

PREPARATION OF HYDROGELS AND THE STUDY OF FACTORS INFLUENCING THE ABSORBENT PROPERTIES OF SAPONIFIED STARCH-G-ACRYLONITRILE**Dr. Harshada Niju¹, Ms Aparna Jadhav² and Dr. Vidyagauri Lele³**¹Assistant Professor, Department of Chemistry, J.V.M.'s Mehta Degree College²Assistant Professor, Department of Chemistry, N. G. Acharya & D.K. Marathe College³Professor, Department of Chemistry, N. G. Acharya & D.K. Marathe College**ABSTRACT**

Sago starch was gelatinised and then grafted with acrylonitrile (AN) using ceric ammonium nitrate (CAN) as an initiator. The grafted copolymer so formed was hydrolysed using an alkali to yield hydrogels. Hydrogels are polymeric networks which contain hydrophilic groups such as $-OH$, $-COOH$, $-NH_2$, $-CONH_2$ and $-SO_3H$. Thus hydrogels are able to absorb and then retain large quantity of water without dissolving themselves. They are widely used in biomedical field namely drug delivery, cell carrier entrapment, wound management and tissue engineering. The effect of various factors such as concentration of initiator and crosslinker, initial dilution of monomers, gelatinisation conditions of starch, and the monomer in feed, on the water absorption capacities of the hydrogels have been studied. The increase in gelatinisation temperature did not result in higher absorption of water. There is a decline in the water absorbency of hydrogels with the increase in initial monomer dilutions as well as with the increase in monomer feed and initiator concentration. The optimum reaction conditions for the said hydrogels prepared using sago starch are: gelatinisation temperature = $75^\circ C$; gelatinisation time = 60 min; AN = 0.152 mol/L; CAN = 0.002 mol/L; N,N' methylene bisacrylamide = 1%.

Keywords: sago starch, graft copolymer, hydrogels. Gelatinisation, crosslinker

INTRODUCTION

Hydrogels are hydrophilic substances that swell in water. Dry hydrogel expands up to an equilibrium extent when submerged in water, while conserving its shape. The shape of hydrogel is stabilized by the partially cross-linked three-dimensional network structure. The hydrophilicity of polymer is favoured by presence of the polar groups which are water soluble. As the water content increases, the three-dimensional network of hydrogel becomes stronger[1].

In a thermally aided, three-step hydration-plasticization of the polymeric network, starch changes into gelatin. First step involves swelling of the hydrophilic starch granules by absorption of water into it. In the second step, starch is heated till it dissolves, thereby resulting in the destruction of starch granules due to leaching of the amylose component. This leads to gelatinization of starch which is an irreversible physical change. Retrogradation is the third step, wherein the starch hydrogel network is built upon cooling and aging, leading to its partial recrystallization and reorganization of the polysaccharide structure. The two main factors affecting the gel formation are, amount of amylose and gelatinization temperature.

In this study we shall discuss the effect of concentration of initiator, effect of % MBA (crosslinker) and effect of time and temperature on the absorption capacity of hydrogels of sago starch, grafted with acrylonitrile [2].

METHOD AND MATERIALS

Gelatinization of starch was carried out by taking a known weight of dried sago starch in a fixed volume of distilled water in a beaker kept in the thermostat with a temperature set to 348 K and continuously stirring it for a fixed time. The gelatinized starch was later brought to room temperature and then placed in thermostat adjusted to 298K. A predetermined amount of CAN was added as an initiator to the gelatinized starch and stirred for 10 minutes, to enable the production of free radical sites on its backbone. Acrylonitrile was added as a monomer in a fixed amount, followed by addition of distilled water to make the total volume of the reaction mixture to a fixed final volume.

To study the effect of addition of cross linker, different known quantities of N, N' – methylene bisacrylamide (MBAM) (cross-linker weight percentage dependent on the total weight of monomers in the monomer feed) were instantly added after monomer addition to the grafting reaction mixture. Further, the reaction mixture was stirred continuously for 2 hours. After the completion of the reaction, the reaction mixture was placed in the

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thermostat which was set to a temperature of 333 K. To this warm solution 5% NaOH solution was added with continuous stirring until its saponification was completed which was indicated by its reddish-brown colour. The saponified solution was digested in the thermostat for further 1200 s till its colour changed to pale yellow. The solution was made to attain room temperature in a water bath and then glacial acetic acid was added to it till a certain pH value. In order to obtain the hydrogel from the solution, methanol was added to it in excessive amounts till its complete precipitation was ensured. The excess of methanol serves the purpose of complete dewatering [3,4], which is important for precipitation of hydrogel. The precipitated hydrogel samples prepared were filtered through Whatmann filter paper and dried in vacuum oven at 343 K [5]. Fine powder of the dried hydrogel samples was kept in desiccator containing anhydrous CaCl_2 to ensure maximum absorbing capacity of the hydrogels.

