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Viscoelastic Behaviors for Optimizing Self-Healing of Gels with Host–Guest Inclusion Complexes

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ABSTRACT

This research showed that the self-healing properties of reversible crosslinked gels with host–guest inclusion complexes depended on the mobility of network chains and the recombination behaviors of reversible complexes, which were affected by changes in the water–glycerol solvent composition. The sticky reptation behaviors of the polymer chains were delayed by the recombination behaviors of reversible bonds. These behavioral characteristics were observed based on a dynamic viscoelasticity. Increasing the glycerol concentration in the mixed solvent decreased the surface tension and increased the mobility of the network chains because the recombination of the complex was slowed by the weak hydrophobic interactions between the host and guest molecules. Consequently, self-healing properties, such as re-adhesion at the cutting surface, were improved by the interdiffusion of polymer chains at the reattached interface. The strong hydrophobic interactions in pure water promoted the formation of complexes within the same cutting surface, thus decreasing the self-healing rates of the mechanical properties. In this study, the solvent was found to be an important parameter for controlling the self-healing properties of reversible crosslinked gels. The competition between the mobility of polymer chains and the recombination behaviors of reversible bonds controlled the self-healing properties of the gels with host–guest inclusion complexes.

Introduction

Self-healing is a biologically inspired process that involves the spontaneous repair of a material after it is physically damaged to recover its structure and function. Polymeric materials with self-healing properties have attracted increasing attention in recent years because improvements in the lifetime and recyclability characteristics of these materials can resolve problems related to the recycling of resources and the environmental burden of polymer waste[1-8].

Self-healing occurs because of the recombination behaviors of dynamic and reversible bonds, such as dynamic covalent bonds[9-12], hydrogen bonds[13-17], ionic bonds[18-22], π - π interactions[23-25], van der Waals interactions[26-30], and host-guest inclusion complexes[31-33]. Recent studies have shown that self-healing is dominated by the strengths and lifetimes of reversible bonds and by the mobility of polymer chains. This mobility is determined by the glass transition, entanglement, and crystallinity. The interdiffusion of polymer chains repairs the damaged interfaces and restores the mechanical properties[34]. According to a simulation based on coarse-grained techniques, the recombination behaviors of dynamic bonds can control the mechanical properties and functions of self-healing polymers[35]. The main techniques for improving the self-healing properties of polymers involve promoting the mobility of polymer chains and recombining reversible bonds.

In the field of polymer dynamics, polymers with reversible bonds have long been studied. Stadler et al. reported the terminal relaxation behaviors of polymer chains with associated functional groups from theoretical and experimental perspectives[36]. Subsequently, some researchers have proposed models that describe the relaxation behaviors of polymers with reversible bonds at crosslinking points (called reversible crosslinks or stickers), such as the sticky reptation[37] and sticky Rouse[38] models. Recently, research on self-healing polymers has increasingly been focused on the dynamics of polymers with reversible crosslinks[39-47]. Sokolov et al. demonstrated the viscoelastic properties of polymers with phase-separated dynamic bonds across large time scales[48,49]. These studies have shown that the

recombination behaviors of reversible bonds affect the fluidity of polymer chains. Nevertheless, the understanding of correlations between the self-healing and viscoelastic properties of polymers with reversible crosslinks is limited in mixed systems, such as polymer gels.

Interactions between polymers and solvents control the network structures and physical properties of polymer gels in polymer hydrogels. Changing the solvent composition of a gel affects the aggregation structure[50-53], viscoelasticity[54,55], and thermoresponsiveness[56,57] of a polymer gel. Consequently, we hypothesize that changing the solvent composition affects the dynamics of polymer network chains, the recombination behaviors of host–guest inclusion complexes, and can control the self-healing and viscoelastic properties of reversible crosslinked gels.

In this study, self-healing gels were prepared by introducing host–guest complexes of β -cyclodextrin and adamantane as reversible crosslinks into the side chain of an acrylamide (P(AAm- β CD-Ad) gel) by changing the water–glycerol solvent composition. Changing the solvent composition influenced the mobility of the network chains and the recombination of the host–guest inclusion complex. The effects of the solvent composition on the self-healing and viscoelastic properties were evaluated based on mechanical measurements and dynamic viscoelasticity analyses to understand the correlations among various parameters of the self-healing gels.

