Carbohydrate Polymers 86 (2011) 872–876

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Microwave assisted synthesis and characterization of *Phaseolus aconitifolius* starch-g-acrylamide

Akhilesh V. Singh [a,*], Lila K. Nath [a], Manisha Guha [b]

[a] Department of Pharmaceutical Sciences, Dibrugarh University, Assam, 786004, India
[b] Central Food Technological Research Institute, Mysore, Karnataka, 570020, India

ARTICLE INFO

Article history:
Received 27 April 2011
Received in revised form 15 May 2011
Accepted 18 May 2011
Available online 26 May 2011

Keywords:
Moth bean starch
SEM
Grafting
XRD
FT-IR

ABSTRACT

Moth bean starch was modified through microwave assisted synthesis using a very low concentration of free radical initiator. Grafted copolymer was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Swelling study was also performed at various temperatures to access its suitability in diverse industrial application. Starch-grafted-acrylamide could be efficiently synthesized using a small concentration of ceric ammonium nitrate (CAN) in aqueous medium under microwave irradiation. The FT-IR spectral analysis confirms group attachment on starch backbone. XRD and SEM studies confirmed more crystalline structure, while TGA confirmed high thermal stability as compared to native starch. Starch-g acrylamide was successfully grafted and this novel biomaterial could be used in various industrial applications like food, textile paper, petroleum and pharmaceutical.

1. Introduction

Starch is one of the main reserve polysaccharides of higher plants, where it occurs as water insoluble granules. Starch is a mixture of two D-glucan homopolymers, composed of α-D-glucopyranosyl (α-D-Glcp) units. The ratio of amylose/amylopectin varies according to the botanical origin of the starch. Starch is widely distributed in the form of small granules and as the major reserve carbohydrate in stems, roots, grains and fruits of all form of green plants. Cereal grains such as wheat, corn, sorghum and tubers like potato are some of the commercial sources of starch for industrial exploitation (Roper, 1996; Tester, Karkalas, & Qi, 2004).

Grafting is a method wherein monomers are covalently bonded (modified) onto the polymer chain backbone. Grafting technique has been utilized as an important technique for modifying the physical and chemical properties of natural polysaccharides. Various techniques of graft copolymerization such as radiation, chemical initiation, etc., were reported in the literature (Bhattacharya & Misra, 2004). Microwave emerged as an efficient source of thermal energy and constitutes original procedure for the heating of materials in different ways from the classical ones. Microwave assisted free radical polymerization is also emerging as a novel technique in the field of polymer science to get grafted biomaterial with or without catalyst (Hoogenboom & Schubert, 2007; Wiesbrock, Hoogenboom, & Schubert, 2004). The polymerization under microwave irradiation of acrylamide and acrylic acid has been investigated with the purpose of developing polyelectrolytes for wastewater treatment. Under microwave irradiation grafting and homopolymerization have been studied without initiators (Misra, Mukul, Sen, & Jha, 2010; Sen, Singh, & Pal, 2010; Singh, Tiwari, Tripathi, & Sanghi, 2004; Singh, Tiwari, Tripathi, & Sanghi, 2006) or in the presence of very low concentration of initiator (Cheng, Zhu, Chen, Chen, & Zhang, 2003; Singh, Tiwari, Pandey, & Singh, 2006).

Moth bean (*Phaseolus aconitifolius* Jacq.) is an underexploited edible Indian legume grown mostly in rain fed region on low fertility soils. It is a very rich source of carbohydrate and proteins. Mostly sprouted seeds and dhal are used for preparation of different types of curries (Kevate, Chavan, Kadam, Chavan, & Amarowicz, 2010). Starch is a principal constituent of many foods and it constitutes not only a major energy source, but also essential to the gross texture or consistency of many food preparations. Physicochemical properties of native moth bean starch were well studied by earlier researchers (Wankhede & Ramteked, 1982).

The aim of present study is to carry out graft copolymerization of acrylamide on the moth bean starch backbone using microwave irradiation technique. This study also reports physicochemical characterization of grafted starch using various analytical techniques.

2. Materials and methods

Raw moth bean seeds were purchased from Indian Institute of Pulse Research, Kanpur, India. Acrylamide (AMD), hydroquinone

* Corresponding author. Tel.: +91 8439265825.
E-mail address: akhileshvikram@gmail.com (A.V. Singh).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.05.029

and ceric ammonium nitrate (CAN) were procured from SD Fine Chem, India. Acetone AR grade were supplied by Qualigens, India. All other chemicals used were of analytical grade.

