

# Synthesis and properties of starch-g-poly(maleic anhydride-co-vinyl acetate)

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**Abstract.** Starch-g-poly(maleic anhydride-co-vinyl acetate) (SMV) was synthesized via the esterification reaction of starch with the copolymer of maleic anhydride and vinyl acetate. The carboxylic unit percentage (CUP) of SMV was tailored with reaction conditions, and it ranged from 29.8 to 46.9%. The structure and the morphology of the copolymers were characterized with Fourier Transform Infrared spectroscopy and X-ray diffraction analysis. It was found that SMV could form complex with some metal cations such as  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  or cationic polyelectrolyte chitosan, and precipitate from the solution. The weight of precipitation increases with an increase of the CUP of SMV. In addition, a physically cross-linked hydrogel of SMV/poly(vinyl alcohol) (PVA) was obtained by freeze/thaw technique. Scanning electron microscopy exhibited the hydrogel was uniform. The gel exhibited pH-responsive re-swelling. The maximum swelling-ratio values of SMV/PVA (9:1, wt/wt) gel were 3.29 and 5.34 in HCl (pH 1.0) and phosphate-buffer saline (PBS) (pH 12) respectively.

**Keywords:** tailor-made polymers, starch, functionalization, properties

## 1. Introduction

As an annually renewable and biodegradable agriculturally derived biopolymer, starch has been receiving growing attention since 1970s [1, 2]. For conserving the petrochemical resources and reducing environmental pollution, many efforts have been exerted to develop starch-based polymers as alternatives of petroleum-based polymers [3–6]. Regenerated from carbon dioxide and water by photosynthesis in plants [7], the totally biodegradable [8], inexpensive and renewable [9] starch is considered as a promising candidate for developing sustainable materials.

However, it is the intrinsic structure and performance of starch itself makes the dream of obtaining polymers of suitable performance from the earth difficult to come true. Starch is the mixture of two homopolymers of D-glucose, linear amylose and branched amylopectin [2, 7–8]. There are two or

three hydroxyl groups in each glucose residue, which render pure starch hydrophilic and poor in its dimensional stability and processability [10]. Thus, native starch is not used directly.

To improve the end-use properties, starch has been modified through the non-covalent blending or oxidation, hydrolysis, and substitution [11]. Chemical modifications of starch are generally carried out via the reaction with hydroxyl groups in the starch molecule [12]. The derivatives have physicochemical properties that differ significantly from the parent starch and maintain its biodegradability. Consequently, substituting the hydroxyl groups with some groups or chains is an effective means to prepare starch-based materials to suit various needs.

Esterification is one of the most important methods to synthesize starch-based polymers [13]. Starch half-esters can be prepared via reaction, such as

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acetylation or succinylation, of starch with anhydrides [14]. An attractive feature of such derivatives is that they usually contain carboxyl groups, which may exhibit some special performances. Carboxymethylation and etherification are another major ways to introduce carboxyl groups onto starch chains [15–17].

In the documented esterification or carboxymethylation methods, each hydroxyl group of starch is transformed into a substituted group that only contains one carboxyl group. Herein, a simple but effective route, i.e. the esterification reaction of starch with a copolymer of maleic anhydride and vinyl acetate, to incorporate numerous carboxyl groups onto starch backbone is presented. The carboxylic derivative of starch, starch-g-poly(maleic anhydride-co-vinyl acetate), shows valuable properties such as cation binding and pH-sensitivity.

## 2. Experimental

### 2.1. Materials

All chemicals, with the exception of polyvinyl alcohol (PVA, kindly donated by Fujian Chemical Fiber and Chemical Factory, China) were obtained from Shanghai Chemical Agents Ltd. Co., China. Water-soluble starch was dried before use. Vinyl acetate (VAc) was purified by distillation. Maleic anhydride (MAn, m.p. 54–55°C) and N,N'-azobisisobutyronitrile (AIBN) were purified by recrystallization from benzene and ethanol respectively. Chitosan (CS, minimum 90% deacetylation), polyvinyl alcohol (PVA, degree of hydrolysis of 99%), sodium hydroxide, calcium chloride, plumbum acetate, hydrargyrum nitrate, 95% ethanol, benzene, hydrochloric acid (HCl) and acetic acid were all analytical grade reagents and used as received.

