

# Peroxydisulfate initiated synthesis of potato starch-graft-poly(acrylonitrile) under microwave irradiation

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**Abstract.** Potato starch-graft-poly(acrylonitrile) could be efficiently synthesized using small concentration of ammonium peroxydisulfate (0.0014 M) in aqueous medium under microwave irradiation. A representative microwave synthesized graft copolymer was characterized using Fourier Transform Infrared Spectroscopy, X-ray Diffraction, Scanning Electron Microscopy and Thermogravimetric Analysis. Under microwave conditions oxygen removal from the reaction vessel was not required and the graft copolymer was obtained in high yield using very small amount of ammonium peroxydisulfate, however using the same amount of ammonium peroxydisulfate (0.0014 M) on thermostatic water bath no grafting was observed up to 98°C (even in inert atmosphere). Raising the concentration of the initiator to 0.24 M resulted into 10% grafting at 50°C but in inert atmosphere.

The viscosity/shear stability of the grafted starch (aqueous solution) and water/saline retention ability of the microwave synthesized graft copolymer were also studied and compared with that of the native potato starch.

**Keywords:** polymer synthesis, biopolymer, starch, peroxydisulfate, microwave irradiation

## 1. Introduction

Starch which is a low cost abundantly available renewable biopolymer on modification may develop properties comparable to synthetic petroleum-based polymers [1, 2] Chemical grafting [3–7] is one of the popular methods for modifying structure and properties of biopolymers. Vinyl grafting on to the polysaccharides improves their shelf life against biodegradation, thermal stability and metal ion binding ability and therefore grafted polysaccharides have a wide range of industrial utility [8]. Considerable amount of research has been published on ceric ion initiated graft copolymerization of acrylic monomers onto starch [9–11]. Potassium permanganate [12] has also been used as initiator to graft poly(acrylonitrile) on to starch. Most of the studies have been focused on grafting of acrylonitrile due to: (a) its superior grafting effi-

ciency [13] and (b) production of the starch-based superabsorbent hydrogels [14] by alkaline hydrolysis of the starch-graft-poly(acrylonitrile). So far voluminous reports are available on the synthesis of starch-graft-poly(acrylonitrile) using redox initiators where inert atmospheric condition is the requirement since O<sub>2</sub> is a very potent inhibitor for most of the common vinyl monomers.

Microwave irradiation [15–19], as efficient thermal energy source constitutes a very original method of heating materials, different from the classical ones. Main advantage is that it results in almost instantaneous bulk heating of materials in a homogeneous and selective manner. Under microwave irradiation grafting and homopolymerization have been studied without initiators [3, 4] or in the presence of very low concentration of initiator [20, 21] and this prompted us to undertake microwave promoted

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grafting of poly(acrylonitrile) onto potato starch using small concentration of ammonium peroxydisulfate as initiator.

## 2. Experimental Section

### 2.1. Materials and Instruments

A Kenstar (Model No. MOW 9811) domestic microwave oven with a microwave frequency of 2450 MHz and a power output from 0 to 1200 W with continuous adjustment was used for all the experiments. The starch sample (Qualigen, Extra pure) containing 30% amylose and 70% amylopectin was used without purification. Acrylonitrile (Lancaster, synthesis grade) was distilled in a stream of nitrogen before use. Ammonium peroxydisulfate (Merck) was used without further purification and double distilled water was used for the grafting reactions. Infrared (IR) spectra were recorded on a Nicolet 5700 of FTIR spectrophotometer using KBr pellet. X-Ray Diffraction (XRD) was carried out on Rigaku D/MAX-2200 X ray powder diffractometer. TGA was done on Perkin Elmer SII Dimond TGA/DTA at a heating rate of 10°C per min under nitrogen atmosphere. For the characterization, sample with maximum grafting was used. The viscosity measurements (of the aqueous solutions) were made on Brookfield LVDVE viscometer at 25°C using small sample adapter (spindle no S-18).

