Carbohydrate Polymers 79 (2010) 933–940

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Synthesis and swelling behavior of acrylatedstarch-g-poly (acrylic acid) and acrylatedstarch-g-poly (acrylamide) hydrogels

A. Pourjavadi [a,*], P. Eftekhar Jahromi [a], F. Seidi [a], H. Salimi [b]

[a] *Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, Tehran, Iran*
[b] *Iran Polymer and Petrochemical Institute, Tehran, Iran*

ARTICLE INFO

Article history:
Received 25 April 2009
Received in revised form 12 August 2009
Accepted 12 October 2009
Available online 20 November 2009

Keywords:
Hydrogel
Acrylatedstarch
Swelling behavior
Acrylic acid (AA)
Acrylamide (AAm)

ABSTRACT

In the present work, synthesis and swellability of acrylatedstarch-based hydrogels was investigated. Acrylic groups were introduced onto starch backbone by a homogeneous synthesis to produce starch monomers with three different degree of substitution (DS). The radical copolymerization of acrylatedstarch (AST) with acrylic acid (AA) and acrylamide (AAm) was carried out in aqueous solution using ammonium persulfate (APS) as an initiator. Infrared spectroscopy (FT-IR) and TGA thermal analysis were carried out to confirm the chemical structure of the hydrogel. Moreover, morphology of the samples was examined by scanning electron microscopy (SEM). Their equilibrium swelling degree was evaluated in various conditions. The absorbency under load (AUL) of the hydrogel was also determined by using an AUL tester at various applied pressures. Finally, dynamic swelling kinetics of the hydrogel was studied.

1. Introduction

Covalent (or chemical) polymer networks are three-dimensional polymers in which the polymer chains are interconnected by chemical crosslinks (Flory, 1953; Yoshihito & Khokhlov, 2005). These networks are composed of homopolymers or copolymers and are insoluble in all solvents, but, depending on their compatibility with the solvent, they can absorb and hold a considerable volume of liquids. The most common hydrogels are polyelectrolyte gels: their high degree of swelling in water is due to the exerting osmotic pressure of counterions. Such gels can acquire up to several hundredweight parts of water per one part of a dry polymer. However, some neutral gels—e.g., based on polyacrylamide or poly(ethylene oxide)—also have high affinity to water, but their degree of swelling is always much lower than that of charged gels (Bajpai & Giri, 2003; Branca et al., 2006).

Hydrogels are used extensively as superabsorbents. For this application high swelling capacity is the most important property. However, there are a number of other areas of use for hydrogels as functional materials (e.g., carriers for controlled drug release (Peppas, Bures, Leobandung, & Ichikawa, 2000), artificial muscles (Lee & Mooney, 2001), membranes with regulated permeability (Dole, Joly, Espuche, Alric, & Gontard, 2004), and sensor devices (Yew, Ng, Li, & Lam, 2007)). For these purposes, high cooperativity of response to the change in external conditions and developed internal microstructure of the gels is required. Therefore, in addition to high swelling capacity, it is necessary to have a counteracting tendency, which favors the gel contraction.

Another important property of hydrogels is their response to external stimuli such as temperature, pH, presence of solutes, electric and magnetic fields, resulting in the absorption or release of water and solutes (Peppas et al., 2000; El-Naggar, Abd Alla, & Said 2006). Usually, these hydrogels are prepared by free-radical copolymerization of the acidic or basic monomers and a chemical crosslinker such as *N,N′*-methylenebis(acrylamide) (Omidian, Rocca, & Park 2005).

Because of the wide range of unique combinations of polymer backbone and crosslinking agent, properties such as hydrogel swelling/degradation, mechanical strength and swelling kinetics are interrelated in a complex and dynamic fashion. However, these characteristics could potentially be tailored to meet a specific biomedical application by modulating hydrogel compositions.

Biodegradable polymers are the youngest members of the materials family with increasing applications in pharmaceutical, medical and biomedical engineering (Bernkop-Schnurch & Kast, 2001; Jayakumar, New, Tokura, & Tamura, 2007; Vandamme, Lenourry, Charrueau, & Chanumeil, 2002). Starch is the main reserve polysaccharide of higher plants where it occurs as water insoluble granules. Starch is readily isolated from plant crops, and major commercial sources include maize, wheat, potato, and rice. The isolated starch finds a very wide range of commercial application, including use in the food, pharmaceutical, paper and packaging industries (Dumitriu, 2005).

---

* Corresponding author.
E-mail addresses: purjavad@sharif.edu, kachal.vay@gmail.com (A. Pourjavadi).

0144-8617/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2009.10.021

The present study reports on (i) the synthesis and characterization of acrylated starch (AST) with three different DS; (ii) the synthesis and characterization of AST-based hydrogels, carried out by radical graft copolymerization of AST with acrylic acid (AA) and acrylamide (AAm); (iii) investigation of swelling properties of the hydrogels in various conditions. As a matter of fact, according to the literature survey based on Chemical Abstract Service, there are some reports on synthesis of acrylate substituted starches itself without any crosslinking. Moreover, there are some reports on preparation of novel acrylate substituted starch-based hydrogels with different crosslinking systems. In the present study, we synthesize novel hydrogels with new type of crosslinking, and investigate their swelling behaviors in various media. According to the basic knowledge of SAP hydrogels (Buchholz & Graham, 1998), "small amounts of crosslinkers play a major role in modifying the properties of SAPs". Recently, some research groups have taken into consideration to study of the chemical nature of crosslinker (Kabiri, Mirzadeh, & Zohuriaan-Mehr, 2008; Metz & Theato, 2009; Ramazani-Harandi, Zohuriaan-Mehr, Yousefi, Ershad-Langroudi, & Kabiri, 2009) and showed that it has a great influence on key parameters such as absorbency under load (Ramazani-Harandi et al., 2009), and also temperature and time of the hydrogel drying (Kabiri et al., 2008).

