

Modification of Sorghum Starch for Production of Superabsorbents

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Abstract - Starch extracted from Sorghum bicolor grains was gelatinized and grafted with acrylic acid (AA) and acrylamide (AAm) using potassium persulphate (KPS) as an initiator. Different parameters of grafting reaction such as reaction time, temperature, initiator concentration, and starch to monomers ratio were optimized. Material thus produced was dried, grounded and characterized using FT-IR and SEM. Grafted starch products were saponified with 0.1 N NaOH solution followed by neutralization and drying. Maximum absorbency of 225.5 $g\ g^{-1}$ in normal water was obtained, qualifying it as super absorbent product (SAP).

Keywords: Grafting, Starch, Superabsorbent

1. INTRODUCTION

Superabsorbent polymers are hydrophilic polymers which are able to absorb and retain a fairly large amount of water within their structure. This becomes possible as the polymers, which are hydrophilic in nature, do not get dissolved in water and hold the water molecules within their swollen three dimensional interconnected structures (hydrogels). There is no definite lower limit of absorbency to call a hydrogel as a superabsorbent, and many authors have referred their hydrogels with high absorbency as superabsorbent when the water retention capacity of the polymer was more than 100 times of its own dry weight (or more than 1000%) [1]. These hydrogels attracted wide interest due to their intriguing properties such as high absorption and swelling capacity, slow release of moisture, etc. Some of these products are widely used in personal care, agriculture and biomedical applications [2].

Although synthetic superabsorbent polymers show very high water retention properties and fair to good gel strength, the biodegradability of these acrylate based SAPs is very poor causing increase in environmental load [3]. Therefore, incorporation of biopolymers for synthesis of SAP became preferred option to the use of their synthetic counterparts. Products made of natural biopolymers are biodegradable and more importantly, their sources are cheap, renewable and sustainable.

Natural biopolymers such as cellulose, starch, etc. are effective alternative of synthetic superabsorbent polymers [4,5]. Starch is basically composed of two fractions, amylopectin and amylose and both constitute 97-98% of dry weight of starch. These are polysaccharides and their ratio varies with the botanical origin of the starch. Great Millet or Sorghum (*Sorghum bicolor* L.Moench) is a cheap and alternative source of starch. Sorghum, commonly known as jowar in India is the world's fourth major cereal in terms of production, and fifth in acreage following wheat, rice, maize and barley, and serves as a staple food crop in India [6]. Sorghum grain contains starch ranging from 68-75% depending upon variation in seed quality, region and climatic conditions [7].

Grafting of starch has been widely reported by different researchers. Different polymerization techniques viz. solution polymerization, emulsion polymerization, suspension polymerization, polymerization via irradiation, etc. are used for producing superabsorbent hydrogels. Different initiation systems such as ceric ammonium nitrate, potassium persulphate etc. also have been used for these processes [8,9]. Chen et al. (2004) utilized batata starch for grafting with acrylic acid and acrylamide under gamma radiation with polyethylene glycol as crosslinker [10]. Cassava starch has been grafted by acrylamide using ceric ammonium nitrate by Jyothei et al. (2012) [3]. Peng et al (2007) on other hand used acrylamide (AAm), diallyldimethylammonium chloride (DMAAC) and sodium starch sulfate for producing SAP using ammonium persulfate as grafting initiator [2].

The present paper deals with extraction of starch from sorghum and its modification as a superabsorbent by grafting hydrophilic monomers onto it. It discusses the optimization of the process as well as the characterization of the modified starch and the product developed as a superabsorbent.

2. EXPERIMENTAL

2.1 Materials

Sorghum grains were bought from the local market. Acrylic acid, acrylamide, potassium persulphate, sodium hydroxide were of analytical grade and were purchased from S. D. Fine Chemical Ltd., Mumbai India.

2.2 Extraction of starch

The starch was extracted from sorghum grains by following the alkali steeping method [11].

