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Synthesis of superabsorbents from Amaranthus starch

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ABSTRACT

A mixture of acrylamide (AM) and acrylic acid (AA) monomers was grafted on gelatinized Amaranthus starch using potassium persulfate (KPS) as an initiator to yield superabsorbent. The effects of different parameters such as time, temperature, monomer feed (AM:AA), starch:monomers ratio and initiator concentration on graft add-on were studied, and the optimized values were found to be 2 h, 65 °C, 1:1 (w/w), 1:1(w/w) and 1% (with respect to starch powder) respectively. The product so formed was saponified with 0.1N NaOH, dried and finely powdered sample was characterized using FTIR, TGA, and XRD. Product showed maximum absorbency of 155 g/g, qualifying itself to be called as superabsorbent.

1. Introduction

Superabsorbent polymer (SAP) is a new kind of functional macromolecule developed in the past 30 years. Different kinds of SAPs are commercially prepared and used in a variety of fields such as disposable diapers, feminine napkins, soil for agriculture and horticulture, water-block tapes, and absorbent pads (Zhang & Liu, 2006). As the interest in this field is growing, newer methods are being attempted to improve the absorption properties in order to widen the application fields of superabsorbents (Li, Dong, & He, 2009). Additionally these processes are also expected to be eco-friendly.

In this context, native starches are very often tailored by modifications, to develop functional properties, such as solubility and absorbency. Polysaccharide based starch hydrogels (SHs) have emerged as promising substitutes for SAPs for they are nontoxic and biodegradable materials and the basic raw material is widely available in the nature (Park, Shalaby, & Park, 1993).

Amaranthus is a plant leaves of which can be eaten as a vegetable and its seeds are used as a cereal grain (Teutonico & Knorr, 1985). Due to the utility of the whole plant and its resistance to drought and hot climate, Amaranthus has a great economical potential. The worldwide annual production of Amaranthus has been estimated to be over at 470,000 ton (Lehmann, 1996). Besides the relative high content of starch (about 60%), particular interest in this polymer is based on its small granule size, 1–3 μm, and low amylose content, 5–8% (Stone & Lorenz, 1984)

Starch constitutes the main component of amaranth grain and plays an important role in its food applications, such as for food thickeners for soups, fat replacers, gravies and sauces, and in breakfast cereals, muffins, cookies, snacks, pastas and health food. Other current and potential commercial uses of amaranth starch are in cosmetics, biodegradable films, paper coatings and laundry starch (Choi, Kim, & Shin, 2004; Teli, Shanbag, Kulkarni, & Singhal, 1996).

The present paper discusses work on application of Amaranthus starch as base material for synthesis of superabsorbent polymer, vis-à-vis wheat starch in order to explore its potential to substitute wheat starch.

2. Experimental

2.1. Material

Amaranthus cereals (Amaranthus paniculate, ash content 4%, moisture content 13%, starch content 60%) used for extraction of starch were obtained from local grocery shop. Chemicals used were of laboratory grade. Acrylic acid (AA), acrylamide (AM), potassium per sulfate, methanol, ethanol and other chemicals were supplied by S.D. Fine Chemical Pvt. Ltd.

2.2. Method

2.2.1. Extraction of starch

The starch was extracted from Amaranthus and wheat using alkali steeping method (Yanez & Walker, 1986). The grains were ground to coarse flour and 20 g wheat was treated 5 times with 500 ml of 0.25% NaOH each, for 4 h followed by draining, and washing it thoroughly until free of NaOH. The grains were ground in a

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warring blender and the slurry obtained was then passed through a 200 mesh bolting cloth and squeezed to extract the crude starch. The extract obtained was kept overnight until separation of two layers. Upper layer was drained and lower layer was centrifuged at 4000 rpm for 10 min. The upper proteineous portion was scrapped and starch obtained was dried in an oven at 50 °C. The starch was then ground to 60 mesh and stored in an air tight container under refrigeration to avoid microbial or fungal attack.

