Tribological Properties of Double-Network Gels Substituted by Ionic Liquids

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Abstract: Since human body joints have a gel-like structure with low friction that persists for several decades, hydrogels have attracted much interest for developing low-friction materials. However, such advantages can hardly be realized in industrial usage because water in the gel evaporates easily and the gel deswells. The substitution of water with an ionic liquid (IL) is one of the effective ways to overcome this problem. In this study, we substituted water in a double network (DN) hydrogel with 3-ethyl-1-methyl-imidazolium ethylsulfate (EMI-EtSulf), a hydrophilic IL, via a simple solvent exchange method to obtain a DN ion gel. A compressive test and thermogravimetric analysis showed that the DN ion gel has a high compression fracture stress and improved thermal properties, with the difference in 10% loss of temperature being $\Delta T_{10} = 234\ °C$. A friction test conducted using a reciprocating tribometer showed that the friction of a glass ball/DN ion gel was relatively higher than that of a glass ball/DN hydrogel. Because the minimum coefficient of friction (COF) value increased after substitution, the increase in polymer adhesion caused by the electrostatic shielding of the surface moieties of glass and poly 2-acrylamidomethylpropanesulfonic acid (PAMPS) was considered the main contributor to the high friction. As the COF value decreased with increasing temperature, the DN ion gel can achieve low friction via the restriction of polymer adhesion at high temperatures, which is difficult in the DN hydrogel owing to drying.

Keywords: double-network gel; ionic liquid; electrostatic interaction; low friction

1. Introduction

Human body joints have a coefficient of friction (COF) as low as 10^{-3} at pressures exceeding 10^2 atm, and they can maintain their lubrication for several decades. Therefore, they are considered a useful model for designing low-friction materials [1]. Since human joints have a gel-like structure comprising proteoglycans and collagen fibrils with high water content (75–80 wt%), gel lubricants have attracted much research attention [2–4]. Gels are soft materials comprising cross-linked polymers and a large amount of swelling agent. They have a high solvent content and a flexible structure; in addition, various functionalities, such as shape memory [5] and self-oscillation [6], can be realized through appropriate design of the chemical structure of the polymer backbone or solvent. The present study aims to clarify gel properties and the potential application of gels as artificial biomaterials.

Despite the attractive properties mentioned above, gels have poor mechanical strength, and this limited their widespread industrial application until the 2000s. Following the report of the slide ring gel [7] in 2001, many researchers have developed mechanically strong hydrogels [8–10]. Gel fracture is mainly caused by stress concentration at the cross-linking point; however, gels can be designed to allow stress to disperse effectively, thereby improving their mechanical strength. For example,

slide ring gels use cyclodextrin as a free and mobile cross-linker to allow flexible polymer chain motion at the cross-linking point and thus reduce stress concentration [7]. Tetra-poly(ethylene glycol) (PEG) gel comprises an ordered PEG network with a uniform chain length that disperses the applied stress homogeneously [10]. Among various tough hydrogels, double-network (DN) gels comprise different polymer networks based on the sacrificial principle, in which one polymer network prevents the fracture of others [9]. DN gels are suitable for fabricating strong gels with various functionalities [11] since they can be produced from various combinations of polymer structures.

Hydrogels show stable low friction as their swelled state is maintained; however, such advantages can hardly be realized in the industrial usage because water in the gel evaporates easily and the gel deswells. Thus, it is important to maintain the swelled state of gels to use their unique tribological properties. In this light, we focused on the use of ionic liquids (ILs). ILs are liquid salts that fully comprise cations and anions, and they generally have a melting temperature lower than 373 K [12]. They have high thermal and oxidative stability, negligible volatility, and low friction [13–15], and therefore, they are expected to be appropriate as swelling agents that will enable low-friction gels to maintain their swelled state. Our previous study on lubricants based on polymer brushes and DN gels comprising IL polymers and ILs showed their potential as robust lubrication systems [16]. IL-type polymer brushes showed low friction under high pressure (440 MPa) over 4000 cycles. By contrast, IL-type DN gels, also called DN ion gels, showed low friction under high temperature (80 °C) and vacuum (2.4×10^{-4} Pa) [17]. However, due to the difference of the polymer backbone between DN ion gels and DN hydrogels, it was difficult to study the difference between water and ILs for lubrication.

