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Preparation of poly(vinyl alcohol) hydrogels with radiation grafted citric and succinic acid groups

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Abstract

Ternary mixtures of PVA/Citric acid (CA)/water and PVA/Succinic acid (SA)/water were gamma irradiated to various doses in air at ambient temperature. Gelation % vs dose curves were constructed and swelling behavior of gels with maximum conversions was studied. In maximum gelled systems 80% of CA used in the feed composition was retained in the gel structure whereas this was only 20% for SA. The volume of swelling of ionic PVA gels increased from 230% to 530% for PVA/CA systems when pH was increased from 2.6 to 7.5. Less significant increase in swelling was observed for PVA/SA gels, from 250% to 330% in the same pH interval. The incorporation of SA and CA groups onto PVA networks improved remarkably the affinity of these structures for Co^{2+} and Ni^{2+} ion uptake.

Keywords: Hydrogel; Poly(vinyl alcohol); Radiation grafting; Citric acid; Succinic acid

1. Introduction

Poly(vinyl alcohol) has been frequently used in the preparation of various membranes and hydrogels (Burczak et al., 1994; Hirai et al., 1996). Being a non-ionic polymer however, it is not possible to use it when some stimuli-responsive properties are sought. In this study to impart pH sensitivity of poly(vinyl alcohol)(PVA) hydrogels, citric (CA) and succinic acid (SA) were grafted on to PVA polymer by irradiation. The swelling behavior of pure PVA, PVA/CA and PVA/SA hydrogel systems in pure water and different pH buffer solutions were investigated. The affinity of grafted hydrogels for the adsorption of Ni^{2+} and Co^{2+} ions were also studied.

2. Experimental

For the preparation of water swellable crosslinked PVA hydrogels, 6 g PVA (Merck, 72000) was dissolved in 94 ml distilled water and placed into PVC straws. For the preparation of CA and SA containing PVA hydrogels 0.2 g acid was dissolved in the 6% (w/w) PVA solutions and then placed into the PVC straws. Before the irradiation they were degassed in an ultrasonic bath. They were irradiated in air at ambient temperature in a ^{60}Co Gamma Cell at a dose rate of 4.2 kGy/h to different doses. The long cylindrical hydrogels obtained were cut into pieces of 1–2 mm in length. They were washed several times with distilled water to remove the unreacted species and dried in air then in vacuum oven.

The percent gelation was calculated by the following equation.

$$\text{Gelation}\% = \frac{w}{w_0} \times 100\% \quad (1)$$

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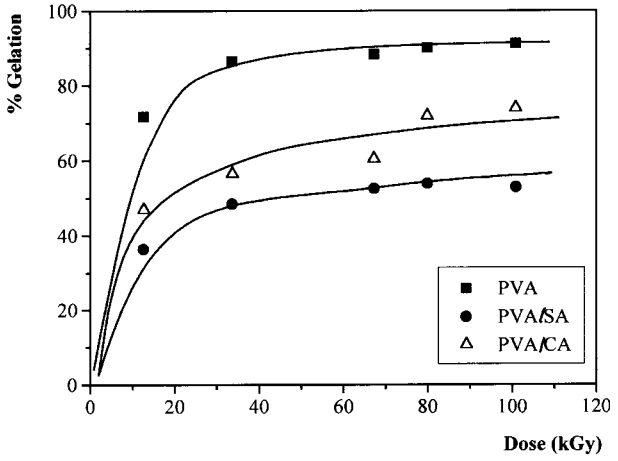


Fig. 1. Gelation % of PVA, PVA/CA and PVA/SA.

where w_0 and w represent the air dried and solubles extracted mass.

The CA and SA content in the hydrogels were determined both spectrophotometrically and titration using 0.01 mol dm^{-3} standard NaOH solution.

Nicolet 520 FT–IR spectrophotometer was used for the spectroscopic characterization of gel systems.

The dry hydrogels were weighed and transferred into water. Water uptake with respect to time was obtained by periodically removing samples from water, surface drying and reweighing at room temperature. Phosphate buffer solutions were used for measurements at different pHs. The following equation was used to calculate the percent of swelling:

$$\text{Swelling}\% = \frac{w_t - w_0}{w_0} \times 100\% \quad (2)$$

Here w_o is the mass of the dry gel before swelling and w_t is the mass after swelling to time t.

