Carbohydrate Polymers 84 (2011) 424–429

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Starch–maleate–polyvinyl alcohol hydrogels with controllable swelling behaviors

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ARTICLE INFO

Article history:
Received 22 July 2010
Received in revised form
30 November 2010
Accepted 1 December 2010
Available online 8 December 2010

Keywords:
Native sago starch
Starch–maleate–PVA
Hydrogel
Swelling behavior

ABSTRACT

Starch–maleate–polyvinyl alcohol (SMP) hydrogels were prepared by reacting polyvinyl alcohol (PVA) with maleic acid (MA) substituted sago starch (SS). The substitution of MA and PVA onto the polysaccharide chain of sago starch was evidenced by the FTIR spectra which showed the presence of the carbonyl group absorption band of maleate ester, and increased intensity of the C–H stretching absorption band. The surface morphology of SMP hydrogels as revealed by SEM micrograph was membrane-like with continuous matrices, and these samples were insoluble in both water and alkaline aqueous solution. TGA analysis showed that the SMP hydrogel exhibited higher thermal stability as compared to the RS, RPVA and SM samples. SMP hydrogel regenerated by freeze-drying showed substantially higher swelling ratio than hydrogel regenerated by direct precipitation under controlled conditions. The swelling behavior of SMP hydrogel could be easily controlled and modulated by varying the feeding composition of precursors or the regeneration methods. The high potential utility of SMP hydrogels in biomedical applications is envisaged by its biocompatibility, low toxicity, ease of preparation and low cost.

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1. Introduction

Hydrogels are hydrophilic polymeric materials that are capable of holding large amount of water or biological fluids in their three-dimensional networks. Hydrogels resemble living tissues in their elasticity, and they swell but do not dissolve when brought into contact with water or aqueous solutions (Alupei, Popa, Hamcerencu, & Abadie, 2002). These unique properties make hydrogels useful materials for biomedical applications such as drug delivery systems, wound dressing, tissue engineering, soft contact lenses, protein sorption and recovery, and artificial implants (Bell & Peppas, 1996; Gehrke, Vaid, & McBride, 1998; Lee, Kung, & Lee, 2005; Muzzarelli, 2009). Other practical applications of hydrogels include as flocculants for treatment of sludge, as well as for the release of agrochemicals, gas separation and removal of toxic heavy metal ions (Han, Chen, & Hu, 2009; Karadag, Saraydin, Caldiran, & Guven, 2000; Okazaki, Hamada, Fujii, Mizobe, & Matsuzawa, 1995; Park & Lee, 2001; Yin, Ju, Zhang, Wang, & Yang, 2008).

Natural biopolymers are more favorable precursors for the preparation of hydrogels as they are nontoxic, biodegradable, renewable and abundant in nature (Li, Xu, Wang, Chen, & Feng, 2009; Tang, Du, Hu, Shi, & Kennedy, 2007). Among these natural biopolymers, starch has been shown to be a good precursor material for the preparation of hydrogels due to its great cross-linking ability in the presence of abundant hydroxyl (OH) groups. However, the hydrophilic nature of starch and its poor mechanical properties have hampered the development of unmodified starch as stable hydrogel (Fang, Fowler, Tomkinson, & Hill, 2002; Swinkels, 1985; Zhang & Sun, 2004). Hence, various biodegradable synthetic polymers such as poly(lactic acid) (PLA), poly(vinyl alcohol), (PVA) and poly(caprolactone), PCL have been blended together with the starch molecules in order to enhance its mechanical properties (Avella et al., 2000; Follain, Joly, Dole, & Bliard, 2005). Among these polymers, PVA is one of the favorite choices due to its excellent compatibility with starch, ease of preparation, non-carcinogenic, inexpensive, biocompatible and biodegradable in nature.

