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Insoluble starch composite foams produced through microwave expansion

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ABSTRACT

An insoluble biocomposite composed of potato starch and chitosan was prepared by microwave treatment. The effect of pH on swelling (liquid absorption) behavior of the composites was investigated at pH 2, pH 6.8 and pH 12. Analysis revealed that the solution uptake ratio of composites depends both on the aqueous pH value and the content of the chitosan. Composites exhibited a relatively high swelling ratio at pH environments lower than the pK_a of amine groups on chitosan (about 6.3). Glucose analysis by ion exchange chromatography showed that there was little hydrolysis of such composites at low pH. When immersed in the same pH solution, composites with higher chitosan content exhibited higher swelling ratios. The microstructure of composites produced was also investigated by FE-SEM.

1. Introduction

Since materials synthesized solely from petroleum result in disposal problems and non-sustainable development, there is increasing interest in developing biomaterials derived from renewable and biodegradable natural polymers (Pieróg, Gierszewska-Drużyńska, & Ostrowska-Czubenko, 2009; Sjoqvist, Boldizar, & Rigdahl, 2009). Low density foams, in particular, can be utilized in areas such as packaging, waste remediation, personal hygiene, and in biomedical applications such as drug delivery and tissue engineering (Castel, Ricard, & Audebert, 2003; Devlieghere, Vermeulen, & Debevere, 2004; Martinez-Ruvalcaba et al., 2009). Chitosan has been extensively investigated due to its special chemical and biological properties (Cunha & Gandini, 2010). Chitosan is derived by deacetylation of chitin, which is the second most abundant natural polymer after cellulose (Lazaridou & Biliaderis, 2002). Chemically, chitosan is a linear cationic polysaccharide mainly composed of β-(1,4)-2-deoxy-2-amino-D-glucose (Lazaridou & Biliaderis, 2002).

Chitosan can form polymer networks by covalent cross-linking or through ionic or polyelectrolyte complexes (Il'ina & Varlamov, 2005). Many studies have attempted to crosslink chitosan covalently with varied chemicals, such as glyoxal, glutaraldehyde, and formaldehyde (Khalid, Agnely, Yagoubi, Grossiord, & Couarraze, 2002; Rohindra, Nand, & Khurma 2004; Singh, Narvi, Dutta, & Pandey, 2006). Covalent crosslinking of chitosan may be undesirable, however, due to the toxicity of many crosslinking agents such as aldehydes which have adverse effects on human health. Another drawback of this type of crosslinking is that the preparation procedure is often tedious and can take days to complete (Khalid et al., 2002; Sakiyama et al., 1993). Polyelectrolyte complexes can be formed between two oppositely charged polyelectrolytes when they are mixed (Sakiyama et al., 1993). Since chitosan is a polycationic polyelectrolyte, another polyanionic polyelectrolyte is required to form the polyelectrolyte complex. Many polyanionic polyelectrolytes such as chondroitin sulfate and k-carrageenan have been used to make a polyelectrolyte complex (Fajardo, Piai, Rubira, & Muniz, 2010; Sakiyama et al., 1993). Such complexes may exhibit characteristics like pH-sensitive swelling (Sakiyama et al., 1993). However, due to the hydrophilic nature of polyelectrolyte complexes (Pieróg et al., 2009), some undesired effects like mass loss and disintegration can be observed when swollen in solutions (Fajardo et al., 2010; Pieróg et al., 2009).

In order to develop an insoluble biodegradable and non-toxic biomaterial with chitosan using an efficient preparation process, the present study used potato starch (PS), a polyanionic polymer (Pérez & Bertoft, 2010), to form a polyelectrolyte complex with chitosan (CS). Due to the unique thermal plastic property of starch, many techniques can be used to process material containing starch in an efficient manner (Glenn, Imam, & Orts, 2011). In this study, we use microwave treatment to process the PS/CS biopolymers.

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Microwave treatment is shown to produce a large expansion of the composites during dehydration, resulting in a low density porous foam-like material. The swelling behaviors of the PS/CS composites in aqueous solutions at varied pHs have been investigated. All composites tested remained insoluble and showed virtually no degradation during testing. The micromorphology of PS/CS composites has also been examined by FE-SEM.

