

# Factors Influencing Absorbent Properties of Saponified Starch-*g*-(acrylic Acid-*co*-acrylamide)

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**ABSTRACT:** Mixtures of acrylamide (AM) and acrylic acid (AA) were grafted onto gelatinized maize starch by using ceric ammonium nitrate (CAN) as an initiator. These graft copolymers were hydrolyzed with alkali to yield hydrogels. The effects of different reaction variables, such as the concentration of the initiator and crosslinker, initial dilution of the monomers, gelatinization conditions of starch, and the ratio of AM and AA in the monomer feed, on the water absorption capacities of these hydrogels have been examined. Absorption increases on gelatinizing starch at a higher temperature for a longer time as smaller granules gelatinize only under these conditions. The higher proportion of AA in the monomer feed enhances absorption due to formation of polyelectrolyte. The optimum conditions for obtaining maximum water absorbency established in the present study are granular maize starch = 2.0 g; gelatinization temperature = 95°C; gelatinization time = 60 min; AM = 1.0 g; AA = 4.0 g; CAN = 0.008 mol/L; *N,N'*-methylene bisacrylamide = 1%. The product so formed was saponified with NaOH and then precipitated in excess of methanol. The dried and finely powdered product showed the maximum water absorbency of 510 g/g. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2480–2485, 2000

**Key words:** hydrogels; starch; acrylamide; acrylic acid; ceric ammonium nitrate

## INTRODUCTION

Hydrogels are water-swollen, hydrophilic, three dimensional networks. Andrade defined it as a polymeric material that exhibits the ability to swell in water and retain a significant fraction of it (generally >20%) within its structure, but which does not dissolve in water.<sup>1</sup> It has been reported that the presence of hydrophilic groups, high polymer chain flexibility, as well as the availability of large free volume between polymeric chains, enhances the swelling capacity of hydrogels.<sup>2</sup> Extent of crosslinking, initial dilution of monomers, and pH of the medium also decide the absorbency values of the resulting hydrogels.

Although the hydrogels based on synthetic polymers such as polyacrylamide and poly(sodium acrylate) gels do have large fluid absorbing capacities, those prepared from saponified starch graft copolymers have a greater demand in industry due to their low cost and also because of the large proportion of starch in these gels which render them biodegradable and thus environmental friendly. The hydrogels based on saponified starch graft vinyl monomers are widely used in consumer products such as adult incontinence pads, diapers, sanitary products,<sup>3</sup> and tissue papers, in addition to their use in soil stabilizers,<sup>4</sup> as microgels in medicine,<sup>5</sup> artificial muscles, water-flood oil recovery,<sup>6</sup> and so on.

Among root starches that possess inherent high water swelling capacity, potato starch shows a very rapid and exceptionally high swelling at relatively low temperature. Therefore, potato

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starch has been preferably used in the preparation of hydrogels. Cassava starch, which has a similar ratio of amylose to amylopectin as that of potato starch, has also been employed in the preparation of hydrogels. However, the cereal starches such as maize starch has comparatively low swelling power and hence there is a need to improve their swelling power by grafting process.

In the present article, we have attempted to enhance the water-absorption capacity of maize starch by simultaneously grafting two hydrophilic monomers, namely acrylic acid (AA) and acrylamide (AM) onto gelatinized starch and then saponifying the resultant graft copolymer. We have further studied the effect of various reaction conditions such as the concentration of initiator and crosslinker, initial dilution of monomers, gelatinization conditions of starch, and the ratio of acrylamide and acrylic acid in the monomer feed on the water absorption capacities of these hydrogels.

## EXPERIMENTAL

### Materials

Maize starch (food grade), supplied by Rajaram and Bros. (India), was dried at 110°C for 10 h to remove the absorbed water/moisture, as we found it to be an optimum time for drying starch to constant weight, and then stored over anhydrous CaCl<sub>2</sub>. AA [(LR), Sisco-Chem Industries, India], having a purity of 99.5%, was stored in a refrigerator and brought to room temperature before use. Ceric ammonium nitrate (CAN) (J. T. Baker Chemical Co., NJ) and AM [(LR), Sisco-Chem Industries, India], being hygroscopic, were dried at 110°C and later stored in a vacuum desiccator. CAN was used as a 0.1M solution in molar nitric acid [analytical reagents (AR), S. D. Fine Chemicals, India].