The cereal grains were first ground into coarse flour, 20g of which was then treated with 500ml of 0.25% sodium hydroxide (NaOH) solution for 4 h at room temperature followed by draining the filtrate. The treatment was repeated for next 3 h, followed by washing it with tap water thoroughly until grains became free of NaOH. After ensuring complete neutralization, coarse grains were ground in a warring blender by adding required quantity of water and the slurry thus obtained was passed through a 200 mesh bolting cloth and squeezed thoroughly to extract the crude starch. The crude starch extract thus obtained was kept overnight inside refrigerator until separation of two layers was clearly visible. The supernatant liquid was drained-off and lower sediment layer was carefully removed and centrifuged at 4000 rpm for 15 min. The upper brown coloured proteinous portion was then scrapped and white coloured starch obtained was dried in an oven at 50 °C. The starch was then ground in a blender in order to obtain fine powder and stored in an air tight bag to protect from moisture and any microbial attack.

2.3 Swelling power

The swelling power of the starch was determined by the method reported by Subramanian et. al. [7]. Starch powder weighing 0.6 g was heated at 95 °C with 30 ml of distilled water for 30 min. The mixture was stirred at an interval of 5 min to avoid any lump formation. The mixture was then cooled to room temperature and then centrifuged for 15 min at 5000 rpm using CRU-5000 centrifuge. After centrifuging, the supernatant liquid was carefully discarded and the swollen starch sediment was carefully weighed. Swelling power was calculated as follows:

$$\text{Swelling power} \left(\frac{g}{g} \right) = \frac{\text{Weight of the wet sediment}}{\text{Initial weight of dry starch}}$$

2.4 Paste clarity

Measurement of paste clarity was carried out by method of Craig et.al. [12]. Starch powder weighing 250 mg was suspended in 20 ml of distilled water in a test tube with its lid closed. The test tubes were then maintained in a water

bath at 95°C for 30 min and were shaken thoroughly at an interval of 5 min to avoid lump formation. The contents were then cooled to room temperature by keeping the test tubes in chilled water bath. The contents were thereafter evaluated for percent transmittance (% T) at 650 nm on a UV-1201 spectrophotometer.

2.5 Estimation of Iodine binding

The amylose content of starch was measured colorimetrically using the iodine method [13]. 100 mg of starch powder was weighed accurately and inserted into a 50 ml Erlenmeyer flask, to which 9 ml of 1N NaOH and 1 ml of 95% ethanol were added in steps. The contents were thoroughly mixed and heated for 10 min in order to gelatinize the starch in a boiling water bath. The mixture was then cooled to room temperature and was subsequently transferred to a 100 ml volumetric flask. The contents were diluted upto 100ml by adding distilled water. Then 5ml of this starch solution was pipetted into a 100 ml volumetric flask. Further in to which, 1 ml of 1 N acetic acid and 2 ml of iodine solution (0.2 g of iodine and 2.0 g of potassium iodide in 100 ml of aqueous solution) were slowly added. Again the contents were diluted to 100 ml with distilled water. The solution was then thoroughly shaken and allowed to stand as it is for 20 min. The absorbance of this solution at 620 nm was then observed using UV spectrophotometer (UV-1201).

2.6 FTIR analysis

The IR spectra of original and various grafted starch samples were recorded using FTIR spectrophotometer (Shimadzu 8400s, Japan) using ATR sampling technique by recording 45 scan in %T mode in the range of 4000–650cm⁻¹.

2.7 SEM analysis

Morphological analysis was done using scanning electron microscopy (Make: JEOL, Japan). Initially the samples were sputter coated with platinum layer and images were taken.

2.8 Water absorbency

The dry sample of starch (0.2 g) was immersed in water for 24 h to reach absorption equilibrium. The fully swollen hydrogel was separated from the unabsorbed water with a 65-mesh screen and thereafter, the hydrogel was weighed. The relative water absorbency was calculated as follows [10]:

$$\text{Water absorbency} \left(\frac{g}{g} \right) = \frac{M_2 - M_1}{M_1}$$

Wherein, M_1 and M_2 are weights of dry sample and of fully swollen hydrogel, respectively.