2. Materials and methods

2.1. Materials

Low molecular weight chitosan (CS) exhibiting at least a 75% degree of deacetylation was purchased from Sigma–Aldrich (Saint Louis, MO). Potato starch (PS) with approximately 75% amylopectin and 25% amylose was purchased from MP Biomedicals (Solon, OH). Corn starch (CNS) with 75% amylopectin and 25% amylose was purchased from Sigma–Aldrich (Saint Louis, MO). Sodium trimetaphosphate and sodium tripolyphosphate were purchased from Alfa Aesar (Ward Hill, MA). Sodium sulfate was obtained from Fisher Scientific (Fair Lawn, NJ). Deionized (DI) water with resistivity 15 MΩ cm at 25 °C (Thermo Scientific Barnstead TII water systems) was used in all aqueous solutions. Analytical grade hydrochloric acid, formic acid and sodium hydroxide were used. Hydrochloric acid (HCl) and nitric acid (HNO_3) were purchased from EMD Chemicals (Darmstadt, Germany), sodium hydroxide (NaOH) was purchased from VWR international (West Chester, PA) and formic acid, 88%, was purchased from Mallinckrodt Baker (Phillipsburg, NJ). All chemicals were used without further purification.

2.2. Starch phosphorylation

Phosphorylated potato starch (PPS) was prepared similar to a previously described method proposed by Błaszczak, Dyrek, Fornal, Michalec, and Wenda (2011). 10 g of potato starch was added to 14 ml aqueous solution at pH 6 (adjusted with 0.2 M HCl) containing 1.05 g of sodium trimetaphosphate/sodium tripolyphosphate (STMP:STPP = 99:1, w/w) and 0.5 g Na_2SO_4. The suspension was then mixed for an hour at room temperature followed by evaporation at temperature 45–50 °C until content of water was equal to 15–20%. Afterwards the material was heated at 130 °C for 2 h. After cooling, 70 ml distilled water was added to the material and pH was adjusted to 6.5 with 0.2 M NaOH solution. Then the suspension was centrifuged at 5000 rpm for 5 min and 80 ml of distilled water was added after supernatant was removed. Washing and centrifugation were repeated three times. The final product was dried at 50 °C for 20 h before further usage.

2.3. Preparation of PS/CS Composites

PS/CS composites were prepared by heating different PS/CS blends in a microwave oven. Preparation was carried out in an Emerson (Hackensack, NJ 07601) MW9339SB microwave oven operating at a frequency of 2450 MHz. Composition and designation of each PS/CS blend are shown in Table 1. 1.67% (w/v), 3.34% (w/v), and 5% (w/v) CS aqueous solutions were made by adding 1.67 g, 3.34 g and 5 g of CS into 100 ml 1% (v/v) formic acid solution, respectively. The CS aqueous solutions were then magnetically stirred for 24 h before blended with PS. 2.7 ml 1.67% (w/v), 3.34% (w/v), and 5% (w/v) CS aqueous solutions were blended manually with 1.8 g PS for 2 min in an 80 ml PFA beaker (Vitlab®, Brandtech Scientific Inc.), respectively. The final weight ratios of the PS/CS blends were 2.5%, 5% and 7.5%, respectively. The beaker containing the PS/CS blend was then placed in the center of the microwave chamber and heated at 100% power (900 W) for 45 s. After microwave treatment, samples were conditioned at 25 °C in 35% RH for 24 h before further characterization.

Table 1
Composition and designation of PS/CS blends.