In this study, we substituted water in DN hydrogels with an IL to study the difference in tribological properties between DN hydrogels and DN ion gels with the same polymer backbone. Substituted-type DN ion gels have been studied as a gas separation membrane [18], but their tribological properties have not been reported. We first fabricated a conventional DN gel comprising poly 2-acrylamidomethylpropanesulfonic acid (PAMPS) and poly dimethylacrylamide (PDAAm) as a DN hydrogel and then substituted the water in the DN hydrogel with 3-ethyl-1-methyl-imidazolium ethylsulfate (EMI-EtSulf), a hydrophilic IL, to obtain a DN ion gel. As these gels have the same polymer backbone, the effect of substituting water with the IL on the tribological and chemical properties can be compared easily.

2. Materials and Methods

2.1. Fabrication of DN Hydrogel and DN Ion Gel

The DN hydrogel was fabricated through a sequential photo-polymerization process [9]. All of the reagents were purchased from Wako pure chemical industry (Tokyo, Japan) except *N,N′*-methylenebisacrylamide (Sigma-Aldrich, Japan, Tokyo) and dimethylacrylamide (Tokyo chemical industry, Tokyo, Japan). A mixed solution of 2-acrylamidomethylpropanesulfonic acid (AMPS) (0.83 g) as the first monomer, α-ketoglutalic acid (0.00029 g) as an initiator, *N,N′*-methylenebisacrylamide (MBAA; 0.012 g) as a cross-linker, and water (1.57 g) as a solvent were charged into a Schlenk tube, and then, argon bubbling was performed for 5 min to deoxygenate the solution. The solution was poured into a reaction cell made from a pair of glass plates separated with 1-mm-thick silicone rubber by using an injection syringe. Then, it was irradiated with ultraviolet (UV) light for 18 h under rotation to obtain the first gel. Polymerization was conducted in an argon atmosphere. After polymerization, the obtained first gel was immersed in the second gel solution until it reached a swelling equilibrium. The second gel solution comprised dimethylacrylamide (DMAAm; 15 g) as a second monomer, α-ketoglutalic acid (0.044 g) as an initiator, MBAA (0.046 g) as a cross-linker, and water (60 g) as a solvent. Then, the swelled first gel was set in the reaction cell and irradiated with UV light for 18 h under rotation. The obtained gel was washed with a 1:1 solution of acetonitrile and EMI-EtSulf, followed by drying at 70 °C under vacuum for 12 h to perform substitution and thereby obtain the DN ion gel.

2.2. Friction Test With Ball-on-Plate-Type Tribometer

A friction test was conducted using a ball-on-plate-type reciprocating tribometer (Tribogear type-15, Shinto Scientific Co., Ltd, Tokyo, Japan). The DN gel sample was fixed on the sliding table, and the glass ball sample (φ10 mm) was set in the ball holder connected to a load cell (Figure 1). The ball/substrate friction force was measured under different loads and sliding speeds to evaluate the lubrication properties.
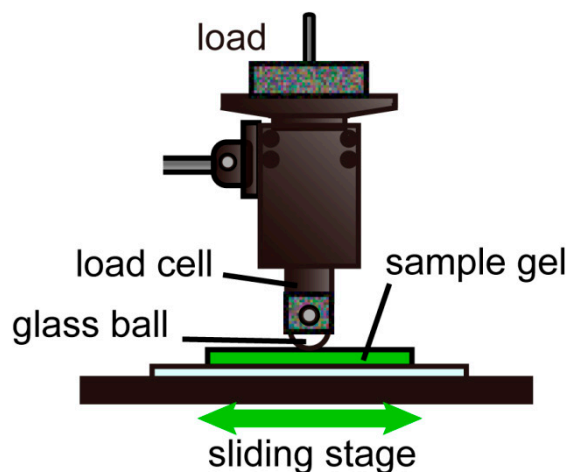

Figure 1. Schematic illustration of friction test by using ball-on-type reciprocating tribometer.