However, blending of polymers may not produce desirable properties due to the poor adhesion between the polymers. Cross-linking is therefore necessary to improve the structural integrity of the polymer blends. Several cross-linkers that are well known for the cross-linking of starch include phosphoryl chloride (Woo & Seib, 1997), epichlorohydrin, (Kuniak & Marchessault, 2006), tri-sodium tri-metaphosphate (Gui-Jie, Peng, Xiang-Sheng, Xing, & Tong, 2006) and glutaradehyde (El-Tahlawy, Venditti, & Pawlak, 2007). However, these cross-linkers are harmful and toxic and therefore have limited their biomedical applications. In this study, we have attempted to use maleic acid (MA) as a cross-linker between starch and PVA through the esterification reaction in order to enhance the mechanical properties and swelling behaviors of the hydrogels formed. MA is being used as a type of food additive, and it is non-toxic and biodegradable in nature. It is therefore a favorable precursor for biomaterial synthesis. However, only few authors have reported the use of MA as a cross-linker with starch (Biswas, Shogren, Kim, & Willett, 2006; Xing, Zhang, Ju, & Yang,

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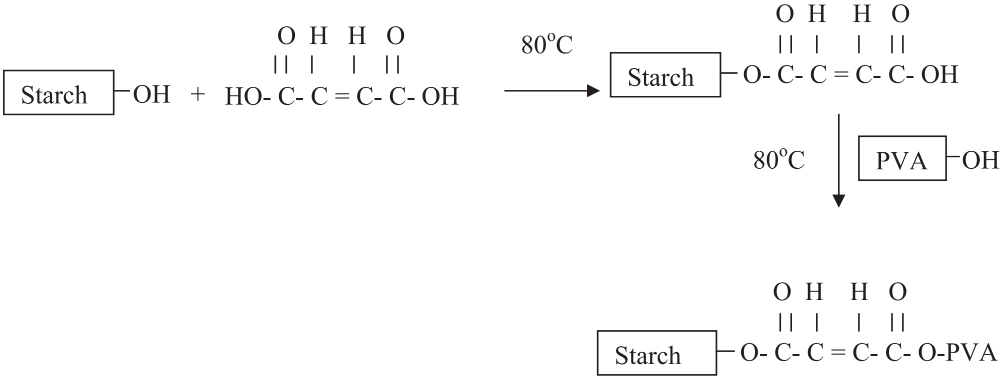
doi:10.1016/j.carbpol.2010.12.002



Scheme 1. Schematic representation of the cross-linking reaction between starch and PVA molecules by maleic acid.

2006). Being a dicarboxylic acid, the esterification of starch as well as PVA can occur through the substitution of carboxylic groups of MA with the free hydroxyl groups of the starch and PVA molecules.

2. Materials and methods

2.1. Materials

Native sago (*Metroxylon sagu*) starch (SS) was purchased from a local grocery store. The maleic acid (MA) was supplied by Fisher Chemicals. Polyvinyl Alcohol (PVA) (MW 89,000–98,000) was obtained from Aldrich, 99% hydrolyzed with an average polymerization degree of 1750 ± 50. Sodium hydroxide (AR grade) was supplied by Mallinckrodt. Ethanol 95% (v/v) denatured was obtained from System. Ultrapure water (∼18.2 MΩ) was generated by the Water Purifying System (ELGA, Model Ultra Genetic). The dialysis tubes used were molecular porous membrane tubing (Spectra/Por–MWCO: 6000–8000).

2.2. Methods

2.2.1. Preparation of starch–maleate–PVA (SMP) hydrogel

The synthesis of hydrogel was carried out by the esterification reaction between the free hydroxyl groups of starch and PVA molecules with the carboxylic groups of MA (Scheme 1). MA acted as the cross-linker between the starch and PVA molecules in the esterification reaction.

In the present study, various SMP hydrogel samples of different compositions were synthesized by varying the initial or feeding molar ratio of anhydroglucose unit (AGU), PVA and MA, as well as the reaction time and hydrogel regeneration method used. Typically, the gelatinized starch solution was prepared by mixing a quantitative amount of native sago starch powder in 10.0 mL of ultrapure water and 1.0 mL of 0.5 M sodium hydroxide (NaOH) solution, and the mixture was heated in a water bath at 80 °C for 10 min with magnetic stirring. A predetermined amount of MA was then added to the gelatinized starch solution and the resulting mixture was further heated in a water bath at 80 °C for 4 h. Subsequently, a quantitative amount of PVA was added to the mixture and continued heating for a further 4 h. Upon being cooled to room temperature, a half-portion of the reaction mixture was added to excess 95% ethanol for direct precipitation of SMP hydrogel. The SMP hydrogel precipitate was rinsed twice with 20 mL of 95% ethanol to remove any unreacted precursors such as MA, PVA and NaOH. The SMP hydrogel obtained was further purified by immersing in 50 mL of 0.5 M NaOH and mechanically stirred for 1 h to dissolve unmodified starch and starch–maleate (SM) ester. The other half-portion of the reaction mixture was dialyzed against ultrapure water and the dialyzed solution was then freeze-dried to obtain the SMP hydrogel. The resulting hydrogel was further stirred in ultra-pure water for 1 hour. All purified SMP hydrogel samples were then dried in an oven at 60 °C until constant weights were achieved.

