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Glow discharge electrolysis plasma initiated preparation of temperature/pH dual sensitivity reed hemicellulose-based hydrogels

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ABSTRACT

The temperature/pH dual sensitivity reed hemicellulose-based hydrogels have been prepared through glow discharge electrolysis plasma (GDEP). The effect of different discharge voltages on the temperature and pH response performance of reed hemicellulose-based hydrogels was inspected, and the formation mechanism, deswelling behaviors of reed hemicellulose-based hydrogels were also discussed. At the same time, infrared spectroscopy (FT-IR), scanning differential thermal analysis (DSC) and scanning electron microscope (SEM) were adopted to characterize the structure, phase transformation behaviors and microstructure of hydrogels. It turned out to be that all reed hemicellulose-based hydrogels had a double sensitivity to temperature and pH, and their phase transition temperatures were all approximately 33 °C, as well as the deswelling dynamics met the first model. In addition, the hydrogel (TPRH-3), under discharge voltage 600 V, was more sensitive to temperature and pH and had higher deswelling ratio.

1. Introduction

Intelligent hydrogels, which exhibit sensitive responses to environment, such as temperature, pH, salt, electric field, and chemical environment, are widely applied in sensors, drug release, tissue engineering and other fields (Gupta, Vermani, & Garg, 2002; Juntanon, Niamlana, Rujiravanit, & Sirivat, 2008; Wu et al., 2008; Hua, Chen, Li, & Zhao, 2008; Chauhan & Chauhan, 2008; Wang, Gao, & Wang, 2012). Temperature and pH sensitive hydrogels, the most important kind of intelligent hydrogels, have been paid special attention. Conventional preparations for temperature and pH sensitive hydrogels are radical polymerization, interpenetrating to introduce thermosensitive or pH sensitive monomers, such as *N*-isopropyl acrylamide (NIPAAm), acrylic acid (AA), etc, then the temperature and pH sensitive hydrogels with three-dimensional network are formed under the effect of crosslinking agents. However, the functional hydrogel displays poor biocompatibility and biodegradability due to petrochemical products as the raw material. Therefore, using renewable resources as raw materials to prepare hydrogels is getting more and more attention.

Temperature and pH sensitive hydrogels were prepared successfully by using natural polymers and their derivatives, such as chitosan, sodium alginate, dextran and cellulose, etc, as base materials and all showed good performance (Baumberger, Caroli, & Martina, 2006; Pourjavadi, Harzandi, & Amini-Fazl, 2008; Yan, Zhang, Lu, Su, & Ge, 2005). Moreover, hemicellulose, one of the three major components in plant biomass (Hansen & Plackett, 2008; Lindblad, Ranucci, & Albertsson, 2001; Goksu, Karamanlioglu, Bakir, Yilmaz, & Yilmazer, 2007), exists in all cytoderm of plants (constituting about 20–30% of the biomass). Statistical information shows hemicellulose, annual production is 3.5×10^{10} t, is one of the most abundant and cheapest renewable resources (Peng, Ren, Zhong, Peng, & Sun, 2011). But as a result of the complexity and diversity of its structure, the application in intelligent hydrogels was rarely reported.

Various initiated techniques have been proposed for the preparation of hydrogels in the past few decades which include chemical initiation, UV-curing technique, microwave or γ-ray irradiation, etc (Peng et al., 2011; Essawy & Ibrahim, 2004; Peng, Zhong, Ren, & Sun, 2012; Sen, Singh, & Pal, 2010; Sun et al., 2012), but all these trigger technologies had residual monomers and initiators, high energy consumption, etc. Glow discharge electrolysis plasma

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(GDEP), which belongs to the non-equilibrium plasma, exhibits the characteristics of non faraday because it produces numerous highly active particles in plasma electrolysis, such as HO•, H•, HO_2•, e_{aq}^-, and H_2O_2 (Gao et al., 2006; Gao, Li, Li, Liu, & Yang, 2012; Lu, Yu, & Gao, 2006; Sengupat & Singh, 1994; Sengupat, Singh, & Srivastava, 1998; Sengupta, Sandhir, & Misra, 2001). In addition, GDEP was used in organic synthesis, wastewater degradation, surface modification and other fields due to its simple equipment, low energy consumption, no environmental pollution (Peng et al., 2011). However, there were scarcely reports about preparation for temperature/pH dual sensitivity reed hemicellulose-based hydrogel through GDEP up to now. Therefore, we used hemicellulose as backbone, hydroxyl radicals which were produced by GDEP as initiators, acrylic acid (AA) and *N*-isopropyl acrylamide (NIPAAm) as monomers, *N*,*N*-methylene double acrylamide (MBA) as crosslinking agents to prepare temperature/pH dual sensitivity reed hemicellulose-based hydrogel. What's more, the formation mechanism, the phase transition temperature, microstructure, properties characterization, discharge parameter, swelling ratio, pH, and salt multiple response behaviors and deswelling kinetics were also examined.

