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Synthesis of superabsorbent from carbohydrate waste

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ABSTRACT

A mixture of acrylamide (AM) and acrylic acid (AA) monomers were grafted on germinated gelatinized wheat 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, 60 °C, 1:1 (w/w), 1:1(w/w) & 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 FT-IR, TGA. Product showed maximum absorbency of 150 g/g.

1. Introduction

Superabsorbent polymers (SAPs) are materials that have the ability to absorb and retain large volumes of water and aqueous solutions. Although there is no specific definition of Super absorbent mentioned in the literature, a number of authors have cited their products of enhanced water absorbency, as "superabsorbent" when , in general the absorbency level was found to be more than 100 times (or >1000%) (Wang, Ge, & Zheng, 2005; Zhang, Wang, & Wang, 2007). This makes them ideal for use in water absorbing applications such as baby nappies, sanitary napkins, agriculture and medicine for drug-delivery system (www.functionalpolymers.basf.com/porta-l/streamer?fid=291074).

Over the past five decades, superabsorbent hydrogel (SHs) have received particular attention as promising material for a series of applications in which the efficient use of water is required such as soil conditioning and disposables. From physical and chemical characteristics points of view, SHs are three-dimensional polymer network capable of expanding upon contact with water which results in the absorption and retention of large amount of liquid (Ratner and Hoffman, 1976).

Recently, there has been increasing interest in the processes which do not cause damage to environment or living organisms. In this context, native starches are very often tailored by modifications. To develop functional properties, such as solubility and absorbency polysaccharide based SHs have emerged as promising substitutes for they are nontoxic and biodegradable materials and are widely available in the environment (Park, Shalaby, & Park, 1993).

In India, untimely rains and hail storms at harvest time and inadequate storage facility for the food grains, a lot of wheat, maize, jowar, rice etc. often get dampened and damaged and these grains slowly start germinating making them unacceptable for edible consumption (Pandey & Raja, 1992). Preharvest sprouting occurs in wet or humid conditions in many regions of the world, including Northwest Europe, North and South America, Australia and New Zealand (Rohera, 2007). This carbohydrate waste instead of dumping can be effectively utilized for extraction of starch which can be used in textiles for sizing and printing. The present paper discusses work on application of germinated wheat starch as base material for synthesis of superabsorbent polymer.

2. Experimental

2.1. Materials

"Lokawan" variety of wheat (Gluten content 14%, Moisture content 11%, Ash content 4%) commonly grown in India was used for extraction of starch. Chemicals used were of laboratory grade. Acrylic acid, acrylamide, potassium per sulfate, methanol, ethanol and other chemicals were supplied by S.D. Fine Chemical Pvt. Ltd.

2.2. Methods

2.2.1. Germination

Germination of wheat was done by imitating the actual poor conditions during storage. Wheat grains were packed and allowed to suffocate in a jute sack. Sprinkling of water was done every 2 h

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for 24 h to keep it in a damp condition. After 24 h the grains were removed and without rinsing, they were completely dried in an oven at 50 °C.

2.2.2. Extraction of starch

Extraction of starch was done by alkali steeping method (Yanez & Walker, 1986). The grains were ground to coarse flour and 20 g wheat was treated five 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 waring 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

Swelling power was determined by the method reported by Subramanian and coworkers. (Subramanian et al., 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

Measurement of paste clarity was carried out by method of Craig and coworkers (Craig, Maningat, Seib, & Hoseney, 1989). Starch sample (250 mg) 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).

4. Grafting of starch

The grafting reaction was carried out in a round bottom flask equipped with reflux condenser and a nitrogen inlet. 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 wheat starch was obtained by heating the slurry at 85 °C in the flask for 30 min. Gelatinized starch was cooled to 60 °C 1% (on wt. of starch) potassium persulphate 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 starch grafting 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 (%) calculated as follows (Fakhru'l-Razi et al., 2001)

$$\text{Graft add-on, }\% = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

where in, W_1 and W_2 are the weights of wheat starch and grafted starch, respectively.

