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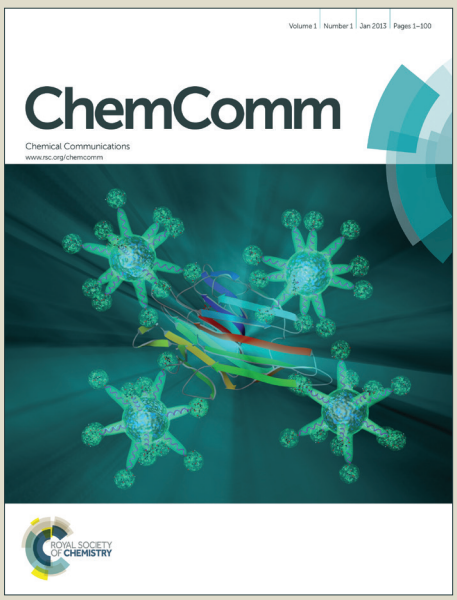

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Control of rheological properties of clay nanosheet hydrogel with guanidinium-attached calix[4]arene binder

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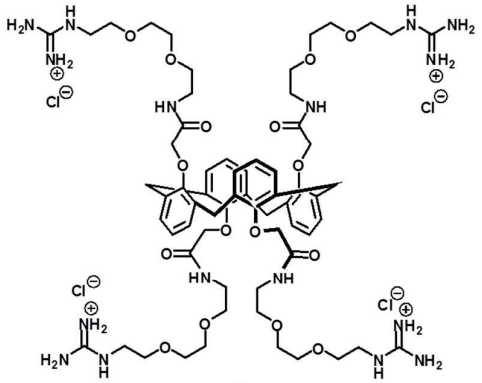
The 1,3-alterate calix[4]arene derivative 1 possessing four guanidinium moieties was synthesized as a molecular binder. The clay nanosheet (CNS) hydrogels were prepared upon addition of 1 and sodium polyacrylate (ASSP), and their mechanical properties were measured by rheometry. The CNS hydrogels prepared by combining calix[4]arene 1 with dispersed CNS surrounded with ASSP showed an enhancement of mechanical properties such as viscosity and elasticity.

Hydrogels have attracted much attention as environmentally friendly renewable soft-materials.[1-7]Hydrogels can be broadly classified into two categories depending on whether the crosslinked gel network that accommodates water molecules is formed with covalent bonds or by noncovalent processes. Hydrogels formed of covalently crosslinked networks are mostly brittle and opaque due to structural heterogeneity; gelation is not reversible by heating. These types of hydrogels are also called 'permanent' or 'chemical' gels.[8-9] In contrast, nanocomposite hydrogels formed by noncovalent forces may be defined as crosslinked polymer networks swollen with water in the presence of nanostructures. The physical crosslinking is noncovalent in nature, often the result of hydrogen bonding, hydrophobic forces, and ionic interactions; these gels are termed 'physical' gels.[10-12] The crosslinked polymer networks are capable of reversible volume changes in response to external stimuli.[13] For example, xerogel prepared by external stimuli such as dry or heating can recover the same volume by soaking water. Additives such as nanomaterials and molecular binders can be used to either crosslink the hydrogel, to adsorb or attach to polymer chains, or to add new properties to the hydrogel by entrapment of the additives within the hydrogel network. In particular, the presence of additives in the polymer hydrogels can generate unique physical properties including mechanical responsiveness,[2, 14,15] the ability to act as a physical barrier, and also can influence optical, thermal, sound, magnetic, and electrical characteristics. These unique properties have led to the application of these materials in sectors such as electronics, optics, sensors, actuators and microfluidics as well as in catalysis, separation devices, drug delivery and many other biotechnological areas.[16-20]

