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# Development of Low-Friction Ion Gels for Industrial Applications

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and Takaya Sato*

## Abstract

Friction reduction is imperative for improving the service life and energy efficiency of mechanical systems. Ion gels using ionic liquids (ILs) as swelling agents are expected to be stable gel lubricants owing to the high thermal stability and negligible volatility of ILs; they can maintain their swollen state even under harsh conditions. Therefore, we investigated two types of ion gels: an IL-substituted double-network gel (DN ion S-gel), in which the water in the DN hydrogel is replaced by the IL 3-ethyl-1-methyl-imidazolium ethylsulfate; and a DN ion gel containing N,N-diethyl-N-(2-methoxyethyl)-N-methyl-ammonium bis(trifluoromethylsulfonyl) imide (DEME-TFSI), where one of the polymer backbones is a network of poly(N,N-diethyl-N-(2-methacryloylethyl)-N-methylammonium bis(trifluoromethylsulfonyl) imide), an IL-type polymer based on our previous synthetic study of IL polymer technology. The DN ion S-gel and DN ion gel achieved compression strengths of 25 and 30 MPa, respectively, and were thermally stable until 196°C and 335°C (10% weight-loss temperature), respectively. The coefficient of friction remained stable and low (0.02) after repeated measurements under harsh conditions (high temperature or vacuum conditions), affirming the durability of the DN ion gel.

**Keywords:** double-network gel, ionic liquid, low friction, highly robust, high vacuum

## 1. Introduction

Low-friction materials are demanded for energy and resource conservation. As 75% of machine failures are attributed to friction wear [1], friction reduction would improve the service life and energy efficiency of mechanical systems [2]. Low-friction materials can be modeled on the human joint, which has a low coefficient of friction (CoF =  $10^{-3}$ ) at pressures above  $10^2$  atm and remains lubricated for decades [3]. The gel-like structure of human joints, comprising proteoglycans and collagen fibers with a high water content (75–80 wt%), has inspired extensive research on gel lubricants [2–4]. In the early 2000s, researchers in Japan developed hydrogels with high mechanical strength [4–7], promoting the application of gel as biomaterials. Double-network (DN) hydrogels with high mechanical strength, low friction, and biocompatibility are representative gel-lubricant materials [8] and suitable candidates for artificial human joints or cartilages [9]. However, the evaporation of the solvent (water) and

consequent loss of the swollen state have limited the industrial exploitation of gels with these benefits.

Previously, we developed ion gels comprising monodisperse silica nanoparticles and ionic liquids (ILs). In these gels, the silica surface is densely grafted by a well-defined polymer, forming a colloidal self-assembled crystal with a face-centered cubic structure [10]. The ionic conductivity and diffusion coefficients of our gels exceeded those of the bulk polymer. We thus considered the possibility of introducing the highly mobile ions in ion gels to a low-frictional gel surface. To test this idea, we combined ILs with gel lubricants. Owing to their high thermal and oxidative stability, ultralow volatility, and low friction [11–13], IL swelling agents are expected to retain the swelling state of low-friction gels. Whereas DN hydrogels have been targeted as tough hydrogels for biomaterial applications [14], DN ion gels have been mainly studied as gas separation membranes obtained by replacing the water in DN hydrogels with amino-acid-based ILs [15]. As shown in our recent study, IL-based lubrication systems and compatible polymer brushes grafted on Si substrates are efficient and robust lubricants [16]. These lubricants are composed of an IL called N,N-diethyl-N-(2-methoxyethyl)-N-methyl-ammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI) and high-density IL-type polymer brushes comprising N,N-diethyl-N-(2-methacryloylethyl)-N-methylammonium bis(trifluoromethyl-sulfonyl)imide (DEMM-TFSI), which is a derivative of DEME-TFSI with a polymerizable group. The CoF of the IL-type polymer brushes remained as low as 0.003 over 4,000 cycles.

The present study proposes two types of DN ion gels: an IL-substituted gel in which the water in the DN hydrogel is replaced by an IL [17], and a gel in which one of the polymer backbones of the DN ion gel is a network of poly(DEMM-TFSI) (hereafter, these two gels will be named DN ion S-gel and DN ion gel, respectively). The IL-type polymer in the latter gel is based on our previous synthetic study [18].

