) Flat and Concave gels sliding against the FDTS-treated flat glass substrate, and (3) gel sliding against gel. A schematic of the measurement system is shown in Fig. 1.

In measurement (1), Flat gel was slid against five kinds of glasses with different roughness. The substrates were prepared by sandblasting soda glass plates (thickness, $t=3$ mm) with different particle sizes (Niki Token. Co. Ltd), the ten-point average roughness, R_z values were 53, 31, 18, 12, and 7.9 μm , respectively. The surface images of the glass substrates are presented in Fig. 2. All rough glass substrates were cleaned by soaking in 10 wt% HCl aqueous solution before the measurements.

In measurement (2), two kinds of gels, Flat and Concave, were slid against the FDTs-treated glass substrate. The preparation method of the substrate is as follows. For surface cleaning, cover glasses (micro cover glass, C050701; Matsunami Glass Ind. Ltd.) were soaked in 10 wt% HCl aqueous solution for 3 days and washed with deionized water. Furthermore, the glass pieces were kept in vacuum and UV irradiated with a light having a wavelength of 172 nm for 1 minute. The cleaned glasses were exposed to FDTs vapor at 20 kPa for 8 hours in a vacuum desiccator at room temperature. The contact angle to water θ of the FDTs-coated glass substrate was $110\pm 1^\circ$.

Measurement (3) was performed for three configurations: Flat-on-Flat, Concave-on-Flat, and Concave-on-Concave. Both gels were cut into disc shapes, and each sample was glued onto the lower stage or upper jig of the rheometer. The size of the lower gel was 24.80 mm in diameter and 2.70 mm in thickness, and that of the upper gel was the same with the one in measurements (1) and (2).

Sliding tests in this work take 7200 seconds at maximum, and although stress relaxation is expected to occur, it is very small and can be negligible. Here, the characteristic time of stress relaxation due to the flow of water in the gel was calculated to be on the order of a^2 / D_c according to the work by Hui et al.[24] a^2 / D_c was on the order of 10^4 - 10^5 seconds. In this calculation, the radius of the indenter compressing the gel, a , was set to 7.85 mm, which is the radius of the gel, and D_c is the cooperative diffusion coefficient, which was calculated as $D_c = k_B T / 6 \pi \eta \xi_h$ and was in the order of 10^{-10} to 10^{-11} m^2/s . k_B , T , η , ξ_h are the Boltzmann constant, temperature, viscosity, and hydrodynamic shielding length respectively. Since the temperature is 25°C and the solvent is water, $k_B T = 4.11 \times 10^{-21}$ Nm, $\eta = 0.894 \times 10^{-3}$ Ns/m². ξ_h was assumed to be the order of 10^{-9} to 10^{-8} m. Since the calculated time (10^4 to 10^5 seconds) is longer than the time scale in this work (10^3 seconds), the stress relaxation due to water flow is considered to be negligible.

2.5 Wear evaluation

2.5.1 Observation by optical microscope

An optical microscope (SZX-12, OLYMPUS) was used for the observation. To avoid the influence of swelling and drying of the gel, the sample surface was observed in air soon after the sliding test.

2.5.2 UV spectrometry

After the sliding test, the lubricant (water in this work) was syringed, and the UV spectrum of the lubricant was acquired using a UV-vis spectrometer (V-660 Spectrophotometer, JASCO), and PVA was detected in

the lubricant. Deionized water was used as the baseline. Prior to the measurement, the lubricant was heated in a water bath at 80°C for 30 minutes to unlink the crosslinks of the wear particles of the PVA gel, resulting in a uniform solution of PVA polymer (Fig. 3).

To prepare a calibration curve, PVA powder was dissolved in deionized water to prepare solutions with concentrations of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, and 1 wt%. Because the un-saponified part of the PVA chain has been shown to have an absorption band near the wavelength of 280 nm (Fig. S1a)[18, 19], a calibration curve was prepared using the absorbance at a wavelength of 280 nm (Fig. S1b).

The amount of PVA *polymer* contained in the lubricant was defined as the wear amount. In addition, the specific wear rate was calculated by dividing the wear amount by the sliding distance.

2.5.3 TOC measurement

The amount of TOC contained in the lubricant was quantitatively evaluated as non-purgeable organic carbon (NPOC) using a total organic carbon meter (TOC-V CSH, Shimadzu Corp.). Because the detection sensitivity is very high compared with UV spectrometry, the TOC of solutions of 0.0001, 0.0005, and 0.001 wt% prepared by dissolving PVA powder in deionized water was measured. In addition, the TOC of deionized water was measured and the calibration curve in the low concentration region was prepared by adopting that value (Fig. S2).

After acquiring the UV spectrum, the solution was used as the measurement sample for TOC. The calculation of the wear amount and specific wear rate is the same as that described in the UV spectrometry section.

3. Results And Discussion

3.1 UV spectra and TOC

The UV-vis spectra of the three types of PVA solutions are presented in Fig. 4. One was prepared by dissolving the PVA polymer powder in water. The second was prepared by heating the PVA gel in water. The last was prepared by heating the lubricant, which is considered to contain the wear particles of the PVA gels. All the aqueous solutions had absorbance bands around 280 nm, and the shapes of the spectra were similar. Therefore, it can be said that quantitative evaluation of PVA concentration in the lubricant is possible using the calibration curve, which is obtained from the absorbance of PVA solutions prepared from PVA *powder*.

