



Research Paper

Gum Arabic: A promising candidate for the construction of physical hydrogels exhibiting highly stretchable, self-healing and tensility reinforcing performances



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ABSTRACT

The preparation of tough and healable hydrogels in one step remains a big challenge throughout the field of hydrogel methodology. Herein, we fabricated a series of Poly(*N,N*-dimethyl acrylamide)-TiO₂-gum arabic (PDMAA-TiO₂-GA) hybrid hydrogels by simply introducing nanoparticles TiO₂ and vinyl-modified gum arabic (GMAGA) into polymer networks. Without complicate molecular design and post-treating process, the hydrogel molding process was simple and effective. The hydrogel exhibited highly stretchable, self-healing and tensility reinforcing performances with the optimized compositions of 30% DMAA, 0.6% GMAGA and 0.13% TiO₂. The maximum elongation of the hydrogel after self-healing recover could reach nearly 700% after only 20 min healing time. The hydrogel could ensure 20 times continuous compressive or tensile tests without obvious deformation. Amazing was the significantly enhanced tensile modulus from 5 kPa to 40 kPa after 20 stretch-release cycles. The facile preparation and fascinating tensility reinforcing performance benefit the potential application of the carbohydrate GA in hydrogels.

1. Introduction

As one of the most attractive soft and wet materials, polymer hydrogels possess unique porous 3D network structure and tunable chemical-physical properties (Lu, Le, & Zhang, 2017). They are usually composed of hydrophilic polymer chains where covalently and/or physically cross-linked points are formed, with the capability of holding a large amount of water. Due to their excellent biocompatibility and environmental friendliness, hydrogels find widespread applications in various fields such as electronic skin (Hur et al., 2014), tissue scaffolds (Han et al., 2013; Singh, 2017), sensing (Wada, Tamaru, Ikeda, & Hamachi, 2009) and capacitance gate insulator (Ko, Kim, & Kim, 2016) etc. Recently, healable hydrogels with good fatigue-resistant performance offer substantial benefits to maintain the integrity of network structure and mechanical level of bulk hydrogels, contributing to their long-term use with stable functionality (Yesilyurt et al., 2016; Wei et al., 2015).

Much effort has been committed to improve mechanical strength of hydrogels by optimizing their network structure and toughening mechanisms. Typical strategies include the use of double network (DN) (Gong, Katsuyama, Kurokawa, & Osada, 2003; Cong, Wang, & Yu,

2013), nanocomposite reinforcement (Haraguchi and Takehisa, 2012; Haraguchi, Uyama, & Tanimoto, 2011; Yang, Han, Duan, Xu, & Sun, 2013; Zhang, Yang, Bao, Wu, & Wang, 2013; Wu et al., 2016a; Zheng et al., 2014; Wu, Yi, Duan, Xu, & Wang, 2016; Liao et al., 2014; Liu, Song, He, & Wang, 2013; Liu et al., 2012), diamond-like structures with homogeneous spacers (Sakai et al., 2008), sliding-ring connecting (Mayumi & Ito, 2010), and dynamic crosslinking systems (Zhong, Liu, & Xie, 2015; Gong et al., 2016; Zhong et al., 2016; Sun et al., 2012; Jeon, Cui, Illeperuma, Aizenberg, & Vlassak, 2016; Sun et al., 2013). Among them, nanocomposite reinforcement and double network (DN) structure are both regarded as the most efficient approaches to obtain tough hydrogel. Clay nanosheets (Haraguchi and Takehisa, 2012; Haraguchi et al., 2011), silica (Yang, Deng et al., 2013; Yang, Han et al., 2013), conductor nanoparticles (Zhanget al., 2013; Wu et al., 2016a; Zheng et al., 2014; Wu, Yi, Duan, Xu, & Wang, 2016), layered inorganic nanosheets (Liao et al., 2014) or graphene oxide (Liu, Song, He, & Wang, 2013; Liu et al., 2012) are always employed as crosslinking reagents filled into the nanocomposite hydrogels. These nanocomposite hydrogels demonstrate excellent toughness, stiffness and self-healing abilities resulting from the supramolecular interactions between nanoparticles and polymer chains, but are lack of enough functionality,

