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Synthesis of radiation crosslinked poly(acrylic acid) in the presence of phenyltriethoxysilane

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HIGHLIGHTS

- Phenyltriethoxysilane (PTES) has been used to crosslink poly(acrylic acid).
- Radiation crosslinking of poly(acrylic acid) in the presence of PTES has been studied.
- The synthesized hydrogel showed switchable swelling response against pH changes.
- Highest swelling of 247 g/g is achieved at neutral pH.

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ABSTRACT

Acrylic acid based superabsorbent hydrogel was prepared using phenyltriethoxysilane (PTES) as polyfunctional monomer. Different amounts of PTES were incorporated in acrylic acid and irradiated at different doses upto maximum of 30 kGy. The crosslinked acrylic acid showed hydrogel properties and its swelling kinetics, gel fraction and equilibrium degree of swelling (EDS) were studied. It was found that the increased PTES concentration decreased the EDS of the hydrogels. Infrared spectroscopy confirmed the crosslinking reaction between the feed components and the existence of siloxane bond. Thermogravimetric analysis showed an increase in the stability of the hydrogels having high PTES content. The swelling of the hydrogel was affected by pH, ionic strength and temperature. These hydrogels showed low swelling in acidic and basic pH range and high swelling around neutral pH. This switchable pH response of these hydrogels can be exploited in environmental and biomedical applications.

1. Introduction

Crosslinking of polymer either by physical or chemical process is very useful method to fix the conformational geometry of the polymer chains (Rosiak and Ulanski, 1999). The crosslinked hydrophilic monomers or polymers showed hydrogel properties. The three dimensional network of the hydrogel retains significant amount of water and also freely exchange it with the external media (Bhat, 2002; Francis et al., 2004). These hydrogels are being used in drug delivery (Ratner and Hoffman, 1976), agriculture (Chanda and Rempel, 1997) and environmental applications (Saglam et al., 2001). The swelling response of hydrogel against different external media such as: pH value, polarity of the solvent, ionic strength and temperature can be controlled by varying the chemical composition of reactant and degree of crosslinking (Hariharan and Peppas, 1993).

Poly(acrylic acid) (PAA) is a versatile synthetic polymer which is used in many commercial applications (Chanda and Rempel, 1997; Saglam et al., 2001). The crosslinked PAA hydrogel showed pH sensitivity and mucoadhesive properties. Generally, the high water solubility of PAA in aqueous medium is resulted the breakdown of the gel structure. Therefore, there is need to find out some other crosslinking agents or methods to obtain stable PAA gel. Jabbari and Nozari synthesized radiation crosslinked PAA and studied the swelling behavior as a function of concentration of PAA in aqueous solution during γ-irradiation and dose. The degree of swelling of crosslinked PAA at pH 4 is ranged from 30 to 300 for doses ranging from 5 to 25 kGy (Jabbari and Nozari, 2000). Ali and Hegazy prepared pH-sensitive hydrogel from poly(ethylene glycol) and acrylic acid using γ-radiation-induced copolymerization and crosslinking. The swelling response of this hydrogel is Fickian diffusion at pH 1 and changed to non-Fickian diffusion at pH 7 (Ali and Hegazy, 2007). Carbopol and polycarbophil are the commercially available crosslinked PAA based products (Chu and Liu, 2008).

The objective of the present study is to prepare radiation crosslinked PAA hydrogel with good stability and pH sensitivity. PTES is selected as polyfunctional monomer (PFM) for the first

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time to crosslink acrylic acid. In acrylic acid, PTES reacted in two steps, utilizing ionizing radiation in the first step and radiation generates free radicals on PTES which then incorporated in to the growing polymer chain. In the second step, the silanol groups of PTES reacted with each other by condensation and formed cross-linking network.

2. Materials and methods

2.1. Materials

Acrylic acid, PTES, sodium hydroxide, hydrochloric acid, potassium chloride, acetic acid and sodium acetate were purchased from Sigma-Aldrich. All others chemicals were of analytical grade.

2.2. Synthesis of hydrogels

Acrylic acid was first neutralized with NaOH upto 75%. The 100 mL of acrylic acid was taken into the flasks and appropriate amount of PTES was added slowly. The samples were irradiated under Co-60 gamma source at a dose rate of 1.05 kGy/h. After irradiation, the resultant hydrogel was washed and dried. The compositions and codes of synthesized hydrogels are shown in Table 1.

