学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士(ソフトマター科学)　氏　名　吉田　匡宏

学 位 論 文 題 名

A Study on Yielding Process of Double Network Hydrogel via Trans-scale Direct Observation: From Macro to Molecular Level
(マクロから分子レベルまでのトランススケール直接観察による DN ゲルの降伏過程に関する研究)

Hydrogels are materials composed of a polymer network capable of retaining water within its crosslinked structure. Thanks to their excellent biocompatibility, hydrogels hold significant potential for applications in biomaterials and bioelectronic devices. However, conventional hydrogels are often brittle, which limits their practical use in many fields. Recent advancements have addressed this issue, leading to the development of high-strength and tough hydrogels, such as the double-network (DN) hydrogel created by our research group. DN hydrogels are particularly notable for their exceptional toughness, which stems from their unique network structure. This structure consists of a rigid, brittle first network interwoven with a flexible, stretchable second network. Under stress, the first network undergoes extensive internal fracturing before the material completely breaks, dissipating strain energy and allowing for significant deformation prior to failure.

One of the most remarkable features of DN hydrogels is the occurrence of a "yielding" phenomenon, a behavior traditionally associated with high-toughness materials, such as metals and plastics. Unlike conventional yielding, which involves permanent plastic deformation, DN hydrogels fully recover their original shape once the stress is removed, suggesting a novel yielding mechanism. This unique behavior has drawn considerable attention as a new strengthening strategy for materials, sparking numerous studies aimed at uncovering its underlying mechanisms. While much research has focused on the macroscopic mechanical properties of DN hydrogels at their yielding points, the localized structural changes that occur prior to large-scale yielding remain poorly understood.

This study aims to investigate the local fracture processes that lead to yielding in DN hydrogels across multiple scales, from macroscopic to molecular-level. Chapter 1 introduces the objectives and context of the study by providing an overview of the research focus. Chapter 2 reviews recent developments in the field by identifying key challenges and outlining the approaches taken in this research.

Chapter 3 explores the macroscopic internal fracture of DN gels by using birefringence imaging during uniaxial stretching. Birefringence imaging is a technique used to visualize the orientation of polymer chains within a material. In DN gels, this method allows for the selective identification of regions where the first network undergoes extensive internal fracturing, with the second network aligning to support the load of the fractured areas. By combining birefringence imaging with uniaxial tensile testing, we tracked the formation and growth of internal fracture regions both before and after yielding. The results revealed that during uniaxial stretching, internal fractures first appear at the sample edges and gradually expand toward the center. Eventually, these fractures propagate across the entire cross-section, leading to yielding. This finding confirms that the yielding phenomenon in DN gels is driven by the progression of localized internal fractures from the edges toward the center of the material.

In Chapter 4, we present the development of a novel nanoscale imaging technique that combines mechanoradical polymerization and transmission electron microscopy (TEM) to visualize bond breakages within the polymer network. While birefringence imaging effectively captures large-scale internal fractures, it lacks the sensitivity and spatial resolution to visualize smaller fractures occurring before yielding. To address this limitation, we developed a new visualization method from scratch to directly observe the breaking of individual bonds in the polymer network. By applying mechanical stress to DN gels, we induced small-scale

internal fractures that generated active radicals, which is called mechanoradicals, at the fracture sites. These mechanoradicals initiated the polymerization of short polymer chains, which were then stained using a mineral-based staining method. The stained chains aggregated near the fracture ends, enabling visualization of rupture points in the first network through TEM. Our observations revealed that under small strains, multiple polymer chains experience localized breakage along the direction of applied stress, suggesting a stress concentration effect at the nanoscale.

Finally, Chapter 5 summarizes the key findings of this research and discusses their implications for designing and fabricating tougher DN hydrogels. The insights gained into the local fracture processes of DN hydrogels have the potential to inform the development of more durable materials. Moreover, the novel imaging technique developed in this study is not limited to DN gels but can be applied to other hydrogel systems, offering valuable insights into their mechanical behavior under stress.

In conclusion, this research provides a comprehensive understanding of the local fracture processes leading to yielding in DN gels, observed across macroscopic and molecular scales. These findings have important implications for the development of tougher hydrogels and could inform advancements in a wide range of material applications, further driving innovation in the field of hydrogel research.