

Preparation and Characteristic of Electric Stimuli Responsive Hydrogel Composed of Polyvinyl Alcohol/Poly (Sodium Maleate-co-Sodium Acrylate)

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ABSTRACT: Maleic anhydride was used to prepare polyvinyl alcohol/poly (sodium maleate-co-sodium acrylate) hydrogels (PVA/poly(SMA-SAA)) by a repeated frost-defrost process because of its higher charge density and potential electric stimuli sensitivity. The bending angle was measured in a noncontact electric field using carbon as plate electrodes. It was found that the bending angle was dependent on various factors, including composition of hydrogel, concentration of NaCl solution, types of electrolyte solution, and electric voltage. It exhibited that the bending angle

increased when the concentration of NaCl solutions and the electric voltages increased. An abnormal bending direction was observed, and it was affected not only by the kinds of hydrogels, but also by the exterior variations. The hydrogel showed good reversibility in on-off electric field and could be a candidate for practical application. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 391–395, 2008

Key words: crosslinking; hydrogels; stimuli-sensitive polymers; swelling

INTRODUCTION

Hydrogels are three-dimensional (3D) hydrophilic polymer networks that can absorb and retain a large amount of water.¹ Some hydrogels are found to reversibly change their volumes and shapes in response to external stimuli, such as pH, solvent composition, ionic strength, temperature, and electric field.^{2–5} Recently, there have been many reports about electric stimuli responsive phenomena in charged polymer networks because of their potential application in intelligent materials.^{6–8} Kim et al.^{9–12} reported electric behaviors of a series of anionic hydrogels based on polyacrylic acid or its derivatives in NaCl solution, which can be used as biosensors and artificial muscles. To improve mechanical strength and biocompatibility of hydrogels, polyvinyl alcohol (PVA), chitosan, or alginate was chosen to build the interpenetrating polymer networks (IPNs).^{13–16} Besides, hydrogels with

different type of charges were also found to show electric stimulus responsive behaviors: Sun et al.^{3,4} reported mechanic-electro-chemical behaviors of cationic chitosan/poly (propylene glycol) composite fibers in aqueous HCl solution. Yuk and Lee demonstrated the reversible bending of crosslinked acrylamide gel induced by electric current in aqueous NaCl and proposed a mechanism for the bending phenomenon.¹⁷ It is found that the response behaviors of electric stimulus responsive hydrogels are affected by many parameters, including fixed charge density, ionic concentration, electrical potential, and so forth.¹⁸

In this paper, maleic anhydride was chosen as a comonomer because of the higher charge density induced by the hydrophilic carboxyl groups in the molecules, which were potentially sensitive to electric stimuli. Moreover, it was testified that poly(maleic anhydride) was high biocompatible and was of low toxicity, providing a potential application in biological fields. Therefore we reported a hydrogel based on poly(sodium maleate-co-sodium acrylate) (poly(SMA-SAA)), physically crosslinked with PVA to make a strong mechanical strength and easy processing. The electric responsive behaviors in a noncontact electric field were investigated.

EXPERIMENTAL

Materials

PVA with an average molecular weight of 7.7×10^4 was purchased from Tianjin Fuchen Chemical Co.,

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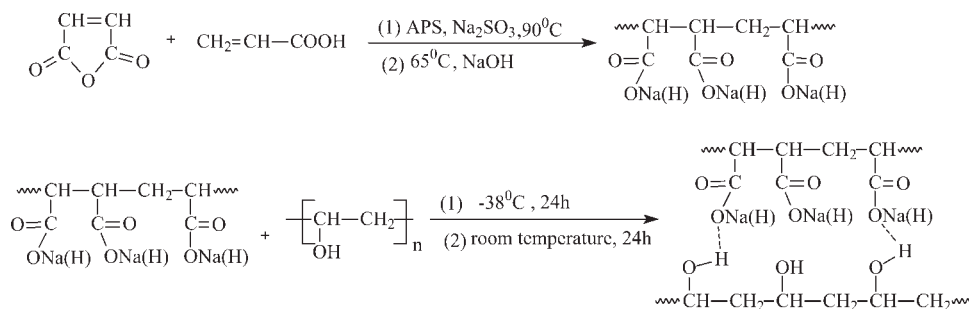
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Scheme 1 A proposed preparation process of Polyvinyl Alcohol/Poly (Sodium Maleate-co-Sodium Acrylate).

and acrylic acid was provided from Tianda Chemical Co., maleic anhydride and ammonium persulfate was obtained from Xi'an Chemical Co. Sodium hydroxide, sodium chloride, sodium bisulfate, ammonia sulfate, sodium carbonate, and absolute ethanol were of analytical grade, and used as received without further purification.

