

# Synthesis and swelling properties of a poly(vinyl alcohol)-based superabsorbing hydrogel

Hossein Hosseinzadeh\*

Department of Chemistry, Payame Noor University, 19395-4697, Tehran, Iran

## CHRONICLE

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## ABSTRACT

Superabsorbent hydrogels based on poly(vinyl alcohol) were prepared by a crosslinking technique using glutaraldehyde as a crosslinker. The hydrogel structure was confirmed using scanning electron microscopy (SEM). Results from SEM observation showed a porous structure with smooth surface morphology of the hydrogel. We have systematically optimized the certain variables of hydrogel synthesis (i.e. the crosslinker concentration, poly(vinyl alcohol) content, time and temperature of crosslinking reaction) to achieve a hydrogel with maximum water absorbency. It was concluded that under the optimized conditions, maximum capacity of swelling in distilled water was equal to 231 g/g. The absorbency under load (AUL) of hydrogels was also measured. In addition, swelling ratio in various salt solutions was determined and the hydrogels exhibited salt-sensitivity properties.

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## 1. Introduction

Superabsorbent polymers (SAPs) are cross-linked networks that can absorb a great amount of water or aqueous solutions<sup>1</sup>. Due to unique properties of SAPs, these polymers were synthesized and characterized by the several research groups in the world<sup>2-5</sup>.

SAPs are mainly used in various industries such as hygienic, foods, cosmetics, and agriculture<sup>6-8</sup>. Since they responded to changing environmental conditions such as temperature<sup>9</sup>, pH<sup>10</sup> and solvent composition<sup>11</sup>, SAPs have been attracting much attention in medical and mechanical engineering fields.

Polyvinyl alcohol (PVA) is a synthetic polymer that is soluble in water. Because of desirable characteristics, PVA hydrogels have been used in various pharmaceutical and biomedical applications

\* Corresponding author.

E-mail addresses: [h\\_hosseinzadeh@pnu.ac.ir](mailto:h_hosseinzadeh@pnu.ac.ir) (H. Hosseinzadeh)

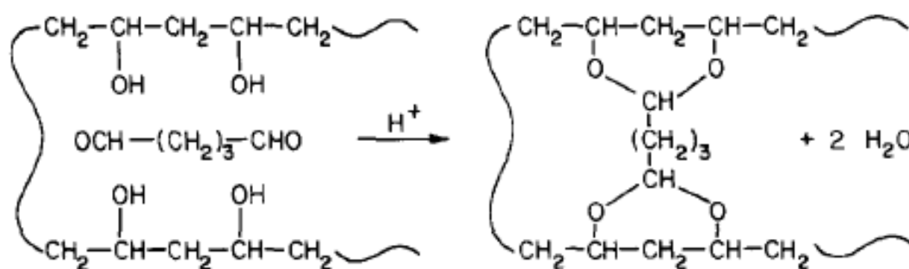
<sup>12-21</sup>. However, PVA must be cross-linked in order to that can be useful for a wide range of applications. Cross-linked PVA can be synthesized by chemical or physical methods. The use of chemical crosslinkers such as glutaraldehyde and the use of electron beams are the most common methods of chemical crosslinking of PVA. Physical crosslinked PVA hydrogels can be prepared using methods such as “freezing-thawing”.

In the present report, we describe the preparation and characterization of a poly (vinyl alcohol)-based hydrogel. The effect of reaction variables affecting the swelling capacity of the hydrogel and swelling behavior in various salt solutions was investigated.