### 2.2. Synthesis of carboxylation agent

The carboxylation agent, copolymer of maleic anhydride and vinyl acetate (MV), was prepared by radical copolymerization using AIBN as initiator [18]. Briefly, MAn (16.11 g, 0.164 mol) and benzene (20 ml) were added into a 250 ml three-necked flask and kept constant stirring at 65°C until MAn completely dissolved. Then a mixture of VAc (15.6 ml, 0.164 mol), AIBN (2.5885 g) and ben-

zene (15 ml) was added dropwise into the solution within 1.5 h. Some benzene (50 ml) was added when the solution became turbid. The reaction mixture was allowed to react for 5 h with agitation. It was cooled, filtered, dried and extracted with benzene in a Soxhlet apparatus for 24 h. The dried powder was pure copolymer MV.

The sample was weighed, kept in NaOH (30 ml, 0.09674 M) at 70°C for 4 h, and titrated with HCl (0.07289 M) in the presence of thymol blue. Then the content of MAn in MV could be calculated according to Equation (1):

$$\text{MAn}[\%] = \frac{(30 \cdot C_{\text{NaOH}} - V_{\text{HCl}} \cdot C_{\text{HCl}}) \cdot 9.8}{2m} \quad (1)$$

where  $C$ ,  $V$  and  $m$  were the concentration, volume and weight of NaOH, HCl and MV respectively. The average MAn% was taken from four samples.

### 2.3. Synthesis of starch-g-poly(maleic anhydride-co-vinyl acetate)

Starch-g-poly(maleic anhydride-co-vinyl acetate) (SMV) were synthesized via the esterification reaction of starch with MV. Typically, starch (4.0 g) was mixed with MV in different feeding ratios and dissolved in ca. 15 ml water. The solution was carefully heated to remove the majority of water, then the concentrated slimy mixture was kept in an air oven at 100°C. At predetermined time, the reaction mixture was removed, extracted with 95% ethanol and dried to obtain the product SMV.

The sample was weighed, kept in NaOH (30 ml, 0.09674 M) at 60°C for 3 h, and titrated with HCl (0.07289 M) in the presence of thymol blue. Then the carboxylic unit percentage (CUP) of SMV could be calculated according to Equation (2) [19]:

$$\text{CUP} = \frac{(30 \cdot C_{\text{NaOH}} - V_{\text{HCl}} \cdot C_{\text{HCl}}) \cdot 45 \cdot 100}{m \cdot 1000} \quad (2)$$

where  $C$ ,  $V$  and  $m$  were the concentration, volume and weight of NaOH, HCl and SMV respectively. The average CUP was taken from four samples. SMV-xx.x in the following represented the CUP of a SMV sample is xx.x%, e.g. the CUP of SMV-45.5 was 45.5%.

SMV (0.5000 g) was dissolved in NaOH (50 ml, 0.1 M) and neutralized with HCl (0.1 M). Some more distilled water was added till the volume of

the solution was 100 ml. Then the intrinsic viscosity of SMV was measured using an Ubbelohde viscometer at 30°C.

#### 2.4. Preparation of SMV/PVA complex hydrogels

A mixture (0.4 g) of PVA and SMV-46.9 in the ratios of 1:9, 3:7, and 5:5 (wt/wt) was dissolved in 5 ml distilled water respectively. The solution was poured into moulds. Then it was subjected to two repeated freeze/thaw cycles, 16 h at –16°C and 5 h at 25°C. The obtained hydrogels were dried under vacuum at 37°C to constant weight.