Preparation of polyvinyl alcohol/ Poly(maleate-co-acrylate)

10 g maleic anhydride and 0.38 g ammonium persulfate were dissolved in deionized water to make a 6% (w/w) maleic anhydride solution in a three-neck flask. Then, 10 g acrylic acid and 13 g 6% (w/w) sodium bisulfite were added, respectively. The resulting mixture polymerized at 90°C under magnetic stirring. After 3 h, the solution was cooled to 65°C, and was neutralized to pH 6.5–7.0 by dropping a sodium hydroxide solution. The resulting copolymer poly (SMA-SAA) was precipitated and washed with absolute ethanol and deionized water for three times, respectively, then dried in oven at 80°C.

5 g PVA was dissolved in deionized water at 80°C, and afterwards 5 g poly (SMA-SAA) was added. The mixture was stirred for 6 h to make an even solution. Then, the solution was poured into a container, and placed in a freezer at -38°C for 24 h, followed by a 24 h defrost process at room temperature. After repeating the frost-defrost process for three times, the sample was dried at room temperature (see Scheme 1).

The hydrogels were immersed in different electrolyte solutions (NaCl, Na₂CO₃ and (NH₄)₂SO₄) with various concentrations for 12 h to achieve a swelling equilibriums before test.

Bending behaviors under an electric stimulus

To test the electric response, a gel sample in cube shape with dimension 3 cm × 0.4 cm × 0.2 cm was placed in a transparent glass container. Two carbon electrodes are of a size of 2 cm × 4.2 cm and a distance of 3cm from each other. The gel was placed in the center of the container, having an equal distance from

each electrode, and one end of the hydrogel sample strip was fixed. The container was filled with the various concentrations of different electrolyte solutions. In the bending angle measurement, the initial position (bending angle = 0°) of the hydrogel strip was the position under nonapplied electric field. When an electric stimulus was applied, the angle of bending was measured by recording the deviated angle from the position of nonapplied electric field. The deformation process was recorded using a digital camera (Nikon, Japan).

RESULTS AND DISCUSSION

FTIR spectroscopy

The IR spectra of maleic anhydride and poly (SMA-SAA) were recorded by a Bruker spectrophotometer (EQINOX55) (see Fig. 1 and Fig. 2, respectively). The characteristic absorption peaks observed 1850 cm⁻¹ and 1780 cm⁻¹ contribute to the typical C=O stretching in O=C—O—C=O and the peaks observed 1270 cm⁻¹ contribute to the C—O stretching in O=C—O—C=O are shown in Figure 1. In comparison, the peaks disappeared in IR spectra of poly

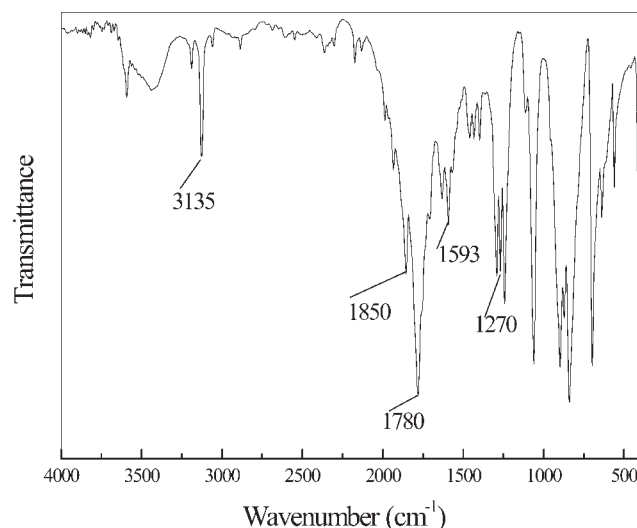


Figure 1 The IR of maleic anhydride.

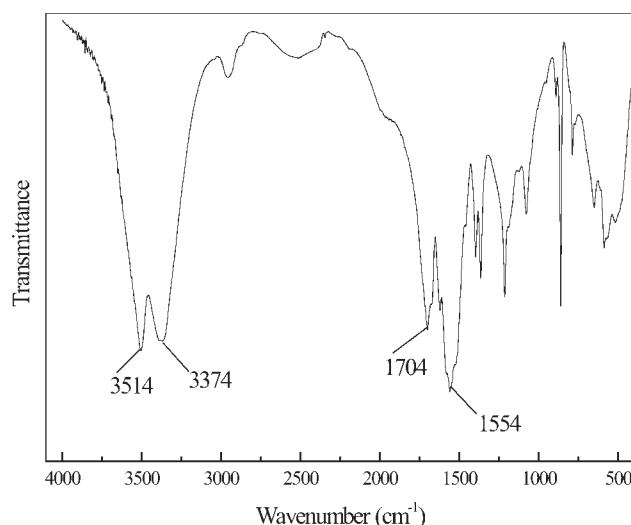


Figure 2 The IR of poly(sodium maleate-co-sodium acrylate).

