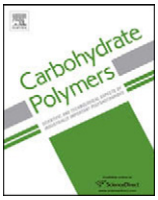
Carbohydrate Polymers 83 (2011) 1016–1019

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Short communication

Preparation of porous starch and its use as a structure-directing agent for production of porous zinc oxide

Peter R. Chang[b,*], Jiugao Yu[a], Xiaofei Ma[a,**]

[a] School of Science, Tianjin University, Tianjin 300072, China
[b] Bioproducts and Bioprocesses National Science Program, Agriculture and Agri-Food Canada, 107 Science Place, Saskatoon, SK, Canada S7N 0X2

ARTICLE INFO

Article history:
Received 4 August 2010
Received in revised form 27 August 2010
Accepted 27 August 2010
Available online 6 September 2010

Keywords:
Porous starch
Citric acid
Zinc oxide
Structure-directing agent

ABSTRACT

In this communication, a facile and green method is introduced for the preparation of porous starch (PS), citric acid-modified PS (CAPS) and porous ZnO. PS was created by replacing ice crystals in frozen starch gel with selected solvent using a solvent exchange technique. The porosity of PS was greatly affected by the ethanol/water volume ratios. PS was further modified with citric acid (CA) in order to preserve or maintain its porous state, especially upon contact with aqueous solution. CAPS was subsequently used as a structure-directing agent to prepare ZnO with a porous network structure. The thus obtained PS, CAPS and porous ZnO may find their niche in applications such as adsorbent, structure-directing agents for porous metal oxides or as sensors.

1. Introduction

Porous starch (PS) is an economical and biodegradable adsorbent that has been widely used in food, pharmaceuticals, agriculture, cosmetics, pulp and paper, and other industries. PS can be produced by reacting various raw starches with starch hydrolyzing enzymes (α-amylase and amyloglucosidase) at a temperature below that of starch gelatinization (Wang et al., 2009; Yao & Yao, 2002). The starch granules are not destroyed, although pits/craters on their surface and/or extensive interior erosion result due to hydrolysis of the amorphous regions of the starch. PS can also be prepared when starch granules have been completely destroyed. Guan and Hanna (2004) prepared starch foam by extruding a native corn starch/starch acetate blend in a twin-screw extruder. El-Tahlawy, Venditti, and Pawlak (2008) prepared microcellular foams by reacting starch with alkyl ketene dimer in an alkaline medium, followed by precipitation by solvent exchange. A microwave foaming process was used to produce PS where the water content played a noticeably important role in foam capacity and expansion (Sjöqvist & Gatenholm, 2007). Torres, Boccaccini, and Troncoso (2007) used a microwave technique to produce PS-based scaffolds from different starches. Recently, supercritical CO_2 technology was introduced and promoted as an innovative technique for the production of PS. Soluble starch was dissolved in water. The water in the gel was then replaced by ethanol, resulting in monolithic starch aerogels after drying using a supercritical CO_2 technique (Miao et al., 2008). Reactive supercritical fluid extrusion was also investigated on the cross-linking of starch blends by phosphorylation. A starch blend was mixed with sodium trimetaphosphate and extruded at 60–70 °C with NaOH solution and supercritical CO_2 as a blowing agent to generate starch foams (Manoi & Rizvi, 2010). It is worth mentioning that the processing method greatly influenced the structure and controllability of the resultant holes in the starch foams. Generally, the size of the holes in the starch foams was larger than that from PS prepared by the hydrolysis method. But both of them were uncontrollable. Zinc oxide is a semiconducting metal oxide that has potential as an integrated multi-sensing platform, which simultaneously detects parameters like change in field effect, mass and surface resistivity (Eriksson et al., 2009). Porous ZnO is in high demand as the larger surface area contributes to higher sensitivity in the resultant devices or sensors (Yoon & Choi, 1997). However, there are fewer reports on porous ZnO structures. Polarz, Orlov, Schuth, and Lu (2007) prepared mesoporous ZnO by using an organometallic ($Zn–CH_3$) as a precursor and mesoporous carbon or liquid crystals as a template. A simple polyglycol-assisted wet chemical method was also used to prepare the nano-sized tetragonal pyramid-shaped porous ZnO structure (Dai et al., 2008). The polyglycol had a significant influence on the nucleation and pore formation in the ZnO nanostructure. In this paper, PS was produced by replacing ice crystals in frozen starch gel with selected solvent using a solvent exchange technique, and chemically modifying with citric acid (CA) to improve the structure stability in aqueous solu-

