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ScienceDirect
Carbohydrate Polymers 72 (2008) 248–254
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Preparation and characterization of porous polysucrose microspheres

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Received 18 May 2007; received in revised form 6 August 2007; accepted 9 August 2007
Available online 23 August 2007

Abstract

A set of novel porous polysucrose microspheres were prepared by the inverse suspension polymerization using soluble polysucrose, epichlorohydrin (EP) as crosslinker and dimethyl ether of polyethylene glycol (DMPE) as porogen. The fourier transform infrared spectrometer (FTIR), optical microscope (OM), scanning electronic microscope (SEM) and laser diffraction method were utilized to characterize the structure and morphology of the porous microspheres. The results indicated that these beads had spherical shape with the mean particle size of around 340 μm, narrow distribution, and porous structure. The equilibrium water contents of these porous microspheres ranged from 92.1% to 96.6% with the increasing contents of porogen. The porosities ranged from 82.3% to 90.3% with the increasing hydroxyl contents from 19.3 to 21.8 mmol/g, and bovine serum albumin (BSA) was used as adsorbate model to examine the adsorption behavior of the porous microspheres. The saturated adsorption capacities of these microspheres ranged from 42.6 to 98.5 mg/g.

Keywords: Polysucrose; Porous microspheres; Inverse suspension polymerization; Adsorption

1. Introduction

Recently, the preparation and application of polysaccharide microspheres have been paid attention due to the good performance of these microspheres such as low toxicity, good biocompatibility and biodegradability. The microspheres including cellulose, dextran and chitosan have been widely used in absorbents (Gustavsson, Axelsson, & Larson, 1998; Kim, Kim, Yang, & Cho, 2004), affinity bioseparators (Fu et al., 2006; Per-Erik, Anders, & Per-Olof, 1999), drug and enzyme carriers (Mi, Shyu, Chen, & Schoung, 1999; Remunan-Lopez, Lorenzo-Lamosa, Vila-Jato, & Alonso, 1998). These microspheres have been prepared directly by emulsion polymerization (Caglayan, Unsal, Camli, Tuncel, & Tuncel, 2006; Kang, Kan, Du, & Liu, 2006), dispersion polymerization (Camli, Tuncel, Senel, & Tuncel, 2002) and suspension polymerization (Lu, Liu, & Liu, 2003). Usually, these hydrophilic microspheres were ''gel-type'' with low surface area and low porosity, which limited their applications. Porous microspheres with large specific surface area and high porosity would be favorite to be used in the separation field. The porous structures of polysaccharide microspheres could be able to obtain via double emulsification procedure (Gustavsson & Larsson, 1996), wet phase inversion method (Fwu-Long, Shin-Shing, Chin-Ta, & Juin-Yih, 2002), or adding porogen such as inorganic particles (Shi, Zhou, & Sun, 2005) in the preparation of microspheres.

Sucrose, a disaccharide, is liable to be crosslinked because it has eight chemically active hydroxyl groups. In this paper, our aim is to synthesize porous hydrophilic polysucrose microspheres by the inverse phase suspension polymerization. The chemical structures, morphology, mean particle size and polydispersity index of the microspheres were characterized. The porosity, equilibrium water content and hydroxyl content of porous microspheres were investigated as well. Bovine serum albumin (BSA) was used as adsorbate model to examine the adsorption behavior of the porous microspheres.

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doi:10.1016/j.carbpol.2007.08.011

2. Experimental

2.1. Materials

Soluble polysucrose was purchased from Polymer Science & Commerce Co. Ltd. (Tianjin). DMPE ($\overline{M_n} = 7798, \mathrm{PDI} = 2.78$) was purchased from Tianjin chemical engineering stock company (Jiangsu Province). Epichlorohydrin (EP) was obtained from Tianjin No. 1 Chemical Reagent Plant (Tianjin, China). Chlorobenzene was purchased from Beijing Chemical Agents Company (China). Sodium hydroxide (NaOH) (50 wt% aqueous solution) was prepared in laboratory. Acetic anhydride and pyridine were purchased from Tianjin Kewei Company (Tianjin, China). All the chemical regents were analytical pure grade and used without further purification.

