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Graft copolymerization onto starch. II. Grafting of acrylic acid and preparation of it's hydrogels

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The grafting of acrylic acid (AA) onto granular maize starch in aqueous medium initiated by ceric ion has been studied gravimetrically under nitrogen atmosphere. The effect of concentration of ceric ion, concentration of AA, reaction temperature, polymerization time and material-to-liquor ratio on the grafting has been studied in terms of %GE and %Add-on. The optimum conditions obtained for the grafting of AA onto 2 g of granular maize starch were: [AA] = 0.2775 mol/L; [CAN] = 0.004 mol/L; time = 240 min; temp = 35°C; material-to-liquor ratio = 1:10. The graft copolymers were characterized by infra-red spectroscopy, XRD, TGA and scanning electron microscopy. XRD showed that the crystallinity of starch decreases owing to grafting. SEM revealed that grafting is essentially a surface phenomenon. Grafting of acrylic acid affects the thermal stability of starch. Hydrogels were prepared by grafting AA onto gelatinized starch followed by neutralization with NaOH. The maximum water absorption obtained was 250 g/g. © 1998 Published by Elsevier Science Limited. All rights reserved.

INTRODUCTION

Chemically modified starches with improved properties are gaining increasing importance in industry not only because they are low in cost, but mainly because the polysaccharide portion of the product is biodegradable. The product then, in a period of time, looses it's integrity and gets reduced to particles small enough to be of minimal damage to the environment. For the last few decades, chemical modification of starch via graft copolymerization of vinyl monomers onto it has been a subject of academic as well as of industrial interest. Though much work has been reported on the grafting of acrylonitrile, methyl methacrylate, acrylamide onto starch, comparatively less attention has been paid to the grafting of acrylic acid (AA) on starch (Trimnell and Stout, 1980; El-Rafie *et al.*, 1995; Mostafa, 1995).

Since the discovery of ceric ammonium nitrate (CAN) as an initiator by Mino and Kaizerman (1958), it has been used by many investigators for initiating graft copolymerization of vinyl monomers onto various natural and synthetic polymers. CAN helps in reducing the extent of homopolymerization during graft copolymerization thereby yielding a pure and uncross-linked graft copolymer (Mino and Kaizerman, 1958).

The ability of starch slurry to swell on heating, by absorption of water, is it's most important practical property. Maize starch has very low swelling capacity in aqueous medium compared with potato, tapioca, sago, arrowroot (Swinkles, 1985). It has been reported that polyacrylic acid (PAA) gives more stability to starch when grafted onto it, owing to the hydrogen bonding between it's carboxylic groups and the hydroxyl groups of starch (Gruber *et al.*, 1976; Masuda and Tanaka, 1980). Masuda *et al.* (1976) and Wong (1987) have patented the water absorbing resins prepared from starch using AA as one the components. The literature survey revealed that the water absorption capacities of hydrogels based only on maize starch-graft-AA have not been investigated.

The present work, therefore, is aimed: (1) at optimizing the conditions of grafting of AA onto granular maize starch using CAN as an initiator and (2) synthesizing the hydrogels (N-SPAA) by grafting AA onto gelatinized maize starch followed by neutralization with NaOH.

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EXPERIMENTAL

Materials

Maize starch (Food grade), supplied by Rajaram and Bros., Mumbai, India was first dried at 110°C and then was stored over anhydrous $CaCl_2$. Acrylic acid (AA) [(LR), Sisco-Chem Industries, India] having purity of 99.5% was stored in refrigerator and was brought to room temperature before use. CAN (J.T. Baker Chemical Co., NJ, USA) was dried at 110°C and later stored in a vacuum desiccator. It was used as a 0.1 M solution in molar nitric acid [(AR), S.D. Fine Chemicals, India].

Graft copolymerization

A mixture of 2 g of dried starch and 70 mL of distilled water was stirred magnetically under an N_2 atmosphere and was then treated with a predetermined quantity of CAN for 10 min. to facilitate free radical formation on starch (Fernandez *et al.*, 1990). This treatment was followed by the addition of monomer and then the total volume of the reaction mixture was made to 100 mL with distilled water. The polymerization proceeded under N_2 atmosphere generally for 180 min. and at 30°C unless stated otherwise.

Control reactions were carried out with 2 g of starch under identical experimental conditions except the addition of monomer in each set of reactions.

