

Graft copolymerization of acrylic acid onto gelatinized potato starch for removal of metal ions and organic dyes from aqueous system

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Received: 14 March 2012, Revised: 28 April 2012, and Accepted: 30 April 2012

ABSTRACT

The graft copolymerization of acrylic acid onto gelatinized potato starch has been carried out at 70 °C using chromic acid as an initiator. The different reaction parameters such as reaction temperature, initiator and monomer concentrations were optimized to get the maximum percentage grafting. The maximum grafting (93.54%) was observed at 60 °C, 0.57 molL⁻¹ of acrylic acid and 0.03 mmolL⁻¹ of chromic acid. The grafted samples were evaluated for other physico-chemical properties such as swelling behavior, moisture absorption and chemical resistance. The grafted samples were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) techniques. The graft copolymers have been successfully used for the removal of metal ions and organic dyes from aqueous system. Copyright © 2012 VBRI Press.

Keywords: Potato starch; acrylic acid; graft copolymerization; metal ions.



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Introduction

Polysaccharides are polymeric carbohydrate structures which are formed by repeating units joined together by glycoside linkages and contain various degrees of branching. Polysaccharides have a general formula C_x(H₂O)_y where y is usually a large number between 200 and 2500. Starch and glycogen are storage polysaccharides whereas cellulose and chitosan act as the structural materials. They provide mechanical strength to plants [1] which make them fit for applications like fibers [2], films [3], adhesives [4], melt processing plastics [5], hydrogels [6], drug delivery agents [7] and emulsifiers [8]. Modification of polysaccharides through graft copolymerization improves the properties of natural polysaccharides. Grafting is known to improve the characteristic properties of the backbones. Starch is a

at a scan speed of 20/min. TGA measurements were made on Perkin Elmer Pyris Diamond thermal analyzer in air at heating rate of 10 °C/min. The surface morphologies of the starch and graft copolymers were studied with the help of scanning electron microscope (Leo 435 VP).

Physico-chemical behaviour of graft copolymers

Swelling studies: Swelling studies were carried out on original starch and starch-g-copolymers in water, carbon tetrachloride and n-butanol. For this study, 40 mg of sample was kept in 20 ml of solvent for 24 hours at room temperature. Then after filtration, the surface water on the swollen sample was removed by softly pressing between the folds of filter paper. An increase in weight was noted. Percent swelling (P_s) was calculated as follows:

$$P_s = \frac{W_f - W_i}{W_i} \times 100$$

where W_f is the weight of the swollen polymer and W_i is the weight of dry polymer.

Moisture absorption behavior: A sample of known weight was placed in the humidity chamber maintained at a definite humidity level for 2 hours. After 2 hours, sample was taken-out and final weight was noted immediately. Percent moisture absorbance was calculated as follows [20].

$$\% M_{abs} = \frac{W_f - W_i}{W_i} \times 100$$

where W_i is the initial weight of the sample and W_f is the final weight of the sample.

Chemical resistance

Chemical resistance of graft copolymers was studied as a function of percent weight loss by immersing the known weight of grafted sample in the solution of HCl and NaOH of known concentrations for 72 hours. The samples were then taken out and dried to constant weight in hot air oven. The final weight of the sample was noted and percent weight loss was calculated by the following expression:

$$\% \text{ Weight loss} = \frac{W_i - W_f}{W_i} \times 100$$

where W_i is the initial weight of the sample and W_f is the final weight of the sample.

Applications of starch graft copolymers

Removal of metal ions: In this study, graft copolymer was used for removal of three metal ions namely magnesium, nickel and zinc from water system. Adsorption was carried out by stirring 0.04 g of grafted starch for 30 minutes in 25 ml solution containing ions (Ni, Zn, Mg). After filtration, the remaining metal ions in the filtrate were determined.

$$\% \text{ Adsorption} = \frac{C_o - C_e}{C_o} \times 100$$

Dye adsorption behavior: The graft copolymers were used for dye adsorption behavior. The known weight of grafted sample was put into the solution of different concentration of methylene blue for 3 hours. Then after filtration, the absorbance of the filtrate was determined at 663 nm using UV-visible spectrophotometer.

$$\text{Dye Adsorption } (q_e) = \frac{C_o - C_e}{W} \times V$$

where q_e is amount of dye adsorbed, C_o is the initial concentration, C_e is the adsorption of sample, V is volume and W is the weight of starch-g-copolymer respectively.

