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Synthesis and characterization of lignosulfonate-*graft*-poly (acrylic acid)/hydroxyethyl cellulose semi-interpenetrating hydrogels

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ABSTRACT

Maximizing the use of waste is an important part of the strategy for sustainable development. Lignosulfonate, a waste product with sufficient reactive functional groups, can be used as reinforcing materials in polymer composites. In this work, composite hydrogels composed of lignosulfonate-*graft*-poly (acrylic acid) AA network and hydroxyethyl cellulose (HEC) polymer chains are synthesized through *in situ* polymerization and cross-linking reaction. The composite hydrogels have semi-interpenetrating network (semi-IPNs) structure, which is driven by the hydrogen bond interactions between proton-donating PAA and proton-accepting HEC. The mechanical properties of these composite hydrogels, including fracture stress, critical compression and elastic modulus and elongation are investigated by tensile measurements. These composite hydrogels exhibit higher toughness and extensibility compared to conventional PAA polymer hydrogels. Moreover, full recovery of their original shape after the removal of compression stress indicates their excellent shape-recovery property. Due to their porous structure, these hydrogels show stimuli responsive swelling properties in aqueous solution depending on the pH or ionic strength, which facilitate the repeating absorption and removal of dyes. Therefore, this work may open a new pathway to synthesize functional materials based on lignosulfonate.

1. Introduction

Stimuli responsive polymer hydrogels have long been investigated as potential intelligent materials for various applications, such as controlled drug release, tissue culture substrates, diagnostics, enzyme immobilization and separation, *etc.* [1–7]. Poly acrylic acid (PAA), one of the pH-sensitive synthetic polymers, is widely used to construct stimuli responsible hydrogels for biomedical applications [8–10]. However, conventional PAA based hydrogels show poor mechanical properties, which restricts their application. To address this shortcoming, much effort has been made to develop PAA hydrogels having optimized network structures to reinforce their mechanical strength, including double-network (DN) hydrogels [11], nanocomposite hydrogels [12], triblock copolymer hydrogels [13], hydrogen bonding hydrogels [14], and some other hydrogels with carefully designed and manipulated microstructures [15].

Recently, there are dramatically increasing interests in bio-renewable materials arising from environmental awareness [16,17] and health concerns [18–20]. Lignin, a heterogeneous aromatic biopolymer, is the second most abundant natural polymer as well as one of the well-known environmentally friendly bio-renewable resources [21–23], and it has been reported that the chemical pulp industries generate nearly 30 million tons all over the world every year [24]. As the most recalcitrant component of lignocelluloses biomass (cellulose, hemicelluloses and lignin) [25,26], lignosulfonate generally has been treated as a waste product in the pulping mill and its basic component is derivatives of benzyl oxide, which is as well as lignin. According to reports [27–29], lignosulfonate offers sufficient reactive functional groups, good elasticity, improved hydrophobicity and better surface activity, rheological properties, mechanical properties, *etc.* making it a potential candidate to be used as reinforcing material in research.

In the past decades, lignosulfonate has emerged as potential materials for various polymer composite applications, *e.g.*, stabilizing agents [30], lubricants [31], coatings [32], surfactants [33], superabsorbent hydrogels [34], and so on [35,36]. Therefore, the preparation of functional materials from lignosulfonate will improve their economics as well as perhaps solve the problem of their waste disposal.

Despite many reports on the synthesis of lignosulfonate–polymer composites, only a few work reported the construction of lignosulfonate-based polymer hydrogels [37]. Some authors reported the chemical cross-linking of kraft lignin or water-soluble

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lignosulfonates by formaldehyde to prepare lignosulfonate-based hydrogels [38]. However, the preparation of lignosulfonate-based hydrogels having both stimulus sensitivity and good strength are rarely reported. In this paper, we prepared lignosulfonate-*graft*-poly (acrylic acid)/hydroxyethyl cellulose composite hydrogels (lignosulfonate-*g*-PAA/HEC hydrogels) with semi-IPNs structure by *in situ* polymerization in HEC solution. HEC is known as a hydrogen-bond acceptor, while acrylic acid is a potent hydrogen-bond donor. Polymerization of AA along with HEC leads to multiple intermolecular hydrogen bonds, which cause the formation of lignosulfonate-g-PAA/HEC hydrogels. These as-prepared hydrogels showed good mechanical strength and stimuli responsible swelling properties, which could be used to treat the dye contained waste water.

2. Experiments

2.1. Materials

Hydroxyethyl cellulose (HEC, vis: 1000–1500 mPa·s), acrylic acid (AA), N,N′-Methylenebisacrylamide (MBAAm),were purchased from Aladdin Chemical Company and used as received. Lignosulfonate was kindly supplied by Liya Technology Co. Ltd. (Shandong, China). All other solvents and agents were analytical grade and used without further purification.

2.2. Synthesis of lignosulfonate-g-PAA/HEC hydrogels

The lignosulfonate-*g*-PAA/HEC hydrogels were prepared by polymerization and crosslinking of lignosulfonate and AA in HEC aqueous solution in the presence of MBAAm. Typically, 3 g of HEC, 1.2 g of lignosulfonate and 0.4 g of MBAAm were dissolved in 30 mL of 2.7% (w/v) AA solution. The solution was stirred at room temperature until it became clear. Then 500 μL of 1% ascorbic acid solution and 500 μL of 5% hydrogen peroxide (H_2O_2) aqueous solution were added into the reaction system to initiate polymerization at room temperature. The reaction was allowed to proceed at 37 °C for 24 h. After that, the hydrogel was obtained and dried under vacuum at 40 °C to constant weights, and stored in desiccators for further use. Other hydrogels were also synthesized in the same way.