After 180 min., the reaction mixture was allowed to stand up to about 10 min. The supernatant solution was replaced by fresh distilled water and was stirred again for 15 min. This procedure was repeated twice to extract the homopolymer. At higher monomer concentration, four to six washings with water were sufficient to remove the homopolymer completely.

The residue was separated by filtering through preweighed Whatman filter paper No.41 and was dried under vacuum at 70°C.

The percentage grafting efficiency (%GE) (Eromosele, 1994) and percentage add-on (%Add-on) (Vera-Pacheco *et al.*, 1993) were calculated as follows:

$$\%\mathrm{GE} = 100 \times \frac{(W_2 - W_1)}{W_3}$$

$$\%\mathrm{Add\text{-}on} = 100 \times \frac{(W_2 - W_1)}{W_2}$$

where W_1, W_2 and W_3 are the weights of pure starch, graft copolymer and monomer charged, respectively.

Infra-red spectral analysis

The infra-red spectra of grafted and ungrafted starch were run in the form of KBr pellets on Shimadzu FTIR 4200 Spectrophotometer in the frequency range of 4000–600 cm^{-1}.

Thermogravimetric analysis

The samples of pure starch and graft copolymer were tested on Mettler TA 4000 TGA System in the temperature range of 35–496°C with a rising rate of 20°C/min.

X-ray diffraction studies

The X-ray diffraction studies were carried out using a Phillips-Hollond (Netherlands) diffractometer (Model PW1729) with copper as the target material in an X-ray tube under the operational conditions of 40 KV, 30 mA and wavelength ranging between 0.154060 and 0.154438 nm. The representative graft copolymer and pure granular maize starch samples were scanned on XRD between 5° and 80°.

Scanning electron microscopy

The surface morphology of polymer samples was studied using a scanning electron microscope (SEM) of Cameca (France) model SU-30. The specimen in the form of films were mounted on the specimen stabs and coated with gold by the ion spattering method. The micrograph were taken at a magnification of 700, 1000 and 1500.

Preparation of hydrogels

The gelatinized starch was prepared by constantly stirring a mixture of 2 g of dried starch and different quantities of distilled water at 75°C for 30 min. The slurry was cooled to 30°C, treated with CAN solution for 10 min and then variable quantities of AA were added to obtain different monomer to starch ratios (Tables 7 and 8). The volume of the reaction mixture (80–40 mL) was made up using distilled water. The polymerization was continued with constant stirring under nitrogen atmosphere. After 120 min., the reaction mixture was warmed up to 60°C and neutralized by dropwise addition of 5% NaOH with stirring until it assumed a reddish-brown colour. The slurry was further digested at 60°C in a water bath for about 20 min. when it turned pale yellow. After cooling the slurry to room temperature, it's pH was adjusted to desired value using glacial acetic acid and it was then precipitated in excess of methanol. The precipitate (N-SPAA) was washed with ethanol to neutrality and dried under vacuum at 70°C. The dried N-SPAA was finely powdered and stored over anhydrous $CaCl_2$ (Vera-Pacheco *et al.*, 1993).

Measurement of water absorption

The water absorption capacities of these hydrogels (N-SPAA) were assessed by filtration method. This method works satisfactorily for discrete type of hydrogels such as starch based hydrogels as the excess water gets removed through internal 'channels' of swollen hydrogel globules (Dave *et al.*, 1995). Hence, samples of powdered precipitates of neutralized starch-graft-AA (N-SPAA) weighed up to 0.1 g were immersed in 100 mL distilled water in a beaker at room temperature. After 30 min., slurry was filtered through weighed porous sintered glass (G-1) crucible. The excess water was removed by applying partial vacuum. Water absorption was measured in terms of amount of water absorbed in gram per gram of dried N-SPAA after weighing the hydrogel retained in the crucible (Giri *et al.*, 1990; Vera-Pacheco *et al.*, 1993). No correction was made for the percentage of the polymer that was soluble in water; the absorbency values would, thus, be higher if based only an insoluble polymer (Fanta *et al.*, 1979).

RESULTS AND DISCUSSION

Evidence for grafting

(1) *Gravimetric estimation.* The graft copolymerization reaction was monitored gravimetrically. The remarkable gain in the weight of starch, after extraction of homopolymer, over the control reaction, gives strong evidence for grafting of PAA onto starch. This weight gain in starch forms the basis for the determination of %GE and %Add-on.