2.9 Grafting of acrylic acid and acrylamide

The reaction was carried out in a round bottom borosilicate glass flask equipped with a reflux condenser, a nitrogen inlet and overhead stirrer. The reaction temperature was properly controlled by carrying out the reaction system in a thermostated water bath. 10 g of starch was mixed with 300 ml of water and poured inside the reactor. The flask was then flushed with nitrogen. Temperature was raised to 85°C and kept for 15 min till the gelatinization of starch occurred and the translucency was observed. Then the temperature was lowered to 65°C and initiator was added to the flask in order to produce free radicals onto starch molecules. After 10 min, the monomers (AA or AAm or mixture of AA and AAm) were added. The reaction was carried out under nitrogen condition with continuous stirring. The reaction was quenched by addition of methanol and the product was precipitated with this. The precipitate was filtered and dried at 60°C till a constant weight was achieved [14]. Homopolymer formed during reaction was washed and separated from grafted polymer by Soxhlet extraction for 8 hour. The homopolymers of acrylic acid was extracted using ethanol-water mixture (80:20). Morpholine was used as solvent for homopolymer extraction in case of grafting of starch with acrylamide. The extraction process was repeated 3 times to ensure the complete removal of the homopolymer for each sample till the constant weight of grafted starch was obtained.

Graft add on (%) was calculated as reported by Teli et al. [5].

$$\text{Graft add-on}(\%) = \frac{W_2 - W_1}{W_1} \times 100\%$$

Wherein, W_1 and W_2 are the weights of sorghum starch and sorghum grafted starch, respectively.

2.10 Saponification of grafted starch

Saponification was carried out by taking 1 g of dried sample in 100 ml of 0.1 N NaOH solution and keeping it at 80°C for 90 min. It was then cooled to room temperature and washed with water till pH 7 was obtained. It was dried, ground and stored in air tight packets. Its swelling capacity was tested in the same way as described earlier.

3. RESULTS AND DISCUSSION

Sorghum starch was extracted from grains as per the method described earlier. A pure starch of 65 g per 100 g

of sorghum grain was obtained. Moisture content of the starch was found to be 10.6%. The physical parameters of sorghum starch were compared with those of the wheat starch as reported by Teli et al (Table 1) [1]. The results indicate that the transmittance for sorghum starch is higher than that for wheat starch. This may be because of the better paste clarity which is reflected in higher swelling power of sorghum starch than that of wheat starch. Lower Iodine binding value in case of sorghum starch indicates the more amount of amylopectin present in this starch as compared to that in wheat starch.

Table 1. Characterization of starch

Property of starch	Wheat starch (Lokwan)	Sorghum starch
Swelling Power(g/g)	8.067	9.83
Transmittance %	2.733	2.77
Absorbance % with Iodine	0.283	0.030

Initial experiments of grafting were carried out using acrylic acid and acrylamide monomers individually and also in 1:1 mixture at 65°C, for 2 h and with 2% initiator concentration and 1: 1.5 starch to monomer ratio. The grafted samples were then analysed for add-on values. The grafted samples were then analysed for graft add-on values, FTIR and SEM characterization.

When both the monomers namely acrylic acid and acrylamide were used in 1:1 proportion keeping overall concentration same, as shown in results from Table 2, it distinctly increased the graft add on as compared to similar values obtained for grafting of individual monomers. This occurred due to the synergistic effect of grafting of acrylic acid and acrylamide in presence of each other. Such a trend has been already reported on grafting of acrylic acid and acrylamide in presence of each other onto polyester fibre and the mechanism of synergism is also described in the same paper from our laboratory [15].

Table 2. Vinyl monomer graft add-on (%) values on starch

Sr. No.	Monomer	Graft add-on (%)
1	Acrylic acid(AA)	27.42
2	Acrylamide(AAm)	22.62
3	AA + AAm(1:1) (w/w)	48.05

3.1 Evidence of grafting on starch

FTIR spectrum of starch grafted with acrylic acid (S-g-AA) clearly shows the peak for -COOH group at 1660 cm^{-1} and that of starch grafted with acrylamide (S-g-AAm) exhibits the peak for N-H stretching vibration at 3200 cm^{-1} confirming the introduction of -NH_2 group onto the starch. These peaks were missing in case of FTIR spectrum of unmodified starch. In case of starch grafted with both acrylamide and acrylic acid mixture, both the peaks of -NH stretching and -COOH group were obtained at 3329 cm^{-1} and 1655 cm^{-1} , respectively (Fig 1).