(SMA-SAA). Instead, a strong adsorption band at 1704 cm^{-1} associated with the stretching vibrations of the uncharged form of carboxylic groups and, when charged, a second band at 1554 cm^{-1} from the asymmetric stretching vibrations of the carboxylate groups in sodium maleate or sodium acrylate molecules. Besides, 3135 cm^{-1} attributed to unsaturated C—H stretching in maleic anhydride, as well as the absorption peak at about 1593 cm^{-1} attributed to the ethylenic bond that conjugated with carbonyl group vanished and testified further the copolymerization (see Fig. 2). Furthermore, two strong bands at 3514 cm^{-1} and 3374 cm^{-1} assigned to O—H stretching vibration in acrylic acid and maleic acid accordingly. So it may

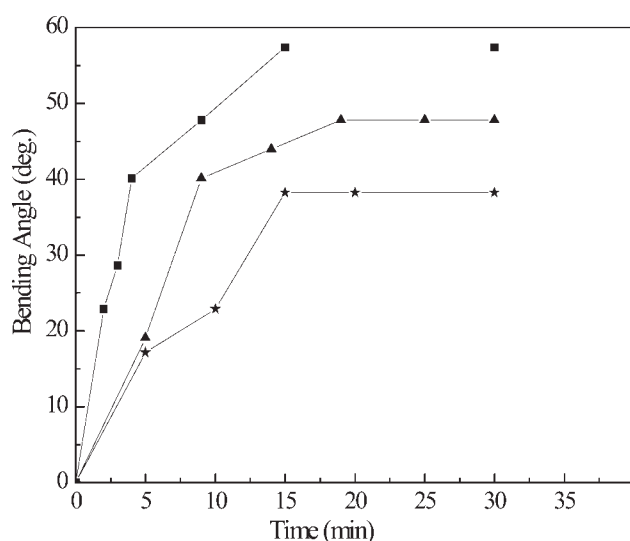


Figure 3 Effect of composition of hydrogels on the bending angle as a function of time in 0.1 M NaCl at 15 V (■—SMA-SAA-VA11; ▲—SMA-SAA-VA21; ★—SMA-SAA-VA12).

TABLE I
Designation and Composition of the Hydrogel

Designation	Composition	
	PVA (wt %)	Poly (SMA-co-SAA) (wt %)
SMA-SAA-VA12	2	1
SMA-SAA-VA11	1	1
SMA-SAA-VA21	1	2

be concluded that maleic anhydride and acrylic acid carried out copolymerization under our experimental condition.

Effect of composition of hydrogel

Figure 3 showed time-dependent bending behaviors of PVA/poly(SMA-SAA) hydrogels with various compositions (Table I) in 0.1 M NaCl aqueous solution at 15 V .

It was observed that the hydrogels rapidly bended and reached equilibrium within 20 min with a maximum bending angle of 57.39° , 38.23° , 47.8° for SMA-SAA-VA11, SMA-SAA-VA12, and SMA-SAA-VA21, respectively. It is widely accepted that the osmotic pressure is a driving force to deform the hydrogels. Such osmotic pressure can be caused by the ion concentration gap between the internal hydrogel and the external solution. Usually, according to the Donnan osmotic pressure equilibrium, with an increase of ionic groups in hydrogels, or movable counterions in solution, the osmotic pressure will increase, thus leading to an increase of bending angle.¹⁹ Similar results were obtained in our experiment that the bending angle of the hydrogels increased with increasing the content of poly (SMA-SAA). The bending angle for the hydrogel at a mass ratio of 1 : 1 of poly (SMA-SAA) to PVA was bigger than at the ratio of 1 : 2. However, a further increase in the content of poly (SMA-SAA) produced a decrease of the bending angle instead. It was probably caused by nonuniform distribution of ionic charge in hydrogels.²⁰ It may be caused by the uneven crosslinking between poly (SMA-SAA) and PVA during the course of frost-defrost.

