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Synthesis of biosuperabsorbent hydrogel based on Acrylonitrile-Sucrose and investigation pH and Salinity properties

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ABSTRACT

In the present paper, attention is paid to synthesis and investigates swelling behavior of a superabsorbent hydrogel based on sucrose and polyacrylonitrile (PAN). The physical mixture of sucrose and PAN was hydrolyzed by NaOH solution to yield sucrose-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel. The nitrile groups of PAN were completely converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis followed by in situ crosslinking of the PAN chains by the alkoxide ions of sucrose. A proposed mechanism for hydrogel formation was suggested. Absorbency of the synthesized hydrogels was also measured in various salt solutions. In addition, swelling capacity was conducted in solutions with pH ranged from 1 to 13.

Key words: sucrose; polyacrylonitrile; hydrogel; superabsorbent; swelling behavior.

Introduction

Loosely crosslinked hydrophilic polymers (hydrogels) being able to absorb and retain hundreds of their own weight of water are known as superabsorbents [1]. The swelling properties of these hydrogels have attracted the attention of researchers and technologists, and have found wide-spread applications in drug delivery systems, agriculture, separation processes and many other fields [2-5].

The modification of natural polymers is a promising method for the preparation of new materials. Graft copolymerization of vinyl monomers onto natural polymers is an efficient approach to achieve these materials. Superabsorbing resins were first developed with a view to utilizing agricultural materials, and are typed by the hydrolyzed corn starch-*g*-poly(acrylonitrile), H-SPAN [6]. Since then, starches from different resources as well as other polysaccharides, for example, cellulose [7,8], hydroxyethyl cellulose [9,10], agar [11], sodium alginate [12,13] and guar gum [14] were graft copolymerized to achieve water absorbing polymers. Polyacrylonitrile (PAN), polyacryamide, and poly(acrylic acid) [15] have been frequently grafted, mostly onto starch, using different initiators especially the ceric-saccharide redox system [16]. Radical polymerization, however, has several disadvantages. The reproducibility of this method is poor, and there is little control over the grafting process, so the molecular weight distribution is polydisperse. In addition, the necessity for inert gases (e.g., argon) to prepare an oxygen-free atmosphere and the need for initiators, toxic and/or expensive monomers, and crosslinkers are other disadvantages of free-radical polymerization reactions. These problems have been reviewed in detail [17]. For the first time, Fanta *et al*. [18], with a new method, tried to synthesize of HSPAN superabsorbent hydrogel. They indicated by a solubility test that crosslinks were formed during graft copolymerization, by coupling of the two growing PAN radicals, and during saponification, by the attack of starch alkoxide ions on the nitrile groups as the initioation reaction of nitrile polymerization in the early stages of saponification. The nitrile groups of PAN were converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis followed by *in situ* crosslinking of the grafted PAN chains. The initially formed oxygen–carbon bonds between the starch hydroxyls and nitrile groups of the PAN chains remained crosslinking sites. Then, Fanta and Doane [19] attempted to extend this idea to the preparation of superabsorbent hydrogels by the saponification of PAN in the presence of polyhydroxy polymers.

To the best of our knowledge, based on a precise survey of the Chemical Abstracts, there is no published report on the synthesis of a superabsorbing hydrogel via alkaline hydrolysis of sucrose-

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polyacrylonitrile physical mixture. Hence, the objectives of this study were to synthesize of a superabsorbent hydrogel made of sucrose and polyacrylonitrile.

Experimental:

Materials:

The disaccharide sucrose was purchased from Merck Chemical Co. (Germany). Polyacrylonitrile was synthesized through a method mentioned in the literature [22]. The drug, verapamil hydrochloride, was received from Aldrich Chemical Co. Double distilled water was used for the hydrogel preparation and swelling measurements.