---

* Corresponding author.
** Corresponding author. Tel.: +86 22 27406144; fax: +86 22 27403475.
E-mail addresses: peter.chang@agr.gc.ca (P.R. Chang), maxiaofei@tju.edu.cn (X. Ma).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.08.076

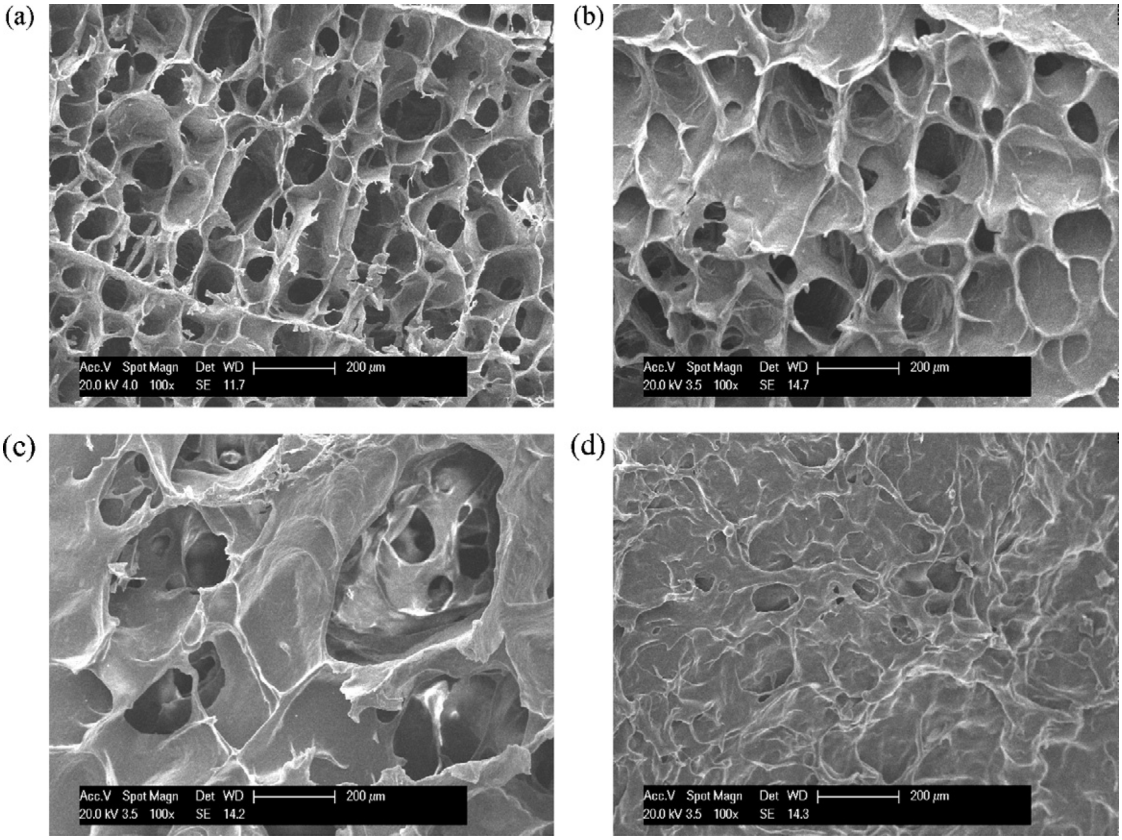


Fig. 1. SEM micrograph of the fractured surface of PS, prepared from different ethanol/water volume ratios (a, PS10; b, PS7; c, PS5; d, PS3).

tion. The resultant CAPS can be used as structure-directing agents for preparation of porous ZnO materials.

2. Materials and methods

2.1. Materials

Potato starch was supplied by Manitoba Starch Products (Manitoba, Canada). Soybean oil was provided by COFCO Northsea Oils & Grains (Tianjin) Co., Ltd., China. Ethanol and citric acid were analytical reagents purchased from Tianjin Chemical Reagent Factory, China.

2.2. Preparation of PS

Potato starch (5 g) was added into 100 mL of distilled water. The mixture was heated at 90 °C for 0.5 h for complete gelatinization of the starch. It was then stored at 5 °C for 48 h to obtain a starch gel. The gel was cut into cubes (about 1 cm × 1 cm × 1 cm), and frozen at −10 °C for another 48 h. The frozen cubes were immersed in mixtures of ethanol/water with different volume ratios (10/0, 7/3, 5/5, 3/7 or 1/9) at room temperature. The cubes were immersed three times, for about 1 h each time, in fresh ethanol/water solution of their respective ratios. The cubes were dried at 50 °C for 6 h, and then heated at 105 °C for 2 h to remove the ethanol and water, and to obtain white solid PS cubes. PS10, PS7, PS5, PS3 and PS1 represent the PS cubes which have been immersed in the ethanol/water mixtures with volume ratios of 10/0, 7/3, 5/5, 3/7 and 1/9, respectively.