Blend	Potato starch (PS) (g)	Chitosan (CS) (aq.) (wt.%)	Chitosan (CS):potato starch (PS) (wt.%)
PS/CS 2.5	1.8	1.67	2.5
PS/CS 5.0	1.8	3.34	5.0
PS/CS 7.5	1.8	5	7.5

2.4. Solution uptake measurements of PS/CS composites

Swelling experiments were performed using a method modified from Fajardo et al. (2010). Swelling ratio (S) was determined to evaluate the swelling capacity of the PS/CS composites in solutions with different pH. Preweighted PS/CS composites were immersed in 60 ml 0.01 M HCl (pH ~ 2.0), DI water (pH ~ 6.8), and 0.01 M NaOH (pH ~ 12) at 30 °C, respectively. 1.8 g corn starch (CNS) mixed with 2.7 ml 2.5% chitosan solution and 1.8 g PPS blended with 2.7 ml 2.5% chitosan solution dehydrated by microwave treatment were used as controls. After excess liquid on the sample surfaces was absorbed using a paper towel, the swollen samples were weighed. All samples were weighed at a set time interval until 120 h was reached. The solution uptake ratio was calculated according the formula:

$$S\% = \frac{M_s - M_d}{M_d} \times 100$$

where M_s is the weight of sample at the swollen state and M_d is the dry PS/CS composite before immersed in solution. The swelling ratio at 24 h was used as the equilibrium swelling ratio for each PS/CS composite.

2.5. Elemental analysis of starch samples by ICP-AES

For inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements, 500 mg of dried potato starch and phosphorylated potato starch were placed in a Teflon vessel, respectively, and 10 mL of 50% HNO_3 was added to each vessel. Each mixture was heated on a hot plate at 80 °C to decompose organic carbon. When the mixture dried, the residue was then dissolved with 1% HNO_3 and analyzed using the ICP-AES (Optima 5300 UV, Perkin Elmer, Norwalk, CT, USA) to measure the phosphorus content.

2.6. Morphology of PS/CS composite by FE-SEM

The morphology of the PS/CS composite before and after swelling was investigated by field emission scanning electron microscopy (FE-SEM) (FEI, Nova™ NanoSEM630). Samples immersed in different pHs for 24 h were frozen in −80 °C for 24 h. Samples were then lyophilized at −48 °C, 0.035 mbar for 48 h. Dried samples were sputter coated with platinum for 40 s before imaging. The electron accelerating voltage for the FE-SEM was 5 kV. Average pore size (μm) was measured by the software ImageJ, NIH. The average was derived from the measurement of 100 randomly selected pores.

2.7. Ion exchange chromatography detection of glucose content after swelling

PS/CS 7.5 composites were placed in beakers with 60 ml of deionized water and pH 2 solutions, respectively. After soaked for 0 h, 12 h, and 24 h, 1.5 ml of liquid from each beaker was

