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Preparation and characterization of starch crosslinked with sodium trimetaphosphate and hydrolyzed by enzymes

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ABSTRACT

Crosslinked porous starch samples were produced by first crosslinking corn starch with sodium trimetaphosphate (STMP) and then partially hydrolyzing it with a mixture of α-amylase and glucoamylase. The granule morphology, porosity, swelling power, adsorption capacity, crystalline nature, molecular structure, melting and viscometric properties of these starch samples were measured and analyzed. The results showed that the porous starch which was crosslinked with 6% (w/w) STMP (ScPS-6) possessed remarkable superiority in terms of thermal and shear resistance among all the starch samples tested. The ScPS-6 also had the highest porosity and largest average pore diameter values. The swelling power of crosslinked porous starch was 56.3% lower than that of uncrosslinked porous starch. First order reaction kinetics equation was found to excellently ($R^2 \geq 0.99$, average error = 6.03%) predict the experimental adsorption kinetics data of methylene blue for the crosslinked porous starch samples.

1. Introduction

Starch is an abundant, biodegradable and renewable biopolymer which is immensely important as food as well as industrial ingredient (Szabo-Revesz, Szepes, Ulrich, Farkas, & Kovacs, 2007). Starch contributes greatly to the textural properties of many food products and it is commonly used in food and other industrial applications as a thickener, a stabilizer, a gelling agent, a bulking agent and water retaining agent (Svegmark & Hermansson, 1993; Singh, Kaur, & McCarthy, 2007). However, starch has intrinsic disadvantages such as very weak resistance against shear and heat, very high susceptibility to thermal decomposition and high tendency to undergo retrogradation (Singh et al., 2007; Jobling, 2004; Raina, Singh, Bawa, & Saxena, 2007; Peng et al., 2011a,b; Yan & Zhengbiao, 2012). Starch has the potential for much greater application in food and other industries if the above mentioned intrinsic disadvantages are technologically overcome. The physical and chemical characteristics of starch can be modified to overcome its inherent limitations and to improve its functionality (Chen, Zhang, & Chen, 2011; Chen, Huang, Tang, Chen, & Zhang, 2011; Hermansson & Svegmark, 1996).

The modification of starch can be carried out by using a number of physical and chemical methods or the judicious combination of these methods. Physical modification is achieved by using hydrothermal processing (gelatinization). The chemical treatments involve the introduction of suitable functional groups into the starch molecule using derivatization reactions such as etherification, esterification, crosslinking and grafting or decomposition reactions such as acid or enzymatic hydrolysis and oxidation (Loacutepez, Zaritzky, & Garciacutea, 2010; Wurzburg, 1986; Singh et al., 2007). Chemical modification is commonly used for improving the properties of starch in order to meet the requirements of specific applications (Han & BeMiller, 2008). One of the most commonly used ways to modify starch is the crosslinking, which is intended to add intra- and inter-molecular bonds at random locations of a starch molecule (Acquarone & Rao, 2003). Sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin (EPCH), phosphoryl chloride ($POCl_3$), a mixture of adipic acid and acetic anhydride, and vinyl chloride are some of the common crosslinking agents currently used to crosslink with starch (Wattanchant, Muhammad, Hashim, & Rahman, 2003; Woo & Seib, 1997; Wu & Seib, 1990; Yook, Pek, & Park, 1993). Epichlorohydrin (EPCH) has been reported as a common crosslinker used to modify starch (Yu & Liu, 1994; Hamdi, Ponchel, & Duchêne, 1998; Atyabi, Manoochehri, Moghadam, & Dinarvand, 2006; Zhou et al., 2006). However, EPCH is known to be toxic and the presence of small quantity of its residue or unreacted fraction can lead to toxic side effects (Li et al., 2009). More recently, sodium trimetaphosphate (STMP) has been proposed as a non-toxic crosslinker of starch (Li et al., 2009) because it does not

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have adverse effects on humans (Woo & Seib, 1997). Because of this reason we have selected STMP as a crosslinker of starch. STMP is reported to efficiently crosslink with semidry starch at high temperature (60–70 °C) (Kerr & Cleveland, 1962). STMP is also reported to efficiently crosslink with hydrated starch in starch slurry at moderately high temperature (40–45 °C) (Singh et al., 2007).

Porous starch (PS) is a versatile, cheaper and biodegradable adsorbent containing large number of micron-sized pores. It has been widely used in food, pharmaceutical, agriculture, cosmetics, pulp and paper industries (Qian, Chang, & Ma, 2011). Earlier investigations have shown that enzymatic hydrolysis is a better method in preparing porous starch (Zhang et al., 2012; Chen et al., 2011; Wu, Du, Ge, & Lv, 2011; Uthumporn, Zaidul, & Karim, 2010). However, the enzymatic hydrolysis, if the process is not properly designed, can easily destroy the granular structure of porous starch. When the granular structure is destroyed, some physical properties such as gelatinization temperature, freeze-thaw stability, tackiness and the stability against shear are negatively impacted. In order to maintain the physical properties of crosslinked starch superior to those of native starch, a proper selection of crossliker and crosslinking method is essential.