#### 2.5. Cation-binding property of SMV

SMV-45.5 (0.005 g/ml) solution was mixed with 10 ml calcium chloride, plumbum acetate or mercury nitrate aqueous solution (0.01 g/ml) in different ratio respectively. After being kept for 30 min, the formed precipitation was filtered, dried and weighed. The cation-binding property of SMV-29.8, SMV-33.7, SMV-38.6 and SMV-42.3 were examined by assuming the best ratio between SMV and cation-contained solution.

Chitosan was dissolved in 1% acetic acid and mixed with SMV-29.8, SMV-33.7, SMV-38.6, SMV-42.3 and SMV-46.4 aqueous solution in the ratio of 1:1 (wt/wt of chitosan:SMV) respectively. The precipitation was filtered, dried and weighed.

#### 2.6. pH-responsive re-swelling behavior of SMV/PVA complex hydrogels

The dried SMV-46.9/PVA gels were weighed and placed in vials that contained 3 ml HCl (0.1 M, pH 1.0) and maintained at 37°C. At timed intervals, the samples were removed; the surface liquid of the samples was blotted up with soft paper and the samples were weighed. HCl was replaced with phosphate-buffer saline (PBS) (0.1 M, pH 12) when the weight of the samples became constant, and then the aforementioned procedure was repeated. The swelling ratio (SR) of the samples was calculated from the weight of sample at different time ( $W_t$ ) and the weight of dried sample ( $W_d$ ) according to Equation (3):

$$SR = \frac{W_t}{W_d} \quad (3)$$

An average of triplicate measurements was taken.

#### 2.7. Spectroscopic and morphological characterization

Powdered MV, starch, and SMV were mixed with dry KBr and compressed into disk respectively. Then, Fourier transform infrared spectra (FTIR) of the samples were recorded using a Nexus 470 FTIR spectrometer (Thermo Nicolet, USA).

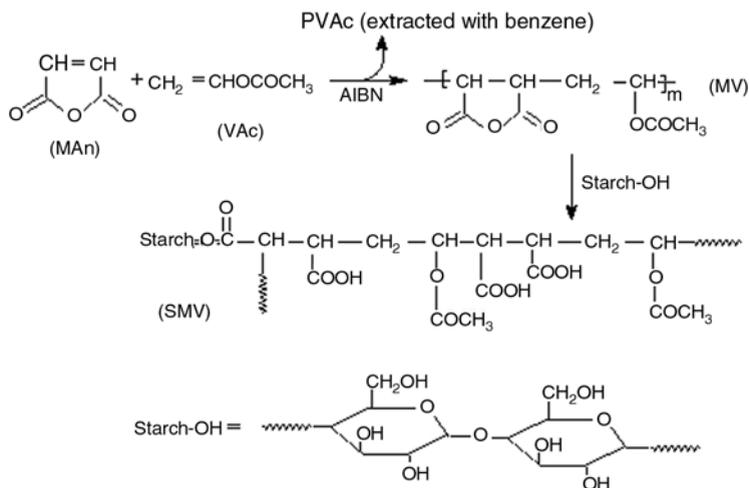
X-ray diffraction (XRD) analysis profiles of dried starch, MV and SMV powder were collected with a Bruker D8-Advanced diffractometer (Bruker, Germany) using Nickel-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406$  nm) and scanned from 2 to 60°C at a scan speed of 2°/min.

The Au-coated cross-section of SMV-46.9/PVA gels was examined with a Hitachi S-3500N scanning electron microscope (Hitachi, Tokyo, Japan).