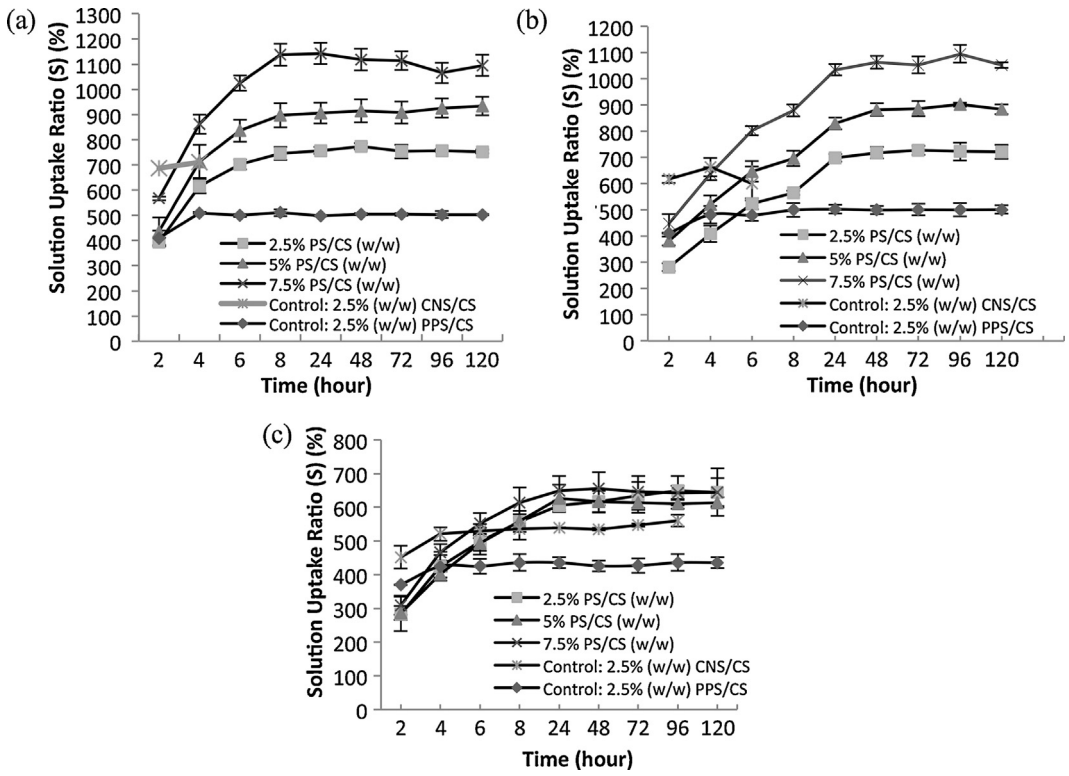

Fig. 1. Swelling behavior of various starch–chitosan composites (2.5% (w/w) PS/CS, 5% (w/w) PS/CS, 7.5% (w/w) PS/CS, 2.5% (w/w) CNS/CS, and 2.5% (w/w) PPS/CS) in different pHs at 30 °C (a) pH 2; (b) pH 6.8 and (c) pH 12.

filtered through a 0.2 μm nylon syringe membrane filter (VWR International, USA) and was injected into a 1.5 ml IC vial for ion chromatography. 0 h sample was prepared by submerging sample in solution and removing immediately. The ion-exchange chromatograph used in this study was Dionex ICS-3000 (Dionex Corporation, Sunnyvale, CA), consisting of an autosampler, a detector compartment (contain injection valves, columns and electrochemical detector) and a dual pump with vacuum degasser. The anion-exchange column CarboPac PA20 (with Borate trap, 3 mm × 3 mm guard column, and 3 mm × 150 mm analytical column) was from Dionex. The detector compartment was maintained at 30 °C, and the flow rate is set at 0.5 ml/min. The eluent used in this study was a mixture of 200 mM sodium hydroxide and nanopure water. 2 mM NaOH was used to run the program. Data acquisition was accomplished using a Chromeleon Chromatography Management Software v. 6.8 (Dionex Corporation, Sunnyvale, CA).

2.8. Statistical analysis

The significant difference of the data was evaluated using Tukey's Comparison (Minitab Statistical Software; Release 15.1; Penn State University, University Park, PA). Each data point was an average of three replicates.

3. Results and discussion

3.1. Swelling characteristics of PS/CS

The solution uptake behaviors of the PS/CS composites were investigated using the swelling ratio (S) described in Section 2.3. Fig. 1 shows the swelling profiles of PS/CS composites immersed in various pH solutions at 30 °C. Regardless of the CS content, composites swollen in the pH 2 solution reached equilibrium faster than those swollen in higher pH solutions. While it took 8 h to achieve a stable equilibrium swelling ratio in the pH 2 solution (Fig. 1a), it required 24 h for composites immersed in the pH 6.8 solution (Fig. 1b) and pH 12 solution (Fig. 1c) to achieve a stable equilibrium swelling ratio. The pK_a of amine group is about 6.3 (Gunasekaran, Wang, & Chai, 2006). In that case, chitosan will be ionized at a pH environment lower than 6.3. Moreover, it is believed that pH 4.0 is sufficient to complete the protonation: $-NH_2 + H^+ \rightarrow -NH_3^+$ (Il'ina & Varlamov, 2005). Fig. 2 depicts an illustration of potentially how PS/CS composite transits from an expanded state to a relatively contracted state under different pH environments. When the PS/CS composite was immersed in the pH 2 solution, the amine groups of chitosan were protonated. These positively charged groups will induce electrostatic repulsion and extension of the glucosamine chain, which contributes to the swelling of the polyelectrolyte network. In contrast, if immersed in a pH environment higher than the pK_a of the amine group, then the ionization of the amine group of chitosan will largely decrease. Thus, in a pH solution much higher than pK_a of amine group there will be a much weaker electrostatic repulsion among the polymer chains, which prevents excessive swelling of the PS/CS composite. Therefore, PS/CS composites more readily absorbed solution at pH 2 than at pH 6.8 or pH 12.

