Materials Science and Engineering C 74 (2017) 374–381

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Bioinspired fully physically cross-linked double network hydrogels with a robust, tough and self-healing structure

Mohammad Sabzi [a,*], Navid Samadi [b], Farhang Abbasi [c], Gholam Reza Mahdavinia [d], Masoud Babaahmadi [a]

[a] Department of Chemical Engineering, Faculty of Engineering, University of Maragheh, Maragheh 55181-83111, Iran
[b] Department of Materials Engineering, Faculty of Engineering, University of Maragheh, Maragheh 55181-83111, Iran
[c] Institute of Polymeric Materials, Sahand University of Technology, Tabriz 55181-83111, Iran
[d] Department of Chemistry, Faculty of Science, University of Maragheh, Maragheh 55181-83111, Iran

ARTICLE INFO

Article history:
Received 23 June 2016
Received in revised form 19 November 2016
Accepted 6 December 2016
Available online 7 December 2016

Keywords:
Hydrogel
Polyvinyl alcohol (PVA)
Agar biopolymer
Physically cross-linked
Double network
Self-healing
Toughness
Elastic modulus

ABSTRACT

The conventional covalently cross-linked double network (DN) hydrogels with high stiffness often show low toughness and self-healing property due to the irreversible bond breakages in their networks. Therefore, scarcity of hydrogels that possess simultaneous features of stiffness, toughness, and autonomous self-healing properties at the same time remains a great challenge and seriously limits their biomedical applications. While, many natural materials acquire these features from their dynamic sacrificial bonds. Inspired by biomaterials, herein we propose a novel strategy to design stiff, tough and self-healing DN gels by substitution of both covalently cross-linked networks with strong, dynamic hydrogen bond cross-linked networks. The prepared fully physically cross-linked DN gels composed of strong agar biopolymer gel as the first network and tough polyvinyl alcohol (PVA) biopolymer gel as the second network. The DN gels demonstrated multiple-energy dissipating mechanisms with a high modulus up to 2200 kPa, toughness up to 2111 kJ m^{-3}, and ability to self-heal quickly and autonomously with regaining 67% of original strength only after 10 min. The developed DN gels will open a new avenue to hydrogel research and holds high potential for diverse biomedical applications, such as scaffold, cartilage, tendon and muscle.

1. Introduction

Self-healing ability is one of the remarkable properties of biological materials such as skin, bone and wood. Furthermore, hydrogels for biomedical applications require simultaneously high stiffness, toughness and self-healing ability to retain shape, resist fracture and heal possible created cracks, respectively. Whereas, most of the synthetic hydrogels with good self-healing performance show low stiffness and/or toughness, which limits their use in many biomedical applications, including scaffold, cartilage, blood vessel, tendon and muscle. Therefore, many works have been done to improve toughness and strength of the self-healing hydrogels, including preparation of various nanocomposite [1–5], double network (DN) [6–8] and hydrophobically associated hydrogels [7,9–13]. However, most of the developed self-healing hydrogels still suffer from low strength and stiffness [5,7,10–16]. Among the developed self-healing hydrogels, DN hydrogels [6–8] exhibited relatively higher mechanical properties, which was correlated to their strong network entanglement [17]. Design of DN hydrogels are commonly based on using two chemically cross-linked networks [18], and only a few hybrid physically/chemically cross-linked DN hydrogels were recently designed by replacing covalent bonds of the first network with non-covalent bonds [14,19–21]. For instance, Chen et al. designed a DN gel including hydrogen bond cross-linked agar as the first network, and a covalently cross-linked polyacrylamide (PAAm) as the second network [6,22,23]. Furthermore, other researchers have synthesized a series of hybrid ionically/covalently cross-linked DN gels using anionic polysaccharides (alginate, gellan gum and carrageenan) as the first ionically cross-linked network and PAAm as the second, covalently cross-linked network. In spite of good strength and toughness of the developed hybrid cross-linked DN gels, their autonomous self-healing is still a slow and low efficient process due to slow chain diffusion and irreversible breakages of covalent bond in chemically cross-linked network(s) [7,24,25].