### Preparation of Hydrogels

In general, the gelatinized starch was prepared by constantly stirring a mixture of 2 g of dried starch and 35 mL of distilled water at 75°C for 30 min. The slurry was cooled to 30°C, purged with a stream of nitrogen, and treated with CAN solution for 10 min to facilitate free-radical formation on the starch backbone. Then variable quantities of AA and AM were added simultaneously to obtain different monomer ratios, followed by the addition of distilled water to make the total vol-

ume of the reaction mixture to 60 mL unless stated otherwise. While studying the effect of crosslinker, *N,N'*-methylene bisacrylamide (MBAM) (wt % of crosslinker based on total weight of monomer in monomer feed) was added to the reaction mixture just after the addition of monomers. The polymerization reaction was allowed to proceed for 120 min with constant stirring under nitrogen atmosphere. The exact details of the reaction conditions are given in the footnotes to the tables. No attempt was made to extract the homopolymers of AA and/or AM, as they are soluble in the medium of reaction (water) and would be filtered off during filtration except where higher percentages of crosslinker is used. Moreover, no method of extraction is efficient enough to extract the homopolymers of AA and AM completely from the reaction mixture and the presence of these homopolymers eventually help in enhancing the water absorption capacity of the final product.

After 120 min, the reaction mixture was warmed in a water bath up to 60°C and hydrolyzed by dropwise addition of 5% NaOH with stirring until it assumed a reddish-brown color. The slurry was further digested at the same temperature in a water bath for about 20 min when it turned pale yellow. After cooling the slurry to 30°C, its pH was brought down to about 10 by using glacial acetic acid and it was then precipitated repeatedly in large excess of methanol for achieving complete dewatering as well as neutrality.<sup>7</sup> The hydrogel so prepared was dried under vacuum at 70°C. To enhance the absorbency, the dried hydrogel was finely powdered<sup>8</sup> and stored over anhydrous CaCl<sub>2</sub>.

### Measurement of Water Absorption

The water absorption capacities of these hydrogels were assessed by filtration method. This method works satisfactorily for a discrete type of hydrogels such as starch-based hydrogels as the excess water gets removed through internal channels of swollen hydrogel globules.<sup>9</sup> Hence samples of powdered hydrogels weighed up to 0.1 g were immersed in 100 mL of distilled water in a beaker at room temperature. After 30 min, the slurry was filtered through a weighed porous sintered glass (G-1) crucible. The excess water was removed by applying partial vacuum. Water absorption was measured in terms of the amount of water absorbed in grams per gram of dried hydrogel after weighing the swollen hydrogel in the crucible.<sup>7,10</sup> No correction was made for the per-

**Table I Effect of Initiator Concentration on the Water Absorbency Values of Hydrogels**

[CAN] <sup>a</sup> /mol L <sup>-1</sup>	Water Absorbency Values (g/g)
0.002	210
0.004	240
0.008	290
0.012	230
0.016	170

The experimental conditions were 2.0 g of maize starch gelatinized at 75°C for 30 min in 35 mL of distilled water, reacted with acrylamide = 1.0 g and acrylic acid = 3.0 g at 30°C for 120 min. The total volume of the reaction mixture = 60 mL.

<sup>a</sup>Ceric ammonium nitrate.

centage of the polymer that was soluble in water; the absorbency values would thus be higher if based only on insoluble polymer.<sup>11</sup>

## RESULTS AND DISCUSSION

All the samples of dried hydrogels were yellowish in color. The color turned reddish for those samples which had a higher component of acrylic acid in the monomer feed. The samples having larger proportion of AM in the monomer feed were in the powder form whereas those with larger component of acrylic acid showed granular nature. All the hydrogels showed high absorption rate in the first 1–2 min, which decreased thereafter.

### Effect of Initiator Concentration

The water absorbency values obtained by altering the CAN concentration are tabulated in Table I. It can be noted that with the increase in the concentration of CAN, the water absorbency of the hydrogels increased and reached a maximum of 290 g/g at [CAN] of 0.008 mol/L and a further increase in CAN resulted in the decline of water absorbency of hydrogels.

At low concentration, CAN must have been mostly utilized in producing a large number of free-radical sites on the starch backbone at which the monomers can be grafted at. Therefore, the grafting yield and in turn the absorbency of the graft polymer increases with increase in CAN concentration. However, above a critical concentration of 0.008 mol/L, the excess of CAN was utilized in the homopolymerization of monomers.

It is a known fact that CAN is an effective initiator for the homopolymerization of AA as well as AM. In other words, even in the presence of starch macroradicals, homopolymerization is a favored process. Poly(acrylamide) (PAM) as well as poly(acrylic acid) (PAA) both are soluble in water. Nevertheless, the absorbencies reported in Table I are only due to insoluble graft copolymer having low percentages of grafted AM and AA.

### Effect of Crosslinker Concentration

Table II depicts the effect of crosslinker on the water absorbency of the starch-*graft*-(acrylic acid-*co*-acrylamide) [starch-*g*-(AA-*co*-AM)]. The preferential use of MBAM as a crosslinking agent in the preparation of hydrogels can be ascribed to the presence of hydrophilic amide groups on it which probably augments the water absorbency of the hydrogels. Crosslinking increases the mechanical strength of these hydrogels, making them suitable for use in surgical dressings and consumer products.