Similar swelling profiles can be found in other studies (Fajardo et al., 2010; Pieróg et al., 2009; Qu, Wirsén, & Albertsson 1999). Interestingly, chitosan composites immersed in alkaline or acidic solutions have been reported to exhibit either mass loss (Fajardo et al., 2010) or disintegration (Pieróg et al., 2009) in a short period of time, even though they have already been crosslinked. The PS/CS composites developed in the present study do not exhibit any mass loss or disintegration within five days (Fig. 1). One possible reason for this might be attributed to the electrostatic linkage between amino groups of chitosan and phosphate groups of potato starch. It is well known that glucose-6-phosphate is the major structure of the esterified phosphate in the potato starch (Tabata & Hizukuri, 1971), and glucose-6-phosphate esters (pKa_1 = 0.94, pKa_2 = 6.11)

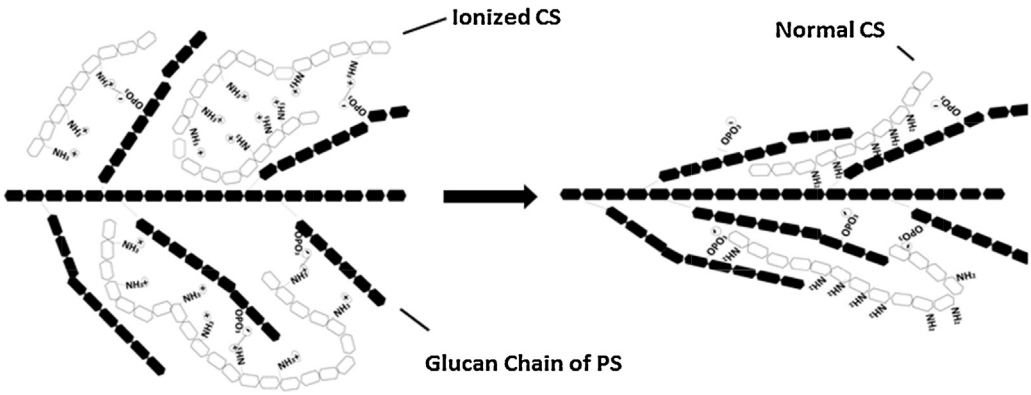

Fig. 2. Schematic of PS/CS composite as it transitions from an expanded state to a contracted state.

are more acidic than orthophosphoric acid (Woodbury, 2011). In that case, phosphate groups of potato starch will be negatively charged at all pH levels in the present study. Therefore, such negatively charged groups will interact with the positively charged amino groups to prevent disintegration of the whole PS/CS composite.

Furthermore, the maximum swelling ratio increases with increasing chitosan content (Fig. 1). Take pH 2 solution (Fig. 1a), for example, PS/CS composite reached 1137% swelling ratio for PS/CS 7.5, while PS/CS 5.0 and PS/CS 2.5 reached 897% and 746%, respectively. Likewise, in pH 6.8 solution the swelling ratio was also following the order of PS/CS 7.5 > PS/CS 5.0 > PS/CS 2.5. However, such an order did not exist in the pH 12 solution, and no significance is detected in swelling ratio among PS/CS 7.5, PS/CS 5.0, and PS/CS 2.5. This is because at a low pH level, as it is mentioned above, the amine groups will be protonated. A higher chitosan content, which is the case for PS/CS 7.5, means more amine groups are available for ionization, and if more amine groups are ionized, there will be more electrostatic repulsion formed. Thus, a larger swelling 'volume' is created due to the formation of more electrostatic repulsion. But in pH 12 solutions, a pH level much higher than the pK_a of amine group on chitosan, almost all the amine groups are at their neutral state, where pronounced electrostatic repulsion is eliminated. Negatively charged phosphate groups also have electrostatic repulsion, but the content of potato starch is the same for all PS/CS composites, plus, phosphate esters only account for a small portion of potato starch. Thus, the repulsion effect induced by ionized phosphate groups is limited, and no significance difference is found in swelling ratio for all the PS/CS composites at pH 12.