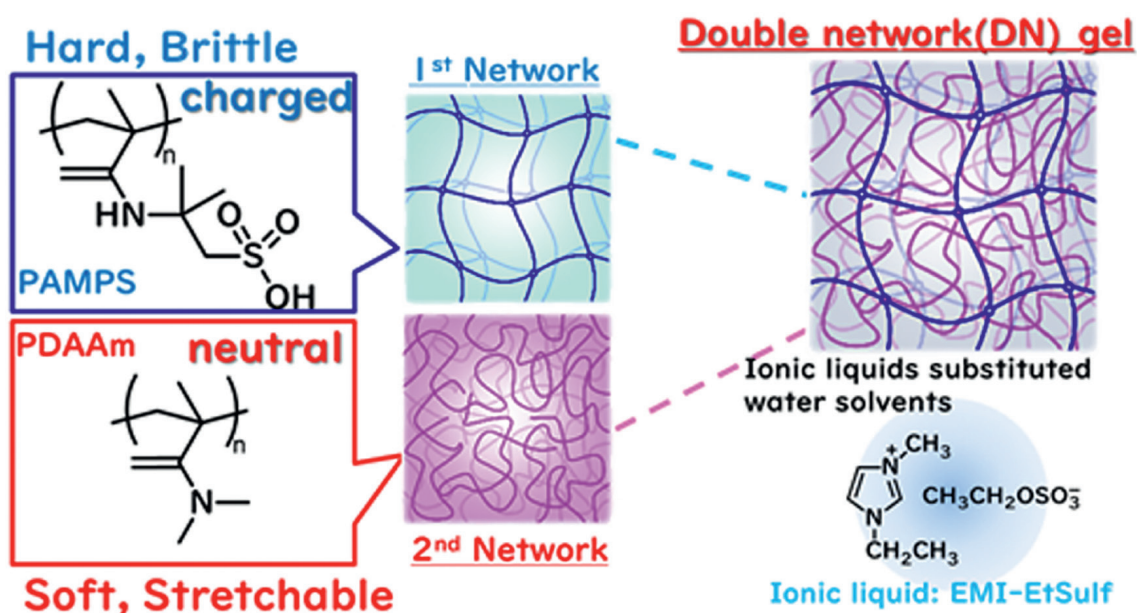
The ILs we used, 3-ethyl-1-methylimidazolium ethyl sulfate (EMI-EtSulf) and DEME-TFSI, are commercially readily available and were selected for their compatibility with the gel networks. EMI-EtSulf was also chosen because it can easily substitute water in the hydrogels and has low toxicity. DEME-TFSI has been used for a long time in our material development due to its low viscosity and high electrochemical and thermal stability [13, 16–20]. We are also considering its eventual industrial applications. This IL has been approved by the Japan Chemical Substances Control Law, thereby indicating its potential for industrial mass production and significant cost reductions. Considering the compatibility with this IL, we designed monomers and developed polymerization technology. Therefore, we are developing functional materials by combining DEME-TFSI and poly(DEMM-TFSI) with a maximum consideration of compatibility.

The present study discusses and compares the different tribological properties of DN hydrogels, DN ion S-gels, and DN ion gels. Specifically, it evaluates the gel immobilization techniques of the gels on substrates, the mechanical and thermal stabilities of the ion gels, their lubrication properties in a vacuum, and other required functions for industrial applications.

## **2. Two types of DN ion gels for industrial applications**

### **2.1 IL-substituted DN gel (DN ion S-gel)**

**Figure 1** is a schematic of an IL-substituted DN gel. First, a DN hydrogel was fabricated via sequential photopolymerization [6]. A solution of 2-acrylamido



