Postprint: Preparation and Properties of SA/PAM/GO Nanocomposite Hydrogel

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Abstract

Sodium alginate (SA)/polyacrylamide (PAM)/graphene oxide (GO) nanocomposite hydrogels were prepared via in situ polymerization. The structure and properties of GO and the composite hydrogels were characterized using X-ray diffraction, atomic force microscopy, infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. The effects of GO content on the structure, mechanical properties, and swelling behavior of the materials were investigated. The results demonstrate that uniformly dispersed GO nanosheets in the polymer system enhanced intermolecular interactions and participated in the formation of the gel network, thereby significantly improving the strength and toughness of the material. Compared with the pure SA/PAM gel, the tensile strength and elongation at break increased by nearly 200%, the compressive strength increased from 2.95 MPa to 4.3 MPa, while the swelling ratio exhibited an initial increase followed by a decrease with increasing GO content, and increased with increasing SA content.

Full Text

Preamble

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Preparation and Properties of Sodium Alginate/Polyacrylamide/Graphene Oxide Nanocomposite Hydrogels

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Abstract

Nanocomposite hydrogels of sodium alginate (SA)/polyacrylamide (PAM)/graphene oxide (GO) were prepared via in-situ polymerization. The structure and properties of GO and the composite hydrogels were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG), and scanning electron microscopy (SEM). The effects of GO content on the material structure, mechanical properties, and swelling behavior were investigated. The results demonstrate that uniformly dispersed GO nanosheets in the polymer system enhanced intermolecular interactions and participated in the formation of the gel network, significantly improving material strength and toughness. Compared with pure SA/PAM hydrogels, the tensile strength and elongation at break increased by nearly 200%, while compressive strength rose from 2.95 MPa to 4.3 MPa. The swelling ratio exhibited an initial increase followed by a decrease with increasing GO content, but increased consistently with higher SA content.

Keywords: composites, sodium alginate, polyacrylamide, graphene oxide, hydrogel, mechanical properties

Introduction

Hydrogels are crosslinked polymers that form three-dimensional network structures through covalent bonds, hydrogen bonds, or van der Waals forces, capable of swelling in water while retaining large amounts of water without dissolution [1]. Based on their response to environmental stimuli, hydrogels are classified as conventional or smart hydrogels. Smart hydrogels can respond effectively to external stimuli such as temperature, pH, electric fields, and magnetic fields, finding widespread applications in biomedical engineering, agriculture, and environmental protection [2-4]. However, smart hydrogels typically suffer from low mechanical strength and toughness. Simply increasing crosslinking density reduces network elasticity and increases brittleness, providing limited improvement in mechanical strength, which restricts their practical applications. Therefore, developing hydrogels with excellent comprehensive properties, particularly mechanical performance, holds significant importance for soft matter research and applications [5, 6].

Preparing organic-inorganic nanocomposite hydrogels represents an important approach to enhancing hydrogel mechanical properties, with nanomaterials such as clay, carbon nanotubes, and silica being commonly employed. Graphene is an emerging star nanomaterial whose unique structure and properties can substantially improve the mechanical performance and thermal stability of composites [7, 8]. Graphene oxide (GO), a key derivative of graphene, possesses abundant hydroxyl, epoxy, and carboxyl groups on its surface, enabling good dispersibility in aqueous and polar solvents and facilitating the formation of nanocomposite hydrogels with hydrophilic polymers. These hydrophilic functional groups enhance interfacial interactions between GO and the matrix material, ensuring good compatibility and significantly improving mechanical properties [9, 10]. For instance, Zhang et al. [11] incorporated GO into PVA hydrogel networks, achieving substantial mechanical enhancement through uniform GO dispersion. Similarly, Shen et al. [12] found that GO improved both the mechanical and thermal properties of PAA/GO composite hydrogels.

