

Non-covalent Tough Hydrogels for Functional Actuators

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ABSTRACT

Tough and responsive hydrogels have recently attracted great research interests for potential applications in artificial muscles, soft robotics, and actuators, etc. This paper overviews our recent progresses in the design and synthesis of hydrogels with very high strength and toughness, and actuators based on these hydrogels. Inorganic nanospheres, nanorods, and nanosheets are exploited as multi-functional crosslinkers to adsorb or bond with hydrophilic chains, leading to hydrogels with very high strength, toughness, fatigue resistance, and/or self-healing. Introduction of functional groups including ionic monomers and amino groups results in hydrogels responsive to pH, ionic strength and electric field. Besides, ionoprinting has been used to change local crosslink density based on reversible chelating/decomposition of metal ions with functional groups. This process is rapid and thus enables reversible and rapid actuation of hydrogel devices. Our studies will further aim to develop sophisticated devices by assembling hydrogel actuators.

INTRODUCTION

Hydrogels have been widely recognized as soft and wet materials with great potentials applications as tissue engineering scaffolds, artificial muscles, and soft robotics, etc. The weakness and fragility of conventional hydrogels have seriously limited their applications [1, 2]. Recently, numerous strategies have been proposed to improve the mechanical properties of hydrogels [3]. Representative ones include slide-ring hydrogels [4], double network (DN) hydrogels [5, 6], nanoparticle-crosslinked hydrogels [7-9], and hydrogels comprised of non-covalent or supramolecular polymer networks [10-12]. The reversible non-covalent or supramolecular interactions may serve as synergistic energy dissipation mechanism, and result in high strength and toughness. Moreover, non-covalent interactions, including hydrogen bonding [13], hydrophobic association [14], electrostatic interaction [15], and supramolecular recognition [16], etc, may decompose, weaken, or re-build upon external stimulus. Therefore, many non-covalent hydrogels are responsive, which are also known as smart hydrogels, and have been demonstrated with great success in fabricating hydrogel actuators that are actuated by light, pH, salt, magnetic field, and electric field, etc.

Recent studies in Ningbo Institute of Materials Technology and Engineering of Chinese Academy of Sciences have developed a series of new concept tough and responsive hydrogels. Inorganic nanospheres, nanorods, nanosheets, and triblock copolymer micelles are exploited as multi-functional crosslinkers to adsorb or bond with hydrophilic chains, leading to hydrogels with very high strength, toughness, fatigue resistance, and/or self-healing. Such new concept hydrogels are introduced with functional groups including ionic monomers, amino groups, and/or host/guest units to create hydrogels responsive to pH, ionic strength, electric field, and competitive molecules, etc. Such polyelectrolyte hydrogels have been used to create actuators that are actuated by electric field or redox-induced ionoprinting.

EXPERIMENTAL DETAILS

Nanoparticles including silica nanospheres and attapulgite (ATP) nanorods (diameter 21 nm, average length 760 nm), as well as those modified with vinyltriethoxysilane (VTEOS), were used for in situ polymerization of 2-acrylamido- 2-methylpropanesulfonic acid (AMPS monomers) with the presence of very small amount N,N'-methylenebis (acrylamide) (MBAA) crosslinkers and potassium persulfate (KPS) initiator at 60 °C for 10 h. The obtained nanoparticle/PAMPS hydrogels were swollen in acrylamide (AAm) solution for a second free radical polymerization with very low MBAA content [17].

Sodium Montmorillonite (MMT) was exfoliated in water under rigorous agitation and further exfoliated by AAm monomers with the presence of KPS and N,N,N',N'-tetramethylethylenediamine (TEMED) as catalyst. In situ free radical polymerization was conducted at 50 °C [18].

Pluronic F127 (PEO₉₉-PPO₆₅-PEO₉₉) triblock copolymer was acrylated on both ends by using acryloyl chloride. The obtained F127DA formed nanomicelles in water and solutions of AAm and ionic monomers (e.g., methyl chloride quaternized N,N-dimethylamino ethylacrylate or DMAEA-Q) for subsequent free radical polymerization initiated by KPS at 50 °C [19, 20].

Mechanical tests were conducted by using an Instron 5567 machine (Instron, MA) in both compression and tensile modes. Tensile tests were conducted on dumbbell samples (5.5 mm diameter, 45mm length, and 5 mm gauge length) at 100 mm/min. Compression tests were performed on cylindrical samples (diameter and height) at 10% strain/s for up to 98% strain to protect the load cell. Cyclic compression tests were performed with specified maximum strains in order to investigate the energy dissipation and fatigue resistance of the hydrogels.