### 2.2. Acrylonitrile grafting on to starch under microwave irradiation

A calculated amount of the starch was dissolved in minimum required amount of warm distilled water in a 150 ml open necked flask. To this solution, calculated amount of the ammonium peroxydisulfate and acrylonitrile were added and the total volume was made up to 25 ml. The flask was exposed to fixed microwave power and exposure time. The graft copolymer was separated from poly(acrylonitrile) (PAN) by pouring the reaction mixture into 100 ml dimethylformamide (DMF) [3]. The copolymer was repeatedly washed with DMF to remove adhered PAN. The grafting experiment was also repeated in presence of hydroquinone (20 mg). The grafting ratio and grafting efficiency were calculated from the increase in weight in the following manner [8].

$$\text{Grafting ratio } [\%G] = \frac{W_1 - W_0}{W_0} \cdot 100 \quad (1)$$

$$\text{Grafting Efficiency } [\%E] = \frac{W_1 - W_0}{W_2} \cdot 100 \quad (2)$$

Where  $W_1$ ,  $W_0$ , and  $W_2$  denote, respectively, the weight of the starch-graft-poly(acrylonitrile) (S-g-PAN) the weight of original starch, and weight of the acrylonitrile used.

### 2.3. Graft co-polymerization of starch on thermostatic bath

Starch (0.1 g) was dissolved in 10 ml of hot distilled water in a two-necked flask. To this acrylonitrile (0.17 M) was added and the total volume was made up to 25 ml. The reaction mixture was purged with purified nitrogen for about 30 min and thermostated at 50°C. Ammonium peroxydisulfate (0.0014 M) was added to the reaction flask and this time was taken as zero time and the graft copolymerization was carried out for one hour. Reaction mixture was finally poured in to 100 ml of DMF [3] to precipitate the graft copolymer. The copolymer was repeatedly washed with DMF to remove the adhered PAN if any and dried. The above experiment was repeated at 98°C. Under identical conditions the reaction was also performed in presence of O<sub>2</sub> at both the temperatures. Grafting was also done with different persulfate concentration ranging from 0.0020–0.24 M at 50°C.

### 2.4. Hydrolysis of grafted starch in aqueous alkali

Starch-graft-poly(acrylonitrile) (2 g on dry basis) was dispersed in 2% NaOH at 100°C for 1.5 h. After hydrolysis [8] the sample was precipitated in 600 ml methanol, washed with methanol followed by ethanol, dried and weighed.

### 2.5. Water and saline (1% NaCl) retention

The sample (0.5 g on dry basis) was swollen in 100 ml distilled water for 30 minutes. The suspension was poured into a G-4 sintered glass filter at 93.32 kPa pressure. Water retention [8] was calculated as gram of water absorbed per gram of dry material. Similarly saline retention [8] capacity was determined using 1% aqueous sodium chloride solution.

## 2.6. Viscosity measurement

A weighed quantity of the samples were dissolved separately (Starch was dissolved in hot distilled water by stirring while the graft copolymer and saponified graft copolymer were dissolved in cold water by soaking them overnight) and then the resulting solutions were made up to desired concentrations and agitated vigorously for about 15 min till they became viscous and homogeneous. Viscosities of starch, starch-graft-poly(acrylonitrile) and saponified starch-graft-poly(acrylonitrile) were measured after different time intervals.

## 3. Results and discussion

Using low concentration of the ammonium peroxydisulfate, poly(acrylonitrile) could be very efficiently grafted on to the potato starch under microwave irradiation. Maximum grafting ratio and efficiency (225% and 98% respectively) were obtained at 0.17 M acrylonitrile, 0.0014 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , 0.1 g potato starch, 70 seconds exposure and 1200 W microwave power keeping total reaction volume fixed at 25 ml. The temperature of the reaction mixture just after the microwave exposure was measured to be 98°C. However at same concentrations of acrylonitrile (0.17 M) and starch (0.1 g/25 ml) on thermostatic water bath at 98°C, 0.0014 M peroxydisulfate was unable to trigger graft copolymerization (both in the nitrogen as well as in oxygen atmosphere) indicating that under conventional conditions, 0.0014 M peroxydisulfate is unable to furnish sufficient primary free radicals required for the graft copolymerization. However when the peroxydisulfate concentration was raised to 0.24 M (in conventional procedure), 10% grafting in nitrogen atmosphere was observed.

$\text{O}_2$  is a very potent inhibitor for most of the common vinyl monomers since it combines with active primary free radicals to give relatively inactive radicals, which are incapable of propagating the chain reaction. Thus the reaction media are usually thoroughly purged with inert gas to remove  $\text{O}_2$ , otherwise the reaction may not work, however under microwave conditions presence of  $\text{O}_2$  does not effect the normal graft copolymerization reaction. It can be assumed that under the influence of microwaves the oxygen reversibly combines with the primary free radicals and thus is unable to inhibit the chain propagation; however more investigations are required on this issue.