3. Results and Discussions

### 3.1. Mechanical Strength of DN Ion Gel

The mechanical strength of the DN ion gel was evaluated by using a universal testing system (Instron 3342, Instron Japan, Kawasaki, Japan) at 25 °C and 40% of relative humidity. The obtained stress–strain curve showed that the compression fracture stress of the DN hydrogel and DN ion gel was 20 and 25 MPa, respectively (Figure 2). The obtained values were comparable to those of the DN ion gel substituted by tetrabutylphosphonium prolinate [18]. The initial slope of the stress-strain curve of the DN ion gel was more gradual than that of the DN hydrogel, indicating that the former is softer than the latter. This is attributed to the loss of hydration force. Because PAMPS is an electrolyte polymer, it swells in pure water via the hydration of negatively charged AMPS. Furthermore, its surface charge is easily shielded in a high concentration of ionic salts. As the DN ion gel showed shrinkage after substitution, its softening was attributed to the loss of hydration force caused by the high ionic strength of EMI-EtSulf.
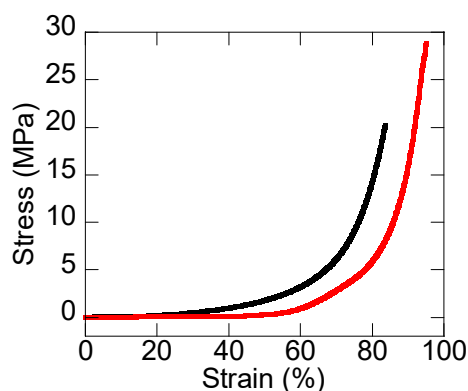
Figure 2. Stress–strain curves of DN hydrogel (black line) and DN ion gel (red line). Compression rate was 10% strain/min for both samples.

3.2. Thermal Properties of DN Ion Gel

The thermal properties of the DN ion gel and DN hydrogel were verified using thermogravimetric analysis (TGA). Figure 3 shows TGA curves of the DN ion gel, DN hydrogel, and EMI-EtSulf. The TGA curves of the DN ion gel and EMI-EtSulf showed initial weight loss until 100 °C, probably due to absorbed water. Secondary weight loss was observed at ≈150 °C for both samples, indicating the thermal decomposition of the sulfate moiety of PAMPS and EMI-EtSulf [19]. Assuming that the initial weight loss of the DN ion gel and EMI-EtSulf were attributable to water, the temperature for 10% weight loss (T_{10}) in the DN ion gel and EMI-EtSulf after water desorption were 273 °C and 288 °C, respectively. In contrast, T_{10} for the DN hydrogel was much lower (39 °C), indicating that substitution of water with an IL effectively improved the thermal stability of the DN gel (ΔT_{10} = 234 °C).
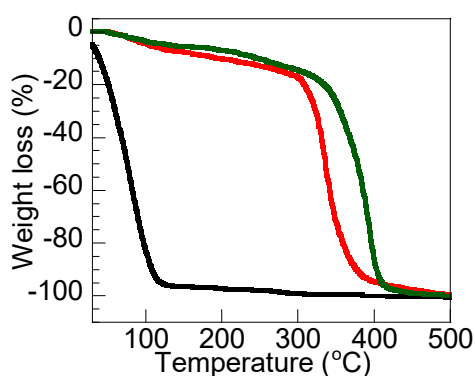
Figure 3. TGA curves of DN hydrogel (black line), DN ion gel (red line), and EMI-EtSulf (green line) measured at 10 °C/min.