DISCUSSION

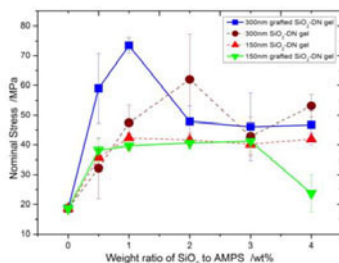


Fig. 1 Compression strength of silica reinforced PAMPS/PAAm double network hydrogels.

PAMPS/PAAm double network hydrogels have showed outstanding mechanical strength [5], but are softened after first loading due to the internal fracture of PAMPS network[6]. Herein, PAMPS/PAAm DN gels showed a compression strength of 20 MPa and fracture strain of 92%. By using silica nanoparticles as fillers and crosslinkers, the compression strength (σ_c) of PAMPS/PAAm DN gels were improved. With the presence of silica nanoparticles, the σ_c was increased from about 18 MPa to 40 MPa (Figure 1). As the nanoparticles are modified with vinyl groups, the σ_c values are further improved, showing a maximum of 73 MPa at 1wt% silica

content (Figure 1). These results suggest that there are synergistic contributions from both chemical bonding and physical adsorption of polymer chains to the vinyl-modified silica nanoparticles.

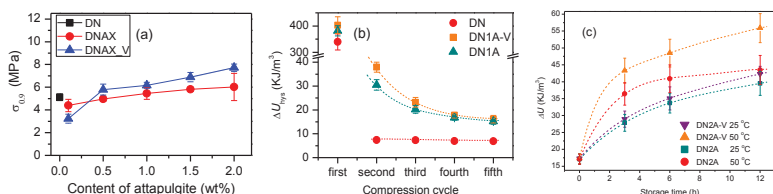


Figure 2 (a) compression strength at 90% strain of DN gels composited with bare ATP (DNAX) and vinyl-modified ATP nanorods (DNAX_V) as a function of ATP content. (b) Residual energy dissipation of DN1A-V and DN1A gels upon cyclic compression loadings, in comparison to conventional DN gels. (c) Recovery of energy dissipation after storage at different temperatures.

Similar toughening effects are also observed for nanocomposite double network hydrogels containing vinyl-modified ATP nanorods (Figure 2a). With increasing ATP nanorods, the compression strength could be higher than 65 MPa and the hydrogels did not fracture at 98% strain. At given ATP contents, the modified ATP nanorods showed better reinforcement than bare ATP nanorods (Figure 2a). Moreover, the compression toughness of these hydrogels decreased upon cyclic loading/unloading tests, but leaving a small hysteresis. This residual hysteresis or energy dissipation increased with increasing ATP content. Besides, the residual energy dissipation (ΔU_{hys}) is higher for gels containing vinyl modified ATP nanorods than those with bare ATP nanorods (Figure 2b). After five cycles, the gels could partly recover to the energy dissipation level of the second cycle by restoring at elevated temperatures for different durations (Figure 2c). This behavior is quite different from conventional DN gels, which completely lose energy dissipation capability after first loading. It is likely that, in addition to chemical bonding to ATP surface, physical adsorption of PAAm chains to ATP surfaces may contribute to the toughening effect. Besides, such physical adsorption is reversible, which allows for partial recovery of energy dissipation mechanism under appropriate conditions.

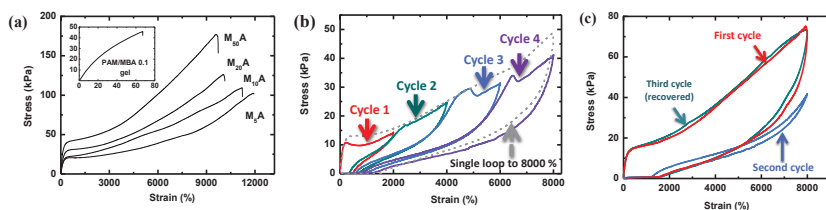


Figure 3 (a) Representative tensile stress-strain curves of PAAm/MMT nanocomposite hydrogels, (b) Cyclic loading-unloading curves of nanocomposite hydrogels with 5wt% MMT, and (c) stress-strain curves of first, immediate second, and third loading-unloading tests after recovery of hydrogels with 10wt% MMT.