5. Chemical characterization

5.1. IR spectra

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 to 600 cm^{-1}.

5.2. TGA

The thermograms of germinated starch and grafted starch sample were recorded using Shimadzu 60H DTG using aluminum pan between temperature range 30–510 °C and under inert atmosphere of N_2 at a flow rate of 50 ml/min.

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 by formula (Chen, Zhang, Luo, & Fang, 2004)

$$\text{Water absorbency (g/g)} = \frac{(M_1 - M_2)}{M_2} \qquad (2)$$

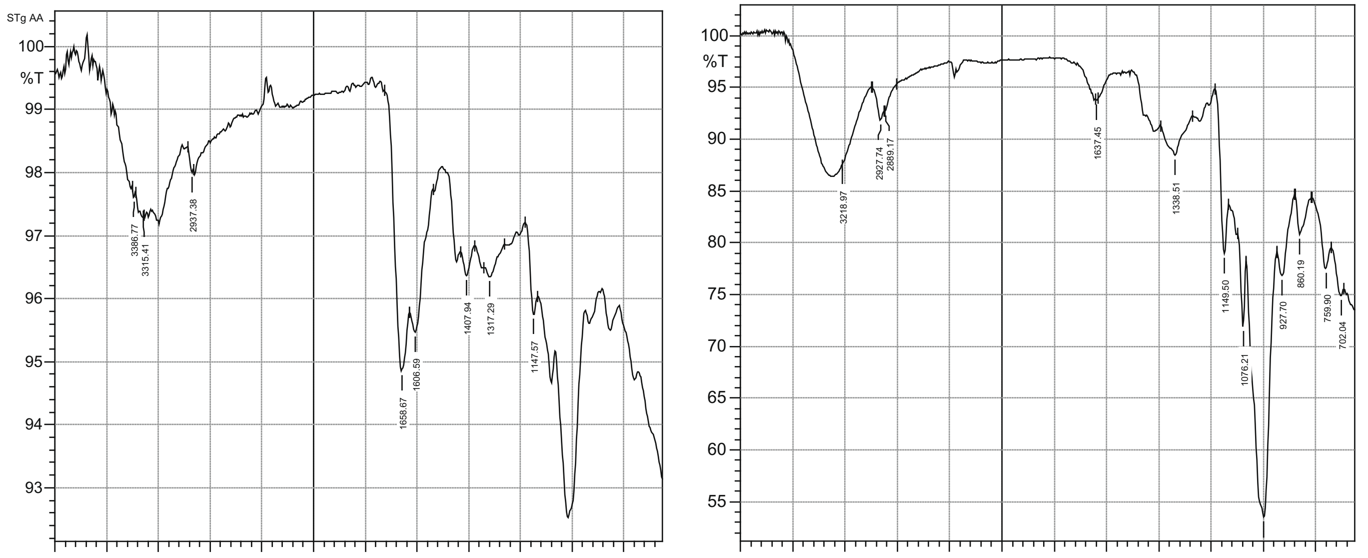
where in, M_1 and M_2 are weight of fully swollen hydrogel and of dry sample, respectively.

7. Results and discussion

The starches from germinated and non-germinated wheat were extracted, characterized and the results are given in Table 1. These results indicate that the swelling power of the non-germinated wheat starch is 1.36 times of that of germinated one. The transmittance is also higher for non-germinated starch than that of germinated one because of the better paste clarity which was consequent to higher swelling power. The enhanced iodine binding capacity of germinated starch shows relative increase in amylose content as a result of germination.

