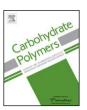
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Modification mechanism of sesbania gum, and preparation, property, adsorption of dialdehyde cross-linked sesbania gum



Tang Hongbo*, Gao Shiqi, Li Yanping, Dong Siqing

Science School, Shenyang University of Technology, Shenyang 110870, China

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ABSTRACT

This paper studied the modification mechanism of Sesbania gum (SG) by means of the variations in the numbers of surface hydroxyl groups on the granules, Schiff's agent coloration of aldehyde groups, Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), energy dispersive spectrum (EDS), etc., and also examined the preparation, property and adsorption of dialdehyde cross-linked sesbania gum (DCLSG). The results showed that the surface hydroxyl numbers of cross-linked sesbania gum (CLSG) decreased with increasing the cross-linking degree. The distribution of the aldehyde groups on the DCLSG particles was nonuniform because most of aldehyde groups mainly located on the edge of particles. The cross-linking occurred only on the surface of SG particles. The oxidization occurred not only on the surface of SG particles, but also in the interior of particles. The cross-linking or oxidization changed the thermal properties, and reduced the swelling power, viscosity, alkali and acid resistance of SG.

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1. Introduction

In recent years, the natural polymers have attracted more and more attention (Baran, Mentes, & Arslan, 2015). They have been extensively used in many fields due to their good performances, worldwide abundance, and renewability (Baran, Açıksöz, & Mentes, 2016; Lawal, 2009; Singh, Kaur, & McCarthy, 2007). But as the demand rises, so does the price of the familiar natural polymers. It is, therefore, necessary to find some substitutes. Sesbania gum is one of the natural polymers which can be used as a substitute for arabic gum or guar gum because of its similar performances and relatively low price. Sesbania gum is extracted from the seeds of sesbania. Sesbania is a kind of annual herbs widely planted because of its good nitrogen fixation ability (Jian, Shen, & Yang, 2009; Ståhl, Högberg, Sellstedt, & Buresh, 2005), salt tolerance (Muhammad & Alweena, 2003), barren tolerance and flooding tolerance (Shiba & Daimon, 2003). The structure of the SG involves β (1 \rightarrow 4) glycosidic bonds linked mannose and α (1 \rightarrow 6) glycosidic bonds linked galactose on the side chains. The ratio of mannose to galactose is about 2:1. The physicochemical characteristics and chemical structures of the SG are similar to those of guar gum. Like other galactomannans, SG is insoluble in organic solvents, but partially soluble in water (Ogwal, Wu, & Hu, 2011).

The SG is composed of galactomannan, and a small amount of protein and fat. Many of its properties are intermediate between starch and polysaccharide. The SG is widely used in the modern industry as a carrier, fortifier, densifier, gelatinizer, catalyst support, and so on (Sarkar & Sharma, 2012; Gayatri & Madhabhai, 2009). However, the SG has poor viscosity stability, high viscosity, and high content of water insoluble substances, as well as long process of decomposition (Wang et al., 1997; Liu, Qi, Gao, Xue, & Shen, 2012) so that its application is limited to some extent. The modification can improve the properties of SG, and expand the application field of SG. In present, the modification methods can be mainly divided into two subsets: physical method and chemical method. By the physical method, the modified SG can be created by the wet milling or grinding to develop the speed of the hydration and the viscosity of the glue solutions. It also can be made by flaking or cooking to increase its viscosity and thermostability. By the chemical method, the SG can be modified by reacting SG with some of chemical reagents to obtain optimal performances. These chemical methods include oxidization (Shen et al., 2011), graft (Liu, Gao, Xue, Shen, & Cui, 2012), esterification (Zhang, Zhang, Li, & Cui, 2007), etherification (Rekaby, Abd El-Thalouth, Rahman, & Abd El-Satar El-Khabery, 2010), and so on.

Few studies have centered on the chemically modified or the composite chemically modified SG. Therefore, the research of dialdehyde cross-linked sesbania gum, as a novel material, is significant owing to the degradation, renewability and biocompatibility of SG. The cross-linking is a common modification for a natural

^{*} Corresponding author.