The control used in this study was a corn starch (CNS) expanded with 2.5% chitosan solution (CNS/CS 2.5). Please notice that the corn starch has the same ratio of amylopectin to amylose (75:25), but one significant difference is that potato starch has phosphorus content much higher than that of corn starch (Swinkels, 1985). Interestingly, the control hydrated very quickly and reached 700% uptake ratio at pH 2 (Fig. 1a), however, it also collapsed much sooner than other PS/CS composites. As can be seen in Fig. 1b and c, the higher the pH environment, the longer the control can remain intact. While it only took 4 h for CNS/CS 2.5 to collapse at pH 2, it took as long as 4 days for CNS/CS 2.5 to collapse at pH 12. Such phenomenon can be largely due to the response of amine groups in CNS/CS 2.5 to pH changes. Since at lower pH, amine groups were ionized, and interaction between chitosan and corn starch was not as strong as chitosan and potato starch, so it was easier for CNS/CS to collapse. However, when swelling in higher pH environments, amine groups were deprotonated. In that situation, chains become stiffer and entanglement between chitosan and corn starch become stronger, and this could protect CNS/CS from disentanglement so quickly.

Another control in our study was phosphorylated potato starch expanded with 2.5% chitosan solution (PPS/CS 2.5). Based on our ICP-AES elemental analysis, the degrees of substitution by phosphate group (DS_p) of potato starch and phosphorylated potato starch were 0.039 and 0.101, respectively. Two significant changes were demonstrated in Fig. 1 for PPS/CS 2.5. On one hand, it only took 4 h for PPS/CS 2.5 to reach solution uptake equilibrium, which was much faster than the normal PS/CS composites. On the other hand, the solution uptake ratios of PPS/CS 2.5 after equilibrium were significantly lower than PS/CS composites at all pH conditions. Such changes might be due to the increase of DS_p in PPS. Compared to normal PS/CS composites, there were more ionized amine groups to interact with phosphate groups in PPS, which led to a weaker electrostatic repulsion among ionized amine groups, and this in turn, could give rise to less solution uptake. More phosphate groups were available on the glucan chain of potato starch, which resulted in a stronger network with protonated amine groups in chitosan.

Fig. 3 shows the equilibrium swelling ratio of PS/CS 2.5, PS/CS 5, and PS/CS 7.5 at varied pH solutions. A similar trend was found for all composites in terms of solution uptake ratio. Composites immersed in pH 2 environment have the highest uptake ratios, while those immersed in pH 12 have the lowest uptake ratios. This phenomenon can be explained by the electrostatic repulsion theory mentioned previously. The extent of which one specific PS/CS composite is ionized will be different, if immersed in varied

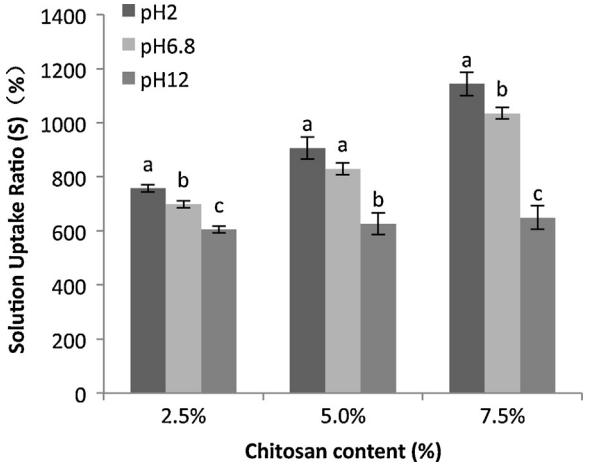

Fig. 3. Equilibrium solution uptake ratio of PS/CS composites at different pH values at 30 °C. A different letter means significantly different at the 95% confidence level (Tukey's multiple comparison).