Results and discussion

Optimization of grafting parameters

The maximum grafting of 93.54% was obtained at optimized reaction temperature (60 °C), monomer concentration (0.57 molL⁻¹) and initiator concentration (0.03 mmolL⁻¹).

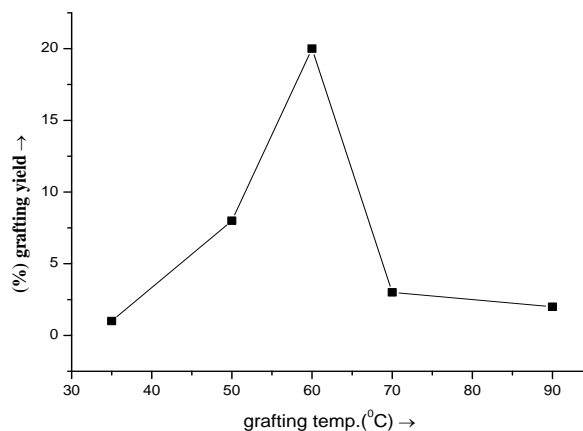


Fig. 1. Variation of grafting yield with reaction temperature for Starch-g-poly(AA).

Reaction temperature: Reaction temperature has a considerable effect on the grafting reaction (Fig. 1). Grafting yield increases with increase in reaction temperature and reached to maximum value at 60 °C and then decreases beyond the optimum reaction temperature. This generally occurs due to the setting up of various hydrogen abstraction reactions and increase in viscosity of reaction medium due to homopolymerization. Increase viscosity of the medium creates hindrance in the path of free radical in reaching the active site on the backbone. Moreover decrease in percentage graft yield beyond optimum reaction temperature could be due to the predominance of homopolymerization over graft copolymer [20-22].

Monomer concentration: It is clear from the **Fig. 2** that grafting yield increases with increase in monomer concentration and further increase in monomer concentration results in decreased grafting yield. This is due to the predominance of homopolymerization over graft copolymerization. With homopolymerization, the system become heterogeneous and creates obstacles in the path of free radical in reaching active sites present on backbone of polymer [20-22].

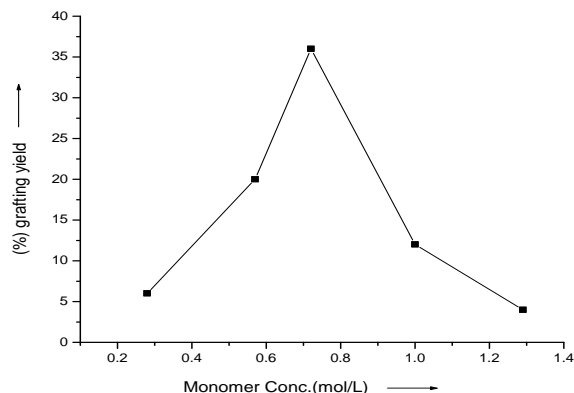


Fig. 2. Variation of grafting yield with monomer conc. for Starch-g-poly(AA).

Ceric ion concentration: The effect the initiator concentration on the grafting parameters at various monomer concentrations was investigated in order to obtain the maximum grafting. The grafting yield and grafting efficiency were increased on increasing the initiator concentration upto 0.03 mmol/L (**Fig. 3**). This was due to increase in the active sites on starch at optimum value of initiator. Further increase in initiator concentration leads to homopolymerization due to increase in number of active radical species, which results in decreased grafting [20].

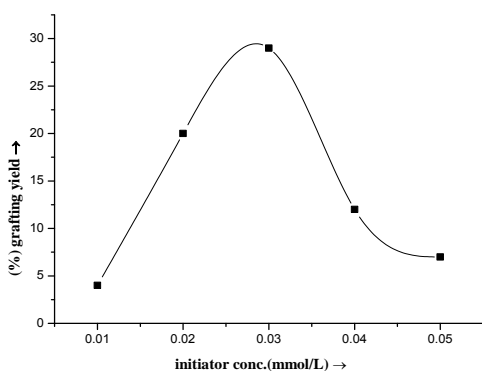


Fig. 3. Variation of grafting yield with initiator conc. for Starch-g-poly(AA).