It is possible to distinguish the contaminants that have absorbance at a different wavelength from PVA, if the solution is contaminated. In addition, TOC measurements were performed for the solution prepared by heating the PVA gel in water, similar to UV spectrometry, and a peak of carbon was detected (data not shown). The PVA concentration calculated by using the calibration curve was almost consistent with the predicted value from the weight of PVA gel considering the polymer fraction of the gel. Therefore, the PVA concentration in the lubricant can also be quantitated using the calibration curve for TOC. Wear scars

reflect the result of complex wear derived from surface deformation, the transfer of wear particles to the counter surface, and the loss of gel as wear particles to the lubricant. On the contrary, the concentration of wear particles in the lubricant can only reflect the loss of gel, making it possible to analyze wear by combining the results of the optical observation of wear scars.

Hereafter, the results of each measurement system for evaluating friction, wear scars, and wear particle concentration in the lubricant are discussed.

3.2 Wear of PVA gels

3.2.1 Gel vs. rough glass

Wear measurement of hydrogels should be conducted in water for the stability because the gels easily change their volume due to drying. However, when lubrication occurs, the viscous resistance of lubricant also donates to the friction force, and wear is reduced because the contact of gel/substrate is hindered. That makes it difficult to understand the relationship between friction and wear and to judge whether this evaluation method is appropriate. Therefore, we first performed the sliding test in the gel vs rough glass system, in which the gel and the counter substrate are expected to surely form contact due to very fast drainage.

To our best knowledge, the equation for wear of gels has not been developed, we use the wear model of rubber and polymer. From the classical wear model developed by Archard, Schallamach and Tabor, the abrasive wear of the gels was assumed to be described by the friction force F (Eq. (1)), or the normal load N for more simple expression (Eq. (2))[25–27].

$$W = kFl(1)$$

$$W = k'NI(2)$$

These are based on the premise that the real contact area A_r is proportional to the normal load N . In the classical wear model, the wear amount W is proportional to the friction force F or normal load N , and the sliding distance l , as in Eq. (1) and Eq. (2), regardless of the material. If it is described by Ratner's wear model for polymer materials[28], $k = k_2 / H\sigma\epsilon$, and $k' = k_2\mu / H\sigma\epsilon$. H is the hardness, σ is the tensile strength, ϵ is the breaking elongation, μ is the friction coefficient, and k_2 is the constant.

For soft matters including gels, the real contact area is equal to the apparent contact area. When the gel is in contact with the bottom surface of the rough glass substrate, Eq. (1) is expected to describe the result well rather than Eq. (2) because the real contact area A_r is not proportional to the load N anymore.

In Fig. 5, the relationship between friction stress and sliding time, which was measured under the condition that Flat, the gel with a flat surface, slid against the glass substrate with surface roughness, $R_z = 53 \mu\text{m}$, is presented. The friction stress tended to decrease with time, which perfectly follows the

decrease in normal force (Fig. S3). Also, the decrease in normal force depends on the volume change caused by the wear loss of gels and not the stress relaxation due to the solvent flow in the gel (Fig. S4).

The results of the wear amount measured by UV spectrometry and TOC are shown in Fig. 6. In Fig. 6a, the *wear amount* on the left axis means the amount of PVA *polymer* released into the lubricant as wear particles. The *loss of PVA gel*, wear amount divided by the polymer fraction (~14%) in PVA gel, is also shown on the right axis and it refers to the weight of PVA *gel*. If the polymer fraction of the gel is known, it can be described in both formats, but we discuss wear behavior hereafter using the value of wear amount.

Since the UV spectrometry only measures 1.5 mol% of PVA, which is the un-saponified fraction, and is easily affected by the contamination, TOC is expected to be more reliable. An approximate straight line was drawn (not shown in Fig. 6) for the PVA concentration obtained from the UV spectrometry, and the modified values, denoted as “modified-UV” in Fig. 6, were calculated by setting the intercept to 0. The modified values were similar to those obtained from the TOC measurements. In UV spectrometry, the absorbance at 280 nm was considered to be affected by contamination, such as the adhesive agent or others. The contaminant had the absorbance at the wavelength of 280 nm and molar absorptivity was relatively higher than PVA. However, the amount of contaminant might be so small that it did not affect the TOC results in this measurement system.

It was confirmed that the wear amount increased with the sliding time in both UV and TOC. Especially in TOC, the wear amount changes more moderately as the sliding time is longer. The wear amount was approximately 400–1100 times the volume derived from the surface roughness of the glass; hence, it can be said that abrasive wear occurred when the gel was ground by the rough glass. In this measurement, the indentation depth of the gel was more than approximately 300 μm ; hence, the gel was compressed sufficiently compared with the surface roughness of the glass substrate.

In the microscopic image of the sample surface taken immediately after the wear measurement (Fig. 7), it was confirmed that there were obviously more severe annular wear scars with longer test time. This corresponds to the wear amount obtained from the UV spectrum and the TOC measurement. Because rotational sliding friction and wear tests were performed in this work, annular wear scars were generated concentrically from the center of rotation.