RESULT & DISCUSSION

A preweighed amount of powdered hydrogel samples was soaked in a beaker containing fixed volume of distilled water for 24 hours at room temperature. After the said period, the fine powdered particles of hydrogel were observed to be swollen with water, which were then filtered through a wet filter paper. The residue thus obtained was weighed and the amount of water absorbed in gram per gram of dry hydrogel served as the unit of measurement for water absorption.

i) Effect of Initiator Concentration

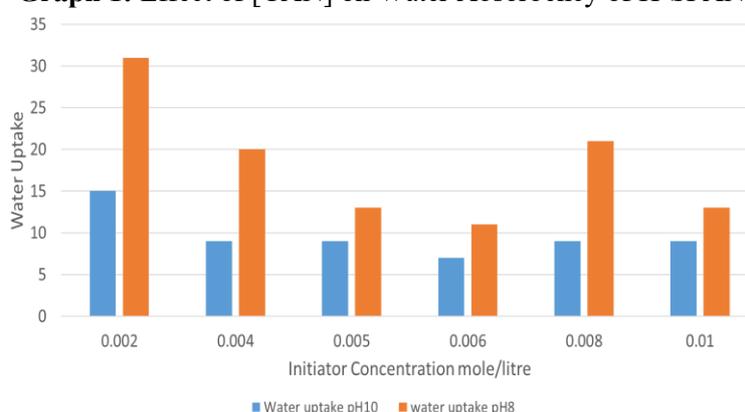
The effect of concentration of CAN on the water absorption capacity H-SPAN is depicted in Graph 1. It is evident, the water absorbency of H-SPAN increased, as the concentration of CAN increased. The water absorbency reached a peak value at at 0.002 mol/L for H-SPAN, beyond which decrease in absorbency value was observed.

The increase in water absorbency with the increase in concentration, at low CAN concentration may be attributed to:

- Significant increase in number of macroradicals at starch backbone
- Higher grafting yield due to grafting of more monomer molecules onto macroradicals

Whereas decrease in absorbency beyond the optimum concentration of CAN, can be explained on the basis that homopolymerisation of the monomer occurs in presence of excess amount of CAN. This is due to the fact that CAN acts as an effectual initiator for causing homopolymerisation of AN, even in presence of starch macroradicals.

Graph 1: Effect of [CAN] on Water Absorbency of H-SPAN

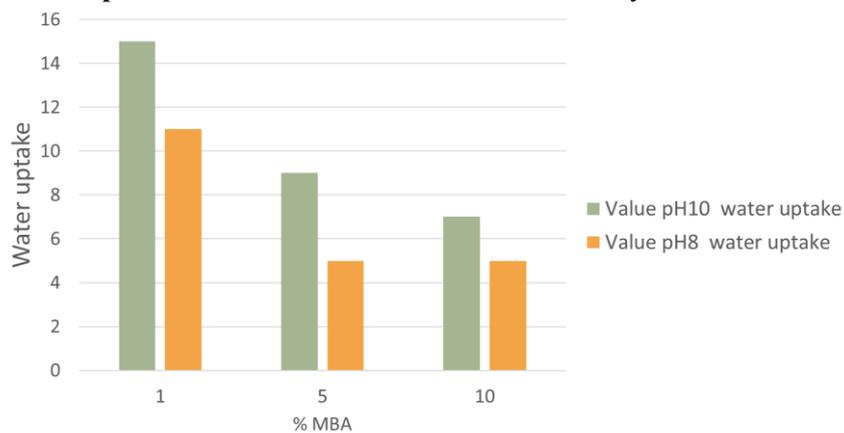


ii) Effect of Crosslinker Concentration

Hydrogels synthesized using chemical cross-linkers exhibit increased stability, longer shelf life, and superior mechanical qualities (tensile, shear, bending, etc.). In order to synthesize chemically crosslinked hydrogels, functional monomers are grafted into the polymer network or two polymer chains are linked together using a crosslinker. The reaction between this cross-linking agent and other groups, such as $-\text{NH}_2$, $-\text{OH}$, and $-\text{COOH}$, can result in the formation of a three-dimensional network. [6-8]