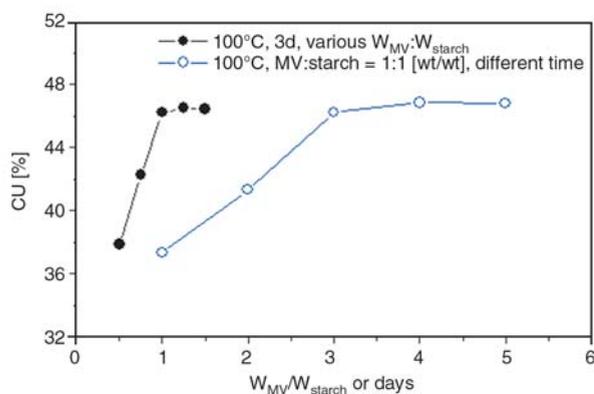
### 3. Results and discussion

#### 3.1. Synthesis of starch-g-poly(maleic anhydride-co-vinyl acetate)

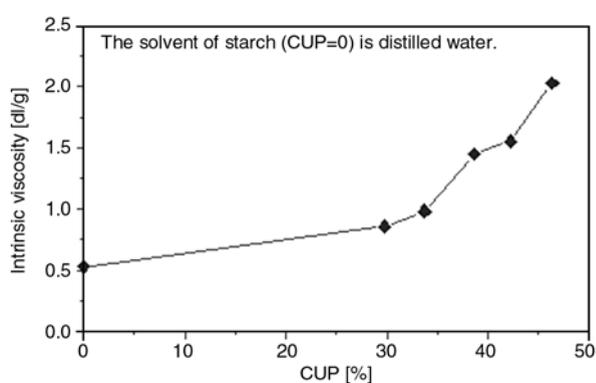
As mentioned above, esterification is an effective way to transform the hydroxyl groups of starch into carboxyl groups. It is used to synthesize starch-based anionic polyelectrolyte too, and the copolymer MV is used as a carboxylation agent. It is found that the percent content of MAn unit in MV is 44.4% and the copolymer is water-soluble. The reactive groups in the chain of MV make it useful for carboxylation. To ensure that MV is uniformly mixed with starch and to focus the examination on the reaction between two reactants, soluble starch i.e., amylose is used as a raw material. The esterification is carried out gradually by water evaporation in an air oven. As a result, starch-g-poly(maleic anhydride-co-vinyl acetate) is readily obtained by two simple steps (Figure 1). More MV added or longer reaction time will increase the CUP of SMV, and CUP will level off when equal weights of reactants fed or 72 h used (Figure 2). In addition, CUP of SMV is 29.8, 36.2 and 46.2% when equal weight of MV and starch is kept at 80, 90 and 100°C for



**Figure 1.** The synthesis of starch-g-poly(maleic anhydride-co-vinyl acetate)



**Figure 2.** The effect of feeding ratio of reagents and reaction time on the carboxylic unit percentage of starch-g-poly(maleic anhydride-co-vinyl acetate)



**Figure 3.** The relationship between the carboxylic unit percentage of starch-g-poly(maleic anhydride-co-vinyl acetate) and its intrinsic viscosity

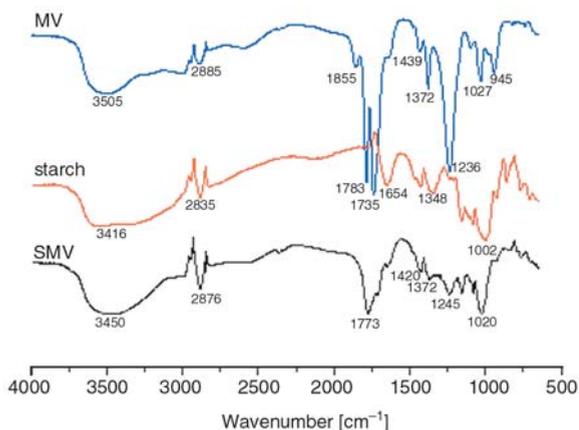
72 h respectively. In other words, the content of carboxyl groups in starch can be easily tailored with reaction conditions such as reaction time, reaction temperature and the feeding ratios. Not higher than 100°C is suggested for reaction temperature to avoid adverse reactions such as cross-linking, oxidation or decomposition.