Characterization techniques

FTIR spectroscopy: The absorption peaks at 2924 cm^{-1} and 1018 cm^{-1} are due to C-H stretching and bending vibrations, respectively. The absorption peaks at 1647 cm^{-1} are due to O-H bending vibrations in original sample. The additional peaks was observed in FTIR spectra of grafted sample at

1427 cm^{-1} and 1155 cm^{-1} due to C-H bending and C-O stretching, respectively. It has been observed that the absorption peaks shift towards low intensity. These additional peaks confirmed the grafting of poly(AA) sample onto potato starch backbone [22].

Scanning electron microscopy study: The surface morphologies of the starch-g-poly(AA) was studied by scanning electron microscope as shown in **Fig. 4**. Pure starch has irregular oval shape granule with a smooth surface. Whereas, starch-g-poly(AA) have course surface rather than smooth surface which was due to grafting of poly(AA) onto starch [20-22].

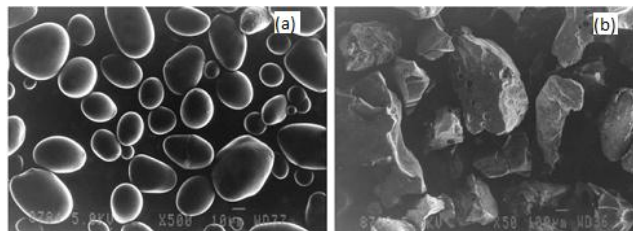


Fig. 4. SEM of (a) Starch (b) Starch-g-poly(AA).

Thermogravimetric analysis: In the pure starch, two stages decomposition was observed and the major weight loss of 66% was found in second step within temperature range of 200-500 $^{\circ}\text{C}$. In case of starch-g-poly(AA) 8.13% weight loss was observed as compared to potato starch where 12.19% weight loss was found upto 160 $^{\circ}\text{C}$. But in case of starch-g-poly(AA), three stages decomposition was observed (**Fig. 5**). The initial weight loss occurs below 200 $^{\circ}\text{C}$ was due to the loss of water of the hydrophilic polymer. Maximum weight loss was observed in the temperature range of 200-500 $^{\circ}\text{C}$, which is due to degradation of starch in graft copolymer. Beyond the 500 $^{\circ}\text{C}$, the weight loss was observed due to degradation of polymer chain and matrix.

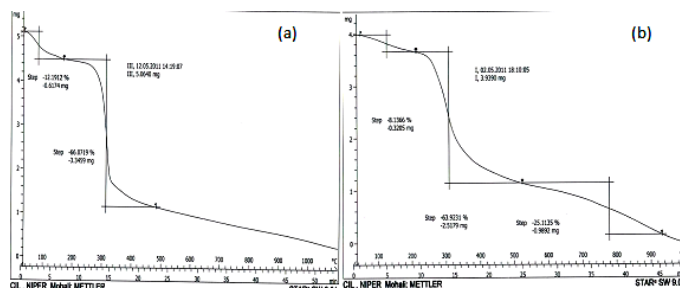


Fig. 5. TGA of (a) Starch (b) Starch-g-poly(AA).

Physico-chemical properties

Swelling behavior: The swelling studies of starch-g-poly(AA) was carried-out in different solvents as shown in **Table 1**. The maximum swelling was observed for starch-g-poly(AA) in water is 150%. This may be due to possible porosity of particles originated due to grafting of AA onto potato starch. The starch-g-poly(AA) shows the following swelling behaviour in different solvents: water > n-butanol > CCl_4 [20-22].

Moisture absorbance: The moisture absorbance study was carried out in humidity chamber. It is clear from **Table 2** that % moisture absorbance was found to decrease in grafted sample, which was due to blockage of active sites by graft copolymerization of AA. Therefore, affinity of grafted starch toward –OH group of water decreases, which leads to the decrease in the hydrophilic character [20].

Table 1. Swelling studies of starch-g-poly(AA) in different solvents.

Solvent	Initial weight (mg)	Final weight (mg)	%Swelling
Water	40	100	150
n-butanol	40	80	100
CCl ₄	40	70	75

Table 2. Moisture absorbance studies of starch-g-poly(AA) sample.