Effect of electric voltage

The dependence of the bending behavior of the SMA-SAA-VA11 hydrogels on the electric voltage in 0.01 M NaCl aqueous was investigated (Fig. 4). It was exhibited that the bending angle of the hydrogels increased with increasing the voltage attributed to an increase of the gap of ion concentration and diffusion rate. Similar behaviors are found in the case of hydrogel composed of poly(methacrylic acid) and alginate.⁹ The SMA-SAA-VA11 reached the highest bending angle at

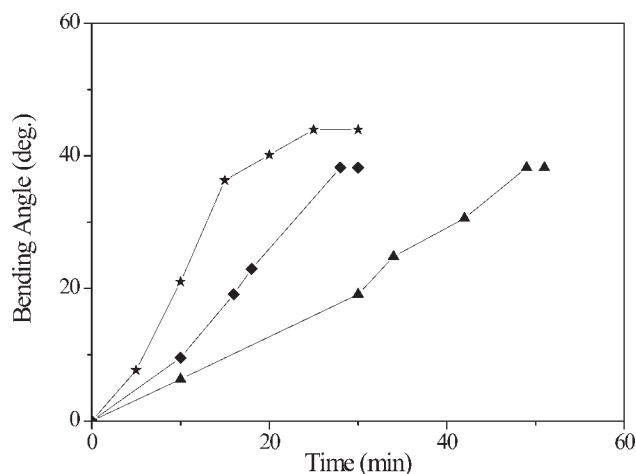


Figure 4 Effect of voltage on the bending angle of SMA-SAA-VA11 hydrogel as a function of time in 0.01 M NaCl (▲—10 V; ◆—15 V; ★—20 V).

20 V within 25 min. However, the hydrogel showed an abnormal bending direction when the voltage was varied. For SMA-SAA-VA11, it was observed to bend to anode at 15 V and 20 V, while bending to cathode at 10 V. Bending direction can be affected by a process of voltage-induced diffusion of ions and the concomitant expansion of one side of the polymer and contraction of the other. At a low electric voltage, as a polyanion-type hydrogel, PVA/poly(SMA-SAA) tended to bend toward cathode due to greater swelling pressure on the side near the anode than on the side near the cathode. It was different from the bending behavior of polycations.¹¹ With increasing applied electric voltage, the diffusion coefficient of free ions moving from the surrounding solution to the counter electrode or into the polymer network increased and produced different pH gradients between two sides of hydrogel due

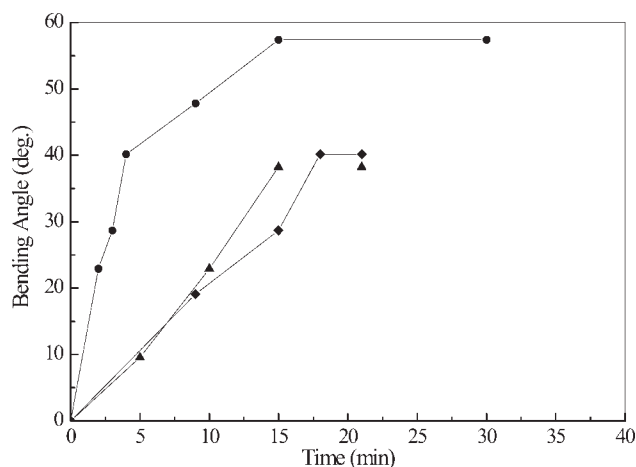


Figure 5 Effect of kinds of electrolyte solutions on the bending angle of SMA-SAA-VA11 hydrogel as a function of time at 15 V (●—0.1 M NaCl; ◆—0.1 M Na₂CO₃; ▲—0.1 M (NH₄)₂SO₄).

to a larger diffusion coefficient of OH⁻ compared with Na⁺,²¹ so an increased bending angle was found. However, the hydrogel bent towards anode instead of cathode. The phenomenon was not reported at other documents. It has not been completely explained because of still a lack of well-developed theories for such chemo-mechanical kinetics.

Effect of kinds of the electrolyte solutions

Figure 5 showed the bending angles for the SMA-SAA-VA11 hydrogels as a function of various electrolyte solutions. Even under the same concentration, the ion strength in Na₂CO₃ and (NH₄)₂SO₄ solution was higher than in NaCl solution, which was supposed to lead to an increased bending angle. However a contrary phenomenon was observed: the bending angle in NaCl solution was obviously higher than that in the other two solutions. One reason was that excessive free cations in the latter solutions would partly shield the negative charges in the polymer chain after diffusing into the gel. Besides, the electrochemical reactions taken place near the electrodes could cause a pH gradient between outside and inside of the hydrogel. In contrast, there were similar electrolysis processes, so no big difference in bending angle was found for Na₂CO₃ and (NH₄)₂SO₄ solution.