Materials and preparation

Acrylamide (AAm), 6-acrylamido- β -cyclodextrin (β CD), and 1-adamantyl acrylamide (Ad) were provided from Yushiro Chemical Industry. Glycerol was purchased from Nacalai Tesque, Inc., and used without further purification. β -Cyclodextrin and 1-adamantanecarboxylic acid were used as model molecules to evaluate the association constant. P(AAm- β CD-Ad) gels were prepared according to a previous report[58] (**Fig. 1a**). The composition of the P(AAm- β CD-Ad) gel is listed in **Table 1**. The contents of the network polymers and solvents were 20 wt% and 80 wt%, respectively. The molar ratio of the monomers AAm, β CD, and Ad in P(AAm- β CD-Ad) was constant at 96:2:2 mol%. The glycerol concentrations in the mixed solvents of water–glycerol (c_g) were varied from 0 wt% to 74 wt%. We obtained transparent samples at all c_g values and confirmed that no phase separation occurred (**Fig. S1**). A viscous sample was obtained at $c_g = 74$ wt%. The mechanical and self-healing properties at $c_g = 74$ wt% were impossible to evaluate by tensile testing. **Fig. 1b** shows schematic images of the network structures of the P(AAm- β CD-Ad) gels with different c_g values. The host–guest inclusion complexes of β CD and Ad were reversible crosslinks between the AAm chains. The network structures of the AAm backbones swelled with mixed solvents of water–glycerol. The hydrophobicity increased with increasing c_g because glycerol was slightly more hydrophobic than water.

(Fig. 1)

(Table 1)

Experimental methods

A tensile test was performed using an Autograph AG-X plus (SHIMADZU Co.) at a strain rate of 0.1 s^{-1} at approximately 25°C . Dynamic mechanical analysis (DMA) was carried out with a DMA system DVA-250 (IT-KEISOKU SEIGYO Co., Ltd.) to measure the dynamic modulus of tensile deformation. The frequency sweep experiments were conducted in the range of angular frequencies of $\omega = 628\text{--}0.314$ rad/s at each temperature during stepwise heating from 273 K to 313 K and a strain of 10%, which was in the linear viscoelastic region. Dynamic viscoelastic measurements were performed using an MCR302e (Anton Paar GmbH) instrument equipped with a parallel-plate fixture with a diameter of 25 mm to measure the shear modulus. The strain was evaluated in the linear viscoelastic regime at a frequency of 10 rad/s. Surface tension was evaluated with pendant drop measurements by using DMe-211FE (Kyowa Interface Science Co., Ltd.). The volume of the sample liquid was 10 μL . Differential scanning calorimetry (DSC) was performed using a DSC 200 (Hitachi High-Tech Co.) instrument with N_2 gas flow (50 mL/min). A 5 mg sample was placed in an aluminum pan. An empty aluminum pan was used as a reference. The thermal properties were measured in the temperature range of 173–303 K by heating and cooling at 10 K/min. Isothermal titration calorimetry (ITC) was conducted to evaluate the association constants of βCD and Ad in a mixture of glycerol and water by using MicroCal PEAQ-ITC (Malvern Panalytical Ltd.). The βCD solution (1 mM, 0.4–2 μL) was added to Ad (0.1 mM, 200 μL) every 2 min.

Results and discussion

1. Effects of the solvent composition on the mechanical properties

The mechanical properties of the P(AAm- β CD-Ad) gels are evaluated based on the stress–strain (S–S) curves obtained by tensile testing (**Fig. S2**). The slope of the tensile stress (σ) at a tensile strain (ε) in the range of 0–5% is defined as the Young’s modulus (E). The elongation at break (ε^*) represents the ε at which the specimens break. The tensile strength (σ_u) is the maximum stress during extension. In this research, all the specimens break at the maximum stress. The toughness (U_T) is represented as the integral of the S–S curves at ε values from 0 to ε^* . The mechanical properties related to the c_g values are shown in **Fig. 2**.

