様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

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研究課題名（和文）Fatigue behavior and underlying mechanism of tough and self-healing hydrogels

研究課題名（英文）atigue behavior and underlying mechanism of tough and self-healing hydrogels

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研究成果の概要（和文）：筋肉などの耐荷重性の生体組織は高い耐疲労特性を持ちますが、生体組織の精巧な階層構造が、それらの優れた耐疲労特性にどのように寄与するかはよく理解されていません。 このプロジェクトでは、単純なモデルシステムとして高分子両性電解質ハイドロゲル（PAゲル）を用いて、階層構造を持つソフトマテリアルの疲労回復特性を研究しました。 疲労サイクル時にPAゲルの2つの連続した相ネットワークが過渡的な配向構造を形成し、その結果、顕著な亀裂の鈍化および亀裂進展を減速させる効果を誘発することを発見しました。これらの調査結果は、丈夫で疲労耐性のある材料設計の指針となることが期待されています。

研究成果の学術的意義や社会的意義
We revealed the antifatigue mechanism of tough and self-healing polyampholyte hydrogels, which not only give important hints to understand fatigue-resistant behavior of biotissues with complex hierarchical structures, but also provide design strategy for tough and fatigue-resistant hydrogels.

研究成果の概要（英文）：Load-bearing biological tissues, such as muscles, are highly fatigue resistant, but how the exquisite hierarchical structures of biological tissues contribute to their excellent fatigue resistance is not well understood. In this project, we studied antifatigue properties of soft materials with hierarchical structures using polyampholyte hydrogels (PA gels) as a simple model system. PA gels are tough and self-healing, similar to biotissues. By combining fatigue measurement and time-resolved synchrotron radiation small-angle X-ray scattering we discovered that, upon fatigue cycling, the bicontinuous phase networks in PA gels form a transient oriented structure to induce a pronounced crack blunting and crack deceleration effect. We further revealed that the phase contrast between soft and hard phase is vital important for suppressing the fast crack growth. These findings provide design strategy for tough and fatigue-resistant materials.

研究分野：polymer physics

キーワード：hydrogels　tough and self-healing　multiscale structure　fatigue resistance

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

Hydrogels are materials consisting of crosslinked polymer network and abundance of water, which bear similar soft and wet nature as biological tissues, and thus are considered as the best candidate for the artificial soft tissues to substitute damaged real ones. However, conventional hydrogels tend to be brittle and weak, like tofu or jellies, in stark contrast to the tough and strong biological tissues. In the recent decade, there is an exploration in the development of tough and strong hydrogels, some of them even possess self-healing ability. The high toughness endows those gels many potential applications, such as load-bearing biomaterials, soft robots and soft machines. Most of those applications not only require hydrogels to possess high toughness, but require them to sustain cyclic loading. For example, an artificial knee joint needs to experience 1 million cycles per year. Therefore, studying the fatigue behavior and revealing the underlying mechanism of hydrogels is vital important and urgently needed.

２．研究の目的

The purpose of this research is two-fold:

(1) to develop an effective methodology for studying fatigue behavior of hydrogels by combing multiscale structure measurements;

(2) to study the fatigue behavior of polyampholyte gels and to elucidate the underlying mechanism with this method.

３．研究の方法

In this research, we combined the small-angle X-ray scattering (SAXS), optical technique, and mechanical measurement to study the fatigue behavior of a type of tough and self-healing hydrogels. SAXS was used to track the phase structure change of the gel, optical technique was used to track the crack growth, and mechanical measurement was used to quantify the energy release rate.

４．研究成果

We chosen a type of tough and self-healing hydrogels composed of polyampholytes as a model system. The effect of phase separation structure and the contrast of the soft and hard phases on the fatigue behavior was revealed. In addition, we also studied the structure formation mechanism of this gel and collaborated with Prof. Chung-Yuen Hui of Cornell university to construct the theory to describe the time-dependent behavior of this system. What is more, we used this gel to realize the memorizing-forgetting behavior, in analogy to human brain. This research generated 11 academic papers, including 3 in *Proceedings of the National Academy of Sciences of the United States of America*, 1 in *Science Advance*, and 3 in *Macromolecules*. A brief summary of the research results is listed below.

(1) Mechanism of hierarchical structures in delaying fatigue fracture.