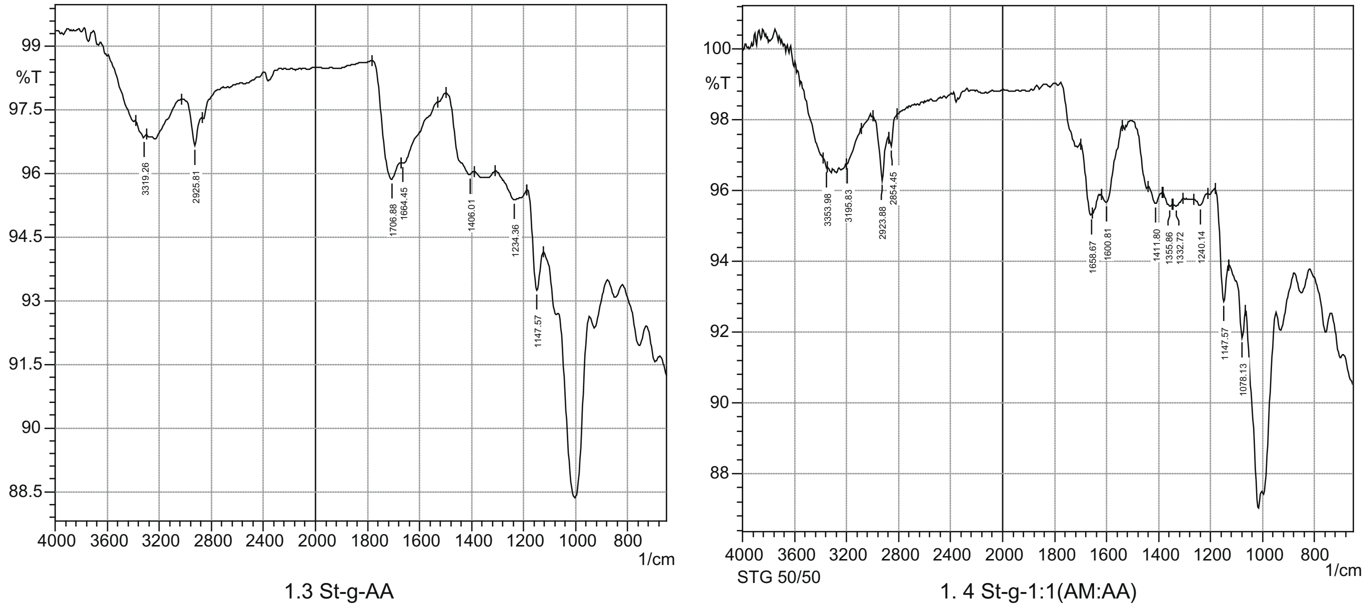
Table 1
Effect of germination on characteristics of starch.

Sr. no.	Characteristics	Germinated starch	Non-germinated starch
1	Swelling power (g/g)	5.932	8.067
2	Transmittance of starch paste (%)	2.266	2.733
3	Iodine binding	0.371	0.283



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 germinated starch and grafted germinated starch. 1.1, starch; 1.2, St-g-AM; 1.3, St-g-AA; 1.4, St-g-1:1 (AM:AA).

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 3386 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. 1.3) the peak for –COOH group was obtained at 1706 cm^{-1} while for starch grafted using mixture of acrylamide and acrylic acid (St-g-AM-AA1:1) (Fig. 1.4) shows the peak for –NH stretching as well as –COOH at 3353 cm^{-1} and 1710 cm^{-1}, respectively.

Fig. 2 shows the thermogram of germinated and grafted starch. In the initial stage weight loss values of both the samples were 11% and 9% at 270 °C (refer A′ and A in the figure), respectively. However, beyond this temperature drastic decomposition of the sample resulted in to significant weight loss which was 58% for germinated and 28% for grafted starch at 330 °C (refer B′ and B in the figure). However, beyond this temperature loss in weight was slowed down and finally at 510 °C, weight loss values of 94% and 66% were observed (refer C′ and C in the figure). This clearly indicates that the grafted starch sample showed relatively higher thermal stability as compared to that of ungrafted germinated starch. This could be attributed to the formation of crosslinked network as a result of grating of vinyl monomers.