Sodium alginate is a linear natural polymer composed of irregularly linked (1,4)-β-D-mannuronic acid (M) and (1,4)-α-L-guluronic acid (G) units. Sodium alginate can be used to prepare pH-sensitive hydrogels through ionic crosslinking [13], graft copolymerization [14], and composite formation with synthetic polymers and inorganic nanomaterials [15]. These hydrogels offer advantages including good biocompatibility, biodegradability, non-toxicity, and low cost. Li et al. [16] prepared SA/PNIPAM/GO temperature/pH dual-sensitive hydrogels with improved mechanical properties through GO incorporation. While SA can enhance pH responsiveness, reports on using GO to reinforce and toughen SA/PAM composite hydrogel systems remain scarce. This study employs in-situ free radical polymerization to prepare sodium alginate/polyacrylamide/graphene oxide nanocomposite hydrogels and investigates their structure and properties.

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1 Experimental

1.1 Materials

Acrylamide (AM), sodium alginate, ammonium persulfate (APS), tetramethylethylenediamine (TEMED), N,N' -methylenebisacrylamide (MBA), graphite (>99.8%, 325 mesh), and all other reagents were of analytical grade.

1.2 Preparation of Graphene Oxide

Graphene oxide was prepared using a modified Hummers method. Under ice bath conditions, 2 g of natural flake graphite and 1 g of $NaNO_3$ were slowly added to 46 mL of concentrated sulfuric acid with stirring. After uniform mixing, 6 g of potassium permanganate was slowly added, and the mixture was reacted at below 5°C for 3 h, followed by stirring at 35°C for 1 h. A certain amount of water was then added dropwise, and the reaction continued at no more than 80°C for 40 min. The product was transferred to a beaker, treated with H_2O_2 until bright yellow, and then washed, centrifuged, and dialyzed to neutral pH for subsequent use.

1.3 Preparation of SA/PAM/GO Nanocomposite Hydrogels

Quantitative AM was mixed with GO aqueous solution, SA, and deionized water. Under ice bath conditions, predetermined amounts of initiator APS, accelerator TEMED, and crosslinker N,N' -methylenebisacrylamide (BIS) were added. The mixture was stirred thoroughly, allowed to stand at low temperature to eliminate bubbles, sonicated for 30 min, transferred to sealed test tubes, and reacted at 10°C for 48 h. The products were removed and stored sealed.

Various hydrogel samples were prepared by varying SA and GO contents. SA concentrations of 0.5%, 0.8%, 1.0%, and 1.3% were used, while GO concentrations of 0, 0.7%, 1.3%, 2.4%, and 3.0% were employed. For example, a sample with 1% SA and 1.3% GO was designated SA1/PAM/GO1.3.

Partial products were cut into 4 mm × 4 mm × 4 mm pieces and immersed in distilled water for 48 h, with water changes at intervals to remove unreacted monomers and small molecules. The purified samples were then dried at 40°C to constant weight.

1.4 Characterization

X-ray Diffraction (XRD): A X' Pert MPD Pro diffractometer with Cu Kα radiation and Ni filter was used at 40 kV and 100 mA, scanning from 1° to 50°.

Atomic Force Microscopy (AFM): Dilute GO aqueous dispersions were deposited on mica sheets. After solvent evaporation, a Nanoscope IIIa Multimode AFM was employed in tapping mode to analyze morphology and sheet thickness.

Fourier Transform Infrared Spectroscopy (FTIR): Dried hydrogel thin films were analyzed using a Nicolet IS-10 FTIR spectrometer in reflectance mode over 650–4000 cm^{-1}.

Scanning Electron Microscopy (SEM): Swelling-equilibrated gel samples were pre-frozen in an ultra-low temperature freezer, freeze-dried for 24 h, sputter-coated with gold, and observed using a JSP-5610LV SEM.

Thermogravimetric Analysis (TGA): A NETZSCH STA409 PC analyzer was used from 30°C to 600°C at 10°C/min heating rate under 100 mL/min nitrogen flow.

Mechanical Testing: Tensile and compressive properties were measured using a TY8000 servo-controlled testing machine according to GB/T1040-92 and GB/T1041-2008 standards at 25°C. Tensile samples (diameter 10.25 mm, length

60 mm) were tested at 50 mm/min crosshead speed with 25 mm gauge length. Cylindrical compression samples (diameter 10.25 mm, height 13 mm) were tested at 2 mm/min. Five specimens were tested per group.