E-mail address: tanghb6666@163.com (H. Tang).

polymer such as starch or guar gum, which can increase the degree of gelation, and develop the resistance of machinability, heating, shearing, acid and alkal (Ačkar et al., 2015). The cross-linked SG can be used in the drilling and petroleum cracking. Common cross-linking agents include phosphorus oxychloride, epoxy chloropropane, and sodium trimetaphosphate. In this paper, glutaraldehyde was selected as a cross-linking agent (Tian et al., 2010; Tong, Gao, & Möhwald, 2008). The oxidation of sodium periodate is a common oxidation one, which can make the modified polymer to develop alkali solubility, cohesiveness, and fungus resistance. Sodium periodate, as a highly selective oxidizing agent, is capable of cleaving the C2 and C3 linkage of the anhydroglucose units with the formation of the dialdehyde groups (Kim, Kuga, Wada, Okano, & Kondo, 2000).

The aim of the current work is to study the modification mechanism of SG based on cross-linking and oxidization, and also the preparation and properties of DCLSG as a novel material in order that DCLSG is well used for the sustained release and removal of amine compounds. Moreover, the adsorption of DCLSG was researched using L-asparagine as an adsorbate, a drug used for lowering the blood pressure, the treatment of bronchiectasia, peptic ulcer, and gastric dysfunction (Boev, Kuznetsova, Baykova, & Urazova, 2011).

2. Materials and methods

2.1. Materials

Sesbania gum was purchased from Xiangshui Unified Guar Gum Co., Ltd. Glutaraldehyde was purchased from Tianjin Rgent Chemical Reagents Co., Ltd. Sodium periodate was purchased from Tianjing Fuchen Chemical Reagents Factory. Ethanol was purchased from Shenyang Xinxing Reagents Factory. Potassium sulphate and selenium were purchased from Shenyang Dongxing Reagents Factory. Copper sulphate and sodium hydroxide were purchased from Shenyang Huizhong Physical and Chemical Products Factory. Methyl red and basic fuchsin were purchased from Shenyang Third Reagents Factory. Methylene blue was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Zinc was purchased from Tianjin Bodi Chemical Co., Ltd. Bonic acid was purchased from Kaiyuan Reagents Factory. L-Asparagine was purchased from Henan Jinrun Food Additives Co., Ltd. Sodium metabisulfite was purchased from Shenyang Xinhua Reagents Factory. Sodium chloride was purchased from Tianjin Damao Chemical Reagents Factory. Sulfuric acid and hydrochloric acid were purchased from Shenyang Economical and Technological Development Reagents Factory. Potassium bromide was purchased from Pike Company in USA.

2.2. Preparation of cross-linked sesbania gum (CLSG)

 $90.0\,\mathrm{g}$ of dried sesbania gum and $288.0\,\mathrm{g}$ of ethanol were put into a $500\,\mathrm{mL}$ flask and then heated in a water bath until the required temperature was reached. The pH of the slurry was adjusted with

0.1 mol/L hydrochloric acid to 4.0. 18.0 g of glutaraldehyde aqueous solutions with a concentration of 50% (w/w), and 63.0 g of distilled water were added into the slurry to prepare the slurry with a concentration of 25% (w/w, dry basis). The pH of the slurry was adjusted with 0.1 mol/L hydrochloric acid to 4.0 again. After the reaction was carried out for 1.5 h, the slurry was filtrated, the obtained cake was washed by ethanol aqueous solutions with a concentration of 50% until it was neutral, and then dried under the infrared lamp until the moisture content achieved about 10%. The dried products were ground to pass through an 80 mesh sieve. Finally, the CLSG was obtained (Chen, Zhang, Dang, & Shu, 2013). The chemical formula of SG reacting with glutaraldehyde is as follows:

2.3. Preparation of dialdehyde cross-linked sesbania gum (DCLSG)

10.0 g of dry cross-linked sesbania gum and 140.0 g of ethanol were put into a 500 mL flask with three necks, stirred, and heated to 30–60 °C. 60.0 g of sodium periodate solution with a mass concentration of 30% was then added to produce a slurry with a mass concentration of 4.76%. After the reaction was carried out for 2.5 h, the slurry was filtrated, the obtained cake was washed by the distilled water until it had no periodate or iodate ions. The cake was dried under the infrared lamp until its moisture content achieved about 10%. After that, the dried products were ground to pass through an 80 mesh sieve. Finally, the DCLSG was obtained (Zhang, Wang, Zhang, Yang, & Wang, 2010). The chemical formula of CLSG oxidized by sodium periodate is as follows:

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