



Processing tough supramolecular hydrogels with tunable strength of polyion complex



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ARTICLE INFO

Article history:

Received 23 February 2016

Received in revised form

19 April 2016

Accepted 20 April 2016

Available online 22 April 2016

Keywords:

Tough hydrogels

Processibility

Stimuli-triggered healing

Viscoelasticity

Polyion complex

Dynamic bonds

Supramolecular gels

ABSTRACT

The rapid developments of tough hydrogels have promoted the applications of this kind of soft materials in loading bearing systems. However, tough gels usually have poor processibility, which is crucial for the construction of complex structures with gels. In this paper, we demonstrate the processing of tough polyion complex (PIC) hydrogels by simple compression moulding or extruding, which relies on the distinct strength of ionic bonds during and after the processing. The PIC precipitates formed by mixing the solutions of polycation and polyanion, poly(3-(methacryloylamino)propyl-trimethylammonium chloride) and poly(sodium p-styrenesulfonate), are plasticized by saline solution with selected concentration. These raw materials, initially weak and viscoelastic, are easily processed into different shapes. After swelling the as-prepared gels in water to dialyze out the salt and counterions of PIC, tough equilibrated gels are obtained with the imposed shapes during processing. These gels with 50–70 wt% water show good mechanical properties, with tensile fracture stress, fracture strain and tearing fracture energy being 3.7 MPa, 700% and 8×10^3 J/m², respectively. These mechanical properties can be effectively tailored by tuning the charge ratio of PIC. However, the concentration of saline water has negligible influence on the mechanical properties of final equilibrated gels. The resultant PIC gels also exhibit stimuli-triggered healing properties owing to the dynamic and reversible nature of the ionic bonds. This study should promote the applications of tough PIC gels in structural elements of soft actuators and synthetic tissues.

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1. Introduction

Hydrogels are fascinating soft materials with large similarities to biological tissues, smart responsiveness to external stimuli and promising applications in tissue engineering, artificial organs, drug delivery, soft actuators, etc. [1–7] Conventional hydrogels are often mechanically weak and limited to the applications in which the mechanical strength is not highly concerned, such as drug delivery vehicles, cell cultural scaffolds and water absorbent materials [7,8]. However, many gel-like biological tissues, such as cartilages,

possess excellent mechanical properties rooted in their specific structures and combinations of different biomacromolecules [9]. In particular, the combination of rigid collagen fibrous matrix and abundant ground substance such as proteoglycan renders the cartilages with high toughness. Inspired by this, Gong et al. have developed double-network (DN) hydrogels with extremely high strength: the reported tensile strength and failure strain were 1–10 MPa and 1000–2000%, respectively, and the tearing fracture energy was 1000–6000 J/m² [10–12]. These DN gels usually consist of a highly crosslinked rigid polyelectrolyte network and a lightly crosslinked dense and ductile neutral polymer. There have been other kinds of tough hydrogels, including nanocomposite hydrogels and slide-ring gels, which greatly broaden the use of such soft materials in load bearing systems [13–20]. However, one major

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limitation of these tough gels is the lacking of processibility due to their permanent network structure.

More adaptive materials can be constructed by involving dynamic covalent bonds responsive to external stimuli [21–23] or noncovalent interactions such as hydrogen bond, metal coordination, and host–guest interaction [24–26]. Supramolecular hydrogels assembled from these dynamic noncovalent interactions may bear the capacity of processibility and stimuli-triggered healing. If the total strength of multiple weak interactions acting on one polymer chain is ensured to be comparable to that of strong covalent bonds, the supramolecular polymeric hydrogels would have high ultimate strength and toughness as well. Indeed, researchers have recently developed tough physical hydrogels based on this strategy. Short-range interactions such as multiple hydrogen bonding [27–29], metal coordination [30], hydrophobic association [31–33], and long-range electrostatic interaction [34–38] have been employed to toughen physical hydrogels. By copolymerizing oppositely charged monomers, or polymerizing one monomer in the presence of oppositely charged polyelectrolyte with equivalent charge, tough supramolecular hydrogels, termed as polyampholyte gels or polyion complex (PIC) gels, respectively, can be obtained due to the formation of compact PIC [34,37]. For example, the tensile strength and tearing energy of equilibrated PIC hydrogels of poly(3-(methacryloylamino)propyl-trimethylammonium chloride)/poly(sodium p-styrenesulfonate) (PMPTC/PNaSS) reached 4 MPa and $8 \times 10^3 \text{ Jm}^{-2}$, respectively, after dialyzing out the counterions [36,37]. These excellent mechanical performances are contributed by the wide spectrum of bonding strength in PIC: the relatively strong associations serve as quasi-permanent crosslinks to maintain the integrity and shape of gels, whereas the relatively weak associations behave as reversible and sacrificial bonds to dissipate energy in resisting fracture [34,36]. These gels also exhibit stimuli-triggered healing ability due to the dynamic nature of ionic bonds, which is not feasible for most chemical hydrogels.