2.2.2. Characterization of starch–maleate–PVA (SMP) hydrogel

The morphology of SMP hydrogel was investigated using a scanning electron microscope (SEM) (JEOL Model JSM 6390LA) at various magnifications. FTIR spectra of the hydrogel samples pelleted with potassium bromide (KBr) were generated using a Fourier Transformed Infrared Spectrometer (SHIMADZU Model FTIR-8201PC) within the range of 400 and 4000 cm^{-1}. Thermogravimetric analyses of samples were performed using a thermogravimetric analyzer (Rigaku, Model TAS100) between 30 °C and 600 °C at a heating rate of 10 °C/min, and air was being used as the purge gas. The swelling ratios of various SMP hydrogel samples prepared with different feeding compositions in ultrapure water (pH 7) at room temperature were determined. Besides, the swelling ratio of SMP hydrogels regenerated by direct precipitation and freeze-drying at different pH and temperature of the swelling medium was investigated. Typically a pre-weighed sample (0.3 g) was immersed in ultrapure water (50 mL) for 24 h at ambient temperature until the hydrogel had reached the equilibrium state of swelling through absorption of water into the hydrogel network (Paranhos et al., 2007). The swollen hydrogel was recovered by filtering through a 100- to 150-mesh sieve and reweighed immediately after removing residual water on its surface. The wet weight of the hydrogel sample (W_w) was recorded. The swollen SMP hydrogel sample was then dried in an oven at 60 °C for up to 24 h or until a constant dry weight (W_d) was obtained. All experiments were conducted in duplicate. The swelling ratio (SR) of hydrogel samples was calculated according to Eq. (1).

$$\text{Swelling ratio (SR)} = \frac{W_w - W_d}{W_d} \qquad (1)$$

where W_w and W_d are the wet and dry weight of the hydrogel sample, respectively.

3. Results and discussion

3.1. Synthesis and characterization of SMP hydrogels

In this study, SMP hydrogels were prepared through the esterification reaction between starch, MA and PVA in aqueous media. This esterification reaction was, in fact, an acid auto-catalyzed reaction which took place at the medium pH of between 3 and 4. The use of NaOH solution was necessary for the gelatinization of the native starch sample. The subsequent addition of MA to the gelatinized starch solution had resulted in lowering the medium pH

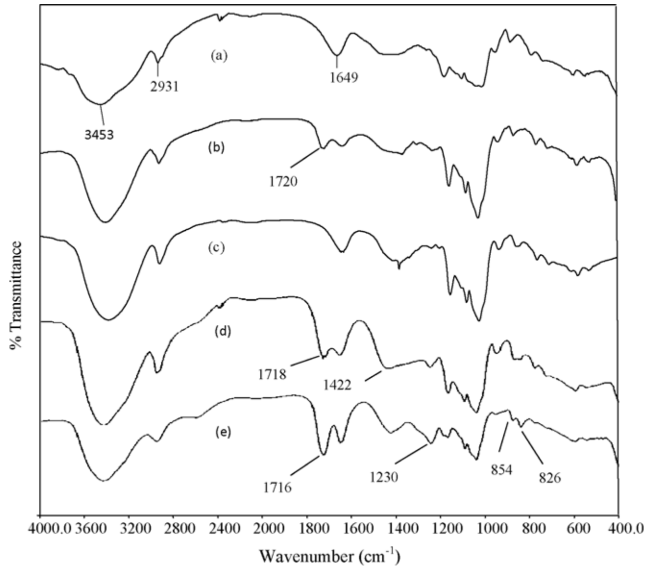


Fig. 1. FTIR spectra of (a) native sago starch; (b) sago starch–maleate; (c) sago starch/PVA; (d, e) SMP hydrogels prepared by direct precipitation and freeze drying, respectively.