2.3. Preparation of CAPS

CA modification was based on the method of Ma, Chang, Yu, and Stumborg (2009) with some modifications. CA (30 g) was dissolved in 100 mL of ethanol. The PS10 cubes were immersed in citric acid solution and conditioned for 12 h at room temperature. They were subsequently dried and reacted with CA at 130 °C for 1.5 h in a forced air oven. CA-modified PS (CAPS) was immersed in ethanol and washed three times to remove unreacted CA, and then dried and used for testing.

2.4. Preparation of porous ZnO

CAPS cubes were immersed in a 0.5 mol/L $ZnNO_3$ solution for 0.5 h, and then immersed in a 1.0 mol/L NaOH solution for 0.5 h. The obtained cubes were immersed in water and washed three times then dried for 6 h at 50 °C. Porous ZnO was obtained after incinerating the dried cubes in an air current at 800 °C for 2 h.

2.5. Determination of the molar degree of substitution by CA

Molar degree of substitution (MS) is the number of CA per anhydroglucose unit (AGU) in starch. MS was determined using the method of Ma, Jian, Chang, and Yu (2008) with minor modifications. CAPS was ground to a powder in order to test the MS. Approximately 1.0 g of dry CAPS was accurately weighed and placed into a 250 mL conical flask. Then 50 mL of 75% ethanol solution was added and the conical flask was agitated and warmed at 50 °C for 0.5 h before cooling to room temperature. Standard 0.500 M aqueous sodium hydroxide solution (20 mL) was added; the conical flask was tightly stoppered and agitated with a magnetic stirrer for 24 h.

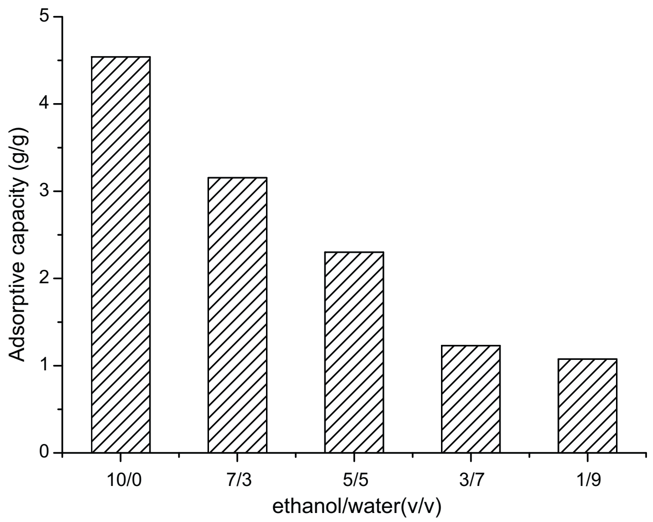


Fig. 2. Effect of different ethanol/water volume ratios on oil adsorption capacity.

The excess alkali was back-titrated with a standard 0.200 M aqueous hydrochloric acid solution and re-titrated 2 h later to account for any further alkali that may have leached from the starch. The sample was measured in triplicate. MS of CA substitution was 0.092 for CAPS.

2.6. Scanning electron microscopy (SEM)

Porous ZnO and the fracture surfaces of PS were examined using a Philips XL-3 scanning electron microscope. PS was cooled in liquid nitrogen and then broken. The fracture surfaces of PS and porous ZnO were vacuum coated with gold for SEM.

2.7. Oil adsorption capacity

The dried PS cubes (weight = w_0) were immersed in soybean oil for 0.5 h at room temperature with constant stirring. The mixture was filtered in the funnel under gravity. When there is no more oil dripping from the filter paper, PS was weighed (w). The oil adsorption capacity was calculated as follow:

$$\text{Adsorptive capacity} = \frac{w - w_0}{w_0} \tag{1}$$

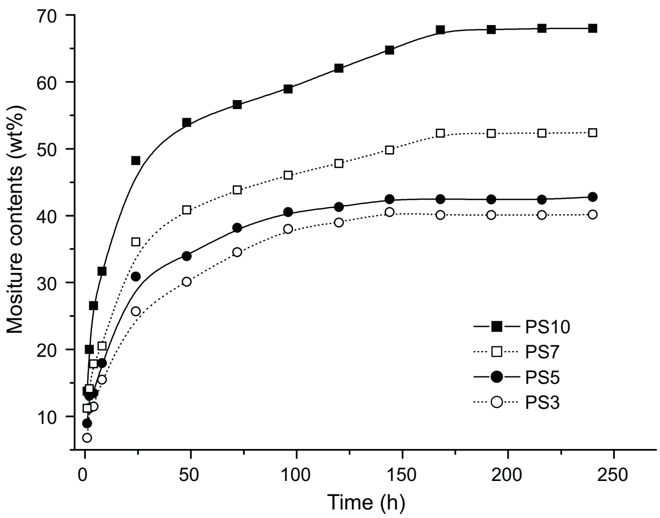


Fig. 3. Effect of different ethanol/water volume ratios on moisture absorption of PS.

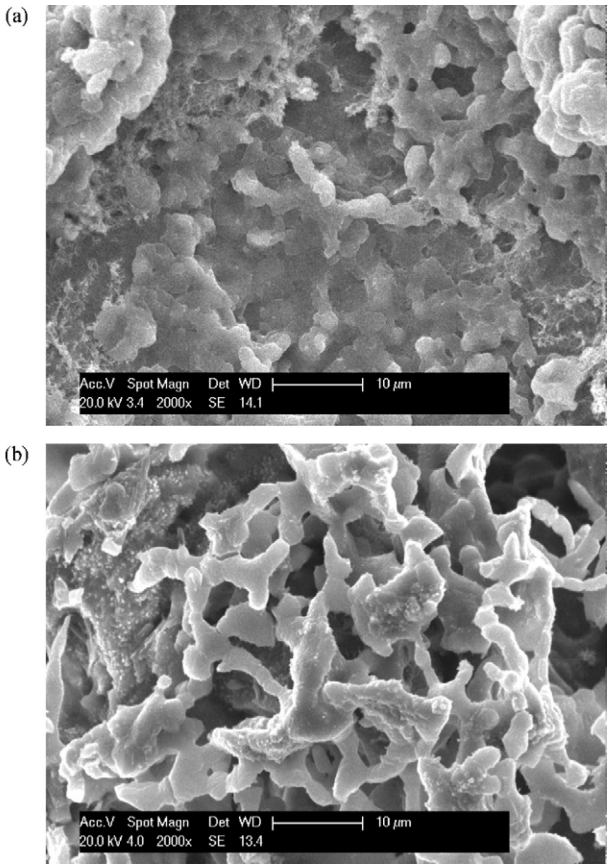


Fig. 4. SEM micrograph of CAPS filled with ZnO (a) and porous ZnO (b).

2.8. Moisture absorption

Dried PS cubes were stored in a closed chamber with a relative humidity (RH) of 75% at 20 °C for a period of time. The moistures of the PS cubes were calculated based on the final weight (w) and original weight (w_0) as follows:

$$\text{Moisture content (wt\%)} = \frac{w - w_0}{w_0} \times 100\% \tag{2}$$

3. Results and discussion

3.1. Morphology

The preparation of PS seems straightforward and effective. Native potato starch granules were destroyed by heat during preparation of the paste. Water was immobilized in the gel after cooling the paste to room temperature and freezing it. Porous structures were created after replacement of ice crystals in the frozen gel with various ethanol/water solutions. As shown in Fig. 1, different porous structures resulted when ice crystals were replaced with different ethanol/water solutions. By increasing the water content from 0% to 70%, the size of the holes in the resulting PS gradually decreased until ultimately the opening was closed.

3.2. Oil adsorption and moisture absorption

As shown in Fig. 2, the oil adsorption capacity of PS10 reached 4.5 g/g (oil/PS) while PS1 had merely 1.07 g/g. With a decreasing ethanol ratio, the oil adsorption capacity of PS also decreased. Despite the hydrophilic nature of starch, PS showed good capacity for oil adsorption; this could be attributed to the porous structures which trap and retain oil. When ethanol was progressively substituted by the ethanol/water solvent, many PS holes collapsed or closed (as shown in Fig. 1), resulting in a lower oil adsorption capacity. The effect of different ethanol/water volume ratios on moisture absorption of PS is shown in Fig. 3. When the ethanol/water volume ratio decreased from 10/0 to 3/7, the PS moisture content at equilibrium decreased from 68% to 40.1%. This was caused by a decrease in surface area resulting from a reduction in porosity.