Swelling Ratio: Dried gel samples were immersed in deionized water at set temperatures until swelling equilibrium. After removing surface water with filter paper, the swelling ratio was calculated as (W - W)/W , where W is the dry gel mass and W is the mass at swelling equilibrium. Three parallel measurements were averaged.

2 Results and Discussion

2.1 AFM Analysis

[Figure 1: see original paper] shows the AFM image and corresponding height profile of the prepared graphene oxide. The average thickness of GO sheets was 0.60 nm, indicating successful preparation of monolayer GO sheets [9].

2.2 XRD Analysis

[Figure 2: see original paper] presents XRD patterns of GO and natural graphite. The sharp diffraction peak at approximately 2 = 26.5° corresponds to graphite with high crystallinity and an interlayer spacing of 0.34 nm. After oxidation, a new peak appeared at approximately 2 = 10.8°, corresponding to an expanded interlayer spacing of 0.83 nm, while the original graphite peak disappeared. This significant expansion indicates the introduction of numerous oxygen-containing groups between graphite layers during oxidation [16]. Notably, SA/PAM/GO nanocomposite hydrogels showed no distinct GO diffraction peak around 2 = 10.8°, exhibiting only a broad diffraction peak around 2 = 15° from sodium alginate and polyacrylamide. This absence confirms uniform dispersion of GO sheets within the polymer matrix without aggregation.

2.3 FTIR Analysis

[Figure 3: see original paper] displays FTIR spectra of SA/PAM, GO/SA/PAM, and graphite. After oxidation, graphite showed significantly increased polar groups: a strong broad peak around 3405 cm^{-1} from -OH stretching, peaks at 1730 cm^{-1} and 1630 cm^{-1} from typical C=O and COOH groups, 1425 cm^{-1} and 1225 cm^{-1} from C-OH and C-O-C, and 1049 cm^{-1} from C-O stretching. These characteristic peaks confirm successful oxidation of graphite to GO [9].

In SA, SA/PAM, and SA/PAM/GO spectra, peaks at 2930 cm^{-1} and 2853 cm^{-1} correspond to symmetric and asymmetric C-H stretching, while 1416 cm^{-1} and 1611 cm^{-1} represent symmetric and asymmetric COO^{-} stretching. After GO addition, the broad absorption peaks for -N-H and -OH at 3340 cm^{-1} and 3190 cm^{-1} intensified. With increasing GO content, the N-H in-plane bending vibration at 1654 cm^{-1} shifted to lower wavenumbers with enhanced intensity, attributed to hydrogen bonding between GO nanosheet O-H groups and PAM chain N-H groups. Additionally, the C-O stretching peak of alkoxy groups at 1116 cm^{-1} shifted to lower wavenumbers with increased intensity, indicating hydrogen bonding between dispersed GO and SA molecular chains. These interactions demonstrate that GO participated in the SA/PAM hydrogel network formation during in-situ polymerization, altering the gel microstructure [17].

2.4 Thermogravimetric Analysis

[Figure 4: see original paper] shows TGA results for SA1/PAM and SA1/PAM/GO hydrogels with varying GO content. GO exhibited thermal instability with 25% mass loss below 200°C, primarily from decomposition of unstable oxygen-containing groups into CO, CO_2, and water vapor, reaching approximately 50% total weight loss by 600°C. SA1/PAM and SA1/PAM/GO gels showed similar degradation profiles: ~5% weight loss below 150°C from water evaporation, 150-250°C decomposition of oligomers and oxygen functional groups, and major weight loss at 300-400°C from polymer matrix decomposition and carbonization. Compared with SA1/PAM gel, the SA1/PAM/GO gels exhibited elevated decomposition temperatures (e.g., 317°C, 328°C, and 337°C at 33% weight loss) and higher residual masses at 597°C (16.22%, 19.22%, and 21.05%). This improved thermal stability arises from strong hydrogen bonding or covalent interactions between oxygen-rich GO nanosheets and the polymer network, enhanced interfacial adhesion, and GO participation in the gel crosslinking network, which increased crosslinking density. Additionally, the large specific surface area of GO provided a physical barrier effect, protecting polymer chains [17].