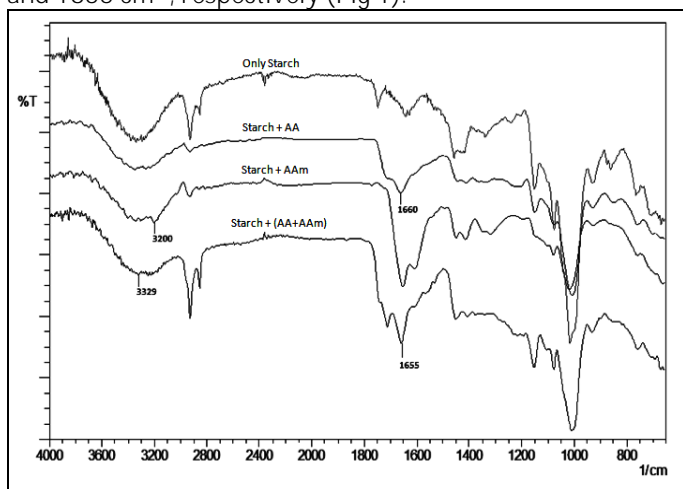


Fig 1. FT-IR analysis of ungrafted and grafted starch

The SEM images of raw and grafted starch clearly show the surface modification of the starch. While the raw starch (Fig. 2.1) depicts comparatively smoother surface, the grafted materials (Fig. 2.2) clearly show rough surface with more surface deposition of graft co-polymers.

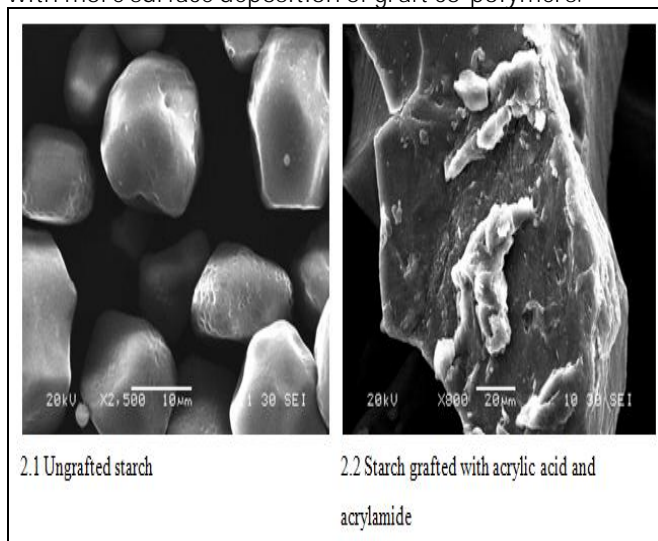


Fig. 2: SEM images of ungrafted and grafted starch

Optimization of various parameters of grafting reaction with respect to graft add-on and water absorbency of unsaponified and saponified samples was carried out and the results are shown in Table 3. The temperature of 65°C was found to be the best and below or above this temperature, the graft add-on level was lower than that at 65°C . Initial increase in graft add-on with increase in temperature may be attributed to increase in number of free radical sites and rate of diffusion of monomers due to increased mobility. However, beyond 65°C , further increase in temperature bringing down the graft add-on level may be due to either increased extent of parallel reaction of the copolymerization of monomers in the bath at the expense of grafting or the initiator radicals may be getting deactivated by recombination. With increase in time graft add-on level increased which is quite obvious. However, beyond two hours grafting period there was no significant increase in the graft add-on observed. Optimized concentration of initiator was found to be 2% on the weight of starch, whereas starch to monomer concentration was found to be 1:2. In order to retain the biodegradable nature of the final product the concentration of monomer was not further increased. Hence, optimized conditions of grafting were selected as 65°C , 2 h time, initiator concentration 2%, and starch to monomer (1:1 acrylic acid : acrylamide) ratio 1:2.

