学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Development of Nano-scale Direct Observation Method for Hydrogel Network Structure and Study on Fracture Mechanism of Hydrogel
（ハイドロゲル網目直接観察法の開発及びハイドロゲル破壊メカニズム究明に関する研究）

Hydrogels are widely using soft materials, such as food, cell culture substrate, artificial biomaterials, and wearable device. Their attractive nature, flexibility and reversibility, comes from entropic elasticity from polymer network's thermal motion. However, state-of-the-art understanding about network structure are still limited at the average structure level derived from bulk measurements. Polymer science has not reached to completely link physical property with structure. There are still several unsolved problems especially with the local structure like chain length distribution and topological inhomogeneity. The main limitation is lack of suitable method to directly observe nano scale network structure. Despite of many challenges, it has not been achieved to capture individual polymer chain by microscopy from among polymers fluctuated by Brownian motion.

Because of such situation, the fracture mechanism of hydrogel is also not well understood. Since gel research ignores how gel breaks on a microscale, it is very difficult to understand the origin of the toughness of the gel. This problem also exist with some strong gels developed in recent years. On the other hand, the fracture mechanism of hard materials such as metals and ceramics has been clarified in detail, through the direct observation results of the fracture surface feature. Therefore, to establish true fracture mechanics of hydrogel via direct observation is promising way to understand and to design tough hydrogels.

The aim of this dissertation is to address these problems by developing novel methods.

In **Chapter 1**, outline of the dissertation is discussed.

In **Chapter 2**, a brief view of the hydrogel observation methods and fracture mechanics of hydrogel is introduced. Meanwhile, major difficulties on observing nanoscale structure of hydrogel is explained. This chapter is helpful to understand why direct observation of soft chemical gels which consisted from thermal fluctuating polymer is so hard.

In **Chapter 3**, a soft lithography technique to make mineral nanoparticle patterned hydrogel is described. This work gave a big hint for developing the hydrogel network direct observation method introduced in **Chapter 4**. Osteoconductive Hydroxyapatite (HAp) mineral nano particle was selectively patterned on the Double Network (DN) hydrogel surface. This kind mechanically tough hydrogels are the promising biomaterial as artificial soft tissue such as cartilage, tendon and ligament. However, their practical application in living body has been limited, because high water content and low friction nature of hydrogel makes difficult to immobilize in the body. Thus, hybridization with osteoconductive HAp, which induces spontaneous bonding with bone, is promising way. Selective dissolution of HAp with acidic gel stamp achieved simple and fast HAp patterning on DN gel surface. Furthermore, selective bone bonding at HAp coated area in the living body was confirmed. In addition, during this study, it was confirmed that HAp inorganic crystals were not uniformly precipitated inside the gel, but that there were some HAp non-exist area. This result suggest that mineral particles selectively mineralized on the hydrogel network.

In **Chapter 4**, we report the novel nanoscale direct observation method for hydrogel network structure by applying inhomogeneous mineralization and double network strategy. Polyelectrolyte gel having sulfonic acid groups was selected as observation target, because they can act as nucleation point and induce selective iron oxide mineralization on the polymer network. Since iron oxide nanoparticles have a sufficiently high electron density, the mineral composite gel network can be observed with a transmission electron microscope (TEM). In addition, the problem of inter-polymer agglomeration during mineralization process was solved by introducing a neutral gel network that does not interact with the mineral. Physical entanglement with neutral network can keep the unperturbed structure of polyelectrolyte gel network. The observed nanoscale gel network structure was well agreed with the network structure predicted from rubber elastic theory. We also

checked that distribution of sulfur element (from target gel network) and iron element (from iron oxide nanoparticle) were overlapped in STEM elemental mapping. This result proved hydrogel network structure was successfully stained by iron oxide nano particles. Furthermore, using this method, we observed various phenomena in which the local structure has an important role (e.g. surface dangling chain, internal voids, gel interface, gel fracture surface).

In **Chapter 5**, mirror radius on the brittle fracture gel surface is investigated. Brittle fracture is a fracture processes in which a material show almost no plasticity or viscosity and fracture starts instantly from a small initial crack. It is known that the brittle fracture surface has a two characteristic feature: 1) Circular smooth region (mirror surface) starting from the initial crack, and 2) uneven region (hackle surface) around smooth region. For hard brittle materials such as glass, it has been reported that there is a correlation between the size of this mirror surface and the fracture stress. In this chapter, by using the hydrogel direct observation method described **in Chapter 4**, it was confirmed that brittle hydrogel also forms mirror-hackle area, but that hydrogel shows different mirror size-fracture stress correlation compared with glass.

In **Chapter 6**, brittle fracture mechanism of pure elastic gel is clarified. It is known that when the brittle materials (e.g. ceramics and thermosetting plastics) fracture, cracks propagate on the weakest path in the material on a microscale. Unfortunately, no studies have been conducted on hydrogels to investigate how cracks grow on a microscale. In this study, we clarified how crack proceed in the hydrogel by combining various observation methods. As the result, we confirmed the inter-microgel fracture is the fracture mechanism for pure elastic gel. Furthermore, by calculating the Hurst index, which represents fractal property of fracture surface roughness, it was suggested that the crosslink density dominated the fracture mechanism on a microscale.

In **Chapter 7**, conclusion of the whole dissertation are summarized.