Materials Letters 228 (2018) 104–107

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Featured Letter

Preparation of high strength and transparent nanocomposite hydrogels using alumina nanoparticles as cross-linking agents

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ARTICLE INFO

Article history:
Received 17 October 2017
Received in revised form 17 May 2018
Accepted 31 May 2018
Available online 1 June 2018

Keywords:
Nanocomposites
Polymers
Hydrogels
High strength
Alumina

ABSTRACT

High strength and transparent nanocomposite hydrogels (AD gels) were prepared by photo-initiated free radical copolymerization of acrylic acid (AA) and N, N-dimethylacrylamide (DMAA) in the colloidal solutions of alumina nanoparticles (Al_2O_3 NPs). The obtained hydrogels displayed well-defined porous structures and outstanding mechanical properties with tensile and compressive strength up to 1.88 MPa and 28 MPa, respectively. The FT-IR spectra indicate that there exist strong chelation reactions between Al_2O_3 NPs and polymer matrix, which are responsible for the formation of AD gels and their excellent mechanical performance. Moreover, AD gels with low swelling ratios could be prepared by choosing appropriate monomer ratios, endowing the hydrogels with considerable mechanical strength even at swollen state.

1. Introduction

For decades, hydrogels that consist of cross-linked hydrophilic polymer chains and large quantities of water have found varieties of biomedical applications because their "soft and wet" feature as well as other physicochemical properties including hydrophilicity, biocompatibility and stimuli sensitivity [1,2]. However, most of the synthetic hydrogels are commonly fragile and brittle due to their intrinsic structural heterogeneity and/or the lack of efficient energy dissipation mechanism, which severely limited their applications in load-bearing systems. To overcome this limitation, much effort has been devoted to developing tough and strong hydrogels, such as double-network hydrogels [3], nanocomposite hydrogels (NC gels) [4], tetra-PEG gels [5], and others [6–8]. Among them, NC gels that prepared by the employment of inorganic nanoparticles as cross-linking agents are considered most promising due to their outstanding mechanical properties, facile preparation as well as other unique features [9]. For now, a variety of inorganic nanomaterials, including clay nano-sheets [4], graphene oxide [10], layered double hydroxide [11], titania [12], and zirconium hydroxide [13], have been utilized to prepare hydrogel materials with superior mechanical strength and toughness. However, despite of their outstanding mechanical properties, the practical applications of NC gels were still limited due to their large swelling ratios originated from their low cross-linking density. After swelling, the mechanical performance of NC gels would be dramatically weakened, making them unable to be used in load-bearing systems under water environments. Therefore, it is of crucial importance to develop novel NC gels with both high mechanical strength and low swelling ratio so as to expand the application range of NC gels.

Here we report on a preparation of novel NC gels by using alumina nanoparticles as the inorganic cross-linking agents. The formation mechanism of hydrogels was supposed to be the chelation reactions between nano-alumina and polymer matrix. The resultant hydrogels were transparent and strong, and possessed considerable mechanical strength at both as-prepared and swollen states due to their low swelling ratios, which could overcome the limitation of practical applications of NC gels.

2. Materials and methods

2.1. Materials

Acrylic acid (AA) and N, N-dimethylacrylamide (DMAA) were purchased from Kohjin Co., Japan and purified by reduced pressure distillation and filtering through activated alumina, respectively. Photo-initiator 2-Hydroxy-4′-(2hydroxyethoxy)-2-methylpropio phenone (IR 2959) was provided by Energy Chemical Co., China and used as received. A transparent colloidal solution of alumina nanoparticles (γ-Al_2O_3 NPs,) with particle size of 10–20 nm and concentration about 10% (w/w in water) were obtained from Jing Rui New Materials Co., China. Deionized water was used in all experiments including swelling measurements.

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https://doi.org/10.1016/j.matlet.2018.05.135
0167-577X/

2.2. Hydrogel preparation

Firstly, homogeneous precursor solutions consisting of 10 g alumina colloidal solution, extra 1.0 g water, 30 mg IR2959 and different molar ratio of AA and DMAA were prepared under nitrogen atmosphere. Then, the solutions were transferred into different glass molds after being degassed by vacuum. Finally, photo-initiated free radical polymerization was carried out under 365 UV light (8 W) for 30 min and transparent and uniform hydrogels were obtained. The resultant hydrogels were denoted as A*m*D*n* gels, in which A and D stand for the abbreviations of AA and DMAA, and *m*/*n* (*m* + *n* = 10) represents the molar ratio of two monomers with the total monomer concentration fixed at 3 mol/L.

2.3. Characterizations

The mechanical properties of hydrogels were performed on an AGS-J (Shimadzu Co., Japan) electronic universal testing machine. The as-prepared hydrogel samples with size of Φ 6.3 mm × 50 mm (gauge length 20 mm) were used for tensile test at the speed of 60 mm/min. The compressive test were conducted on the sample of Φ 10 mm × 10 mm at the slow speed of 1 mm/min. As for the swollen samples, the mechanical properties were measured with the same method based on their actual sizes at swollen state. The SEM observation was conducted on a Quanta 250 (FEI Co., USA) instrument using the freeze-dried as-prepared A2D8 gel. The FTIR spectra of Al2O3 NPs, neat copolymer and AD gels were recorded on a Nicolet 6700 (Thermal Scientific Co., USA) spectrometer using a KBr method.