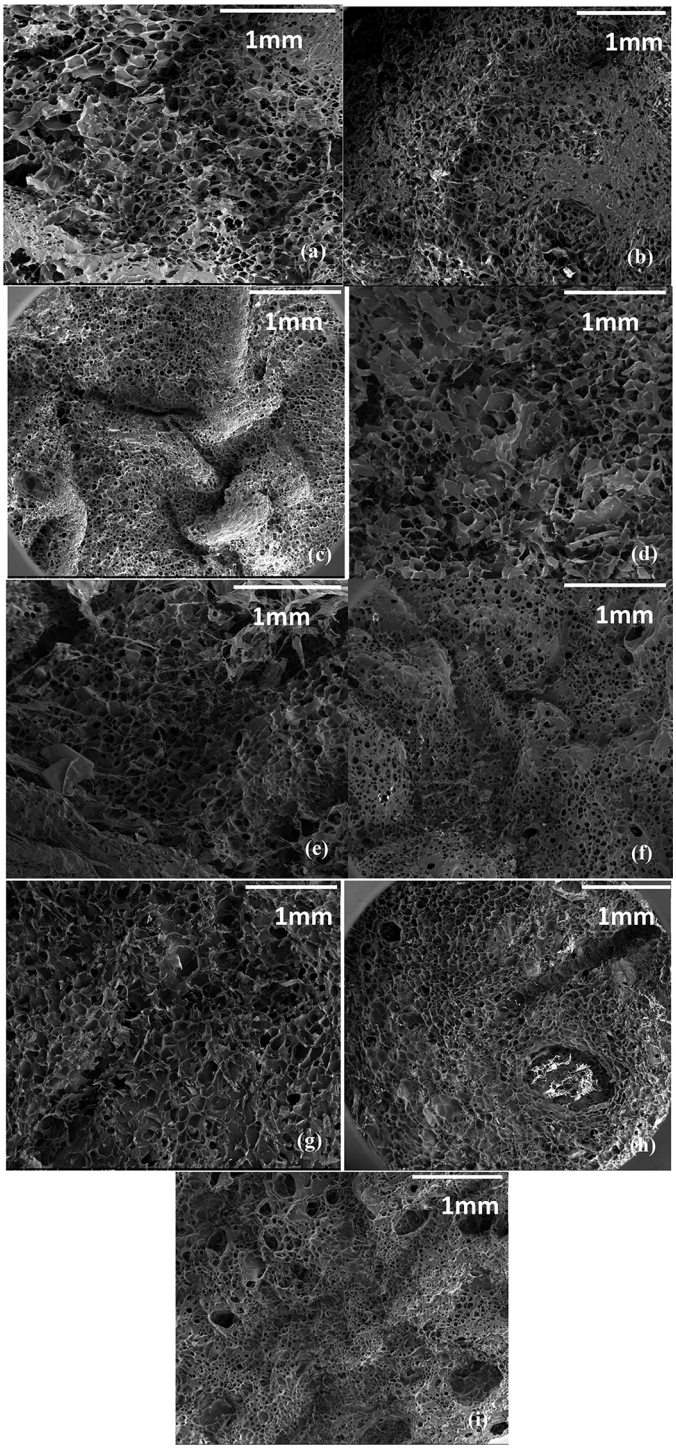

Fig. 4. FESEM images obtained from PS/CS composites freeze dried after swelling for 24 h: (a) PS/CS 2.5 swells at pH 2, (b) PS/CS 2.5 swells at pH 6.8, (c) PS/CS 2.5 swells at pH 12, (d) PS/CS 5.0 swells at pH 2, (e) PS/CS 5.0 swells at pH 6.8, (f) PS/CS 5.0 swells at pH 12, (g) PS/CS 7.5 swells at pH 2, (h) PS/CS 7.5 swell at pH6.8, and (i) PS/CS 7.5 swell at pH 12.

pH solutions. At a lower pH environment the PS/CS will be more protonated, and thus there will be more repulsion among polymer chains. When the pH environment is much higher than the pK_a of the amine groups, which is the case at pH 12, the repulsion effect is largely prevented, which prevents good swelling of PS/CS composites at pH 12.

Table 2
Average pore size of PS/CS samples swelling in varied pH solutions for 24 h.