Effect of concentration of electrolyte solution

Figure 6 showed the bending behavior of the SMA-SAA-VA11 hydrogel to the electric stimuli with varying concentrations of the NaCl solution, among 0.01, 0.05, and 0.1 M. It was observed that an increase in the concentration of NaCl solution was accompanied by a rise in the bending angle. The hydrogel approached

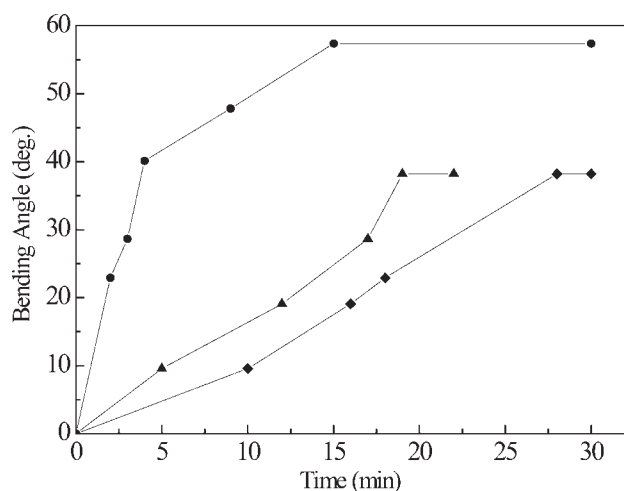


Figure 6 Effect of concentration of NaCl solution on the bending angle of SMA-SAA-VA11 hydrogel as a function of time at 15 V (●—0.1 M NaCl; ▲—0.05 M NaCl; ◆—0.01 M NaCl).

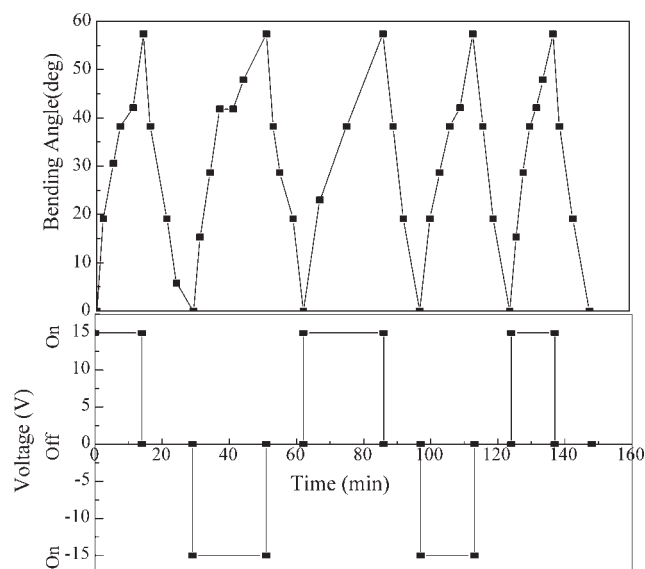


Figure 7 Effect of On-Off switching of electric field on the bending angle of SMA-SAA-VA11 hydrogel as a function of time at 15 V.

the maximum bending angle in 0.1M NaCl solutions, while it exhibited the minimum bending angle in 0.01M NaCl. As described above, the increase of electrolyte concentration induces the increase of the free ions moving from the surrounding solution toward their counter electrode, or into the hydrogel itself. As a result, the bending angle of the SMA-SAA-VA11 could increase.¹¹

Effect of on-off switching of electric field

Figure 7 showed the electric response of the SMA-SAA-VA11 hydrogel with on-off switching of electric field at 15V. When an electric field was applied to the hydrogel in 0.1M NaCl solution, the gel bended toward the anode at a rate of 3.9°/min. Furthermore, it was found the gel returned to its initial position almost at equal rate when the electric field was removed. The bending direction and bending angle varied periodically with changing the voltage periodically. Therefore, it can be concluded that PVA/poly (SMA-SAA) hydrogel showed an outstanding reversibility and can be repeatedly used in practical application.

CONCLUSIONS

The hydrogels composed of polyvinyl alcohol and poly (sodium maleate-*co*-sodium acrylate) was found to be electrically sensitive and outstandingly reversible. Its bending behaviors at noncontact parallel plate carbon electrode were dependent of various factors, including composition of hydrogels, concentration of NaCl solution, types of electrolyte solution, and electric voltage. The bending angle did not show a proportional increase with the increase of charged hydrophilic groups in the hydrogels. It was indicated to bend towards anode at a high voltage, while towards cathode at a low voltage. It was further testified that it exits different factors deciding the bending behaviors of hydrogels.

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