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Adhesion between Semihard Polymer Materials Containing Cyclodextrin and Adamantane Based on Host–Guest Interactions

Takahiro Kakuta, Yoshinori Takashima, Takaaki Sano, Takashi Nakamura, Yuichiro Kobayashi, Hiroyasu Yamaguchi, and Akira Harada*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

S Supporting Information

ABSTRACT: The adhesion between hard materials without any glue is difficult but challenging topic because hard materials inhibit molecular mobility and have a large gap on the adhesive interface. Here we show that host–guest interactions realize a strong adhesive strength between semihard materials based on polyacrylamide xerogel by using a minimal amount of water. The adhesive strength between β CD xerogel(x) and Ad xerogel(y), where β CD and Ad denote β -cyclodextrin and adamantane, respectively, increases as the molar ratio (mol %) of host (x) or guest (y) molecules increases, which indicates that adhesion between β CD xerogel(x) and Ad xerogel(y) is due to complexation between the β CD and the Ad units. Adhesion between β CD xerogel(10) and Ad xerogel(5) displays a robust adhesive strength (5.1 MPa). Competitive experiments using small molecules confirmed the importance of host–guest interactions in adhesion. Optical microscopic observations of the adhesion interfaces reveal that both sides of β CD xerogel(x) and Ad xerogel(y) pull together, reflecting the specific adhesive nature between the two materials. Furthermore, a self-healable semihard material, β CD-Ad xerogel(0.3, 0.4) modified with both 0.3 mol % of β CD and 0.4 mol % of Ad, shows an 88% stress recovery ratio. These results indicate that β CD and Ad moieties function as glue on the molecular level in the solid state.



1. INTRODUCTION

Adhesives, which have a long history as glue and bonding agents, are a fundamental part of everyday life. Recently, adhesion phenomena have been related to many scientific and technological fields, and as polymer chemistry advances, adhesive materials are shifting toward intelligent polymeric adhesives.^{1–7} Typically, after a polymeric solid material is fractured, its fragments cannot be restored to the original solid state. Adhesion between fractured materials requires suitable bonds and primer reagents. On the other hand, a polymeric solid material possessing selective adhesion abilities would eliminate the need for bonds and primer reagents. Macromolecular self-assembled materials through noncovalent interactions have the potential to create a new paradigm in adhesion science based on its dynamic nature (e.g., reversible adhesives^{8–10} and self-healing materials^{11–22}).

Adhesive and self-healing behaviors between soft materials such as gels have been achieved utilizing magnetic interaction,²³ host–guest interaction,^{25,26} and metal–ligand interaction.^{27,28} Recently, we realized selective adhesion through host–guest interactions using a supramolecular hydrogel possessing host or guest polymers.^{29–33} Additionally, a hydrogel without chemical cross-linking units inside a hydrogel has been reported to exhibit self-healing^{34,35} and highly elastic³⁶ properties through molecular recognition. In soft materials, high molecular mobility and material flexibility realize these properties. On

the other hand, adhesion and self-healing properties between hard materials are difficult to achieve without glues, adhesive reagents,²⁰ light,¹⁹ or heat.¹² Because the molecular mobility is restricted and the gap between hard materials does not bridge without artificial glues in dry conditions, adhesion of hard materials has only been reported for hard materials adhered in a water.³⁷

To realize adhesion between hard materials, we have focused on semihard materials based on polyacrylamide xerogel possessing host and guest molecules due to two reasons. First, xerogels will show the adhesion through the host–guest interaction by the addition of small amounts of water on the surface because the flexibility and the molecular mobility of the xerogel surface restore under the wet condition. Second, xerogels (tensile strength ~12 MPa) are much harder than hydrogels (~6.3 kPa). Once xerogels adhere each other through the host–guest interaction, the strong adhesion strength that hydrogel cannot perform will be formed after drying. Herein we demonstrate the strong adhesion strength between the interfaces of xerogels via host–guest interactions. Furthermore, we create self-healing semihard xerogels that

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recover to material strengths close to the initial strength through supramolecular cross-linking.

