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研究課題名(和文) Creating tough and fatigue-resistant hydrogels with hierarchical structures

研究課題名(英文) Creating tough and fatigue-resistant hydrogels with hierarchical structures

研究代表者

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研究成果の概要(和文)：自己修復性ハイドロゲルの強靱化と耐疲労性に及ぼす階層構造とレオロジー応答の影響に焦点を当てた研究を行っている。本研究では物理と化学的パラメータを変化させて階層構造と動的な機械的挙動を調整し、レオロジー応答からゲルの伸長・破壊挙動を明らかにしました。その一方で遅延疲労破壊は相分離構造によって支配されることを明らかにしました。本研究結果は、強靱で疲労耐性のある次世代ソフト材料の設計指針になると考えています。この成果は、Nat. Rev. Mater., Sci. Adv., Macromolecules、およびJ. Mech. Phys. Solidsに掲載されました。

研究成果の学術的意義や社会的意義

This study reveals the relationship between the microscopic structures, rheological response and mechanical performance, and proposes general principles for the design of next-generation tough and fatigue-resistant soft materials.

研究成果の概要(英文)：The applicant focuses on studying the influence of hierarchical structure and rheological response on toughening and fatigue resistance of self-healing hydrogels, which are composed of a hierarchical structure including ionic bonds, transient and permanent polymer networks, and bicontinuous hard/soft phase networks. By tuning the hierarchical structures and dynamic mechanical behavior using physical (changing salt concentrations and performing cyclic training) and chemical strategies (applying different monomers and varied crosslinker contents), it was revealed that the tensile and fracture behavior of the gels are mainly determined by the rheology response, while the delayed fatigue fracture is dominated by the phase-separated structure. Additionally, general principles for the design of next-generation tough and fatigue-resistant soft materials are proposed. The achievements have been published in Nature Reviews Materials, Sci. Adv., Macromolecules, and J. Mech. Phys. Solids.

研究分野：polymer physics

キーワード：Phase separation fatigue resistance fracture toughness dynamic bonds in-situ SAXS

1. 研究開始当初の背景

The soft and wet nature of hydrogels endows them with great application potential in biological and biomedical applications such as artificial soft tissue, sensors, wound dressings, models for biological studies, etc. However, common synthetic hydrogels are unstructured and usually soft, weak, and brittle with a fatigue threshold G_0 only on the order of 10 J/m^2 , unable to meet the basic requirement for high strength, extensibility, and long-term mechanical stability. The toughness of hydrogels can be strengthened to 10^3 to 10^4 J/m^2 by introducing covalent or noncovalent sacrificial bonds to dissipate energy. Nonetheless, the energy dissipation structures contribute little to the fatigue threshold as they break down under continuous cyclic loading. This is in stark contrast with biological tissues, composed of hierarchical structures with characteristic dimensions spanning from the nanoscale to the macroscale, that exhibit excellent fatigue resistance along with high toughness. It inspires us that the hierarchical structures could be beneficial for long-term mechanical stability under a high load. However, enhancing the fatigue resistance of synthetic hydrogels through hierarchical structure design is challenging.

In previous work, the applicant group found that the tough and self-healing polyampholyte hydrogels (PA gels), prepared from random copolymerization of a cationic monomer methyl chloride quarternized N,N-dimethylamino ethylacrylate (DMAEAQ) and an anionic monomer sodium p-styrenesulfonate (NaSS) at the charge balance point, are composed of hierarchical structure, containing reversible ionic bonds at the 0.1-nm scale, a cross-linked polymer network at the 10-nm scale, and bicontinuous hard/soft phase networks at the 100-nm scale. The PA gels exhibit multi-scale fatigue resistance under cyclic loading, shown by multi-level threshold of energy release rate for crack growth, resulting in strong anti-fatigue-fracture. Particularly, the bicontinuous phase networks can alleviate stress concentration, contributing to the slow crack growth mode. The synergy effect of the hierarchical structure not only endows hydrogels with significant energy dissipation and high fracture energy but also imparts strong fatigue resistance. However, the hierarchical structure also results in a rich variety of dynamic mechanical behaviors in PA gels. It remains unclear whether the hierarchical structure or the rheological response is more crucial for enhancing fracture toughness and fatigue resistance.