2.3. Infrared spectroscopy

Infrared spectra were recorded using Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700) purchased from Thermo Electron Corporation, USA. The FTIR was used in ATR mode and diamond crystal was used in ATR assembly. Before analysis, the samples were washed with excess of distilled water and dried under vacuum. The spectra were scanned from 4000 to 500 cm^{-1} at 4 cm^{-1} resolution and averages of 200 scans were reported.

2.4. Thermogravimetric analysis

The thermal behavior of the samples was studied using TGA from Mettler Toledo, (model: TGA/SDTAEN55011) under nitrogen atmosphere (50 mL/min). The sample (3–5 mg) was heated at a rate of 20 °C/min from 30 to 600 °C.

2.5. Gel content

The dried hydrogel samples were extracted with water for 8 h using soxhlet apparatus. After extraction, samples were dried at room temperature and then in vacuum oven at 100 °C until the weight became constant. The gel content was determined from the following equation:

$$\text{Gel content } (\%) = (W_f/W_i) \times 100 \quad (1)$$

here 'W_i' is the initial weight of dried gel and 'W_f' is the weight after extraction.

Table 1
Composition and codes of formulations.

Code	AA40/15	AA60/15	AA80/15	AA40/30	AA60/30	AA80/30
Dose (kGy)	15	15	15	30	30	30
PTES amount [a]	0.83	1.25	1.65	0.83	1.25	1.65

[a] μmol/100 mL of acrylic acid.

2.6. Swelling studies

2.6.1. Swelling in water

The swelling response of crosslinked acrylic acid was studied under different conditions. Sample (50 mg) of uniform size was placed in a beaker filled with distilled water (100 mL) at given temperature. At fixed time intervals, the weight of the swollen sample was determined after removing the excess of surface water. After weighing, the sample was placed again in the same solution and weight again. The swelling of the sample was determined gravimetrically by using the following equation

$$\text{Swelling} = (W_s - W_i)/W_i \quad (2)$$

here, 'W_i' is the initial weight of the sample and 'W_s' is the swollen weight of the sample after time 't'.

2.6.2. Swelling in non-buffer, buffer and salt solutions

The swelling response of hydrogels against pH was studied in non-buffer and buffer solutions. Non-buffer solutions were prepared from the dilution of the stock solution of HCl (0.1 M) and NaOH (0.1 M). Buffer solutions were prepared using standard method and the pH values were rechecked by pH meter. Hydrogels response against different salts concentration was investigated. Sodium chloride (NaCl) and barium chloride ($BaCl_2$) were selected for this study.

3. Results and discussion

Radiation technology has been effectively used to prepare hydrogel by crosslinking hydrophilic monomer. The properties of these hydrogels can be controlled by changing the dose which influences the structure and crosslinking density of final product (Nagasawa et al., 2004).

3.1. Infrared spectroscopy

The FTIR spectra of the crosslinked hydrogels are shown in Fig. 1. The spectra of crosslinked hydrogels show a very intense broad absorption band centered at 3330 cm^{-1} is due to the associated OH groups. Highest intensity of this band is observed in AA80/15 containing higher amount of PTES, which might be due to the presence of high concentration of Si–OH groups. Three bands at 2949, 2922 and 2841 cm^{-1} are due to different CH stretching bands present in the sample. The 1695 cm^{-1} band of acrylic acid (AA) representing the C=O stretching is reduced and shifted to 1712 cm^{-1}. The intensity of C–O stretching vibration of

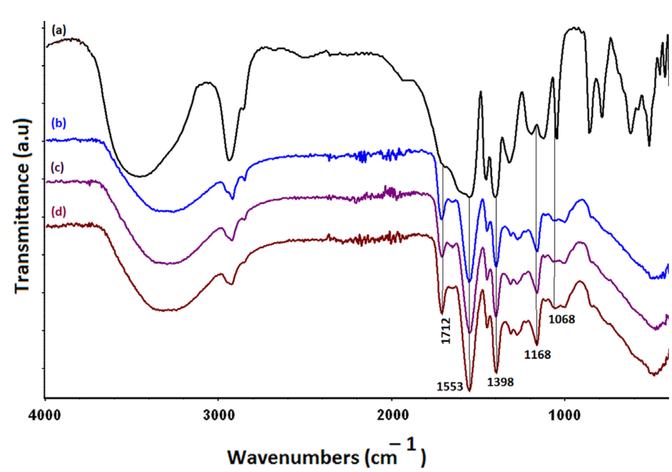

Fig. 1. FTIR spectra of (a) poly(acrylic acid) and hydrogels, (b) AA40/15, (c) AA60/15, (d) AA80/15.