3.3. Tribological Properties of the DN Ion Gel

Figure 4 shows the sliding speed dependence of the COF for glass ball and gel samples under an applied load of 0.98 N. The COF of the glass ball/DN hydrogel was 0.01–0.02 in the measured sliding speed range, and it reached its minimum value at 3.0×10^{-2} ms^{-1}, indicating a shift in the lubrication regime from elastic to mixed lubrication. By contrast, the COF of the glass ball/DN ion gel showed a relatively higher COF of 0.04–0.05 in the same sliding speed range as that for the glass ball/DN hydrogel, and it reached its minimum value at 5.0×10^{-3} ms^{-1}; this is six times lower than that for the DN hydrogel.
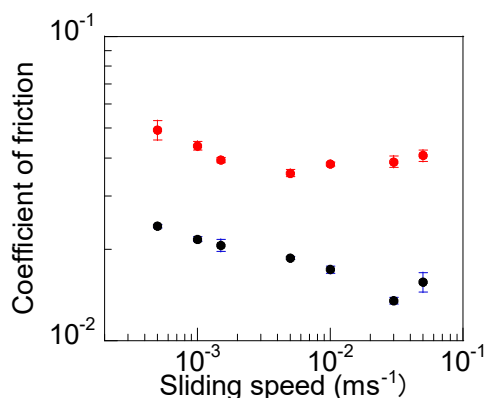
Figure 4. Sliding speed dependence of COF at the glass ball/DN hydrogel (black circle) and glass ball/DN ion gel (red circle) interfaces under an applied load of 0.98 N.

These results can be explained by two factors. One factor is the viscosity of the swelling agent incorporated in DN gels. The viscosity of water and EMI-EtSulf at 25 °C is 0.89 and 71 mPa·s, respectively, leading to a thicker fluid film in the case of IL. The DN ion gel showed a shift in the

lubrication regime at lower sliding speeds compared with the DN hydrogel, indicating the contribution of a thicker fluid film due to higher viscosity. However, the sliding speed ratio at which the lubrication regime shifted was only 6.0; this was much lower than the viscosity ratio (80) of EMI-EtSulf and water. Therefore, the viscosity change was not considered the main factor responsible for the different lubrication properties between the DN ion gel and DN hydrogel.

Another factor is the increase in polymer adhesion caused by substituting water with an IL. Because PAMPS and the glass surface easily dissociate to possess negative charge in pure water, electrostatic repulsion leads to a separation of PAMPS and glass surface, which is to preserve the fluid film thickness [20,21]. Electrostatic repulsion is a very important factor in achieving low friction at the electrolyte interface. Raviv et al. studied the friction between polymer brush layers adsorbed on a molecularly smooth mica surface in water by using a surface force apparatus (SFA) [20]. The shear force between polyelectrolyte brush layers showed lower friction (COF: 0.0006–0.001) compared with that in the case of neutral brush layers, where electrostatic repulsion of a negatively charged tribopair of polymer brush led to decrease friction. Dunlop et al. measured the normal and shear forces between polyelectrolyte brush layers grafted on a mica surface to examine the contribution of the ionic strength to friction [21]. They showed that the electric double layer was shielded at higher salt concentrations, leading to higher shear forces. Due to the high salt concentration ($\approx$5 molars) of EMI-EtSulf which is fully composed of cations and anions, almost all of the hydroxyl groups on the glass surface and sulfate groups on PAMPS were strongly shielded. The higher friction of the DN ion gel compared with that of the DN hydrogel was therefore attributed to the increase in polymer adhesion on the glass surface induced by the electrostatic shielding of the glass and PAMPS surface.

The frictional stress caused by the elastic deformation of the polymer layer can be expressed as follows [17,22]:

$$f_{el} \propto m \nu \tau_b \qquad (1)$$

where m, ν, and τ_b represent the number of adsorbed site per unit area, sliding speed, and lifetime of adsorption lifetime, respectively. Each adsorbed polymer chain desorbs from the surface via thermal agitation after τ_b and then repeats adsorption and desorption on the surface as follows:

$$\tau_b = \tau_f \, exp[(F_{ads} - F_{el})/T] \qquad (2)$$

where τ_f, F_{ads}, F_{el}, and T represent the readsorption lifetime, adsorption energy per unit area, elastic energy of each polymer chain, and absolute temperature, respectively.

In scaling theory, a partial chain of gels can be considered as an isolated polymer chain with a Flory radius R_f. Here, τ_f can be expressed in terms of the solvent viscosity η as follows:

$$\tau_f \approx \eta R_f{}^3 / T \qquad (3)$$

From Equations (1)–(3), we can derive $f_{el} \propto exp[1/T]/T$, which monotonically decreases as T increases. Thus, we next examined the temperature dependence to confirm the contribution of polymer adhesion to the friction of the DN gel.