2. RESULTS

2.1. Preparation of Dried Materials. Hydrogels based on polyacrylamide were used to obtain host–guest interactions on the macroscopic scale because of their ease of preparation and the weak or absent interaction between polyacrylamide and CDs.²⁹ To achieve adhesion through host–guest interactions between the host and guest plastics, xerogel, which is the dried hydrogel modified with β -cyclodextrin (β CD), and adamantanone (Ad) were prepared because β CD has a relatively high affinity for Ad ($K_a = 4.0 \times 10^4 \text{ M}^{-1}$).³⁸ Figure 1 depicts the chemical

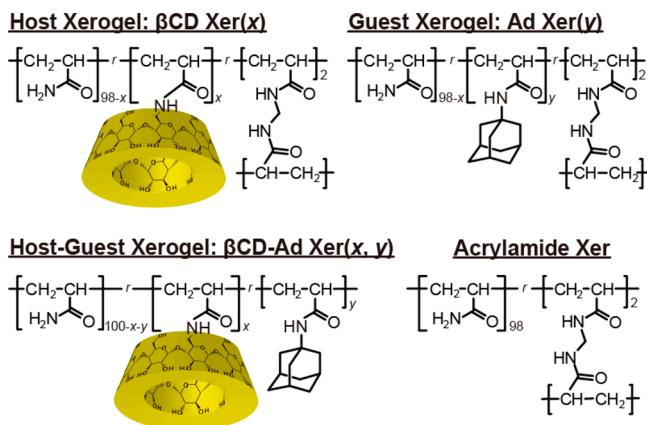


Figure 1. Chemical structures of β CD Xer(x), Ad Xer(y), β CD-Ad Xer(x,y), and AAm Xer. x and y represent the feed ratios of the host and guest molecules, respectively. AAm Xer has 2 mol % of MBAAM as a cross-linking unit.

structures of the β CD xerogels(x) [β CD Xer(x)], Ad xerogels(y) [Ad Xer(y)], β CD-Ad xerogels(x,y) [β CD-Ad Xer(x,y)], and acrylamide xerogels (AAm Xer). x and y represent the mol % of the β CD and Ad units, respectively. To discriminate β CD Xer(x) from Ad Xer(y), these materials were stained by dyes, which do not affect the adhesive behavior. AAm Xer, which serves as the control material, was prepared in the same manner as β CD Xer(x).

A creep meter (Yamaden Ltd., RE-33005B) was used to measure the materials strength of these xerogels. Every xerogel has a higher strength [β CD Xer(10): 2.1 MPa, Ad Xer(5): 1.0 MPa, β CD-Ad Xer(0.3, 0.4): 3.7 MPa, and AAm Xer: 12 MPa] than the hydrogels [β CD hydrogel: 8.7 kPa, Ad hydrogel: 1.4 kPa, β CD-Ad Xer(0.3, 0.4): 3.2 kPa, and AAm hydrogel: 6.3 kPa].

We prepared the β CD polymer, Ad polymer, and AAm polymer under the same conditions as model polymers without cross-linking units to determine the roles of the β CD and Ad units inside the xerogels (Supporting Information Schemes S1–S3). The molar ratio of β CD and Ad units in these polymers was determined by ^1H NMR spectroscopy. ^1H NMR studies showed that both monomer units are introduced into these polymers along the lines with these feed ratio (Supporting Information Figures S3–S5), suggesting that the β CD and Ad units in the xerogel mix during polymerization regardless of the presence of the cross-linking unit.

2.2. Adhesion Behavior between β CD Xer(x) and Ad Xer(y). The adhesive strength between β CD Xer(x) and Ad Xer(y) was analyzed by tensile experiments (Figure 2c). β CD

Xer(x) was placed on top of Ad Xer(y) after applying water (2 μL) onto the surface of Ad Xer(y), which increases the molecular mobility on the surface. The xerogels do not adhere without water. Subsequently, β CD Xer(x) and Ad Xer(y) adhere at room temperature due to the own weight. After drying for 24 h, the adhesive strength of β CD Xer(x)/Ad Xer(y) was measured using a creep meter at 1 mm/s of the tensile velocity for a sample size of $3 \times 3 \times 10 \text{ mm}^3$. Figure 2d shows the adhesive strength between β CD Xer(x)'s ($x = 1, 3, 5$, and 10) and Ad Xer(y)'s ($y = 3$ and 5). Adhesion did not occur when two pieces of the same kinds [β CD Xer(x)'s or Ad Xer(y)'s] were contacted. In contrast, heterogeneous connections between β CD Xer(x) and Ad Xer(y) resulted in adherence. The adhesive strength of β CD Xer(x)/Ad Xer(y) increases with x or y , which are the feed ratios of β CD in β CD Xer(x) and Ad in Ad Xer(y), respectively.

The combination between β CD Xer(10) and Ad Xer(5) shows the highest adhesive strength (5.1 MPa). This adhesive strength is 4600 times larger than the adhesive strength between β CD gel and Ad gel (1.1 kPa).³⁰ When we used hydrogels, including the β CD or Ad units, the adhesive strength is too large to be detected by the breaking hydrogels. However, the higher adhesive strength (5.1 MPa) was confirmed using xerogels. The improvement of materials strength using xerogel allows the measurement of the strong adhesion strength through host–guest interactions.