Very recently, Aida and co-workers reported the enhancement of mechanical properties of clay nanosheet (CNS) hydrogels upon the addition of dendritic molecular binders and small amounts of acrylic sodium salt polymer (ASSP).[24-29] Although several groups have demonstrated the control of the mechanical properties of hydrogels by additives,[24-29] the development of simple molecular binders remains important for the improvement and control of the mechanical properties of supramolecular hydrogels. Thus, we selected a 1,3-alternate calix[4]arene derivative as a molecular binder, because its molecular shape is similar to that of low dimensional dendritic molecules and because of its easy synthesis. Furthermore, calix[4]arene derivatives composed of four benzene groups could act as excellent rigid intercalators. Thus, we report here a 1,3-alternated calix[4]arene derivative having four guanidinium groups as a molecular binder for crosslinking CNS



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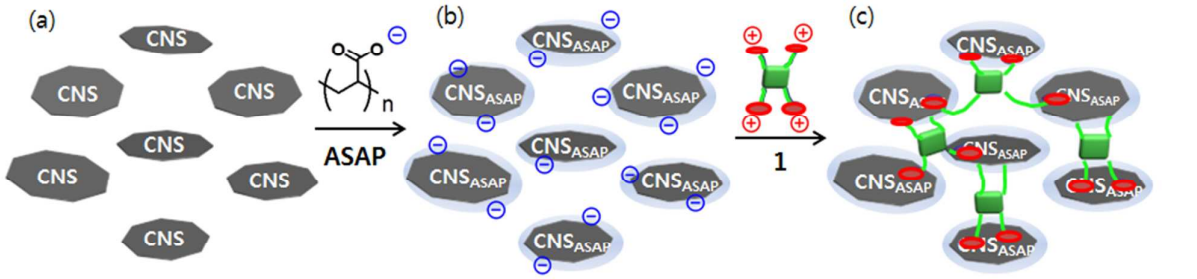
with ASSP in water to afford supramolecular hydrogels. New binder **1** possesses two guanidinium groups at the upper and lower sides to the electrostatic interaction between CNS and binder. Addition of the binder **1** in the hydrogel resulted in enhancement of the elastic properties mediated by noncovalent bonding.

Calix[4]arene-based binder (**1**) was synthesized according to the following steps in multigram quantities: The starting compound **2** was prepared according to a modified literature procedure.[30] Compound **3** was treated with $AlCl_3$ in DCM/toluene to remove the tert-butyl group. Compound **4** was reacted with ethyl 2-bromoacetate in the presence of Cs_2CO_3 to obtain compound **5** in acetone. Then, to introduce guanidinium moieties, compound **5** and compound **8**, synthesized from diamine, were coupled in a reaction using toluene and methylene chloride to produce desired ligand **1** in 70% yield, as confirmed by ^1H, ^{13}C NMR, mass spectroscopy and elemental analysis.

The formation mechanism of CNS hydrogels in the presence of ASSP and binder **1** represented in Scheme 1. ASSP has anion charge. When ASSP is add in CNS solution, anion type of ASSP is surround onto the surface of clay nanosheet (CNS). Then, cationic type of binder **1** is effectively binds to the anionic CNS by electrostatic interaction, which improves the mechanical properties of CNS hydrogel.

We prepared CNS hydrogels in the presence of molecular binder **1** and ASSP under various conditions. The typical progress of a reaction is shown in Scheme 1. To a stirred aqueous suspension (2.4 mL) of CNS (60 mg) was added an aqueous solution (0.6 mL) of ASSP (DP = 22000–70000, 0.3-0.7 wt%) at 20 °C. To this aqueous dispersion of CNS was added an aqueous dilute solution (0.15 mL) of **1** (3-5 wt%) or ASSP (0.3-0.7 wt%) with vortex stirring. After the addition of **1**, the mixture was allowed to stand without stirring at 20 °C. In 10 min, the mixture lost its fluidity. As this solid mixture was allowed to stand further, water was expelled due to completion of the network formation. A mixture of CNS and ASSP formed mechanically weak translucent hydrogel (Fig. S1). In contrast, the mechanically weak hydrogel obtained from a mixed CNS and ASSP became to mechanically strong transparent hydrogel upon addition of binder **1** (Fig. S2).