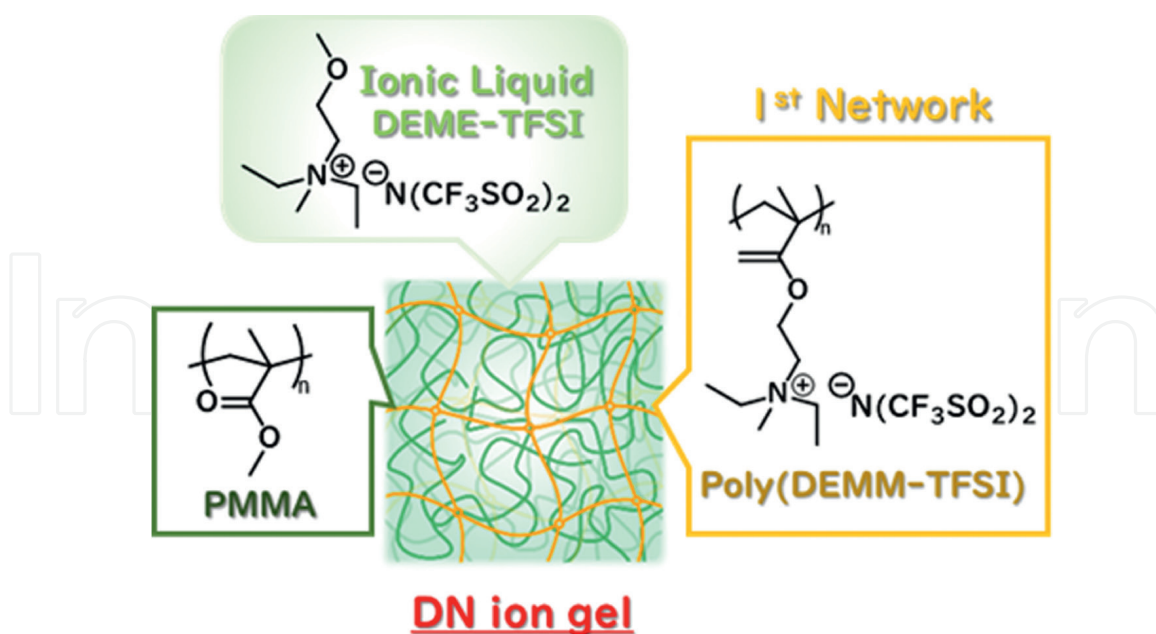
**Figure 1.**  
 Schematic of the IL-substituted DN gel (DN ion S-gel).

methylpropane sulfonic acid (AMPS) as the first monomer,  $\alpha$ -Ketoglutaric acid as the initiator, N,N-methylene bisacrylamide (MBAA) as the cross-linker, and water as the solvent was mixed and transferred to a Schlenk tube. Using an injection syringe, the solution was inserted into a reaction cell formed by sandwiching 1-mm-thick Si rubber between two glass plates. After 18 h of rotation under ultraviolet (UV) irradiation, the first gel was obtained. This gel was polymerized under Ar atmosphere, then immersed in a second gel solution comprising dimethylacrylamide as a second monomer,  $\alpha$ -Ketoglutaric acid as the initiator, MBAA as the cross-linker, and water as the solvent. Once swelling equilibrium was reached, the second gel solution (i.e., the swelled first gel) was set in the reaction cell and rotated for 18 h under UV light irradiation. The obtained gel was washed with acetonitrile and EMI-EtSulf (volume ratio 1:1), then vacuum-dried at 70°C for 12 h to obtain the substituted DN ion gel. The gel prepared using this method is called DN ion S-gel. The synthesis is detailed elsewhere [17].

## 2.2 DN ion gel comprising IL and IL polymer, DN ion gel

**Figure 2** schematizes the DN ion gel comprising an IL and its polymer (DN ion gel). The first and second networks were composed of DEMM-TFSI and poly (methylmethacrylate) (PMMA), respectively. DEMM-TFSI as the IL monomer, IRGACURE 369 as the initiator, triethyleneglycol dimethacrylate (TEGDMA) as the cross-linker, and DEME-TFSI as the solvent were mixed in a Schlenk tube and deoxygenated by Ar bubbling for 5 min. Using an injection syringe, the solution was injected into a reaction cell formed by sandwiching 2-mm-thick Si rubber between a pair of glass plates. The first gel was rotated for 18 h under UV light irradiation to promote polymerization in an Ar atmosphere. The polymerized gel was washed with acetonitrile to remove impurities and then swollen with DEME-TFSI (poly(DEMM-TFSI) gel as a reference material. PMMA gel was prepared similarly by replacing DEMM-TFSI with methyl methacrylate (MMA) at the same weight ratio. The first gel was polymerized and immersed in a second gel solution comprising MMA monomer, benzophenone





**Figure 2.**  
Schematic of the DN ion gel composed of an IL and an IL polymer (DN ion gel).

as the initiator, TEGDMA as the cross-linker, and propylene carbonate as the solvent. After immersion for 2 days to reach swelling equilibrium, the swollen first gel was placed in a reaction cell and rotated for 18 h under UV irradiation. The resulting second gel was washed with an acetonitrile and DEME-TFSI (volume ratio 1:1) to remove the impurities and then vacuum-dried at 70°C for 12 h. The resulting DN ion gel was rich in DEME-TFSI (75 wt%). The synthesis is detailed elsewhere [18].