In conclusion, crosslinker type and concentration has a great influence on the physical properties of SAPs. Therefore, new types of crosslinkage should be investigated systematically to achieve hydrogels with improved properties. This new practical research represents deeper physicochemical studies on the structure–property relation in SAP hydrogels.

2. Experimental

2.1. Materials

Acrylic acid (AA, from Merck) as ionic monomer distilled before use. Starch (ST) was obtained from Merck Chemical. Ammonium persulfate (APS, from Merck) as a water soluble initiator, acrylamide (AAm, from Merk), acryloyl chloride (from Merk) were of analytical grade and used without further purification. The solvents (all from Merck) were used as received. All other chemicals were also analytical grades. Double distilled water was used for the hydrogel preparation and swelling measurements.

2.2. Instrumental analysis

^{1}H-NMR spectra were obtained using a Bruker DPX 500 MHz spectrometer with D_2O as solvents. The extent of the esterification was determined from the ^{1}H-NMR.

Thermogravimetric analyses (TGA) of synthesized hydrogels were performed using Polymer Laboratories systems at a heating rate of 20 °C/min under nitrogen atmosphere.

FTIR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer. Morphology of the dried gel structures was studied by scanning electron microscopy (SEM). Dried superabsorbent powder was coated with a thin layer of gold and was imaged in a SEM instrument (Philips, XL30).

2.3. Acryloyloxystarch (AST) Synthesis

Twenty grams of dried starch was dissolved in 75 mL dimethyl sulfoxide (DMSO) in 100 °C. After cooling to room temperature 20 mL *N*,*N*-dimethylformamide (DMF) and an appropriate amount (1–2.6 mL) of pyridine were added. Then the reaction medium cooled to 0 °C and a suitable amount (1–2.6 mL) of ACOCl diluted in 5 mL DMF was added dropwise to the reaction medium under stirring. After addition was completed, the derivatization reaction developed 2 h in 0 °C and 3 h in room temperature. The product was precipitated and washed thoroughly by acetone, and then dried in air at r.t. The DS was determined by the ^{1}H–NMR spectroscopy.

2.4. Hydrogels synthesis

(a) With acrylic acid (AA):

A 200-mL, three-necked, round-bottomed flask, equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 200 rpm) is charged with 40 mL of water and 1.4 g of AST and the mixture is stirred for 10 min at r.t. until a clear solution is obtained. The reactor was immersed in a thermostated water bath preset at 75 °C. Then, 40% neutralized acrylic acid (AA, 5.0 g) dissolved in 10 mL H_2O was added. After 5 min, ammonium persulfate (APS, 0.07 g) in 5 mL H_2O was added. After 10–15 min obtained gel was cooled at room temperature and poured to excess non-solvent acetone (200 mL) and remained for 3 h to dewater. Then, acetone was decanted and the product was cut into small pieces (diameter ~5 mm). Again, 200 mL fresh acetone was added and the hydrogel remained for 48 h. Finally, the filtered gel was dried in oven at room temperature for 48 h. After grinding, the powdered hydrogel was stored away from moisture, heat and light.

(b) With acrylamide (AAm):

It is similar to the method mentioned above; just the amount of AST is 1 g, the amount of AAm is 3 g and APS is 0.05 g.

2.5. Measurement of monomer conversion

To determine monomer conversion values, a weighed, dried, and powdered sample was washed with non-solvent methanol several times. After filtration, the sample was dried, and reweighed. Monomer conversion was calculated by following equations:

(a) AAm-based hydrogel: monomer conversion $\% = \left(\frac{m_f - 1}{3}\right) \times 100$,

(b) AA-based hydrogel: monomer conversion $\% = \left(\frac{m_f - 1.4}{5.6}\right) \times 100$,

where m_f stands for final weight of sample after several washing. 1 and 1.4 values are related to weights of AST were used. 3 and 5.6 values are related to amounts of acryl amide and total weights of acrylic acid and sodium acrylate, respectively.

The results are as follows:

Sample	Monomer conversion %
AST-g-poly (AA) (DS = 0.08)	82
AST-g-poly (AA) (DS = 0.15)	80
AST-g-poly (AA) (DS = 0.24)	79
AST-g-poly (AAm) (DS = 0.08)	94.66
AST-g-poly (AAm) (DS = 0.15)	95.3
AST-g-poly (AAm) (DS = 0.24)	93

2.6. Swelling measurements

The tea bag (i.e. a 100 mesh nylon screen) containing an accurately weighed powdered sample (0.1 ± 0.001 g) was immersed entirely in 200 ml distilled water or 0.15 M of NaCl solution and allowed to soak for 1 h at room temperature. The sample particle sizes were 40–60 meshes (250–400 µm). The tea bag was hung up for 15 min in order to remove the excess water. The equilibrium swelling (ES) was calculated according to following equation:

$$ES\left(\frac{g}{g}\right) = \frac{W_2 - W_1}{W_1} \qquad (1)$$

where W_1 and W_2 are the weights of dry and swollen gel, respectively.