In this study, starch was crosslinked by sodium trimetaphosphate (STMP) followed by partial enzymatic hydrolysis of starch using a mixed enzyme system. The crosslinked porous starch samples were examined using a scanning electron microscope to observe the change in the starch granules. The effect of crosslinking on the molecular structure of starch was assessed by using FTIR. The thermal properties such as glass transition and melting temperatures of the crosslinked porous starch granules were determined using a DSC. The uncrosslinked porous starch and native starch samples were also investigated along with the crosslinked porous starch for comparison purpose.

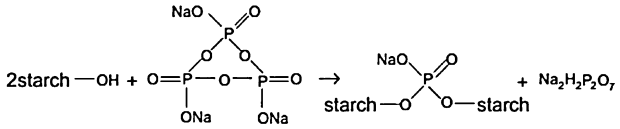
2. Materials and methods

2.1. Materials

Corn starch was obtained from Yujing Food Co. Ltd (Henan, China). Sodium trimetaphosphate (STMP) was purchased from Beijing Chemical Company (Beijing, China). α-Amylase (activity = 3.7 unites/mg) and glucoamylase (activity = 100 unites/mg) were purchased from Aoboxing Biological Technology Co. Ltd. (Beijing, China). The methylene blue was provided by Jinke Chemical Industry Research Institute (Tianjin, China). All of these reagents were of analytical grade and were used without further purification. Deionized water was used throughout the work.

2.2. Preparation of STMP-crosslinked starch

STMP-crosslinked starch samples were prepared using STMP as crosslinker according to the method of Mao, Wang, Meng, Zhang, and Zheng (2006). Corn starch (50 g) was added into 100 mL distilled water which contained 1 g Na_2CO_3 (2 g/100 g dry starch) and 2.5 g NaCl (5 g/100 g dry starch). The crosslinking agent (STMP), was dissolved in the starch containing slurry varying its amount from 1 g to 4 g to form four samples having four different crosslinking degrees (2%, 4%, 6%, and 8%, w/w). Then, the mixture was stirred using a magnetic stirrer at 200 rpm for 80 min at 50 °C in a thermostated water bath. Hydrochloric acid (1 M) was used to adjust the pH of slurry to 6.5. After the solid portion was precipitated, the supernatant was discarded and the solid portion was washed with deionized water. In this way crosslinked starch samples having different degree of crosslinking were obtained. The crosslinking reaction involved in the STMP-starch crosslinking is given below (Liu, 2001).



2.3. Preparation of STMP-crosslinked porous starch (ScPS)

Starch slurry (25% w/v) containing the crosslinked starch (described in Section 2.2 above) was prepared using 200 mL of sodium acetate buffer (pH = 4.6). This slurry was stirred for 20 min at 150 rpm in a water bath maintained at 40 °C as proposed by Whistler (1991). After preheating the slurry for 20 min, a mixture of α-amylase and glucoamylase at the ratio (α-amylase to glucoamylase) of 1:4 was added into the slurry. The enzyme to starch ratio was 1:100 (w/w). The slurry samples were then stirred using a magnetic stirrer at 150 rpm for 14 h while maintaining the temperature at 40 °C. Upon completion of the enzymatic reaction (14 h), the enzymes were inactivated and the hydrolysis was stopped by adding 20 mL of NaOH solution (4%, w/w). The resultant hydrolyzed starch suspension was centrifuged at 1007.1*g* for 5 min. The starch product obtained by centrifugation was washed three times in order to remove the non-starch components (Zhang et al., 2012; Chang, Yu, & Ma, 2011). Finally, the washed product was collected and dried using a vacuum freeze dryer (LGJ-18C, Four-Ring Science Instruments Plant Co. Ltd., Beijing, China). The starch product was first frozen at −30 °C for 1 h and then it was dried in the vacuum chamber by maintaining the pressure at 1.0 Pa. The heating rate within the dryer was maintained at 5 °C/h until the temperature reached 25 °C. The total drying time was 12 h.

2.4. Examination of morphology

The morphology of starch granules was observed using a scanning electron microscope (S-3400N, Hitachi Instruments Ltd., Japan). The sample particles were evenly distributed on SEM specimen stubs with double-sided adhesive tape, and sputtered with gold. The shape and the surface characteristics of the sample particles were observed and analyzed at an operating voltage of 15 kV.

2.5. Porosity test

The porosity of samples was measured using an automatic mercury porosimeter (AutoPore IV 9510, micromeritics Inc., America). Starch samples (1 g) were dried at 105 °C, placed in a dilatometer attached with the porosimeter and then out-gassed under high vacuum. The pores of the out-gassed samples were filled with mercury under the pressure varying from 0.0036 MPa to 413 MPa. Mean pore radius (r) was calculated according to Eq. (1) based on the assumption of cylindrical pores. Five replicate tests were made to determine the average diameter for each ample.

$$R = \frac{(2 \times \gamma/\cos\theta)}{p} \quad (1)$$

where γ is the surface tension of mercury (0.48 J/m^2), θ is the contact angle (140°) and p is the applied pressure (MPa).

2.6. Degree of swelling

The degree of swelling was determined using a mass gain method reported by Lin, Yu, and Yang (2005) with some modification. Briefly, 2.5 g of porous starch samples (having different degree of crosslinking) were added into 50 mL of deionized water and heated at 45 °C, 70 °C, 90 °C for 5 h. Then, these samples were centrifuged at 11,190*g* for 10 min. The surface water of the centrifuged starch samples was removed by using blotting paper and