2.1. Microwave assisted synthesis of starch grafted acrylamide

Firstly, moth bean starch was pregelatinized by heating the starch dispersion at 75 °C. The pregelatinized moth bean starch was grinded in an electric grinder (Philips, India) and sieved through 100 mesh. 1 g of pregelatinized moth bean starch was dispersed in 50 mL of double distilled water. Various amounts of acrylamide (2.5–10.0 g) were dissolved in 15 mL of water and further added to starch dispersion. They were mixed well using stirrer and transferred to the glass conical flask (250 mL) and CAN (0.25 g) were added. The flask was subsequently placed on the turntable of a microwave oven (CE1111L, Samsung Electronics, India) and microwave irradiated at various values (150–600 W). The reaction was also performed at various durations (1–4 min) in order to get the optimized reaction duration. After completing the reaction (formation of gel mass) the flask was placed in ice cooled water. The flask was kept undistributed for 12 h to complete the grafting reaction. After 12 h, 0.5 mL saturated hydroxyquinone solution was added to terminate the grafting reaction. Now, the gel mass was poured into excess of acetone. The grafted copolymer was purified by solvent extraction method using a mixture of formamide and acetic acid (1:1;v/v) to remove the homopolymer. The resulting precipitate of graft copolymer was collected and was dried in hot air oven at 45 °C for 12 h. The grafted material was grinded until a homogenous powder was obtained. The grafted materials were evaluated for percentage grafting (%G):

$$\%G = \frac{\text{Wt. of grafted copolymer}}{\text{Wt. of native starch}} \times 100 \quad (1)$$

Three reaction parameters, i.e., effect of monomer concentration, effect of microwave power and exposure time were optimized in respect to %G, and during optimization of one parameter, other parameters were kept constant.

2.2. Fourier transform infrared spectroscopy (FT-IR)

A Bruker FT-IR spectrophotometer (Model Vector-22, Germany) was used to record the IR spectra in the range of 4000–450 cm^{-1}. The IR spectra of MBS, AMD and MBS-g-AMD were recorded in the solid state using the KBr pellet method.

2.3. Scanning electron microscopy (SEM)

The surface morphology of native and grafted starch were studied using SEM. Sample was studied using a scanning electron microscope of JEOL model JSM-240 (Japan). The specimens in the form of films were mounted on the specimen stabs and coated with thin film of gold by the ion sputtering method.

2.4. X-ray diffractometer

The X-ray diffraction (XRD) studies were carried out using a Perkin Elmer diffractometer with copper as target material. The voltage, the current, and the wavelength of the X-ray source were 20 kV, 30 mA, and 0.154060–0.154438 nm, respectively. The representative moth bean starch, acrylamide and graft copolymer sample were scanned on XRD between 3° and 70°.

2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of MBS, AMD and their graft copolymer was carried out using thermal analyser (Model TGA-400, Perkin Elmer, USA) in nitrogen atmosphere. Samples of approximately 5 mg were heated in an aluminum cell between 30 °C and 500 °C temperature at a heating rate of 10 °C/min.

2.6. Swelling study

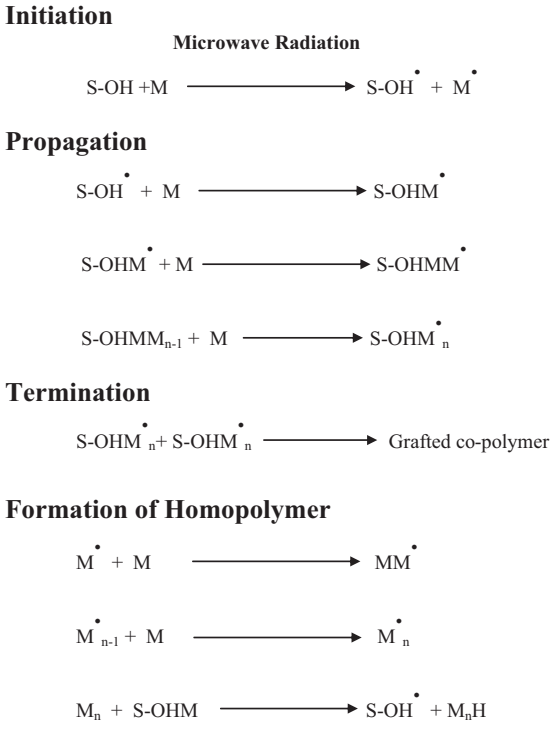
Swelling power was determined using the method described elsewhere (Liu, Ramsden, & Corke, 1999) in triplicate. Effect of temperature on swelling power was carried out in the temperature range of 30–90 °C. A total of 1.0 g of starch samples was accurately weighed and quantitatively transferred into a clear dried test tube and weighed. Ten milliliters of distilled water was added to the test tube, and the mixture was mixed thoroughly with a cyclomixer for 1 min. The resultant slurries were heated at desired temperatures, varied between 30 and 90 °C for 30 min in a constant temperature water bath (The FinePCR, Korea). The mixture was cooled to room temperature and centrifuged for 15 min. The residue obtained from the above experiment (after centrifugation) with the water is retained and the test tube was weighed. Swelling power was calculated as follows:

$$\text{Swelling power} = \frac{\text{Sediment weight (g)}}{\text{Dry weight (g)}} \quad (2)$$

3. Results and discussion

3.1. Optimal grafting conditions under microwave irradiation

The grafting of acrylamide on starch backbone in the presence of catalyst (CAN) was occurred by free radical reaction mechanism. The scheme of free radical reaction is given in Scheme 1. Reaction parameters like exposure time, monomer concentration and microwave power in respect to percentage grafting (%G) were optimized keeping the total reaction volume fixed.



Scheme 1. Schematic representation for microwave assisted synthesis of starch-g-acrylamide.

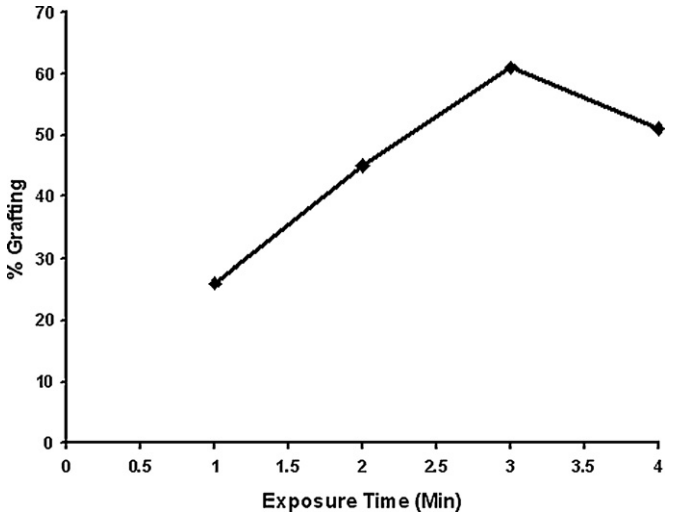


Fig. 1. Effect of exposure time on percentage grafting.

3.1.1. Effect of exposure time

The %G was increased with increase in exposure time, and the optimized reaction duration at constant microwave power was found to be 3 min (Fig. 1). Increase in %G, might be due to availability of more microwave energy resulting into more free radical generation that increased the %G.

3.1.2. Effect of monomer concentration

Grafting efficiency was increased on increasing the monomer concentration and the optimized concentration came 5.0 g; at 600 W power with exposure time of 3.0 min. The increase in %G may be due to the availability of more monomer on grafting site of polysaccharide (Fig. 2).

3.1.3. Effect of microwave power

To optimize the microwave power, reaction was proceeded from 150 to 600 W. The %G was increased up to 600 W microwave power at fixed monomer concentration (5.0 g) with exposure time of 3.0 min. Increase in %G with increasing microwave power may be due to the formation of more free radicals, resulting into more availability of grafting site and higher grafting (Fig. 3).