To examine the relation of wear amount and friction or normal load in detail, the plot in which the wear amount is on the vertical axis and the product of friction force F and sliding distance l , calculated as $Fl = \sum_i f_i(t_i) \cdot \Delta t \cdot v$, is on the horizontal axis is presented in Fig. 6b. The $f_i(t_i)$ is the friction force at the sliding time $t = t_i$, Δt is the data acquisition time, and v is the sliding velocity. In the system where the gel slid against the rough glass, the result was consistent with the classical wear model in which the wear amount is proportional to the product of friction and sliding distance (Eq. (1)). The fact that the results of Flat on rough glass fit well with Eq. (1) means that the friction and wear behavior of this system is as follows:

1. The asperity of the glass substrate makes firm contact with the gel, also the gel is in contact with almost the entire glass surface until it reaches the bottom of the asperity because the gel is sufficiently compressed. Then, the contact area of the gel and the glass substrate with the asperity becomes smaller as the load decreases with the stress relaxation of the gel.
2. Friction is dominated by the resistance of gel/glass, and the viscous resistance of lubricant is small because the system is not lubricated, due to the firm contact of gels and glass asperity.
3. Wear particles are easily released into the lubricant, and the rate of transfer to the glass or the gel itself is small.

Also, the results of the wear amount follow Eq. (2) well, and the plot is presented in Fig. S5.

We would like to claim that the results are consistent with the classical wear model because this method accurately measures the wear particles in the lubricant. In particular, the TOC indicated a remarkable linearity in Fig. 6b, suggesting that the wear amount can be accurately quantified.

The relationship between the surface roughness of the substrate and the specific wear rate is shown in Fig. 8. The specific wear rate is defined as the value at which the weight of the PVA (polymer) contained in the lubricant is divided by the total sliding distance. As shown in Fig. 8a, the specific wear rate increased as the surface roughness of the substrate increased, and the rate of change gradually decreased. It is known that the wear rate is proportional to the surface roughness, and this trend is observed for metals[14], polyethylene[29], and rubber in lubricant[30]. The results shown in Fig. 8a depend on the fact that the volume that can be ground is large because the contact area between the gel and the glass is large as the surface roughness of the substrate increases. The larger the surface roughness, the easier it is for the contact area to change with stress relaxation. Therefore, the specific wear rate changes moderately as the surface roughness gets larger.

The microscopic images taken after the tests (Fig. 8b-f) also show that the sample slid against the substrate with a larger surface roughness was more severely worn. However, the friction stress did not show a clear correlation with the size of the surface roughness on the substrate and the specific wear rate (Figs. S6a and S6b).

3.2.2 Gel vs. flat hydrophobic glass

Next, the results for the hydrophobically treated glass substrate with a flat surface used as the counter substrate of the gel will be described. The schematics of the system are shown in Fig. 9. In this system, two kinds of gels, Flat and Concave, were used. It is predicted that mostly adhesive wear occurs because the substrate with a flat surface was used, unlike the case the rough substrate was used.

The friction stress of Flat was slightly lower than Concave (Fig. 9c). It is predicted that Concave exhibits lower friction than Flat, due to the smaller contact area by the difference in surface geometry, and we have already obtained the results that the friction stress of Concave was lower than that of Flat under the normal pressure of 11 kPa. (The description for this is stated in supporting information for review only. The data is now submitted to the journal, *Soft Matter*, published from The Royal Society of Chemistry.)

The reason for the relatively low friction of Flat under the normal pressure of 28 kPa (Fig. 9c) is considered as follows. When Flat contacts the FDTs-treated hydrophobic substrate, both wetting and dewetting domains are formed by lodging the lubricant water between the gel and the glass substrate[31]. Then, forced wetting occurs during the sliding motion and shows low friction[30, 31]. For Concave, it is difficult for a water film to exist between the gel and the glass substrate due to higher pressure at the flat region than that of Flat, this makes firm contact with gel and glass, and the water inside the dimples may be relatively difficult to contribute to lubrication under 28 kPa of normal pressure; hence, it can be said that the effect of lubrication in the high-velocity region is small. Owing to these effects, the friction of Flat was considered to be relatively low compared with Concave.

The specific wear rate measured in the tests with Flat and Concave sliding against the FDTs-treated glass substrate are displayed in Fig. 10. The results of the gel sliding against the other gel are also shown, but they are described later. The specific wear rates adopted in Fig. 10 are the values calculated from the TOC.

Although friction stress of Flat was slightly lower than that of Concave (Fig. 9c), the specific wear rate of Flat was higher than that of Concave. Since the friction stress does not correspond to the wear amount, it can be seen that the classic wear model cannot be applied to systems with different geometries, Concave and Flat. Wear reduction of Concave is predicted considering its surface geometry, because the contact area of Concave is smaller than that of Flat. However, the real contact area under sliding cannot be easily compared because there are both wetting and dewetting domains for Flat, as mentioned earlier. The contact area or normal pressure may define the wear of the gels, but there is no evidence that the difference in wear amount of Flat and Concave is attributed to these parameters.

Annular wear scars were observed concentrically for Flat, but almost no wear scars were observed for Concave (Fig. 11). From the friction behavior, the microscopic images and the wear evaluation using the lubricant, we predict that the effect of determining the degree of wear is not the contact area or friction, but the ability of the dimples to trap the wear particles into them. The small wear particles generated by the sliding motion are expected to be taken into the dimples, which suppresses further wear of the surface due to the wear particles[32].

3.2.3 Gel-on-gel

Finally, the results on friction and wear when a gel slides against the other gel are discussed. The sliding tests were conducted under three configurations: Flat-on-Flat, Concave-on-Flat, and Concave-on-Concave, using two types of gels, Flat and Concave, which had different surface geometries (Fig. 12a). The sliding velocity dependency of the friction stress is available in the Supporting Information (Fig. S7). We evaluated friction and wear of the gels at the sliding velocity of 0.01 m/s for 7200 seconds, in this work.