We observed the morphological influence of CNS hydrogels formed with amounts of ASSP ranging from 0.3-0.7 wt% on the binding with **1** (3.0-5.0 wt%) by scanning electron microscopy (SEM). As shown in Fig. 1, CNS hydrogels prepared at different concentration of ASSP in the presence of **1** showed honeycomb-like structures at low magnification. These honeycombs consisted of fibrous structures with diameters of 200-500 nm (Fig. S3). However, the morphologies of CNS gels prepared with different concentrations of ASSP seem to be the



Scheme 1. Schematic representation for hydrogelation by mixing CNS_{ASSP} and molecular binder **1**: (a) CNSs, (b) CNSs dispersed with ASSP and (c) CNS_{ASSP} with binder **1**.

honeycombs-like structures with fibrous structures, but different pore size.

We also varied the concentration of ASSP in CNS hydrogels and systematically measured the rheological properties. All hydrogels were allowed to stand at 20 °C for 50 h, in order for their cross-linked gel networks to develop completely. As shown in Fig. 2A, the rheological properties of CNS hydrogels with different concentrations of ASSP in the absence of **1**, upon strain sweep at $\omega = 6.28$ rad s^{-1}, showed that the storage (G') value was larger than the loss modulus (G'') value when γ (G''/G' ratio). was smaller than 136% (Fig. 2A;a). In contrast, when γ exceeded 1000%, the G' value decreased more than the G'' value (G''/G': ~0.06 → ~5.7), indicating a breakdown of the gel network. It is worth noting that the G'' value increased as γ changed from 10% to 100% and then declined at γ > 100%. This tendency suggested that sliding of cross-linked CNSs preceded this breakdown event.[27,28,31] In addition, increasing the concentration of ASSP in CNS hydrogels enhanced G' values. From the results of Figs. 2A;b and 2A;c, in a comparison with the hydrogel prepared with 0.3 wt% of ASSP, the G' value of the CNS hydrogel prepared with 0.7wt% of ASSP decreased at a lower γ value than that of a hydrogel obtained with a lower concentration of ASSP (Fig. 2A;d). These findings indicate that the network strength of the CNS hydrogel prepared with high concentration of ASSP was relatively weaker than that of a hydrogel polymerized with a lower concentration of ASSP. The G' value of the CNS hydrogel prepared was enhanced by increasing concentration of ASSP without **1** (Fig. S4), because

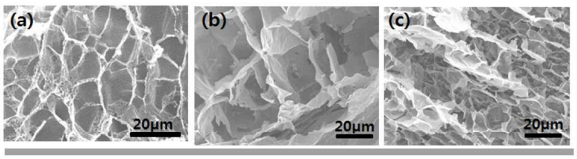


Fig. 1 SEM images of hydrogels of CNS (60 mg) with different concentrations ASSP (a) 0.3 wt%, (b) 0.5 wt% and (c) 0.7 wt% in the presence of binder **1**.

upon addition of high concentration of ASSP maybe suppressed the motion of CNS molecules in hydrogel state.

Furthermore, we observed the rheological properties of CNS hydrogels in the presence of molecular binder **1** and ASSP (Fig. 2B). In compared to Fig. 2A, the addition of 3 wt% of **1** in CNS hydrogels induced the 4~10 fold enhancements of G′ and G″ values (Fig. 2B), which may be attributed to electrostatic interaction between **1** and ASSP. In particular, the G′ value of the CNS hydrogel prepared with 0.7wt% of ASSP in the presence of **1** (3.0 wt%) was highest than those of hydrogels with 0.3 wt% and 0.5 wt% of ASSP (Fig. 2B;d), which was attributed to strongest interaction between anionic type CNS surrounded with ASSP and cationic type **1**. Once again, the enhancement of G′ values of CNS gels upon addition of binder **1** is due to stronger interaction between negative charge of CNS gel prepared with ASSP and positive charge of binder **1**. As shown in Fig. S5, γ value of CNS hydrogels did not strong dependent on the concentration of ASSP in the presence of **1** in compared to Fig. 2A;d.