To discuss the dependence of each mechanical property on the solvent composition, we evaluated the association constant (K_a) values of β CD and Ad in mixed solvents (**Figs. S3 and S4**). K_a was correlated with the number of reversible crosslinking points in P(AAm- β CD-Ad) gels because P(AAm- β CD-Ad) gels are designed with the same molar ratio of host to guest molecules regardless of the solvent composition[59]. The K_a values decrease with increasing c_g (**Fig. S5**). The formation of host–guest inclusion complexes should change with the c_g value. Since the hydrophobic interaction between β CD and Ad contributes to complex formation, the surface tension (S) of the mixed solvent was an important parameter for complex formation. The S of the mixed solvent decreases with increasing c_g (**Fig. S6**) because the S value of glycerol (63.4 mN/m at 20 °C) is slightly lower than that of water (72.8 mN/m at 20 °C).

E was constant regardless of the c_g (**Fig. 2a**). The elastic modulus of a polymeric network structure is generally corrected by either the concentration of elastically effective chains or the density of crosslinking points. The dependence of K_a on c_g shows that the number of reversible crosslinking points decreases with increasing c_g , indicating that E decreased with c_g . Conversely, the extension of AAm chains

in water is greater than that in glycerol[60,61]. In this research, the polymer concentrations in the gels were fixed at 20 wt%, which is considerably greater than the entanglement concentration. The spreading chains in water form additional entanglements and improve E . E was affected by a decrease in the number of crosslinking points and an increase in the level of entanglement. Incidentally, the increase in E with increasing c_g is similar to the relationship between the viscosity and glycerol content of a mixed water–glycerol solvent[62].

ε^* increased linearly with increasing c_g (**Fig. 2b**). The number of reversible crosslinking points decreases with increasing K_a , and the length of the strand between two crosslinking points increases, resulting in an increase in the elongation at break (ε^*) with increasing c_g . Additionally, the AAm chains in water are more dispersed than those in glycerol, and the hydrodynamic radius of poly(AAm) decreases linearly with increasing the glycerol concentration(**Fig. S7**)[60]. Consequently, the network chains of the P(AAm- β CD-Ad) gels are tight in water. Stretching strains the network chains, and P(AAm- β CD-Ad) gels break at a low ε value. In contrast, at high c_g values, AAm chains shrink compared to the chains in water and can reform the network structure with elongation. Hence, P(AAm- β CD-Ad) gels with high c_g values exhibited high ε^* values.

The σ_u value was the highest at $c_g = 0$ wt% and decreased with increasing c_g . Recombining the crosslinking points increased σ_u because the network structure remains the same after undergoing a large deformation. The P(AAm- β CD-Ad) gel had a much greater σ_u than the chemically crosslinked gels (**Figs. S8 and S9**). A decrease in σ_u with an increase in the c_g value suggests that the recombination behaviors of host–guest inclusion complexes during deformation differ according to the solvent composition. The recombination of the complex slowed with increasing c_g because a decrease in the surface tension reduced the K_a value.

U_T exhibited the same trend of a decrease in σ_u with an increase in c_g . The similarity between U_T and σ_u shows that σ_u is the primary factor influencing the U_T values of the gels and that the reversible crosslinking network improved the toughnesses of the polymeric materials.

(Fig. 2)

2. Readhesion on the cutting surface

The self-healing properties of the readhered gels were evaluated by the healing ratio of toughness. The readhered gels were prepared by cutting the gels, reattaching them to the cutting surface, and allowing them to stand for 24 h while preventing solvent evaporation (**Fig. 3a**). The healing ratio of toughness ($H_{\text{toughness}}$) can be defined as follows:

$$H_{\text{toughness}} = \frac{U_T \text{ of readhered}}{U_T \text{ of original}} \quad (1)$$

The U_T values of the readhered and original gels represent their toughnesses before cutting and after readhering, respectively. **Figs. 3b** and **3c** show snapshots of **Movie S1**, in which the tensile tests of the original and readhered gels were filmed. **Fig. 3d** shows the S–S curves of the original and readhered gels at $c_g = 0$ wt% and 46 wt%. The S–S curves of the original and readhered gels at $c_g = 46$ wt% almost overlapped, and the gels were healed. At $c_g = 0$ wt%, the increase in σ at the initial elongation was consistent, but the readhered gel broke at a significantly smaller ε than the original gel. **Fig. 3e** shows the dependence of $H_{\text{toughness}}$ on the c_g value. $H_{\text{toughness}}$ increased with increasing the c_g value.

