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Author(s)	黄, 以万
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学位論文内容の要旨  
Abstract of Doctoral Dissertation

博士の専攻分野の名称 博士 (生命科学) 氏名 黄以万  
Degree requested Doctor of Life Science Applicant name Yiwan Huang

学位論文題名  
Title of Doctoral Dissertation

Developing Extremely Tough Fiber Reinforced Soft Composites  
(超強靱な繊維強化ソフト複合材料の開発)

In general, producing materials that possess both high strength and toughness is extremely difficult and has rarely been realized. This is because these two properties are often contradicting. Nature has overcome this conflict and developed materials exhibiting both excellent load-bearing capacity and fracture resistance, as can be observed from both hard tissues (*e.g.*, nacre and bone) and soft tissues (*e.g.*, ligament and tendon), by combining rigid, brittle components (either inorganic or organic) and soft, organic components into composite materials. As a vital class of soft materials, tough hydrogels have shown strong potential as structural biomaterials. These hydrogels alone, however, still possess limited mechanical properties (low modulus) when compared to some load-bearing tissues, *e.g.*, ligaments and tendons. Developing both strong and tough soft materials is still a challenge.

Recently, our group has developed a new class of tough hydrogels, polyampholyte (PA) gels, based on multiple ionic bonds acting as reversible sacrificial bonds in the gel network. Interestingly, PA gels also demonstrate unique interfacial bonding to charged surfaces, either positive or negative, due to the self-adjustable Coulombic interaction of the dynamic ionic bonds of the PA. The PA gels are synthesized from radical polymerization of oppositely charged monomers. In contrast to traditional hydrogels that swell in water, the as-prepared PA gels undergo a deswelling process in water by dialysis of small counter-ions, which favors the enhancement of both gel toughness and surface adhesion to charged surfaces. The combined superior properties of PA gels provide us with the raw materials necessary to realize our target of achieving *fiber reinforced soft composites* (FRSCs) with both superior strength and toughness. In this dissertation, I strategically combined commercially available glass fiber fabric with soft PA gels to develop extremely tough FRSCs and to systematically understand the influence parameters on the mechanical properties.

In **Chapter 3**, focus is on the size-dependent fracture behaviors and synergistic toughening in the fiber reinforced hydrogel composites. To address this issue, firstly, we typically chose the P(NaSS-*co*-DMAEA-Q) tough hydrogel as a model PA gel matrix and a woven glass fabric (GF) to qualitatively study the width-dependent tearing properties, failure modes resisting tearing, and the synergistic toughening in the PA-GF hydrogel composites. Secondly, we selected another PA hydrogel, *i.e.*, P(NaSS-*co*-MPTC) gel, to further verify the priority of the tough PA gel matrix in the development of fiber reinforced soft composites and to better understand the size-dependent tearing behaviors. Finally, to achieve the saturated process zone in the hydrogel composites at a relatively small sample size, we used a *thin* woven glass fabric (*t*-GF, possessing smaller single fiber diameter and lower fiber bundle fracture strength in relation to GF) to explore the process zone influence on the size-dependent tearing behaviors and the synergistic effect of the PA-*t*-GF composites. Despite being water-rich and encompassed by biocompatible hydrogel, the composites still show exceptional fracture toughness ( $\sim 1,000 \text{ kJ m}^{-2}$ ), high tensile strength ( $> 300 \text{ MPa}$ ), and good bending flexibility, which make them bridge the gap between the soft, tough hydrogels and general rigid materials. This chapter thus not only gives us some insight into this new composite system, but also open up a simple pathway to design robust soft and wet materials with extraordinary fracture resistance.