## 2. Results and Discussion

### 2.1. Synthesis of hydrogel

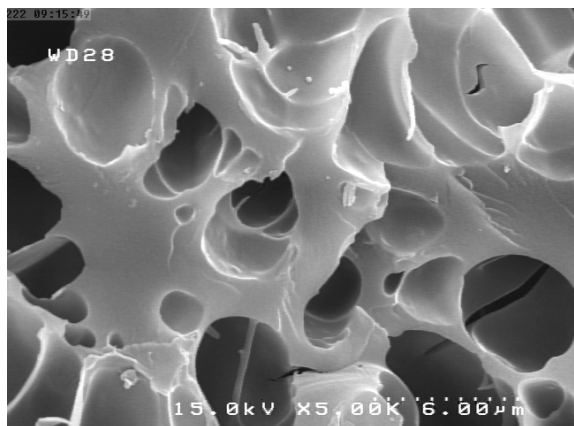
A general reaction mechanism for PVA-based hydrogel formation is shown in Scheme 1. As seen from this Scheme, the acetal linkage was formed between aldehyde groups of glutaraldehyde and hydroxyl groups of PVA backbones.



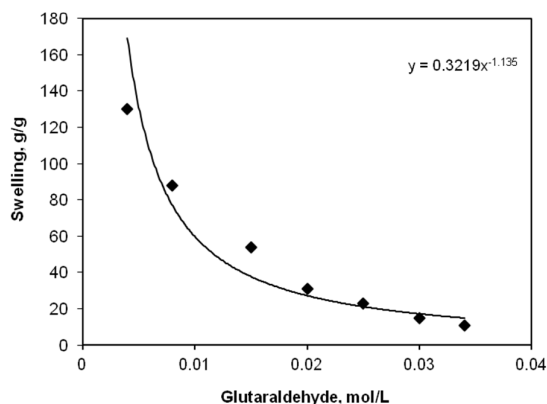
**Scheme 1.** Proposed mechanistic pathway for synthesis of the PVA-based hydrogels.

### 2.2. Characterization

In general, the scanning electron microscopy (SEM) shows microstructure morphologies of hydrogels. The SEM of the synthesized hydrogel is shown in Fig. 1. This picture verifies that the synthesized PVA-based hydrogel in this work has a porous structure. Existence of these pores in hydrogels strongly increases the swelling kinetics of the resulted product.



**Fig. 1.** SEM photograph of the hydrogel. Surfaces were taken at a magnification of 500, and the scale bar was 6  $\mu\text{m}$



**Fig. 2.** Effect of crosslinker concentration on swelling capacity

### 2.3 Effect of crosslinker concentration

As mentioned in "Introduction" section, in order to the PVA hydrogel to be useful, it must be cross-linked. In the hydrogel synthesis, crosslinking agents prevent dissolution of the hydrogels. As shown in Scheme 1, glutaraldehyde acts as crosslinker. Fig. 2 shows the influence of the crosslinking agent on the swelling capacity of hydrogel. As indicated in Fig. 2, higher crosslinker concentration decreases the space between the copolymer chains and, consequently, the resulted highly crosslinked rigid structure cannot be expanded and it holds a large quantity of water.

### 2.4 Effect of PVA concentration

The swelling dependency of the hydrogels on PVA amount is shown in Fig. 3. Maximum swelling capacity (187 g/g) has been observed at 2.4 wt% of PVA, while other factors were kept constant. Swelling of hydrogel is considerably increased with the increase of PVA value from 1.2 to 2.4 wt%. This behavior is attributed to the availability of more sites for crosslinking. However, upon further increase in the substrate concentration, increase in the reaction medium viscosity restricts the movements of PVA chains, thereby decreasing the absorbency.