2. 研究の目的

Creating tough and fatigue-resistant self-healing hydrogels and understanding the underlying mechanism is one important but challenging topic. At present, few principles can guide the design of self-healing hydrogels with tissue-like toughness, resilience, and fatigue resistance. This propose aims to 1) reveal the intrinsic correlations between the multiscale structures/rheological response and mechanical/physical properties; 2) create a series of self-healing hydrogels exhibiting high strength, toughness, and fatigue resistance, and elucidate the toughening and fatigue-resistant mechanisms; 3) propose a general principle for the design of next-generation tough and fatigue-resistant soft materials.

3. 研究の方法

Since phase separation in PA gels arises from the competition between the free energy gain of polyion complexation and the entropic penalty of chain elasticity, tuning the two parameters (the polyion complexation and the chain elasticity) is expected to tune the hierarchical structure effectively. Consequently, systematically investigating the effects of such tuning on fracture toughness and fatigue resistance can reveal the intrinsic correlations between the multiscale structures/rheological response and mechanical/physical properties. The applicant tuned the hierarchical structure and rheology response in PA hydrogels via physical (changing salt concentrations and performing cyclic training) and chemical (applying different monomers and varied crosslinker contents) strategies. The polymerization kinetics of monomers were monitored using nuclear magnetic resonance (^1H NMR). The formed phase-separated structures and their evolution under monotonic and cyclic loading in real-time were tracked by small-angle X-ray scattering (SAXS) and ultra-small angle X-ray scattering (USAXS). Rheology tests and cyclic stretching were employed to measure the dynamic mechanical behavior. Tensile, pure shear, and cyclic fatigue tests were conducted to characterize mechanical properties, such as self-healing, extensibility, energy dissipation, fracture toughness and fatigue resistance. During fracture, mechanical training and fatigue tests, circle birefringence was utilized to characterize stress concentration and de-concentration around the crack tip.

4. 研究成果

(1) Tensile behavior and fracture toughness are dominated by the rheological response, regardless of the phase structure

The applicant group investigated the salt effect on rheological response and mechanical behaviors. Through a systematic study on one poly(sodium *p*-styrenesulfonate-*co*-3-(methacryloylamino)propyl-trimethylammonium chloride) [P(NaSS-*co*-MPTC)] gel (PA-p) without a chemical crosslinker and one P(NaSS-*co*-MPTC) gel (PA-c) with a small amount of chemical crosslinker, the applicant group demonstrate that the salt effect on mechanical properties, including small-strain moduli, large deformation energy dissipation, fracture stretch ratio, and fracture toughness can be effectively converted into frequency or strain rate dependences following the time–salt superposition principle, regardless of the phase-separated structure change (**Figure 1**). Accordingly, one

can access a wide range of observation time scales from 10^{-9} to 10^2 rad/s at room temperature, covering three regimes: (I) the high-frequency plateau regime from the dynamic and primary networks, (II) the viscoelastic regime from sticky Rouse motion of ionic associations, and (III) the low-

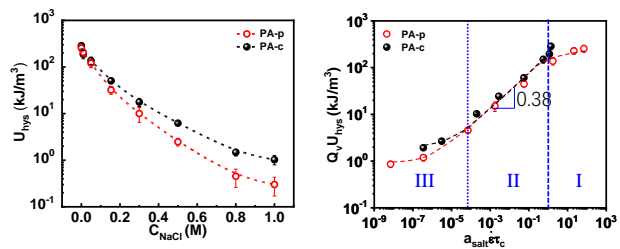


Figure 1. Effect of ionic bond strength on energy dissipation of PA gels.

frequency plateau regime from the primary network. This work is published in *Macromolecules* (*Macromolecules* 2023, **56**, 535). Additionally, the applicant and coworkers revealed that the relaxation of dynamic bonds of the PA gel accelerates crack propagation under static fatigue loading. This work is published in *Journal of the Mechanics and Physics of Solids* (*J. Mech. Phys. Solids* 2024, **186**, 105595).

