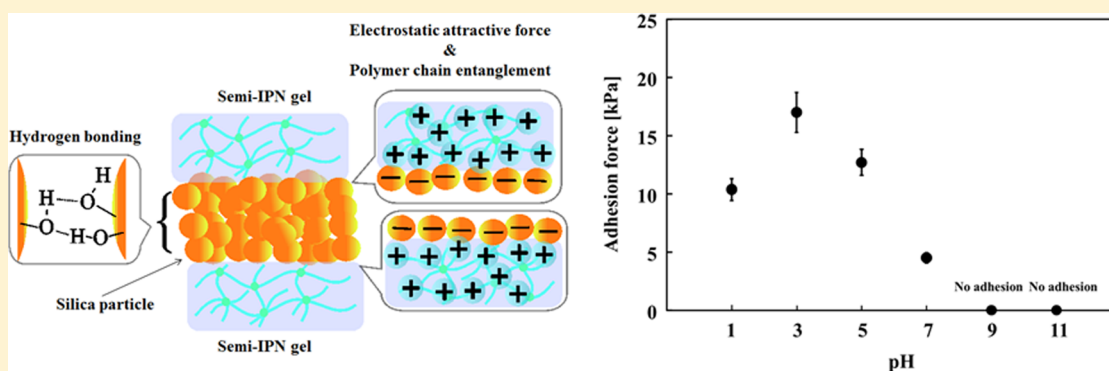# Adhesion of Gels by Silica Particle

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Ⓢ *Supporting Information*

ABSTRACT: In this study, a method for achieving adhesion between two positively charged gels with high mechanical strength was developed. By utilizing a silica particle dispersion as a binder, the gels easily adhered to each other and remained stable for up to 11 days when immersed in aqueous solution. The adhesion force between the two positively charged semi-interpenetrating network gels with the silica particle was measured to be up to approximately 20 kPa, which is around 10 times larger than that with a charged polymer-rich liquid as a cross-linker (approximately 1.5 kPa). It was demonstrated that the adhesion force was a result of two types of interactions: an electrostatic attractive force between the cationic gel surface and hydrogen bonding among the silica particles. In addition, it was shown that the adhesion force was dependent on solution pH, which was attributed to changes in the charge of the silica particles.

INTRODUCTION

A wide variety of soft and wet materials have been the subject of extensive research in recent years. In particular, stimuli-responsive polymers and gels that swell or shrink by changing the physicochemical conditions have been studied from the point of view of both fundamental and applied research.[1−3] Of particular interest are biologically inspired soft robotic actuators that can move in a manner similar to that of living creatures.[4,5] For example, by simply changing the external physicochemical conditions, these devices can move through their environment. In one case, a polymer gel actuator composed of a bigel was able to bend under the appropriate stimulus.[6] This bigel was prepared from interpenetrating an *N*-isopropylacrylamide (NIPAAm) gel, which is a thermosensitive polymer, into a polyacrylamide (PAAM) gel network. This structure was able to bend in water in response to a change in temperature as a result of the characteristics of the responsive NIPAAm component. The design and construction of a gel robot consisting of many types of stimuli-responsive gels via a bigel method can give gel robots with superior motion capabilities.