Therefore, designing a new generation of DN gels comprising two non-covalent associated networks is required to prepare robust and autonomous self-healing gels. Chen et al. [7] have recently designed first fully physically cross-linked DN gels comprising of hydrogen bond associated agar gel as the first network and hydrophobically associated PAAm as the second network. The developed DN gels exhibited high-energy dissipation and extensibility. However, these hydrogels were relatively soft with tensile strength of 267 kPa, and also their self-healing efficiency and speed were relatively low (≈40% recovery of initial strength after 24 h at room temperature) [26].

Many natural materials gain their high strength and toughness from dynamic sacrificial bonds and hidden length [27,28]. Since, the dynamic sacrificial bonds break and re-form dynamically before the fracture of

* Corresponding author.
E-mail address: m.sabzi@maragheh.ac.ir (M. Sabzi).

http://dx.doi.org/10.1016/j.msec.2016.12.026
0928-4931/

the main molecular backbone, therefore, giving a "self-healing" property to materials. For instance, random coil PEVK (Pro-Glu-Val-Lys) domains of Titin (the largest known protein), are believed to reversibly unfold by breakage of sacrificial hydrogen bonds to permit extension of the muscle [29]. Herein, inspired by toughening and healing mechanisms of biological materials, we propose a novel strategy to design stiff, tough DN gels with self-healing ability by substitution of both covalently cross-linked networks with strong, dynamic hydrogen bond cross-linked networks.

Moreover, different from the network structures of hybrid cross-linked and chemically cross-linked DN gels that the second network remains intact during loading, here both the networks of Agar/polyvinyl alcohol (PVA) DN gel can participate in energy dissipation during the deformation process. The second PVA network helps to bear force as the first agar network does, resulting in a DN gel with high toughness. We expect that the ductile and tough (not soft) PVA as the second network will provide an additional platform to dissipate energy, and heal the broken network structure.

To the best of our knowledge, this is the first report for the preparation of biopolymer-based DN gels with neutral physically cross-linked networks, demonstrating strong mechanical properties and fast, efficient self-healing behavior using a simple one-pot method.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA Mowiol 28–99, M_W ~145,000 g/mol and degree of hydrolysis > 99%) was obtained from Aldrich. Agar powder (with gel strength of 750 ± 50 g/cm^2 and melting point of 85 ± 5 °C) was purchased from Scharlau, Spain.

2.2. Preparation of Agar/PVA DN gels

Briefly, a homogeneous solution of PVA was first obtained by dissolving desired amount of PVA in 100 ml distilled water at ~95 °C under vigorous stirring for nearly 2 h; the flask was sealed with plastic film in the whole process to prevent water loss. Subsequently, a predetermined amount of the agar powder was added to the stirring solution of PVA. After 30 min, the obtained clear solution was poured into 5 ml syringes to obtain cylindrical shape specimens. By gradually cooling down the solution to room temperature, agar formed gel at 30–40 °C. Afterward, through a freezing/thawing (F-T) cycle (freezing at − 10 °C for 1 h followed by thawing for 2 h at room temperature) a large number of crystallites were generated in PVA. The PVA SN (single network) gel was prepared with the same procedure, except no agar was added. The sealed samples were kept at refrigerator (at 5–10 °C) until conducting experimental works. Total concentration of Agar/PVA in water was kept constant at 22 wt%, and DN gels were prepared with different proportions of agar and PVA; DN gels were designated as Agar-x/PVA-y, where x and y indicate the weight percentage of agar and PVA in the total amount of the Agar/PVA hydrogel, respectively (e.g. Agar-1/PVA-21 stands for Agar/PVA DN gel containing 1 wt% agar and 21 wt% PVA).