3.2. FT-IR study

The FT-IR spectra of native starch (a), acrylamide (b) and grafted copolymer (c) are shown in Fig. 4. The native starch showed

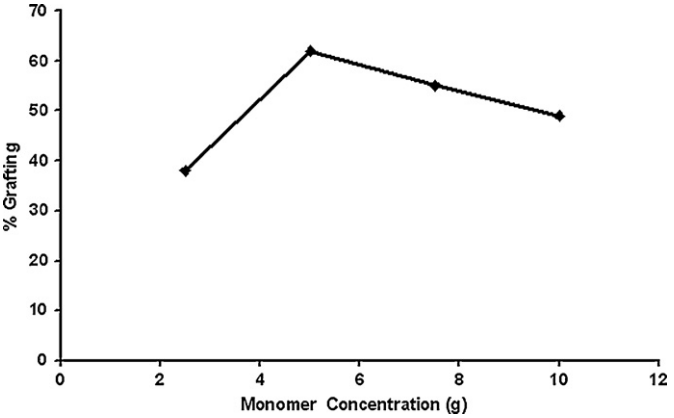


Fig. 2. Effect of monomer concentration on percentage grafting.

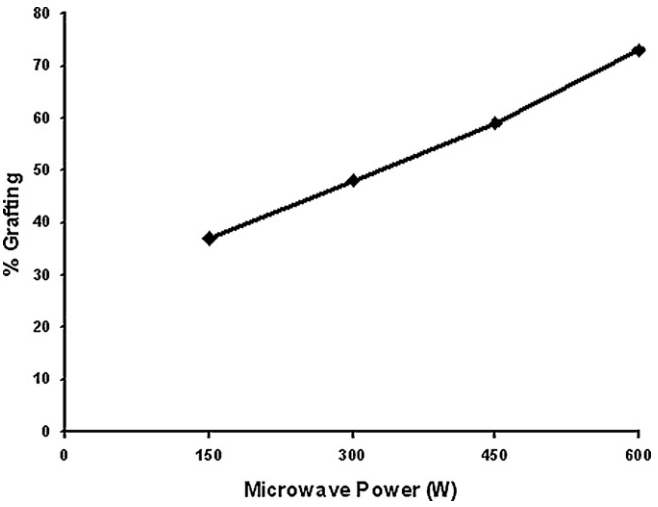


Fig. 3. Effect of microwave power on percentage grafting.

broad peaks at 3383.15 cm^{-1} due to stretching vibration of O–H, a smaller peak at 2927.4 cm^{-1} attributed to the C–H stretching vibration. The bands peak at 1636.28 cm^{-1} assigned for water molecules and 1021.8 cm^{-1} for C–O–C stretching vibration. In case of starch grafted acrylamide (Fig. 4(b)), O–H stretching band of hydroxyl group of starch and N–H stretching band of amide group present in acrylamide overlap with each other and lead to a peak at 3471.94 cm^{-1} and 3413.41 cm^{-1}. Strong absorption peaks at 1637.5 cm^{-1} and 1617.38 cm^{-1} attributed to C–O–C stretching vibrations and N–H stretching vibrations in the $-CONH_2$, suggesting the existence of grafting.

3.3. SEM characterization

In Fig. 5(a), the scanning electron micrograph of native starch clearly exhibits smooth surface, whereas acrylamide possessed

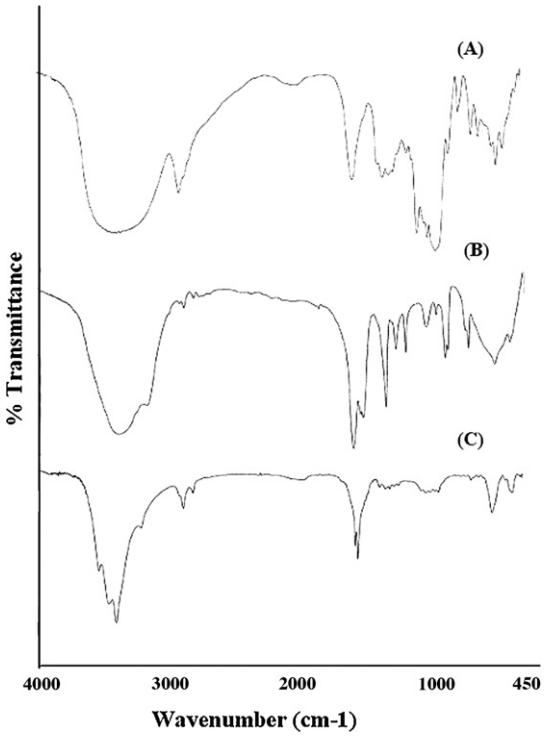


Fig. 4. FT-IR spectrum of (A) starch, (B) acrylamide and (C) starch-g-acrylamide.

