

Supramolecular approach to novel composite hydrogels reinforced by inorganic/organic 2D-nanosheets

(無機・有機二次元ナノシートよりなる新規複合ヒドロゲルの開発に向けた超分子のアプローチ)

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Introduction

Hydrogels, which consist of crosslinked network structure and large amounts of water, have received greater attention from a standpoint of their biocompatibility and environmental sustainability. Traditional polymer hydrogels are usually prepared by *in-situ* polymerization of aqueous mixtures of acryl monomers and crosslinking agents.^{1a} However, their poor mechanical strength and low possibility of further functionalization have limited practical applications of hydrogels.

As one of the most promising and seminal approaches, nanocomposite hydrogels, based on the hybridization of organic polymers and two-dimensional (2D) nanosheets, have emerged in the last decade. Recent progress in nano sciences has made various types of 2D nanosheets available, such as clay, metal oxides, metal hydroxides, and grapheme derivatives. When such 2D nanosheets are embedded in polymeric networks that hold hydrogels, they are expected to offer unique structures and functions, considering the following aspects: (i) Owing to characteristic high specific surface area, 2D nanosheets can efficiently interact with polymer chains at multiple sites, thereby mechanical properties. (ii) Because of their anisotropic susceptibility to external fields, 2D nanosheets can be oriented in the fields, allowing for the formation of anisotropically ordered hydrogels. (iii) Some 2D nanosheets intrinsically possess optoelectronic functions, which should be reflected on the properties of the resultant hydrogels.

Here in this philosophy doctoral (Ph.D.) thesis, the author describes a supramolecular approach for developing novel composite hydrogels reinforced by inorganic/organic -nanosheets. In Chapter 1, high-water-content 2D-inorganic clay nanosheet reinforced composite hydrogels with the mechanical and swelling properties tuning by multiple supramolecular interactions has been discussed. In Chapter 2, the graphene oxide nanosheet reinforced composite hydrogels with stable macroscopic alignment induced by magnetic field has been described. Throughout this thesis, new strategies towards development of highly functionalized hydrogel materials will be described.

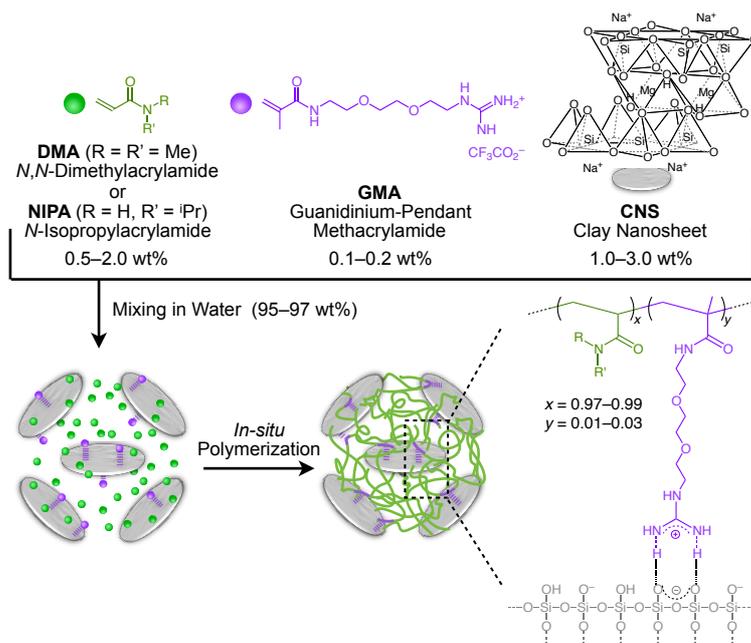
[Chapter 1] Mechanically tough, high-water-content clay-nanocomposite hydrogels based on multivalent salt-pair interactions

For practical application of hydrogels as soft materials mimicking biological tissues, a long-standing problem is how to increase their mechanical strength with maintaining high water-content. To address this issue, some pioneering works have succeeded in realizing excellent mechanical properties, by elaborating polymer networks that hold hydrogels. However, these hydrogels usually contain relatively large amount of organic component (*ca.* 10 wt%), which is not ideal in terms of environmental loading and biocompatibility. Therefore, it still remains a challenge to develop new hydrogels, which cope with high-mechanical strength and high water-content at the same time.

