学 位 論 文 の 要 約
Summary of Doctoral Dissertation

博士の専攻分野の名称　博士（生命科学）　氏　名　　黄　以万
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学 位 論 文 題 名
Title of Doctoral Dissertation

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

In this dissertation, four issues were proposed in the general introduction: i) Fabrication and mechanical properties of robust woven fabric reinforced polyampholyte hydrogel composites; ii) Understanding the role of energy dissipation of the matrices in the synergistic toughening of the soft composites; iii) Understanding the role of the interfacial adhesion in the synergistic toughening of the soft composites; iv) Developing robust nonwoven microfiber reinforced polyampholyte hydrogel composites with very low fiber loadings. Based on the systematic study, the conclusions of each chapter are summarized as follows:

In **Chapter 3**, we have systematically studied the width-dependent fracture behaviors of the composites and understood the synergistic effect in mechanical properties. The hydrogel composites show width-dependent tearing properties and follow different failure modes depending on the different fracture mechanisms. Interestingly, the composites can achieve a tearing energy plateau (T_p) in a much smaller width compared with the neat GF, and the T_p value highly reaches ~1,000 kJ m^{-2}. By optimizing the geometry of the neat GF, the sample width of the composites for achieving the T_p value can be further shifted to a relatively tiny size (~10 mm), which makes the material more useful for practical applications. Additionally, the composites exhibit strong synergistic increases in fracture energy and tensile properties far beyond the simple combination of the neat components. Our composites also contain sufficient water (~38 vol%) and are encompassed by biocompatible hydrogels, structurally similar to some load-bearing fibrous tissues. We believe that this study may provide a simple strategy to develop extremely strong, tough, flexible, and biocompatible soft materials. Therefore, this work is very important not only for the design of structural biomaterials, but also for some general applications, for example, soft robotics and load-bearing flexible devices.

The highly energy-dissipative polyampholyte (PA) hydrogel matrix has been proven to play a critical role in achieving extremely tough fabric reinforced hydrogel (PA-GF) composites that far exceed what could be expected from simply mixing the neat components. In **Chapter 4**, to *universally* explore the relationship between matrix toughness and composite toughness in fabric reinforced soft composites (FRSCs), a series of matrices, including *weak* polyacrylamide hydrogels and a commercially available polydimethylsiloxane *elastomer*, were further selected as soft matrices to create soft composites. The results demonstrate that for a given fabric geometry, the composite toughness is correlated to the matrix toughness, following an empirical power-law equation, $T_c = 220 T_m^{0.64}$, over two orders of magnitude. This relationship is associated with the energy dissipation of the soft matrix phase by the deformation and fracture of the matrix during fiber pull-out. By selecting soft matrix materials that can dissipate large amounts of energy and possess optimized interfacial bonding, strong synergetic effects can be achieved, and one can develop composites with toughness far beyond what would be achieved by simple additive rule of mixtures. The results match the synergistic increase in mechanical properties seen in tough biological materials. This work provides a good guide towards the design of FRSCs with extraordinary fracture resistance capacity.

In **Chapter 5**, the interfacial adhesion has been understood to play a role in achieving extremely tough fabric reinforced hydrogel (PA-GF) composites. To understand 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. Firstly, a fiber pull-out test was performed, and the results showed 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 showed 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. Then, it was found that the PA-*s*-GF hydrogel composite showed 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 decreased accordingly compared to the PA-GF composite. Therefore, the above evidences demonstrate 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**, to further confirm the priority of the material concept proposed in this dissertation for achieving robust soft composites, nonwoven microfiber reinforced hydrogel composites have been developed by incorporating *nonwoven* glass microfiber fabric (*n*GF) into the tough PA hydrogel matrix. The resulting PA-*n*GF composites have showed structural anisotropy due to the orientation of microfibers and the good interfacial adhesion between the components. Compared with neat PA hydrogel, the reuslts show that the fracture strength and modulus of PA-*n*GF composites were enhanced from ~0.35 to ~3.5 MPa and from ~0.11 to ~13.5 MPa, respectively. Also, the fracture energy reached >30,000 J m^{-2}. 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 was also carried out in this chapter. The results are in agreement with the mechanical properties. Therefore, this work has further proved the universality of the material concept proposed in this dissertation for achieving robust soft composites.