

# Synthesis and Mechanism of Tough Hydrogels Reinforced by Microgels as Sacrificial Bonds

(微粒子ゲルを犠牲結合とする高靱性ハイドロゲルの創製とその原理に関する研究)

## 学位論文内容の要旨

Hydrogels are polymeric materials that maintain a distinct three-dimensional structure when swollen in water. They possess some unique properties, such as volume phase transition, excellent biocompatibility and low surface friction, which have them drawn great attention for their potential biomedical applications as drug and cell carriers, and as tissue engineering matrices. However, traditional synthetic hydrogels show the low mechanical strength due to their low polymer density and heterogeneous network structure, which remains the largest barrier to them as load-bearing materials in extensive practical applications, such as artificial cartilage, fuel cell films, wound dressings, etc. Over the past decade, several famous mechanically robust hydrogels with different network topologies have been developed, such as double-network (DN) hydrogels, slide-ring (SR) hydrogels, and nanocomposite (NC) hydrogels. Among them, DN gels created by our lab, combining highly cross-linked, rigid and brittle polyelectrolyte poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) network (the first network) with lowly cross-linked, soft and flexible neutral polyacrylamide (PAAm) network (the second network), show the highest toughness, even as tough as some solvent-free elastomers. However, in the practical applications of DN gels, it is quite difficult to fabricate various desired shapes of DN gels, due to the fragility of the PAMPS gels upon swelling. Therefore, we synthesize DN gels from PAMPS powder precursors (the first network) that are obtained by grinding the dried bulk PAMPS hydrogels. Surprisingly, these so-called P-DN gels exhibit comparable strength and toughness with those of standard DN gels even though the first network is no longer the continuous phase. We attempt to reveal the similarities and differences in fracture mechanism between P-DN gels and DN gels, but it is unpromising for the further study on the fracture mechanism of P-DN gels due to an irregular shape and a wide size distribution of the grinded PAMPS particles.

In this dissertation, we firstly prepared quasi-monodisperse polyelectrolyte microgels (diameter  $\approx 5 \mu\text{m}$ ) by SPG (Shirasu Porous Glass) membrane emulsification, which were used to replace the above grinded PAMPS particles. Through two-step sequential UV polymerization of PAAm networks in the presence of these microgels, we fabricated strong and tough microgel-reinforced hydrogel films (thickness  $\approx 300 \mu\text{m}$ ), named as MR hydrogels. By the selective dyeing of the embedded microgels in MR gels with Alcian Blue, we visualized the microgels clearly under an optical microscope both in the real-time stretching state and in the reswollen pre-stretched state of MR gels. Based on the observation of the deformation of the embedded microgels, we can pursue the fracture mechanism of MR gels in depth.

In Chapter 2, synthesis condition and mechanical model of MR gels are discussed. The relationships between synthesis conditions and physical properties of MR gels were systematically explored to determine the optimal formulation, under which the MR gel showed the highest mechanical strength and toughness comparable to conventional DN gels. The molar ratio of the

PAAm to the PNaAMPS in the microgels is found to be a critical parameter of MR gels and shall reach the optimal value of 20–30 for the high mechanical strength, similar to conventional bulk DN gels. Based on the fact that the observed strain of microgels is far smaller than the applied strain on MR gels, we conclude that isostress model (Reuss's model) is more applicable to MR gels than isostrain model (Voigt's model). The modulus of PAAm matrix  $E_2$  estimated from isostress model and the equilibrium swelling ratio  $q$  show a power law relation ( $E_2 \sim q^{-x}$ ) with the scaling exponent  $x = 2.33$  for sMR gels (MR gels with single PAAm network) and  $x = 2.77$  for MR gels, both of which are in the range  $2.3 < x < 3$ , in good agreement with the Flory–Rehner theory. This result, in turn, confirms the validity of isostress model for MR system.

In Chapter 3, effect of microgel species on the mechanical strength of MR gels and visible mesoscale fracture structure of MR gels are discussed. Several kinds of MR gels are prepared in the presence of microgel precursors of various chemical species with different charges, and all of them show the reinforced mechanical strength comparing with the pure PAAm gels, which indicates that the reinforcement phenomenon based on microgels incorporation has the universality. Considering the embedded microgels as probe during or after elongation, we have certified visible mesoscale fracture structure in MR gels, which will bridge the gap between macroscopic mechanical properties and microscopic structure change.

In Chapter 4, fracture mechanism of MR gels is explicitly discussed. Through the mechanical analyses in modulus  $E$  and dissipated energy  $W$  of MR gels as a function of applied maximum strain  $\epsilon$ , as well as the observation of the deformation of the embedded microgels both in the real-time stretching state and in the reswollen pre-stretched state of MR gels, the stress-strain curve of MR gels can be divided into four regions, as elastic region ( $0 < \epsilon < 1$ ), fast fracture region ( $1 < \epsilon < 3$ ), large deformation region ( $3 < \epsilon < 7$ ), and hardening region ( $\epsilon > 7$ ). In essence, the microgels included in MR gels can be considered as DN structure, and the high mechanical strength and toughness of MR gels root in the sacrificial bonds of the microgels that fracture during deformation, similar to the fracture mechanism of DN gels. Dissipated energy  $W$  is calculated from the area encompassed by hysteresis loop, and can be used to estimate the fraction of broken carbon-carbon (C-C) bonds in the rigid and brittle polyelectrolyte network. According to the fraction of broken C-C bonds, DN microgels in MR gels show four times higher in fracture efficiency than that of bulk DN gels at a certain  $\epsilon$ , which is attributed to the stress concentration on the microgels in MR gels.

In summary, in this study, we have fabricated strong and tough microgel-reinforced (MR) hydrogels comparable to the conventional DN gels (at macroscale). These MR gels are with the two-phase composite structure, where the disperse phase is viewed as DN microgels, and the continuous phase is the flexible PAAm matrix, which is well described by isostress model (at mesoscale). Furthermore, the fracture mechanism of MR gels has been elucidated that the included microgels serve as sacrificial bonds to increase the resistance against the crack propagation, similar to the fracture mechanism of DN gels (at microscale).

# 学位論文審査の要旨

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## 学位論文題名

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