The self-healing properties of polymer materials are improved by increasing the healing temperature because the segmental and chain dynamics are relatively fast, and the reversible bonds can be rearranged[14]. Controlling these dynamics is important for self-healing. Moreover, the self-healing

properties of the P(AAm- β CD-Ad) gels were affected by the solvent composition. $H_{\text{toughness}}$ depended on c_g . To confirm the mobility of the network chains and the recombination behaviors of the complexes, we measured the viscoelastic properties of the P(AAm- β CD-Ad) gels.

(Fig. 3)

3. Mobility of network chains

The exponent of the dependence of the frequency (ω) on the elastic modulus characterizes the dynamics of a polymer. The terminal flow region of a linear polymer is generally characterized by the dependence of the storage modulus on ω^2 and the dependence of the loss modulus on ω . Polymers with reversible bonds, such as host–guest inclusion complexes, exhibit characteristic viscoelastic behaviors in the flow region[36-38]. This process can be modeled by the sticky reptation or sticky Rouse models, and it occurs because the recombination behaviors of reversible bonds prevent the flowing of the main chain. We measured the frequency dependence of the viscoelasticity of P(AAm- β CD-Ad) gels to elucidate the relationships among their self-healing and viscoelastic properties.

Fig. 4a shows the angular frequency dependences of the storage (E') and loss (E'') moduli of the tensile deformation of the P(AAm- β CD-Ad) gels. The E' and E'' curves at a given temperature were superimposed to construct master curves by following the time–temperature superposition (TTS) principle (**Fig. S10**). Each modulus was both horizontally and vertically shifted by using the time (a_T) and modulus (b_T) shift factors. The reference temperature is 303 K (**Table S1** and **Fig. S11**). DSC measurements confirmed that no transition was observed in the measured temperature range of DMA (**Fig. S12**). However, the TTS principle failed for the gels with low c_g values. The presence of several relaxation events with different relaxation times leads to the failure of the TTS principle at low c_g .

E' was greater than E'' within the measurement frequency range, indicating that the samples are elastic gels. The moduli of gels with $c_g = 0$ wt% and 23 wt% were characterized by $E' \sim E'' \sim \omega^n$, which represent gels with rheological characteristics determined based on the Winter–Chambon criterion[63]. The scaling exponents (n) at $c_g = 0$ wt% and 23 wt% are 0.15 and 0.24, respectively. The dissociated host and guest molecules immediately reform another inclusion complex at low c_g values. The reversible crosslinks behaved like permanent crosslinks over large time scales, resulting in gels with low c_g values

following the Winter–Chambon criterion. We observed a rubbery plateau region that arises due to the presence of entanglements and crosslinks, but the terminal flow region could not be observed at $c_g = 0$ wt% or 23 wt%. The gels with $c_g = 46$ wt%, 60 wt%, and 74 wt% showed plateau region and relaxation behaviors according to the sticky Rouse model. Therefore, we clearly confirmed the occurrence of relaxation from the peak of the loss tangent ($\tan \delta$) at approximately $\omega = 0.5\sim 1.5$ s⁻¹, as shown in **Fig. 4b**. The n values in the flow region at $c_g = 46$ wt%, 60 wt%, and 74 wt% were 0.36, 0.37, and 0.40, respectively. Similar behavior to that of the sticky Rouse model occurred as c_g increased because the recombination behaviors of reversible crosslinks was suppressed and did not delay the flow of polymer chains.