Clay nanosheets have been demonstrated to adsorb hydrophilic monomers and initiators etc for in situ free radical polymerization to generate physically crosslinked hydrogels. Such nanocomposite hydrogels have showed extraordinary extensibility, strength, and toughness. Different from synthetic clays (e.g., laponite, diameter ~ 30 nm), sodium MMT has larger lateral dimensions (> 100 nm) and thus may adsorb more hydrophilic monomers (AAm) and polymer chains. By using exfoliated MMT nanosheets as physical crosslinkers, PAAm/MMT nanocomposite hydrogels were obtained and showed ultra high stretchability. As MMT content was increased from 0.5wt% to 5wt%, 10wt%, 25wt% and 50%, the fracture elongation were higher than 9000% and up to 12000% (Figure 3a). Besides, the fracture energy was as high as 10 MJ m^{-3} . Upon stretching, the PAAm chains gradually detached from clay surface, resulting in yielding and a large hysteresis upon an immediate subsequent loading. The second loading to a higher strain resulted in overlapping to the previous unloading till a higher strain. Interesting, new yielding occurred, indicating further chain detachment (Figure 3b). Such chain detachment resulted in a nearly complete loss of energy dissipation capability. After the first loading-unloading cycle, an immediate second cycle showed very low hysteresis loop (Figure 3c). After restoring at 50°C for 10 h, a third cycle test showed a complete overlapping to the first loop (Figure 3c), suggesting a full re-adsorption of polymer chains to MMT nanosheets. These results imply that these hydrogels are self-healable. In fact, short rods of these nanocomposite hydrogels spontaneously and completely healed upon contacting, dehydrating, and rehydrating[18].

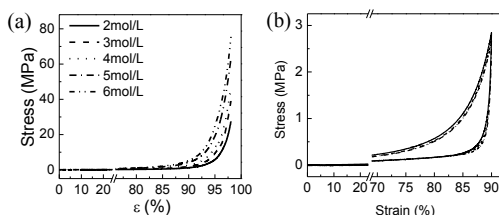


Figure 4 (a) Representative compression stress-strain curves of F127DA micelle crosslinked PAAm gels with different AAm monomer concentrations (2, 3, 4, 5, and 6 mol/L). (b) Cyclic compressive loading-unloading stress-strain curves of nanomicelle crosslinked PAAm gels.

Despite of the high stretchability and self-healing, these nanocomposite hydrogels are lack of adequate tensile and compression strength and fatigue resistance. Alternatively, vinyl functionalized triblock copolymer (F127DA) micelles were used as crosslinkers for in situ copolymerization with hydrophilic monomers. No chemical crosslinkers are needed. This one-pot procedure is convenient for the synthesis of hydrogels in any moulds and leads to hydrogels with accurate replication of mould details. The obtained hydrogels show outstanding strength, toughness, and fatigue resistance. No fracture occurred upon compression at 98% strain and 80 MPa stress (Figure 4a). The hydrogels showed remarkable energy dissipation hysteresis upon loading/unloading tests. Interestingly, completely overlapping hysteresis loops are observed upon cyclic loading-unloading tests, suggesting outstanding fatigue resistance that has rarely been observed for most other tough hydrogels (Figure 4b). The self-assembled micelles, based on amphiphilic interactions, may serve as reversible energy dissipation mechanism for these novel hydrogels.

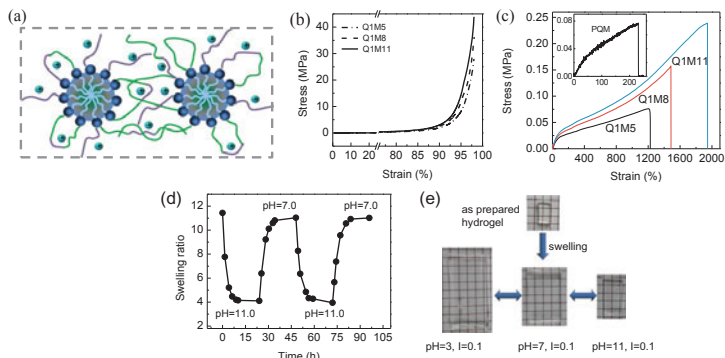


Figure 5 (a) Schematic illustration to the structures of F127DA micelle-crosslinked DMAEA-Q/PAAM hydrogels. Representative (b) compressive and (c) tensile stress-strain curves of nanomicelle crosslinked DMAEA-Q/PAAM (Q_xM_y) gels (x and y are molar ratio of Q and M monomers). (d) Cyclic swelling/deswelling of DMAEA-Q/PAAM gels upon exposure to pH 7 and 11. (e) Photo images of the gels swollen in pH 3, 7, and 11 buffer solutions.