3. Results and discussion

3.1. Hydrogel formation

Fig. 1a illustrates the preparation of AD gels. Due to the uniform dispersion of the Al2O3 NPs in the colloidal solution and the water miscibility of AA and DMAA, the obtained hydrogel precursors were highly transparent, making them suitable for UV-initiated polymerization. After UV irradiation for 30 min, transparent and uniform hydrogels with well-defined porous structures (Fig. 1b) were obtained. Here, it should be noted that no organic cross-linkers were used in the preparation process, and the Al2O3 NPs acted as the inorganic cross-linking agents, responsible for the formation of 3D network structures of AD gels. To the best of our knowledge, this is the first report on preparing NC gels using Al2O3 NPs as the cross-linking agents. To preliminarily study the cross-linking mechanism of AD gels, FT-IR spectroscopy was performed and the results were shown in Fig. 1c. It can be seen that the absorption bands at 3417 cm^{-1}, 1717 cm^{-1}, and 1253 cm^{-1}, which are the characteristic peaks of carboxyl groups on polymer side chains almost disappeared in the spectra of AD gels. Furthermore, the peak centered at 3441 cm^{-1} corresponding to the stretching vibration of –OH on the surface of Al2O3 NPs also significantly weakens. These results indicate that there exist strong chelation reactions between carboxyl groups and Al2O3 NPs according to the literatures [14], although the exact interaction modes need further investigation. These strong chelation reactions were not only responsible for the cross-linking structures of AD gels, but also contributed to their excellent mechanical properties as will be discussed later.

3.2. Mechanical properties

Similar to NC gels cross-linked by other nanomaterials, currently reported AD gels also displayed excellent mechanical toughness, which could withstand various deformations without breaking (Fig. 2a). In order to quantitatively investigate the mechanical properties of AD gels, uniaxial tensile and compressive tests were conducted. As shown in Fig. 2b, the prepared AD gels with the AA to DMAA ratios of 1/9, 2/8, 3/7 and 4/6 could be stretched 308 –1516% of their original length before fracture, revealing tensile strength between 0.6 MPa and 1.88 MPa, which are much higher than those of conventional organically cross-linked hydrogels and some other NC gels. The excellent mechanical properties of AD gels can be attributed to the strong chelation reactions between Al_2O_3 NPs and polymer matrix, which could break preferentially to dissipate large amount energy before the fracture of the polymer chains. It also can be found from Fig. 2b that the elongations at break of AD gels monotonously decrease as the increasing of AA ratio, while the elastic moduli gradually increase. This finding indicates the increasing of cross-linking density of hydrogels, which is similar to our previous report [12]. Furthermore, the results from compressive tests also revealed the excellent mechanical properties of AD gels as shown in Fig. 2c. All of the prepared AD gels except the A4D6 gel could be compressed 90% of their original heights without damage, showing compressive strength from 6 MPa to 28 MPa, depending on their monomer ratios. Additionally, after releasing the external forces, the compressed hydrogels were able to restore their original heights within 1 min. As for the A4D6 gel, although it fractured when compressed 75% due to its high cross-linking density, a fracture stress up to 8.2 MPa was observed. To our knowledge, NC gels that possess both such strong tensile and compressive strength as AD gels have not been reported yet.

3.3. Swelling properties

Fig. 3a shows the time-dependent swelling ratios of AD gels with respect to their as-prepared weight. It can be seen that the

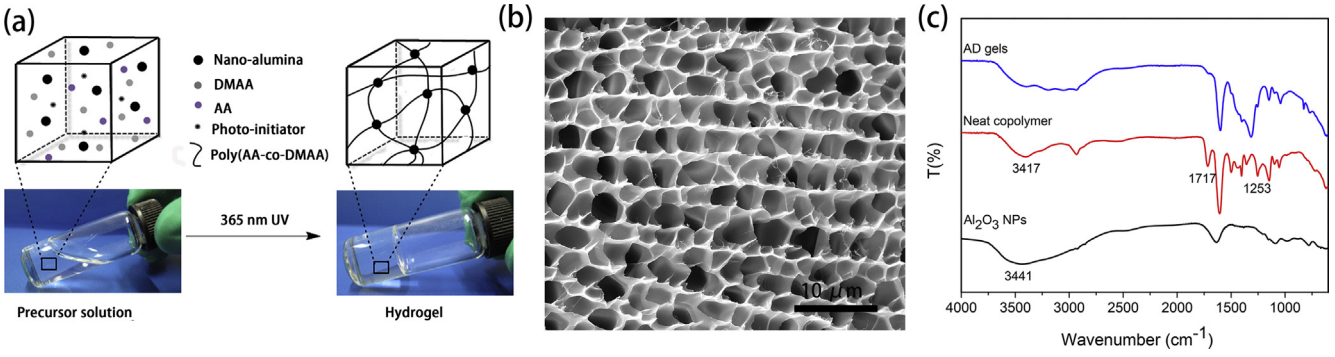

Fig. 1. (a) Illustration of the preparation of AD gels; (b) Typical SEM image of AD gels; (c) FT-IR spectra of Al_2O_3 NPs, neat copolymer and AD gels.