The results in Table 2 indicate that good degree of grafting to the tune of 30% and 31% was observed in case of AM and about 20% and 21% in case of AA. In general the germinated and non-germinated starches gave comparable graft add-on with the monomers studied. When both these monomers were taken in mixture in 1:1 proportion keeping the overall concentration same (1:1 starch to total monomer ratio), distinctly enhanced level of grafting was observed. This may be attributed to synergestic influence of AM on grafting of AA and that of AA on grafting of AM. This has been already reported in case of grafting of AA and AM on polyester fibre (Lokhande & Teli, 1984). It has been attributed to possibility of Acrylamide (AM) and acrylic

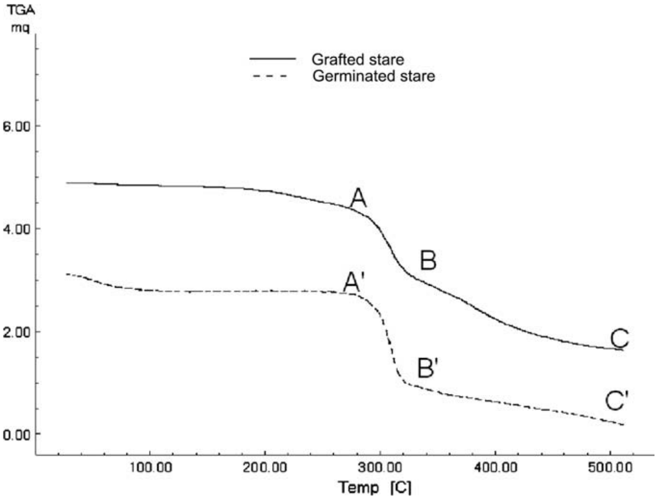


Fig. 2. TGA of germinated St-g-AM: AA, 1:1 (w/w) and germinated starch.

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

Sr. no.	Monomer	Graft add-on (%)	
		Germinated starch	Non-germinated starch
1	Acrylamide (AM)	30	31
2	Acrylic Acid (AA)	20.4	21.2
3	AM:AA 1:1 (w/w)	35	36.7

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.

- Due to the complex formation, mobility of the reacting species in the solution gets reduced, thereby retarding the rate of homopolymerisation.

Table 4
Water absorbency of grafted starches.

Sr. no.	Product name	Water absorbency of grafted starch (g/g)	
		Germinated starch	Non-germinated starch
1	St-g-AM	26.8 (110.4)*	31.2 (125.3)*
2	St-g-AA	29.7 (49.9)*	31.0 (55.4)*
3	St-g-AM:AA1:1 (w/w)	87.2 (150)*	95.0 (163.5)*

* Corresponds to saponified samples.

- 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-copolymer 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 synergestic 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 60 °C, time 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 non-germinated starch is found to be higher than that of grafted germinated starch (refer Table 4). This is because of relatively higher graft add-on obtained in case of grafting on non-germinated starch than that on germinated starch and also its higher molecular weight as compared to germinated one.

Table 3
Effect of different parameters on graft add-on and water absorbency of modified germinated starch.

Sr. no.	Starch monomer ratio (w/w)	Monomer feed AA:AM (w/w)	Temp (°C)	Time (h)	Initiator concn. (%)	Graft add-on (%)	Water absorbency of grafted starch	
							Unsaponified	Saponified
1. Effect of temperature								
A	1:1	1:1	50	2	1	27	70	110
B	1:1	1:1	60	2	1	35	90	150
C	1:1	1:1	70	2	1	32	80	140
2. Effect of time								
A	1:1	1:1	60	1	1	24	70	110
B	1:1	1:1	60	1.5	1	30	80	120
C	1:1	1:1	60	2	1	35	90	150
D	1:1	1:1	60	2.5	1	35	90	150
3. Effect of monomer feed								
A	1:1	0.3:0.7	60	2	1	20	50	100
B	1:1	1:1	60	2	1	35	90	150
C	1:1	0.7:0.3	60	2	1	30	70	120
4. Effect of initiator								
A	1:1	1:1	60	2	0.5	20	50	100
B	1:1	1:1	60	2	1	35	90	150
C	1:1	1:1	60	2	1.5	31	80	120
5. Effect of monomer ratio								
A	1:0.5	1:1	60	2	1	20	65	100
B	1:1	1:1	60	2	1	35	90	150

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 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 affect 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 that of their own weight. The results in Table 4 clearly indicate that alkali treated or saponified samples of St-g-AM, both the germinated and non-germinated and St-g-AM:AA fall in the category of superabsorbents. Similarly the mixture of monomers when used for grafting, due to synergism giving enhanced level of grafting on the starch, there is clear potential of such sample to qualify to be superabsorbents even before saponification.