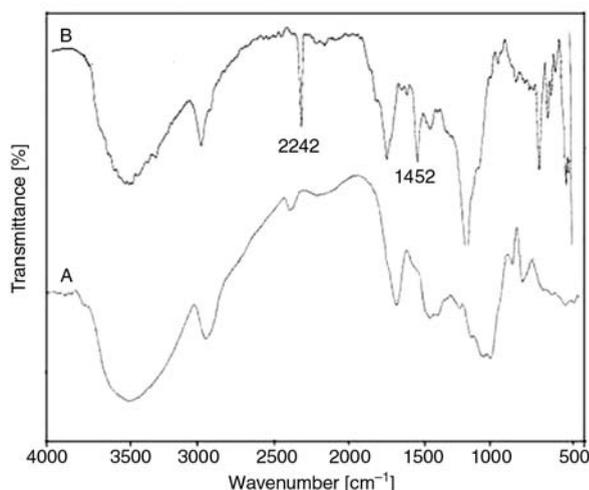
## 3.1. Characterization of the grafted starch

A representative microwave synthesized graft copolymer sample (sample with maximum grafting ratio), was characterized using IR, XRD and TGA. IR spectrum (Figure 1) of pure starch has a broad strong absorption at 3310–3425  $\text{cm}^{-1}$  (O–H stretching) and a peak at 2947  $\text{cm}^{-1}$  (C–H stretching) while IR spectrum of starch-graft-PAN has additional absorption peaks at 2242  $\text{cm}^{-1}$  (–CN stretching) and 1453  $\text{cm}^{-1}$  ( $\text{CH}_2$  deformation vibration) which can be attributed to grafted PAN chains at starch backbone. Physical blends of gum and PAN after selective removal of PAN with DMF showed no absorption in –CN stretching and – $\text{CH}_2$  bending region. This substantiates the formation of the graft copolymer.

TGA of Starch (Figure 2) and starch-graft-PAN showed that grafted starch to be more thermally stable than the pure Starch. Up to 650°C, 49% loss in total weight was observed for grafted starch in comparison to 58% weight loss in starch.

Comparison of XRD of the starch, poly(acrylonitrile) (PAN) and starch-graft-PAN further confirms grafting (Figure 3). XRD spectra of the grafted starch showed increased crystallinity in the region of  $2\theta$  28–32° due to the presence of PAN grafts on starch backbone, while peak at  $2\theta$  18° originally present in the starch has been significantly reduced after grafting.

Grafting is also evidenced by the SEM picture of the starch, picture clearly shows change in the surface topology of the starch after grafting due to the growing poly(acrylonitrile) grafts (Figure 4).



**Figure 1.** IR spectra of starch (A) and starch-graft-poly(acrylonitrile)

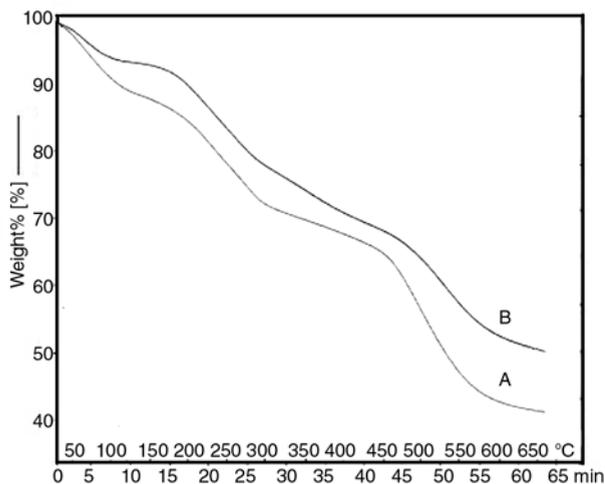


Figure 2. TGA of starch (A) and starch-graft-poly(acrylonitrile) (B)

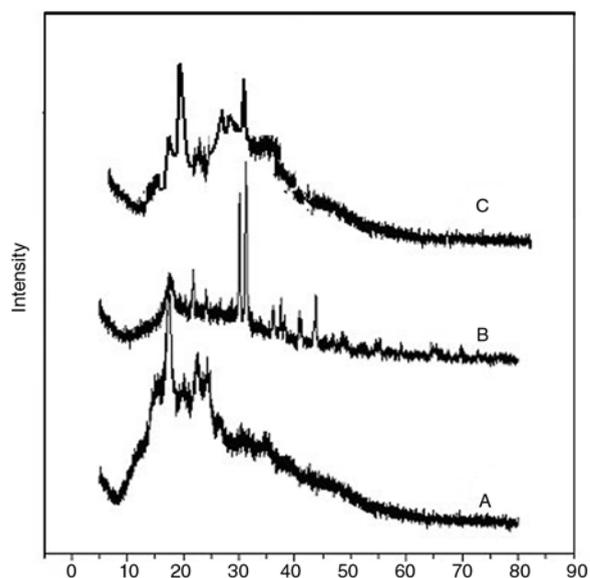


Figure 3. XRD of starch (A), starch-graft-poly(acrylonitrile) (B) and poly(acrylonitrile)