Due to its very reactive carbon-carbon double bonds, N, N'-methylene-bis-acrylamide (MBA) is frequently utilized as a cross-linking agent in the preparation of hydrogels [9,10]. Graph 2 illustrates the effect of variation in concentration of MBAM on the water absorbency of H-SPAN. The addition of cross linker improves the water absorbency, provided that it is added in a very low concentration (less than 1%). This can be explained on the basis of the following points: (i) the development of a three – dimensional network of moderately cross-linked graft copolymer (ii) generation of insoluble cross-linked homopolymers also contributes to absorption (iii) generation of an insoluble graft copolymer by minimal grafting of MBAM onto sago starch

Graph 2: Effect of MBAM on Water Absorbency of H-SPAN

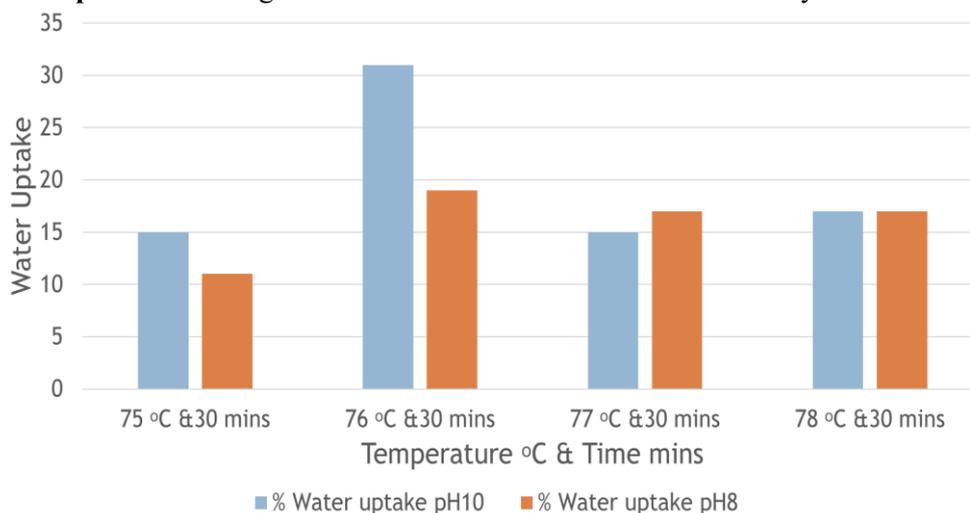


iii) Effect of Gelatinisation Temperature and Time

When the temperature of the aqueous starch slurry was raised up to the gelatinization temperature range (341K to 346 K), a rapid increase in swelling of starch granules was observed due to the absorption water by it along with an instantaneous increase in its viscosity of the solution. The revelation that hydrogels synthesized by gelatinization of starch at 348 K had better absorbency values than those gelatinized at 368 K, was unexpected. This can be the result of smaller starch granules being degenerated at higher temperatures.

However, when the gelatinization time is increased, the absorbency values increase substantially, as indicated in Graph 3. Based on the swelling pattern of starch granules, the trend can be better understood. Exterior surface of starch granules absorb water at first, and then water gradually diffuses in to the interior of the granules. Granules of starch that become swollen possess larger surface area, thus facilitating increased rate of grafting of monomer onto its surface. This further leads to its improved water absorbency values with the increase in gelatinization time. The optimum gelatinization temperature and time in this study were establishment to be 348 K and 3600 s. respectively.

Graph 3: Effect of gelatinization conditions on Water Absorbency of H-SPAN



CONCLUSION

By grafting acrylonitrile onto gelatinized sago starch employing ceric ion initiation and then being saponified by NaOH, the hydrogels were synthesized. Following optimum conditions have been determined after studying the effects of different reaction conditions:

Reaction Parameters	H-SPAN
Initiator Concentration (mol/L)	0.002
Cross-linker Concentration (w/w %)	1
Gelatinization Temperature (K)	348
Gelatinization Time (seconds)	3600

The exceptional potential of hydrogels based on starch graft copolymers to absorb aqueous fluids has gained prodigious attention from researchers over the past several decades. A review of the literature indicates that while extensive research has been done on hydrogels based on starch graft copolymers, the majority of that research has been protected by patents. For over the years, potato, tapioca or cassava and maize starch were preferred by the researchers because of their higher natural swelling properties. Nevertheless, we have concentrated our attention to hydrogels made from sago starch grafted with vinyl monomer like AN and have successfully produced hydrogels.

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