3. Results and discussions

Gelation % versus dose curves were calculated by using Eq. (1). Fig. 1 shows the gelation % of PVA, PVA/CA and PVA/SA gel systems. As it can be seen from Fig. 1 the gelation reaches a plato at about 80 kGy dose.

The results of the UV spectrophotometric analysis and titration showed that the citric acid content in the gel system is higher than the succinic acid content. The reason of this observation is assumed to be due to the fact that citric acid can easily release OH group upon irradiation in aqueous solutions and be grafted onto PVA backbone. But radical formation and subsequent grafting are less favorable for succinic acid.

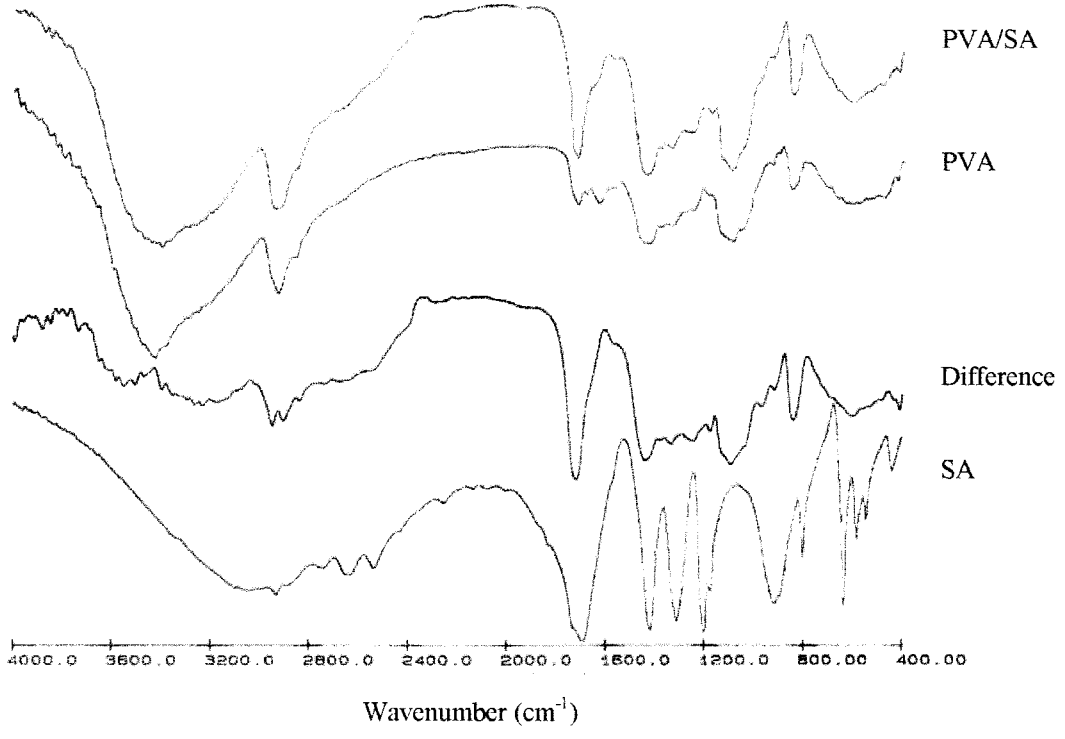
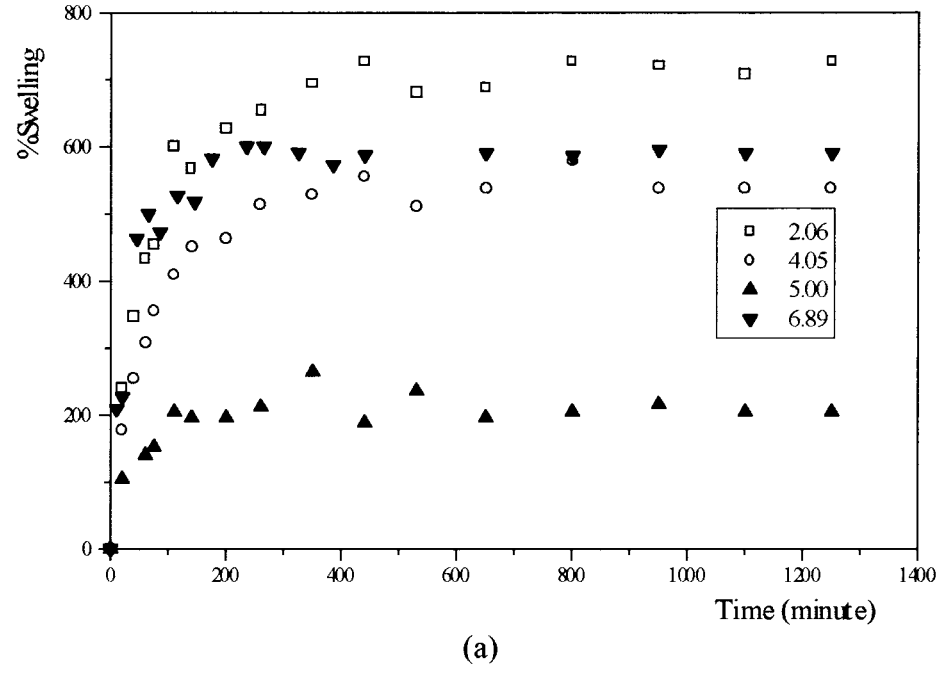