PS/CS composites	Average pore size of PS/CS (μm)		
	pH 2	pH 6.8	pH 12
PS/CS 2.5	111 ± 34	70 ± 18	59 ± 14
PS/CS 5.0	110 ± 37	75 ± 21	48 ± 15
PS/CS 7.5	137 ± 31	100 ± 18	66 ± 28

3.2. Morphology analysis of PS/CS

The FESEM images of PS/CS composites swollen in pH 2, pH 6.8 and pH 12 solutions for 24 h are shown in Fig. 4, and the statistical results obtained from image analysis are given in Table 2.

As shown in Table 2, the average pore size decreases with increasing solution pH. PS/CS composites swollen at pH 12 showed a reduction in the average pore size, while composites swollen at pH 2 had the largest pore size. Such changes of pore size can be observed in the FESEM images in Fig. 4, which further supports the pH sensitive response of PS/CS composites. As emphasized previously, with the presence of basic groups at higher pH, the ionized effect on amino groups of chitosan was largely compromised, which led to the neutralization and contraction of the chains. Thus, average sizes of pores decreased at higher pH environment.

The formation of the pores is due to the expansion of potato starch. According to Sjoqvist and Gatenholm (2005), before the expansion, starch is going through a process called gelatinization where starch granules swell and transform into a paste-like material. When the temperature reaches the boiling point, water will turn into gas bubbles and act as a blowing agent (Glenn et al., 2011). After the bubbles are formed, they will be trapped by the viscous starch paste, and the following evaporation process of water stabilizes the material (Sjoqvist & Gatenholm, 2005). Furthermore, it is possible that the expansion of the starch glucan chains due to gelatinization could facilitate the entanglement with chitosan, which, according to Sperling (2001), has a similar effect on elasticity as chemical crosslinking. If entanglement did exist, to some extent, that might explain why an insoluble PS/CS composite is formed and could absorb solution and respond to pH changes without disintegration over the timeframe studied.

3.3. Glucose detection by ion exchange chromatography

As mentioned previously, PS/CS composites swollen in pH 2 solution had pore size significantly larger than those swollen in higher pH value. In order to make sure such change of pore size was not caused by acid hydrolysis of the composite, an ion exchange chromatography was used to detect whether any significant

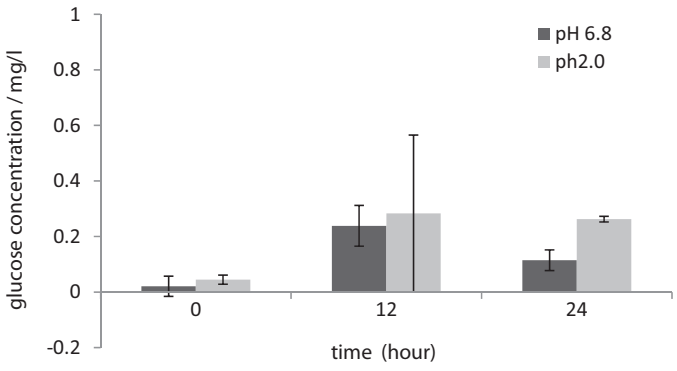

Fig. 5. Glucose concentrations in different solutions after composite swelling.

amount of glucose was released during composite swelling. As can be seen in Fig. 5, glucose concentration in pH 6.8 and pH 2 solution after swelling of PS/CS 7.5, regardless of the swelling time, are all lower than 1 ppm (1 mg/L). In that case, limited amount of glucose was released during swelling of PS/CS composite.

4. Conclusions

An insoluble foam-like composite consisting of potato starch and chitosan was formed using microwave treatment. Crosslinking of the composite was achieved through electrostatic interactions where a polyelectrolyte complex was formed. Solution uptake behavior was examined as a function of the solution pH. The micro structure and swelling mechanisms of the composites are different for pH values lower and higher than the pK_a of chitosan. The uptake capacity of the composites at varied pH solutions can be explained by electrostatic repulsion. The equilibrium swelling ratio was influenced by both pH environment and content of chitosan. Electrostatic interaction between amine groups of chitosan and phosphate groups of potato starch might enhance the structural strength of PS/CS composites and prevent disintegration over the timeframe studied (5 days). The average pore size of the composites became larger at lower solution pH, and limited acid hydrolysis happened during swelling of PS/CS composite.

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