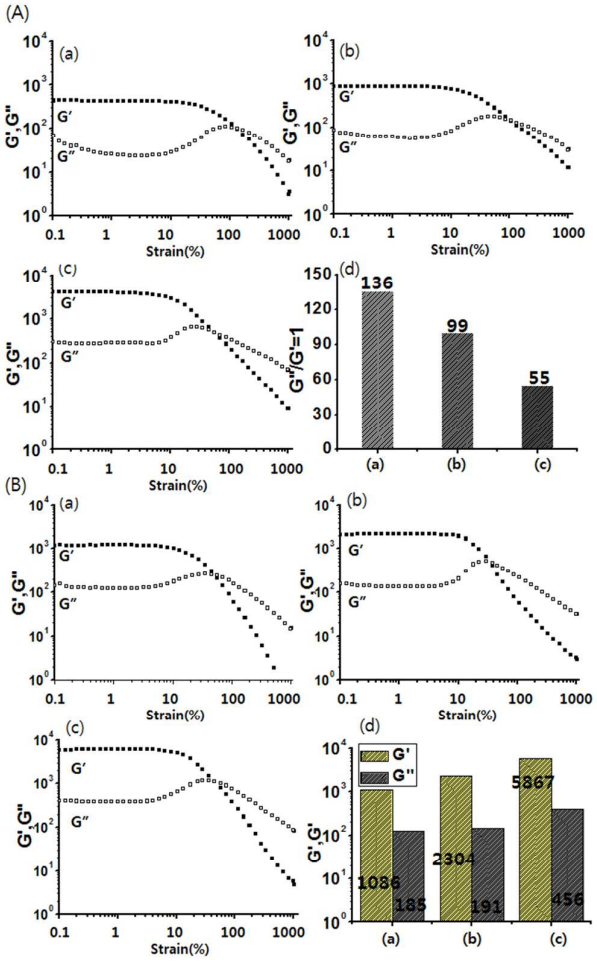


Fig. 2 (A) Rheology property of hydrogels with different concentrations of CNS (60 mg) with ASSP (a) 0.3 wt%, (b) 0.5 wt% and (c) 0.7 wt% in the absence of **1**. (d) Graph of γ values at G″/G′=1 in figure 2A (a-c). (B) Rheology property of (A) hydrogels with different concentrations of CNS (60 mg) with ASSP (a) 0.3 wt%, (b) 0.5 wt% and (c) 0.7 wt% in the presence of **1** (3.0wt%). (d) Graph of G′ and G″ at γ =0.1% in figure 2B (a-c). These data were average values by measurement with 3 times.

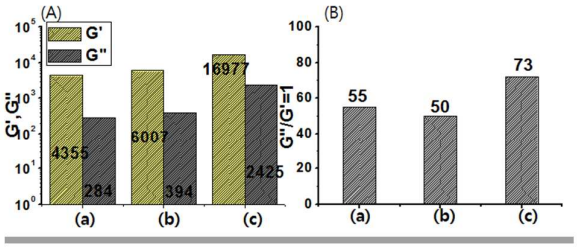


Fig. 3 (A) The graphs of G′ and G″ at γ =0.1% value of CNS gels with **1** (a: 0 wt%, b: 3.0 wt% and c: 5.0 wt%). (B) Graph of γ values at G″/G′=1 of CNS gels with **1** (a: 0 wt%, b: 3.0 wt% and c: 5.0 wt%). These data were average values by measurement with 3 times.

The continuous step strains of CNS hydrogels prepared with different concentrations of **1** were observed at γ=0.1 and 100%, respectively (Figs. 3 and S6). G′ and G″ values of CNS hydrogel with 5wt% of **1** were 2-3 fold higher than that obtained with gel prepared with 3 wt% of **1** (Fig. 3A). Furthermore, the G′ values of CNS hydrogels prepared with different concentrations of **1** dropped at different γ values (Fig. 3B), suggesting that the concentration of **1** had a strong influence on the breakdown of the gel network.

