Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Polymers 72 (2008) 500–505
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Heterogeneous degradation of chitosan with H_2O_2 catalysed by phosphotungstate

Qun Zeng Huang *, Li Hong Zhuo, Ying Chen Guo

College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang, China

Received 24 June 2007; received in revised form 17 September 2007; accepted 21 September 2007
Available online 29 September 2007

Abstract

Phosphotungstate (PTA), an insoluble catalyst synthesized with phosphotungstic acid (PWA) and chitosan in acidic reaction system by electrostatic attraction. The catalyst was characterized by DRS and FTIR spectra. Under the catalysis of PTA, the heterogeneous degradation of chitosan with H_2O_2 was achieved. The effect of volume of H_2O_2, dosage of catalyst, reaction temperature and time on the degradation was discussed by orthogonal tests. The experimental results show that chitosan can be effectively degradated with H_2O_2 under the catalysis of PTA. The catalyst, PTA, may have a promising application in oxidative degradation of polymer.

Keywords: Chitosan; Phosphotungstate; H_2O_2; Catalysis; Degradation

1. Introduction

Chitosan, a (1→4)-2-amino-2-deoxy-β-D-glucan derived from full or partial deacetylation of chitin, has been receiving great attention as novel functional material for its excellent properties such as biodegradation, immunological, antioxidant and antibacterial activities (Carmen & Roland, 1997; Cheng et al., 2003; Kofuji et al., 2005; Qi, Xu, Jiang, Hu, & Zou, 2004; Zhao, Wang, Zhao, & Pan, 2002). However, the utilization of chitosan has been scarcely developed because of its high molecular weight, water-insolubility and high viscosity of its solution. Compared with the ordinary chitosan, low molecular weight chitosan (LWCS) without altering its chemical structure has much improved water-solubility and some special biological, chemical and physical functions. LWCS has been prepared with different methods (Hsu, Don, & Chiu, 2002; Huang, Wang, Huang, Zhuo, & Guo, 2007; Tanioka et al., 1996; Terbojevich, Cosani, & Muzzarelli, 1996; Vårum, Ottøy, & Smidsrød, 2001; Wang, Huang, & Wang, 2005; Zhang & Neau, 2002), some of which show advantages, but also disadvantages.

H_2O_2 is a strong oxidant, producing free radicals in acidic, neutral and basic reaction systems, which can attack the β-D-(1–4) glycosidic bond and degrade chitosan. This technique is easy to handle, easily available and environmentally friendly (Chang, Tai, & Cheng, 2001; Qin, Du, & Xiao, 2002; Shao, Yang, & Zhong, 2003; Tian, Liu, Hu, & Zhao, 2003). However, the formation of radical groups is inefficient when H_2O_2 is used alone. Recently, to improve the efficiency, the combined degradation method using H_2O_2 and chemical or physical techniques such as catalysis of PWA (Huang et al., 2007), irradiation of ultraviolet light (Wang et al., 2005), radiation of microwave (Shao et al., 2003) and gamma radiation of ^{60}Co source (Kang, Dai, Zhang, & Chen, 2007) have been studied. But to date there have been few reports about the degradation with H_2O_2 in heterogeneous phase under the catalysis of PTA.

PWA is a representative heteropoly acid with Keggin type, which is the most often studied due to their favorable acid and redox characteristics, greater stability and availability (Misono, 2001; Okuhara, Mizuno, & Misono, 1996; Pope, 1983). In a previous work, our group has

* Corresponding author. Tel./fax: +86 377 63513540.
E-mail address: qz_huangny@126.com (Q.Z. Huang).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2007.09.022

shown that chitosan can be effectively degraded with H_2O_2 under the catalysis of PWA (Huang et al., 2007). However, PWA is often difficult to separate from the products due to its high solubility in water, methanol and acetone. Therefore, the catalysts supported PWA are widely applied. The supports including oxides such as Al_2O_3, SiO_2, TiO_2, diatomite, bentonite and active carbon, etc., apparently affect the structure and acidity, as well as the redox property of PWA (Wu et al., 1996). Moreover, chitosan is a cationic biopolymer, previous studies have shown that chitosan can interact with anionic matter to form either soluble or insoluble complexes which stabilized by electrostatic, ion-dipole and hydrophobic interactions (Vikhoreva, Babak, Galich, & Gal'braikh, 1997; Wei & Hudson, 1993). Thus, according to above theory, PTA was synthesized with protonated chitosan and PWA due to electrostatic attraction.

