Design, Synthesis, Investigation of Mechanical Properties and Functional Applications of Metal ion Cross-Linked Strong and Tough Polymer Hydrogel Materials

Abstract

Recently, interest has surged in creating strong, flexible multifunctional hydrogel materials. Polymer hydrogels with dynamic cross-linked networks show promise, yet conventional hydrogels still face mechanical issues like weakness, brittleness, and low fatigue resistance, often fracturing under stresses below 1 MPa. In this thesis, metal ion cross-linking strategy was exploited to access mechanically robust and tough hydrogels and the multifunctional applications of these materials were demonstrated. A simple polymer hydrogel poly(acrylamide-co-maleic acid) was taken as the basic material and incorporation of metal ion-dicarboxylate cross-links into this network was systematically investigated. By incorporating Ca^{2+}-dicarboxylate cross-links in situ (Ca^{2+} ions added before polymerization), a moderately strong (tensile strength ~ 250 kPa), highly stretchable (breaking strain ~ 1500%), self-healing and adhesive, tough (fracture energy ~ 1500 J m^{-2}) hydrogel with anti-freezing and anti-dehydration characteristics was accessed. To enhance the mechanical strength of these materials, the as prepared poly(acrylamide-co-maleic acid) hydrogel was cross-linked by Fe^{3+} ions post polymerization to furnish hydrogels with high tensile (~ 1 MPa) and compressive strength (~ 13 MPa). These hydrogels demonstrated shape memory and programmable actuation behaviour. To address the issue of reduced stretchability (breaking strain ~ 400%) of the Fe^{3+} cross-linked hydrogels, hydrophobic association as additional cross-links was introduced to synthesize poly(acrylamide-co-maleic acid-co-butyl acrylate) polymer hydrogels, which were then cross-linked with Fe^{3+} ions. The tensile (~ 3 MPa) and compressive (~ 60 MPa) strengths increased significantly with improved stretchability (~ 600%). The presence of Fe^{3+}-dicarboxylate cross-links resulted in colorimetric changes in response to pH change of the medium, which was utilized to demonstrate application in data encryption-decryption. Synergistic effects of hydrophobic association, anisotropic orientation and salting-out effect induced aggregation were also studied to further enhance the hydrogel mechanical properties (tensile strength ~ 11 MPa, stiffness ~ 3 MPa) without compromising toughness (work of fracture ~ 15 MJ m^{-3}) of these hydrogel materials. All the hydrogels discussed in this work showed good self-recovery and anti-fatigue characteristics, suitable for repeated load-bearing applications. Multifunctional applications of the hydrogels - as flexible resistive strain sensors, for monitoring human limb movements, as electrolytes in flexible supercapacitor devices and as EMI shielding materials – have been demonstrated.

Keywords: Tough hydrogel, Anti-fatigue, Anti-freezing, Strain sensing, Flexible supercapacitor, Shape memory, Anisotropy