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Swelling behaviors of starch-g-polyacrylamide hydrogel: before and after saponification

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Abstract: Biodegradable starch based hydrogels have been attracting much attention of the researchers owing to concerns related to environmental pollution by the synthetic polymers. In this article green hydrogel is prepared by the free radical polymerization of acrylamide on the starch backbone. The amide groups of the starch-g-PAAm hydrogel were saponified and its swelling behavior was compared with unsaponified starch-g-PAAm and crosslinked polyacrylamide. The pH responsive swelling behaviors of the hydrogels were also investigated. The swelling percentage of saponified starch-g-PAAm was found higher than that of unsaponified hydrogel. Swelling percentage of crosslinked PAAm and starch-g-PAAm hydrogels normally increase with the pH value. But in case of extremely basic medium the swelling percentages were found to be lowered. The structures of the hydrogels were confirmed by FTIR spectroscopy.

Keywords: Hydrogel, Swelling percentage, pH responsive, Starch, Saponification.

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I. Introduction

Crosslinked hydrophilic polymer which are able to absorb and retain large volume of water are known as superabsorbent polymer or hydrogels [1]. Hydrogels can swell and retain a significant fraction of water within its three dimensional structure without being dissolved in it. The water absorbing capacity of hydrogels arises from the hydrophilic functional groups attached to the polymeric backbone [2], chemically crosslinked network [3] and physical entanglement [4]. Due to wide range of applications, hydrogels have received considerable attention in the past 50 years. According to the definition, both biomaterials and synthetic materials can be considered as hydrogels. Many naturally occurring materials can absorb water but their capacity to swell and retain the water is comparatively poor with respect to synthetic hydrogels. But the increasing focus on environmental problems associated with synthetic polymers, there is an emerging tendency toward the development of biodegradable polymers. Research works for modification of natural polymers and development of new products by using renewable biomaterials are growing rapidly [5]. Graft co- polymerization of vinyl based monomers onto natural polymers like starch, cellulose etc. is an efficient and promising approach for the development of new bio-based materials [6, 7]. Many research works have been done by using starch as substrate for grafting because of the ease with which vinyl monomers undergo grafting onto it [8-10]. Moreover abundant resources, non-toxicity, biodegradability, low cost and adhesive property make starch suitable substrate for grafting [11]. Starch is easily extractable from various natural sources like potato, corn, wheat, maize, cassava etc. Other polysaccharide like cellulose, hydroxyethyl cellulose [12], guar gum [13] have been graft copolymerized to prepare water absorbing polymers. J.R. Witono *et al.* were prepared graft copolymer using cassava starch and acrylic acid [14]. Mohammad Sadeghi & Mojgan Yarahmadi have reported on pH-sensitive hydrogel prepared via graft copolymerization of mixtures of acrylic acid (AA) and 2-hydroxy ethyl methacrylate (HEMA) onto starch backbones by a free radical polymerization technique [15].

In this investigation crosslinked polyacrylamide (PAAm) was synthesized. Polyacrylamide (PAAm) was grafted on starch by free radical polymerization and their pH responsive swelling behaviors were investigated. The amide groups of the hydrogel were saponified and swelling behaviors of the hydrogels before and after saponification were also investigated.

II. Materials And Method

2.1 Raw materials:

Reagent grade starch (DaeJung chemicals and metal Ltd. Korea), Acrylamide (Loba Chemie Pvt. Ltd. India), N,N-methylenebis acrylamide ((Loba Chemie Pvt. Ltd. India), Potassium persulphate (Merck Specialities Pvt. Ltd. India) were used without any purification for the synthesis of hydrogel. Reagent grade NaOH (Merck Germany) and HCl (Merck Germany) were used for further treatments.

2.2 Grafting of acrylamide on starch:

The starch was gelatinized at 80°C for 30 mins. After that a cold mixture of acrylamide (AAm), potassium persulphate and N,N-methylenebis acrylamide was slowly added to the gelatinized starch with continuous stirring. Starch and acrylamide were used in 1:1 ratio and 0.1% crosslinking agent was used with respect to total monomers. The polymerization reaction was continued for 2 hours with continuous stirring. Polyacrylamide (PAAm) was prepared under same reaction conditions. The starch-g-PAAm gel was comparatively opaque than the polyacrylamide gel.

2.3 Saponification of starch-g-PAAm gel:

The starch-g-PAAm gel was saponified with 200 mL of 2% NaOH solution. The saponification reaction was carried out for 2 hours at 80°C. After the reaction the excess alkali was neutralized with 0.1N HCl solution. Then the hydrogels were dried in oven at 90°C with continuous air flow.