### 3.2. Mechanism of grafting

Since the grafting was not observed when the radical scavenger hydroquinone was added to the reaction mixture, a free radical mechanism for the grafting is the most probable and is proposed as under.

The grafting is being carried out in aqueous medium and the water being polar, absorbs microwave energy. This results in dielectric heating of the reaction medium. Microwaves are also reported to have the special effect [15] of lowering of Gibbs energy of activation of the reactions. These two effects cause quick decomposition of peroxydisulfate into sulphate ion radicals (Figure 5).

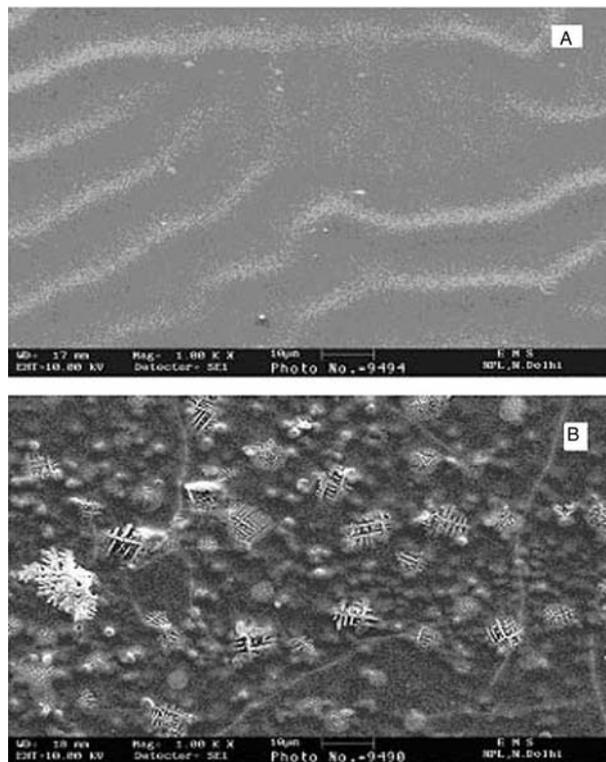


Figure 4. SEM picture of starch (A) and starch-graft-poly(acrylonitrile)(B)

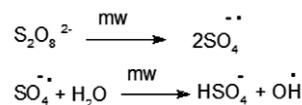
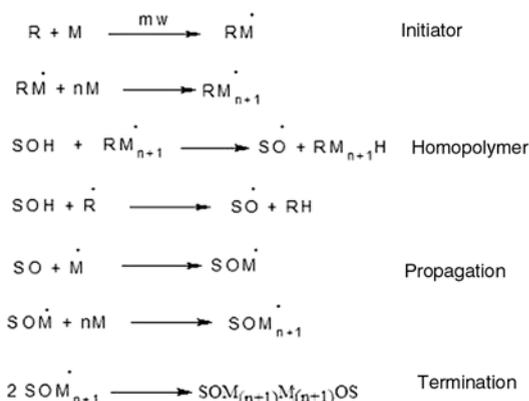


Figure 5. Generation of primary free radicals by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  under microwave irradiation



Where  $\text{R}^{\cdot}$  stands for primary free radicals  $\text{SO}_4^{\cdot-}$ ,  $\text{OH}^{\cdot}$   
 $\text{SOH}$  for Starch &  $\text{M}$  stands for acrylonitrile  
 mw stands for microwave irradiation

Figure 6. Graft copolymerization initiated by primary free radicals

$\text{SO}_4^{\cdot-}$  and  $\text{OH}^{\cdot}$  are the primary radicals, generated in the above sequence of reaction, and are expressed as  $\text{R}^{\cdot}$  in Figure 6. They initiate the vinyl polymerization as the vinyl polymerization is

reported to be faster than the H abstraction from the polysaccharide starch backbone [5]. The macro radical ( $SO^{\cdot}$ ) may be generated by abstraction of H by the growing vinyl polymer radical, which may add onto the vinyl monomer (M) generating new radical  $SOM^{\cdot}$  and this chain will grow till it combines with other such chains to give the graft copolymer (Figure 6).