To verify the adhesive behavior through the host–guest interactions between the β CD and Ad units, a solution of competitive molecules was used to inhibit the adhesion of these xerogels. Figure 2e shows the stress–strain curves with and without aqueous solutions of competitive molecules [β CD and 1-adamantanecarboxylic acid sodium salt (AdCANa)] to the interface between β CD Xer(10) and Ad Xer(5). The adhesive strength (5.1 MPa) between β CD Xer(10) and Ad Xer(5) decreases upon adding competitive molecules. Moreover, the adhesive strength of β CD Xer(10)/Ad Xer(5) decreases as the concentration of competitive molecules increases (Supporting Information Figure S6). The addition of β CD or AdCANa as competitive molecules inhibits the formation of the inclusion complex between the β CD and Ad units on the interface because the competitive molecules cover the free host and guest molecules on the surface.

Next, AAm Xer adheres to β CD Xer(x) or Ad Xer(y), but the β CD and Ad units do not cross-link, confirming the effect of host–guest interactions because this represents the blank condition in which host–guest interactions are absent. The measured adhesive strengths of β CD Xer(10)/AAm Xer (0.40 MPa), Ad Xer(5)/AAm Xer (0.34 MPa), and AAm Xer/AAm Xer (0.40 MPa) show very weak stress values, which are one-tenth of the original stress of β CD Xer(10)/Ad Xer(5) (5.1 MPa) (Supporting Information Figure S7). Because AAm Xer does not possess both host and guest molecules, β CD Xer(x)/AAm Xer, Ad Xer(y)/AAm Xer, and AAm Xer/AAm Xer lack adhesive abilities through host–guest interactions, suggesting that the weak adhesive behavior is due to the weak anchor effect. These results indicate that host–guest interactions at the interface result in the strong adhesive strength between β CD Xer(x) and Ad Xer(y).

On the basis of a strong adhesive strength (5.1 MPa) of β CD Xer(10)/Ad Xer(5), we anticipated that this adhered xerogel would show an excellent performance and could lift a dumbbell (1 kg). To demonstrate the adhesive strength between β CD Xer(10) and Ad Xer(5), a 1 kg dumbbell was attached to