2.4 Fourier transform-infrared (FTIR) spectroscopy:

The FTIR absorption spectra of synthesized PAAm, unsaponified starch-g-PAAm and saponified starch-g-PAAm hydrogels were taken using the Agilent Cary 630 FTIR spectrometer in the range of 4000–350 cm⁻¹.

2.5 Swelling percentage measurements:

In this series of experiments the swelling percentages of PAAm, starch-g-pAAm and saponified starch-g-PAAm hydrogels were measured in different pH solutions. Stock HCl and NaOH solution were used to reach desired pH values 3.0, 5.0, 7.0, 9.0, 11.0 and 13.0. PHS-25 digital pH meter was used for the measurements. Then 0.5g of each hydrogels were immersed in 200 mL of solvent and allowed to swollen for 48 hours. After 48 hours the swollen hydrogel beads were separated through filtration and the swollen weight of the hydrogels were taken by an analytical balance. Swelling percentages (S%) were measured by the following equations:

$$SR = W_i / W_o \quad \dots\dots\dots (a)$$

$$\text{Swelling percentage (S\%)} = SR \times 100 \quad \dots\dots\dots (b)$$

Where, W_o is the initial weight of dry hydrogel and W_i is the weight of swollen hydrogel bead after 48 hours. SR represents the swelling ratio [16].

III. Results And Discussion

The grafting of PAAm on starch was confirmed by FTIR spectrum. The FTIR Spectra of PAAm, unsaponified starch-g-PAAm and saponified starch-g-PAAm are presented in figure 1. In the PAAm spectrum weak band in the region of wave number 3400-3100 cm⁻¹ was found for N-H stretching vibration. Comparatively broad and strong bands were found in the region of wave number 3600-3200 cm⁻¹ for starch-g-PAAm and saponified starch-g-PAAm hydrogels. These bands arise due to the stretching vibrations of more polar O-H groups on starch. The C=O stretching band at 1600-1560 cm⁻¹ was found stronger for saponified starch-g-PAAm due to presence of more polar carboxylic groups. Moreover a band at 1340 cm⁻¹ arises for starch-g-PAAm and saponified starch-g-PAAm hydrogel spectra. This is for the O-H bending vibration of hydroxyl group in starch.

The maximum swelling capacity of the prepared hydrogels has been found for saponified starch-g-PAAm at pH 7. The swelling percentages of saponified starch-g-PAAm at pH 3, 5, 7, 9, 11, 13 were found 6650, 8995, 15650, 12905, 11550 and 4880 respectively. Whereas the swelling percentages of unsaponified starch-g-PAAm at pH 3, 5, 7, 9, 11, 13 were found 920, 972, 1140, 1202, 1265 and 2350 respectively. For polyacrylamide these values were found 1795, 1870, 1988, 2390, 2714 and 4207. The swelling behavior of PAAm, starch-g-PAAm and saponified starch-g-PAAm hydrogels are presented in figure 2. The saponified starch-g-PAAm hydrogel showed higher swelling percentage than starch-g-PAAm and PAAm at all pH values. During the hydrolysis process under basic condition the amide group converted to hydrophilic carboxylic group. Crosslinked Polyacrylamide and unsaponified starch-g-PAAm gel are flexible enough to swell in water but in case of saponified starch-g-PAAm, the presence of more carboxylic groups on the surface of the polymer make it more hydrophilic hydrogel.

The pH responsive properties of the hydrogels are shown in figure 3. In acidic medium the functional groups in the saponified starch-g-PAAm polymer chain should undergo protonation and in basic condition similar ions on the aqueous medium lower the swelling capacity of the hydrogel. In case of PAAm and unsaponified starch-g-PAAm hydrogels, the swelling capacity increases with the increase in pH. At basic medium slow hydrolysis of amide group leads to the formation of carboxylic group. Moreover, in presence of NaOH the hydroxyl groups of the starch can form an alkoxide ion (St-O⁻) [17].