Preparation of Hydrogel:

A general one step preparative method for synthesis of sucrose-based hydrogel was conducted as follows. Sucrose (0.25–1.50 g) and 35 mL doubly distilled water were added to a three necked reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm). The reactor was immersed in a thermostated water bath. After complete dissolution of sucrose to form a homogeneous solution, required amount of sodium hydroxide (1.0–15.0 wt %) was added to the sucrose solution at desired temperature (60^{o}C). The mixture was stirred for a certain time period (30 min). Different hydrogels were prepared by varying the amount of PAN (0.25–1.50 g) dispersed in the reaction mixture to saponify for 100 min at 80^{o}C. During saponification, NH_3 gas was evolved and the color changed from red to light yellow. This discoloration was an indication of the reaction completion. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8.0 by addition of 10 wt % aqueous acetic acid solution. Then the gelled product was cut to small pieces and put in methanol (200 mL) for 5 h to remove water. The hardened particles were filtered and dried in oven (50^{o}C, 10 h). After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat, and light.

Swelling behaviour of hydrogels:

The swelling ratios of hydrogel samples were measured gravimetrically. Weights of swollen hydrogels were obtained after being wiped off the excess water on the surfaces with moistened filter paper. The average value of three measurements from three parallel specimens in the same hydrogel was taken for each sample.

The swelling ratios were measured by immersing hydrogel samples in water at room temperature for 2h. The swelling ratio S was calculated as follows:

$$S = \frac{W_t - W_d}{W_d} \quad (1)$$

For the equilibrium swelling ratio S_{eq}:

$$S_{eq} = \frac{W_e - W_d}{W_d} \quad (2)$$

where W_t, W_e are the weights of swollen hydrogels at a time interval t or at equilibrium state under a given condition, respectively; W_d is the dry weight of the hydrogel.

FTIR analysis:

FTIR spectra were measured using an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature in the range from 4000 to 500 cm^{-1}, with a resolution of 2 cm^{-1} and 20 scans. Samples were prepared by well dispersing the complexes in KBr and compressing the mixtures to form disks.

Morphological analysis:

Morphology is a critical factor to analyze final result. In this work, the morphology of the hydrogels was observed by a scanning electron microscope (SEM; Leo, 1455 VP) operating at an accelerating voltage of 20 kV. All samples were mounted on a copper stub and sputter-coated with gold to minimize charging.

Results and discussion

Mechanism of hydrogel formation:

Alkaline hydrolysis of the sucrose–PAN mixture was carried out using aqueous sodium hydroxide solution. A general reaction mechanism for sucrose-poly(NaAA-co-AAm) hydrogel formation is shown in Scheme 1. At the first step, the hydroxyl ions abstract hydrogen from the OH group of sucrose substrate to form corresponding alkoxide anions. Then, these macroalkoxides initiate crosslinking reaction between some adjacent PAN pendant chains. This reaction leads to intermediate formation of naphthyridine cyclic structures (including imine, C=N, conjugated bonds), with dark red color. The intermediate was then saponified using residual sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups. During the alkaline hydrolysis, ammonia was evolved and an orange-red color developed due to conjugated imine formation. This sharp color change was used as an indication to stop the alkaline treatment. As shown in Scheme 1, crosslinking reaction also occurred between some nitrile groups of adjacent PAN pendant.