9. Conclusion

The level of grafting in germinated and non-germinated starches was found to be comparable and hence starch obtained from germinated wheat which is otherwise treated as carbohydrate waste could be used effectively for the preparation of superabsorbent materials without significant loss in performance. 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 germinated and non-germinated and St-g-AM:AA (1:1) qualified to be called as superabsorbents.

References

Chen, P., Zhang, W., Luo, W., & Fang, Y. (2004). Synthesis of superabsorbent polymers by irradiation and their applications in agriculture. *Journal of Applied Polymer Science, 93*(4), 1748–1755.

Craig, S. A., Maningat, C. C., Seib, P. A., & Hoseney, R. C. (1989). Starch paste clarity. *Cereal Chemistry, 66*, 173–182.

Fakhru'l-Razi, A., Qudsieh, I. Y. M., Wan Md, Z. W., Zaki, Ab., & Rahman, M. Z. (2001). Graft copolymerization of methyl methacrylate onto sago starch using ceric ammonium nitrate and potassium persulfate as redox initiator systems. *Journal of Applied Polymer Science, 82*(4), 1375–1381.

Juliano, B. O. (1971). A simplified assay for milled rice amylose. *Cereal Science Today, 16*, 334–360.

Lokhande, H. T., & Teli, M. D. (1984). Grafting onto polyester fibers. IV. Synergism during graft copolymerization of binary mixtures of vinyl monomers onto polyester fibers. *Journal of Applied Polymer Science, 29*(5), 1843–1856.

Pandey, A., & Raja, K. C. M. (1992). Recent trends in carbohydrate research. *Proceedings of eighth conference* (p. 248). Trivandrum, India.

Park, K., Shalaby, W. S. W., & Park, H. (1993). *Biodegradable hydrogels for drug delivery* (pp. 35–66). Basel: Technomic Publishing.

Qudsieh, I. Y. M., Fakhru'l-Razi, A., Muyibi, S. A., Mansor, B., Ahmad, M. Z., Rahman, Ab., et al. (2004). Preparation and characterization of poly (methyl methacrylate) grafted sago starch using potassium persulfate as redox initiator. *Journal of Applied Polymer Science, 94*(5), 1891–1897.

Ratner, B. D., & Hoffman, A. S. (1976). In Andrade (Ed.), *Hydrogels for medical and related applications* (pp. 1–29). Washington, DC: ACS.

Rohera, P. (2007). *Studies in process intensification*. M.Tech. Thesis. University of Mumbai.

Subramanian, V., Hoseney, R. C., & Bramel-Cox, P. (1994). Shear thinning properties of sorghum and corn starches. *Cereal Chemistry, 71*, 272–275.

Wang, Y.-J., Ge, J.-H., & Zheng, Y. D. (2005). Carboxymethyl-cellulose superabsorbent materials prepared by two-step heating process. *Huaxue Gongcheng/Chemical Engineering (China), 33*(5), 50–52.

Wu, J., Wei, Y., Lin, J., & Lin, S. (2003). Preparation of a starch-*graft*-acrylamide/kaolinite superabsorbent composite and the influence of the hydrophilic group on its water absorbency. *Polymer International, 52*, 1909–1912.

Yanez, G. A., & Walker, C. E. (1986). Effect of tempering parameters on extraction and ash of pros millet flours, and partial characterization of proso starch. *Cereal Chemistry, 63*, 164–167.

Zhang, J., Wang, L., & Wang, A. (2007). Preparation and properties of chitosan-g-poly(acrylic acid)/montmorillonite superabsorbent nanocomposite via in situ intercalative polymerization. *Industrial and Engineering Chemistry Research, 46*(8), 2497–2502.