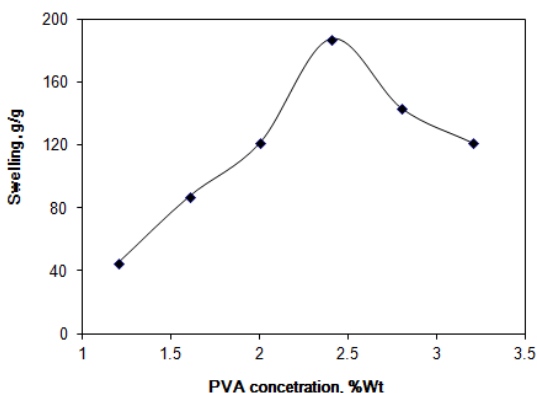


Fig. 3. Effect of PVA content on swelling capacity

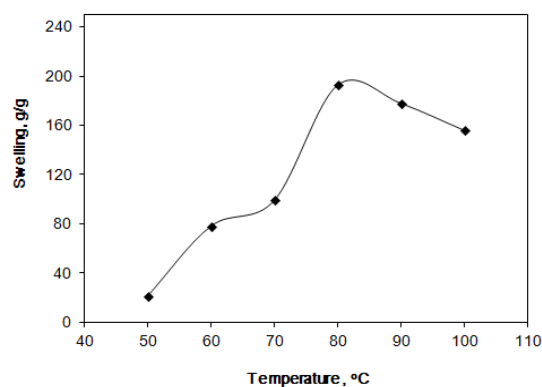


Fig. 4. Effect of reaction temperature on swelling capacity

### 2.4 Effect of the reaction bath temperature

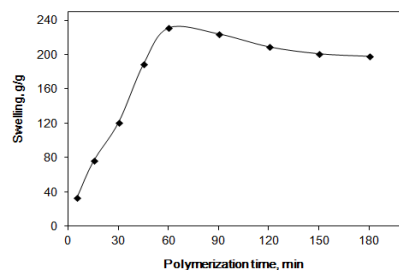
In this series of experiments, the swelling ratio as a function of the reaction temperature was studied by varying the temperature of the water bath from 50 to 100°C (Fig. 4). Increase in swelling values with increasing the temperature up to 80°C can be attributed to the rising of the rate of diffusion of glutaraldehyde into PVA backbones. At the temperatures higher than 80°C, however, a possible "thermal crosslinking" of the PVA backbones may play a major role in leading low-swelling hydrogels. In addition, the swelling loss may be related to an increase of crosslinking extent via completion of the di-acetal formation by further reaction of the possible mono-acetal species with another PVA chain (Scheme 1).

### 2.5 Effect of reaction time

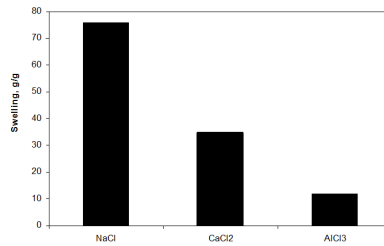
Fig. 5 demonstrates the swelling variations as a function of time of the crosslinking reaction. Swelling capacity is gradually increased up to 1 h. Meanwhile, the swelling capacity of the hydrogel synthesized after 1 h (i.e. 231g/g) is appreciably decreased to 20-30g/g in longer reaction time due to enhancement of the crosslinking extent. No remarkable change of water absorbency was observed in the case of longer time of the reaction.

## 2.6 Swelling in Various Salt Solutions

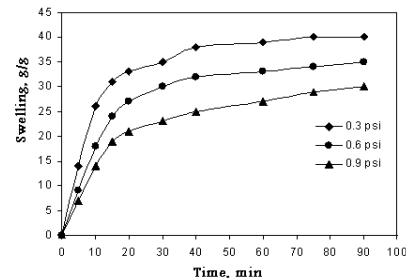
Swelling capacity in salt solutions has prime significance in many practical applications such as water release systems in agriculture. In the present study, swelling capacity was studied in 0.15M various chloride salt solutions (Fig. 6). As shown in the Fig. 6, the swelling ability of hydrogels in various salt solutions is decreased compared to the maximum swelling values in distilled water (231 g/g).