to the desired level. Several successful esterification of starch in aqueous media have been reported in the literature during the past recent years (Fang, Fowler, Sayers, & Williams, 2004; Wang & Wang, 2002; Xu, Miladinov, & Hanna, 2004). Since the esterification reaction between carboxylic acid and alcohol is a reversible reaction, the volume of water used was being kept at a minimum level to ensure higher concentrations of the native starch such that the equilibrium would be shifted towards the direction of forward reaction, and hence lead to increased yield of product. The SMP hydrogel obtained was soft and elastic whereas the SM sample was in the form of white amorphous powder. The incorporation of PVA had enhanced the elasticity of the SMP hydrogels. Fig. 1a shows the FTIR spectra of native sago starch with the characteristic absorption bands of O–H stretching and bending at 3453 cm^{-1} and 1649 cm^{-1}, and of C–H stretching at 2931 cm^{-1} (Dumoulin, Alex, Szabo, Cartilier, & Mateescu, 1998). For the SM sample, a characteristic peak of the carbonyl functional group was observed at 1720 cm^{-1} (Fig. 1b), which was absent in the native sago starch sample (Lutfor et al., 2001). The same characteristic absorption band was observed for the SMP hydrogel, but not for the starch/PVA sample (Fig. 1c). A distinct absorption peak attributed to the carbonyl group (at 1716-1718 cm^{-1}) was observed in both FTIR spectra of SMP hydrogel samples regenerated by freeze drying and direct precipitation (Fig. 1d and e). The presence of carbonyl group in the SMP hydrogel indicated the occurrence of esterification reactions between MA, starch and PVA molecules. The substitution of MA was also confirmed by the absorption band observed at 1230 cm^{-1} which indicated the C–O–C stretching of an ester (Liebert, Kulicke, & Heinze, 2008).

The incorporation of PVA onto the SM molecule was collectively indicated by the increased intensity of the C–H stretching absorption band at 2931 cm^{-1}, C–C stretching vibrational band at 1422 cm^{-1}, CH_2 wagging band at 854 cm^{-1} (Kayal & Ramanujan, 2010; Murugan, Mohan, & Bigotto, 1998), and substantial changes in the texture and morphology of the SMP hydrogel samples before and after the esterification reaction. The SM and SMP samples were observed to be powdery and elastic (or rubbery) in nature, respectively. Furthermore, the SM samples were observed to be very soluble in both water and aqueous NaOH solution, whereas the SMP samples were insoluble under the same conditions.

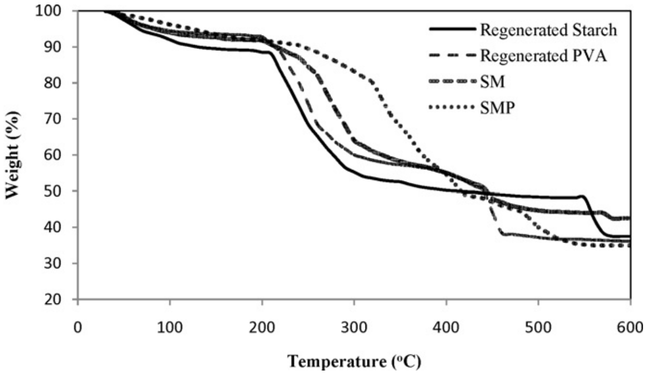


Fig. 2. The TGA thermograms of regenerated starch, regenerated PVA, SM and SMP hydrogel samples.

The esterification reaction between PVA and MA is expected to be easier than reaction between MA and starch molecules. The hydroxyl groups of PVA are more susceptible for substitution due to the comparatively less complex PVA molecular structure as compared to those of the polysaccharide chains in the aqueous state. Polysaccharide chains are reported to show molecular structure of multiple helical order (Brant, 1997; Trommsdorff & Tomka, 1995), whereas PVA shows helical conformation with four PVA units per helix turn (Gribanov, Izmailov, & Arbonin, 2001; Satokawa & Shikata, 2008). Besides, extensive intra-molecular hydrogen bonds occurring within the polysaccharide molecules would tend to stabilize and render them less prone to deprotonation during the esterification reaction.

