Abstract of Doctoral Dissertation

Degree requested Doctor of Soft Matter Science

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Title of Doctoral Dissertation

Study on Bone-Inspired Soft/Hard Composite with Unique Toughening Mechanism Through Multiple Sacrificial Structure
(骨に着想を得た複数の犠牲構造による強靭化機構を備えたソフト/ハード複合材料に関する研究)

Bones exhibit exceptional mechanical properties, such as stiffness and toughness, due to their hierarchical organization and energy dissipation mechanisms. These properties arise from a synergistic interaction between calcium phosphate (CaP) minerals, collagen fibrils, and non-collagenous proteins (NCPs), which form static and dynamic cross-links. At the molecular level, covalent bonds transfer mechanical stress to ionic sacrificial bonds, dissipating energy and preventing catastrophic fracture. This sacrificial bond mechanism, combined with bone's hierarchical porous architecture, enables bones to achieve superior toughness and load-bearing capacity. Inspired by this natural system, this dissertation introduces a bioinspired composite material that mimics bone's intrinsic toughening mechanisms.

The composite consists of a porous biphasic calcium phosphate (BCP) ceramic skeleton and a poly(acrylic acid) (PAAc) hydrogel matrix. The ceramic skeleton is fabricated using a sponge templating method that replicates the trabecular architecture of spongy bones. In this process, a polyurethane sponge is coated with hydroxyapatite (HAp) slurry, followed by sintering, which results in a highly porous, interconnected structure. This sintering process preserves the hierarchical porosity of the template while also partially converting HAp into β-tricalcium phosphate (β-TCP), forming a biphasic ceramic structure. The coarse and intermediate pores (ranging from 540 to 760 μm) mimic the size range of trabecular bone pores, while intermediate and fine pores, created during the combustion of the sponge and sintering, enhance the surface area available for interaction with the hydrogel matrix.

The biphasic structure of the skeleton optimizes both its mechanical and chemical performance. HAp ensures structural integrity, while β-TCP facilitates the controlled release of calcium ions, enabling ionic bonding with the hydrogel. This hierarchical, porous architecture ensures efficient stress transfer, energy dissipation, and enhances the adhesion between the hard ceramic skeleton and the soft hydrogel matrix, closely mimicking the toughening mechanisms observed in natural bone.

Mechanical testing revealed that the composite exhibits an exceptional combination of high toughness and flexibility, attributed to its unique structural design and energy dissipation mechanisms. Uniaxial tensile tests demonstrated that energy dissipation occurs through multiple sacrificial bonds formed by the fracture of the ceramic skeleton, calcium-mediated ionic bonding within the hydrogel matrix, and the new interactions between the newly exposed ceramic surfaces and the PAAc hydrogel. The contribution of these sacrificial bonds is further validated by cyclic tensile tests, which show significant energy dissipation

(91.78 kJ/m³) in the composite compared to conventional hydroxyapatite-particle composites. This underscores the critical role of these sacrificial bonds in enhancing the composite's mechanical performance.

Furthermore, the fracture of the ceramic skeleton generates new bare surfaces that establish additional interfacial interactions with the hydrogel matrix, creating another sacrificial structure within the composite system. These calcium-mediated interactions between the newly exposed ceramic surfaces and the PAAc hydrogel matrix contribute to the composite's self-healing abilities. Healing ratios of up to 76% were observed in composites with a lower cross-linker concentration in the hydrogel matrix, following a 1-hour waiting period between cycles. This highlights the importance of flexible polymer chains, which readily adapt to the new surfaces, re-establish ionic interactions, and enable partial recovery of mechanical properties.

Optimization of the composite's properties was achieved by tuning the ceramic skeleton's pore architecture. Two skeletons, S1 and S2, were fabricated with differing pore sizes and strut lengths. The S2 skeleton, characterized by smaller and more uniform pores, exhibited superior mechanical performance due to its increased surface area and more homogeneous stress distribution. The composite containing the S2 skeleton achieved a strain at break of 5.4 mm/mm and an energy absorption capacity of 1002 kJ/m³, compared to 4.8 mm/mm and 625 kJ/m³ for the S1-based composite. The smaller pore structure of the S2 skeleton enabled stronger interfacial adhesion and efficient load transfer between the ceramic and hydrogel phases.

These findings conclude that the multiple sacrificial bonds, formed through the fracture of the ceramic skeleton, calcium-mediated ionic bonding, and the new interactions between exposed ceramic surfaces and the hydrogel matrix, work synergistically to enhance the composite's toughness, energy dissipation, and self-healing capabilities. By integrating these mechanisms, the composite achieves superior performance, paving the way for advanced applications in biomimetic materials and tissue engineering.