	Initial weight of sample (mg)	Final weight of sample (mg)	% M _{abs}
Raw sample	70	105	50%
Starch-g-poly(AA)	70	90	28.571%

Evaluation of chemical resistance: It has been resulted that chemical resistance of starch-g-poly(AA) polymer was more than raw sample (**Table 3**). This was due to deactivation of active sites on grafted Polymer backbone in 1N HCl whereas, both raw and grafted samples were completely dissolved in 1N NaOH.

Table 3. Percent weight loss shown by starch-g-poly(AA) sample in HCl and NaOH.

	Initial weight (mg)	Final weight in 1N HCl (mg)	% Weight loss	Final weight in 1N NaOH	% Weight loss
Raw sample	40	5	87.5%	0	Completely Dissolved
Starch-g-poly(AA)	40	10	75%	0	Completely Dissolved

Applications of graft copolymers

Removal of metal ions: In this study Mg, Zn and Ni metals are taken under investigation. Structural aspects of the polymeric backbone are important factors affecting metal ions sorption. The synthesized starch-g-poly(AA) remove metal ions both by adsorption on COO⁻ of acrylic groups and also by sorption in the bulk of grafted copolymer hydrogel. Therefore, the structure of a polymeric hydrogel affects the level of polymer interaction with water and the provision of active sites to absorb or coordinate metal ions. It is revealed from Table that the metal ions uptake percentage of Mg was higher than for Zn and Ni. This can

be attributed to the fact that the Mg ion has a lower atomic radius than other metal ions and consequently its adsorption by polymer is high. The sequence of metal ions sorption was as follows: Mg > Ni > Zn (**Table 4**) [20].

Table 4. Results of metal ions adsorption by starch-g-poly(AA).

Sr. No.	% Adsorption	Metal ions
1.	12.6	Zn
2.	16.0	Ni
3.	18.7	Mg

Dye adsorption from water system: The results of dye adsorption of starch-g-poly(AA) are shown in **Table 5**. Starch, due to its high contents of carboxylic and hydroxyl functional groups, has high affinity for many classes of dyes. Carboxylic group and hydroxyl group grafted onto starch also serve as donor in alkaline environment and responsible for adsorption of dye on starch-g-poly(AA) [20].

Sr.No.	Dye in ml/L	Adsorption of dye (q _e) (mg/ml)
1.	50	12.6
2.	100	20.5
3.	150	45.9

Table 5. Adsorption of dye by starch-g-poly(AA) at 663 nm.

Conclusion

The FTIR spectrum of starch-g-poly(AA) gives the characteristic absorption peaks, which confirmed the grafting of poly(AA). Thermal stability of potato starch was found to enhance on grafting of poly(AA) onto starch. SEM micrographs clearly indicated that the grafting of poly(AA) onto gelatinized starch remarkably alters the structure of potato starch. Grafted starch is more resistant to the chemicals as compared to potato starch. Starch graft copolymers have been successfully removed the metal ions and organic dyes from aqueous system.

Reference

- Lapasin, R.; Prich, S. *Food Hydrocolloids*. Rheology of industrial polysaccharides Theory and Applications. **1995**, New York: Aspen Publishers.
DOI: [10.1016/j.foodhyd.2010.08.014](https://doi.org/10.1016/j.foodhyd.2010.08.014)
- Pillai, C.; Paul, W.; Sharma, C. P. *Prog. Polym. Sci.* **2009**, *34*, 6418.
DOI: [10.1016/j.progpolymsci.2009.04.001](https://doi.org/10.1016/j.progpolymsci.2009.04.001)
- Bastos, D. C.; Santos, A. E. F.; Silva, M. L. V.; Simao, R. A. *Ultramicroscopy*, **2009**, *109*, 1089.
DOI: [10.1016/j.ultramic.2009.03.031](https://doi.org/10.1016/j.ultramic.2009.03.031)