Fig. 2 shows TGA thermograms of the regenerated starch (RS), regenerated PVA (RPVA), SM and SMP hydrogel samples. The thermogram of regenerated starch (RS) showed three stages of weight loss. The first minor weight loss of about 5% occurred at about 100 °C which was attributed to the removal of moisture. The subsequent major weight loss was observed to occur within the temperature range of 210–280 °C due to the degradation of saccharide structure (Tang, Dou, & Sun, 2006). The third minor weight loss was observed within the temperature range of 560–580 °C which could be due to the presence of trace amount of combustible impurities in the regenerated starch. Regenerated PVA showed very similar thermogram as the RS sample except for the minor weight loss observed at the temperature range of 440–460 °C.

The SM sample showed similar initial weight loss as the RS and PVA samples due to the removal of moisture. However, the subsequent major weight loss due to thermal degradation of SM was observed to occur within the temperature range of 220–300 °C, and followed by a minor weight loss at the temperature range of 400–460 °C. In contrast, the SMP hydrogel exhibited different stages of weight loss at somewhat different ranges of temperature. The initial stage of minor weight loss attributed to the removal of moisture was observed to extend beyond 100 °C to about 150 °C. The subsequent major weight loss due to thermal degradation of SMP hydrogel was observed to occur within the temperature range of 250–400 °C. Further minor weight loss was observed within the temperature range of 460–520 °C which could be due to degradation of SMP hydrogels with higher degree of cross-linking. As a whole, the onset degradation temperature of SMP hydrogel (250 °C) was comparatively higher than those of SM (220 °C), RS and RPVA (210 °C). The higher thermal stability of the SMP hydrogel as compared with RS, RPVA and SM samples was clearly evident.

Fig. 3a shows SEM micrograph of native sago starch which consisted of oval-shaped granules of diameters within the typical range of 20–40 μm. Native sago starch granules exhibited smooth surface morphology with no observable fissures, cavities or pores. Fig. 3b shows the surface morphology of starch–maleate of tightly packed

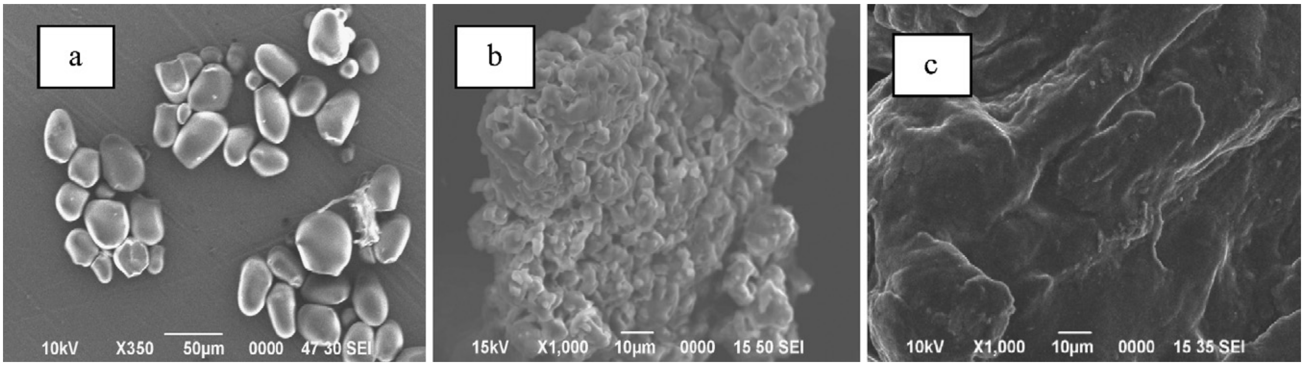


Fig. 3. SEM micrographs of (a) native sago starch; (b) SM; and (c) SMP hydrogel.

macro-clusters. In contrast, the SMP hydrogel (Fig. 3c) showed smoother surface morphology of continuous gel network structure, which could be attributed to more extensive cross-linking between the sago starch, MA and PVA molecules.