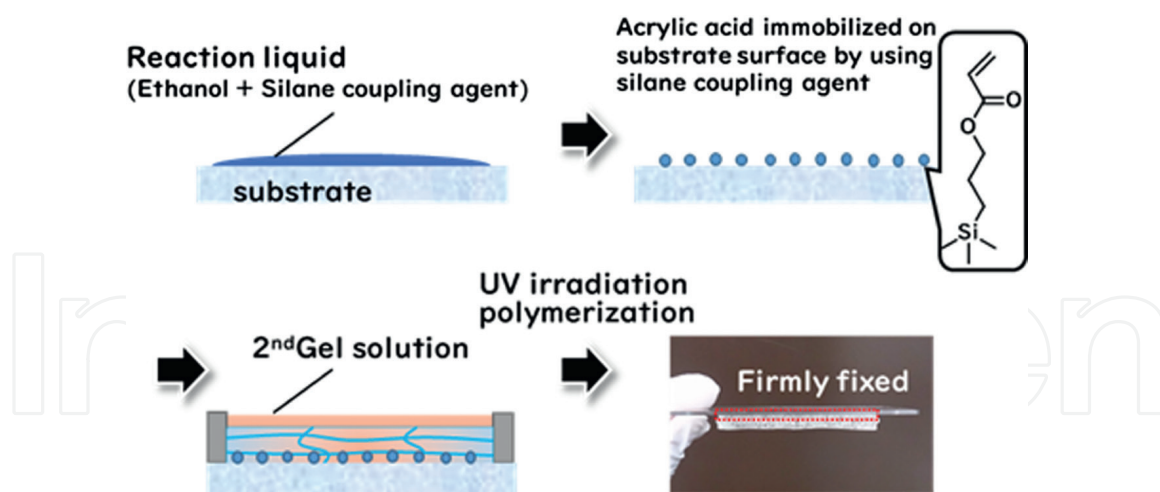
### 2.3 Gel immobilization technology on substrates

**Figure 3** is a schematic of the gel immobilization technique. The DN ion gels were covalently immobilized on glass substrates via a silane coupling reaction [21]. Briefly, a mixture of ethanol and 3-(trimethoxysilylpropyl) methacrylate was slowly dropped into mixed ethanol and 25-wt% ammonia solution while stirring. The solution was used to immerse a washed glass substrate for 16 h at room temperature to impart the vinyl moieties that covalently anchor the gel to the glass surface. The resulting substrate coated one side of the reaction cell. During the second gel synthesis, the DN ion gel was covalently bonded to the surface silanol groups of a glass substrate. The same technique can prepare DN hydrogels. It is also applicable to other substrates if their surfaces possess hydroxyl groups that can be modified by a silane coupling reagent with vinyl groups, which can help anchor the gel.

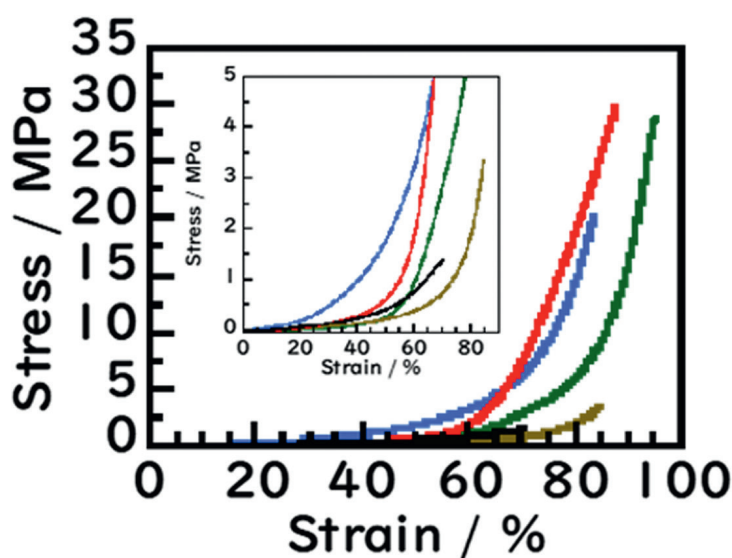
## 3. Characterization of DN and DN ion gels

### 3.1 Mechanical properties from stress-strain curves

The mechanical strengths of the DN ion gels were evaluated at 25°C and 40% relative humidity using a universal testing machine (Instron 3342, Instron Japan, Kawasaki, Japan). From the stress-strain curves, the compression fracture stresses of the DN



**Figure 3.**  
Schematic of gel immobilization technology.



**Figure 4.**  
Stress-strain curves of DN hydrogel (blue), DN ion S-gel (green), single DEMM-TFSI gel (brown), and DN ion gel (red). Inset is an expansion of the change region of the curves.