2.5 Hydrogel Morphology

[Figure 5: see original paper] presents SEM images of SA1/PAM/GO hydrogels with different GO contents. Both SA1/PAM and SA1/PAM/GO hydrogels exhibited porous structures, though GO significantly influenced the network architecture. As GO content increased, network density increased while pore size decreased and pores became shallower. This resulted from interactions between polar organic groups on exfoliated GO sheets and polymer chains, creating new crosslinking points that densified the network and reduced pore dimensions. The images also reveal uniform GO dispersion within the matrix, with more homogeneous network structures at higher GO loadings, likely related to GO arrangement and directly affecting mechanical performance [18].

2.6 Swelling Properties

[Figure 6: see original paper] illustrates the equilibrium swelling ratio in deionized water for hydrogels with different SA contents as a function of GO content. Small amounts of GO ($GO < 0.3\%$) enhanced swelling performance, but further

GO addition decreased the swelling ratio. This behavior stems from the abundant hydrophilic oxygen-containing groups on GO surfaces and edges, which initially increased hydrophilic group density in the network and enhanced swelling. However, at higher GO concentrations, hydrogen bonding interactions between GO and the matrix acted as multifunctional crosslinkers, modifying polymer network microstructure and increasing effective crosslinking density, thereby reducing swelling capacity [19]. Additionally, at constant GO content, higher SA concentrations yielded greater swelling ratios due to sodium alginate' s strong hydrophilicity, which enhanced network hydrophilicity and equilibrium swelling [20].

2.7 Mechanical Properties of SA/PAM/GO Hydrogels

Polymer fracture mechanisms involve initial disruption of local van der Waals forces or hydrogen bonds, followed by stress concentration on oriented main chains and eventual covalent bond rupture. Consequently, maximum polymer strength depends on main chain chemical bond forces, intermolecular interactions, and polymer chain flexibility. During tensile testing, hydrogels exhibit distinct responses: initial polymer chain alignment under load, subsequent network elongation, and final chain/network rupture. Thus, polymer type and network structure critically determine tensile performance. SA1/PAM/GO hydrogels demonstrated excellent strength and flexibility, withstanding bending, entanglement, compression, and repeated high-strain deformation.

[Figure 7: see original paper] shows tensile and compressive stress-strain curves for hydrogels with varying GO content. With increasing GO content, tensile strength, compressive strength, and elongation at break all improved substantially. The maximum elongation at break reached 2250%, tensile strength increased from 0.04 MPa to 0.11 MPa, and compressive strength rose from 2.95 MPa to 4.3 MPa. This enhancement originates from GO sheets' high strength and modulus, large specific surface area, and good hydrophilicity, which create strong hydrogen bonding interactions with hydrophilic PAM and SA polymers. Initiators adsorbed on GO surfaces triggered free radical polymerization, generating numerous flexible long polymer chains between GO sheets. Additionally, GO' s polar groups likely participated in chain transfer reactions during polymerization, grafting some macromolecular chains onto GO surfaces. During stretching, GO sheets could slide relative to each other, eliminating stress concentration. The long, flexible polymer chains between GO sheets could move freely without rupturing, substantially improving elasticity. In contrast, hydrogels without GO contained randomly distributed crosslinking points with broad molecular chain length distributions, restricting chain mobility and causing non-uniform stress distribution that led to premature failure at low strains [16, 20].

3 Conclusion

SA/PAM/GO nanocomposite hydrogels were successfully prepared via free radical aqueous solution polymerization. Graphene oxide was uniformly dispersed in the hydrogel matrix, forming strong hydrogen bonding interactions with polymer chains that created new physical and chemical crosslinking points. Partial macromolecular chains grafted onto GO sheets modified the original gel network microstructure. When subjected to external forces, the long flexible chains between GO sheets could move relatively freely, enhancing mechanical strength and toughness. GO addition also improved thermal stability. The swelling ratio generally decreased with increasing GO content but increased with higher SA concentrations.

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