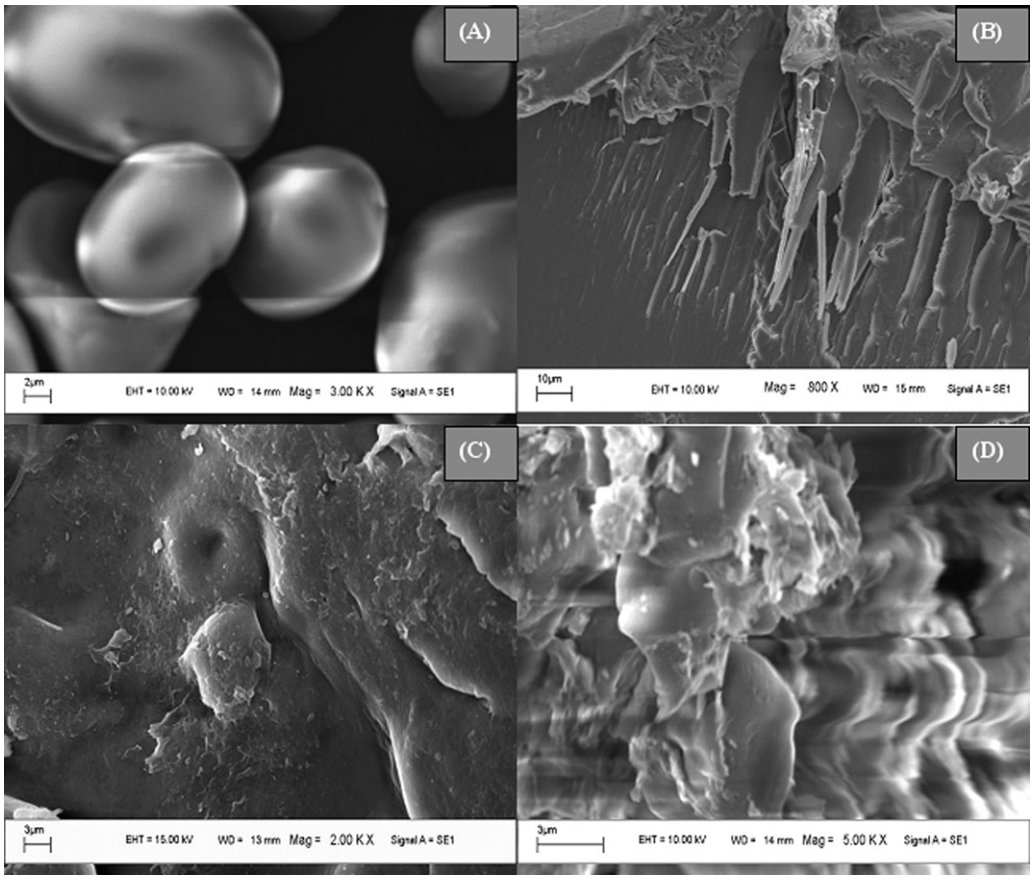


Fig. 5. Scanning electron micrographs of (A) starch, (B) acrylamide, (C) starch-g acrylamide and (D) swelled grafted copolymer.

crystalline structure (Fig. 5(b)). The grafted copolymer showed loss of smooth surface because of grafting of acrylamide on to starch backbone (Fig. 5(c)). The SEM of swelled copolymer confirms formation of three dimensional network of copolymer (Fig. 5(d)), and also increase in the size due to grafting.

3.4. XRD study

The XRD pattern of native starch (a), acrylamide (b) and grafted copolymer (c) is shown in Fig. 6. Native starch granules are semicrystalline in nature. The crystallinity is due to amylopectin fraction present in the starch granule. The pure acrylamide is crystalline in nature (Fig. 6(B)). Due to microwave heating and grafting of acrylamide, the grafted copolymer exhibited strong diffraction peaks that confirms its transformation into crystalline form. The result suggests that starch crystallinity increased following graft copolymerization.

3.5. TGA characterization

The results of thermogravimetric analysis (Fig. 7) were employed to characterize the thermal stability of moth beam starch after acrylamide grafting. Pure starch shows a three step characteristic thermogram at 24.48 °C, 246.21 °C and maximum weight loss occurred at 403.28 °C was due to degradation of the starch backbone. Starch-g-acrylamide (Fig. 7(c)), in addition to the above zones of weight loss, has two extra zones of weight loss (326.33 °C and 588.19 °C), due to the grafted acrylamide chains.