In 2002, Haraguchi *et al.* reported the creation of “nanocomposite hydrogel” with a unique organic–inorganic network structure and exhibited extraordinary mechanical, optical, swelling/de-swelling properties by using the inorganic clay nanosheet to act as multipoint crosslinkers which could simultaneously overcome the limitations of conventional hydrogels.^{1b}

More recently, we reported another class of hydrogels with extraordinary high water content (95–98 wt%), formed by the supramolecular interaction of inorganic clay nanosheet (2–5 wt%) with a dendritic macromolecule (<1 wt%).^{1c} In this system, crosslinked network is developed via the multiple noncovalent interactions between the oxyanionic surface groups of clay nanosheets with the guanidinium groups at the termini of the dendritic macromolecules. Although individual ion-pair interactions were weak and reversible, a cooperative effect significantly enhanced the kinetic and thermodynamic stability of the overall association.

These pioneering works on clay-nanocomposite hydrogels prompted the author to create a similar network by using *in-situ* generated poly(acrylamide)s in place of dendritic macromolecules. If a monomer bearing a guanidinium cation is copolymerized with conventional neutral monomers, the guanidinium cations incorporated in the resultant polymer chains should serve as adhesive units to reinforce the interactions between the polymer chains and the nanosheet surfaces (**Scheme 1**). Based on this concept, we succeeded in developing high-water-content (95–98 wt%) inorganic nanosheet-polymer composite hydrogels with excellent mechanical toughness and elasticity. As depicted in **Scheme 1**, an extremely small amount of guanidinium-pendent methacrylamide (GMA; 0.05–0.2 wt%) was copolymerized with an acryl monomer such as *N,N*-dimethylacrylamide (DMA; 1–2 wt%) in an aqueous suspension of clay nanosheet (CNS; 1–3 wt%). By the addition of GMA, the self-standing ability of the resultant hydrogels was highly improved, particularly in the case of hydrogels with >97 wt% water



Scheme 1. Schematic representation of clay nanosheet (CNS)-polymer composite hydrogels reinforced by the incorporation of guanidinium-pendent methacrylamide (GMA).

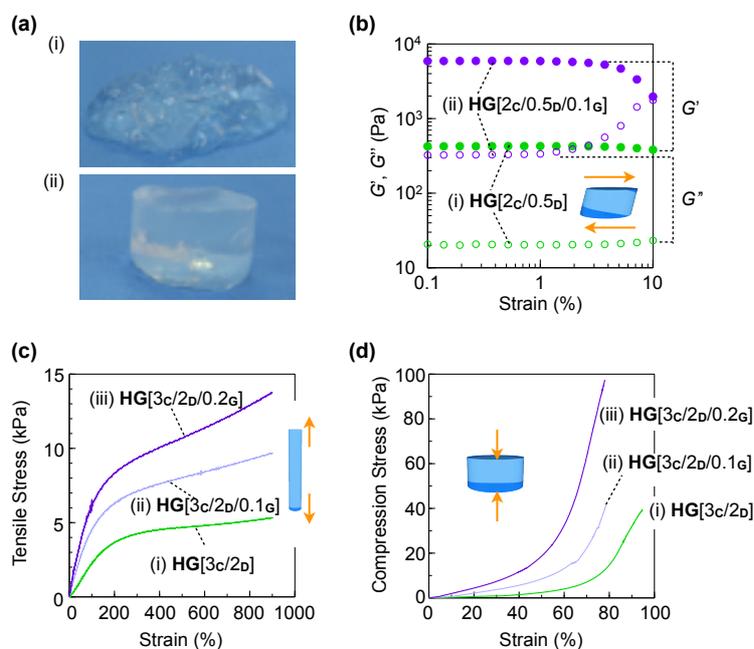


Figure 1. Self-standing ability and mechanical properties of CNS-polymer composite hydrogels. (a, b) Photograph and rheological tests of (i) HG[2c/0.5D] and (ii) HG[2c/0.5D/0.1G]; (c, d) Tensile and compression tests of (i) HG[3c/2D], (ii) HG[3c/2D/0.1G], and (iii) HG[3c/2D/0.2G].