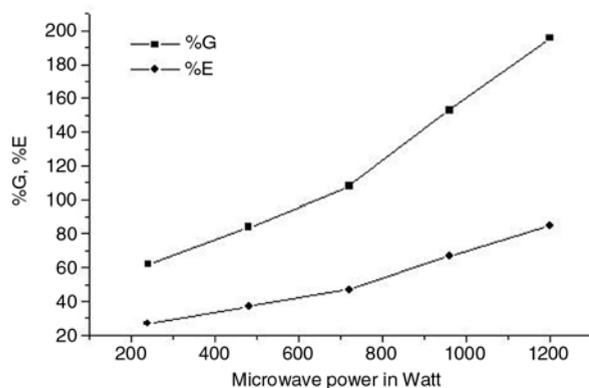
Since under identical reaction conditions, 0.0014 M persulfate could not initiate graft copolymerization in conventional grafting method (on thermostatic water bath) even at 98°C, some microwave effect cannot be ruled out in the microwave accelerated grafting procedure.

### 3.3. Determination of optimal grafting conditions under microwave irradiation

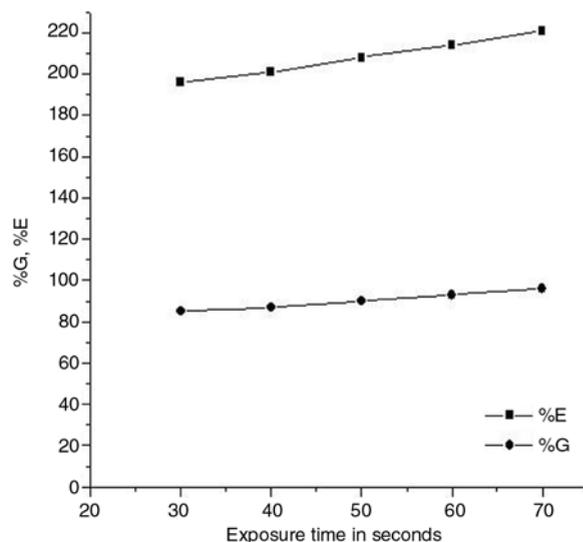
The microwave power, exposure time and concentration of the reactants (ammonium peroxydisulfate, acrylonitrile and starch) were varied keeping the total reaction volume fixed at 25 ml. The maximum grafting ratio and efficiency that could be reached were 225% and 98% respectively.

#### 3.3.1. Effect of microwave power

On increasing microwave power from 240–1200 W, grafting ratio and efficiency increased (up to 1200 W microwave power) at fixed concentration acrylonitrile (0.17 M),  $(NH_4)_2S_2O_8$  (0.0010 M), starch (0.1g), exposure time (30 sec) and reaction volume (25 ml) (Figure 7). Increase in %G and %E with increasing microwave power may be due to the formation of more  $M^{\cdot}_n$  and  $SO^{\cdot}$  radicals, resulting into more  $SOM^{\cdot}_n$  radicals for graft co-polymerization.



**Figure 7.** Effect of microwave power on %G and %E at  $[(NH_4)_2S_2O_8]$  0.001 M; [acrylonitrile] 0.17 M; [starch] 0.1 g/25 ml and exposure time 30 sec



**Figure 8.** Effect of exposure time on %G and %E; at  $[(NH_4)_2S_2O_8]$  0.001 M; [acrylonitrile] 0.17 M; [starch] 0.1 g/25 ml and 1200 W microwave power

#### 3.3.2. Effect of exposure time

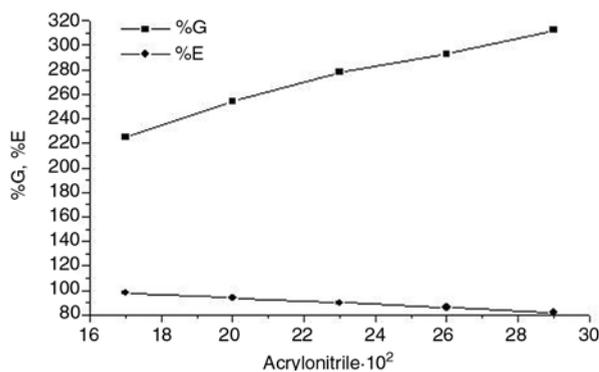
Grafting increased with increase in exposure time and was most for 70 sec exposure at fixed concentration of acrylonitrile (0.17 M),  $(NH_4)_2S_2O_8$  (0.0010 M), starch (0.1 g), microwave power (1200 W) and reaction volume (25 ml) (Figure 8). On increasing the exposure time, grafting ratio and efficiency increased. This may be due to the availability of more microwave energy resulting in to extra  $SOM^{\cdot}_n$  radicals for the graft copolymerization.