2.3. Characterization

For the spectroscopic studies, the dried samples were milled and mixed with dried KBr powder to make pellets. The Fourier transform infrared spectroscopy, FTIR (Perkin Elmer Spectrum 1) analysis was conducted with the subtraction of KBr background to investigate possible molecular interactions between PVA and agar interpenetrating networks, as well as the crystallization of PVA. For microscopic investigation, the frozen hydrogels in liquid nitrogen were fractured, freeze-dried and gold sputtered. Cross-sectional micrographs were taken using scanning electron microscopy, SEM (MIRA3 FEG-SEM, Tescan). The mechanical properties of cylindrical hydrogel samples (diameter of 1 cm and length of 6 cm) were determined using a Zwick Roell test machine with 1 kN load cell and crosshead speed of 10 mm/min. For reproducibility, at least 6 samples were measured for each gel, and the results were averaged.

3. Results and discussion

3.1. Design and preparation of Agar/PVA DN gels

Compared with synthetic materials, natural materials are gaining increasing interest because of their high biocompatibility and biodegradability without toxic by-products. Completely different from other chemically cross-linked and hybrid cross-linked DN gels, Agar/PVA DN gels in the present study were prepared by a green and one-pot method using water as solvent, without using any chemical cross-linkers, organic surfactants, monomers and initiators. Fig. 1 schematically shows the

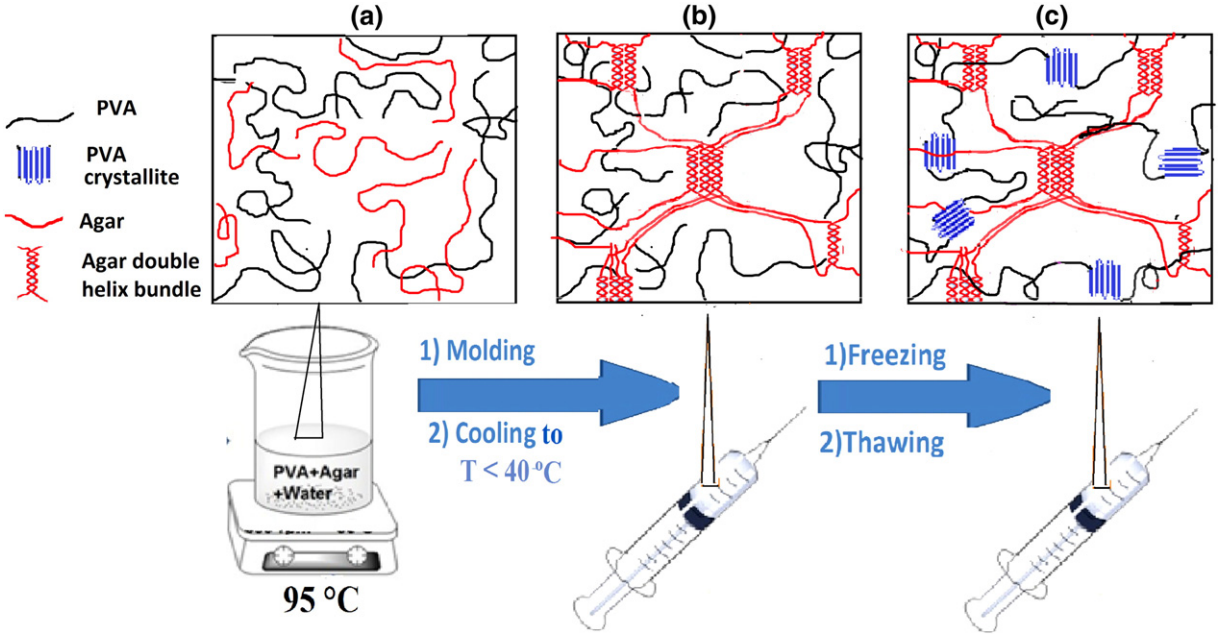

Fig. 1. Schematic illustration of the preparation process and the networks formation of Agar/PVA DN gels.