Figure 5 shows the variations in the measured COF of the glass ball/DN ion gel at different temperatures under an applied load of 0.98 N at 5.0×10^{-3} ms^{-1}. The COF of the glass ball/DN ion gel at 25 °C was 0.067; it changed to 0.057, 0.054, and 0.037 at 50 °C, 80 °C, and 100 °C, respectively. This monotonic decrease in COF with increasing temperature was also observed in the case of the hydrophobic DN ion gel. Although this temperature increase may induce the softening of the DN ion gel to reduce P_{av}, it will increase the fluid thickness and thereby increase the viscous resistance. Therefore, the decrease in polymer adhesion is considered the main contributor to low friction. In contrast, previous study showed that the COF of the DN hydrogel at 50 °C suddenly increased to 0.1 within 400 friction cycles probably owing to the heat-induced aggregation of dried polymers [17]. In contrast, the DN ion gel showed a stable COF after 500 friction cycles even at 100 °C. These results

showed that the DN ion gel has much higher thermal stability than the DN hydrogel; therefore, they are expected to find use as lubricant gels at higher temperatures at which hydrogels cannot easily be applied.
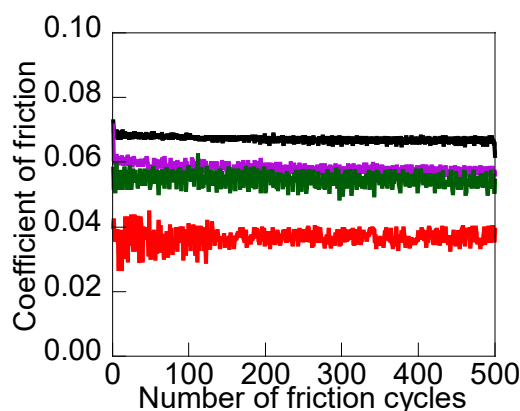
Figure 5. Variation of measured COF with number of friction cycles in a glass ball/DN ion gel at 5.0×10^{-3} ms^{-1} under an applied load of 0.98 N at temperatures of 25 °C (black line), 50 °C (purple line), 80 °C (green line), and 100 °C (red line).

4. Conclusions

In this study, we substituted water in a DN hydrogel with EMI-EtSulf, an IL, to clarify the different tribological properties between a DN hydrogel and a DN ion gel with the same polymer backbone. Compression tests revealed that the DN ion gel was relatively softer than the DN hydrogel, indicating the effect of electrostatic shielding of sulfate moieties on the PAMPS network. The compressive fracture stress of both samples was similar. TGA showed that the loss of the liquid lubricant incorporated in the DN gel was restricted by the substitution of water with the IL; the difference in 10% loss of temperature was $\Delta T_{10} = 234$ °C. A friction test conducted using a reciprocating tribometer showed that the friction of the glass ball/DN ion gel was relatively higher than that of the glass ball/DN hydrogel. Because the minimum COF increased after substitution, the increase in polymer adhesion caused by the electrostatic shielding of the surface moieties of glass and PAMPS was considered to contribute to the high friction. As the COF value decreased with increasing temperature, the DN ion gel could achieve low friction via the restriction of polymer adhesion at high temperatures; this is relatively difficult in the DN hydrogel owing to drying.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "Conceptualization, H.A., T.K., T.M. and T.S.; Methodology, H.A., F.M. and T.K.; Software, H.A. and F.M.; Validation, H.A., F.M. and T.K.; Formal Analysis, H.A. and F.M.; Investigation, F.M.; Resources, F.M, S.H. and T.M.; Data Curation, H.A. and F.M.; Writing-Original Draft Preparation, H.A. and T.S.; Writing-Review & Editing, H.A., T.K. and T.S.; Visualization, H.A. and F.M.; Supervision, T.K. and T.S.; Project Administration, T.K. and T.S.; Funding Acquisition, H.A., T.K. and T.S.

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