The effect of synthesis parameters on the morphology of starch–maleate–PVA (SMP) hydrogel was investigated. Fig. 4 shows SEM micrographs of SMP hydrogels prepared at different cross-linking reaction times between SM and PVA, and regenerated by different methods. The SMP hydrogel prepared with two hours of cross-linking reaction times and regenerated by direct precipitation consisted mainly of individual spherical particles and particle agglomerates of various sizes (Fig. 4a). In contrast, the SMP hydrogel prepared with 4 h of cross-linking reaction time and regenerated by direct precipitation showed smooth surface morphology with continuous matrix of gel network structure (Fig. 4b). The observed effect of cross-linking reaction time on the surface morphology of SMP hydrogel formed could be attributed to the different extent of cross-linking formed between the SM and PVA molecules. We speculate that individual granular particles of very fine sizes were formed initially, which subsequently grew continuously through agglomeration of particles with the progress and extent of cross-linking reaction between SM and PVA molecules. A prolonged cross-linking reaction time between the SM and PVA would therefore lead to increased extent of cross-linking and hence the formation of larger agglomerates of particles. Due to the inherent instability of these individual SMP particles and agglomerates, they eventually coalesced together to form continuous matrix of gel network structure. Fig. 4c shows the SMP hydrogel prepared at 4 h of cross-linking reaction time and subsequently regenerated by freeze drying. The freeze-dried SMP hydrogel showed regular porous network structure which could be attributed to the removal of water molecules retained within the gel network structure during freeze drying. The texture of freeze-dried SMP hydrogel was observed to be soft and brittle, whereas its surface morphology was observed to be fractured, rough and interspersed with many cracks on the surface of the hydrogel sample.

3.2. *Swelling behavior of SMP hydrogel*

The swelling behavior of hydrogel depends on the nature of polymer network such as the presence of hydrophilic groups, cross-linking density, elasticity of polymer network, pH and temperature of the swelling medium (Yang, Liu, Chen, Yu, & Zhu, 2008). As such, any variation of the SMP hydrogel network structure should directly influence its swelling behavior. In the present investigation, the swelling ratio (SR) of SMP hydrogels prepared by varying the feeding precursor compositions such as the molar ratio and mole fraction of anhydroglucose unit of sago starch (AGU), MA and PVA, and the use of different hydrogel regeneration methods and conditions were determined. Fig. 5a shows the effect of various feeding precursor composition on the swelling ratio (SR) of the resulting SMP hydrogels regenerated by direct precipitation at pH 7 and 25 °C. The mole fraction of native sago starch was being varied between 0.08 and 0.18, whereas those of MA and PVA were varied between 0.17 and 0.49, and between 0.27 and 0.49, respectively. At a fixed MA/PVA molar ratio of 1, the swelling ratio of SMP hydrogel was observed to vary substantially over a rather narrow range of mole fraction of native sago starch, with the peak swelling ratio of 6.9 occurred at 0.12 mole fraction of native sago starch. Low swelling ratios of SMP hydrogel were observed at both low and high contents of native sago starch. The initial increase in the swelling ratio of SMP hydrogel at low starch content could be due to the hydrophilic nature of incorporated hydroxyl (OH) functional groups of starch molecules within the gel networks. However, the increase in viscosity and filling up of free spaces or voids by starch molecules within the gel network could arrest entry

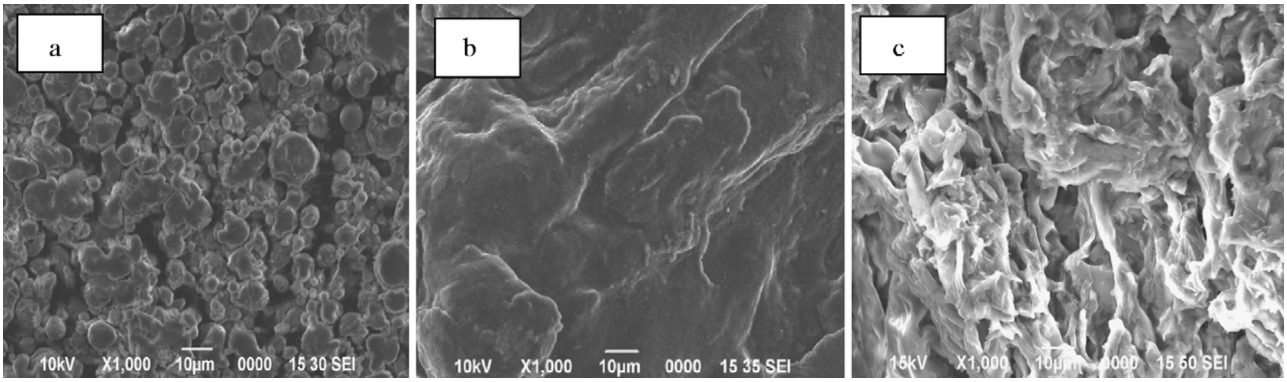


Fig. 4. SEM micrographs of SMP hydrogels prepared at various cross-linking reaction times and regeneration methods. (a) 2 h: direct precipitation; (b) 4 h: direct precipitation; and (c) 4 h: freeze-drying (magnification: 1000×).