Muscles, composed of exquisite hierarchical structures, exhibit high fatigue resistance and can resist crack propagation even after injury. The mechanism of the hierarchical structures on suppressing crack advance under reciprocating movement is poorly understood. Tough and self-healing hydrogels are good candidates as simplified model systems for studying the mechanical behaviors of load-bearing biotissues. We found that that polyampholyte hydrogels, having a hierarchical structure, demonstrate high fatigue resistance through a synergistic effect between different scales. Such an antifatigue mechanism based on hierarchical structure not only gives important hints to understand fatigue-resistant behavior of biotissues with complex hierarchical structures, but also provides design strategy for tough and fatigue-resistant hydrogels, by forming multiscale network structures using noncovalent bonds as building blocks.

(2) Effect of mesoscale phase contrast on fatigue-delaying behavior

We investigated the fatigue resistance of polyampholyte hydrogels with a hierarchical structure due to phase separation and find that the details of the structure, control the mechanisms of crack propagation.

When gels exhibit a strong phase contrast and a low cross-linking level, the stress singularity around the crack tip is gradually eliminated with increasing fatigue cycles and this suppresses crack growth, beneficial for high fatigue resistance. On the contrary, the stress concentration persists in weakly phase-separated gels, resulting in low fatigue resistance. A material parameter, λ_{tran}, is identified, correlated to the onset of non-affine deformation of the mesophase structure in a hydrogel without crack, which governs the slow-to-fast transition in fatigue crack growth. The detailed role played by the mesoscale structure on fatigue resistance provides design principles for developing self-healing, tough, and fatigue-resistant soft materials.

(3) Phase separation behavior in polyampholyte hydrogels

We systematically studied the phase network formation of polyampholyte gels aiming to answer the following three questions: (1) how the phase separation occurs? (2) what determines the phase structure? and (3) is this structure in thermodynamic equilibrium or not? Our results show that the phase separation occurs during dialysis of counterions from the gels and it is driven by the Coulombic and hydrophobic interactions. The phase size d_0 and the number of aggregated chains in a unit cell of the phase structure n scale with the molecular weight of the partial chain between permanent effective cross-linking M_{eff} as $d_0 \sim M_{eff}$ and $n \sim M_{eff}^2$, respectively. A chemical cross-linker and topological entanglement suppress phase separation, while hydrophobic interaction favors phase separation. An intrinsic correlation between the polymer density difference ($\Delta\rho$) between two phases and d_0 is observed ($\Delta\rho \sim d_0^2$) as a result of the competition between the driving force to induce phase separation and the resistance to suppress the phase separation. The phase-separated structure is metastable, which is locally trapped by strong intermolecular interactions.

(4) Constitutive modeling of bond breaking and healing kinetics of polyampholyte gel

We developed a three-dimensional finite strain nonlinear viscoelastic model is developed to study the mechanical behavior of a physically cross-linked polyampholyte gel. We divided the physical cross-links broadly into weak and strong bonds, depending on their survival and reformation characteristics. Our constitutive model connects the strain dependent bond breaking and reforming kinetics in the microscopic regime to the deformation of the gel at the continuum level. We compared the predictions of our model with uniaxial tension, tensile-relaxation, cyclic, and small strain torsional relaxation tests. The material parameters in our model are obtained using least squares optimization. Our theory agrees well with the experimental behavior of the gel.

(5) Using polyampholyte hydrogels to construct dynamic memorizing-forgetting device

The memory of our brain, stored in soft matter, is dynamic, and it forgets spontaneously to filter unimportant information. By contrast, the existing manmade memory, made from hard materials, is static, and it does not forget without external stimuli. We proposed a principle for developing dynamic memory from soft hydrogels with temperature-sensitive dynamic bonds. The memorizing–forgetting behavior is achieved based on fast water uptake and slow water release upon thermal stimulus, as well as thermal-history-dependent transparency change of these gels. The forgetting time is proportional to the thermal learning time, in analogy to the behavior of brain. The memory is stable against temperature fluctuation and large stretching; moreover, the for- getting process is programmable. This principle may inspire future research on dynamic memory based on the nonequilibrium process of soft matter.

５．主な発表論文等

〔雑誌論文〕　計11件（うち査読付論文　11件／うち国際共著　11件／うちオープンアクセス　0件）

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３．雑誌名 Proceedings of the National Academy of Sciences	６．最初と最後の頁 7606～7612
掲載論文のDOI（デジタルオブジェクト識別子） 10.1073/pnas.2000189117	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

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〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関