3. Physical characterization of starch

3.1. Swelling power

The estimation of swelling power was carried out using the method reported by Subramanian, Hoseney, and Bramel-Cox, (1994). Starch (0.6 g) was heated with 30 ml of distilled water at 95 °C for 30 min. Lump formation was prevented by stirring this mixture at every 5 min interval. The mixture was then cooled and centrifuged (using CRU-5000 centrifuge) at 5000 rpm for 15 min. The supernatant liquid was carefully removed and the swollen starch sediment was weighed. Swelling power (g/g) was calculated as the ratio of the weight of the wet sediment to the initial weight of the dry starch.

3.2. Paste clarity

The paste clarity was measured using the method of Craig, Maningat, Seib, & Hoseney (1989). 250 mg of starch sample was suspended in 20 ml of distilled water in a 40 ml test tube with plastic cap. The tubes were then placed in a boiling water bath for 30 min, shaken thoroughly every 5 min and then cooled to room temperature (25–30 °C) for about 10 min. The percent transmittance (%*T*) was determined at 650 nm against water as blank on a UV-1201 spectrophotometer (Shimadzu, Japan).

3.3. Estimation of iodine binding

The amylose content of starch was measured colorimetrically using the iodine method (Juliano, 1971; Teli et al., 1996). The sample (100 mg) was weighed accurately and placed into a 50 ml Erlenmeyer flask, to which 1 ml of 95% ethanol and 9 ml of 1 N NaOH were added. The sample was heated for 10 min in boiling water to gelatinise the starch. After cooling, the gelatinized sample to room temperature, it was transferred to 100 ml volumetric flask; then the total volume was made to 100 ml by adding distilled water. The starch solution (5 ml) was pipetted into a 100 ml volumetric flask and 1 ml of 1N 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 added. The solution was diluted to 100 ml with distilled water, shaken and then allowed to stand for 20 min. The absorbance was then measured at 620 nm using UV-1201 spectrophotometer (Shimadzu, Japan).

4. Grafting of starch

A round bottom flask equipped with reflux condenser and a nitrogen inlet was used to carry out grafting reaction. To control the reaction temperature, the flask was placed in a thermostated water bath. The starch slurry was prepared by adding 10 g of starch in 300 ml water. Gelatinized starch was obtained by heating the slurry at 90 °C in the flask for 30 min. Gelatinized starch was cooled to 65 °C and 1% (on wt. of starch) potassium persulfate was added to it, to produce free radicals onto starch followed by addition of monomer (AA or AM or AA:AM) after 15 min. The reaction (gelatinization, initiation, and propagation) was carried out under nitrogen atmosphere and the mixture was stirred continuously. At the end of reaction (2 h after addition of monomer) the product was precipitated in methanol, filtered and dried at 60 °C in an oven to a constant weight (Qudsieh et al., 2004). The homopolymers formed during the graft-copolymerization reaction, was separated from the grafted polymer by Soxhlet extraction for 8 h. Morpholine was used as solvent for homopolymer extraction in case of grafting of starch with acrylamide. The homopolymers of acrylic acid was extracted using ethanol–water mixture (80:20). To ensure the complete removal of the homopolymer, the above extraction was carried out three times for each sample till the constant weight of grafted starch was obtained. Graft add-on (%) was calculated as follows (Fakhru'l-Razi, Qudsieh, Wan Md, Zaki, & Rahman, 2001).graft add-on (%) = $\frac{W_2-W_1}{W_1} \times 100$where in, W_1 and W_2 are the weights of Amaranthus starch and Amaranthus grafted starch, respectively.

5. Chemical characterization

5.1. IR

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 4000–600 cm^{-1}.

5.2. TGA

The thermograms of Amaranthus starch and grafted Amaranthus starch sample were recorded using Shimadzu 60H DTG using aluminum pan between temperature range 30 and 500 °C and under inert atmosphere of N_2 at a flow rate of 50 ml/min.

5.3. XRD

5.3.1. X-ray diffraction analysis

X-ray Diffraction analysis was carried out to determine the changes in crystallinity of Amaranthus and wheat starch using XRD 6000 (Shimadzu, Japan) at an angular (2θ) range of $4°–32°20'$. In order to have precise results XRD analysis was carried at four different places for both the starches and the average % crystallinity was calculated. From the radial scans of intensity versus 2θ, the lateral order or the crystallinity index was determined using Shimadzu's crystallinity software.