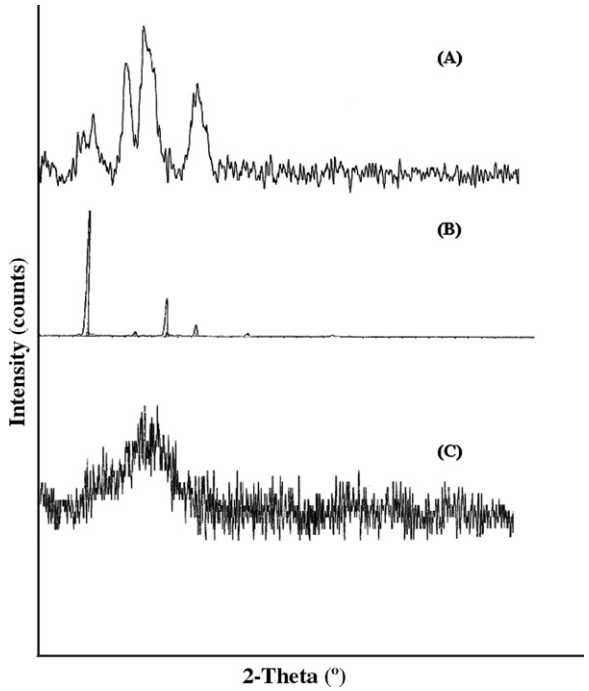


Fig. 6. XRD pattern of (A) starch, (B) acrylamide and (C) starch-g-acrylamide.

3.6. Swelling study

Native starch contains amylose and amylopectin but when starch is heated the crystalline structure is disrupted and water

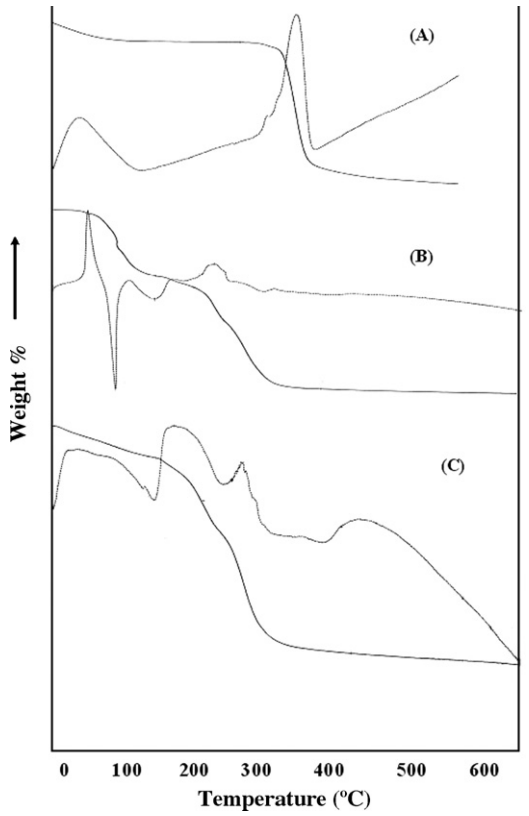


Fig. 7. TGA thermogram of (a) starch, (b) acrylamide and (c) starch-g-acrylamide.

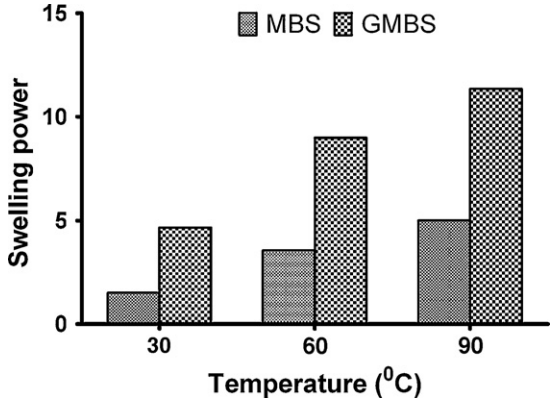


Fig. 8. Swelling study of moth bean starch (MBS) and starch-g-acrylamide (GMBS) at various temperatures ($n = 3$).

molecules become linked to free hydroxyl groups of amylose and amylopectin by hydrogen bonding. There is an increase in swelling power of native starch as the temperature of medium increased. Increase in swelling power at higher temperature is achieved due to increase in mobility of starch molecules, which facilitates percolation of water in the starch granules. Graft copolymerization of vinylic monomer increased swelling power of native starches that might be due to introduction of free hydrophilic groups. Due to introduction of more hydrophilic groups strong interchain hydrogen bonding takes place between the grafted side chain of acrylamide. Probably, strong hydrogen bonding favors the formation of strong three dimensional network that can hold more water in it, which is also confirmed by SEM analysis of grafted copolymer (Fig. 8).