2. Experimental

2.1. Materials

Reed hemicelluloses were isolated according to the experiment by Peng et al. (2011) using 10% KOH at 25 °C for 10 h with a solid to liquor ratio of 1:20 (g/ml) from holocellulose obtained by delignification of reed with sodium chlorite in acidic solution (PH 3.7–4.0, adjusted by 10% acetic acid) at 80 °C for 2 h. Acrylic acid and *N*-isopropyl acrylamide (AA and NIPAAm, analytical reagent grade, Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China), were purified by distillation under reduced pressure to remove the inhibitor hydroquinone before use. *N*,*N*-Methylene-bis (acrylamide) (MBA) was purchased from Shanghai Chemical Reagent Corporation (Shanghai, China). All other reagents used were of analytical grade and without further purification.

2.2. Experiment apparatus

The experimental apparatus consisted of a direct current power supply and a reactor, as shown in Fig. 1. The power supply was a LW100J1 DC power supply (Shandong, China) providing the voltage of 0–1000 V and the current of 0–1 A. The reactor was a cylindrical plexiglas chamber (Φ 30 mm × 100 mm), containing a reflux condenser, a thermometer, a nitrogen conduit, a platinum anode with a diameter of 0.5 mm sealed into a glass tube to generate a glow discharge plasma in the aqueous solution, and a graphite cathode with a diameter of 10 mm. A magnetic stirring bar was placed at the bottom of the flask to keep the solution mixed well.

2.3. Preparation of temperature/pH dual sensitivity reed hemicellulose-based hydrogels

The isolated hemicelluloses (1.0 g) and Na_2SO_4 (0.6 g) were dissolved in distilled water (20.0 mL) in the reactor as shown in Fig. 1 with a magnetic stirrer at 80 °C for 2 h before the solution was cooled to room temperature. The solution was continuously purged with gaseous N_2 for 15 min. The glow discharge lasted 90 s with various applied voltage of 500–650 V. The same quality of AA (1.0 g) and NIPAAm (1.0 g) were added, and 0.05 g MBA was added to the solution after monomers were dissolved completely. The mixture was allowed to stir for 2 h under nitrogen gas atmosphere, and then the reaction was allowed to proceed at room temperature for 24 h without stirring. Thereafter, the temperature/pH dual

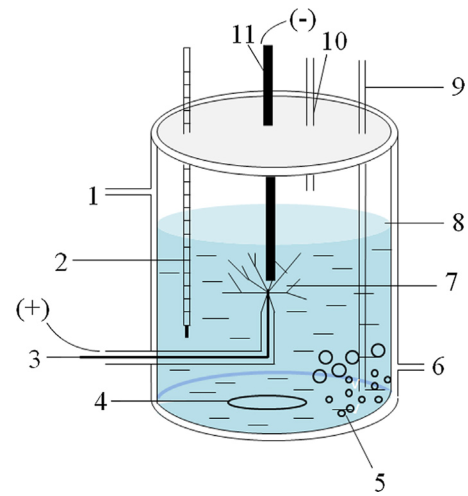

Fig. 1. The experimental apparatus of the glow discharge electrolysis plasma. (1) Cooling water outlet, (2) thermometer, (3) anode, (4) stirring pill, (5) gas bubbles, (6) cooling water inlet (7) glow discharge area, (8) solution level, (9) gas inlet, (10) gas outlet, (11) cathode.

sensitivity reed hemicellulose-based hydrogels were obtained. The hydrogels were marked for TPRH-1, TPRH-2, TPRH-3 and TPRH-4 under discharge voltage of 500 V, 550 V, 600 V and 650 V, respectively. The hydrogels were again carefully washed thoroughly in distilled water and acetone, and then were dried to a constant mass at 60 °C.

2.4. Properties characterization of temperature/pH dual sensitivity reed hemicellulose-based hydrogels

2.4.1. FT-IR analysis

FT-IR spectra of reed hemicellulose and temperature/pH dual sensitivity reed hemicellulose-based hydrogels were investigated by using Fourier Transform Infrared Spectrophotometer (Thermo Nicolet380). All measurements were carried out using the KBr disk technique.

2.4.2. VPTT (volume phase transition temperature) determination

The VPTT of the temperature/pH dual sensitivity reed hemicellulose-based hydrogel was analyzed using a differential scanning calorimeter (DSC) (Mettler Toledo 822). All the hydrogels were immersed in deionized water at room temperature and allowed to swell for at least 48 h to reach equilibrium state. The DSC analysis of the swollen hydrogels were performed from 25 °C to 45 °C at a heating rate of 3 °C/min under nitrogen atmosphere with a flow rate of 40 mL/min. Deionized water was used as the reference in DSC analyses.

2.4.3. Morphology of temperature/pH dual sensitivity reed hemicellulose-based hydrogels

The temperature/pH dual sensitivity reed hemicellulose-based hydrogels were first immersed in distilled water to reach equilibrium swelling, and then the swollen hydrogel samples were freeze-dried. The morphology of reed hemicellulose-based hydrogels was investigated by scanning electron microscopy (SEM, Quanta FEG). Specimens were coated with gold for 30 s in SEM coating equipment.

2.4.4. Temperature sensibility of reed hemicellulose-based hydrogels

Preweighted dry hygrogels (m_d) were immersed into excessive distilled water to reach a state of equilibrium swelling under different temperatures. The weight of the samples was monitored