博 士（理 学） ムハンマド アナムル ハック

学 位 論 文 題 名

Creation of Anisotropic Hydrogel with Hierarchical Structure Based on Bilayers and its Emergence of Functions

（二分子膜に基づく階層構造を有する異方性ゲルの創製とその機能創発）

学位論文内容の要旨

Most conventional soft and wet hydrogels usually show extremely poor mechanical performance due to their amorphous structure in contrast with the soft natural bio-tissues that possess well-defined hierarchy structure from molecular level to macroscopic scale. Creating soft and wet synthetic materials with an excellent mechanical performance had been a challenging task for material scientists. Although several hydrogels with high strength, such as slide ring and tetra-PEG gels, and toughness, such as nanocomposite and double network gels, have been successfully developed, they also possess amorphous structure in contrast with the natural bio-tissues. However, these hydrogels have negligible self-recovery and fatigue resistance. On the other hand, the well ordered structures are important for the hydrogel to exhibit color that further underpin the wide applicability of them as a photonic sensor material. A few of the photonic materials, that exhibit mechanically stimulated color tuning ability, have been synthesized based on the periodic array of colloidal crystal. However, they are isotropic in their structure; they have poor color quality, weak mechanical response, and their color tuning ability is limited over small wavelength region (20-70 nm) and irreversible. The hybrid hydrogel with periodic lamellar structure might be an excellent system to combine the two novel phenomena, tunable structural color under mechanical stimulation and excellent mechanical functions, in one material. This system was initially developed by Tsujii *et al.* However, their synthesized hydrogel is far from perfect anisotropy due to microscopically oriented lamellar domains are randomly oriented in the bulk gel, and exhibits poor structural color and negligible enhancement on mechanical property.

In this research, by developing a single-domain macroscopic lamellar bilayer structure, we have found that the hydrogel exhibits robust anisotropic functions, excellent mechanical performances, and superb color tuning ability under mechanical stimuli which might play important roles in diverse applications.

Chapter 2 is a review about the polymerizable surfactant (dodecyl glyceryl itaconate:DGI) and its self-assembly and polymerization behavior in hybrid hydrogel system.

In chapter 3, a novel anisotropic hydrogel with a unidirectionally aligned membrane-like lamellar bilayer structure of macroscopic size has been synthesized in a one-pot polymerization reaction from a polymerizable surfactant (dodecyl glyceryl itaconate:DGI) and acrylamide in presence of a cross-linker. Prior to the polymerization, by applying shear flow to the precursor solution, thousands of lamellar bilayers of self-assembled DGI are aligned in one direction parallel

to the substrate surface. Polymerized lamellar bilayers are stacked periodically and entrapped in the polyacrylamide network to give a mechanically strong hydrogel (PDGI/PAAm). This hydrogel shows one-dimensional swelling, strong anisotropy in the elastic modulus, and magnificent structural color due to the Bragg's diffraction of visible light on the lamellar bilayer planes. Owing to the softness and large deformability of the gel, the color of the gel can be reversibly tuned by the compressive strain over a wide wavelength range, which might be used as a soft tactile sensor that is able to detect a complicated force field. The color of the gel further can be selectively changed by selective compression that could guide the gel to be used as deformation based color display.

In chapter 4, we report the extra-ordinary toughness, hysteresis, self-recovery, and persistent fatigue resistance of the anisotropic PDGI/PAAm hydrogel with single-domain lamellar structure, consisting of periodical stacking of several thousands of rigid, hydrophobic bilayers in the ductile, hydrophilic polymer matrix. The stratified lamellar bilayers not only diffract light to exhibit magnificent structural color, but also serve as a reversible sacrificial bond that dissociate upon deformation and give rise to the excellent mechanical functions such as toughness, self-recovery, and persisting fatigue resistance. Both the molecular dissociation and lipid-like mobile nature of bilayers dramatically enhance the resistance to crack propagation by suppressing the stress concentration at the crack tip with the formation of extra-ordinary blunting. This unique toughening phenomena might allow deep insight into the toughening mechanism of the hydrogel-like soft materials such as biological soft tissues.

In chapter 5, we successfully develop a rubber-like elastic hydrogel with the formation of periodically ordered bilayer micro-domains from the single-domain macroscopic lamellar bilayer of the PDGI/PAAm gel. By applying double network principle, we developed a 2^{nd} PAAm network in the existing PAAm network of the PDGI/PAAm gel. The obtained hydrogel (PDGI/PAAm^2) is able to tune the magnificent structural color reversibly over the entire wavelength range of the visible spectrum as fast as the uni-axial tensile stretching and compressive deformation are applied and released. The color of the hydrogel can also be tuned reversibly from blue to red by applying compression perpendicular to the observation direction. Owing to the strength, softness, and rubber-like elastic deformability, the tunable hydrogel might be used extensively as a soft tactile sensor or stress sensor which is more potentially able to detect a local deformation of a complicated force field.

Finally, this study has indicated the successful development of the perfectly anisotropic hydrogel by forming uni-axial lamellar bilayer structure in the polymer gel network that exhibits stress induced tunable structural color and excellent mechanical performance. We believe that the research will open a new class of soft tactile photonic sensor, bio-compatible material that further allow insight into the toughening mechanism of bio-tissue, and drug delivery system.

学位論文審査の要旨

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Most conventional soft and wet hydrogels usually show extremely poor mechanical performance due to their amorphous structure in contrast with the soft natural bio-tissues that possess well-defined hierarchy structure from molecular level to macroscopic scale. Although several hydrogels with high strength have been successfully developed, they also possess amorphous structure in contrast with the natural bio-tissues. On the other hand, the well ordered structures are important for the hydrogel to exhibit color that further underpin the wide applicability of them as a photonic sensor material. A few of the photonic materials, that exhibit mechanically stimulated color tuning ability, have been synthesized based on the periodic array of colloidal crystal. However, they are isotropic in their structure; they have poor color quality, weak mechanical response, and their color tuning ability is limited over small wavelength region and irreversible. The hybrid hydrogel with periodic lamellar structure might be an excellent system to combine the two novel phenomena, tunable structural color and excellent mechanical functions, in one material. This system was initially developed by Tsujii *et al.* However, their synthesized hydrogel is far from perfect anisotropy due to random orientation of bilayer domains in the bulk gel, and exhibits poor structural color and mechanical property.

In this study, the author has developed an anisotropic hydrogel by forming uni-axial bilayer ordered structure inside into a polymer matrix. This hydrogel exhibits robust anisotropic functions, excellent mechanical performances, and superb color tuning ability under mechanical stimuli which might play important roles in diverse applications.

In conclusion, the author has new findings of an hydrogel which possesses the hierarchical structure in accordance with the biological soft tissues and we believe that the research will open a new class of soft tactile photonic sensor, bio-compatible material that further allow insight into the toughening mechanism of bio-tissue, and drug delivery system.

Therefore, we acknowledge that the author is qualified to be granted the doctorate of Science from Hokkaido University.