hydrogel and DN ion S-gel were found to be 20 and 25 MPa, respectively (**Figure 4**), which were comparable to those of DN ion gel substituted with tetrabutylphosphonium proline [14]. The stress-strain curve of DN ion gel presented a smaller initial slope than that of DN hydrogel; the loss of hydration force softened the DN ion gel. PAMPS is an electrolyte polymer that swells in pure water via hydration of negatively charged AMPS. In addition, its surface charge is easily shielded in ionic salt at high concentration. The DN ion gel shrank after displacement, suggesting that it softened through loss of hydration power caused by the high ionic strength of EMI-EtSulf.

Moreover, the compressive fracture stress of the DN ion gel was 30 MPa at 87% strain (**Figure 4**), which is 10 MPa higher than that of the DN hydrogel (20 MPa) and DN ion S-gel (25 MPa). The compressive fracture stresses of single-network gels were much lower (1 MPa for poly(DEMM-TFSI) and 3 MPa for PMMA), suggesting that the high mechanical strength of the combined materials derives from the formed DN structure. Because conventional DN gels substituted with amino-acid-based

ILs exhibit similarly high mechanical strengths (>25 MPa) [14], we concluded that combining ILs with compatible polymers can boost the mechanical strength without hydration assistance from electrolyte polymers.

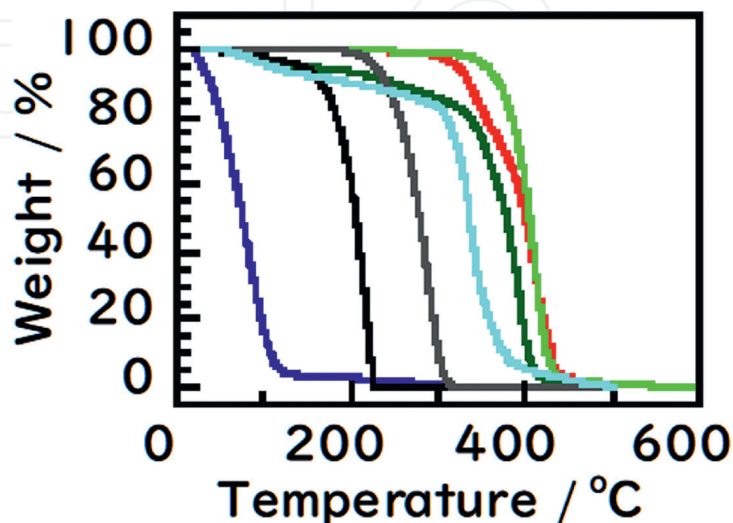
### 3.2 Thermal properties of the gels

The thermal properties of DN ion S-gel, DN ion gel, and DN hydrogel were evaluated using thermogravimetric analysis (TGA), and the results were compared with those of pure ILs and the conventional lubricants poly- $\alpha$ -olefin (PAO) and glycerol. **Figure 5** compares the TGA curves of DN hydrogel (blue), DN ion S-gel (light blue), EMI-EtSulf (green), DN ion gel (red), DEME-TFSI (light green), PAO (gray), and glycerol (black). The initial weight loss (up to 100°C) in the TGA curves of DN ion S-gel and EMI-EtSulf was attributed to release of absorbed moisture. The secondary weight loss at ~150°C indicated pyrolysis of the sulfonate and sulfate portion of PAMPS and EMI-EtSulf [22]. The 10% weight-loss temperatures ( $T_{10}$ ) of DN ion S-gel and EMI-EtSulf were determined as 196°C and 247°C, respectively. The  $T_{10}$  of DN hydrogel was much lower (39°C), thereby indicating that replacing water with ILs decidedly improves the thermal stability of DN gels ( $\Delta T_{10, \text{DN ion S-gel}} = 157^\circ\text{C}$ ). The DN ion gel thermally decomposed at nearly 300°C with a weight loss 10% at 335°C. The obtained  $T_{10}$  value of DN ion gel was much higher than that of the DN hydrogel ( $\Delta T_{10, \text{DN ion gel}} = 295^\circ\text{C}$ ) and 139°C higher than that of the S-gel. The 10% weight loss of DN ion gels occurred at a much higher temperature than that of glycerol (165°C) and PAO (241°C); therefore, DN ion gel can be used as stable and efficient lubricant under high-temperature conditions for industrial applications.