2.3. Mechanical properties tests

The compressive properties of hydrogels were measured by compressive test using Instron 5565 (Instron Co. USA). Hydrogel samples with cylindrical shape were placed at the center of the lower compression plate and then compressed by the upper plate at a speed of 10 mm/min until the breakdown of the hydrogel. The strain under compression is defined as the change in the thickness relative to the pre-compressed thickness of the specimen. The ultimate stress in the compressive destruction test was determined from the peak of the stress–strain curve.

For the tensile test, samples of 1.34–2.5 mm in thickness were cut into a dumbbell shape. Tensile velocity was 10 mm/min. For both compressive test and tensile test, the fracture strain and stress were determined as the nominal strain and stress at the failure point, respectively. Work of extension was determined from the area under the stress–strain curve of the tensile test. Measurements were performed at least three times for each sample.

2.4. Swelling properties tests

Swelling studies were carried out by comparing the fully swollen weight and the dry weight of hydrogels. The dried hydrogels (W_1) were immersed in an excess amount of deionized water at 25 °C until swelling equilibrium was attained. The wet weight of the sample (W_2) was determined after removing the surface water with filter paper. Equilibrium swelling ratio (Q_{eq}) was determined by the following equation.

$$Q_{eq} = (W_2 - W_1)/W_1 \tag{1}$$

To measuring the swelling characteristics of hydrogels at different pH and salt solutions, buffer solutions with various pH values were prepared with $C_6H_8O_7 \cdot H_2O$, $Na_2HPO_4.12H_2O$ and NaOH properly. pH values were precisely measured by a pH meter at room temperature. The various salt solutions were adjusted with NaCl, $CaCl_2$ and $AlCl_3$, and their concentrations were adjusted to 0.6%. The equilibrium swelling ratio (Q_{eq}) of the hydrogels in various pH buffer solutions and salt solutions were measured according to a method similar to that for distilled water.

2.5. Adsorption studies

Dried hydrogel samples (0.5 g) were immersed in 50 mL 9 mg/mL of Congo Red (CR) solutions at 25 °C. During the adsorption process, 3 mL of the CR solution was taken out from the system at regular time interval and the CR concentrations were measured and analyzed using a 1800 model UV–vis spectrophotometer.

2.6. FT-IR

FT-IR analysis was recorded on Nicolet iS10 FT-IR spectrometer (Nicolet iS10, Nicolet, USA). The samples were lyophilized to dry powder, and the obtained dried powder was mixed with KBr and pressed to a plate for measurement. Range: 4000–500 cm^{-1}, resolution: 4 cm^{-1}, number of scans: 16.

3. Results and discussion

3.1. Preparation of lignosulfonate-g-PAA/HEC hydrogels

In this work, hydrogel with semi-IPNs structure was synthesized, which composed of lignosulfonate-*graft*-PAA cross-linking networks and hydroxyethyl cellulose (HEC) polymer chains. The lignosulfonate-*g*-PAA/HEC (LS-A/H) hydrogel was prepared through *in situ* polymerization of lignosulfonate and acrylic acid in HEC solution, using H_2O_2/ascorbic acid as a redox initiator and MBAAm as a cross-linking agent. The polymerization and grafting process of AA on the lignosulfonate chain was demonstrated in Fig. 1. Firstly, hydroxyl radicals were formed from the reduction of H_2O_2 by ascorbic acid. Then the phenoxy radicals were obtained through the oxidation of Ph-OH groups from lignosulfonate by the hydroxyl radicals [39]. Finally, phenoxy radicals initiated the polymerization of AA to form the grafted copolymer lignosulfonate-g-PAA. Fig. 2 presents FT-IR spectra of pure HEC, lignosulfonate, PAA and dried LS-A/H hydrogels respectively. It was observed that in the LPH hydrogel spectrum, the peak for non-etherified –OH group from Ph-OH at 1418 cm^{-1} was much weaker than that in the lignosulfonate. This is reasonable that due to the polymerization of AA initiated by phenoxy radicals, some of the Ph-OH groups in the lignosulfonate forms ether bonds with PAA, which consequently reduces the content of non-etherified Ph-OH groups. This result verified the successfully grafting of AA onto the lignosulfonate chains.

Furthermore, HEC chains were randomly distributed throughout the lignosulfonate-*g*-PAA networks to form the LS-A/H hydrogels. The selection of HEC as a semi-IPNs polymer cross-linking agent in LPH hydrogels is due to the formation of strong hydrogen bonds between the hydroxyl groups of HEC and carboxyl groups of PAA chains, which can significantly improve mechanical properties of the lignosulfonate-*g*-PAA networks. The existence of hydrogen bonds between the HEC and PAA was verified by FT-IR analysis as shown in Fig. 2. For the HEC, the characteristic absorption bands of –OH groups at 3431 cm^{-1} shifted to 3420 cm^{-1} in the LS-A/H hydrogels spectrum. Moreover, the broad