3.3. CAPS and porous ZnO

There is genuine concern over the stability of the porous structure of PS, particularly when PS is in contact with aqueous solutions. In our previous study, we demonstrated that citrate starches did not swell and gelatinize in hot water as a result of a cross-linking reaction (Ma et al., 2009). It was therefore decided that CAPS be used in this study, instead of PS, as the structure-directing agent for porous ZnO. The obtained CAPS with 0.092 MS had an oil adsorption capacity of 7.0 g/g and moisture content of 55.9% at equilibrium. Compared to PS, the hydrophobic surface of CAPS contributed to an improvement in the oil adsorption capacity and a reduction of moisture absorption. Fig. 4(a) shows that CAPS was full of ZnO. When incinerated, the organic CAPS disappeared. As shown in Fig. 4(b), the obtained ZnO exhibited a porous network structure.

4. Conclusion

A facile and green method was developed to prepare PS and CA-modified PS for the production of porous ZnO with network structures. The porous structure of PS, as revealed by SEM, oil adsorption capacity, and water absorption were greatly affected by ethanol/water volume ratios during the solvent exchange process. The oil adsorption capacity and moisture content at equilibrium were 4.5 g/g and 68% for PS10, and 1.23 g/g and 40.1% for PS3, respectively. Other parameters, for instance starch concentration (or water content) and CAPS/ZnO ratios, affecting the porosity and performance will be studied in detail and reported in the near future. It is hoped that the method described here will be extended to other porous metal oxides and higher value applications in areas such as food, pharmaceuticals, agriculture, cosmetics, and sensors.

References

Dai, Z. H., Liu, K., Tang, Y. W., Yang, X. D., Bao, J. C., & Shen, J. (2008). A novel tetragonal pyramid-shaped porous ZnO nanostructure and its application in the biosensing of horseradish peroxidase. *Journal of Materials Chemistry*, *18*, 1919–1926.

El-Tahlawy, K., Venditti, R., & Pawlak, J. (2008). Effect of alkyl ketene dimer reacted starch on the properties of starch microcellular foam using a solvent exchange technique. *Carbohydrate Polymers*, *73*, 133–142.

Eriksson, J., Khranovskyy, V., Söderlind, F., Käll, P. O., Yakimova, R., & Spetz, A. L. (2009). ZnO nanoparticles or ZnO films: A comparison of the gas sensing capabilities. *Sensors and Actuators B: Chemical*, *137*, 94–102.

Guan, J. J., & Hanna, M. A. (2004). Extruding foams from corn starch acetate and native corn starch. *Biomacromolecules*, *5*, 2329–2339.

Ma, X. F., Chang, P. R., Yu, J. G., & Stumborg, M. (2009). Properties of biodegradable citric acid-modified granular starch/thermoplastic pea starch composites. *Carbohydrate Polymers*, *75*, 1–8.

Ma, X. F., Jian, R. J., Chang, P. R., & Yu, J. G. (2008). Fabrication and characterization of citric acid-modified starch nanoparticles/plasticized-starch composites. *Biomacromolecules*, *9*, 3314–3320.

Manoi, K., & Rizvi, S. S. H. (2010). Physicochemical characteristics of phosphorylated cross-linked starch produced by reactive supercritical fluid extrusion. *Carbohydrate Polymers*, *81*, 687–694.

Miao, Z. J., Ding, K. L., Wu, T. B., Liu, Z. M., Han, B. X., An, G. M., et al. (2008). Fabrication of 3D-networks of native starch and their application to produce porous inorganic oxide networks through a supercritical route. *Microporous and Mesoporous Materials*, *111*, 104–109.

Polarz, S., Orlov, A. V., Schuth, F., & Lu, A. H. (2007). Preparation of high-surface-area zinc oxide with ordered porosity, different pore sizes, and nanocrystalline walls. *Chemistry – A European Journal*, *13*, 592–597.

Sjöqvist, M., & Gatenholm, P. (2007). Effect of water content in potato amylopectin starch on microwave foaming process. *Journal of Polymers and the Environment*, *15*, 43–50.

Torres, F. G., Boccaccini, A. R., & Troncoso, O. P. (2007). Microwave processing of starch-based porous structures for tissue engineering scaffolds. *Journal of Applied Polymer Science*, *103*, 1332–1339.

Wang, X. Y., Wang, H. Q., Dai, Q. F., Li, Q. Y., Yang, J. H., Zhang, A. N., et al. (2009). Preparation of novel porous carbon spheres from corn starch. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *346*, 213–215.

Yao, W. R., & Yao, H. Y. (2002). Adsorbent characteristics of porous starch. *Starch-Starke*, *54*, 260–263.

Yoon, D. H., & Choi, G. M. (1997). Microstructure and CO gas sensing properties of porous ZnO produced by starch addition. *Sensors and Actuators B: Chemical*, *45*, 251–257.