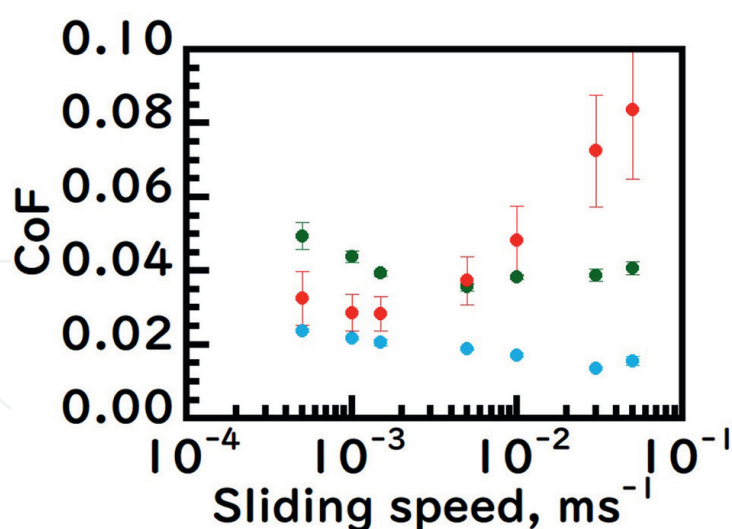
## 4. Tribological properties of the DN ion gel

### 4.1 Sliding-speed dependence of CoF on gel properties

For the friction test using a ball-on-plate-type reciprocating tribometer (Shinto Scientific Co., Ltd, Tokyo, Japan), the gel sample was fixed on a sliding table and a glass ball sample ( $\phi 10$  mm) was placed in a ball holder connected to a load cell. To



**Figure 5.** TGA curves of DN hydrogel (blue), DN ion S-gel (right blue), EMI-EtSulf (green line), DN ion gel (red), DEME-TFSI (light green), PAO (gray), and glycerol (black).



**Figure 6.**

Sliding-speed dependence of CoF at glass ball/DN hydrogel (light blue circles), glass ball/DN ion S-gel (green circles), and glass ball/DN ion gel (red circles).

evaluate the lubrication properties, the ball/substrate frictional force was measured at different loads and sliding speeds. **Figure 6** plots the CoFs as functions of sliding speed for the ball/DN hydrogel (light blue circles), glass ball/DN ion S-gel (green circles), and glass ball/DN ion gel (red circles) under an applied load of 0.98 N. The CoF of the glass ball/DN hydrogel remained within 0.01–0.02 over the range of measured sliding speeds. The minimum CoF at  $3.0 \times 10^{-2} \text{ ms}^{-1}$  indicated a shift from the elastic lubrication regime to mixed lubrication. By contrast, the CoFs of the glass ball/DN ion S-gel ranged from 0.04 to 0.05 over the sliding-speed range and were minimized at a speed six times slower ( $5.0 \times 10^{-3} \text{ ms}^{-1}$ ) than that of the DN hydrogel. These results can be attributed to the following factors: (1) high viscosity of the swelling agent incorporated in the DN gels, and (2) increased polymer adhesion after substituting water with IL. As the viscosities of water and EMI-EtSulf at 25°C are 0.89 and 71 MPa·s, respectively, a fluid film of IL is much thicker than a water film. Therefore, the viscosity change could not explain the disparate lubrication properties of DN ion S-gel and DN hydrogel. Regarding factor (2), PAMPS and the glass surface easily dissociate to produce negative charges in pure water, and the fluid film thickness is preserved by electrostatic repulsion between the glass surface and PAMPS [23, 24]. Electrostatic repulsion is essential for lowering the friction at an electrolyte interface. Using a surface force apparatus, Raviv et al. [23] studied the friction between polymer brush layers adsorbed on a molecularly smooth mica surface in water. The friction induced by the shear force between the polyelectrolyte brush layers (CoF = 0.0006–0.001) was lower than that induced between neutral brush layers. In the former case, friction was decreased by electrostatic repulsion between the negatively charged tribopaired polymer brushes. Dunlop et al. [24] measured the normal and shear forces between polyelectrolyte brush layers grafted on a mica surface. After examining the contribution of ionic strength to friction, they found that salt at high concentrations shielded the electric double layer, thereby increasing the shear forces. Being fully composed of cations and anions, EMI-EtSulf has a high salt concentration ( $\approx 5$  molar); therefore, it shielded almost all of the hydroxyl groups on the glass surface and the sulfonate groups on PAMPS. The higher friction of the DN ion gel than of the DN hydrogel was thus attributed to polymer adhesion on the glass surface, enabled by electrostatic shielding of the glass and PAMPS surfaces.