2.2. Preparation of porous polysucrose microspheres

To a 250 mL three-necked flask were added subsequently soluble polysucrose (5.0 g), epichlorohydrin (2.54 mL), DMPE (2.0 g) in distilled water (35 mL) at room temperature. Then chlorobenzene (160 mL) and span80 (3 g) were added to the mixture under stirring. The pH value of the mixture was adjusted to 14 by aqueous NaOH solution (50 wt%). The microspheres were formed during the crosslinking reaction carried out at 70 °C for 90 min with appropriate mechanical stirring. The temperature was then raised to 90 °C and the reaction continued for 4 h. The microspheres were washed by ethanol and water several times to eliminate the chlorobenzene and DMPE.

Five microsphere samples were synthesized using the method above, labeled as PPS-1, PPS-2, PPS-3, PPS-4, PPS-5, respectively, where the numbers following the PPS indicated the mass of porogen (g) used in the reaction.

2.3. Characterization of porous polysucrose microspheres

2.3.1. Fourier transform infrared spectra

The fourier transform infrared (FTIR) spectra were obtained using Bio-Rad FTS 135 FTIR instrument (Bio-Rad, USA), the dry samples were powdered and mixed with KBr and then pressed into pellets under reduced pressure.

2.3.2. The morphology of porous microspheres

The Optical microscope (Olympus BX51, Japan) and scanning electron microscope (PHILPS XL-30 apparatus) were used to determine the size and morphology of porous polysucrose microspheres. The samples were sputter coated with a thin layer of gold to enhance the surface contrast and reduce surface charging prior to SEM examination.

2.3.3. The particle size and distribution

The particle sizes and the size distribution of PS microspheres were determined using Mastersizer S particle size analyzer (Malvern Instrument, UK).

2.3.4. Pore volume and porosity of microspheres

It is important to investigate the porosity, which reflects the pore volume and the ability of adsorption of microspheres. The excess surface-adhered water on the microspheres was removed by blotting. Then the microspheres were dried to constant weight at 25 °C in vacuum oven for 24 h. The average pore volume V_p and porosity P_r were calculated according to Eqs. (1) and (2) (Zhang, Zhou, Yang, & Chen, 1998):

$$V_p\ (\mathrm{mL/g}) = (V - W_d/d)/W_d \quad (1)$$

$$P_r\ (\%) = V_p/(V_p + 1/d) \quad (2)$$

where V was the volume of the wet microspheres, W_d was the dried weight of microspheres, d was the density of porous microsphere framework.

2.3.5. Hydroxyl content (Dong, 2004, pp. 94–95)

Acid number was determined through the following method: 0.1 g of dried porous polysucrose microspheres were introduced into ethanol (20 mL). The solution of NaOH (1.0 mol/L) was used to titrate the excess of acetic acid using a phenolphthalein solution as the indicator. Blank titration was performed in the same way to avoid systematic errors. The acid number was calculated according to:

$$\text{Acid number}\ (\mathrm{mg/g}) = \frac{40 \times (V - V_0) \times c}{m} \quad (3)$$

where V and V_0 were the volume of NaOH solution for the experimental and blank titration, respectively, c was the concentration of NaOH solution (mol/L) and m was the mass of sample (g).

Non-aqueous titration was employed to determine the hydroxyl content in porous polysucrose microspheres: to a pyridine solution of acetic anhydride (20 mL, 25%, v/v) was added 0.30 g of porous polysucrose microspheres at room temperature, and then raised to 100 °C to acetylate for 1 h. Afterwards, to the reaction system was added 5 mL of distilled water and the system was allowed to stand for another 30 min. The aqueous solution of NaOH (1.0 mol/L) was used to titrate the excess of acetic acid using phenolphthalein solution as indicator. A blank titration was performed in the same way to avoid systematic errors. The hydroxyl content was calculated according to Eqs. (4) and (5):

$$\text{Hydroxyl number}\ (\mathrm{mg/g}) = \frac{40 \times (V_1 - V_2) \times c}{m} + \text{Acid number} \quad (4)$$

$$\text{Hydroxyl content}\ (\mathrm{mmol/g}) = \frac{\text{Hydroxyl number}}{N} \quad (5)$$

where V_2 and V_1 are the volume of NaOH solution for the experimental and blank titration, respectively, c is the concentration of NaOH solution (mol/L), m is the mass of sample (g), and N was the mole mass of NaOH (g/mol).

2.3.6. Equilibrium water content

The swelling behavior of the porous polysucrose microspheres was determined by monitoring the equilibrium