The relaxation time (τ_r) values for the mobility of network chains of P(AAm- β CD-Ad) gels was determined from the inverse frequencies at the maximum E'' value. τ_r is considered the shortest relaxation time for the main chain, whose flow is suppressed by the recombination behaviors of host–guest inclusion complexes. For gels with $c_g = 0$ wt% and 23 wt%, τ_r cannot be estimated from **Fig. 4a** because the recombination behaviors of host–guest inclusion complexes accelerated by hydrophobic interactions reduced the mobility of the network chain to a location outside the frequency window considered in this research. The dependence of τ_r on c_g is shown in **Fig. 4c**. Increasing the c_g decreased the τ_r . A large τ_r indicates that the mobility of network chains is low. τ_r should be very large at $c_g = 0$ wt% and 23 wt%. The gels with high c_g values had shorter τ_r values and greater network chain mobilities. Specifically, the recombination behaviors of host–guest inclusion complexes were not active due to the K_a value being low. After dissociation by deformation, it is difficult for the host and guest molecules to form complexes with weak hydrophobic interactions in the high- c_g solvent. The dependence of a_T deviated from the Arrhenius dependence owing to the presence of several relaxation events with different relaxation times or activation energies and because of the failure of the TTS principle (**Fig. S11**). A comparison of $H_{\text{toughness}}$ and τ_r suggests that the high mobility of network chains improves the self-healing properties (**Table S2**). We

consider that the high mobility of the network chain promotes the interdiffusion of network chains and the reformation of the complex at the reattached gel interface.

(Fig. 4)

4. Dynamics of complex recombination

To clarify the details of the recombination behaviors of host–guest inclusion complexes in P(AAm- β CD-Ad) gels, we measured the relaxation modulus when applying a certain shear strain (γ).

We measured the shear storage modulus (G') when a nonlinear γ (= 100%) was applied to the gels. The nonlinear γ was determined from the strain sweep measurements (**Fig. S13**). When nonlinear γ was applied to the gels, G' decrease because the network structure was broken. Then, the G' values were either constant or slowly decreased due to the reconstruction of the network structure resulting from the recombination behaviors of the reversible crosslinking points and unraveling behaviors of the entanglements (**Fig. 5a**). The relaxation behavior depended on the solvent compositions.

The recombination behaviors of the host–guest inclusion complexes was evaluated from the relaxation time (τ_e) when the relaxation modulus $G'(t)$ is 1/e of $G'(t_0)$. The relaxation behavior depended on the solvent composition, and the relaxation rate decreased as c_g increased. The dependence of τ_e on the c_g value is shown in **Fig. 5b**. τ_e decreased with increasing c_g above 23 wt%, which is similar to the trend of τ_r in relation to c_g , as shown in **Fig. 4c**. The low τ_r indicated that the recombination behaviors of the complexes were not active due to the K_a values being low. After dissociation by deformation, it is difficult for the host and guest molecules to form complexes with weak hydrophobic interactions in the high- c_g solvent. The S values of the solvents evaluated by the pendant drop method monotonically decreased with increasing c_g . A decrease in S (**Fig. S6**) reduces the hydrophobic interactions between β CD and Ad. In addition, the recombination rates of host–guest inclusion complexes decreased with increasing c_g .

(Fig. 5)

5. Influence of solvent composition on self-healing properties

We discuss the influences of the solvent composition on self-healing properties, such as readhesion at the gel cutting surface, in relation to the mobility of network chains and the dynamics of complex recombination processes. The low- c_g gels had relatively fast recombination rates for their host–guest inclusion complexes. Hence, the host and guest molecules reformed complexes within the same cutting surface. Then, the numbers of free host and guest molecules decreased at the cutting surface. Complex formation did not proceed between the other cutting surfaces, resulting in a decrease in $H_{\text{toughness}}$. In contrast, the relatively low recombination rates of the complexes of the high- c_g gels suppressed the reformation of the complexes within the same cutting surface. In addition, the high mobility of network chains at high c_g promoted polymer chain interdiffusion at the reattached gel interface and improved $H_{\text{toughness}}$. Nonselective repair of the cutting surfaces for the gel at $c_g = 46$ wt% suggests that the interfacial diffusion of polymer chains contributes to the high healing ratio (**Fig. S14**).