Table 3. Effect of different parameters on graft add-on and water absorbency of grafted sorghum starch

Sr No	Starch: monomer ratio (w/w)	Monomer feed AA:AAM (w/w)	Temperature (°C)	Time (hour)	Initiator concentration (%)	Graft add-on (%)*	Water absorbency of grafted starch in (g/g)*	
							Unsaponified	Saponified
1. Effect of temperature								
A	1:1	1:1	55	2	1	15.2	40.01	61.21
B	1:1	1:1	65	2	1	24.1	65.20	89.43
C	1:1	1:1	75	2	1	17.5	42.29	64.36
2. Effect of time								
A	1:1	1:1	65	1	1	4.9	14.10	25.2
B	1:1	1:1	65	2	1	24.1	65.20	89.43
C	1:1	1:1	65	3	1	24.1	62.35	90.24
3. Effect of initiator concentration								
A	1:1	1:1	65	2	0.5	14.6	35.70	45.11
B	1:1	1:1	65	2	1	24.1	65.20	89.43
C	1:1	1:1	65	2	2	30.2	69.70	110.50
D	1:1	1:1	65	2	3	22.3	64.00	94.90
4. Effect of starch: monomer								
A	1:1	1:1	65	2	2	30.2	69.70	110.50
B	1:1.5	1:1	65	2	2	48.1	83.20	152.11
C	1:2	1:1	65	2	2	70.1	95.50	225.50
5. Effect of monomer feed								
A	1:2	1:1	65	2	2	70.1	95.50	225.50
B	1:2	0.3:0.7	65	2	2	51.6	78.95	160.55
C	1:2	0.7:0.3	65	2	2	50.8	82.67	175.20

* All experiments were carried out in triplicate and the standard deviation was found to be $\pm 0.5\%$.

3.2 Absorbency of grafted starch

The water absorbency of grafted sorghum starch was found to be quite good. When the starch was grafted with mixture of acrylic acid and acrylamide (1:1 w/w), the absorbency was found to be having positive dependence on extent of graft add-on (Table 3). This grafted starch contains both carboxylic and amide groups which are polar, having capacity to form hydrogen bonds with water resulting in enhanced swelling and water absorption.

When saponified, grafted starches showed further enhancement in absorbency of water irrespective of monomers used. On saponification, $-COOH$ groups convert into $-COONa$ groups whereas $-CONH_2$ groups are converted into first $-COOH$ groups and then $-COONa$ groups. The amounts of these hydrophilic groups in turn govern the extent of water absorbency of the product. Alkali saponified S-g-(AA+AAM)1:1 (w/w) sample showed maximum water absorbency among all the samples. This phenomenon can be attributed to the highest graft add-on and combined effect of the presence of the hydrophilic groups enhancing the absorbency.

An another experiment was carried out using acrylic acid and acrylamide individually and also in 1:1 mixture at the

optimized conditions. The results of graft add-on and water absorbency are shown in Table 4. These results clearly substantiate that the 1:1 acrylic acid and acrylamide monomer mixture gives synergistic enhanced graft add-on levels as high as 70.1% and commensurately the water absorption values before and after saponification were found to be maximum i.e. 95.5 and 225.5 (g/g).

In general, those products which are able to absorb and retain water more than 100 times of their own dry weight are generally called as superabsorbents. From Table 4, it is clear that sorghum starch grafted with either acrylic acid or acrylamide or a mixture of both the monomer and saponified fall in the category of superabsorbent. Among these the product that is grafted with the 1:1 mixture of acrylic acid or acrylamide showed the highest amount of absorbency.

Table 4. Water absorbency of grafted starches

Sr No.	Product Name	Graft Add-on	Water absorbency of grafted starch (g/g)	
			Unsaponified	Saponified
1	S-g-AA	40.1	75.23	126.44
2	S-g-AAm	33.6	72.10	120.37
3	S-g-AA+AAm 1:1(w/w)	70.1	95.5	225.5

4. CONCLUSION

Sorghum starch on grafting was found to be useful for producing superabsorbent polymers. Graft add-on and water absorbency values were higher when starch was grafted with a mixture of acrylic acid and acrylamide 1:1(w/w) monomer, than when these monomers were used individually. Water absorption was further increased when the samples were saponified with alkali at higher temperature. The saponified samples of grafted sorghum starch displayed water absorbency higher than 100 g/g and thus can be categorized as superabsorbents.

ACKNOWLEDGEMENT

Authors are grateful to University Grant Commission, India for funding this project.

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BIOGRAPHIES



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