6. Water absorbency measurement

The dry sample was weighed (0.2 g) and 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 (Chen, Zhang, Luo, & Fang, 2004):

$$\text{water absorbency (g/g)} = \frac{M_2 - M_1}{M_1}$$

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

7. Results and discussion

The starches from Amaranthus and wheat were extracted and characterized. These results indicate that the swelling power of the wheat starch (6.23) and Amaranthus starch (6.01) were comparable. The transmittance value of wheat starch (2.75) and that of

Table 1
Physical characteristics of starch.

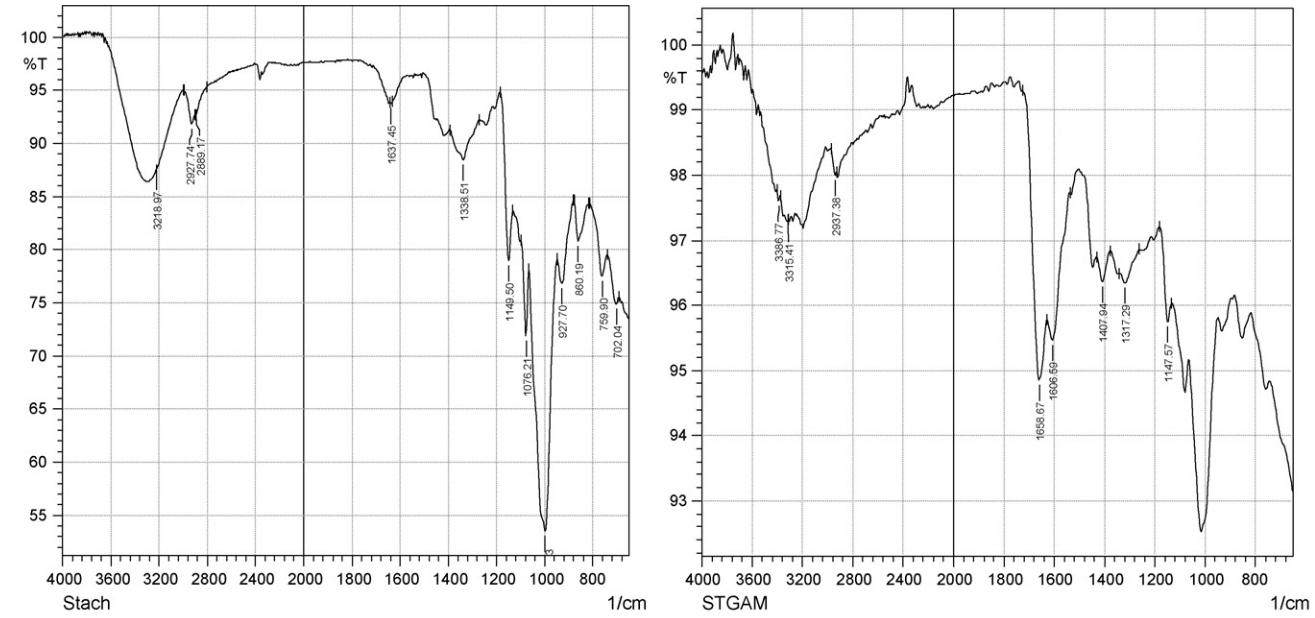
Sr. no.	Characteristics	Amaranthus starch	Wheat starch
1	Iodine binding	0.031	0.283
2	Average Crystallinity (%)	45	30

Amaranthus starch (2.64) were also found to be similar. The results in Table 1 indicate the lower iodine binding capacity of Amaranthus starch than that of wheat starch which shows less amylose content of the former.

X-Ray Diffraction analysis was done to determine the amorphous and crystalline structure of the starches and the crystallinity (%) was calculated by using reported formula. The crystallinity of Amaranthus starch was 45.80% and that of wheat starch was 30.48% (refer Table 1). Higher crystallinity of Amaranthus is because of amylopectin (98%) being its major constituent which significantly contributes to the orientation of chain molecules. For wheat starch the presence of amylose along with amylopectin reduces the orientation and hence reduces the overall crystallinity too.