Improvements in self-healing properties require the repair of chemical and physical structures at the damaged interface. Chemical repair involves the reformation of reversible bonds. Physical repair involves the interdiffusion of polymers. We demonstrated that the self-healing of the gel can be enhanced by promoting the repair of the physical structure at the interface. This interface can be repaired by controlling the viscoelastic behavior with the solvent composition. In addition, the solvent composition controls the self-healing properties of the gels by changing the viscosity and surface tension of the solvent.

Conclusion

We demonstrated correlations between the self-healing and viscoelastic properties of reversible crosslinked gels with host–guest inclusion complexes based on the water–glycerol solvent composition. The $H_{\text{toughness}}$ and τ_r values were correlated, indicating that the self-healing properties improved as the mobility of the network chains increased (i.e., as τ_r decreased).

Increasing the glycerol concentration in the mixed solvents decreased the surface tension of the solvents and the association constants of the host–guest inclusion complexes, thereby degrading the recombination behaviors of the complexes because the hydrophobic interactions of the host–guest inclusion complexes weakened. The mobility characteristics of network chains in the gels abided by the sticky Rouse model and increased with increasing glycerol concentration. The high mobility of network chains enhanced polymer chain interdiffusion at the reattached interface, improving the self-healing properties through readhesion at the cutting surface. When the recombination rate of the host–guest inclusion complex was high, complex formation proceeded on the same cutting surface, and gel readhesion decreased.

According to this research, solvent characteristics, such as surface tension and viscosity, were considered important parameters for controlling the self-healing properties of reversible crosslinked gels. The competitive effects of the mobility of polymer chains and the recombination behaviors of reversible bonds controlled the self-healing properties of gels with host–guest inclusion complexes.

ASSOCIATED CONTENT

Supporting information

Photographs, stress–strain curves, dynamic viscoelasticity, relaxation modulus, and thermal properties of P(Aam- β CD-Ad). Mechanical properties of the chemical crosslinked gels. Surface tension values of the solvents. Hydrodynamic radius of polyacrylamide. Movie of a tensile test for the evaluation of self-healing properties. Association constants of β CD and Ad in the mixture solvent.

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Figure legends

Fig. 1. (a) Chemical structures and molecular models of P(AAm- β CD-Ad) gels (**1**), glycerol (**2**), and water (**3**). (b) Schematic images of P(AAm- β CD-Ad) gels with different glycerol concentrations (c_g).

Fig. 2. (a) Young's modulus (E), (b) elongation at break (ϵ^*), (c) tensile strength (σ_u), and (d) toughness (U_T) values of P(AAm- β CD-Ad) gels depending on the glycerol concentration in the mixture solvent (c_g).

Fig. 3. (a) Preparation processes of the readhered gels. Snapshots of the tensile tests of the original and readhered gels at $c_g =$ (b) 0 wt% and (c) 46 wt% (**Movie S1**). (d) Stress-strain curves of P(AAm- β CD-Ad) gels with glycerol concentrations (c_g) of 0 wt% (blue) and 46 wt% (green). The solid and dotted lines represent the original and readhered gels, respectively. (e) Healing ratio of toughness ($H_{\text{toughness}}$) that depends on c_g .

Fig. 4. Angular frequency dependences of the (a) storage ($b_T E'$) and loss ($b_T E''$) moduli of P(AAm- β CD-Ad) gels. Each spectrum is vertically shifted to avoid data overlapping. (b) Angular frequency dependences of $\tan \delta$ of the P(AAm- β CD-Ad) gels. (c) Relaxation time (τ) as a function of the glycerol concentration in each mixed solvent (c_g). The black dashed line is a visual guide.

Fig. 5. (a) Relaxation modulus at $\gamma = 100\%$. Dotted line: $1/e (= 0.367)$. (b) Dependence of the relaxation time (τ_c) on c_g estimated from the dotted line in (a).

Table 1. Weights of the polymer, water, and glycerol in the P(AAm- β CD-Ad) gels and the glycerol concentration in each solvent (c_g).

Polymer [wt%]	Water [wt%]	Glycerol [wt%]	c_g [wt%]
20	80	0	0
20	61	19	23
20	43	37	46
20	32	48	60
20	21	59	74