

A novel fabrication method of temperature-responsive poly(acrylamide) composite hydrogel with high mechanical strength



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ABSTRACT

High strength, stimuli-responsive poly(acrylamide) composite hydrogels (PAAm CH gels) were prepared by grafting polymerization of acrylamide (AAM) onto temperature-sensitive core–shell microgels. These microgels, composing of poly(N-isopropylacrylamide) as core and polyvinylamine (PVAm) as shell, were used as both initiator and crosslinker to form a robust three-dimensional network via bonding the poly(acrylamide) (PAAm) backbone. The CH gels exhibited a remarkably rapid shrinking rate and transmittance switch in response to the environmental temperature change, which the conventional chemically cross-linking PAAm hydrogels (PAAm OR) were short of. Even compared to the bulk PNIPAAm hydrogels (PNIPAAm OR) crosslinked with N,N'-methylenebisacrylamide (MBA), the CH gels were featured with faster responsive rate, which could be attributed to the formation of interconnected water transportation channels between the microspheres and PAAm gel matrix due to the fast shrinking of microgels. Moreover, the effects of microgel species and content on swelling and mechanical properties of CH gels were also systematically investigated. The results elaborated that the CH gels could be compressed almost 99% without breaking and completely recovered their original shape when the stress was removed. And the optimized compressive strength of CH gels could be up to 21.94 MPa. Based on the analysis of CH gel mechanical properties, the influence of microsphere content on effective network chains density of CH gels was discussed through rheology measurements. Finally, the essential reinforcement on mechanical properties was mainly contributed to the homogeneous microstructure of hydrogel network and the energy dissipation mechanism of microgels in gel matrix.

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1. Introduction

Due to the integrated mimic nature of liquid and solid, poly(acrylamide) hydrogels (PAAm gels) have been one of the most promising hydrogel materials for potential biomedical applications such as drug delivery vehicles [1,2], tissue-engineering scaffolds [3,4], and sensors [5]. However, one significant disadvantage that PAAm gels are scant of the stiffness and toughness limits their utilization. Meanwhile, the lack of stimuli-response for PAAm gels, particularly lack of fast stimuli-response, is also another fatal defect hindering their application.

To date, several robust PAAm-based hydrogels with various enhanced network have been fabricated, such as double-network hydrogels [6], topological gels [7], nanocomposite gels [8],

microspheres composite gels [9] and hydrophobically associated hydrogels [10,11], and various toughening mechanisms [12–15] have been demonstrated based on aforementioned studies. In contrast to abundant investigations of toughening hydrogels, the facile method that can endow stimuli-response to PAAm hydrogels is still limited. The most representative methods are the introduction of chemical reaction of functional groups in polymer chains (as chelation [16], coupling [17], hydrolysis [18], etc...) and the incorporation of stimuli-response monomers, like acrylic acid [19], N-isopropylacrylamide [20]. In order to obtain the rapid responsive hydrogels, many attempts have been done, including the use of pore-forming agents [21–23] to prepare microporous structure and the introduction of hydrophilic microdomains [24] or interpenetrating structure [25] to modify the network. At the same time, nanoparticles incorporating [26], freeze-dried [27] and crosslinking aggregation of nanogels [28] can also significantly improve the response rate of hydrogels. Unfortunately, the mechanical and swelling performance cannot be improved simultaneously via these methods. Therefore, the development of new fabrication

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method that can simultaneously endow PAAm gels with excellent mechanical performance and smart stimuli–response becomes extremely important.

Recently based on the investigations of micro-, nano-particles reinforced composite hydrogels, a successful approach to fabricate high mechanical performance composite hydrogels through incorporating microspheres as crosslinker into hydrogels has been proposed in our laboratory [29–31] and others groups [32,33]. For example, Wang et al. [9,34] and Zhu [35] two groups prepared hydrophobic macromolecular microsphere composite hydrogels with high mechanical strength. Chu and coworkers [36] used hydrophilic microgels as crosslinkers to improve the response rate of PNIPAAm hydrogels. Gong's investigation [33,37] on the microgel-reinforced hydrogels demonstrated the entanglement between the PAAm matrix and incorporated microgels played a crucial role in stress transmission. However, microspheres referred to in aforementioned literature cannot supply smart stimuli–response properties to PAAm hydrogel at all. One of few exceptional cases is reported by our group, in which composite hydrogel [30] exhibited temperature response without volume change stemming from the addition of tem-responsive microgels. Unfortunately, the existence of small molecular crosslinker (MBA) impaired their response rate to stimuli and the simplicity of structure of composite hydrogel.