The connection of a thermosensitive sheetlike gel to a pH-sensitive sheetlike gel could produce a bigel that is able to bend in water in response to both temperature and pH changes. By connecting many types of gels, it should be possible to construct a novel gel that can respond to multiple stimuli. However, there are few studies regarding the development of an appropriate adhesion method for connecting gels. In a previous investigation, electrostatic interactions between anionic and cationic gels were exploited in order to bond them in an air environment.[7] Furthermore, charged gels were attached to one another by utilizing a charged polymer-rich liquid as a cross-linker (approximately 1.5 kPa).[8] These studies concerned adhesion methods for normal gels with low mechanical strength; however, in order to combine many types of actuators and soft robots, an adhesion method for mechanically strong gels is required. To date, there have been
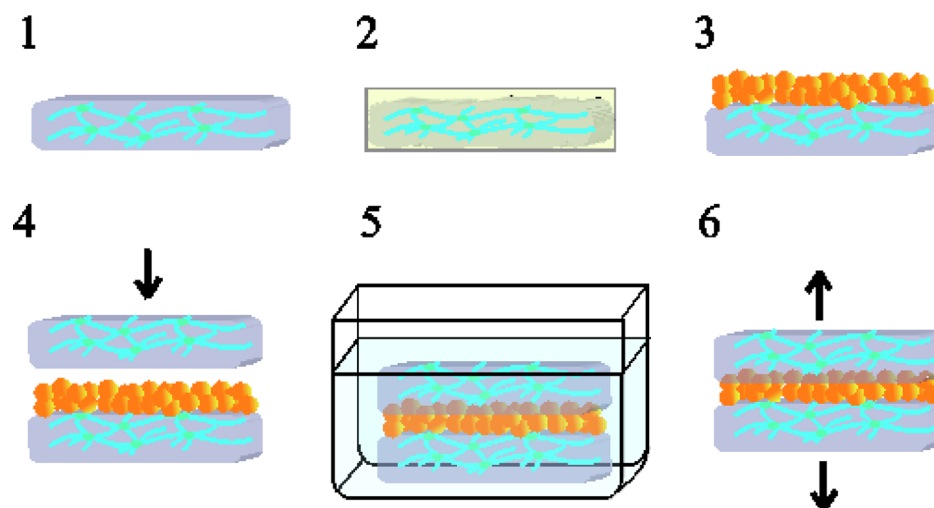
Figure 1. Steps of the adhesion processing procedure. (1) Gels were immersed in a pH 3 aqueous solution and then left to dry to 65% water content. (2) Gels were wrapped in Saran Wrap and then stored for 1 week. (3) A 20 wt % silica particle dispersion was applied to one surface. (4) A second gel was placed in contact under 0.2 MPa load for 10 min. (5) The aggregate was immersed in pH 3 aqueous solution for 2 days. (6) The gels were separated at a rate of 200 mm/min.

no studies regarding such a protocol, despite the development of many types of gels with high mechanical strength.[9−11]

In this study, we developed a novel adhesion method for positively charged semi-interpenetrating network gels (SI gels) with high mechanical strength by utilizing negatively charged silica particles as a binder. We measured the adhesion force between two polymer gels and suggested a mechanism responsible for the strength of the binding.

■ EXPERIMENTAL SECTION

Synthesis of Cationic SI Gel. A 50 wt % solution of [3-(methacryloylamino)propyl]trimethylammonium chloride (MAPTAC) in water (10.4 g), N,N'-methylenebis(acrylamide) (MBAA; 0.253 g) as a cross-linker, and α-ketoglutaric acid (0.0343 g) as an initiator was added to pure water (15.3 mL). The monomer solution was injected into a cell consisting of a pair of glass plates separated by a silicone rubber spacer (thickness, 2 mm). The cell was then irradiated with a UV lamp for 1 h to initiate the polymerization. The resulting gel was soaked in an aqueous solution of 40 wt % acrylamide containing of 1 mol % α-ketoglutaric acid for 2 days and then irradiated with UV light for 20 min. After polymerization, the SI gel was immersed in pure water for 2 days to remove unreacted compounds. This was repeated three times with fresh water used each time.

Synthesis of Anionic SI Gel. 2-Acrylamide-2-methylpropane sulfonic acid (AMPS; 2.07 g), MBAA (57.9 mg) as a cross-linker, and α-ketoglutaric acid as an initiator were dissolved in pure water (8.21 mL). The rest of the processing procedure was the same as that for the synthesis of the cationic SI gel.

Adhesion Processing Procedure and Adhesion Force Measurements. As shown in Figure 1, the cationic SI gels were first immersed in a dilute aqueous solution of hydrochloric acid (pH 3) for 1 day and then left to dry to 65% water content at 50 °C (step 1). The dried gels were wrapped in Saran Wrap and then stored for a week to equalize the water content throughout the entire gel (step 2). Rectangular block specimens (approximately $4 \times 4 \times 20$ mm^3) were cut from the resulting gels. A 20 wt % silica particle dispersion was then applied to the

top surface of the block (step 3), and this was placed in vertical contact with another gel sample under 0.2 MPa of pressure for 10 min (step 4). The conjoined gels were immersed in dilute hydrochloric acid (pH 3) for 2 days to reach equilibrium (step 5). Finally, the adhesion force between the two cationic SI gels was measured using tensile tests at room temperature. The samples were set on a tensile–compressive tester (Shimadzu, Kyoto, Japan) and vertically separated at a rate of 200 mm/min in an air environment. The force just before their detachment was measured as the adhesion force. The stress was calculated based on the adhesion force divided by the adhesion area between the two cationic SI gels, which was measured with a slide gauge.

