学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Study on Toughening Hydrogels through Sacrificial Bonds Formation via Multiple Equilibrium Reactions
(多重平衡反応を利用した犠牲結合形成による
ハイドロゲルの強靭化に関する研究)

Polymer hydrogels are materials that contain a large amount of water molecules in a three-dimensionally extended network structure, and they are expected to be applied as biomaterials due to their similarity to biological tissues. A critical drawback in applying polymer hydrogels has been their mechanical fragility. Over the past 25 years, numerous studies have reported the development of high-strength and high-toughness polymer hydrogels that overcome this critical weakness. Strategies for toughening polymer hydrogels can be broadly divided into two categories: eliminating the inhomogeneities considered to be the origin of the fragility of polymer hydrogels, and introducing sacrificial bonds, an energy dissipation mechanism, into polymer hydrogels. This paper discusses the creation of novel sacrificial bond-based tough hydrogels and the relationship between the microstructure and mechanical properties of polymer hydrogels.

Sacrificial bonds refer to bonds or structures that break preferentially before the complete failure of the material during deformation, a concept first proposed for the toughening mechanism of biological tissues such as bone and seashells. The double network gel (DN gel) was the first to incorporate this concept into polymer hydrogels. As the name suggests, a DN gel has an interpenetrating network structure composed of two networks, one being brittle and the other being flexible and highly stretchable. Generally, based on the preparation procedure, the brittle network is called the first network, and the flexible, highly stretchable network is called the second network. In DN gels, the sacrificial bonds are formed by the preferential breakdown of the brittle first network during deformation, dissipating energy and thus enhancing toughness. Following the DN gel, various polymer hydrogels have been developed with sacrificial bonds based on hydrophobic interactions, ionic bonds, and other interactions. This paper deals with the preparation of sacrificial bond-based tough hydrogels with self-regulating functions similar to those observed in bone tissue.

Bone is a tough organic-inorganic composite material composed of hydroxyapatite (HAp), collagen, and multiple proteins, and one of the origins of its toughness is believed to be sacrificial bonds. The sacrificial bonds in bone are thought to arise from calcium-mediated ionic bonds between acidic polymers like osteopontin and osteocalcin and calcium ions derived from HAp. These calcium-mediated ionic bonds are self-regulated through metabolic processes in the body, which distinguishes them from sacrificial bonds in synthetic materials. This study aims to reproduce these self-regulating calcium-mediated ionic bonds in synthetic hydrogels to toughen the materials and demonstrate a new toughening strategy. As the calcium source for the calcium-mediated ionic bonds, HAp is used, similar to bone, while the synthetic polymer polyacrylic acid (PAAc) with

carboxyl groups as side chains is used as the acidic polymer. By mixing these two components, a PAAc/HAp gel is prepared to mimic the self-regulating formation of calcium-mediated ionic bonds in bone. When the prepared PAAc/HAp gel is immersed in water, the formation of calcium-mediated ionic bonds is confirmed, and macroscopically, the gel shrinks. Tensile tests on this gel revealed a tough mechanical property with a strength of approximately 2 MPa. The spontaneous formation of calcium-mediated ionic bonds and toughening were observed for PAAc/HAp gels prepared with various compositions. These results suggest the successful creation of an artificial material that reproduces the self-regulating sacrificial bonds found in bone. This outcome is expected to contribute to elucidating the relationship between calcium-mediated ionic bonds and mechanical properties, which is difficult to study in actual bone, and aid in understanding the toughening mechanism of bone.