Fig. 2. FT–IR spectra of PVA/SA hydrogels.



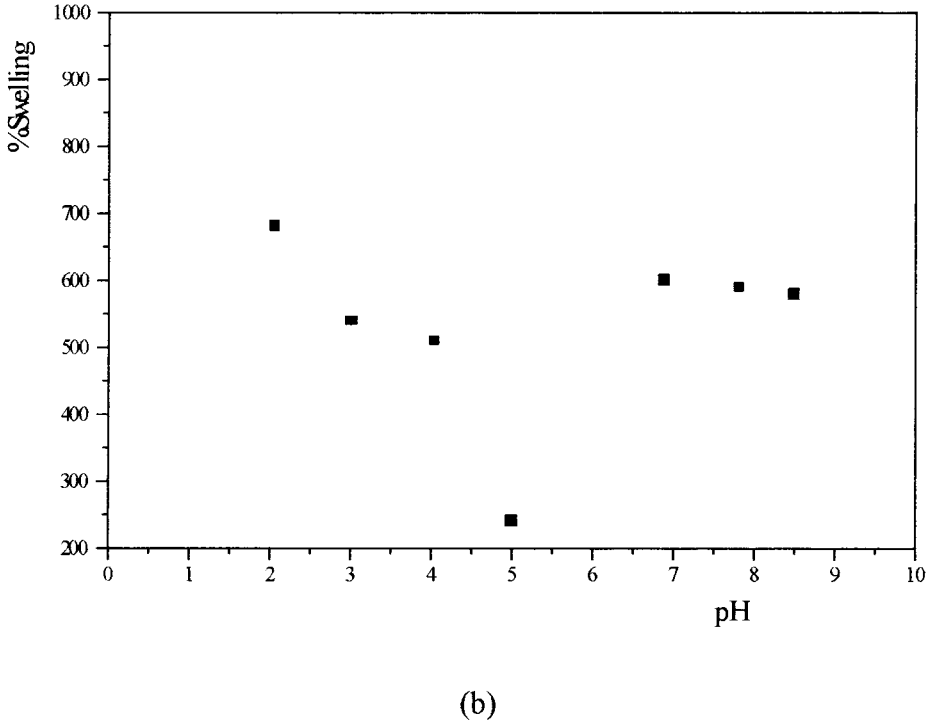


Fig. 3. (a) Swelling curves of PVA hydrogels at different pHs. (b) Maximum swelling of PVA hydrogels at different pHs.