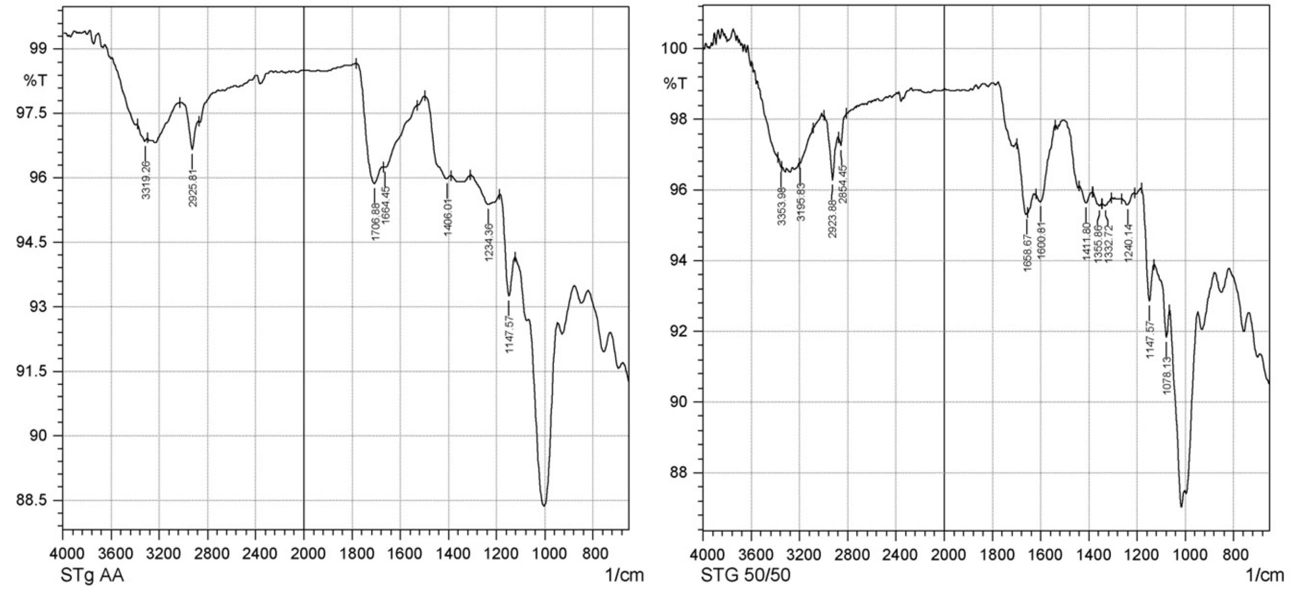
7.1. *Evidence of grafting on starch*

The FTIR spectrum of starch grafted with Acrylamide (St-g-AM) (Fig. 1.2) clearly indicates the peak for N-H stretching vibration at 3387 cm^{-1} which confirms the introduction of NH_2 group after grafting of starch with acrylamide, which otherwise was missing in ungrafted starch (Fig. 1.1). In case of Starch grafted with Acrylic acid (St-g-AA) (Fig. 1 Fig. 1.3), the peak for –COOH group was obtained at 1707 cm^{-1} while for starch grafted using mixture of acrylamide and acrylic acid (St-g-AM-AA1:1) (Fig. 1.4) the peak for –NH stretching



1.1 Starch

1. 2 St-g-AM



1.3 St-g-AA

1. 4 St-g-1:1(AM: AA)

Fig. 1. FTIR spectra of Amaranthus starch and grafted Amaranthus starch. (1.1) Starch, (1.2) St-g-AM, (1.3) St-g-AA, (1.4) St-g-1:1 (AM:AA).