The aim of this work is to show the oxidative degradation of chitosan with H_2O_2 under the catalysis of PTA in heterogeneous phase. One advantage of the system is that PTA is easy to separate from LWCS, which improved the purity of LWCS. Other is that the oxidative degradation of chitosan occurs in heterogeneous phase, which avoided using acetic acid and made the preparation process of LWCS convenient.

2. Experimental

2.1. Materials

Original chitosan, obtained from Yuhuan Biology Engineering (Zhejiang, China), whose degrees of acetylation is 98.26%, its viscosity-average molecular weight (Mv) is about 210,000 determined based on viscosity measurements (Wang et al., 2005). Hydrogen peroxide, PWA , acetic acid, sodium acetate and other reagents, supplied by Nanyang Chemical Agent Corporation (Nanyang, China), are of analytical grade. The water used was distilled.

2.2. Preparation of catalyst PTA

Chitosan solutions were prepared by dissolving 3.0 g chitosan in 300 mL 1.5% (v/v) acetic acid solutions. Then 100 mL chitosan solutions were added into 3.0%, 5.0% and 7.0% (w/v) PWA solutions at a volume flow rate of 3.0 mL min^{-1} (using a burette), respectively. Thus PTA (1), PTA (2) and PTA (3), which are hyaloid insoluble matter, were obtained, respectively. The products were washed thoroughly with distilled water and acetone, collected after drying in vacuum at 60 °C.

2.3. Oxidative degradation of chitosan under the catalysis of PTA

In order to reveal the contrast of catalysis of PTA, four experiments on the degradation of chitosan were designed. For each experiment, 1.5000 g chitosan was placed in a 50 mL conical flask and soaked thoroughly after adding 17 mL distilled water. Then PTA (1), PTA (2) and PTA (3) was added into the corresponding conical flask for experiment 2, 3 and 4, respectively, and the dosage for each catalyst was 0.03 g. But for experiment 1, catalyst was not used. After adding 3.5 mL 30% (wt%) H_2O_2 aqueous solutions for each experiment, the oxidation degradation of chitosan was carried out at 80 °C for 30 min. After reaction, the solutions were filtrated, the collected solid was washed with distilled water until the eluent reached pH 7, and then dried at 50 °C in vacuum. Furthermore, addition of ethanol into the resulting filtrate resulted in a precipitate, which is LWCS. The oligomers were washed thoroughly with acetone, collected after drying in vacuum at 50 °C.

2.4. Characterization techniques

The degradation ratio of chitosan was calculated according to the following equation:

$$R(\%) = \frac{M_0 + M_c - M_x}{M_0} \times 100 \quad (1)$$

where R refers to degradation ratio, M_0, M_c refers to the quantity of original chitosan and PTA, respectively. M_x refers to the quantity of collected solid after degradation at different conditions.

The FTIR spectra of samples were obtained using a Nicolet 5700 FTIR spectrometer using KBr pellets, respectively.

The DRS spectra of samples were recorded on a Cary-500 Scan UV–vis-NIR spectrophotometer equipped with a HARRICK diffuse reflectance accessory.

3. Results and discussion

3.1. The choice of catalyst

For the degradation experiments, the using of different catalyst affected the degradation efficiency. The contrast of degradation ratio under different conditions is depicted in Fig. 1. As can be seen from Fig. 1, the degradation ratio was only 30% without catalyst, which indicated that the yield of free radicals formed by decomposing of H_2O_2 was rather slow when H_2O_2 was used alone. But in the presence of PTA (1), PTA (2) and PTA (3), the degradation ratio increased, which added up to 51%, 98% and 100%, respectively. It indicated that the catalysis of PTA improved as the ratio of the quantity of PWA to that of chitosan increased. Therefore, it can be predicated that the catalysis of PTA (3) is remarkable for oxidative degradation compared with other catalysts.

3.2. DRS and FTIR analyses of PTA (3)

Fig. 2 shows the DRS spectra of chitosan, PWA and PTA (3). For chitosan, a weak absorption band was evi-