



Original article

Tough superabsorbent poly(acrylic acid) nanocomposite physical hydrogels fabricated by a dually cross-linked single network strategy



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ABSTRACT

In this work, we report a facile method for the preparation of tough and highly stretchable physical hydrogels by dual cross-linking composed of vinyl-hybrid silica nanoparticles (VSNPs) as multivalent covalent cross-linking and hydrogen bonding as physical cross-linking. Poly(acrylic acid) nanocomposite physical hydrogels (NCP gels) are obtained without adding any organic chemical cross-linkers. When the content of VSNPs is 0.7 wt% (relative to the monomer), the NCP gels exhibit good mechanical properties (fracture strength = 370 kPa, elongation at break = 2200%) and a high swelling capacity in both deionized water (2300 g/g) and saline (220 g/g). Meanwhile, the NCP gels have good recovery ability.

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1. Introduction

Polymer hydrogels have been extensively studied and used in tissue engineering [1,2], carriers for drug delivery [3,4], wastewater treatment, and disposable diapers [5,6] for their good biocompatibility and stimuli-response ability. Generally, hydrogels are moderately cross-linked networks of a hydrophilic polymer which can absorb and retain a large amount of water or other fluids [1]. In fact, the swelling capacity strongly depends on the cross-linking density, and moderately cross-linked hydrogels exhibit the best swelling performance [2]. Meanwhile, the cross-linking density and swelling capacity also influence the mechanical properties of hydrogels. Although some nanocomposite hydrogels [7–10], especially those based on inorganic nanofillers (e.g., mica, kaolin, silicate, rectorite, vermiculite, attapulgite, and montmorillonite) raise much attention because of their reduced production costs and improved swelling capacity and swelling rate for superabsorbent polymers, their mechanical properties are seldom reported. Recently, silica nanoparticles reinforced nanocomposite hydrogels with good mechanical properties were reported, but their swelling capacities were neglected [11,12].

However, many applications require hydrogels that have exceptional mechanical properties, which are generally limited by low extensibility and toughness, so many strategies to focus on the improvement of the mechanical properties have been investigated recently [13–15]. In particular, nanocomposite hydrogels composed of both an organic polymer and an inorganic compound hold the unique properties of organic–inorganic materials and may be used as high-performance materials [13]. Recently we proposed a “single network, dual (or hierarchical) cross-linking” strategy to prepare various tough and highly stretchable nanocomposite hydrogels [16–20]. For example, nanocomposite physical hydrogels (NCP gels) based on vinyl-hybrid silica nanoparticles (VSNPs) have been prepared by *in situ* free radical polymerization [18,19]. The networks of NCP gels are first enabled by the intermolecular hydrogen bonds among the VSNP/polymer nanobrushes. Once the hydrogen bonds are formed, the VSNP can act as multiple covalent “analogous cross-linking points”, which translate into excellent mechanical properties. Some reports have been published for the improvement of swelling capacity [16–18,21]. However, the mechanical properties (stress and strain) of the hydrogels are relatively low. Therefore, hydrogels with both high toughness and swelling capacity are still a huge challenge.

In this work, we report a facile one pot method for the preparation of tough and stretchable VSNP/poly(acrylic acid) (PAA) nanocomposite physical hydrogels (NCP gels) with superior

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swelling capacity. The effect of the content of VS/NPs on the mechanical properties and swelling behavior are investigated. We find that the NCP gels have excellent and balanced mechanical properties (tensile strength = 370 kPa, elongation at break = 2200%) and excellent swelling capacity (~2300 g/g in deionized water and 220 g/g in saline). Furthermore, when the NCP gels are in a swollen state, they can be stretched by more than 400%. We believe this method may highlight a new way to prepare hydrogels having excellent and balanced mechanical properties coupled with an excellent swelling capacity, which may find their applications in bioengineering, water treatment, chemical separation, as well as hygienic fields.

2. Experimental

VS/NPs with 3 nm diameter were prepared following our previous reports [19,20]. NCP gels were prepared as follows: a calculated amount of acrylic acid was added to deionized water and neutralized by 40% NaOH solution under stirring in an ice bath. After that, a pre-set amount of VS/NPs suspension was redispersed in the above solution by stirring at ambient temperature. After 2 h, 0.25 wt% ammonium persulfate (relative to the monomer) was added to the mixture and stirred for a few minutes. After being degassed by bubbling with N₂ for 1 h, the uniform suspension was transferred to several plastic syringes of 5 mm internal diameter. The polymerization was performed at 45 °C for 30 h in a water bath under N₂ atmosphere. The chemically cross-linked PAA gels were prepared using the same procedure with *N,N'*-methylene diacrylamide (Bis) (0.1 wt% relative to the monomer) as the cross-linker. The total water content and the value of neutralization degree of the hydrogels were fixed at 67 wt% and 70%, respectively.