content (**Figure 1a**, i). In the absence of GMA, a hydrogel with 97.5 wt% water (HG[2_C/0.5_D]) existed as a viscous fluidic material (**Figure 1a**). In contrast, the hydrogel doped with 0.1 wt% GMA (HG[2_C/0.5_D/0.1_G]) existed as a self-standing material despite its high water content (**Figure 1a**, ii). HG[2_C/0.5_D/0.1_G] is a very rare self-standing hydrogel with an organic content of less than 1 wt%.

Mechanical properties of hydrogels were characterized by rheological, tensile, and compression testing, which clearly indicate that a minute amount of GMA (0.1–0.2 wt%) can drastically enhance the mechanical toughness of the composite hydrogels. In rheological measurements, the G' value of the GMA-containing hydrogel was about 15 times higher than that of the GMA-free one (**Figure 1b**). The tensile stresses (at 900% strain) of the GMA-containing gels, were 1.8 and 2.6 times higher than that of the GMA-free one, respectively (**Figure 1c**). Notably, the GMA-containing hydrogels did not break until 900% strain, suggesting that the GMA-induced reinforcement of CNS-polymer composite hydrogels was not accompanied by a loss in elasticity. By the aid of GMA, compression properties of the CNS-polymer composite hydrogels were also highly improved (**Figure 1d**).

Mechanism for the GMA-induced mechanical reinforcement of hydrogels was also investigated. Guanidinium groups in the polymer chains interact with the oxyanions on the CNS surfaces via hydrogen bonding and electrostatic interactions, increased the number of crosslinking points in the 3D networks might be the origin of the improved mechanical properties and the suppressed swelling of the GMA-containing hydrogels.

[Chapter 2] Macroscopically anisotropic hydrogels containing graphene and graphene oxide nanosheets: magneto-induced alignment as a versatile method to regulated the orientation of 2D nanosheets

Graphene and graphene oxide (GO) have attracted exceptional recent attention as a 2D organic materials due to their unique mechanical and optoelectronic properties. For the creation of novel composite materials, these 2D nanosheets have often been employed as excellent nanofillers owing to its light weight and extremely high strength.^{2a,2b} Particularly, GO has a large number of oxygen-containing groups, it makes GO hydrophilic and dispersible in water as well as other solvents, and easily modified to be compatible with polymer for enhancing the mechanical performance of hydrogel.^{2c,2d}

The orientation of 2D nanosheets in composite materials is a key issue to maximize the effect of nanosheets doped in. To control the orientation of nanosheets, one of the most ideal ways is to apply a magnetic field, which can be operated in nondestructive and noncontact manner. For example, nanocomposites with carbon nanofibers and nanotubes aligned in the external magnetic field doped with paramagnetic nanoparticles have been extensively studied. As to 2D nanosheet such as inorganic clay nanosheet and graphene, only few experiments explored so far.^{3a,3b}