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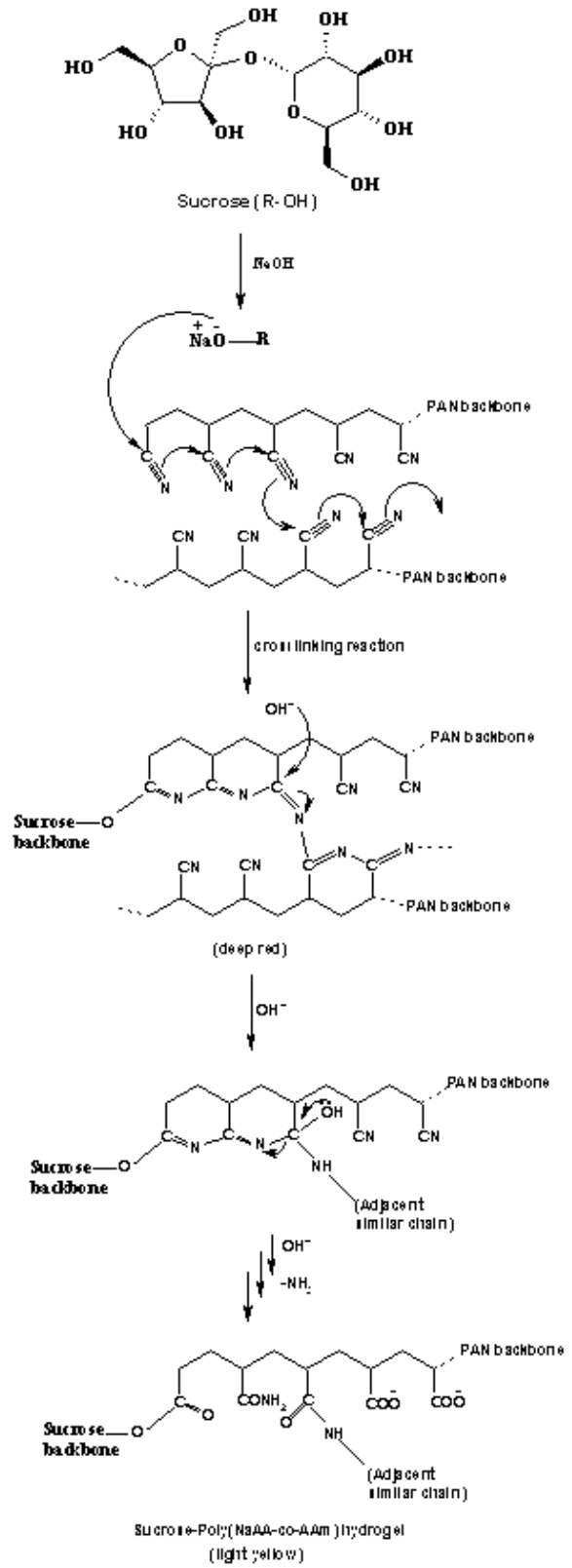

Scheme 1: Proposed mechanism for crosslinking during hydrolyzing nitrile groups of sucrose-PAN mixture to produce sucrose-poly (NaAA-*co*-AAm) hydrogel.

Spectral characterization:

For identification of the hydrogel, infrared spectroscopy was used. Figure 1(a) is the spectrum of the physical mixture of sucrose and PAN. A sharp absorption peak shown at 2251 cm^{-1} is attributed to stretching of CN groups of PAN. After alkaline hydrolysis, the absorptions modes at 1635, 1561, and 1412 cm^{-1} [Fig. 1(b)] can be attributed to C=O stretching in carboxamide functional groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively.

One of the most important properties that must be considered is hydrogel microstructure morphologies. Figure 2 shows the scanning electron microscope images of the hydrogel. This picture verifies that the synthesized polymer in this work have a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

Swelling in various salt solutions:

The swelling ratio is mainly related to the characteristics of the external solution, i.e. the charge number and ionic strength, as well as the nature of polymer, i.e. the elasticity of the network, the presence of hydrophilic functional groups, and the extent of crosslinking density. For instance, swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased comparing to the swelling values in distilled water. This well-known undesired swelling-loss is often attributed to a "charge screening effect" of the additional cations causing a non-perfect anion-anion electrostatic repulsion [23]. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of particles causing an appreciably diminish in swelling capacity.

The swelling capacity of the hydrogels was measured in various salt solutions (NaCl, $CaCl_2$, and $AlCl_3$) with different concentrations. Fig. 3 illustrates a reverse relationship between concentration of salt solutions and swelling capacity of the hydrogel. As mentioned above, charge screening effect and ionic crosslinking are the main explanations for the intense loss of swelling.