■ RESULTS AND DISCUSSION

The dependence of the adhesion force between the two cationic SI gels on the silica particles and the drying process can be seen in Figure 2. It is clear that without the drying out period (Figure 1, step 2) or in the absence of the silica particles (Figure 1, step 3), the two gels did not adhere to one another. On the other hand, when the cationic SI gels bonded by the silica particles after the drying process were immersed in aqueous solution, their adhesion was maintained, despite the
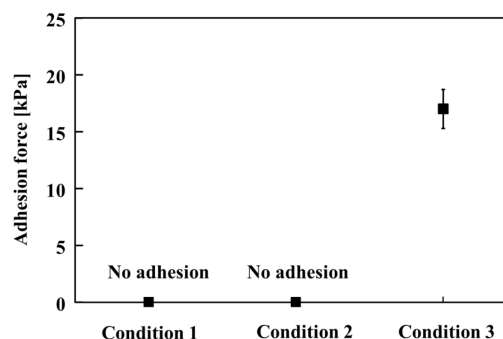

Figure 2. Dependence of adhesion force on various conditions: (condition 1) with silica particles and without the drying process; (condition 2) without silica particles and with the drying process, (condition 3) with silica particles and the drying process.

increase in volume due to swelling. It is reasonable to suppose that the adhesion was a result of an electrostatic attractive force between the cationic SI gel and the silica particles. The negatively charged silica particles have negated the electrostatic repulsive interaction between the two cationic SI gels. The lack of adhesion in the absence of the drying process was attributed to the low polymer chain concentration on the gel surface due to the swollen state of the cationic SI gels. On drying, the loss of water concentrated the polymer chains on the gel surface, resulting in an increase in interactions between the silica particles and the cationic moieties. As the cationic gels were placed in contact with one another without the silica particles, they initially bonded; however, upon immersing the bonded gel in an aqueous solution for 2 days, the cationic gels were separated. The initial adhesion between the gels carrying the same charge was attributed to the entanglement of the polymer chains on the gel surface. Owing to the weak nature of these interactions, on prolonged immersion in aqueous solution, electrostatic repulsive forces become dominant, resulting in detachment of the gels from one another. As a result of this measurement, it was demonstrated that the drying process enhanced the interactions and entanglement strength between the silica particles and the polymer chains.

Figure 3 shows that the adhesion force between the two cationic SI gels was not greatly affected by prolonged
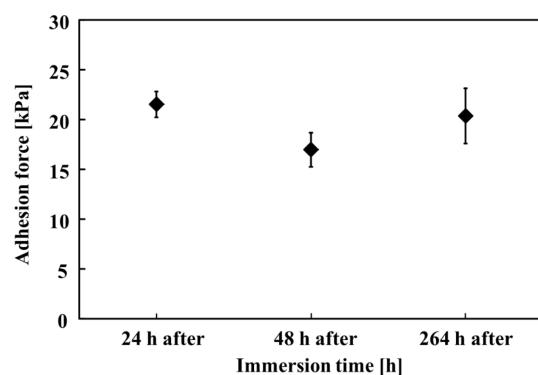

Figure 3. Dependence of adhesion force on immersion time for two cationic SI gels.

immersion. The gels were able to maintain their attached state for 11 days without a significant decrease in the adhesion force. This is an important finding as it is necessary for the successful application of this method that the adhesion force be maintained in solution. On the other hand, anionic SI gels attached via the same silica particle method became detached from one another in less than 2 days, despite them exhibiting almost the same adhesion force (15.7 kPa) at 24 h as that of the cationic gels. The main cause of their detachment was electrostatic repulsive interactions between the polymer chains, similar to the case of the cationic gels in the absence of silica particles. We considered that the retention of the adhered state of the two anionic SI gels for 24 h was attributed to polymer chain entanglement.