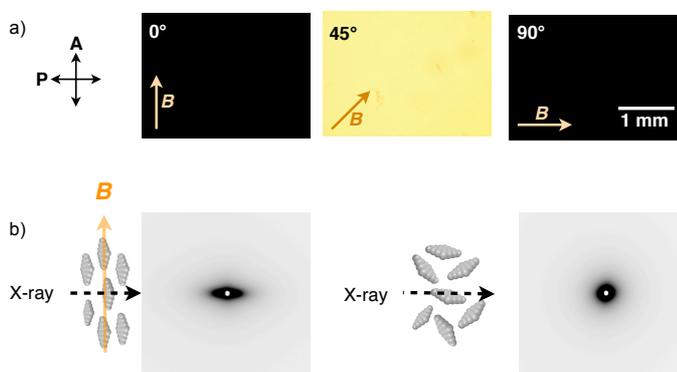


Figure 2. Optical and structural anisotropy of GO–polymer composite hydrogel prepared in a magnetic field (10 T). (a) Polarized optical microscopy images of a GO-doped hydrogel prepared in a magnetic field. (b) 2D SAXS image of GO- hydrogels prepared (i) with and (ii) without applying a magnetic field.

Though many composite materials have been developed based on these 2D sheet structures, macroscopically aligned GO hydrogels has yet to be reported. In Chapter 2, the author discusses a novel methodology to fabricate GO/polymer hydrogels with well-defined macroscopic alignment of GO nanosheet, involving the magneto-induced alignment of the GO suspension in an aqueous solution of a water-soluble acryl monomer, followed by the fixation of the alignment by means of *in-situ* polymerization of the monomer. This provides a new and original way to prepare anisotropic GO–polymer hydrogel films, in which GO/reduced GO nanosheets can orient to any direction over large macroscopic areas.

Through the *in-situ* crosslinking process, aligned hybrid hydrogel films structure was hardly perturbed. The uniform alignment of the system over macroscopic area was observed as a highly optical anisotropy in polarized optical microscope images (**Figure 2a**). As shown in **Figure 2b**, the corresponding 2D-SAXS patterns exhibit an elliptical diffusive pattern and periodic intensity variation against azimuthal angle, indicating the increasing degree of orientation in GO–polymer composite after applying magnetic field. Aligned GO structure was still preserved even after reduction of GO to reduced GO as confirmed by SAXS (**Figure 3**, i and ii). Furthermore, the macroscopic alignment of all samples was still preserved after different solvent (*e.g.* ethylene glycol, ethanol, and ionic liquid) exchange due to the stable chemical crosslinking structure of polymer in our research (**Figure 3**, iii).

The GO/r-GO composite hydrogels presented in this study have potential applications that require macroscopic graphene sheets alignment, such as substrates for growth of cells, actuators, and sensors with improved mechanical and electrical properties.

References

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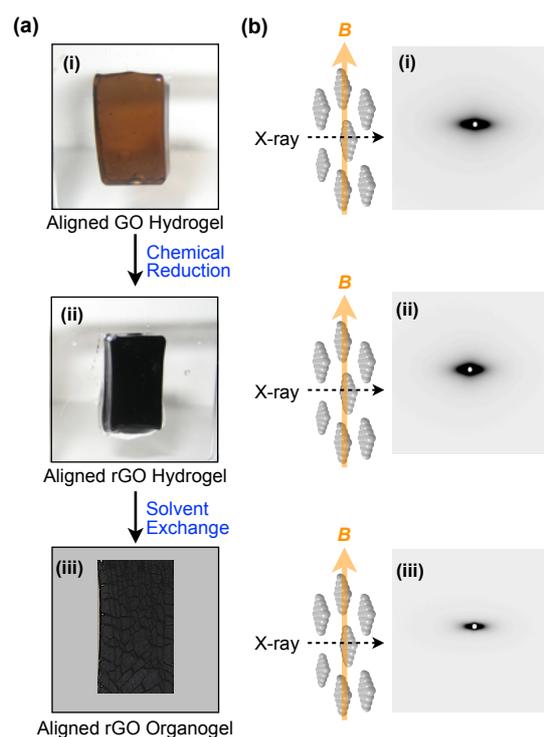


Figure 3. *In-situ* GO chemical reduction (i to ii) and solvent exchange (ii to iii) of magnetically ordered GO–polymer composite hydrogel. (a) Photograph and (b) 2D-SAXS images of GO hydrogel; (i) as prepared, (ii) after chemical reduction of GO, and (iii) after solvent exchange.