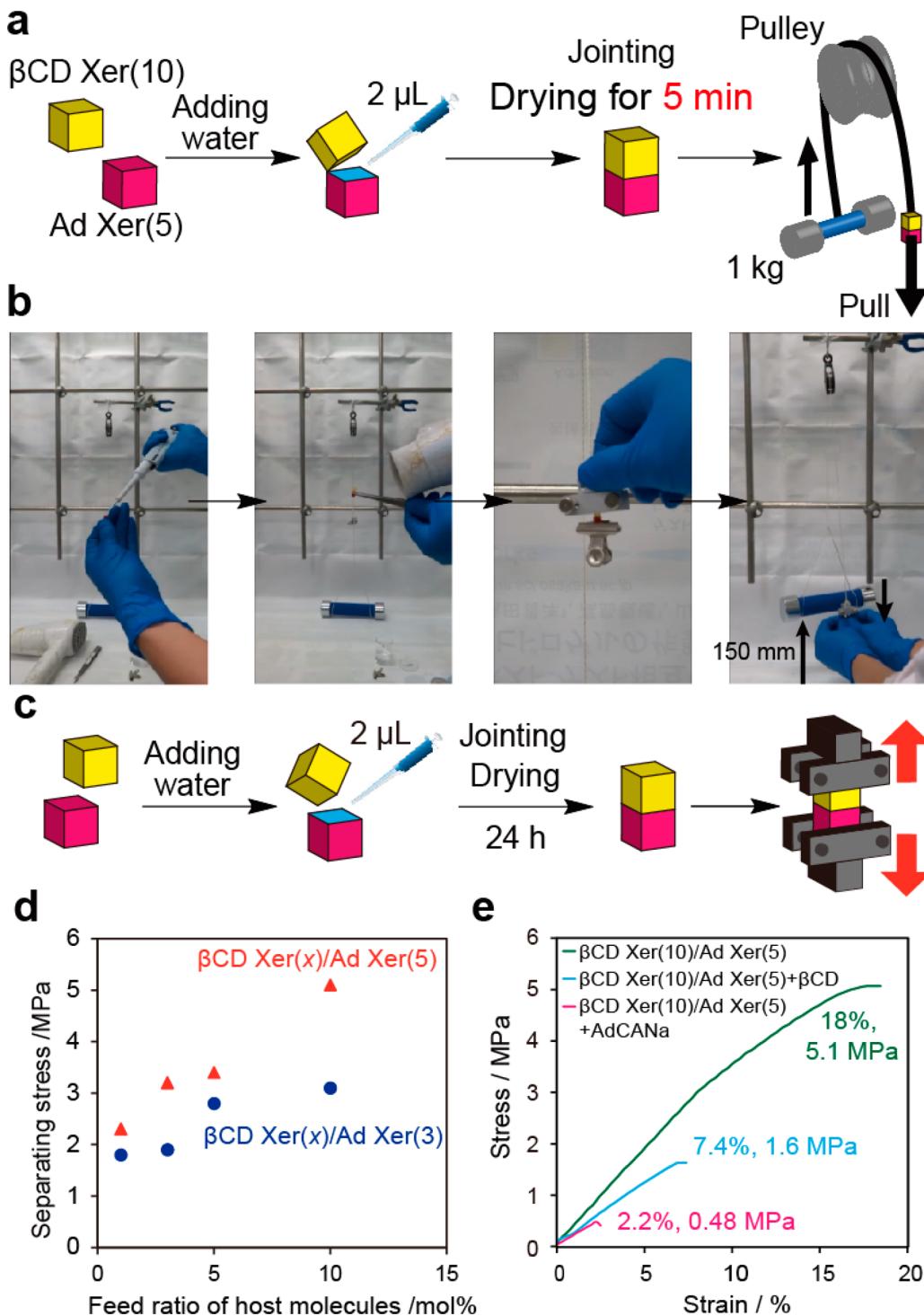


Figure 2. Adhesive strengths between semihard materials based on host–guest interactions. (a) Procedure for the hoisting experiments. (b) Images of the hoisting experiments. After adding water ($2 \mu\text{L}$) to Ad Xer(5) on an adhesive surface, Ad Xer(5) and $\beta\text{CD Xer}(10)$ were joined and allowed to dry for 5 min under a hot dryer. Then the adhesive material was held with clips that were connected to a dumbbell. Finally, a 1 kg dumbbell was hoisted. (c) Experimental procedure to measure adhesive strengths. (d) Dependence of adhesive strength on the feed ratio of host molecules. (e) Stress–strain curves of the competitive experiments using βCD and AdCANa as inhibitor.

bonded hard materials composed of $\beta\text{CD Xer}(10)/\text{Ad Xer}(5)$ and lifted via strings. Figure 2a shows the procedure to attach and lift the dumbbell. First, water ($2 \mu\text{L}$) was placed onto the Ad Xer(5) surface. Then the wet Ad Xer(5) was attached to $\beta\text{CD Xer}(10)$. Next the attached material ($\beta\text{CD Xer}(10)/\text{Ad Xer}(5)$) was dried using a hot dryer for 5 min. Prior to lifting the dumbbell, it was connected to the $\beta\text{CD Xer}(5)$ side of the

adherent sample $\beta\text{CD Xer}(10)/\text{Ad Xer}(5)$ using a clip via a pulley. The Ad Xer(10) side of the $\beta\text{CD Xer}(10)/\text{Ad Xer}(5)$ was also held via a clip. Finally, the dumbbell was hoisted with $\beta\text{CD Xer}(10)/\text{Ad Xer}(5)$. When the Ad Xer(5) side of the $\beta\text{CD Xer}(10)/\text{Ad Xer}(5)$ is pulled, the 1 kg dumbbell is suspended (Figure 2b and Supporting Information Movie S1). These results suggest that the adhesive strength of βCD

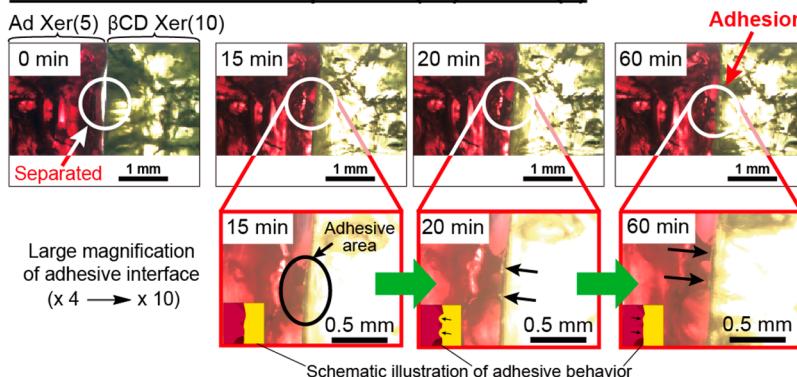
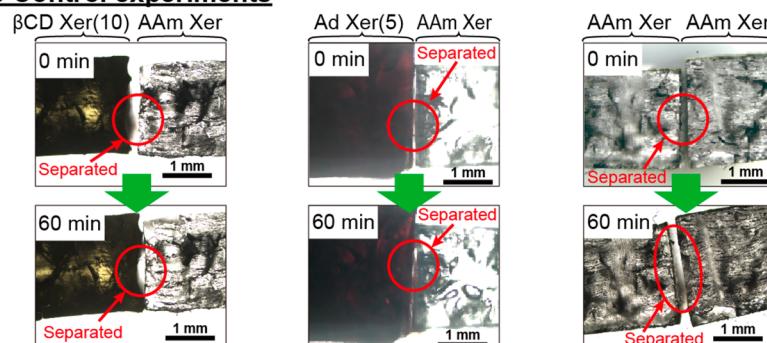
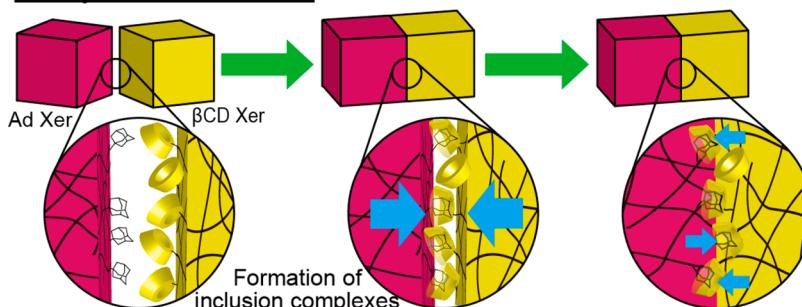
a Adhesive behavior of β CD Xer(10)/Ad Xer(5)**b Control experiments****c Proposed mechanism**