4. Conclusion

Moth bean starch-g acrylamide was synthesized using microwave assisted reaction, using small concentration of catalyst (CAN). The % grafting was found to be highest with exposure time of 3 min and with 600 W microwave power. The monomer concentration also influenced the % grafting and most optimized concentration came 5.0 g. The grafted copolymer was further characterized by FT-IR, SEM and XRD. The semi crystalline nature of native starch was changed after grafting that was proved from XRD analysis, similarly the grafted copolymer exhibited higher thermal stability after grafting which was confirmed with TGA study. Grafting of acrylamide monomer onto starch backbone favored the formation of a three dimensional hydrophilic network that increased water-holding capacity and swelling power of this modified starch and it is increased linearly with temperature.

Acknowledgement

The authors are thankful to Prof. Harkesh B. Singh, Department of Chemistry, IIT Bombay for carrying out XRD and TGA characterization of samples.

References

Bhattacharya, A., & Misra, B. N. (2004). Grafting: A versatile means to modify polymers-technique, factors and application. *Progress in Polymer Sciences*, *29*, 767–814.
Cheng, Z. P., Zhu, X. L., Chen, M., Chen, J. Y., & Zhang, L. F. (2003). Atom transfer radical polymerization of methyl methacrylate with low concentration of initiating system under microwave irradiation. *Polymer*, *44*, 2243–2247.
Hoogenboom, R., & Schubert, U. S. (2007). Microwave-assisted polymer synthesis: Recent developments in a rapidly expanding field of research. *Macromolecular Rapid Communication*, *28*, 368–386.
Kevate, B. N., Chavan, U. D., Kadam, S. S., Chavan, J. K., & Amarowicz, R. (2010). Isolation and characterization of starch from moth bean. *African Journal of Food Science and Technology*, *1*(2), 68–70.
Liu, H., Ramsden, L., & Corke, H. (1999). Physical properties of cross-linked and acetylated normal and waxy rice starch. *Starch/Stärke*, *51*, 249–252.
Misra, S., Mukul, A., Sen, G., & Jha, U. (2010). Microwave assisted synthesis of polyacrylamide grafted starch (St-g-PAM) and its applicability as flocculant for water treatment. *International Journal of Biological Macromolecules*, *48*(1), 106–111.
Roper, H. (1996). Applications of starch and its derivatives. *Carbohydrate Europe*, *15*, 4–21.
Sen, G., Singh, R. P., & Pal, S. (2010). Microwave-initiated synthesis of polyacrylamide grafted sodium alginate: Synthesis and characterization. *Journal of Applied Polymer Sciences*, *115*, 63–71.
Singh, V., Tiwari, A., Tripathi, D. N., & Sanghi, R. (2004). Microwave assisted synthesis of guar-g-polyacrylamide. *Carbohydrate Polymers*, *58*, 1–6.
Singh, V., Tiwari, A., Pandey, S., & Singh, S. K. (2006). Microwave accelerated synthesis and characterization of potato starch-g-poly(acrylamide). *Starch/Stärke*, *58*, 536–543.
Singh, V., Tiwari, A., Tripathi, D. N., & Sanghi, R. (2006). Microwave promoted synthesis of chitosan-grafted polyacrylamide. *Polymer*, *47*, 254–260.
Tester, R. F., Karkalas, J., & Qi, X. (2004). Starch—Composition, fine structure and architecture-review. *Journal of Cereal Science*, *39*, 151–165.
Wankhede, D. B, & Ramteked, R. S. (1982). Studies on isolation and physicochemical properties of starch from moth bean (*Phaseolus aconitifolius*). *Starch/Stärke*, *34*, 189–192.
Wiesbrock, F., Hoogenboom, R., & Schubert, U. S. (2004). Microwave-assisted polymer synthesis: State of the art and future perspectives. *Macromolecular Rapid Communication*, *25*, 1739–1764.