### 3.2. Characterization of starch-g-poly(maleic anhydride-co-vinyl acetate)

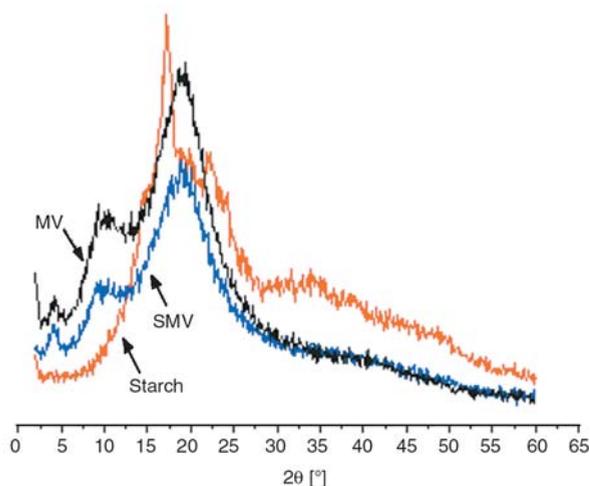
SMV is water-soluble and its solubility can be enhanced with NaOH. The intrinsic viscosity ( $[\eta]$ ) of SMV is determined in presence of a little sodium chloride formed during preparing the solution. It is known that  $[\eta]$  of the copolymer of MAN is in proportion to its molecular weight [20]. On the other hand, the more MV reacted with starch, the higher CUP and molecular weight of SMV will be. Thus,

the  $[\eta]$  of SMV increases with the increase of CUP of SMV (Figure 3), and this indicates the esterification of MV and starch is successfully carried out as expected.

As the difference between the structure of starch and SMV is quite obvious, the structure of SMV can be simply verified with FTIR (Figure 4). The characteristic peaks appeared at 1855 and 1783, 1735 and 1236  $\text{cm}^{-1}$  on the spectra of MV are attributed to the anhydride group of MAN unit and the ester group of VAc unit respectively. Owing to the hydrolysis of some anhydride groups during storage [18], an absorption band appears around 3505  $\text{cm}^{-1}$ . Comparing the FTIR spectra of SMV with starch and MV, the characteristic peaks of the unreacted hydroxyl groups and formed carboxyl groups, carbonyl groups and ester groups are found at 3450, 1773, 1245 and 1020  $\text{cm}^{-1}$  on the spectra of SMV respectively.



**Figure 4.** FTIR spectra of starch, copolymer of maleic anhydride and vinyl acetate and starch-g-poly(maleic anhydride-co-vinyl acetate)

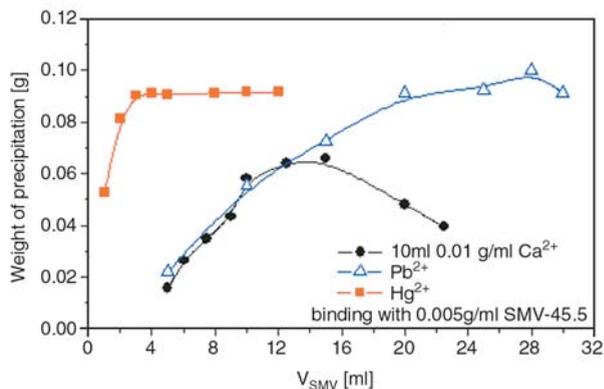


**Figure 5.** X-ray diffraction analysis profiles of starch, copolymer of maleic anhydride and vinyl acetate and starch-g-poly(maleic anhydride-co-vinyl acetate)

XRD analysis results (Figure 5) show that starch, MV and SMV are all semicrystalline. There are two sharp peaks exhibited at ca.17 and 22° on the XRD pattern of starch. The XRD profile of SMV is similar to that of MV whereas different from the one of starch. Both the sharp peaks of MV and SMV appear at about 10 and 19°. These phenomena indicate that the chemical structure and morphology of starch is evidently changed after modification.