Figure 4 shows scanning electron microscopy (SEM) images of the cationic SI gel surface after the tensile test. Figure 4a shows the top view of the adhesion surface. The silica particles are deposited as thin plates on the gel surface. Figure 4b is the side view of the adhesion surface. The thickness of the silica particle plates is approximately 8 μm. The repulsive force of the two cationic gels depends on the distance between them. The
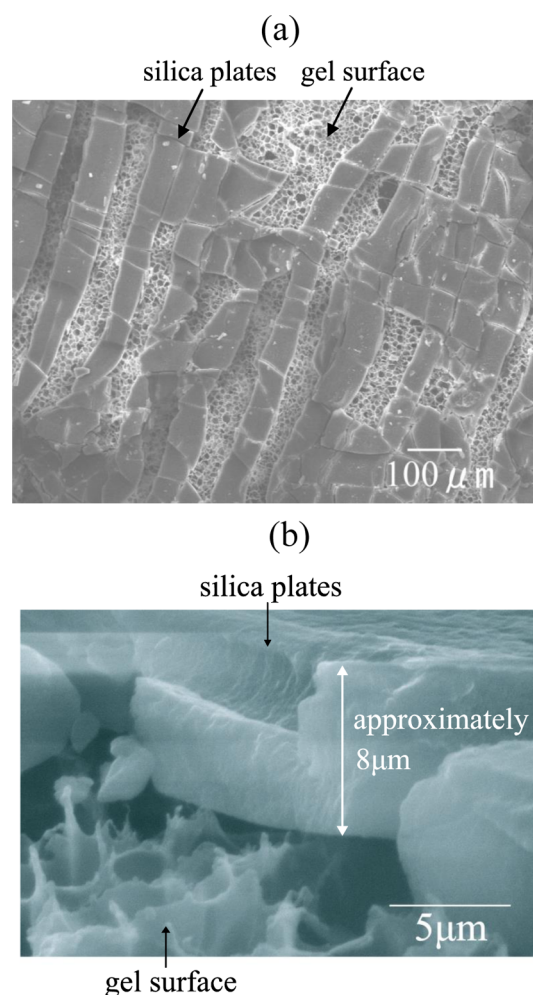

Figure 4. SEM images of adhesion surface between the cationic SI gels with colloidal silica: (a) top view of the adhesion surface; (b) side view of the adhesion surface.

particle layer thickness was sufficient to exclude the repulsive force between the two cationic gels. From these SEM images, it is clear that the silica layer between the two gels is a multilayer (the diameter of the silica particles is 4−6 nm). This phenomenon indicates that the adhesion force is influenced by the interaction between the gel surface and the silica particle as well as that among the silica particles. In general, it is well-known that the silica surface reacts with water to form a layer of the silanol (SiOH) groups. In particular, the charge on the silica particle is influenced by the behavior of the silanol groups in solution. An increase in the pH in solution causes an increase in the negative charge on the SiO$_2$ surface as follows.[12]

$$\equiv SiOH + OH^- \rightarrow \equiv SiO^- + H_2O$$
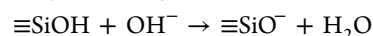
The ζ potential of the silica particles increases with increasing pH in solution.[13] Thus, it is clear that the pH in solution has a direct influence on the adhesion between the cationic SI gels.

The pH of the aqueous solutions used for steps 1 and 5 in Figure 1 was varied, and the effect on the adhesion force between two gels prepared under identical conditions was assessed (Figure 5). It can be seen that the adhesion force was the highest at pH 3, decreasing both above and below this value. At a pH above 9, the two cationic SI gels did not attach at all. The charge of the cationic SI gels does not depend on solution pH because of the quaternary ammonium salt.
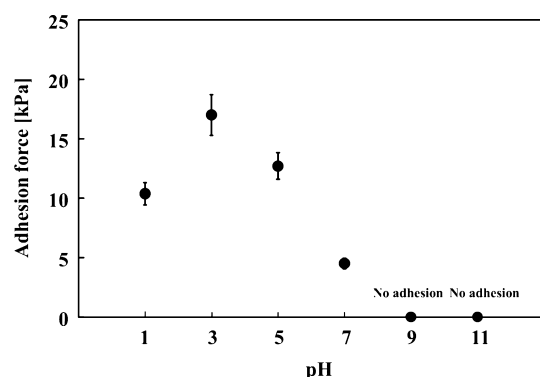
Figure 5. pH dependence of the adhesion force between the two cationic SI gels.

Figure 6. Adhesion forces after immersing the gels in solutions with or without urea.

Therefore, it is suggested that the electrostatic attractive interaction between the cationic SI gel and the silica particles increases with the increasing pH in solution. However, as shown in Figure 5, the adhesion force decreased with the increase in solution pH. This phenomenon can be explained by the interaction among the silica particles. The silica particles are stably dispersed at pH 9−10 because of the electrostatic repulsion between the silica particles (Snowtex XS, Nissan Chemical Industries, Tokyo, Japan).[14] Their stability decreases with decreasing solution pH because of the decrease in the electrostatic repulsion, and the silica particles become a physical gel or aggregate siloxane (Si−O−Si) linkage or hydrogen bonding (see Figure 4).[13] Therefore, the adhesion force was the highest under mildly acidic conditions because the attractive interaction between the silica particles is very strong. At pH 3, the silica surface is essentially neutral ($\equiv$SiOH) and is covered by silanol groups, with an area density of approximately 5 silanol groups/nm^2.[15] As a result, a decrease in the pH in solution enhances hydrogen bonding among the silica particles via the silanol groups. The adhesion force at pH 1 was lower than at pH 3 because the silica particles have a positive charge:

