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Self-healable mussel-mimetic nanocomposite hydrogel based on catechol-containing polyaspartamide and graphene oxide

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ABSTRACT

Stimuli-responsive and self-healing materials have a wide range of potential uses, and some significant research has focused on cross-linking of hydrogel materials by means of reversible coordination bonding. The resulting materials, however, tend to have poor mechanical properties with pronounced weakness and brittleness. In this work, we present a novel mussel-inspired graphene oxide(GO)–containing hydrogel based on modified polyaspartamide with γ-amino butyric acid (GABA), 3.4-dihydroxyphenethylamine (DOPA), and ethanolamine (EA), termed PolyAspAm(GABA/DOPA/EA). Here both GO nanosheets and boric acid (H_3BO_3) act as cross-linkers, interacting with polar functional groups of the PolyAspAm(GABA/DOPA/EA). Compared to PolyAspAm(GABA/DOPA/EA)/B^{3+} gel without GO, the same containing 5 wt% of GO yielded a 10-fold increase in both the storage and loss moduli, as well as 134% and 104% increases in the tensile and compressive strengths, respectively. In addition, the GO-containing polyaspartamide hydrogel exhibited rapid and autonomous self-healing property. Two types of bonding, boron–catechol coordination and strong hydrogen bonding interactions between PolyAspAm side chains and GO nanosheets, would impart the enhanced mechanical strength and good reversible gelation behavior upon pH stimulation to the hydrogel, making this biocompatible hydrogel a promising soft matter for biomedical applications.

1. Introduction

Hydrogels are a class of soft matter possessing three-dimensional polymeric networks and high water content. Hydrogels can be further classified as chemical hydrogels or physical hydrogels, according to whether covalent bonding or noncovalent interactions form their three-dimensional polymeric networks, respectively. Recently, some significant research has been focused on physical hydrogels; the noncovalent bonds in physical hydrogels can include hydrogen bonds, hydrophobic interactions, metal–ligand coordination bonding, or guest–host interactions [1–7]. These physical hydrogels can easily respond to the external environment, including stimuli such as temperature, pH, and light, and can have self-healing properties [8–10]. However, because of the low density of the polymer chains, low friction between the polymer chains, and weak bonding, most noncovalent hydrogels have poor mechanical properties, often restricting their further industrial and biomedical application [11].

Self-healing is a fascinating property of materials to heal or repair their surface or internal damage autonomously and spontaneously. In recent years, there has been increasing interest in the field of self-healing hydrogels, because more safe lifetime and environmental impact of synthetic materials can be achieved by self-healing ability, although self-healing hydrogels have very weak mechanical performance in general [12–14]. Marine mussels withstand high-energy wave impacts in rocky seashore habitats by fastening tightly to surfaces with tough and self-healing proteinaceous fibers called byssal threads, which are heavily decorated with DOPA, a catecholic functionality. In some studies, the catechol moiety of DOPA form strong, reversible interactions with metal ions, leading to the formation of rapid self-healing smart materials [15–17]. Boric acid is a typical Lewis acid, which can react with water to abstract OH^- in aqueous media and convert the trigonal boron to an anionic tetrahedral geometry [18]. Under alkaline conditions, the boron atom has four coordinative bonds to form bis-complexes with diols from catechol groups. In our previous works, we exploited the reversible boron–catechol coordinative bonds to impart self-healing characteristics in dopamine-conjugated polyaspartamide gels with rather week mechanical properties [19].

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Significant approach used to form nanocomposite hydrogels with unique structures and high mechanical strength includes the addition of organic or inorganic nanofillers such as clays, carbon nanotubes, and cellulose. Graphene and graphene oxide have also been identified as nanofillers that can mechanically reinforce hydrogels. Graphene oxide (GO), a two-dimensional single-layer nanomaterial, is prepared from graphite by means of chemical oxidation and exfoliation [20–34]. GO can be stably dispersed in aqueous solutions owing to its various oxygen functional groups, including hydroxyl (—OH), epoxy (—C—O—C), carbonyl (—C═O) and carboxyl (—COOH) [35–42]. Moreover, depending on these functional groups, GO can make strong covalent or noncovalent interactions with polar small molecules or polymers, and also function as nanofillers to mechanically reinforce hydrogels [43–49]. Zhang et al. reported on a high-strength composite hydrogel prepared from GO and PVA by means of a freeze/thaw process [20]. The incorporation of GO in PVA hydrogels resulted in a significant increase of tensile and compressive strength. Without use of organic cross-linkers, GO nanosheets and calcium ions as double cross-linkers trigger the polar groups of the PAM side chains to form the double network with hydrogen bonding and coordination interactions [22]. Cong et al. have reported highly elastic and stretchable GO–PAM nanocomposite hydrogels with high tensile strengths and large stretchability; in these gels, a cross-linked double network is formed by Ca^{2+} ions and a chemical cross-linker [22]. Although many researchers have reported on GO-containing hydrogels with excellent mechanical characteristics, only a few reports have been devoted to highly stretchable smart hydrogels containing GO. Cong et al. also designed a novel kind of GO/PAACA hydrogel endowed with enhanced mechanical properties and self-healing capability [23]. Zhong and coworkers proposed a facile method for fabricating self-healing, super tough graphene oxide (GO)–poly(acrylic acid) (PAA) nanocomposite hydrogels by using Fe^{3+} ions as a cross-linker; the resulting GO–PAA nanocomposite hydrogels exhibit superior toughness, tensile strength, and stretchability [35]. Furthermore, these nanocomposite hydrogels exhibit good self-healing properties after being treated at 45 °C for 48 h. Sun and Wu have demonstrated dual thermal and pH response with good reversibility in hydrogels combining graphene and poly(*N*-isopropylacrylamine) (PNIPAM) [27].