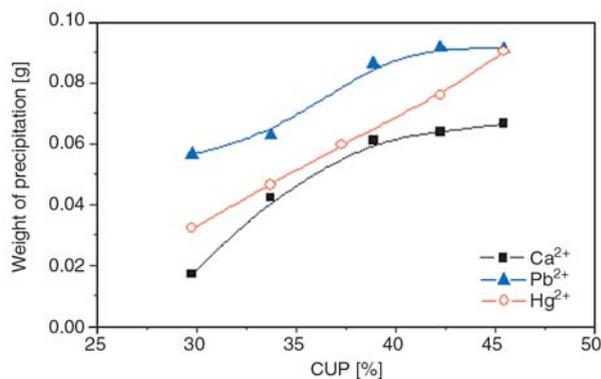
### 3.3. Properties of starch-g-poly(maleic anhydride-co-vinyl acetate)

The carboxyl groups existed in SMV may be changed into negatively charged groups in the solution, which enable SMV binding multivalent-metal



**Figure 6.** The effect of dosage of starch-g-poly(maleic anhydride-co-vinyl acetate) solution on its metal cations' chelation

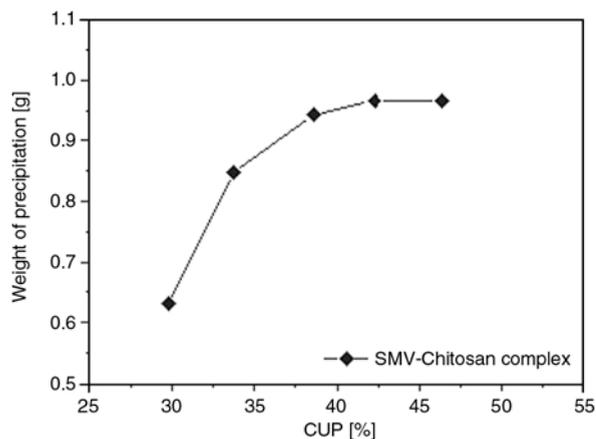
cations [21]. Actually, a precipitation is formed when the SMV solution is mixed with the solution containing  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$  or  $\text{Hg}^{2+}$ . Noting that some of chelating agent SMV will remain in solution due to its water-solubility, the weight of precipitation instead of adsorption capacity is used to investigate the interaction of SMV and cations. As shown in Figure 6, the weight of precipitation is increased with the amounts of SMV added and appears a maximum value for each cation. Since the amount of cations in solution is fixed, the volume of SMV-45.5 solution that forms the maximum weight of precipitation can be regarded as the best one for chelating metal cations. Then 15, 28 and 10 ml SMV solution is assumed to chelate  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$  or  $\text{Hg}^{2+}$  in 10 ml 0.01 g/ml salt solution respectively. As carboxyl groups are the functional groups for binding cations, the weight of precipitation increase with an increase of CUP of SMV (Figure 7). The results also reveal that the amount of carboxyl groups incorporated onto starch chains is high



**Figure 7.** The effect of the carboxyl groups' content of starch-g-poly(maleic anhydride-co-vinyl acetate) solution on its metal cations' chelation

enough to make uncross-linked SMV binding metal cations.

Chitosan can be positively charged in aqueous solution. The electrostatic attraction and additional secondary interaction such as hydrogen bonds between the cationic amino groups of chitosan and the anionic groups of the other polyelectrolyte will produce polyelectrolyte complex (PEC) [22]. The fact, that precipitation is observed when mixing SMV solution with chitosan solution, once more confirms SMV is an anionic polyelectrolyte. Evidently, more carboxyl groups in SMV will enhance the interaction between two oppositely charged polyelectrolytes and obtain more precipitation. The experimental results shown in Figure 8, SMV of higher CUP will form more precipitation with equal weight of chitosan, is consistent with forma-



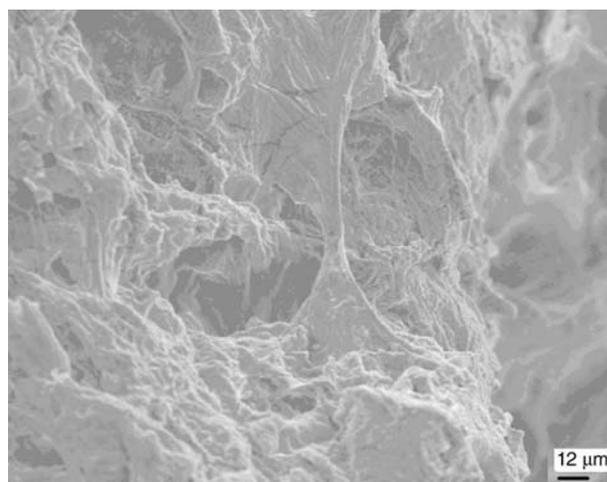
**Figure 8.** The effect of the carboxyl groups' content of starch-g-poly(maleic anhydride-co-vinyl acetate) solution on its complexation with chitosan