Figure 3. Observations of the adhesive interface. (a) Prior to adding water, the surfaces of β CD Xer(10)/Ad Xer(5) are separate. After 60 min, the interface of β CD Xer(10)/Ad Xer(5) shows an adhesive state. Magnification of the adhesive area demonstrates that adhesion progresses. (b) Surfaces of β CD Xer(10)/AAm Xer, Ad Xer(5)/AAm Xer, and AAm Xer/AAm Xer show a gap after standing for 60 min. (c) Schematic illustration of the adhesion mechanism. First, the free Ad units of Ad Xer(y) form inclusion complexes with the free β CD units of β CD Xer(x). Second, β CD Xer(x) and Ad Xer(y) pull the polymer chains toward each other. Finally, inclusion complexes, free Ad molecules, free β CD molecules, and main chain polymers intrude into a proposed adhesive interfaces of β CD Xer(10)/Ad Xer(5).

Xer(10)/Ad Xer(5) is sufficiently strong to withstand a 1 kg weight, and the adhesion is accelerated at higher temperatures.

2.3. Microscopic Observations of the Adherent Boundary.

To investigate the adhesive behavior at the interface, changes in the boundary between the surface of β CD Xer(10)/Ad Xer(5) during the adhesion process were observed via optical microscopy. The start time (0 min) was defined as the moment that water (2 μ L) was added. Figure 3a shows the adhesive interfaces of β CD Xer(10)/Ad Xer(5) at two different magnifications ($\times 4$ and $\times 10$). β CD Xer(10)/Ad Xer(5) has a gap at the initial state (0 min), which is the separated state. After 60 min, β CD Xer(10) and Ad Xer(5) adhere at the interface, and this adhered state is maintained after standing for a day. Moreover, the magnified ($\times 10$) shows that the two surfaces of the β CD Xer(10)/Ad Xer(5) are in contact after 15 min. After 20 min, the gap is minimized for

both surfaces of β CD Xer(10) and Ad Xer(5) through host-guest interactions. After 60 min, the interface of β CD Xer(10)/Ad Xer(5) adheres and the gap disappears.

In contrast, the gaps between β CD Xer(10)/AAm Xer, Ad Xer(5)/AAm Xer, and AAm Xer/AAm Xer do not change at the contact interfaces because AAm Xer lacks host and guest molecules. After standing for 60 min, the gap ranges from 3.6×10^{-1} to $8.1 \times 10^{-2} \text{ mm}^2$ for β CD Xer(10)/AAm Xer, from 2.0×10^{-1} to $2.4 \times 10^{-1} \text{ mm}^2$ for Ad Xer(5)/AAm Xer, and from 4.1×10^{-1} to $4.5 \times 10^{-1} \text{ mm}^2$ for AAm Xer/AAm Xer (Figure 3b). These control experiments reveal that the host-guest interaction is important for adhesion of β CD Xer(10)/Ad Xer(5).