A gel-to-quasi liquid transition showed reversibility, where G′ and G″ values were recovered quickly within 30 s when γ was reduced from 100% to 0.1%. Thus, the CNS gel allows such a rapid thixotropic response (Fig. S7). The recovery process involves regeneration of the gel network.[27] In particular, unlikely a CNS hydrogel prepared with 3 wt% of **1**, the G′ value of a CNS hydrogel prepared with 5 wt% of **1** at γ=100% is the same as the G″ value. The results indicate that the electrostatic interaction between ASSP and **1** in a CNS hydrogel prepared with 5 wt% of **1** was higher than that of a gel with 3 wt% of **1**. The strong gel network interaction led to a gel-to-sol transition at a high γ value.[27,28]

The rheological properties of CNS hydrogels with ASSP (0.7 wt%) and **1** (5.0 wt%) were measured at different pH values (Fig. S8). Among the values of pH=3, 7 and 11, G′ and G″ values of the CNS hydrogel prepared at pH =7 were higher than those of pH=3 and 11. The lowest G′ and G″ values were obtained at acidic condition, suggesting that the acidic proton was bound to the anionic form of ASSP instead of to the cationic type of **1** at pH=3. In contrast, under basic conditions, the lower G′ and G″ values of CNS hydrogels, in comparison to those at neutral conditions, could be attributed due to that to the anionic basic species preventing the electrostatic interactions between ASSP and **1**.

We also measured the influence of the addition of different concentrations of Na^+ ion on the rheological properties of CNS hydrogels (Fig. S9), because Na^+ ion can bind to oxygen or

nitrogen atoms of **1** by coordination bonds. However, Na^+ ion had no essential influence on the mechanical gel properties.

The morphological changes of CNS hydrogels prepared at different pH values were observed by SEM (Figs. S10). As observed at neutral condition, the SEM images of CNS hydrogels at pH 3 and 11 seems to plate-like structures (Fig. S11). These results suggest that the changes in the mechanical properties of CNS hydrogels are slightly influenced the morphological structures.

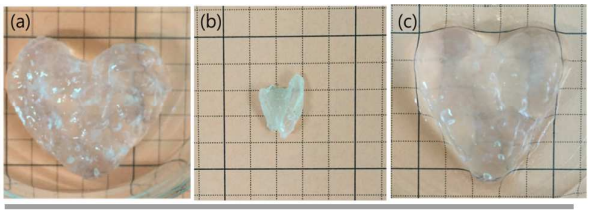


Fig. 4 Shape memory profiles of hydrogel; (a) original CNS hydrogel, (b) dried xerogel and (c) hydrogel by re-swelling in water for 1 hr at 25 °C.

We also observed the swelling effect of CNS hydrogels. As shown in Fig. 4, we removed the water from the CNS hydrogel prepared at pH=7 by freeze drying it under vacuum, whereby we obtained a translucent, shrunken structure. The freeze dried xerogel was then soaked in water at 25 °C for 1 hr. The xerogel swelled and recovered its heart shape and the dimension of the original hydrogel within 1 hr. The swelling volume of the xerogels could be reproduced multiple times.

Conclusions

In conclusion, we have demonstrated that a water soluble 1,3-alterate calix[4]arene derivative acts as an adhesive binder to improve hydrogel mechanical properties. The CNS hydrogels prepared by combining calix[4]arene **1** with dispersed CNS also showed attractive properties. Furthermore, the mechanical properties of hydrogels could be controlled by the addition of ASSP and calix[4]arene-based binder **1**. In particular, the macroscopic shape memory of the gel network without any pre-treatment by drying and re-swelling was also significant. These CNS hydrogels with high water content and with promising mechanical properties can offer materials that should find various uses in environmental and biomedical applications.

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Graphical abstract