**Fig. 5.** Effect of reaction time on swelling capacity



**Fig. 6.** Swelling capacity of the optimized hydrogel in different chloride salt solutions (0.15 M)



**Fig. 7.** The AUL of the optimized hydrogel in various loading

## 2.7 Absorbency Under Load

In general, in order to investigate the gel strength of hydrogels the Absorbency Under Load (AUL) of them was measured. Load-free absorbency usually given in the basic scientific literature and AUL value is a parameter often reported in the technical data sheets and patent articles. Thus, the study of this parameter is of great significance from industrial point of view. The AUL of synthesized hydrogels in this paper in 0.15M NaCl solutions was shown in Fig. 7. This figure shows the AUL of PVA-based hydrogels under various pressures as the function of swelling time. As shown, the minimum time needed for the highest AUL in the case of each load was determined to be 40 minutes. After this time, the AUL values were unchanged. In addition, the final AUL values were decreased with the increase of loaded pressure.

## 3. Conclusions

In the present study, PVA superabsorbent hydrogel was synthesized in an aqueous solution using glutaraldehyde as a crosslinking agent. Swelling capacity of the synthesized hydrogels is affected by the crosslinker concentration. The swelling is decreased by increasing the glutaraldehyde concentration. The effects of PVA content, reaction time and temperature on swelling capacity were also investigated. Swelling measurement of the hydrogels in different salt solutions showed swelling loss in comparison with distilled water. This can be attributed to charge screening effect. Finally, the measurement of absorbency under load of the optimized hydrogels shows that the AUL values were diminished with increasing of loaded pressure.

## Experimental

### Instrumental Analysis

The surface morphology of the gel was examined using scanning electron microscopy (SEM). Dried superabsorbent powder was coated with a thin layer of palladium gold alloy and imaged in a SEM instrument (Leo, 1455 VP).

### Materials

Poly(vinyl alcohol) with molecular weight of 50000 was obtained from Aldrich, Milwaukee, WI, USA and used without further purification. Glutaraldehyde (from Merck) was of analytical grade and was used without further purification.

### Preparation of Hydrogel

Aqueous PVA solution was prepared by dissolving 3.0 g PVA powder in 30 ml deionized water and then heating it at 85 °C for 10 h. Glutaraldehyde with various concentrations as cross-linking agent was added to the resulting solution. After 60 min, the reaction product was allowed to cool to ambient temperature. The hydrogel was poured to exceed non-solvent ethanol (500 mL) and kept for 24 h to remove of absorbed water. Then ethanol was decanted and the product was scissored to small pieces. Again, 100 mL fresh ethanol was added and the hydrogel was stored for 24 h. Finally, the filtered hydrogel was dried in oven at 50°C for 10 h. After being ground by mortar, the powdered superabsorbent was stored by being protected protecting from moisture, heat and light.

### Swelling measurements using tea bag method

The tea bag (i.e. a 100 mesh nylon screen) containing an accurately weighed powdered sample ( $0.5 \pm 0.001$  g) with average particle sizes between 40–60 mesh (250-350  $\mu$ m) was immersed entirely in distilled water (200 mL) or desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excessive fluid. The equilibrated swelling (ES) was measured twice using the following equation:

$$ES(g/g) = \frac{\text{Weight of swollen gel} - \text{Weight of dried gel}}{\text{Weight of dried gel}} \quad (1)$$

The accuracy of the measurements was  $\pm 3\%$ .

### Absorbency under load (AUL)

AUL was measured using a piston assembly allowing the addition of weights on top of the superabsorbent sample.<sup>22</sup> A macro-porous sintered glass filter plate (d=80 mm, h=7 mm) was placed in a petri dish (d=118 mm, h=12 mm), and the weighted dried sample ( $0.5 \pm 0.01$ g) was uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid load (Teflon, d=60 mm, variable height) was put on the dry hydrogel particles while it could be freely slipped in a glass cylinder (d=60 mm, h=50 mm). Desired load (applied pressure 0.3, 0.6, and 0.9 psi) was placed on the hydrogel sample. Then 0.9% saline solution was added so that the liquid level was equal to the height of the sintered glass filter. Whole of the set was covered to prevent surface evaporation and probable change in the saline concentration. After 60 min, the swollen particles were weighted again, and AUL was calculated according to Eq. (1).

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