It is widely known that F127DA micelles are stable in aqueous solutions and insensitive to changes in ion strength. This is advantageous for the synthesis of polyelectrolyte hydrogels, which has been a challenge for some other systems since organic electrolyte monomers may break the ionic equilibrium of reactants [21]. Herein, cationic DMAEA-Q (Q) monomers were copolymerized with F127DA micelles and AAm (M) monomers at 50 °C (Figure 5a). The obtained gels also showed outstanding compressive and tensile properties. With increasing cationic monomer content (from Q1M11 to Q1M8 and Q1M5), the compressive strength was changed from about 30 MPa to 40 MPa (Figure 5b), while the tensile elongation was decreased from 1800% to 1200% (Figure 5c).

The charged hydrogels are responsive to pH changes through swelling/deswelling. As the prepared hydrogels are immersed in pH 7 buffer solution with ion strength of 0.1M, the volume expanded (Figure 5d,e). As pH was decreased to 3, the gel was further swollen. On the other hand, as the pH was increased to 11, the gels shrank. As the gels were shuttled between pH 7 and 11, the volumes were cyclically changed (Figure 5d). Similarly, the hydrogel volume was also sensitive to ion strength. As the ion strength was decreased to 0.05 M, the gel was swollen. As the ion strength was increased to 0.2 M, the gel was shrunk. Such swelling/deswelling behavior was also reversible.

Polyelectrolyte hydrogels have been demonstrated to be actuated under electric field[22]. The mechanical strength of hydrogel actuators is critical to sustain cyclic actuation and for potential loading, which, however, remains challenge. Our nanomicelle-crosslinked hydrogels carrying positive charges with high strength and toughness are responsive to electric field. As a gel beam is immersed in 0.1 M Na_2SO_4 solution, it starts to bend toward the anode under a 2V cm^{-1} electric field is supplied (Figure 6a). The bending rate increases with the increasing electric field strength. As the electric field is reversed, the bending direction is immediately reversed. As the electric field direction is periodically changed at a low frequency, the hydrogel beam experiences cyclic actuations (Figure 6b). Such simple actuation may serve as a basic principle

and unit for the fabrication of complicated actuators by, for example, assembling hydrogels with different actuation behaviors into sophisticated devices. This could be an interesting and promising topic warranting more studies.

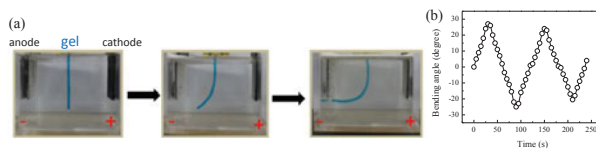


Figure 6 (a) Actuation of micell-crosslinked anionic hydrogel beam in Na_2SO_4 solution under electric field. (b) Cyclic bending of gel beam under alternating electric field.

Electric field-driven actuation is usually slow and limited by the actuation mode. Variation of local crosslink density of hydrogels has been demonstrated efficient to rapidly motivate the gels. We introduced primary amino groups to the PAAM/clay nanocomposite hydrogels in order to chelate with metal ions. As an iron cathode was contacted with the hydrogel, Fe^{3+} was released upon oxidation and chelated with the polymer chains at the contacting area. Thus, the local crosslink density was increased and the gel was bent quickly. Programmed Fe^{3+} printing led to controlled curling of the gel. As Fe^{3+} ions in the gels was reduced to Fe^{2+} , the local crosslinking was decomposed since Fe^{2+} has very low coordination constant with amino groups. Thus, the gel was swollen and recovered to the original shape. This reversible redox reaction was utilized to fabricate clamp-shaped gel actuators with a rapid actuation behavior. Such actuators have potentials for grabbing and release of small objects.

CONCLUSION

Hydrogels with outstanding strength, toughness, stretchability, and fatigue resistance have been synthesized by using nanoparticles and nanomicelles as crosslinkers. It is critical that non-covalent interactions (hydrogen bonding, physical adsorption, and amphiphilic association) serve as reversible energy dissipation mechanisms. As a result, the gels showed recovery or self-healing. Such toughening mechanisms have been utilized to synthesize polyelectrolyte hydrogels, which are responsive to changes in pH or ion strength. Tough polyelectrolyte hydrogels are actuated by electric field. Moreover, ionprinting causes enhanced local crosslinking through chelating metal ions. Reversible redox reaction of metal ions cyclically changes in local crosslink density, which results in reversible actuation of hydrogels. By incorporating non-covalent interactions with functional monomers, more tough, responsive, and functional hydrogels are to be developed for artificial muscles, sensors, and actuators.

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