Figure 3c schematically illustrates a proposed adhesive mechanism between β CD Xer(10) and Ad Xer(5). The host and guest molecules on the surface form inclusion complexes

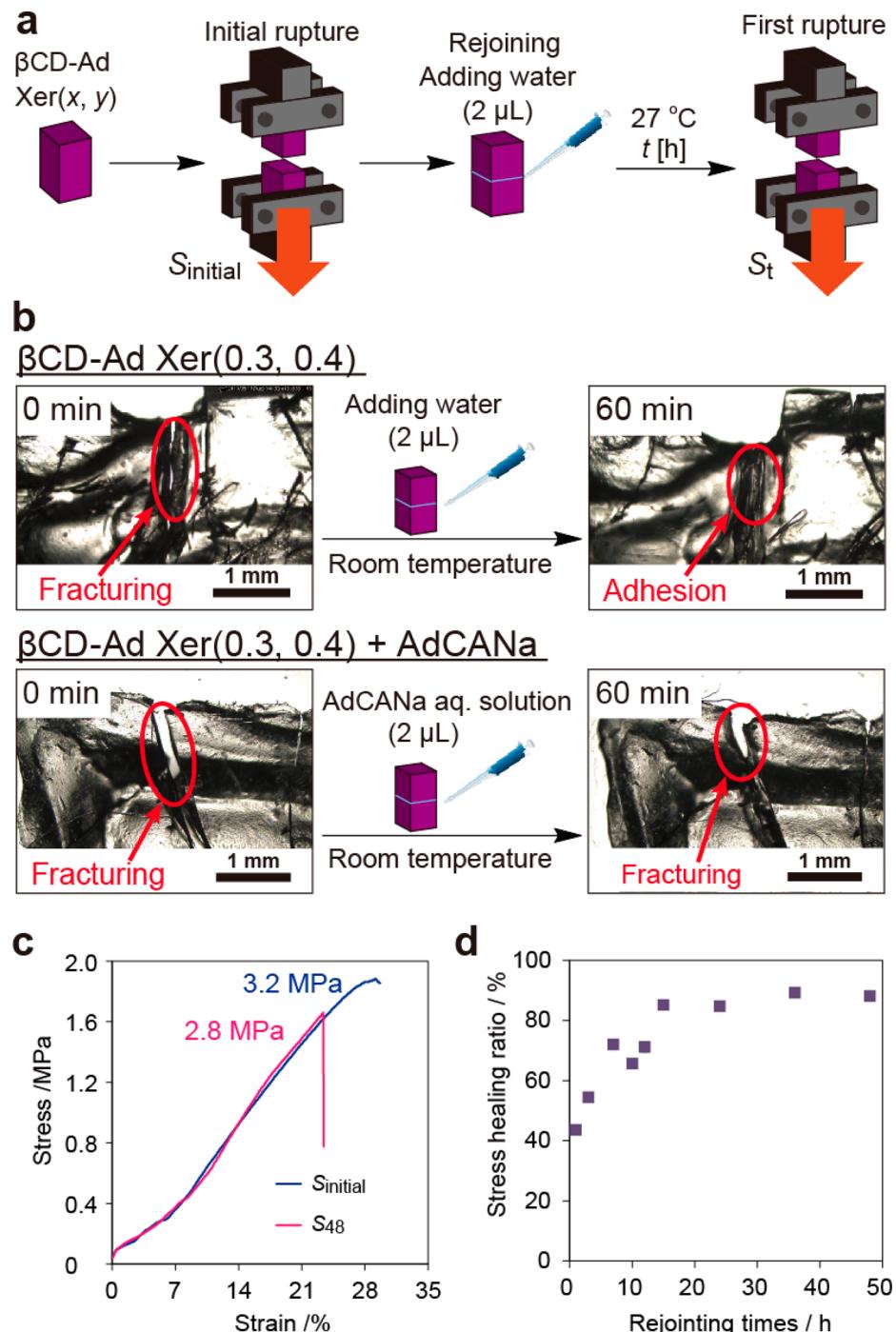


Figure 4. Self-healing property of semihard $\beta\text{CD-Ad Xer}(0.3,0.4)$. (a) Schematic illustration of the tensile test used to measure the rupture stress and stress healing ratio. (b) Microscopic images of the adhesive surfaces. Cut pieces of $\beta\text{CD-Ad Xer}(x,y)$ show an adhesive behavior upon adding water (2 μL). However, adding an aqueous AdCANa solution inhibits adhesion between cut pieces of $\beta\text{CD-Ad Xer}(x,y)$. (c) Stress–strain curves of the initial tensile rupture (blue line: S_{initial}) and the recovery tensile rupture after reattaching for 48 h (pink line: S_{48}). (d) Stress healing ratio as a function of rejoining time.

upon touching each other. These inclusion complexes then pull the polymer chain from the host and guest xerogels to form more inclusion complexes. Thus, each polymer chain intrudes into the interface of the xerogels. Without host or guest moieties, AAm Xer does not show such attractive forces because polyacrylamide gel itself does not have significant intermolecular interactions. In short, host–guest interactions realized discriminative adhesions of semihard materials.

