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Material Properties

Mechanical testing and reinforcing mechanisms of a magnetic field-sensitive hydrogel prepared by microwave-assisted polymerization

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ABSTRACT

A novel magnetic field-sensitive composite hydrogel was prepared by microwave-assisted polymerization of salecan and 3-acrylamidopropyl trimethylammonium chloride in the presence of Fe_3O_4@tannic acid (TA) nanoparticles. FT-IR spectroscopy confirmed the formation of the copolymer structure. XRD patterns clearly showed the crystal planes of Fe. TGA verified that incorporation of Fe_3O_4@TA nanoparticles into the copolymer matrix greatly enhanced the thermal stability of the composite hydrogel. The water uptake, retention, saturation magnetization and pore size can be well modulated by changing Fe_3O_4@TA content. More importantly, mechanical tests revealed that the compressive and storage moduli were significantly improved by the introduction of Fe_3O_4@TA nanoparticles or application of external magnetic field, probably due to the particles alignment and subsequent structural rearrangement of polymer chains under the magnetic field. The reinforcement mechanism reported here offers a universal strategy for enhancing the comprehensive mechanical properties of polysaccharide-based materials.

1. Introduction

Stimuli-responsive hydrogels, which undergo abrupt changes in properties in response to external stimuli such as pH, temperature, light, magnetic field and ionic strength, have potential application in various biotechnological areas [1–6]. Among these intelligent materials, magnetic hydrogels have attracted intensive attention due to their unique features, including low friction, fast response, spatial and temporal control manipulation, as well as non-invasive and remote actuation [7]. Magnetic composite hydrogels can be prepared by embedding magnetic nanoparticles such as $Mn_xFe_{1-x}O$, $MgCr_2O_4$ and Fe_3O_4 nanoparticles in a polymer matrix. However, it is challenging to achieve uniform nanoparticle distribution within the hydrogels, and these nanoparticles may diffuse out of the magnetic hydrogels when immersed in a liquid solution [8]. The introduction of tannic acid (TA) into the hydrogel system can help to circumvent such problems. TA is a water-soluble naturally occurring polyphenol and exists in a variety of plants. Its functional ligands like carboxylic groups and multiple phenolic groups can react with iron Fe^{2+} and Fe^{3+} in salt solution to form stable complex compounds [9,10].

Considerable interest has been focused recently on the polysaccharide-based hydrogels due to their low toxicity, biocompatibility and biodegradability [11–13]. However, the poor mechanical properties have hampered the development of these hydrogels as engineering materials. To overcome this drawback, polysaccharide-based hydrogels can be modified by introducing functional nanoparticles into the polymer network matrix [14,15]. Interactions of the polymer chains with the surface of nanoparticles imply a local heterogeneity with respect to polymer segmental mobility. Due to the high surface-to-volume ratio of the nanoparticles, this effect can be remarkable with low nanoparticle content and will produce improvement in the mechanical properties of the material [16]. In particular, the behavior generally observed as reinforcement can be attributed to the interaction of polymer chains with the nanoparticles, which leads to molecular stiffening and the consequent rearrangement of polymer structure [17].

Microwave-assisted polymerization has been an interesting technique to fabricate hydrogels. Because the microwave heating process has high temperatures it creates reactions faster than under conventional thermal conditions [18]. Compared with the conventional thermal methods, microwave-assisted polymerization presents a potentially fast, efficient and selective method for the thermal treatment of biomass and, therefore, allows the rapid conversion of monomer solution to a gel or solid [19].

Salecan is a linear (1→3)-β-D-glucan composed of β-1-3-linked

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glucopyranosyls with a small number of α-1-3-linked. It is obtained by the fermentation of a salt-tolerant new strain Agrobacterium sp. ZX09. As a water-soluble microbial polysaccharide, salecan with unique rheological properties and biological activity can undergo chemical modification attributed to the presence of hydrophilic hydroxyl functional groups [13,20]. Because of these properties, salecan has emerged as a promising candidate for preparing hydrogels as biomedical materials [21–23]. 3-acrylamidopropyl trimethylammonium chloride (APTAC) is a highly hydrophilic monomer. Its polymer PAPTAC, a typical cationic polyelectrolyte, is known to entail a high charge density generated by a large amount of trimethylammonium chloride groups [24]. It is well known that the mechanical properties of hydrogel network are mainly determined by their crosslink density. The electrostatic interaction is also supposed to have cross-linking role [25]. In this way, the mechanical properties would be improved by the electrostatic interaction between negatively charged carboxyl groups and positively charged ammonium groups.