Figure 12b displays the sliding time dependence of the friction stress, and Fig. 10 shows the specific wear rate. For these measurement conditions, both the upper and lower gels were worn, as shown in Figs. 12c–h; therefore, the specific wear rate shown in Fig. 10 is the sum of the wear of PVA released from both gels.

Comparing the sliding friction, the friction stress was higher in the order of Flat-on-Flat, Concave-on-Flat, and Concave-on-Concave. However, the wear was larger in the reverse order, that is, Concave-on-Concave, Concave-on-Flat, and Flat-on-Flat. In addition, the optical microscope images revealed that there were more severe wear scars on the surface of Flat, but there were few wear scars on the surface of Concave.

The results for Flat-on-Flat shown in Figs. 10 and 12 are counter-intuitive, showing higher friction and more severe wear scars than Concave-on-Flat and Concave-on-Concave, but with very low wear amount. Friction for the configuration of gel-on-gel will be explained as below. The most influential effect for the higher friction of Flat-on-Flat compared with Concave-on-Flat or Concave-on-Concave is predicted to be the high contact ratio because the contact ratio is reduced for the latter two configurations due to the surface dimples of Concave. From the presence of wear scars, it is clear that friction occurs in the condition that the gel is in contact with each other, and the difference in contact area affects the friction. Since they are sliding in a relatively high velocity region, partial lubrication is also expected to occur, and the viscous resistance due to lubrication is also predicted to be higher in Flat-on-Flat than in Concave-on-Flat or Concave-on-Concave, because the water in surface dimples of Concave behaves like a thick lubricating layer, and the viscous resistance does not increase, considering Newton's law of viscosity.

Regarding the wear, the wear amount of Flat-on-Flat was the smallest among all the combinations, including Flat vs. flat glass, although the friction was highest in gel-on-gel configuration and severe wear scars were generated. This result indicates that, unlike the case of abrasive wear, most of the wear particles are not released into the lubricant, but deform the surface and/or transfer to the upper and lower gels as they grow larger (Fig. 13a). This effect is expected to occur because the gel is flat and soft on both sides, making it easy to contact with each other firmly, and there is no pathway for the particles to be released into the lubricant.

Comparatively, Concave increased the wear amount when the counter substrate was gels, and the wear amount was the highest for Concave-on-Concave. One of the reasons for this result is that the gel is soft and easily deformed, the surface of the gel on one side probably enters the dimples of the gel on the opposite side, and wear is likely to occur at the edges of the dimples. Furthermore, the more effective and plausible reason is as follows: when wear particles are generated on the surface, they are considered to be scraped by the dimple's edges, and they are moved from the gel surface to the lubricant (Fig. 13b). Scraping with dimples' edges is expected to release the generated small particles into the lubricant much more efficiently than the case of Flat, therefore, the evaluated wear amount in the lubricant increased. We also predict that the observed wear scars were reduced because the wear particles are less likely to grow large on the gel surface. In particular, the configuration of Concave-on-Concave has the largest number of dimples compared with other configurations, therefore, it is considered to have the largest wear amount and the minimum wear scars due to the scraping effect. The meaning of "scrape" in this paper is that the dimples on Concave merely take the wear particles into them and make the counter surface planar; not that the dimples generate new wear scars on the counter surface. In the case of Concave sliding against a flat glass substrate, fewer wear scars were observed and the wear amount was small compared with

the case of Flat gel sliding against the flat glass substrate. In this system, scraping of the counter gel does not occur, and thus the result is appropriate.

Figure 14 shows the similar plot of wear amount vs. the product of the friction force and the sliding distance as shown in Fig. 6b. Unlike the case of abrasive wear using rough glass, this figure shows that it is impossible to predict the concentration of wear particles released into the lubricant from the friction force when the gel has surface dimples or when the gel slides against the gel. Moreover, we have already shown that these results are not predictable from the observed severity of wear scars. In contrast to the classical model, which assumes simple adhesive or abrasive wear, the effects of trapping and scraping of wear particles by surface dimples have a much larger effect on the particle concentration than the magnitude of sliding friction between gel and substrate.

4. Conclusion

In this work, the wear of poly(vinyl alcohol) (PVA) gels could be evaluated quantitatively using two methods, UV spectrometry and TOC measurement, with a polymer solution derived from the lubricant containing the wear particles of the worn gels after the sliding test. For UV spectrometry, the range limitation of the detectable concentration is higher than that of the TOC measurement, but it has the advantage that the sample can be recovered and measured quickly. It would be able to perform more precise measurements for PVA gels prepared using PVA polymers with a lower degree of saponification. TOC measurement is also able to evaluate the wear with a lower measurable concentration limit than UV spectrometry, down to approximately 2×10^{-4} wt%. Although sample solutions cannot be recovered, TOC is useful to measure the very low wear of gels.

From the results obtained by the aforementioned methods, the following conclusions can be made regarding the wear of the PVA gels. The behavior of wear followed the classical wear model when the gel slid on the rough glass substrate. The wear amount is proportional to the normal force, friction force, and sliding distance, and is also proportional to the degree of wear scars.

When the Concave gel slid against the flat glass substrate, fewer wear scars were observed, and the wear amount was smaller than that of the Flat gel. We predict that the surface wear was hindered by trapping the wear particles in the dimples, considering that the friction of Flat was slightly lower than that of Concave, but the wear of Concave was smaller.

