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ORIGINAL RESEARCH

Self-healing quadruple shape memory hydrogels based on coordination, borate bonds and temperature with tunable mechanical properties

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Abstract
Quadruple shape memory hydrogels were prepared by one-pot in situ copolymerization using acrylamide, acrylic acid, agar, and poly(vinyl alcohol). The hydrogels have multiple reversible shape memory based on the coordination bonds of poly(acrylic acid) with Fe^{3+}, borate bonds based on poly(vinyl alcohol), and hydrogen bonds of agar and poly(vinyl alcohol). The hydrogel demonstrated tunable mechanical properties when the hydrogels immersed in different solutions for various lengths of time. After immersion in the ferric chloride solution, tensile stress and elastic moduli of the hydrogels were enhanced with increasing soaking time. After immersion in the borax solution, tensile stress first increased and then decreased with increasing soaking time. Due to the reversible effect of the borate bond, the hydrogel achieved ultra-fast self-healing. The hydrogel after immersion in borax solution could begin healing in 24 h and healed at 44 h. The tensile stress and tensile strain of the self-healing hydrogel increased when soaking time increased from 48 to 96 h, and tensile stress at healing times of 96 h was nearly as the same as that of the original hydrogel when compared with it. The combination of tunable mechanical properties, efficient recoverability and self-healing abilities coupled with facile preparation endowed the developed hydrogel a high potential for use in biomedical applications.

Keywords Shape memory hydrogels · Borate bonds · Coordination bonds · Hydrogen bonds · Self-healing property

Introduction

Shape memory hydrogels (SMHs) have the advantages of high deformability, good shape recovery performance, and environmental responsiveness [1], and can be applied in biomedicine [2], biomaterials such as artificial tissue [3] and absorbent fiber [4], aerospace [5], and other fields. SMHs can be constructed by various intermolecular and intramolecular interactions and dynamic covalent bonds.

The physical interactions, especially hydrogen bond, and coordination bonds have been applied to fix and recovery the SMHs. The reversibility of hydrogen bonds gives shape memory hydrogel adjustable mechanical properties. The widely used material with hydrogen bond is poly(vinyl alcohol) (PVA). Chen et al. [6] demonstrated a PVA with programmable multistep shape recovery processes in water via a wettability contrast strategy. Different forms of hydrogen bonds give different properties to materials.

Hybrid hydrogels with different hydrogen bonds provide an additional platform to dissipate energy and heal the broken network structure. Wang et al. [7] reported a shape memory hydrogels cross-linked with hydrogen bonding between PVA and tannic acid (TA). The stronger H-bonding between PVA and TA functioned as the “permanent” cross-linked, and the weaker H-bonding between PVA chains as the "temporary" cross-linked. The mixtures of PVA and agar have also been reported.

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