The present paper describes the development of a novel magnetic field-sensitive composite hydrogel based on a salecan/PAPTAC network and Fe_3O_4@TA nanoparticles using microwave-assisted polymerization. To the best of our knowledge, this is the first time salecan/PAPTAC/Fe_3O_4@TA composite hydrogels have been prepared. The embedded Fe_3O_4@TA nanoparticles could act as a physical reinforcement and, therefore, provide an effective approach to enhance the mechanical properties of the composite hydrogels. The structure and thermal stability of the composite hydrogels was characterized by FT-IR, XRD and TGA, respectively. The effect of Fe_3O_4@TA content on their swelling behavior, morphology and magnetic property was studied. In particular, the compressive and rheological properties in response to an external magnetic field were investigated in detail.

2. Experimental section

2.1. Materials

Salecan was made by the Center for Molecular Metabolism, Nanjing University of Science & Technology (Nanjing, China). APTAC, ammonium persulfate (APS) and tetra(ethylene glycol) diacrylate (TEGDMA) were purchased from Aladdin Reagent Corporation (Shanghai, China).

2.2. Salecan/PAPTAC/Fe_3O_4@TA composite hydrogel preparation

Hydrogel precursors were prepared by mixing a calculated amount of salecan solution (2%, w/v), Fe_3O_4@TA nanoparticles dispersion (5%, w/v), 1 mL of APTAC solution (40%, w/v) and 1 mL of TEGDMA solution (2%, w/v) in a 50 mL three-neck flask. The mixture was kept at 0 °C with an ice-water bath and stirred under Ar atmosphere for 30 min. Then, 1 mL of APS solution (5%, w/v) was added under vigorous stirring. The final volume of the solution was made up to 7 mL with deionized water. The resultant mixture was poured into a mold and placed in a domestic microwave oven (Sineo, China) at 500 W for 5 min. After polymerization, the resulting composite hydrogels were sliced into small pieces and immersed in deionized water for 1 week. The water was refreshed four times every day in order to remove the residual unreacted monomer. Subsequently, the swollen composite hydrogels were frozen at −20 °C overnight in a freezer and then lyophilized under vacuum in a freeze dryer (Christ, Alpha 1–2 LD Plus, Germany) for 24 h. The feed compositions of the composite hydrogels are displayed in Table 1. The preparation of Fe_3O_4@TA nanoparticles is shown in supporting information.

Table 1
Composition of initial reaction mixtures used for the preparation of the hydrogels.

Ingredient	Designation			
	SPAP	SPAPFT-1	SPAPFT-2	SPAPFT-3
Salecan solution (2%, w/v) (mL)	1	1	1	1
APTAC solution (40%, w/v) (mL)	1	1	1	1
TEGDMA solution (2%, w/v) (mL)	1	1	1	1
APS solution (5%, w/v) (mL)	1	1	1	1
Fe_3O_4@TA dispersion (5%, w/v) (mL)	0	1	2	3
Deionized water (mL)	3	2	1	0

3. Characterization

3.1. Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra of salecan and the composite hydrogels were obtained on a Nicolet IS-10 spectrometer, using the universal attenuated total reflectance (ATR) attachment. Four scans were registered with a resolution of 4 cm^{-1} in the range of 650–4000 cm^{-1}.

3.2. X-ray diffraction (XRD)

XRD data of salecan and the hydrogels were collected using a D8 Focus X-ray diffractomer (Bruker) with Cu Kα radiation at 40 kV and 40 mA (λ = 0.154 nm) in the 2θ range of 10°–65°.

3.3. Thermogravimetric analysis (TGA)

TGA of salecan and the hydrogels was carried out using a Netzsch TG209F1 thermogravimetric analyzer operating in a temperature range of 50–600 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

3.4. Water uptake and retention

The water uptake of the hydrogels was measured gravimetrically in deionized water and NaCl solution with different concentrations (0.3–1.5 wt%) at room temperature. The dry samples were first placed in deionized water or NaCl solution. At predetermined time intervals, the samples were taken out of the media and the surface water was removed by filter paper. Then, the weight of the samples was measured. Water uptake was calculated using the following equation (1):

$$\text{Water uptake} = (W_t - W_d)/W_d \quad (1)$$

W_t and W_d represent the weights of the swollen hydrogel at time t and dry hydrogel, respectively. All experiments were performed in triplicate.

For the water retention test, the freeze-dried samples were first soaked in excess deionized water for 2 h to ensure equilibrium water absorbency. Then, the swollen samples placed in a 45 °C oven and weighed at selected intervals. The water retention ratio was obtained based on equation (2):

$$\text{Water retention (\%)} = (W_t/W_{eq}) \times 100 \quad (2)$$

W_t and W_{eq} represent the weights of the deswollen composite hydrogels at time t and swollen composite hydrogels at equilibrium, respectively.

3.5. Magnetic property

Magnetization measurements were performed by a Lakeshore 7400-s vibrating sample magnetometer (VSM). Samples were measured in sealed plastic capsules, fixed on a glass sample holder between two poles of an electromagnet and vibrated at a frequency of 70 Hz. The hysteresis loops were obtained by varying the magnetic fields in the range of 0–15 kOe at room temperature. Three replicates were tested for each composition.

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