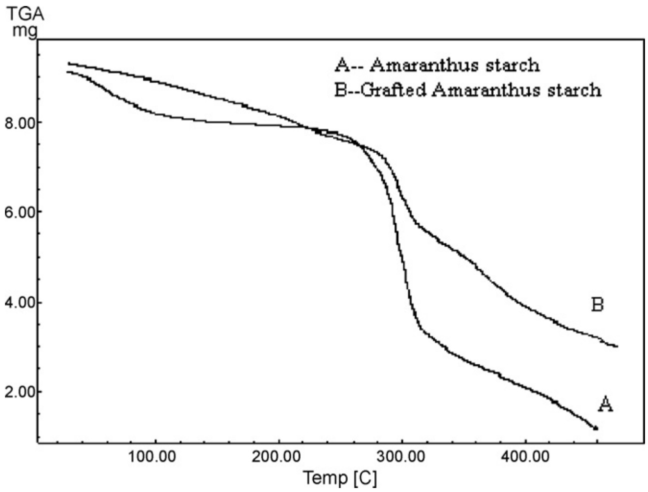


Fig. 2. TGA of Amaranthus St-g-AM:AA, 1:1 (w/w) and Amaranthus starch.

as well as for –COOH were obtained at 3354 cm^{-1} and 1660 cm^{-1}, respectively.

Fig. 2 shows the thermogram of Amaranthus and grafted starch. In the initial stage weight loss values of both the samples were 16% and 17% at 250 °C, respectively. Beyond this temperature, the drastic decomposition of the sample resulted in to significant weight loss which was 56% for Amaranthus and 27% for grafted starch at 350 °C. However, beyond 350 °C the loss in weight was slowed down and finally at 500 °C, weight loss values observed were 92% for Amaranthus and 65% for grafted starch, respectively. This clearly indicates that the grafted starch sample showed relatively higher thermal stability as compared to that of ungrafted Amaranthus starch. This could be attributed to the formation of crosslinked network as a result of grafting of mixture of vinyl monomers on to a starch.

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

Sr. no.	Monomer	Graft add-on (%)	
		Amaranthus starch	Wheat starch
1	Acrylamide (AM)	28.00	30.6
2	Acrylic acid (AA)	20.00	22.1
3	AM:AA 1:1 (w/w)	36.00	38.1

The results in Table 2 indicate that, good degree of grafting on both the starches to the tune of 28% and 31% was observed in case of AM and about 20% and 22% in case of AA. In general wheat starch gave marginal but distinct increase in graft add-on values with the monomers studied. This may be attributed to its lower crystallinity as well as linear chain molecular structure due to higher amylose content. When both these monomers were taken in mixture (1:1 proportion) keeping the overall concentration same (1:1 starch to total monomer ratio), it distinctly enhanced the level of grafting. This may be attributed to synergistic influence of AM on grafting of AA and that of AA on grafting of AM on to the natural biopolymer. Similar trend has been already reported in case of grafting of AA and AM on polyester fibre (Lokhande & Teli, 1984). It has been attributed to the possibility of acrylamide (AM) and acrylic acid (AA) monomer molecules present in solution of the mixture, in the form of labile complex, and extent of its formation seems to have considerable influence in changing the extent and rates of reaction during the grafting process. It is reported that:

- Due to the complex formation, mobility of the individual reacting species in the solution gets reduced, thereby retarding the rate of homopolymerisation.
- When one monomer molecule diffuses inside the polymer structure it automatically carries another monomer present in the complex, thus increasing the monomer concentration in the polymer phase – a very favorable situation for higher graft-co-polymer formation.
- When the monomer molecule reacts with the free radical on the backbone of polymer chain molecule, the chain propagation is enhanced due to the complex, and hence higher amount of molecules is utilized resulting in synergistic influence (Lokhande & Teli, 1984).

Results in Table 3 show the effect of various parameters of reaction on water absorbency of the final product. The optimized conditions for highest absorbency were temperature 65 °C, time

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

Sr. No.	Starch :monomer ratio (w/w)	Monomer feed AA:AM (w/w)	Temperature (°C)	Time (h)	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	30	72	108
B	1:1	1:1	65	2	1	36	93	155
C	1:1	1:1	75	2	1	31	80	140
2. Effect of time								
A	1:1	1:1	65	1	1	20	71	105
B	1:1	1:1	65	1.5	1	30	80	120
C	1:1	1:1	65	2	1	36	93	155
D	1:1	1:1	65	2.5	1	36	93	155
3. Effect of monomer feed								
A	1:1	0.3:0.7	65	2	1	25	60	110
B	1:1	1:1	65	2	1	36	93	155
C	1:1	0.7:0.3	65	2	1	28	70	120
4. Effect of initiator								
A	1:1	1:1	65	2	0.5	20	58	100
B	1:1	1:1	65	2	1	36	93	155
C	1:1	1:1	65	2	1.5	31	80	120
5. Effect of monomer ratio								
A	1:0.5	1:1	65	2	1	20	65	100
B	1:1	1:1	65	2	1	36	93	155

Table 4
Water absorbency of grafted starches.