Table 1
The equilibrium swelling values of hydrogels first kept at pH = 2.06 then swollen at different pHs at room temperature, swelling of unreacted gels are given in parentheses

Gel system	pH = 2.06	pH = 3.01	pH = 4.05	pH = 5.00	pH = 6.01	pH = 6.89	pH = 7.88	pH = 8.56
PVA	121(680)	55(540)	88(510)	67(240)	62(500)	96(600)	107(590)	168(580)
PVA/CA	70(725)	72(690)	54(560)	54(285)	86(475)	88(625)	105(550)	88(510)
PVA/SA	68(840)	22(1080)	79(950)	35(400)	44(730)	43(466)	45(700)	56(462)

Table 2
The equilibrium swelling values of PVA hydrogels first kept at pH = 5.00 then swollen at different pHs at room temperature

Gel system	pH = 2.06	pH = 3.01	pH = 4.05	pH = 5.00	pH = 6.01	pH = 6.89	pH = 7.88	pH = 8.56
PVA	400	546	221	117	313	525	525	385

Table 3
The equilibrium swelling values of hydrogels first kept at pH = 2.06 then swollen at different pHs at 50°C

Gel system	pH = 2.06	pH = 3.01	pH = 5.00	pH = 6.01	pH = 6.89
PVA	117	131	140	192	213
PVA/CA	113	130	218	177	162
PVA/SA	126	150	163	214	214

The FT–IR spectra of PVA and SA grafted PVA hydrogels are given in Fig. 2. The absorption band at 1700 cm^{-1} due to C═O groups shows that SA was grafted on to PVA backbone. Similar results, not shown here, were obtained for CA grafted PVA hydrogels too.

As it can be seen from Fig. 3 the maximum swelling values for PVA/CA (or PVA/SA) hydrogel systems decreased with the increasing pH in the acidic region. But an increase was observed after pH = 5.00 in the alkaline region. This behavior is not characteristic for pure PVA that is known as a non-ionic polymer (Miller and Peppas, 1988). However, the PVA polymer used in this study contains 3% (w/w) non-hydrolized acetate groups. It was assumed that protonation of these acetate groups at low pH values caused an increase in the swelling values because of the newly formed carboxylic groups. At high pH these acid groups complete their ionization so an increase in the swelling value was observed. To investigate the formation of these groups and its effect on the swelling behavior, three gel systems were first kept in pH = 2.06 solution and then swollen at different pHs. Table 1 shows the maximum swelling values obtained from these experiments. Generally a decrease was observed in the equilibrium swelling values. The reason of this decrease was thought to be due to the formation of H-bonding between the carboxylic and OH groups. The FT–IR spectra of soluble PVA kept at pH = 6.89, 5.00, 4.05 and 2.06 were taken and it has been seen from these figures that the band at 1637 cm^{-1} shows the formation of carboxylic groups. Table 2 shows the results of swelling experiments for PVA gels kept at pH = 5.00. According to these results, the formation of carboxylic groups was less at pH = 5.00 and 6.89 and the maximum swelling values were higher than those at pH = 2.06.

In order to increase the swelling of the gels the three gels systems were first kept at pH = 2.06 at room temperature and then swollen at different pH solutions at 50°C. Table 3 shows the equilibrium swelling values. As it can be seen from these values an increase was observed in the maximum swelling that must be due to the cleavage of hydrogen bonds at higher temperature.

The PVA, PVA/CA and PVA/SA gel systems were tested in the metal ion adsorption experiments. Table 4

Table 4
Adsorption of metal ions onto gel systems (mg/g dry gel)

Gel system	Co^{2+}	Ni^{2+}
PVA	82	–
PVA/SA	77	410
PVA/CA	105	792

shows the adsorption results at pH = 6.00 which corresponds to completely ionized forms of CA and SA. Incorporation of citric acid and succinic acids imparts metal ion adsorption affinity into these gels. Citric acid seem to be more efficient for the uptake of ions, and the uptake of Ni^{2+} ions is higher than that of the Co^{2+} ions. Further work is in progress to elaborate this issue.

The incorporation of SA and CA onto PVA networks improved remarkably the affinity of these structures for the uptake of Co^{2+} and Ni^{2+} ions. Very high adsorption capacities were determined especially for CA containing systems.

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