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which greatly limit their uses for other applications. For the DN hydrogels, the current reports from preparation techniques, network structure, to toughening mechanism mainly focus on chemically cross-linked DN gels. The toughening mechanisms are largely based on “sacrificial bonds” theory. Since chemical crosslinks are essential for the construction of DN hydrogels, the resultant gels usually demonstrate poor properties in fatigue-resistance and recovery. To solve the above problems, several research groups introduce reversible and non-covalent interactions to replace sacrificial covalent in the first network to construct hybrid chemical-physical DN hydrogels, even fully physically cross-linked DN hydrogels. These dynamic crosslinks based on supramolecular associations contain hydrogen bonding (Zhong et al., 2015; Gong et al., 2003), ionic bonding (Zhong et al., 2016; Sun et al., 2012), hydrophobic (Jeon et al., 2016) and electrostatic interactions (Sun et al., 2012), supplying more diversity and a wider spectrum of properties. For example, Wu et al., 2016a synthesized PAM-CS DN hydrogels by soaking method (Yang, Wang, Yang, Shen & Wu, 2016). Panhuis and co-workers developed a series of ionic-covalent DN gels using anionic polysaccharides (gellan gum and carrageenan) as the first, ionically crosslinked network and poly (acrylamide) as the second, covalently crosslinked network (Bakarich, Panhuis, Beirne, Wallace, & Spinks, 2013; Kirchmayer & Panhuis, 2014). Recently, fully physically linked DN hydrogel composed of agar and polyacrylamide was synthesized by Chen et al. (Chen et al., 2015). These hydrogels mainly focus on the toughness of hydrogel with limited self-healing ability under ambient conditions. However, most of nature polymers are not a preferable choice as the first network in building tough hydrogels, since they usually have high viscosity even at low concentration, such as alginate and chitosan solutions, and the bubbles generated during the mixing process seriously restrict the formation of uniform network. Besides, the current synthesis procedures for the fabrication of DN polysaccharides-based hydrogels are usually sophisticated and time-wasting. It is almost unavoidable for the above DN hydrogels to become soft and weak after several loadings. Therefore, it is highly desirable to develop simple and effective strategies for designing and constructing powerful hydrogels with good properties in recovery, self-heal and fatigue-resistance.

Gum arabic (GA) is a kind of natural polysaccharide which can be obtained from acacia tree. Due to its low cost, non-toxicity, biocompatibility and biodegradability, GA is being extensively used as stabilizer, emulsifier and thicken agent in the food industry. It has a highly branched structure which is composed of arabinose, rhamnose, galactose and glucuronic acid residues with a backbone consisting of 1, 3 linked β -D-galactopyranosyl units (Sarika, Cinthya, Jayakrishnan, Anilkumar, & James, 2014). This highly branched structure leads to a relatively small hydrodynamic volume and decreased intermolecular interaction between gum arabic molecules. Especially, the viscosity of GA is low, making them easy to be mixed with the other components without the generation of bubbles. Actually, it has been reported that the mechanical level of chitosan-gelatin-based nanofibers was improved by use of gum arabic as a solvent (Tsai et al., 2015). Recently, chemical modification of polysaccharide by reaction with glycidyl methacrylate (GMA) gained our attention in preparation of GA hydrogel (Fan, Shi, Wang, & Yin, 2013). It was observed that vinyl modified gum arabic (GMAGA) could transform uncross-linked polysaccharides into covalent hydrogels whose crosslinks were stable as time went on, preserving the hydrogel properties (Reis et al., 2016). Therefore, we suppose that GMAGA would be a promising candidate for the construction of robust and dynamic physical hydrogels.