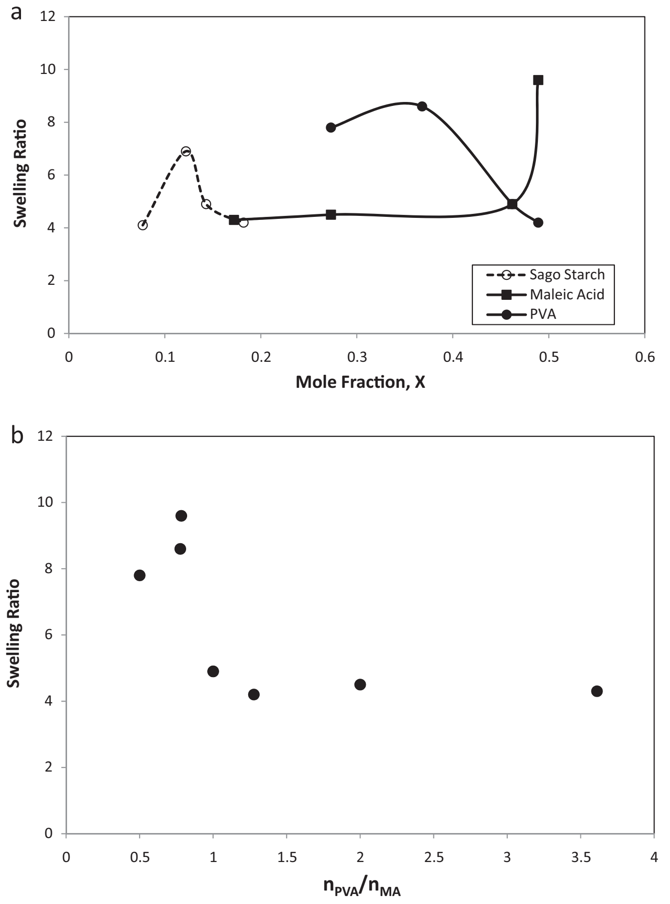


Fig. 5. Effect of feeding composition on the swelling ratio of the SMP hydrogel. (a) Mole fraction of various precursors; and (b) mole ratio of PVA/MA.

Table 1
The swelling ratio of SMP hydrogels prepared by different regeneration methods and at various swelling medium conditions.

Swelling medium		Swelling ratio (g/g)	
pH	Temperature (°C)	Direct precipitation	Freeze-drying
7.00	25	4.9	12.0
7.00	37	6.8	17.0
6.38	25	4.5	11.5
1.23	25	1.8	9.5

Note: Weight of SMP hydrogel used = 0.300 g; volume of swelling medium = 10 mL; feeding mole ratio of AGU:MA:PVA for the preparation of SMP hydrogel = 1:3:3.

of water molecules into the SMP hydrogel, and hence the observed lower swelling ratios at higher starch contents.