In the tests for the configurations of gel-on-gel, the wear amount did not depend on the apparent degree of wear scars. This wear mode cannot be recognized without the evaluation of the lubricant; hence, it can be said that particularly important results were obtained. For the configuration of Concave-on-Flat, fewer wear scars on Concave surface were observed, but the wear amount was larger compared with the Flat-on-Flat configuration. This phenomenon is considered to be caused by the effects that the wear particles generated on the surface are scraped by the dimples. For the configuration of Flat-on-Flat, severe wear scars were generated, but the wear amount was small; hence, the predicted wear amount from the

observation and the measured wear amount in the lubricant was not consistent. In this configuration, it is strongly indicated that the wear particles are not easily released into the lubricant but remain on the surface as transfer particles, or surface deformation occurs solely.

The traditional methods used for wear analysis, such as observation by optical microscope, can only evaluate the degree of deformation on the worn gel surface. It is possible to evaluate the wear amount quantitatively by measuring the lubricant, so we can distinguish the wear mode, which means that the surface is deformed by wear or the surface is damaged by releasing wear particles.

UV spectrometry can be used to detect the wear particles of the gel composed of not only PVA but also other polymers that have any specific absorbance within the measuring wavelength range, such as polymers with aryl groups in their backbone. In addition, as TOC measurement is a method to quantify the amount of carbon in the solution, almost all the polymers composed of organic carbon can be detected as with PVA. However, in any measurement when the wear particles of the gel are not homogeneously dispersed, the measurement accuracy may decrease. Therefore, just as the measurements in this work, crosslinks of the gels made of other polymers may also need to be unlinked. For instance, the addition of an acid or base that does not contain organic carbon or UV irradiation can be considered. It may be easy for gels with reversible cross-linking points, such as cross-linking by Schiff bases.

Declarations

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Electronic Supporting Information

Additional figures as mentioned in the text; UV spectra of PVA aqueous solutions and calibration curve obtained from UV spectrometry of PVA solutions (Fig. S1); Calibration curve obtained from TOC measurements of PVA solutions (Fig. S2); Time variation of the normal force (Fig. S3); Relation of the sliding time and the normal force at the end of the sliding test (Fig. S4); Relation of the wear amount and the product of the normal force and sliding distance (Fig. S5); Relations of the friction stress and the wear (Fig. S6); Sliding velocity dependence of friction stress for gel-on-gel configurations (Fig. S7) (PDF)

Conflicts of Interests

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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Scheme

Scheme 1 is available in the Supplementary Files section.

Figures

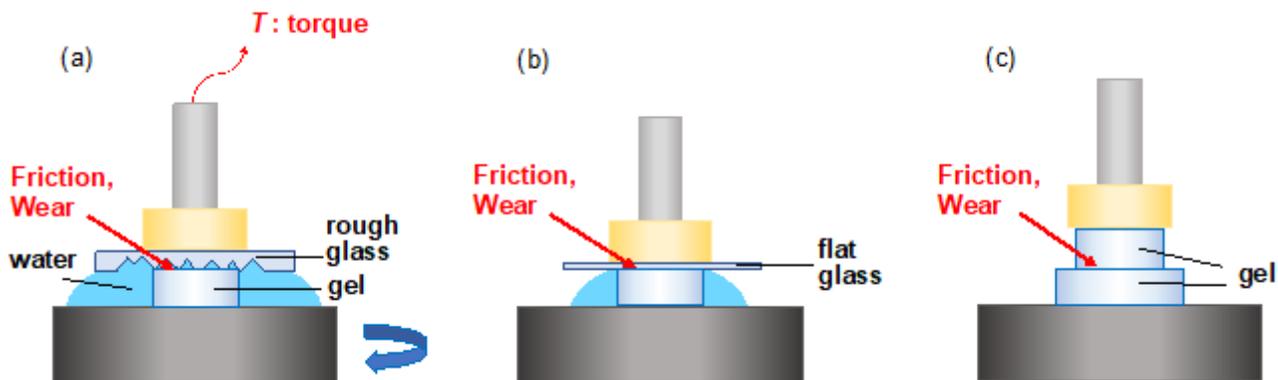


Figure 1

Schematic of the system for the three types of sliding tests. (a) Flat gel sliding against the rough glass substrates. (b) Flat or Concave gel sliding against the FDTS-treated flat glass substrate. (c) Gel sliding against gel.

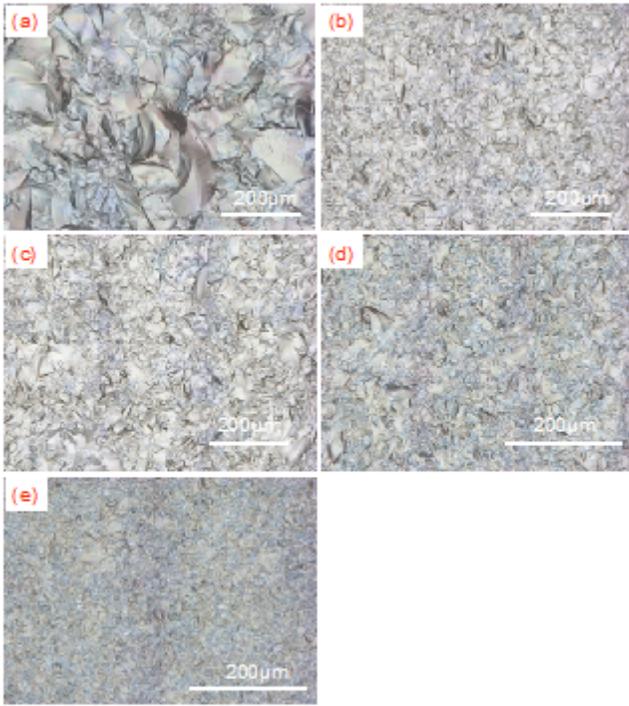


Figure 2

Surface images of the glass substrates with different surface roughness, R_z . The glasses were treated by sandblasting. The R_z values are (a) 53, (b) 31, (c) 18, (d) 12, (e) 7.9 mm, respectively. Scale bar: 200 mm.

