Abstract of Doctoral Dissertation

Degree requested Doctor of (Life Science) / Pharmaceutical Science / Clinical Pharmacy Applicant's name CUI, WEI

Title of Doctoral Dissertation

Design and Development of Soft Fiber-Reinforced Polymer Composites with Extraordinarily High Crack Resistance
(非常に高い亀裂耐性を示すソフト繊維強化ポリマー複合材料の設計と創製)

Many industrial applications require anisotropic structural materials that can bear considerable load in tension while showing flexibility when bent or twisted. Soft fiber-reinforced polymers (FRPs), consisting of soft, rubbery matrices, and rigid fabrics, featuring high strength, high contact compliance, low weight and low flexural stiffness, are uniquely qualified for wide use such as in tires, conveyor belts, soft robotics, etc. However, a common problem of soft FRPs made from conventional rubbery matrices is their relatively low crack resistance (toughness), which consequently results in increased risk of disastrous failure during their lifespan.

The aim of this dissertation is to address this problem by designing extraordinarily tough soft FRPs for industrial applications. In the dissertation, we mainly focus on the following three important parts: 1) Selecting excellent matrices to fabricate extremely tough soft FRPs; 2) Understanding the energy dissipation mechanism of the resulting soft FRPs; 3) Proposing a universal design principle of extremely tough soft FRPs.

In **Chapter 1**, outline of the dissertation is discussed.

In **Chapter 2**, a brief view on the concept of crack resistance (toughness) is introduced. Meanwhile, common experimental methods to characterize the crack resistance of a material are explained. Based on the lessons learned from nature, basic strategy to enhance the crack resistance of materials is put forward. This chapter is helpful to initially understand why materials with a composite structure always show fantastic crack resistance.

In **Chapter 3**, the design strategy of extraordinarily tough soft FRPs by selecting excellent matrices is introduced. Viscoelastic matrices that are adhesive, soft, and tough are utilized to combine with commercial fiber fabrics. The three key properties of the matrices result in composites showing unique features that are totally different from traditional soft FRPs. The strong adhesion between fibers and matrices enables a strong interface, which ensures both fibers and matrices to dissipate energy over a large area; The softness of matrices gives extremely high fiber/matrix modulus ratio, leading to extraordinarily large energy dissipation zones that are on the order of centimeters; The tough matrices also show energy dissipation density comparable to fibers, contributing to the high energy dissipation density of composites in the dissipation zone. Therefore, the fabricated composites are expected to demonstrate an extremely high crack resistance.

In **Chapter 4**, the mechanical properties of the prepared soft FRPs are investigated. The highly anisotropic composites demonstrate multiple fantastic properties such as high strength, high toughness, and low density, which can be rarely achieved by other material systems. The soft FRPs can also be polymerized from thermal initiation besides photo initiation, broadening their potential applications in industry. Moreover, strong and tough soft FRPs can be obtained from a various combination of fabrics and matrices that are adhesive, soft, and tough, enabling diversified choices for fabricating tough soft FRPs according to the operating environment.

In **Chapter 5**, the energy dissipation mechanism of soft composites is elucidated. By relating the tearing fracture energy with the sample width, it is found that the soft FRPs show a size-dependent fracture behavior. When the sample width is below a characteristic width, w_1, the fracture behavior of the soft FRPs is fiber pullout and matrix failure. In this region, the fracture energy of the materials is determined by the matrix toughness, fiber geometry, and sample width based on a fiber pullout model. When the sample width is above w_1 but below another critical width, w_2, the fracture behavior of the soft FRPs is concurrent fiber pullout and fracture, and matrix failure. In this region, the fracture energy of the materials is initially governed by fiber fracture but then by fiber pullout after a certain number of fibers are broken. This mixed-mode fracture process is still not well understood. We expect that this region can be modeled through a serial combination of both

fiber pullout and fracture mechanisms, and we will investigate this mixed-mode region in future work. When the sample width is above w_2, the fracture behavior of composites is mainly fiber fracture and matrix failure, and soft FRPs show the intrinsic size-independent fracture energy. In this region, the intrinsic fracture energy (Γ) is decided by the force transfer length (l_T) as well as the energy dissipation density (W), as $\Gamma = W \cdot l_T$. We show that force transfer length (l_T) is related to the fiber/matrix modulus ratio while the energy dissipation density (W) results from the volume weighed average work of extension at fracture of both components. The results generate a universal design principle of extremely tough composite materials. That is, maximizing force transfer length (l_T) by maximizing the fiber/matrix modulus ratio and enhancing energy dissipation density (W) by using energy-dissipative components. By maximizing both l_T and W, we successfully fabricate composites that show fracture energy as high as 2500 kJ m^{-2}, exceeding any best-in-class tough materials including metals.

In **Chapter 6**, we apply the design principle to hydrogel system, aiming to develop crack resistant composite hydrogels. Alginate hydrogels dried in confined condition are employed as the rigid skeleton. Polyacrylamide hydrogels are incorporated into the skeleton as soft matrices. The modulus ratio of the rigid skeleton to the soft matrix can be as high as 10^5, which is conducive for a large force transfer length. Meanwhile, the alginate skeleton has an energy dissipation density comparable to strong and rigid commercial fibers, which facilitates high energy dissipation density of the resulting composite gels. The resulting composite hydrogels show improved tensile and tearing properties compared with components and demonstrate an extraordinarily high crack resistance that is superior to common tough hydrogels.

In **Chapter 7**, conclusions of the whole dissertation are summarized.