$$\equiv\text{Si}-\text{OH} + \text{H}^+ \rightarrow \equiv\text{Si}-\text{OH}_2{}^+$$
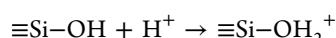
In consequence, the repulsion among the silica particles increased, and hence, the adhesion force decreased. In addition, in this experiment, we did not use the buffer solution. The dilute aqueous solutions with intended pHs were controlled by hydrochloric acid and sodium hydrate. Therefore, we considered that the effect of ionic concentration on the adhesion force was negligible in this experiment.

We considered that the formation of hydrogen bonds among the silica particles at the interface between the two cationic SI gels may have also had an influence on the adhesion. This hypothesis was evaluated by placing two conjoined cationic gels into a 1 M aqueous solution of urea. Urea is known for its ability to disrupt hydrogen bonding, such as that observed in the denaturation of proteins, and was therefore utilized to determine whether hydrogen bonds were involved in the adhesion between the two gels.[16−19] Figure 6 shows that immersion in the urea solution resulted in a reduction in adhesion force. As the data shown in Figure 3 demonstrate that extended periods of immersion did not reduce the adhesion force, it appears that the presence of urea was responsible for the observed reduction. This indicates that hydrogen bonding was at least partly responsible for adhesion of the two cationic SI gels.
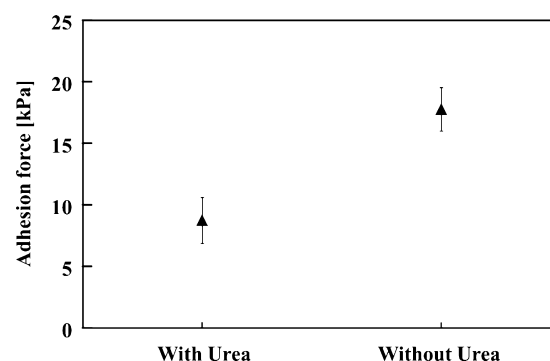
On the basis of the obtained data, we propose the mechanism of adhesion of the gels in the presence of silica particles to be that shown in the schematic in Figure 7. As a 20
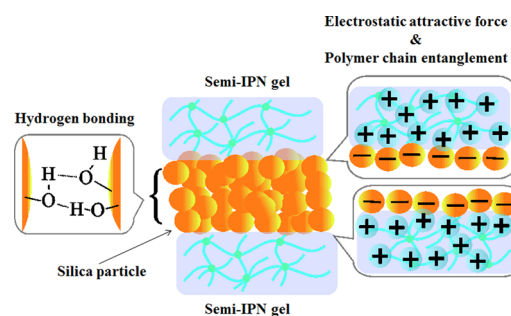

Figure 7. Schematic representation of the adhesion model between cationic SI gels with silica particles.

wt % silica particle dispersion was used, it is likely that the particles assembled in a multilayer between the two cationic SI gels. In this case, there are two interactions occurring. The first of these is the cohesive interaction between the silica particles owing to the hydrogen bonding, with the pH dependence of the adhesion force between the gels being considered to result from the change in stability of the silica particle layer. The second interaction is that between the surface of the gel and the silica particles. The observed detachment of the two anionic SI gels indicated that the interaction was electrostatic in nature.

■ CONCLUSION

Adhesion between the two positively charged SI gels was observed when a silica particle dispersion was utilized as a binder. The adhesion force was measured to be up to approximately 20 kPa, which is more than 10 times the force achieved using a charged polymer-rich liquid as a cross-linker (approximately 1.5 kPa). It was clarified that the origin of the adhesion force was the following: (1) electrostatic attractive interaction between the gel surface and the silica particles, with the anionic SI gels not attached to each other because of electrostatic repulsion; (2) a cohesion force originating from the hydrogen bond between the silica particles themselves. It was found that the adhesion force depended on the environmental pH, and this pH dependence can be explained by the hydrogen bonding between the silica particles.

ASSOCIATED CONTENT

S Supporting Information

Photograph of adhesion between two cationic SI gels. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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