It can be noted that the water absorbency values increase with the addition of the crosslinker, provided it is added in very low concentration (<1%). This can be attributed to (a) formation of moderately crosslinked graft copolymer producing a continuous network; (b) formation of crosslinked, insoluble homopolymers which, too, would participate in the absorption; and (c) marginal grafting of MBAM onto starch producing an insoluble graft copolymer.

However, with an increase in the concentration of the crosslinker, the pendant AA and AM chains on the starch backbone would crosslink to form a tight network. It is known that a highly crosslinked, rigid structure cannot hold a large quan-

**Table II Effect of Crosslinker Concentration on the Water Absorbency Values of Hydrogels**

[MBAM] <sup>a</sup> (w/w %)	Water Absorbency Values (g/g)
0	290
1	330
5	110
10	90

The experimental conditions were 2.0 g of maize starch gelatinized at 75°C for 30 min in 35 mL of distilled water, reacted with acrylamide = 1.0 g and acrylic acid = 3.0 g in presence of [CAN] = 0.008 mol/L at 30°C for 120 min. The total volume of the reaction mixture = 60 mL.

<sup>a</sup>*N,N'*-methylene bisacrylamide.

**Table III Effect of Gelatinization Conditions on the Water Absorbency Values of Hydrogels.**

Gelatinization		Water Absorbency Values (g/g)
Temperature/ °C	Time/ min	
75	30	330
75	60	370
95	30	360
95	60	410

The experimental conditions were 2.0 g of maize starch gelatinized in 35 mL, reacted with acrylamide = 1.0 g and acrylic acid = 3.0 g in presence of [CAN] = 0.008 mol/L and [MBAM] = 1% at 30°C for 120 min. The total volume of the reaction mixture = 60 mL.

tity of fluid. Therefore, the absorbency values decreased on increasing the concentration of cross-linker over 1%.

#### Effect of Gelatinization Conditions

Gelatinization of starch is a unique phenomenon. On increasing the temperature of aqueous starch slurry up to its gelatinization temperature range (62–72°C), a sudden swelling by absorbing an immense amount of water with simultaneous rise in viscosity was observed. Starch is a combination of two polymers, linear amylose and branched amylopectin. At still higher temperature, the amylopectin sacs burst out and the amylose granules leach out of these sacs. The swelling of starch granules in hot aqueous solutions can be quantitatively measured in terms of swelling power. Swelling power, which is the measure of hydration capacity, is determined from a weight measure of swollen granules and their occluded water. At 90°C, the swelling power of potato starch is 350 compared to 65 for tapioca, 60 for waxy corn, and just 16 for regular corn (maize) starch.<sup>12</sup> The considerably low swelling power shown by maize starch suggests the presence of cohesiveness of structure and tendency to disrupt when heated in water. The presence of amylose-lipid complexes in maize starch, too, inhibit the granule swelling.

Table III exhibits the effect of gelatinization conditions on the absorbency values of saponified maize starch-*g*-(AA-*co*-AM). It can be noted that the absorbency values of hydrogels prepared by gelatinizing starch at 95°C were higher than those where the gelatinization temperature used was 75°C. It is known that when the aqueous

starch slurry is heated, the larger starch granules absorb water and swell rapidly, unlike smaller granules, which swell only at higher temperatures (>75°C).<sup>13</sup> Moreover, it has been reported that the smaller starch granules, because of their low lipid contents, had greater swelling capacities by absorbing more fluid than larger granules.<sup>14</sup> Hence the higher absorbency shown by the hydrogels prepared from the starch gelatinized at 95°C (Table III) can be attributed to the participation of smaller granules in the absorption of water.

It can be noted further that the absorbency values increased remarkably with the increase in the gelatinization time (Table III), irrespective of the temperature used for the gelatinization. The higher absorbency at longer gelatinization time can be explained only by considering the actual swelling behavior of the starch granules. The swelling of starch granules by absorption of water initiates at the outer surface of granules and then the water slowly diffuses into the core of the granule.<sup>15</sup> Thus, the longer gelatinization time results in completely swollen starch granules. It can be inferred from the present studies that in addition to temperature, time of gelatinization also plays a vital role in determining the swelling behavior of starch granules.

The swelling of the granules would facilitate the grafting by making a larger surface area available where the monomers can be grafted at. The considerable increase in the absorbency values at higher temperature (>75°C) and with longer time of gelatinization (Table III) must be certainly because of gelatinization and swelling of smaller granules in addition to larger granules, encouraging thereby a higher percentage of grafting.

**Table IV Effect of Initial Dilution of Monomers on the Water Absorbency Values of Hydrogels**

Volume of Reaction Mixture (mL)	Water Absorbency Values (g/g)
40	475
60	410
80	310
100	280

The experimental conditions were 2.0 g of maize starch gelatinized at 95°C for 60 min in 35 mL of distilled water, reacted with acrylamide = 1.0 g and acrylic acid = 3.0 g in presence of [CAN] = 0.008 mol/L and [MBAM] = 1% at 30°C for 120 min.