Sr. no.	Product name	Water absorbency of grafted starch (g/g)			
		Amaranthus starch		Wheat starch	
1	St-g-AM	27.1	112.4[a]	30.6	122.4[a]
2	St-g-AA	30.1	55.2[a]	32.0	60.3[a]
3	St-g-AM:AA 1:1 (w/w)	92.7	155[a]	98.0	166[a]

[a] Saponified samples.

2 h, initiator concentration 1% with respect to starch and monomer mixture concentration 1:1(w/w). Either side of these optimized conditions, product shows the decrease in water absorbency, which may be attributed to reduced extent of grafting due to not so favorable conditions of reactions.

7.2. Absorbency of grafted starch

The water absorbency (as explained in experimental part) of grafted wheat starch is found to be higher than that of grafted Amaranthus starch (refer Table 4). This is because of lower Crystallinity of wheat starch as compared to that of Amaranthus. Also slightly higher graft add-on values in case of the former may also result in enhancing water absorbency further.

The starch when grafted with 1:1 (w/w) mixture of AM and AA, absorbency was found to be higher, as compared to that grafted with individual monomers irrespective of the type of the starch. This is obvious due to the increased add-on observed using mixture of monomers of AM and AA. The grafted starch contains both –COOH and $–CONH_2$ functional groups and this mixed system is more efficient water absorbent than individual AM and AA grafted starch samples. Both these monomers are quite polar and thus form H-bonds with water, showing enhanced swelling, extent of which is directly dependent on extent of graft add-on.

Saponified grafted starches showed increased water absorbency irrespective of the type of monomer or starch. In case of St-g-AA, the –COOH groups are converted to –COONa groups after alkali treatment. Similarly in case of St-g-AM, the $–CONH_2$ groups are converted to –COOH and –COONa groups in saponification. The effect of various parameters of saponification on conversion of $–CONH_2$ to –COOH and –COONa is explained in the literature (Wu, Wei, Lin, & Lin, 2003). The amount and variety of hydrophilic groups such as $–CONH_2$, –COONa and –COOH will govern the absorbency of superabsorbents. The absorbency behavior may be interpreted by postulating that the collaborative absorbent effect of $–CONH_2$, –COONa and –COOH groups is superior to that of single $–CONH_2$, –COONa and –COOH groups (Wu et al., 2003).

The water absorbency of alkali treated St-g-AM:AA (1:1) was found to be highest among all the samples. This may be attributed to highest graft add-on and the combined effect of mixture of functional groups enhancing the absorbency.

In general the superabsorbents are expected to be absorbing the water more than 100 times (or >1000%) that of their own weight (Wang, Ge, & Zheng, 2005; Zhang, Wang, & Wang, 2007). The results in Table 4 clearly indicate that saponified samples, both Amaranthus and wheat starches i.e. of St-g-AM, and St-g-AM:AA fall in the category of superabsorbents. Similarly since the mixture of monomers in 1:1 proportion when used for grafting, results in enhanced level of grafting due to synergism, there is clear potential of such sample to qualify to be superabsorbents even before saponification.

8. Conclusion

The level of grafting in Amaranthus and wheat starches was found to be comparable and hence starch obtained from Amaranthus can be used as an alternative for the preparation of superabsorbent materials without significant loss in performance. This can eventually lessen the burden on wheat, which is used as food grain by the masses. The graft add-on values and consequently water absorbency values were higher in case of grafting using mixture of AM and AA in 1:1 ratio (w/w). The water absorbency however, increased after alkali treatment or saponification of grafted materials. The saponified samples i.e. St-g-AM, both Amaranthus and wheat and St-g-AM:AA (1:1) qualified to be called as superabsorbents. This presents one more avenue for utilization of Amaranthus starch, for high value products.

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