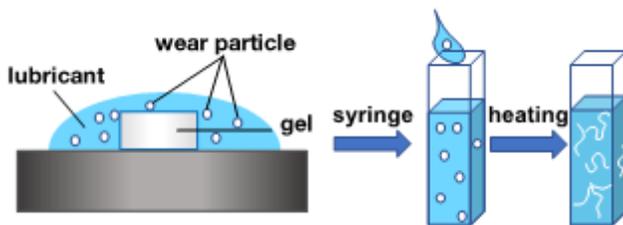


Figure 3

Lubricant that contains the wear particles of the PVA gel was syringed, then heated at 80°C in a water bath to form the homogeneous solution of the PVA polymer by unlinking the crosslinks of the wear particles of the PVA gel.

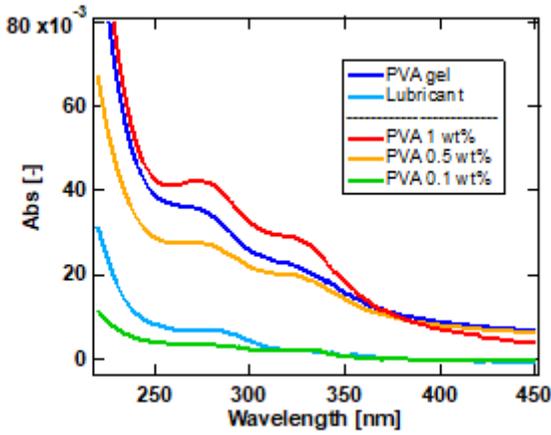


Figure 4

UV-vis spectra of PVA aqueous solutions obtained by dissolving the predefined amount of PVA polymer powder, PVA hydrogel, and by heating the lubricant that contains wear particles of the PVA gel.

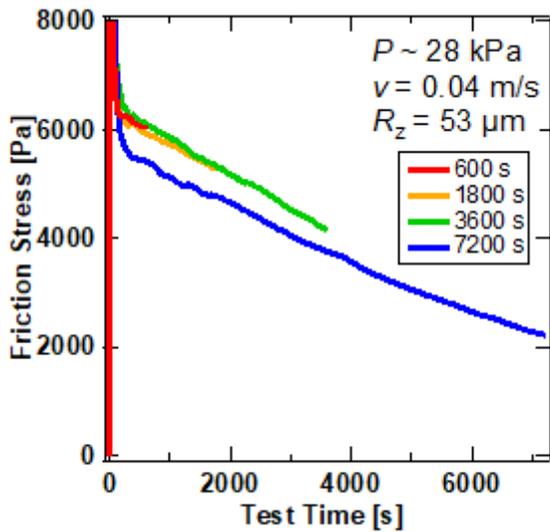


Figure 5

Relationship between the sliding time and friction stress for test where Flat was slid against the glass substrate with surface roughness, $R_z = 53 \mu\text{m}$ for 600, 1800, 3600, and 7200 seconds.

Figure 6

Results of wear amount evaluated by two methods, UV spectrometry and TOC. (a) Sliding time dependence of wear amount and loss of PVA gel. Wear amount on the left axis indicates the weight of PVA polymer contained in the lubricant. Loss of PVA gel on the right axis was calculated by considering the polymer fraction in PVA gel. (b) Relation of wear amount and the product of friction force and the

sliding distance. Straight-line fitting is performed and the coefficient of determination R^2 values are shown.

Figure 7

Surface images of the PVA gels after sliding tests, where they were slid against the glass substrate with surface roughness,

= 53 mm. The sliding time were (a) 600 and (b) 3600 seconds, respectively.



Figure 8

Results of the sliding tests slid against the glass substrate with various surface roughness. (a) Surface roughness, , dependence of specific wear rate. (b–f) Surface images of the PVA gels after the wear tests. Each gel slid against the glass substrate with different surface roughness, , shown under each image. Scale bar: 1 mm.