4. Haag, A. P.; Maier, R. M.; Combie, J.; Geesey, G. G. *Int. J. Adhes. Adhes.* **2004**, *24*, 495.
DOI: [10.1016/j.ijadhadh.2004.01.004](https://doi.org/10.1016/j.ijadhadh.2004.01.004)
5. Shi, R.; Zhang, Z.; Liu, Q.; Han, Y.; Zhang, L.; Chen, D.; Tian, W. *Carbohydr. Polym.* **2007**, *69*, 748.
DOI: [10.1016/j.carbpol.2007.02.010](https://doi.org/10.1016/j.carbpol.2007.02.010)
6. Reis, A. V.; Guilherme, M. R.; Cavalcanti, O. A.; Rubira, A. F.; Muniz, E. C. *Polym.* **2007**, *47*, 2023.
DOI: [10.1016/j.polymer.2006.01.058](https://doi.org/10.1016/j.polymer.2006.01.058)
7. Liu, L. S.; Fishman, M. L.; Hicks, K. B. *Cellulose*, **2007**, *14*, 15.
DOI: [10.1021/jf2047515](https://doi.org/10.1021/jf2047515)
8. Nakauma, M.; Funamia, T.; Nodaa, S.; Ishihara, S.; Al-Assaf, S.; Nishinari, K.; Phillips, G. O. *Food Hydrocolloids*, **2008**, *22*, 1254.
DOI: [10.1016/j.foodhyd.2007.09.004](https://doi.org/10.1016/j.foodhyd.2007.09.004)
9. Tharanathan, R. N. *J. Sci. Critical Reviews in Food Science and Nutrition*, **2005**, *45*, 371.
DOI: [10.1080/10408390590967702](https://doi.org/10.1080/10408390590967702)
10. Tharanathan, R. N. *J. Sci. Ind. Res.* **1995**, *54*, 512.
DOI: [10.1080/10408390590967702](https://doi.org/10.1080/10408390590967702)
11. Lu, D. R.; Xiao, C. M.; Xu, S. J. *Express Polymer Lett.* **2009**, *3*, 366.
DOI: [10.3144/expresspolymlett.2009.46](https://doi.org/10.3144/expresspolymlett.2009.46)
12. Pareta, R.; Edirisinghe, M. J. *Carbohydrate Polymers.* **2006**, *63*, 425.
DOI: [10.1016/j.carbpol.2008.06.004](https://doi.org/10.1016/j.carbpol.2008.06.004)
13. Yoshida, T.; Hattori, K.; Sawada, Y.; Choi, Y.; Uryu, T. *J. Polym. Sci. Polym. Chem.* **1996**, *34*, 3060.
DOI: [10.1007/s10570-006-9080-1](https://doi.org/10.1007/s10570-006-9080-1)
14. Mingzku, L.; Rongshi, C.; Jingjia, W.; Cheng, M. *J. Polym. Sci. Polym. Chem.* **1993**, *31*, 3181.
DOI: [10.1002/app.20883](https://doi.org/10.1002/app.20883)
15. Singh V. *Journal of Applied Polymer Science*, **2006**, *99*, 619.
DOI: [10.1002/app.22189](https://doi.org/10.1002/app.22189)
16. Park, J. S.; Yang, J. H.; Kim, D. H.; Lee, D. H. *Journal of Applied Polymer Science*, **2004**, *93*, 911.
DOI: [10.1002/app.20533](https://doi.org/10.1002/app.20533)
17. Singh, V.; Maurya, S. *International Journal of Biological Macromolecules* **2010**, *47*, 348.
DOI: [10.1016/j.ijbiomac.2010.05.023](https://doi.org/10.1016/j.ijbiomac.2010.05.023)
18. Song, H.; Wu, D.; Zhang, R.Q.; Qiao, L.Y.; Zhang, S.H.; Lin, S.; Ye, J. *Carbohydr. Polym.* **2009**, *78*, 253. DOI: [10.1016/j.carbpol.2009.03.027](https://doi.org/10.1016/j.carbpol.2009.03.027)
19. Song, S. *Carbohydr. Polym.*, **2010**, *82*, 768.
DOI: [10.1016/j.carbpol.2010.05.049](https://doi.org/10.1016/j.carbpol.2010.05.049)
20. Pathania, D.; Sharma, R. *Adv. Mat. Lett.* **2012**, *3*, 136.
DOI: [10.5185/amlett.2011.8297](https://doi.org/10.5185/amlett.2011.8297)
21. Kumari, A.; Kaith, B. S.; Singha, A. S.; Kalia, S. *Advanced Materials Letters* **2010**, *1*, 23.
DOI: [10.5185/amlett.2010.6129](https://doi.org/10.5185/amlett.2010.6129)
22. Kalia, S.; Kumar, A.; Kaith, B.S. *Advanced Materials Letters* **2011**, *2*, 17.
DOI: [10.5185/amlett.2010.6130](https://doi.org/10.5185/amlett.2010.6130)

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