#### 3.3.3. Effect of monomer concentration

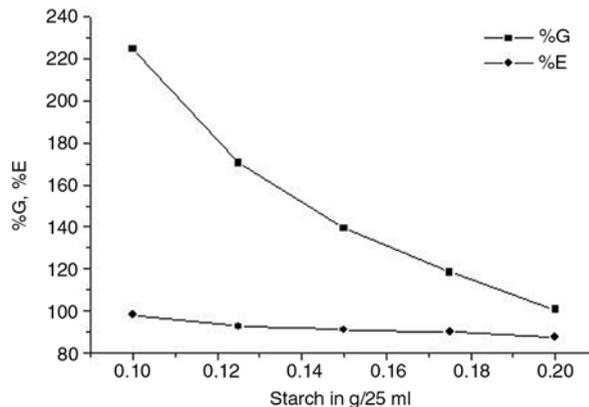
Grafting ratio increased on increasing the monomer concentration after 0.17 M; however efficiency decreases under the fixed concentration of starch (0.1 g/25 ml) at 1200 W microwave power and 70 sec exposure in 25 ml reaction volume (Figure 9). The increase in %G may be due to the formation of more  $M^{\cdot}_n$ , generating more grafting sites and due to availability of extra monomer for grafting. Decrease in efficiency on increasing the monomer concentration beyond 0.17 M may be probably due to more homopolymer formation.

#### 3.3.4. Effect of ammonium peroxydisulfate concentration

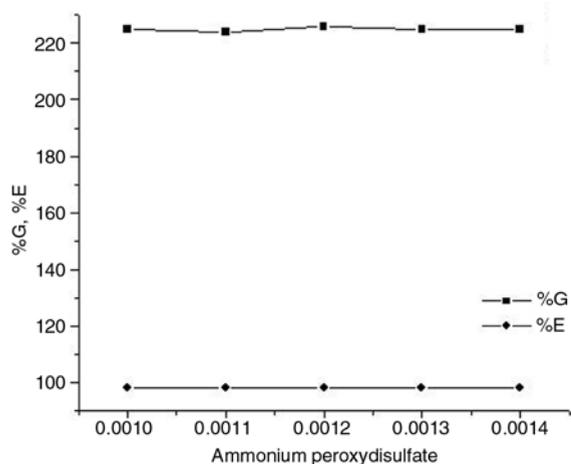
The effect of ammonium peroxydisulfate on the copolymerization was studied in the concentration



**Figure 9.** Effect of acrylonitrile concentration on %G and %E at [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] 0.001 M; [starch] 0.1 g/25 ml; 1200 W microwave power and 70 seconds exposure



**Figure 11.** Effect of starch concentration on %G and %E at [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] 0.0014 M, [acrylonitrile] 0.17 M, 1200 W microwave power and 70 sec exposure



**Figure 10.** Effect of ammonium peroxydisulfate concentration on %G and %E at [acrylonitrile] 0.17 M; [starch] 0.1 g/25 ml; 1200 W microwave power and 70 seconds exposure

range 0.0010–0.0014 M at fixed concentration of acrylonitrile (0.17 M), starch (0.1 g/25 ml) at 1200 W microwave power and 70 sec exposure in 25 ml reaction volume (Figure 10). It was observed that the %G and %E was not significantly affected by change in peroxydisulfate concentration in the studied concentration range. This may be due to very fast reaction taking place under the influence of the microwaves so minor change in the initiator concentration does not affect grafting.

### 3.3.5. Effect of starch concentration

The effect of Starch concentration was studied in the range of 0.1–0.2 g/25 ml at fixed concentration of ammonium peroxydisulfate (0.0014 M), acrylonitrile (0.17 M), microwave power (1200 W), exposure time (70 sec) and reaction volume (25 ml) (Figure 11). It was found that both %G and %E decrease with the increase in the concentration of starch, which may be due to the increase in the viscosity of the reaction medium causing hindrance of the normal reaction and also due to decrease in the monomer: starch ratio.