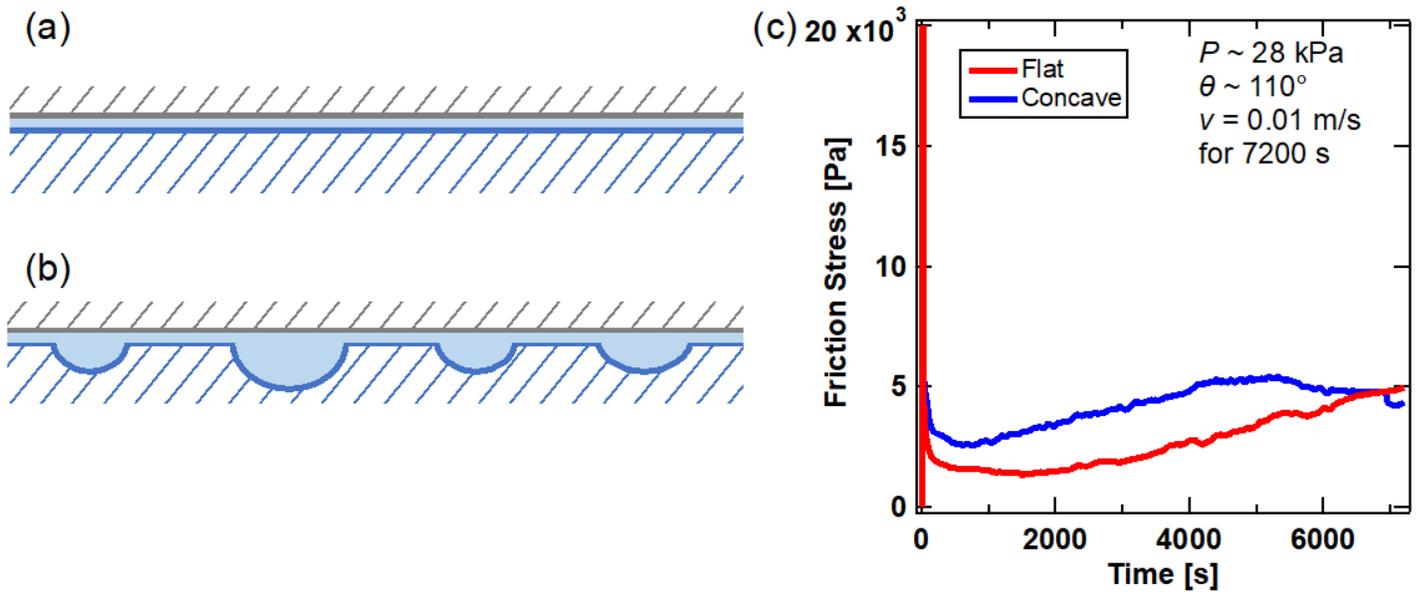


Figure 9

Illustrations of gel/glass interfaces and the result of the sliding test. Schematic of (a) Flat gel/flat glass and (b) Concave gel/flat glass. (c) Sliding time variation of friction stress. Gels, Flat and Concave, slid against FDTS-treated flat glass for 7200 seconds.

Figure 10

Specific wear rate for the test with different conditions; gels sliding against the FDTS-treated flat and gel sliding against the other gel in the gel-on-gel configuration.

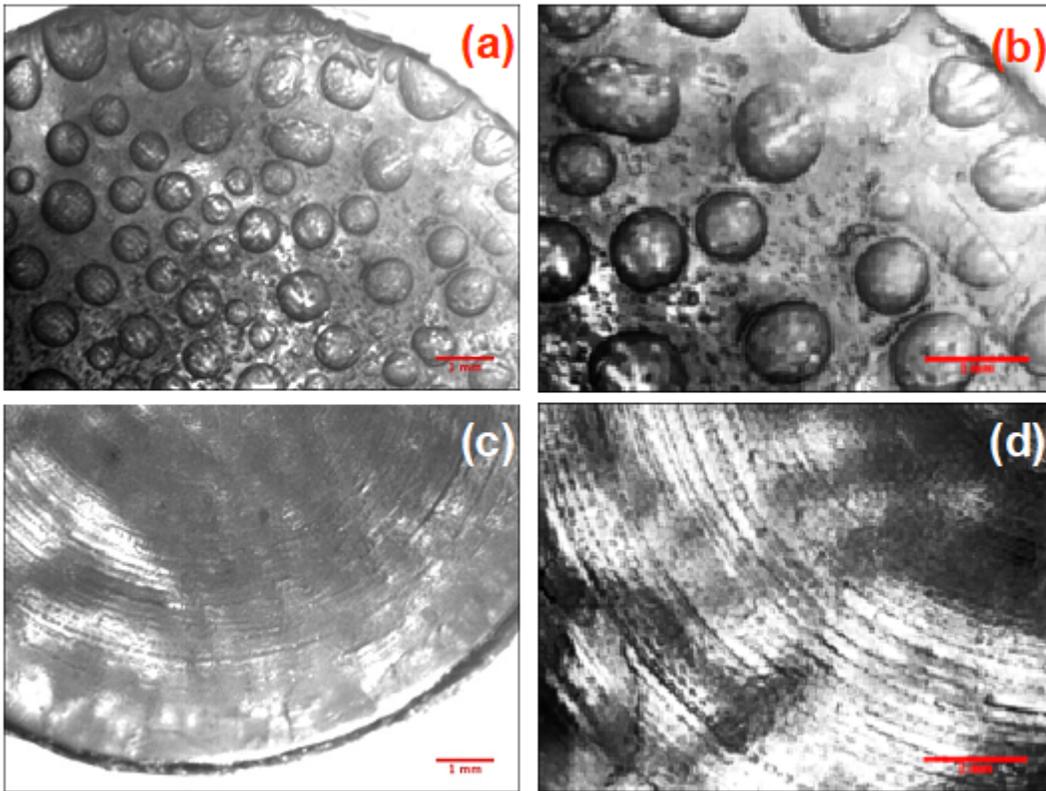


Figure 11

Surface images of the PVA gels after the sliding tests. The test was performed using FDTs-treated flat glasses and lasted 7200 seconds. (a–b) Images of Concave surfaces. (c–d) Images of Flat surfaces. Images in the right column were taken in higher magnification than those in the left column. Scale bar: 1 mm.