IV. Figures And Tables

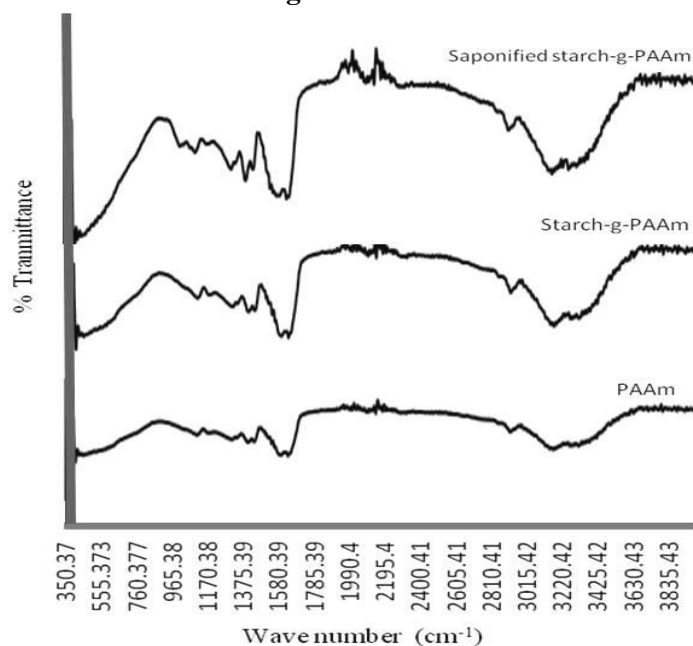


Figure 1: FTIR Spectra of PAAm, starch-g-PAAm and saponified starch-g-PAAm

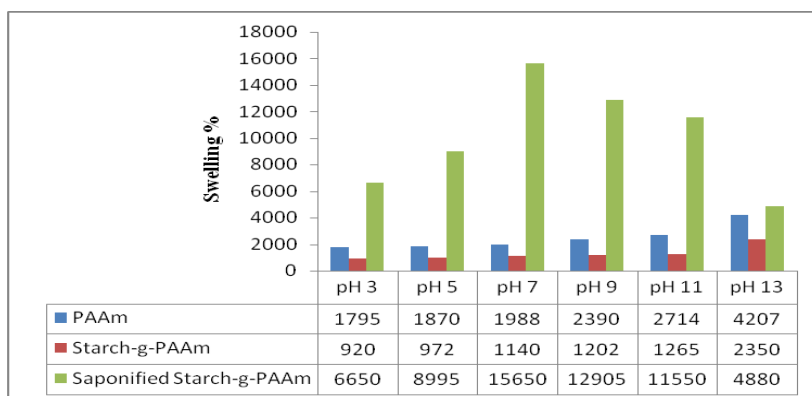


Figure 2: Swelling percentage of PAAm, starch-g-PAAm and saponified starch-g-PAAm hydrogels.

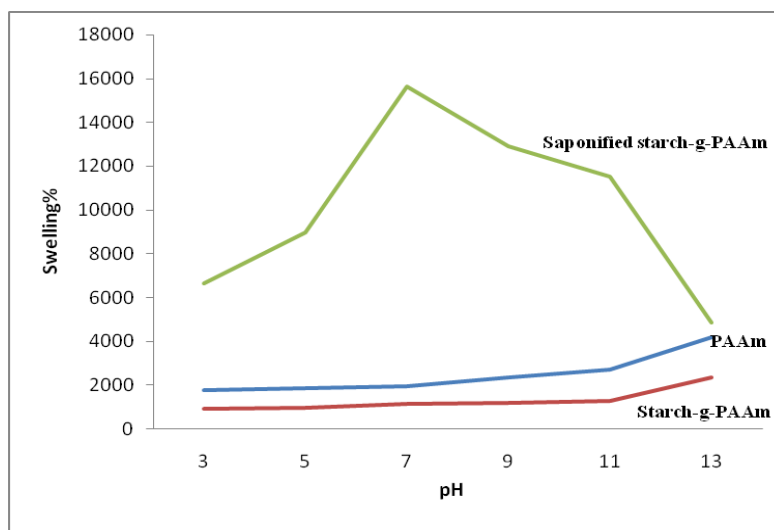


Figure 3: pH responsive swelling properties of PAAm, starch-g-PAAm and saponified starch-g-PAAm hydrogels.

V. Conclusion

A superabsorbent polymer was synthesized by direct grafting of acrylamide onto cassava starch in the presence of N,N-methylenebis acrylamide polymerization crosslinker and free radical initiator. The grafting of polyacrylamide with starch was confirmed by FTIR spectroscopy. The saponified starch-g-PAAm showed better swelling percentage than unsaponified starch-g-PAAm and PAAm. The maximum swelling percentage was found for saponified starch-g-PAAm at pH 7.

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