In the present work, inspired by our previous studies, we prepared a novel GO-containing nanocomposite hydrogel based on GABA, DOPA, and EA-conjugated polyaspartamide, hereafter termed PolyAspAm(GABA/DOPA/EA). Polyaspartamides are promising water-soluble, nontoxic, nonantigenic, and biodegradable polymers and can be obtained from the aminolysis of polysuccinimide (PSI), which is easily prepared by thermal polycondensation of D,L-aspartic acid, the thermal polycondensation product of aspartic acid monomer. The hydrogel networks in GO/PolyAspAm(GABA/DOPA/EA)/B^{3+} are formed by GO nanosheets and boric acid as cross-linkers. The pH-responsive and adhesive catechol group can reversibly undergo gelation through metal boron–catechol coordinative bonding, and the polar functional groups of PolyAspAm(GABA/DOPA/EA) side chains should interact with oxygen-containing groups on the GO nanosheets by means of hydrogen bonding to reinforce the mechanical properties of the hydrogel. Both these types of reversible bonds would impart self-healing characteristics to the PolyAspAm gels.

2. Experimental section

2.1. Materials

L-aspartic acid (98%+), ortho-phosphoric acid (98%), *N,N*-dimethylformamide (99.8% anhydrous, DMF), γ-aminobutyric acid (99%+), chlorotrimethylsilane (99%+), dopamine hydrochloride (DOPA), ethanolamine (99%, EA), dibutylamine (99.5%+), sodium hydrosulfite (ca. 85%), acetic acid (99%+), boric acid (99.5%+), and methanol (99.9%+) were purchased from Sigma–Aldrich. Acetone and ethyl ether were obtained from DaeJung Chemical Co. (Siheung, Korea). All other chemicals purchased were of sufficient quality and were used as received.

2.2. Synthesis of polysuccinimide (PSI)

L-aspartic acid (30 g) and 98% ortho-phosphoric acid (30 g) (50:50 wt. ratio) were put into a round-bottom flask and mixed at room temperature. The mixture was heated slowly from room temperature to 180 °C under reduced pressure in about 30 min and then maintained at 180 °C for 4.5 h. The reaction mixture was then cooled and DMF was added to dissolve the product. The resulting solution was precipitated in excess water and the precipitate was washed several times with water to remove residual phosphoric acid until the solution reached pH 7. The product was finally dried at 70 °C in vacuum for 3 d to obtain PSI in white powder form. The molecular weight was estimated to be approximately 75,000 Da, as calculated from an empirical equation relating the solution viscosity to the molecular weight [50].

2.3. Synthesis of polyaspartamide derivatives, PolyAspAm(GABA/DOPA/EA)

2.3.1. Synthesis of γ-aminobutyric methyl ester hydrochlorides (GABAME)

γ-Aminobutyric acid (0.01 mol) was weighed into a round-bottom flask and dissolved in 30 mL of methanol. Chlorotrimethylsilane (0.02 mol) was then added slowly to this solution with gentle magnetic stirring. The reaction mixture was stirred for 24 h at room temperature. After reaction, the solution was precipitated using ethyl ether. The filtered powder was washed with fresh ethyl ether several times and dried under vacuum.

2.3.2. Synthesis of PolyAspAm(GABA/DOPA/EA)

PSI of 0.97 g (corresponding to 0.01 mol succinimide unit) was dissolved in 20 mL of DMF. GABAME of 6.5 mmol (0.66 g) and 6.5 mmol (1.1 mL) of dibutylamine (DBA) were dissolved in 20 mL of DMF. This solution was then added to the PSI solution under vigorous stirring at room temperature. After reaction for 5 d, 0.005 mol of DOPA and 0.005 mol of DBA were added. The reaction was carried out under a nitrogen atmosphere in the presence of 0.05 g sodium hydrosulfite. The reaction mixture was placed in an 80 °C water bath and stirred for 24 h. EA of 10 mol% excess was added slowly to the reaction mixture and stirred at room temperature for 24 h.

The resulting mixture was precipitated in 300 mL of cold acetone, from which the product, PolyAspAm(GABA/DOPA/EA), was removed by filtration. The product was dispersed in a pH 10 solution of sodium hydroxide in distilled water; additional sodium hydroxide solution was dropped into the dispersion to maintain its pH at about 10. The mixture was stirred overnight and then hydrochloric acid was dropped into the solution until its pH stabilized at pH 4.0. The resulting solution was filtered, dialyzed, and then lyophilized to obtain solid polymer.

2.4. Gelation of PolyAspAm(GABA/DOPA/EA) with GO and boric acid

PolyAspAm(GABA/DOPA/EA) samples of different graphene oxide contents were used for the preparation of aqueous solutions and reversible gels. As an example, 0.5 g of PolyAspAm(GABA/DOPA/EA) was dissolved in 3.5 mL of deionized water, into which a sufficient amount of $B(OH)_3$ solution (catechol/$B(OH)_3$ M ratio: 2.0) was then added. A 5 mg/mL GO solution (5 wt%) was then added; the GO in this solution was prepared by means of a modified Hummer's method (Fig. S.1 and S.2) [36,51]. The pH of the mixture was increased to the desired final pH of 9 by the addition of 0.1 N NaOH solution under a nitrogen blanket. The mixture was mechanically mixed to promote the formation of gel by means of B-catechol coordination bonding.