Inspired by aforementioned investigations, our aim of this work is to fabricate microgel-reinforced PAAm composite hydrogels (named CH gels) with high mechanical strength and rapid temperature-responsive rate by using temperature-sensitive microgels to act as both chemical crosslinker and initiator to bridge PAAm matrix. The mechanism for the formation of a composite hydrogel is proposed in Scheme 1. When the tert-butylhydroperoxide (TBHP) was added into the reaction solution, it can interact with amino groups on the surface of microgels to form redox pairs. One electron was then transferred from nitrogen to ROOH under heat, resulting the formation of an alkoxyl radical ($\text{RO}\cdot$) and a nitrogen cationic radical, which subsequently lost a proton to generate an amino radical [38] (PNH, here P is the microgel). PNH was able to initiate the grafting polymerization of monomers onto the microgels while $\text{RO}\cdot$ initiated the homopolymerization of monomers or terminated the growing polymer chains and the network can be formed finally. Thus obtained CH gels exhibited better mechanical performance than conventional OR gels. On the other hand, they were featured with fast response rate to the environmental temperature stimuli. Meanwhile, we systematically explored the effects of the concentration and the

species of microgels on the mechanical properties of CH gels. The internal microstructure, swelling and deswelling properties of the prepared hydrogels were also investigated experimentally.

2. Experiment section

2.1. Materials

Acrylamide (AAm, Beihua Fine Chemical Co., Ltd) was twice recrystallized from acetone and vacuum dried at 40 °C. N-Isopropylacrylamide (NIPAAm) was obtained from Acros, recrystallized in toluene/cyclohexane (1:5), and dried under vacuum before used. N-Vinylformamide (98%), tert-butylhydroperoxide (TBHP, 70% water solution), 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) and N,N'-methylenebisacrylamide (MBA) were used as received from Aldrich without further purification.

2.2. Synthesis of NIPAAm-PVAm core–shell microgels

PVAm was prepared as following method. Poly(N-vinylformamide) (PNVF) was first synthesized by free radical polymerization in isopropyl alcohol using AIBN as initiator, followed by hydrolysis of PNVF in alkaline solution to obtain PVAm. The weight–average molecular weight of PVAm was $70,000 \text{ g mol}^{-1}$.

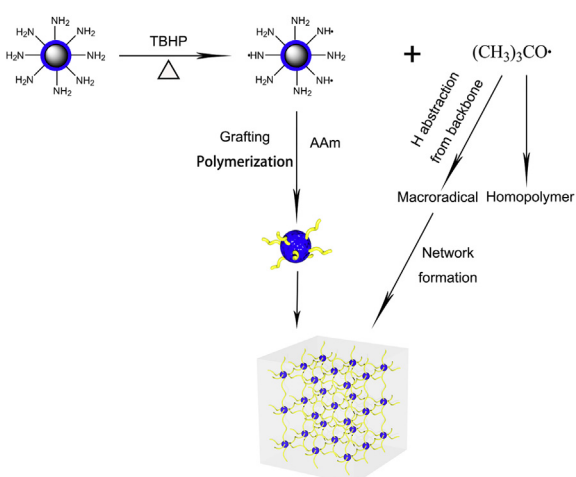
Microgels were prepared according to the previously reported literature [39]. The typical synthetic procedure of core–shell microgels was as follows: Briefly, for a total aqueous solution of 30.00 g, purified NIPAAm (1.20 g, 0.010 mol), MBA (0.0163 g, 1.0×10^{-4} mol) and PVAm (0.30 g) were added sequentially into a three-necked flask equipped with a thermometer, a condenser, a magnetic stirrer and nitrogen inlet. The pH of the reaction solution was adjusted to 7–8 and the solid content was controlled at 5 wt%. After bubbling nitrogen for 30 min at 70 °C, dilute TBHP solution (0.60 g, 0.1 wt% solution) was added to the mixture, and the solution was stirred at 70 °C for 6 h under nitrogen for complete reaction. The final harvest mixture was a stable white translucent latex dispersion.

2.3. Synthesis of composite hydrogels (CH gels)

The synthetic procedure of composite hydrogels was described as follows: at first, a transparent aqueous solution consisting of appropriate mass of water and AAm (1.50 g) was prepared. Next, the aqueous solution including microgel nanoparticles and finally the aqueous solution of initiator (TBHP, 0.1 wt.% solution) were added to the former solution with drastic stirring at ice-water bath. After the agents were completely mixed, the solution was transferred into test tubes of 14 mm internal diameters and oxygen was excluded from the system. Free radical reaction was allowed to proceed in a water bath at 60 °C for 24 h to create the robust hydrogel with the shape of test tube. The composite hydrogel was expressed as CH-Ma(b), where “a” represented the microgel code as shown in Table 1 and “b” stood for the numerical value of the microgel content. For comparison, the PAAm hydrogels with physically trapped core–shell microgels were prepared by using initiator VA-044 instead of TBHP. During the preparation of the conventional PAAm (PAAm OR) and PNIPAAm hydrogels (PNIPAAm OR), MBA was used as the cross-linker.

2.4. Particle size analysis

The particle size and polydispersity index (PDI) of core–shell microgels were measured by dynamic light scattering using a



Scheme 1. The proposed synthesis mechanism of CH gels.

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