2.4. Self-Healing of Xerogels. We have demonstrated that a xerogel with host moiety and that with guest moiety display adhesive properties. Thus, a new hard self-healing material can be created through host–guest interactions. We have reported $\beta\text{CD-Ad hydrogel}(x,y)$ as soft self-healing material, in which the polymer chains are cross-linked only by forming an inclusion complex between the βCD and Ad units.²⁶ Here, a self-healing xerogels, $\beta\text{CD-Ad Xer}(x,y)$ was obtained by drying $\beta\text{CD-Ad}$

hydrogel(x,y) under the same conditions as β CD Xer(x) (Supporting Information Figure S8).

To investigate the self-healing ratio of β CD-Ad Xer(0.3,0.4) at various rejoining times, the material strength and separating stress were analyzed by tensile tests. Figure 4a shows the procedure for the self-healing experiments of β CD-Ad Xer(x,y). First, the initial tensile rupture stress (S_{initial}) of β CD-Ad Xer(0.3,0.4) (size: $2 \times 2 \times 5 \text{ mm}^3$) was measured by a 0.1 mm/s tensile velocity. After fracturing β CD-Ad Xer(0.3,0.4) to give two pieces, water (2 μL) was dropped onto the fractured surface. The ruptured β CD-Ad Xer(0.3,0.4) was allowed to rejoin for a prescribed time (t [h]). After reattaching the fracture surfaces of β CD-Ad Xer(0.3,0.4) for the prescribed time, the recovery rupture stress (S_t) was determined by the tensile test. The recovery ratio (R_t) was calculated as $R_t = S_t / S_{\text{initial}} \times 100$.

Figure 4b shows images of an adhesion surface as a function of time, where the start time (0 min) is defined as the time when the fracture pieces were rejoined. The optical microscope images confirm a self-healing behavior on the rejoined interfaces of β CD-Ad Xer(0.3,0.4). After 60 min, the gap of the fractured β CD-Ad Xer(0.3,0.4) is spontaneously filled, and picking up the sample with tweezers does not separate the rejoined β CD-Ad Xer(0.3,0.4). In contrast, dropping an aqueous AdCANA solution prevents the fractured surface, β CD-Ad Xer(0.3,0.4), from mending, indicating that the self-healing behavior of β CD-Ad Xer(0.3,0.4) results from the host-guest interactions between the β CD and Ad units.

Figure 4c shows the stress-strain curves of the initial tensile rupture (blue line: S_{initial}) and the recovery tensile rupture after reattaching for 48 h (pink line: S_{48}). Both the stress-strain curves are the same until fracturing. After reattaching for 48 h, the material strength recovers to a recovery stress ratio (R_{48}) = 88%, which was calculated using S_{initial} and S_{48} . Figure 4d shows R_t of the β CD-Ad Xer(0.3,0.4) as a function of time. After an hour, R_t exceeds 40%, which is a relatively fast recovery property. Moreover, R_t increases as the rejoining time increases, and R_{48} = 88%. On the other hand, touching the fractured surface of β CD-Ad Xer(0.3,0.4) with a nonfractured surface does not mend the sample, even if it is allowed to sit for 24 h. Of course, the fracture surface of β CD-Ad Xer(0.3,0.4) has roughness. The free host and guest molecules, which appear due to a rupture on the surface of the β CD-Ad Xer(x,y), play important roles in the self-healing ability on an adhesive interface.

We also investigated the durability of adhesions in β CD-Ad Xer(0.3,0.4) (Supporting Information Figure S9). R_{cm} shows the recovery ratio where m denotes the number of cycles. β CD-Ad Xer(0.3,0.4) shows a high R_{cm} after three cycles ($R_{c1} = 88\%$, $R_{c2} = 72\%$, and $R_{c3} = 60\%$). These results suggest that β CD-Ad Xer(0.3,0.4) has high self-healing properties even in hard materials. After the fourth cycle, the mended β CD-Ad Xer(0.3,0.4) ruptured not at the rejoined surface but at another location. This fracturing may be due to the accumulated load.

3. CONCLUSION

We successfully create self-adhesive materials, which exhibit strong and chemically specific adhesive abilities through host-guest interactions using β -cyclodextrin as a host molecule and adamantane as a guest molecule. The adhesive strength between xerogels containing β -cyclodextrin (β CD Xer(x)) or adamantane (Ad Xer(y)) is greatly influenced by adding competitive molecules as well as the molar ratio of the β CD

and Ad units, suggesting that the host-guest interactions between the β CD and Ad units play an important role in the adhesion between β CD Xer(x) and Ad Xer(y). Although semihard materials generally adhere weakly or not at all, β CD Xer(x) and Ad Xer(y) show robust adhesive strengths by increasing the molecular mobility on the surface with a little water even for materials with a low molecular mobility such as xerogels. Dried solid materials selectively adhered by cyclodextrin-guest complex formations through hydrophobic interactions. The jointed xerogels do not split off even after dried off. In addition, we created a self-healable material via inclusion complexes of β CD and Ad (β CD-Ad Xer(0.3,0.4)), which show a relatively high stress healing ratio (88%) and high adhesive strength (2.8 MPa). These results suggest that the host-guest interaction between β -cyclodextrin and adamantane act as glue on the molecular scale in semihard materials to achieve macroscopic adhesion. We believe that host-guest interactions will provide a new adhesive mechanism for semihard materials.