Uniaxial tensile tests were performed by a Zwick 005 tensile machine at ambient temperature on the cylindrical hydrogel specimen, at a constant crosshead speed of 100 mm min⁻¹ and initial sample length between jaws of 15 mm. The tensile strength (from the initial cross-section of 19.62 mm²) and percentage elongation at break were calculated by the recorded fracture tensile force and length. The slope between 20 and 80% strain in the stress-strain curve was used to calculate the initial elastic modulus. The fracture toughness of NCP gels was defined as the work of the fracture, calculated as the integrated area underneath the stress-strain curve of each sample. Hysteresis loops were examined to calculate energy dissipation and were performed on the cell loading-unloading cycles tests using the same experimental setup as uniaxial tensile test with the same tensile speed of 100 mm min⁻¹.

The swelling capacity was examined as follows: a weighed quantity of the as-prepared NCP gels sample was immersed in a large amount of deionized water or saline solution (0.9 wt% NaCl) at ambient temperature to reach swelling equilibrium. The swollen samples were then separated from unabsorbed water by filtering

over a 100-mesh screen. The water absorbency (*Q*) of the hydrogels was determined by weighing the swollen samples, and the *Q* of the samples was calculated using the following equation: $Q = (m_2 - m_1)/m_1$ where *m*₁ and *m*₂ are the weights of the calculated dry sample and the swollen sample, respectively.

3. Results and discussion

Silica nanoparticles are widely used as “nano-fillers” to obtain inorganic-organic nanocomposites due to their easily controllable size, uniform structure, and stable function in aqueous or organic solutions [11]. Uniform and multivalent VS/NPs with a diameter of 3 nm are prepared by a universal sol-gel method [19,20]. As reported in our previous work, we have prepared physically cross-linked PAA hydrogels by *in situ* free radical polymerization with acrylic acid as the monomer, which is grafted from the surface of VS/NPs, thus obtaining VS/NP/PAA nanobrushes. VS/NPs serve as multivalent covalent cross-linking points once the physical cross-links enabled by the hydrogen bonding interactions between the nanobrushes have been established [19,20]. Thus, dually cross-linked, single-network hydrogels with multivalent covalent cross-linking points and hydrogen bonding points are obtained.

The influence of the VS/NPs content on the hydrogels' mechanical properties is investigated first. A typical stress-strain curves of the NCP gels with 67% fixed water content is presented in Fig. 1, which demonstrates that the NCP gels have good mechanical properties with tensile strengths in the range of 110–370 kPa and elongations at break of 1600%–3000%. In contrast, the chemically cross-linked hydrogels exhibit a relatively low tensile strength of 100 kPa and stretchability of 700% only. With increasing VS/NPs content, the elongation at break decreases steadily. Conversely, the tensile strength, modulus, and toughness increase with the increase of VS/NPs content from 0.05 wt% to 0.7 wt% relative to the monomer. Degraded mechanical properties can be observed for the NCP gels when the VS/NPs content is higher than 0.7 wt%. When the VS/NPs content is 0.70 wt%, the NCP gels exhibit excellent mechanical properties with the tensile strength and elongation at break of 370 kPa and 2200%, respectively. The excellent mechanical properties should result from the interplay between the VS/NPs content and the molecular weight of the grafted PAA chains. As mentioned above, VS/NPs act as the “analogous cross-linking points” when the hydrogels are stretched, which can thus absorb and relax the applied stress *via* the numerous flexible polymer chains anchored on their surface. At the same time, the physical cross-links break-recombine to dissipate energy, thus delaying crack propagation. When the VS/NPs content increases, the grafted PAA molecular weight should be reduced [19], because there are a greater number of initiation points on the surface of VS/NPs for polymer growth at a given monomer concentration. Consequently, the average polymer length is reduced as the VS/NPs content increases, thus decreasing the elongation at break of the NCP gels.

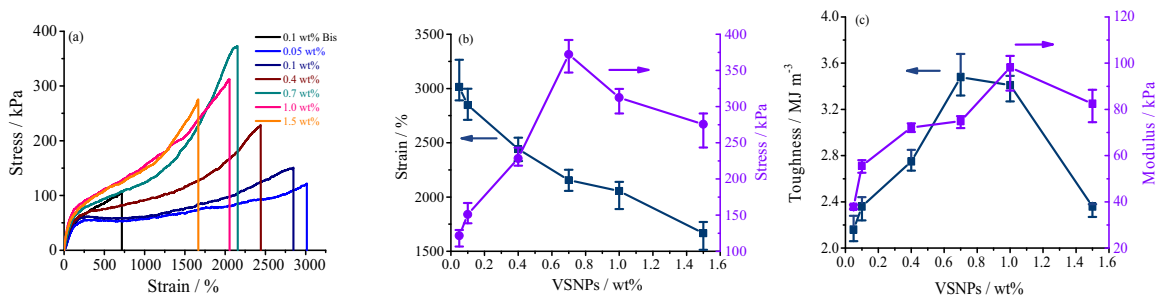


Fig. 1. Mechanical properties of the NCP gels: (a) stress-strain curves; (b) tensile strength and elongation at break; (c) initial elastic modulus and fracture energy; the water content was fixed at 67%.

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