To promote the use of hydrogels in practical applications, typically in diverse configurations, hydrogels are expected to have processibility as well as good mechanical performances. Tough gels usually have poor processibility. It is therefore desirable to find suitable approach to effectively process tough hydrogels by extruding, compression or injection moulding, as done to general polymers. Luo et al. have dissolved PIC gels in concentrated saline solution and reprocessed them into films, fibers and capsules by casting and injection [37]. However, the processibility in their study highly relies on a sol-to-gel transition, which limits the construction of more complex shapes. Weak physical gels can be easily reshaped because the internal noncovalent bonds are reversibly destroyed and reformed during processing [40,41]. If the strength of noncovalent bonds can be tentatively tuned in a single protocol, tough physical gels might be readily processed by extruding or moulding during the stage of relatively weak bonding, without affecting the ultimate strength and toughness after processing. The PIC hydrogels show distinct mechanical strength before and after swelling them in saline solution, implying different status of ionic bonding. Previous studies showed that the PIC gels maintain moderated toughness in saline solution with NaCl concentration (C_{NaCl}) less than 1 M, whereas they are dissolved in 4 M saline solution [37,39]. There should exist an intermediate amount of salt in bulk PIC gels to render them processibility. Schlenoff and co-workers have developed an approach to process compact PIC precipitates by addition of saline water, which plasticizes the precipitates to be thermally processible through normal extruders [42–46]. Thus obtained PIC gels of poly(acrylic acid)/poly(allylamine hydrochloride) (PAA/PAH) showed high strength and self-healing capacities, with tensile strength and fracture strain being 3 MPa and 500%, respectively [44]. This approach may be applicable

to PMPTC/PNaSS supramolecular hydrogels as well. The extruding usually requires specialized instrument and relatively large amount of raw materials; the cleaning up of the set-up takes massive time after processing. Therefore, it should be meaningful to study how to process tough PIC gels by simple compression moulding as well.

In this paper, we demonstrate that PIC precipitates from mixed polyelectrolytes with opposite charges, PMPTC and PNaSS, can be plasticized by saline water and used as raw materials to fabricate tough physical hydrogels. NaCl concentration, C_{NaCl} , together with the relative amount of saline water, serves as a key parameter that enables a processing window for the gels. In the presence of saline water with C_{NaCl} of 2–3.5 M, the polyion complexes form transparent viscoelastic hydrogels with modest strength, hence can be easily processed into different shapes by compression moulding. After peeling off and swelling the samples in water, tough hydrogels with prescribed shapes can be obtained. The effects of charge ratio of PMPTC/PNaSS and C_{NaCl} on the properties of equilibrated hydrogels are investigated. These gels with 50–70% water content show excellent mechanical properties, viscoelasticity and stimuli-triggered healing ability. This combination of processibility and multiple mechanical properties should broaden the application range of supramolecular tough gels in biomedical devices, soft actuators, etc.

2. Experimental section

2.1. Materials

Sodium p-styrenesulfonate (NaSS; anionic monomer, 90 wt% purity), 3-(methacryloylamino) propyltrimethylammonium chloride (MPTC; cationic monomer, 50 wt% aqueous solution), α -ketoglutaric acid (photoinitiator) were purchased from Sigma–Aldrich. NaCl was received from Sinopharm Chemical Reagent Co., Ltd. Millipore deionized water was used in all the experiments.

2.2. Preparation of PIC gels

The procedure to prepare PIC gels is depicted in Fig. 1. PNaSS and PMPTC were synthesized by polymerizing the precursor aqueous solutions of 1 M NaSS and 1 M MPTC, respectively, in the presence of 0.05 mol% (relative to the monomer) 2-oxoglutaric acid under UV light irradiation (365 nm wavelength, 7.5 mW/cm²) for 8 h. The viscous liquid was precipitated in ethanol and dried in the oven. Thus obtained PMPTC and PNaSS are transparent solids with weight-average molecular weight, M_w , of 4×10^3 and 1×10^6 g/mol, and polydispersity (M_w/M_n) of 1.5 and 3.4, respectively. The polymers were dissolved in water to prepare solutions with prescribed concentrations. PMPTC solution was prepared at concentration of 0.1 M repeat units. PNaSS solutions were prepared at concentrations of 0.095, 0.1, 0.105, 0.11, 0.115, 0.12, and 0.125 M repeat units. Then, PNaSS and PMPTC solutions with equal volume were slowly dripped from the syringes into 250 mL water in the beaker intensively stirred by a magnetic stirrer. The PIC precipitates with different charge ratio of PNaSS/PMPTC were dried in the oven at 110 °C and made into powder. To prepare PIC hydrogels, 25 mL saline water with selected concentration was added to 10 g precipitate in a centrifuge tube and kept at 90 °C for 6 h to obtain homogeneous and highly viscous liquid. The PIC solutions were centrifuged (Velocity 18R Refrigerated Centrifuge) under 14,000 rpm for 15 min to remove the bubbles inside. The samples were kept at 90 °C for 10 min to increase their fluidity and poured onto one hot (100 °C) polytetrafluoroethylene (PTFE) plate. Compression moulding was immediately performed on the viscoelastic sample at room temperature for 20 min, before a transparent hydrogel sheet with thickness of 1 mm was peeled off from

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