4. METHODS SECTION

4.1. General Procedures. Acrylamide- β -cyclodextrin (AAm- β CD), acrylamide-adamantine (AAm-Ad), and adamantane carboxylic acid sodium salt (AdCANA) were prepared according to the literature.^{29,39} Dimethyl sulfoxide (DMSO) and the acrylamide monomer were obtained from Wako Pure Chemical Industries, Ltd. β -Cyclodextrin (β CD) was obtained from Junsei Chemical Co., Ltd. *N,N'*-Methylenebis(acrylamide) (MBAAm), ammonium peroxodisulfate (APS), and [2-(dimethylamino)ethyl]dimethylamine (TEMED) were obtained from Nacalai Tesque Inc. DMSO-*d*₆ was obtained from Merck & Co., Inc. Rose Bengal (red dye) and tartrazine (yellow dye) were obtained from Kiriya Chemical Co., Ltd. Water was purified with a Milli-Q system. All reagents were used as received.

4.2. Measurements. The one-dimensional NMR spectra were recorded with a JEOL ECA-500 NMR spectrometer at 30 °C. Chemical shifts were referenced to the solvent value ($\delta = 2.49$ ppm for DMSO-*d*₆). The positive-ion matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) experiments were performed using a Bruker autoflex speed mass spectrometer using 2,5-dihydroxybenzoic acid as a matrix. The mechanical properties of the xerogels were measured using a rupture testing system (creep meter, RE-3300SB, Yamaden Ltd.). GPC was performed in formamide (0.30 mL/min) with 10 mM lithium bromide using a TOSOH GPC-8020 Model II equipped with a TOSOH TSKgel α -M column to determine the molecular weight (M_n). M_n 's of the control samples were measured with respect to polyacrylamide (PAAm) standards (American Polymer Standards Corp.). Adhesion interfaces were measured using a digital inverted microscope (EVOS AME i2111, Advanced Microscopy Group).

4.3. Preparation of Xerogel Materials. β CD hydrogel(x) was prepared by polymerization of AAm- β CD (x mol %), AAm (98 - x mol %), and MBAAm (2 mol %) in water (2 M). After polymerization, the hydrogel material was soaked in DMSO followed by water for 3 days each. β CD xerogel(x) was obtained by cutting (10 × 10 × 15 mm³) samples and drying to remove the absorbed water at rt under atmospheric pressure for 2 days and then at 27 °C in vacuo for a day. Similarly, AAm xerogel was prepared using AAm (98 mol %) and MBAAm (2 mol %) in water (2 M). Ad xerogel(y) was prepared by polymerization of AAm-Ad (y mol %), AAm (98 - y mol %), and MBAAm (2 mol %) in DMSO (2 M). After polymerization, the organogel material was soaked in DMSO followed by water for 3 days each. Ad xerogel(y) was obtained by cutting (10 × 10 × 20 mm³) pieces and drying under the same conditions as the β CD xerogel(x).

4.4. Adhesive Experiments. β CD xerogel(x) and Ad xerogel(y) were adhered by joining the same-size surface area of these xerogels for 24 h after coating with water (2 μL) on the Ad xerogel(y) surface (9 mm²). Other combinations of β CD xerogel(x) and AAm xerogel, Ad

xerogel(*y*) and AAm xerogel, and AAm xerogel and AAm xerogel were also adhered under same conditions as β CD xerogel(*x*) and Ad xerogel(*y*). The adhesive strength was measured using a creep meter at 1 mm/s of the tensile velocity. To measure adhesive surfaces, every combination was touched on the glass plate. Subsequently, 2 μ L of water was added to the surface, and the adhesive behavior was observed by an optical microscope. Competitive experiments used equal amounts of AdCANa aqueous solution (from 1 to 500 mM) and β CD aqueous solution (10 mM).

■ ASSOCIATED CONTENT

§ Supporting Information

^1H NMR spectra, competitive measurements, stress-strain curves, and repeatability. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: harada@chem.sci.osaka-u.ac.jp (A.H.).

Notes

The authors declare no competing financial interest.

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