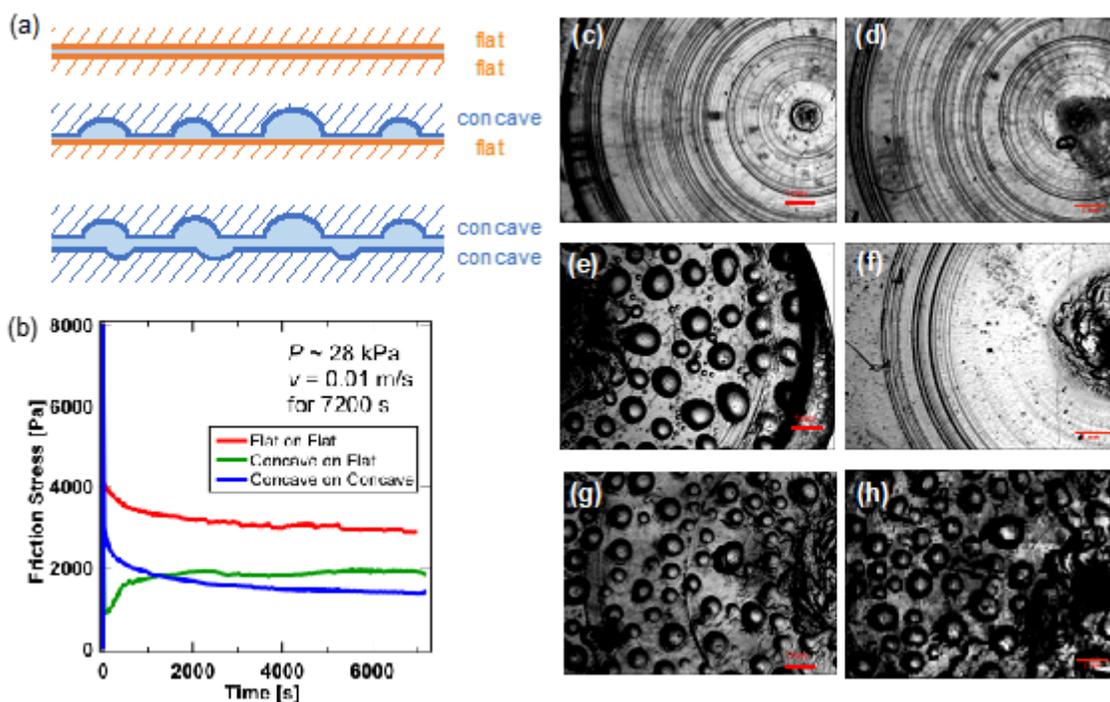


Figure 12

Illustration and results for the sliding test performed in gel-on-gel configurations. (a) Schematic of three types of gel-on-gel configurations. (b) Sliding time dependence of friction stress for the tests of three types of gel-on-gel configurations. (c–h) Optical microscope surface images of the PVA gels taken after the sliding tests. The tests were performed for the configurations of Flat-on-Flat (c, d), Concave-on-Flat (e, f), and Concave-on-Concave (g, h). The images in the left column show the upper gels and the images in the right column show the lower gels. Scale bar: 1 mm.

Figure 13

Schematic of (a) Flat/Flat and (b) Concave/Flat interfaces. (a) Most of the wear particles are not released into the lubricant and deform the gel surfaces. (b) Generated wear particles are scraped by the dimples on the counter surface.

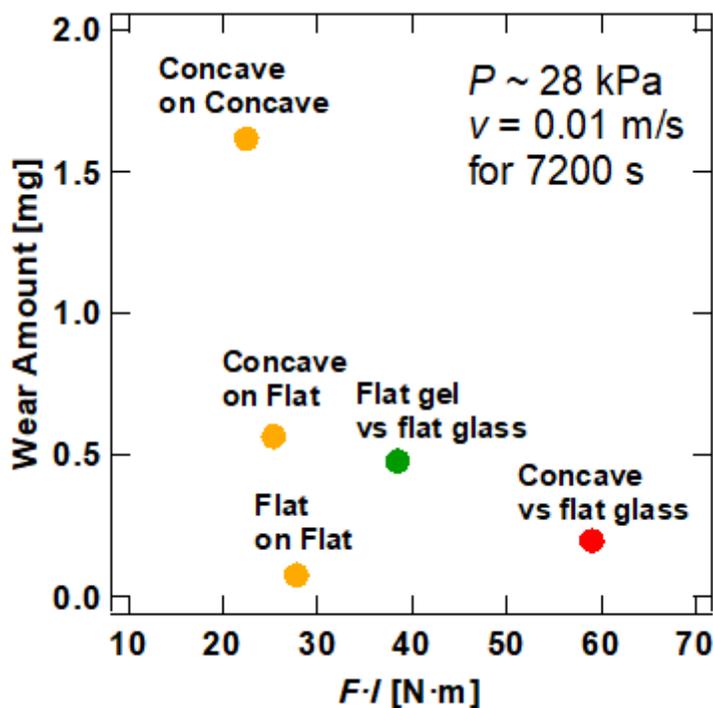


Figure 14

Relation of wear amount and the product of the friction force and the sliding distance.

Supplementary Files

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- [GraphicalAbstract.eps](#)
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