(2) Mechanical training orientates the phase-separated structure, enhancing fatigue resistance

P(NaSS-*co*-DMAEAQ) gels, composed of hierarchical structures including ionic bonds, transient and permanent polymer networks, and bicontinuous hard/soft phase networks, were adopted to investigate the effect of hierarchy structure on the mechanical adaptation of self-healing hydrogels under cyclic stretching training. Conditions for effective training, mild overtraining, and fatal overtraining were demonstrated in soft materials for the first time. Compared with the self-healing gel and elastomer without phase-separated structure, the applicant group revealed that mesoscale hard/soft phase networks dominate the long-term memory effect of training and play a crucial role in the asymmetric dynamics of compliance changes and the symmetric dynamics of hydrogel shape evolution. During cyclic training, the mesoscale hard/soft phase networks become relative stable oriented structure, which alleviates subsequent fatigue crack stress concentrations, enhancing fatigue resistance dramatically

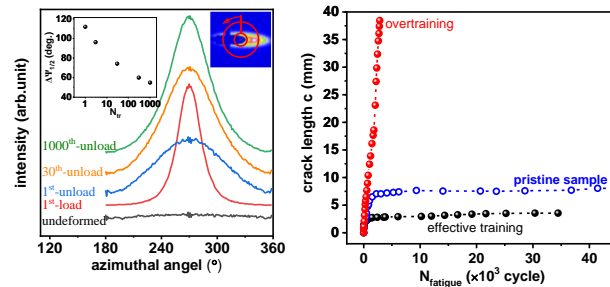


Figure 2. Effective training orientates the phase-separated structure and enhances fatigue resistance.

(**Figure 2**). This work is published in *Science Advances* (*Sci. Adv.* 2023, **9**, eadj6856).

(3) Hard and soft components tuned the phase-separated structure and dynamic mechanical behavior

The applicant group further tuned the phase-separated structure in PA gels by combining two components: one with a glass temperature (T_g) higher than room temperature, and another with T_g lower than room temperature. This strategy resulted in the fabrication of hydrogels with varying phase-separated contrast, domain size, and rheology response. Following systematic rheological, tensile, fracture, and fatigue tests, the applicant group revealed that the tensile and fracture behavior of the PA gels are mainly determined by the rheology response, while the fatigue threshold and delayed fatigue fracture are dominated by the phase-separated structure. In addition, the applicant and coworkers investigated the evolution of the microscopic structure under varied loading temperature conditions, and elucidated that the mechanical performance of the PA gels closely correlates with the deformation of the hierarchical structures, which is dramatically affected by loading temperatures. High loading temperatures result in soft and ductile behavior of the gels, and the microscopic deformation of phase networks follows affine deformation to a large stretch ratio. In contrast, low temperatures lead to hardening, and non-affine deformation of phase

networks occurs from the onset of stretching (**Figure 3**). This work provides an in-depth understanding of the relationship between structural evolution and macroscopic performance. It is published in *Macromolecular Rapid Communications* (*Macromol. Rapid Commun.* 2024, 2400327).

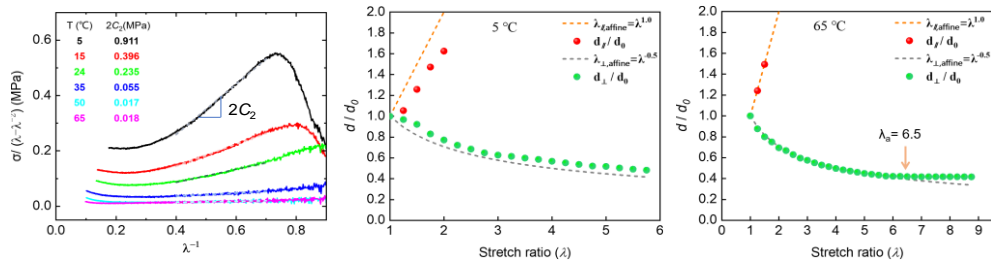


Figure 3. Effective environmental temperature on mechanical performance and deformation in micro-phase separation.

Based on their understanding of toughening and fatigue resistance mechanisms in hydrogels, the applicant and coworker wrote a review paper (*Nat. Rev. Mater* 2024, **9**, 380), providing a comprehensive overview of the design principles for tough hydrogels. The paper also presents strategies for obtaining fatigue-resistant, self-growing and reinforced hydrogels that can adapt to their surrounding mechanical environment. Moreover, it proposes general principles for the design of next-generation tough and fatigue-resistant soft materials.

5. 主な発表論文等

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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
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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			
米国	University of Colorado Boulder	Cornell University		
中国	USTC	Sichuan University	Taiyuan University of Technology	他3機関