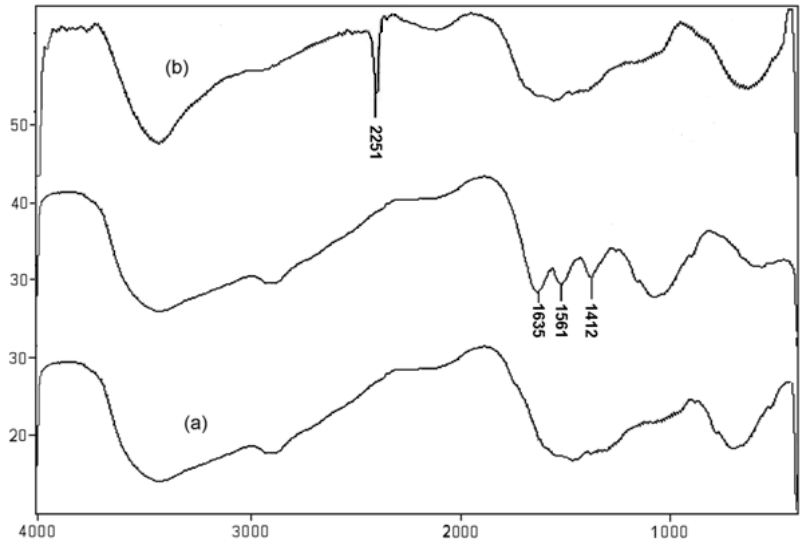

Fig. 1: KBr FT-IR spectra [transmittance versus wave number (cm^{-1})] of (a) the physical mixture of sucrose and PAN and (b) the hydrogel.

Equilibrium swelling at various pH solutions:

Most of ionic hydrogels are pH-sensitive and, therefore, the pH of the swelling medium has direct control over the degree of absorbency capacity of the network. So, in this series of experiments, equilibrium swelling for the synthesized hydrogels was measured in different buffer solutions with pHs ranged from 1.0 to 13.0 (Fig. 4). In the pH region from 1 to 3, most of carboxylate groups are in the form of –COOH and the low swelling values of hydrogels can be attributed to the presence of non-ionic hydrophilic COOH and -OH groups in the hydrogel network. The swelling ratio increased rapidly as the pH of solutions was increased from 4 to 8. At higher pHs (4-8), some of carboxylate groups are ionized and the electrostatic repulsion between COO^- groups causes an enhancement of the swelling capacity. The reason of the swelling-loss for the highly basic solutions (pHs>8) is charge screening effect of excess Na^+ in the swelling media which shield the carboxylate anions and prevent effective anion-anion repulsion.