Overall maximum grafting ratio and efficiency that could be achieved was 225% and 98% respectively at 0.0014 M ammonium peroxydisulfate; 0.17 M acrylonitrile; 0.1 g/25 ml starch, 1200 W microwave power, 70 sec exposure keeping total reaction volume fixed at 25 ml.

### 3.4. Viscosity

Viscosity of 1% solution of starch, starch-graft-PAN (%G-225) and saponified starch-graft-PAN were found to be 0.008 Pas-s, 0.022 Pas-s and 0.203 Pas-s respectively (Table 1). The viscosity of the pure starch solution was found prone to biodegradation and its viscosity was lost slowly on

**Table 1.** Viscosity of starch, starch-graft-PAN and saponified starch-graft-PAN with time at 25°C

No.	Sample	%G	Viscosity of 1% solutions in Pas-s after different time intervals							
			Initial	8 h	12 h	24 h	48 h	86 h	128 h	250 h
1.	Starch	–	0.008	0.006	0.004	0.003	0.003	0.003	0.003	0.003
2.	S-g-PAN	225	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022
3.	Saponified S-g-PAN	225	0.203	0.204	0.205	0.206	0.209	0.209	0.209	0.209

Where S-g-PAN stands for starch-graft-poly(acrylonitrile)

**Table 2.** Water and saline retention for starch, starch-graft-PAN and saponified starch-graft-PAN at 25°C

No.	Sample	%G	Water retention [g/g]	Saline (1% NaCl) retention [g/g]
1.	Starch	–	18.01	15.43
2.	S-g-PAN	225	11.93	8.17
3.	Saponified S-g-PAN	225	58.96	49.31

Where S-g-PAN stands for starch-graft-poly(acrylonitrile)

**Table 3.** %G and %E in microwave and conventional methods in atmospheric and inert conditions at different peroxydisulfate concentration using starch (0.1 g/25 ml), acrylonitrile (0.17 M), total reaction volume 25 ml

No.		Concentration Persulfate in M	Condition	Temperature in °C	%G	%E
1.	Microwave method	0.0014	Atmospheric	98	225	98
2.	Conventional method	0.0014	Atmospheric	50	Nil	Nil
		0.0014	N <sub>2</sub> atm	50	Nil	Nil
		0.0014	Atmospheric	98	Nil	Nil
		0.0014	N <sub>2</sub> atm	98	Nil	Nil
		0.014	N <sub>2</sub> atm	50	Nil	Nil
		0.028	N <sub>2</sub> atm	50	Nil	Nil
		0.14	N <sub>2</sub> atm	50	Nil	Nil
		0.24	N <sub>2</sub> atm	50	10	4

standing while the grafted and saponified grafted starch solutions retain their viscosity even after 250 h (Table 1).

### 3.5. Water retention and saline retention

The water retention property is due to the interaction of the hydroxyl groups of the starch through hydrogen bonding. The grafting of the vinyl monomers onto the starch occurs through the hydroxyl groups of its backbone thereby decreasing the number of available hydroxyl groups for water and saline retention. Thus water and saline retention ability of the graft copolymer proportionally decrease with the increase in the grafting ratio (Table 2 and 3). On hydrolysis with aqueous alkali, the –CN groups on the grafted chains get hydrolyzed to –CONH<sub>2</sub> and –COOH groups and this increases water-binding sites in the saponified starch-graft-PAN and thereby a larger volume of water is bonded.

### 4. Conclusions

Starch-graft-PAN was synthesized in very short time using low ammonium peroxydisulfate concentration under microwave irradiation and for grafting removal of oxygen from the reaction vessel was not required. The highest grafting ratio (225%) and efficiency (98%) were found at 0.17 M acrylonitrile; 0.0014 M ammonium peroxydisulfate; 0.1 g starch, 1200 W microwave power and 70 sec expo-

sure keeping total reaction volume fixed at 25 ml. On grafting viscosity and shear stability of starch solutions increase while water and saline retaining ability decrease.