In **Chapter 4**, focus is on understanding the role of energy-dissipation of the soft matrices in the synergistic toughening of fiber reinforced composites. We consider that the highly energy-dissipative gel matrix and its unique interfacial bonding with glass fabric are the two critical factors for achieving

the synergistic effect in toughness of the composites. To isolate this variable, we select a specific fabric type and geometry, where the glass fibers are woven in a plain weave and the strength of the fibers is relatively high so that the failure of the composites always occurs due to pull-out of the fibers, by fracture either at the fiber-matrix interface or in the bulk of matrix. We use the PA hydrogel, P(NaSS-*co*-DMAEA-Q), as the matrix, and perform experiments to alter the matrix toughness to study its effect on the toughness of the soft composites. Firstly, we varied the effective PA gel toughness by changing the tearing velocity, taking the advantage of the strong viscoelasticity of PA gels due to dynamic Coulombic interactions between oppositely charged ionic groups. Secondly, we tuned the PA gel toughness using saline solutions, because the ionic bonds in the PA gel are sensitive to ionic strength. Finally, to expand our understanding of this system and attempt to understand the universality of the relationship between matrix toughness and composite toughness, we further selected a series of weak polyacrylamide hydrogels and a commercially available polydimethylsiloxane elastomer as soft matrices. Through these experiments, we have discovered a *universal* scaling law between the toughness of soft matrix and that of the composite at the given fiber pull-out mechanism. This discovery on the importance of matrix toughness in FRSC systems gives a good guide towards the design of extremely tough composites from various soft materials such as hydrogels and elastomers.

In **Chapter 5**, focus is on understanding the role of interfacial interaction in the synergistic toughening of woven fabric reinforced hydrogel composites. To address this issue, we tuned the interfacial adhesion while keeping the toughness of the PA hydrogels as constant by using the original and silane-treated glass fibers (*s*-GF). The original glass substrate is hydrophilic; while the silane-treated glass fibers show significant hydrophobicity. To understand the importance of interfacial forces between the hydrogel and fabric, a fiber pull-out test was performed. The results show that the maximum debonding force is significantly lower than that of the untreated fiber bundles in the equilibrium PA hydrogel matrix. By using them to fabricate the fiber reinforced composites, after the tearing test, the fracture samples show that the deformation zone of PA-*s*-GF hydrogel composite also appears to have dissipated less energy than that of the PA-GF hydrogel composite. Accordingly, it was found that the PA-*s*-GF hydrogel composite shows a decreased peak tearing force, demonstrating a reduced crack resistance capacity. The tearing energy,  $T$ , of the PA-*s*-GF hydrogel composite with different sample widths also decrease accordingly compared to the PA-GF composite. The above finding demonstrates that good interfacial adhesion between the tough hydrogel matrix and the woven fabric is necessary for achieving highly tough fabric-reinforced hydrogel composites.

In **Chapter 6**, focus is on developing robust nonwoven microfiber reinforced hydrogel composites with very low fiber loadings. To address this issue, we demonstrate a novel fiber reinforced physical hydrogel composite by incorporating *nonwoven* glass microfiber fabric (*n*GF) into the tough PA hydrogel matrix. Compared to woven fiber fabric, the *n*GF shows relatively good homogeneity and flexibility in geometry, and acts as reinforcement filler in the composites. Because of the high aspect ratio of fibers and the preparation technique, fibers in the *n*GF sheet exhibit a nearly two-dimensional (2D), random orientation in the plane direction during the *in situ* radical polymerization. Due to this orientation, the resultant hydrogel composites show structural anisotropy, similar to natural fibrous tissues. Compared with neat PA hydrogel, the fracture strength and modulus of PA-*n*GF composites were enhanced from  $\sim 0.35$  to  $\sim 3.5$  MPa and from  $\sim 0.11$  to  $\sim 13.5$  MPa, respectively. Also, the fracture energy reached  $>30,000$  J m<sup>-2</sup>. Thus, the PA-*n*GF composites possess extremely high resistance to crack propagation. In addition, systematic understanding of the effect of reinforcement fiber on the structure of the PA-*n*GF hydrogel composites is also carried out in this chapter. The results are in agreement with the mechanical properties. Therefore, this work further confirms the universality of the material concept proposed in this dissertation for achieving robust soft composites.

In brief, in this dissertation the energy-dissipative fiber reinforced hydrogel composites have been successfully developed and demonstrated extremely high stiffness, strength, and toughness. Systematic study on the influence parameters has indicated that the energy-dissipative soft matrix plays a critical role in the synergistic toughening of fiber reinforced composites. In addition, the interfacial adhesion between the tough hydrogel matrix and the fibers may also influence the mechanical properties of the composites. This work provides a good guide towards the universal design of soft composites with extraordinary fracture resistance capacity.