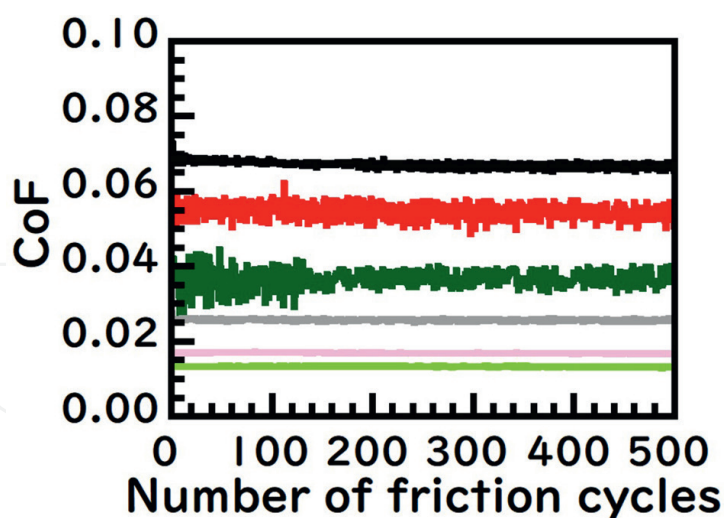
The red circles in **Figure 6** plot the relationship between CoF and sliding speed of the glass ball/DN ion gel under a 0.98-N load. The CoF decreased as the sliding velocity increased to  $1.5 \times 10^{-3} \text{ ms}^{-1}$  and increased slowly thereafter, indicating a transition from a mixed (elastic fluid) to a fluid lubrication regime. The higher CoF of the DN ion gel than of the hydrogels and DN ion S-gel at sliding velocities above  $5.0 \times 10^{-3} \text{ ms}^{-1}$  may be explained by the smaller elastic deformation (and consequent entry to the fluid lubrication regime) of the synthesized DN ion gel. The CoF of the DN ion gel exceeded those of the DN hydrogel and ion S-gel in the same velocity region. Meanwhile, the effect of surface-to-surface contact becomes significant at velocities below  $1.5 \times 10^{-3} \text{ ms}^{-1}$  (in the mixed lubrication regime). The smaller CoF of the DN ion gel than that of the DN ion S-gel in the slow-velocity region means a smaller interaction between the glass surface and DN ion gel than between the glass surface and DN ion S-gel; however, the former interaction exceeded the interaction between the glass surface and DN hydrogel. The CoF of the DN hydrogel was lower at room temperature when water was not volatilized (that is, under the experimental conditions of the present study).

#### **4.2 Repeated durability and thermal stability of gels**

**Figure 7** shows the temporal changes in the measured CoFs of glass balls/DN ion S-gel and glass balls/DN ion gel at different temperatures under a 0.98 N load and a sliding speed of  $5.0 \times 10^{-3} \text{ ms}^{-1}$ . At 25°C, 80°C, and 100°C, the CoF values of the glass ball/DN ion S-gel were 0.067, 0.054, and 0.037, respectively, and those of the glass balls/DN ion gel were 0.025, 0.017, and 0.013, respectively. Both sets of CoFs monotonically decreased with increasing temperature. Higher temperatures promote gel softening and decrease the average contact pressure. They also increase the fluid film thickness and hence the viscous resistance. Therefore, decreased polymer adhesion is considered as the main cause of the friction reduction. At 50°C, the CoF of the DN hydrogels jumped by more than 10-fold during repeated measurements, probably due to thermal aggregation of the dried polymer [18] as the water solvent evaporated. In contrast, the CoF of the DN ion gel remained stable after 500 friction cycles even at 100°C because it did not volatilize, indicating that the DN ion S-gel and DN ion gels were more thermally stable than the DN hydrogel. Therefore, they can potentially be applied as lubricating gels in high-temperature applications that are unsuitable for hydrogels.

#### **4.3 Lubricating properties of gels in a vacuum and future development of gel materials**

**Figure 8** shows the stability of the DN ion gel under a high vacuum during repeated friction measurements of glass balls/DN ion gel. The sliding velocity, load, and pressure were  $5.0 \times 10^{-3} \text{ ms}^{-1}$ , 0.20 N, and  $2.2 \times 10^{-4} \text{ Pa}$ , respectively. For this test, a custom-made ball-on-plate-type tribometer was installed in a vacuum chamber [25]. The tribopairs of DN ion gel with glass balls and SUJ2 balls showed a stable response (CoF = 0.023) after 500 friction cycles, indicating that the low-friction surface of the DN ion gel remained stable under high-vacuum conditions. Along with the temperature stability results in **Figure 7**, this result affirms that DN ion gels can reduce the friction and improve the energy efficiency of mechanical systems operating under high-temperature and high-vacuum conditions, such as bearings and mechanical seals.