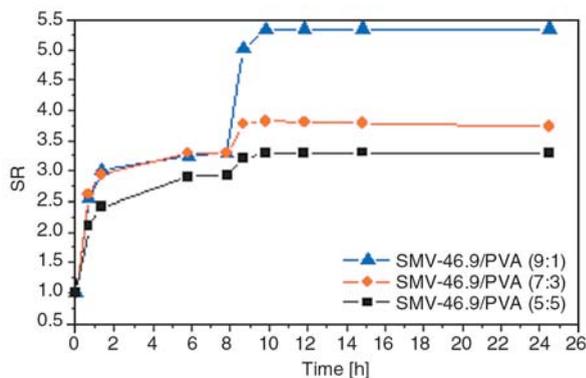
**Figure 9.** The appearance of starch-g-poly(maleic anhydride-co-vinyl acetate)/PVA hydrogel

tion mechanism of PEC. The weight of precipitation is almost kept the same when CUP of SMV is higher than 38.6%, which may be attributed to amino groups of chitosan have been saturated with carboxyl groups.

The pH-sensitive re-swelling behavior of dried SMV-46.9/PVA gels also proves the amount of carboxyl groups on SMV is high enough [23]. After subjecting to several freeze/thaw cycles [24], the solution containing SMV and PVA can be transformed into hydrogels. As can be seen in Figure 9, a uniform, soft and elastic SMV-46.9/PVA hydrogel is successfully prepared via such a physical cross-linking method. Scanning electron microscopy shows that no phase separation happened within the hydrogels (Figure 10). As might have been expected, SR of SMV-46.9/PVA gels in PBS are much greater than that in HCl. Moreover, the higher the content of SMV-46.9, the more evident pH-sensi-



**Figure 10.** Scanning electron microscopy of the cross-section of starch-g-poly(maleic anhydride-co-vinyl acetate)/PVA hydrogel



**Figure 11.** Re-swelling behaviors of starch-g-poly(maleic anhydride-co-vinyl acetate)/PVA gels in HCl (0.1 M, pH 1.0) and phosphate-buffer saline (PBS) (0.1 M, pH 12) at 37°C

tive re-swelling will be exhibited (Figure 11). The maximum SR values of SMV-46.9/PVA gels prepared in the ratio of 9:1, 7:3 and 5:5 (wt/wt) are 3.29 and 5.34, 3.29 and 3.81, 2.92 and 3.30 in HCl (0.1 M, pH 1.0) and in PBS (0.1 M, pH 12) respectively. Undoubtedly, it is the incorporation of SMV-46.9 that renders the gels shows pH-responsive.

#### 4. Conclusions

A convenient two-steps route including radical copolymerization of maleic anhydride with vinyl acetate and subsequent esterification with starch is carried out to incorporate numerous carboxyl groups onto starch chains. The starch-based derivative SMV shows some unique properties such as binding metal cations, forming PEC with a polycationic biopolymer and endowing complex hydrogel pH-responsive re-swelling. The experimental results validate not only that the amount of carboxyl groups incorporated onto starch chains by using the approach presented is high enough, but also suggests that SMV will be a good candidate for environmental or biomedical applications.

These reactions can be easily performed and are controllable, and can be used to modify naturally occurring native starch. Starch, chitosan and PVA are biodegradable. In addition, vinyl acetate units are almost distributed singly in the side-chain of SMV. Thus, synthesis of SMV and formation of PEC with chitosan or hydrogel with PVA may elicit a direction to improve the performance of starch without sacrificing its biodegradable nature.

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