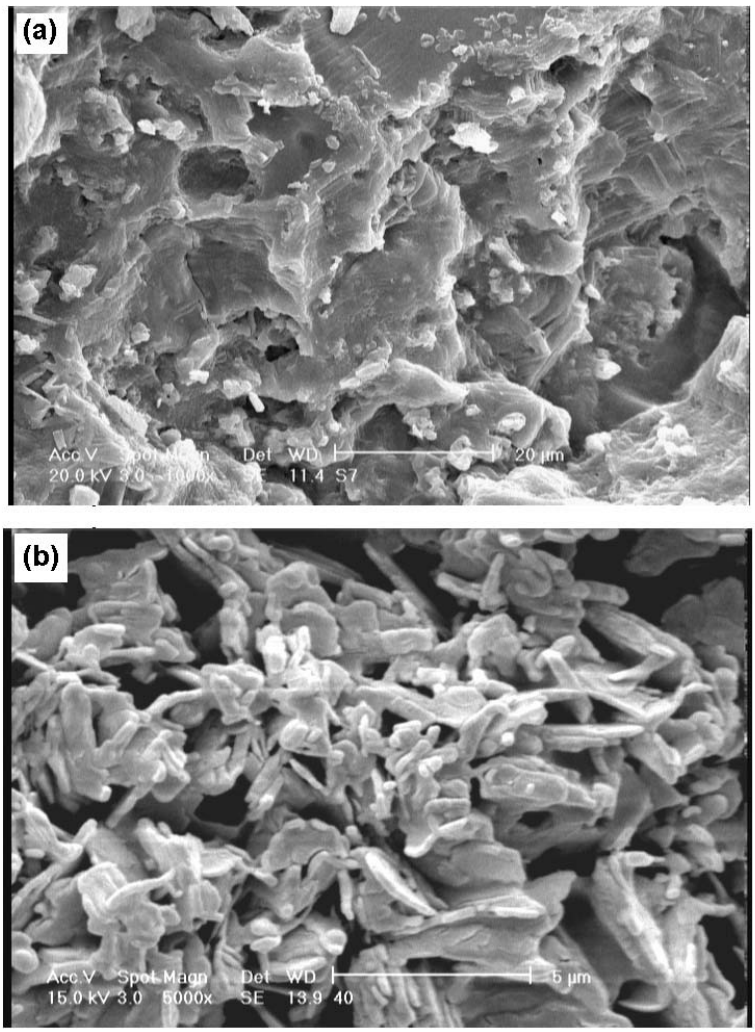

Fig. 2: SEM photographs of the hydrogel. Surfaces were taken at a magnification of 1000X and the scale bar of 20 µm (a) and at a.

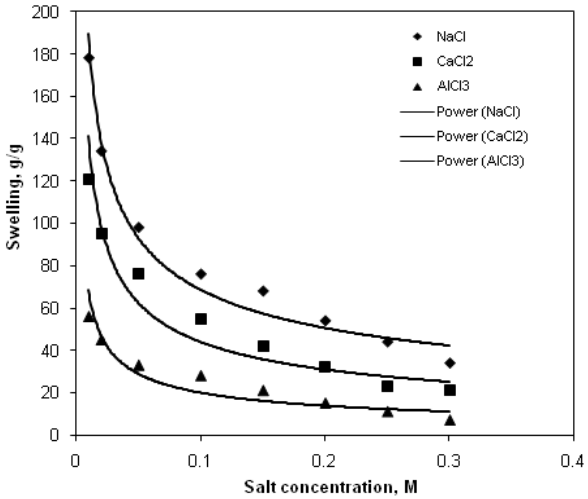

Fig. 5: Swelling capacity variation of sucrose-poly(NaAA-co-AAm) superabsorbent in saline solutions with various concentrations.

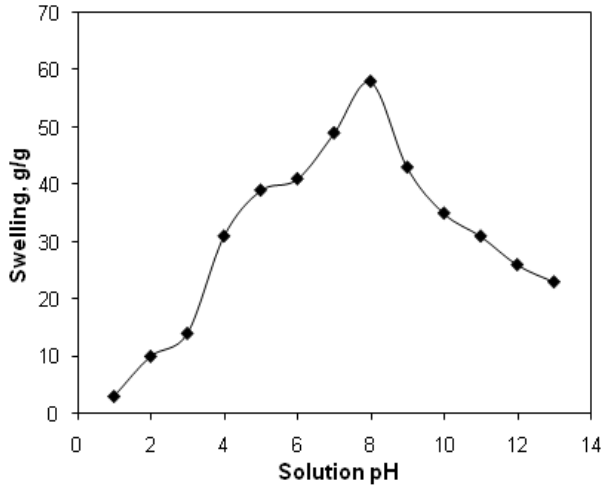

Fig. 6: Effect of pH of solution on swelling of sucrose-based hydrogel.

Conclusion:

In the present study, we prepared a novel superabsorbent hydrogel by alkaline hydrolysis of sucrose-PAN physical mixture. The synthetic approach used in this research to prepare the superabsorbent hydrogel has several advantages. The practical one-step method for hydrogel synthesis is relatively simple and easy in comparison with free radical graft copolymerization method. Also, no initiator and expensive crosslinking agent is used. Therefore, this practical approach may be preferred to as a relatively "green process".Swelling measurement of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in NaCl solutions.

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