In this presentation, a series of PDMAA/GMAGA/TiO₂ hybrid hydrogels were synthesized by combined use of nanoparticles TiO₂ and GMAGA as photo-initiator and crosslinks. The hydrogel could effectively dissipate energy and obtain excellent fatigue-resistance and self-healing abilities through the interactions between different crosslinking agents, e.g. hydrogen bonding, physical entanglement or surface adsorption. An obvious tensility reinforcing behavior was found after the hydrogel was repeatedly stretched and released several times, clearly

indicating a different toughening mechanism from those of the DN hydrogels. Furthermore, the preparation procedure also could be generally applied for other vinyl monomer/gum arabic/nanoparticles crosslinking systems. We expect that this strategy can provide a new perspective for fabricating a unique multi-cross-linked single network (SN) hydrogel with adjustable mechanical strength, as well as recovery, self-heal and fatigue-resistance properties, which would further widen the application of GA in modern high-tech fields.

2. Materials and methods

2.1. Materials

Gum Arabic (GA, Mw = 262.64) was purchased from Aladdin Reagent Co., Ltd. Glycidyl methacrylate (GMA) was provided from Shanghai Saen Chemical Reagent Co., Ltd. Nanoparticles TiO₂ dispersion (15% in wt.%) was bought from Yicheng Ruijing New Material Reagent Company. The size of nanoparticles TiO₂ was around 15–50 nm. N, N-dimethylacrylamide (DMAA), N, N-bis(methylene)acrylamide (BIS) and an organic photo-initiator 2-diethoxyacetophenone (DEAP) were obtained from Shanghai Saen Chemical Reagent Company. All the other reagents were at least of analytical reagent grade and used as received.

2.2. Chemical modification of GA with glycidyl methacrylate (GMA) in aqueous solution

GA solution modified by GMA (GMAGA) was prepared by the method reported elsewhere (Tsai et al., 2015). First, 20 g of GA was dissolved into 200 ml of aqueous-dimethylsulfoxide (DMSO) mixed solution. The volume ratio of aqueous and DMSO was 1: 2.6. Afterward, a known amount of GMA was introduced. The mixture solution was kept stirring for 72 h at 50 °C. Finally, the product GMAGA was alternately precipitated and dissolved in ethanol and water for three cycles. The purified GMAGA solution was filtrated under reduced pressure and the resultant precipitate was freeze dried for 1 week to remove water completely. The ¹H NMR spectra of GMAGA and GA indicated that GA reacted with GMA by an epoxide ring-opening mechanism (Fig. 1 and Fig. 2 d).

2.3. Preparation of PDMAA-GMAGA-TiO₂ gels

PDMAA-GMAGA-TiO₂ nanocomposite hydrogels were synthesized by a simple UV photo-induced radical polymerization method. Typically, 1000 mg DMAA, 240 mg GMAGA and 0.05 ml TiO₂ nanoparticle dispersion was successively added into a distilled water (4 ml), followed by a gentle stirring at ambient temperature. Then, the mixed solution was exposed to the UV light irradiation for 1 h ($\lambda = 365$ nm wavelength, intensity of 8 W). Finally, a nanocomposite PDMAA-GMAGA-TiO₂ hydrogel was formed and stored in the refrigerator (~ 5 °C). The total weight of the precursor solution for hydrogel was kept to be 4.0 g and the mass percent for each component was 25% DMAA, 0.6% GMAGA and 0.13% TiO₂, respectively. For comparison purpose, PDMAA-BIS-TiO₂ hydrogels were synthesized in a similar manner except the use of organic crosslinks (BIS) of 2% relative to DMAA, instead of GMAGA. For the preparation of PDMAA-GMAGA-DEAP hydrogel, the same procedure was followed except the use of organic photo-initiator DEAP of 2% relative to DMAA, instead of TiO₂ nanoparticles dispersion.

2.4. Mechanical tests

All mechanical tests of the gels were carried out at ambient temperature by a CMT6503 stretch-compression electromechanical tester with a 500 N load cell (Shenzhen SANS, China). To obtain reliable values, at least three specimens per experimental point were tested in

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