**Table V Effect of Monomer Ratio in Feed on the Water Absorbency Values of Hydrogels**

Acrylamide/ g	Acrylic acid/g	Water Absorbency Values (g/g)
4	1	130
3	1	210
2	2	310
1	3	475
1	4	510

The experimental conditions were 2.0 g of maize starch gelatinized at 95°C for 60 min in 35 mL of distilled water, reacted with mixture of monomers in presence of [CAN] = 0.008 mol/L and [MBAM] = 1% at 30°C for 120 min. The total volume of the reaction mixture = 40 mL.

### Effect of Initial Dilution of Monomers

Table IV illustrates the effect of initial dilution of monomers on the water absorbency values of these hydrogels. There was a sharp decline in the absorbency values of hydrogels with an increase in the quantity of the solvent in the reaction mixture. Several studies showed that the hydrogel structure and the hydrogel properties strongly depend on the initial degree of dilution of monomers.<sup>16,17</sup>

As the quantity of solvent present in the reaction medium increases, the network structure becomes increasingly loose. No continuous network is formed above a critical quantity of solvent.<sup>18</sup> The decline in the absorbency values with an increase in the initial dilution of monomers may be due to loosening of the network structure, which then cannot hold larger quantity of fluid in it.

### Effect of Monomer Ratio

The absorbency values of the hydrogels prepared by varying the ratio of AA to AM are listed in

Table V. It can be noted that the absorbency values were higher provided the acrylic acid component was higher in the monomer feed. These results can be rationalized as follows.

1. The poly(acrylamide) on alkaline hydrolysis forms poly(acrylic acid) (Scheme I). Alkaline hydrolysis of poly(acrylamide) proceeds rapidly in the early stages (up to 40% conversion); however, the rate of hydrolysis becomes extremely slow when residual amide content falls below about 30%.<sup>19,20</sup> Hence at a higher ratio of AM in monomer feed, the extent of unhydrolyzed grafted PAM may be higher, resulting in lower absorbency values.<sup>21</sup>

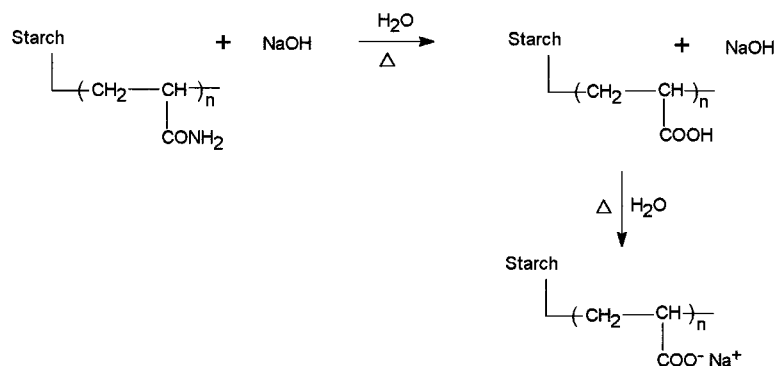
2. Grafted PAA on saponification forms [poly(sodium acrylate)] (Scheme I), which is a highly ionized salt, and hence favors swelling.<sup>22</sup>

The results in Table V are in agreement with our previous work on hydrogels, where we observed that under the same experimental conditions, the neutralized starch-*graft*-polyacrylic acid hydrogels (NSPAA)<sup>23</sup> absorbed water to a higher extent than the hydrolyzed starch-*graft*-polyacrylamide hydrogels (HSPAM).<sup>24</sup>

## CONCLUSIONS

The following conclusions can be made from the experimental research.

1. Low concentration of CAN facilitated higher water absorption.
2. Low concentration of MBAM favored the formation of a better network, which could hold more fluid in it.
3. The smaller starch granules participated in the absorption of fluid, provided the gelatinization was carried out at a higher temperature and for a longer time.



**Scheme I** Saponification of starch-*graft*-polyacrylamide.

4. Higher initial dilution of monomers resulted in a discontinuous network rendering lesser retaining capacity to the hydrogel.

5. AA played a dominant role in deciding the water absorption capacity of the hydrogels due to formation of highly ionized polyelectrolyte.

6. The optimum conditions for obtaining maximum water absorbency established in the present study are as follows: 2.0 g granular maize starch were gelatinized at 95°C for 60 min and graft-copolymerized with a mixture of 1.0 g AM and AA 4.0 g in the presence of 0.008 mol/L CAN and 1% MBAM. The product formed was saponified with NaOH and then precipitated in excess of methanol. The dried and finely powdered product showed the maximum water absorbency of 510 g/g.

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