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### References

- [1] Athawale V. D., Lele V.: Graft copolymerization onto starch. 3: Grafting of acrylamide using ceric ion initiation and preparation of its hydrogels. *Starch-Starke*, **50**, 426–431 (1998).
- [2] Pourjavadi A., Zouhuriaan-Mehr M. J.: Modification of carbohydrate polymers via grafting in air. 1. Ceric-induced synthesis of starch-g-polyacrylonitrile in presence and absence of oxygen. *Starch-Starke*, **54**, 140–147 (2002).
- [3] Singh V., Tiwari A., Tripathi D. N., Sanghi R.: Microwave assisted synthesis of guar-g-polyacrylamide. *Carbohydrate Polymers*, **58**, 1–6 (2004).
- [4] Singh V., Tiwari A., Tripathi D. N., Sanghi R.: Microwave promoted synthesis of chitosan-grafted-polyacrylamide. *Polymer*, **47**, 254–260 (2006).
- [5] Singh V., Tiwari A., Sanghi R.: Studies on K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/ascorbic acid initiated synthesis of Ipomoea dasyperma seed gum-g-poly(acrylonitrile): A potential industrial gum. *Journal of Applied Polymer Science*, **98**, 1652–1662 (2005).
- [6] Singh V., Tiwari A., Tripathi D. N., Sanghi R.: Poly(acrylonitrile) grafted Ipomoea seed-gums: a

- renewable reservoir to industrial gums. *Biomacromolecules*, **6**, 453–456 (2005).
- [7] Athawale V. D., Rathi S. C., Lele V.: Graft copolymerization on to maize starch. I. Grafting of methacrylamide using ceric ammonium nitrate as an initiator. *European Polymer Journal*, **34**, 159–162 (1998).
- [8] Singh V.: Poly(acrylonitrile)grafted Cassia pudibunda seed gum: a potential commercial gum from renewable source. *Journal of Applied Polymer Science*, **99**, 619–627 (2006).
- [9] Lutfor M. R., Rahman M. Z. A., Sidik S., Mansor A., Haron J., Yunus W. M. Z. W.: Kinetics of graft copolymerization of acrylonitrile onto sago starch using free radicals initiated by ceric ammonium nitrate. *Designed Monomers and Polymers*, **4**, 253–260 (2001).
- [10] Fanta G. F., Felker F. C., Shogren R. L.: Graft polymerization of acrylonitrile onto spherocrystals formed from jet cooked cornstarch. *Carbohydrate Polymers*, **56**, 77–84 (2004).
- [11] Geresh S., Gilboa Y., Peisahov-Korol J., Gdalevsky G., Voorspoels J., Kost J.: Preparation and characterization of bioadhesive grafted starch copolymers as platforms for controlled drug delivery. *Journal of Applied Polymer Science*, **86**, 1157–1162 (2002).
- [12] Hebeish I., Abd El-Thalouth I., El-Kashouti M. A., Abdel-Fattah S. H.: Graft copolymerization of acrylonitrile onto starch using potassium permanganate as initiator. *Angewandte Makromolekulare Chemie*, **78**, 101–108 (2003).
- [13] Sugahara Y., Ohta T.: Synthesis of starch-graft-polyacrylonitrile hydrolyzate and its characterization. *Journal of Applied Polymer Science*, **82**, 1437–1443 (2001).
- [14] Taylor N. W., Fanta G. F., Doane W. M., Russell C. R.: Swelling and rheology of saponified starch-g-polyacrylonitrile copolymers. Effect of starch granule pretreatment and grafted chain length. *Journal of Applied Polymer Science*, **22**, 1343–1357 (1978).
- [15] Galema S. A.: Microwave chemistry. *Chemical Society Reviews*, **26**, 233–238 (1997).
- [16] Deshayes S., Liagre M., Loupy A., Luche J. L., Petit A.: Microwave activation in phase transfer catalysis. *Tetrahedron*, **55**, 10851–10870 (1999).
- [17] Loupy A., Petit A., Hamelin J., Texier-Boullet F., Jacquault P., Mathe D.: New solvent free organic synthesis using focused microwaves. *Synthesis-Stuttgart*, **9**, 1213–1234 (1998).
- [18] Varma R. S.: Solvent-free organic synthesis using supported reagents and microwave irradiation. *Green Chemistry*, **1**, 43–55 (1999).
- [19] Kappe C. O.: Controlled microwave heating in modern organic synthesis. *Angewandte Chemie-International Edition*, **43**, 6250–6284 (2004).
- [20] Singh V., Tiwari A., Pandey S., Singh S. K.: Microwave accelerated synthesis and characterization of potato starch-g-poly(acrylamide). *Starch-Starke*, **58**, 536–543 (2006).
- [21] Cheng Z. P., Zhu X. L., Chen M., Chen J. Y., Zhang L. F.: Atom transfer radical polymerization of methyl methacrylate with low concentration of initiating system under microwave irradiation. *Polymer*, **44**, 2243–2247 (2003).