The feeding compositions of MA and PVA at fixed native starch content were observed to have contrasting effect on the swelling ratio of the SMP hydrogel formed (Fig. 5). The peak swelling ratios of SMP hydrogels were observed in the presence of high mole fraction of MA (0.49), but at low mole fraction of PVA (0.27–0.37). According to the reaction in Scheme 1, MA acts as a cross-linker between the starch and PVA molecules in the formation of SMP hydrogel. Higher feeding content of MA could have resulted in higher degree of substitution of the starch molecules to form SM, which in turn, led to increased overall hydrophilicity of the SMP hydrogel formed due to the incorporation of hydrophilic moieties such as MA and PVA molecules. In particular, the ionic and polar characteristics of the carboxylic groups of MA could have contributed significantly towards elevating the hydrophilicity of SMP hydrogels. The swelling ratio of SMP hydrogel could therefore be related directly to the degree of substitution of the starch molecules by MA, and the subsequent cross-linking reaction between the SM and the PVA. As such, the higher feeding PVA content would lead to higher extent of cross-linking within the SMP hydrogel thereby resulted in lower swelling ratio. Such contrasting effect of MA and PVA on the swelling ratio of SMP hydrogel is further illustrated in Fig. 5b, whereby SMP hydrogels of high swelling ratios were obtained only at the feeding molar ratios of PVA/MA < 1. Our findings concurred with report by Yang et al. that pure PVA hydrogel had the smallest swelling capacity (Yang et al., 2008). In addition, the higher feeding composition of PVA would result in the formation of SMP hydrogel of lower swelling ratio due to its higher degree of crystallinity. The swelling ratio of starch-grafted-PVA films was reported to decrease with increasing PVA branch length, and PVA segments would crystallize during the process of film formation (Xiao & Yang, 2006). Grafted PVA of higher molecular weight would lead to the formation of higher crystalline phase in the starch-g-PVA. As a consequence, less water could be absorbed and hence the observed decrease in the swelling ratio of starch-g-PVA films.

Table 1 shows the effect of hydrogel regeneration methods, and swelling medium conditions on the swelling ratio of SMP hydrogels. The freeze-drying method had led to the formation of SMP hydrogel with a highly porous network as shown in Fig. 4c. The swelling ratio of SMP hydrogel regenerated by freeze-drying was also observed to be substantially higher than that of SMP hydrogel regenerated by direct precipitation. Freeze-drying could have the effect of inducing physical entanglement between the PVA and polysaccharide chains thereby creating networks of pores and void spaces within the hydrogel matrix. PVA crystallite domains were reported to act as junction points that physically crosslink the polymeric chains within the hydrogel (Ricciardi, Auriemma, De Rosa, & Laupretre, 2004). Such porous hydrogel network gave rise to higher water holding capacity as reflected by its higher swelling ratio.

The swelling ratio of the SMP hydrogels regenerated by freeze-drying and direct precipitation was observed to increase substantially as the temperature of swelling medium was being increased from 25 °C to 37 °C. Such temperature dependence of swelling ratio of SMP hydrogel could be attributed to induced expansion of the polymer chains within the hydrogel network structure at higher temperature of the swelling medium. Besides, the rate of diffusion of water molecules into the hydrogel network would increase at higher temperature thereby trapping more water molecules within a shorter duration (Lakouraj, Tajbakhsh, & Mokhtary, 2005).

The effect of swelling medium pH on the water absorption capacity of SMP hydrogels is of great importance. A change in the pH of swelling medium would cause fluctuation in the pore volume accessible to penetrating water molecules, thereby affecting the swelling behavior of the hydrogel. The swelling ratio of SMP hydrogel was observed to be substantially lower at the medium pH of 1.23 (pH of gastric juice) as compared to those at medium pH 6.38 (pH of intestinal fluids) and pH 7.0. The higher swelling ratio of SMP hydrogel in less acidic swelling medium could be attributed to the acidic nature of the SMP hydrogel. The acidic nature of the SMP hydrogel was evidenced by immersing the SMP hydrogel into water to form an acidic solution. Such acidic nature could be attributed to the presence of some free carboxylic end groups on the polymeric starch chains of the SMP sample. At higher pH, there would be increased interactions between the swelling medium and hydrogel, which in turn led to higher swelling ratios.

4. Conclusion

We have demonstrated the successful preparation of SMP hydrogels with controllable swelling behavior via the esterification reactions of the hydroxyl groups of sago starch and PVA molecules with the carboxyl groups of MA which also serves as the cross-linking agent in aqueous medium. The synthesis method used in this study is simple, facile and without the use of any toxic chemicals and solvents. The swelling behaviors of the SMP hydrogels are dependent on the feeding precursor compositions, pH and temperature of the swelling medium, as well as the hydrogel regeneration techniques used. As the swelling behavior of SMP hydrogels can be easily modulated by varying the feeding precursor composition of sago starch, MA and PVA, they are therefore promising materials for various biomedical applications such as drug delivery system, tissue engineering, artificial implants and wound dressing.

Acknowledgements

The authors gratefully acknowledge the financial support of this research work rendered by University of Malaysia Sarawak (UNIMAS) through the award of the research innovation grant (No.: D1/09/2008(17)).

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