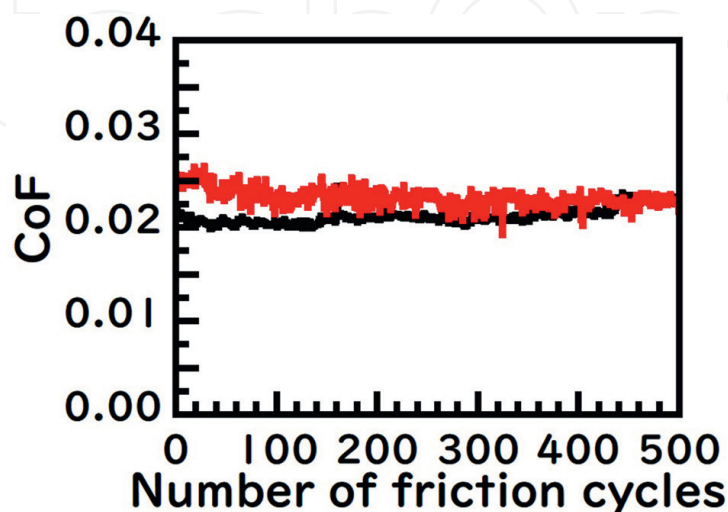


**Figure 7.**

CoF versus number of friction cycles for glass ball/DN ion S-gel (black: 25°C, red: 80°C, green: 100°C) and glass ball/DN ion gel (gray: 25°C, pink: 80°C, yellow-green: 100°C). All measurements were taken at  $5.0 \times 10^{-3} \text{ ms}^{-1}$  under a load of 0.98 N.

Thus, we combined DN gels and ILs and evolved them into an industrially viable material. For widespread usage of this material, we must halt the metal corrosion of ILs and replace the expensive ILs with cheaper alternatives such as deep eutectic solvents (DES) [26]. In DES compounds, hydrogen-bond donors are mixed with hydrogen-bond acceptors (either or both solid) at a certain ratio, forming a liquid at room temperature. DESs exhibit similar properties to ILs but are inexpensive and their combination possibilities are numerous. We plan to develop new materials based on DESs.

In addition, the DN gel with IL in this study requires a two-step preparation, which is difficult to synthesize in large quantities. This issue must also be resolved in industrial preparations. Currently, we are developing a one-step preparation method for DN gels [27].



**Figure 8.**

CoF versus number of friction cycles for glass ball/DN ion gel (black) and SUJ2 ball/DN ion gel (red), measured at  $5.0 \times 10^{-3} \text{ ms}^{-1}$  under a 0.20 N load and  $2.2 \times 10^{-4} \text{ Pa}$ .

## 5. Conclusion

In this study, we investigated gels comprising two types of ILs for industrial applications: DN ion S-gel in which the water in the hydro-DN gel is replaced by an IL EMI-EtSulf, and DN ion gel containing IL DEME-TFSI where one of the polymer backbones of the DN ion gel becomes a network of poly(DEMM-TFSI), an IL-type polymer developed through our previous IL polymer technology.

The obtained DN ion S-gel and DN ion gel achieved high compression strengths (25 and 30 MPa, respectively) and were thermally stable up to 196°C and 335°C (the 10% weight-loss temperature), respectively. The decomposition behavior of the DN ion S-gel and DN ion gel reflects their thermal stabilities after incorporating EMI-EtSulf and DEME-TFSI, respectively. This phenomenon is commonly observed in ion gels. The CoF of the DN ion gel was low (0.02) and stable after repeated measurements at high temperature and under vacuum conditions, confirming the durability of this gel even under harsh conditions.

This study elucidated the fabrication of lubricant gels with high mechanical strength and robustness. The gels are expected to reduce the energy and resource consumption of materials in the temperature range at which conventional hydrogels cannot be used (DN ion S-gel:  $\Delta T_{10, \text{DN ion S-gel}} = 157^\circ\text{C}$ , DN ion gel;  $\Delta T_{10, \text{DN ion gel}} = 295^\circ\text{C}$ ).

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