(2) *Infra-red spectral analysis.* The IR spectra of pure and grafted starch (Fig. 1) both show a broad absorption band characteristic of glucosidic ring of starch between 3450 and 3200 cm^{-1}. Moreover, there is an increment in the intensity of this band in case of grafted sample, owing to the unutilized hydroxyl groups of the grafted acrylic acid. As expected, the grafted product shows an additional band owing to the carbonyl group of PAA, confirming beyond doubt the existence of grafting.

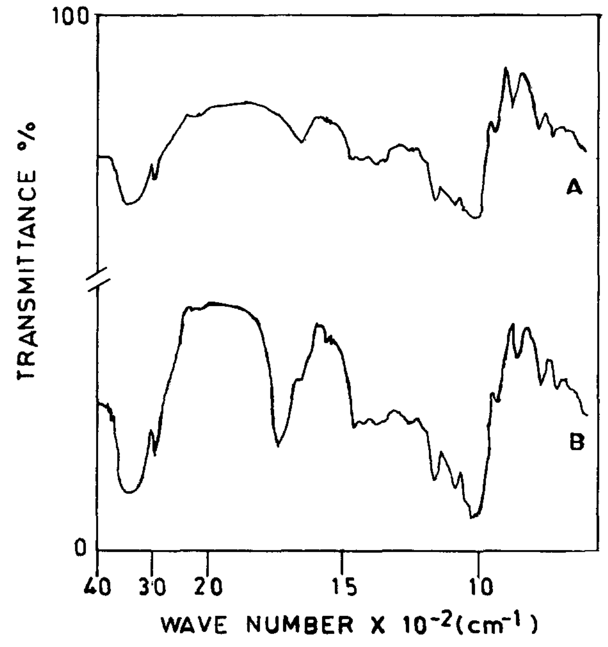

Fig. 1. Infra-red spectra of pure starch and graft copolymer (%Add-on = 25.21).

Table 1. Effect of initiator concentration on the grafting of AA onto maize starch

CAN (mol/l)	%GE	%Add-on
0.001	7.80	7.24
0.002	11.05	9.95
0.004	18.10	15.33
0.006	15.75	13.61
0.008	9.40	11.64

Starch = 2 g and [AA] = 0.2775 mol/l in each case in 100 ml of distilled water; 30°C for 180 min.

Effect of initiator concentration

Table 1 shows the effect of concentration of CAN on the %GE and %Add-on. The %GE and %Add-on initially increase steadily with the increase in [CAN] from 0.001 to 0.004 mol/L, however, these grafting parameters later on decrease gradually with further rise in concentration of CAN.

The initial rise in %GE and %Add-on may be attributed to the formation of increasing number of free radicals on the starch backbone at which the monomer molecules can be grafted at. The decline in %GE and %Add-on at higher concentration of CAN (>0.004 mol/L) may be rationalized as follows:

(1) non-availability of sites on starch molecules at which CAN can react to generate more free radicals;

(2) the initiation of homopolymerization by unutilized CAN.

Effect of monomer concentration

Table 2 shows the effect of concentration of AA on the %GE and %Add-on. In the initial stages, though both the grafting parameters rise with increase in [AA], beyond certain concentration of AA, both %GE and %Add-on decrease. The optimum values for %GE of 18.10% and for %Add-on of 22.33% were obtained at 0.2775 and 0.5551 mol/L of monomer, respectively.

The initial increase in %GE and %Add-on was obviously owing to the greater availability of monomer in the proximity of starch macroradicals, however, the decrease in grafting yield at a later stage may be owing to the wastage of AA molecules in the formation of large amounts of

Table 2. Effect of monomer concentration on the grafting of AA onto maize starch

AA (mol/l)	%GE	%Add-on
0.0694	7.60	1.86
0.1388	11.10	5.26
0.2775	18.10	15.33
0.5551	14.38	22.33
0.8326	6.50	16.32
0.1110	1.76	6.59

Starch = 2 g and [CAN] = 0.004 mol/L in each case in 100 mL of distilled water; 30°C for 180 min.

Table 3. Effect of reaction temperature an the grafting of AA onto maize starch

T (°C)	%GE	%Add-on
25	12.70	11.27
30	18.10	15.33
35	23.70	19.16
40	20.00	16.67
45	14.00	12.28
50	8.60	7.92
55	6.70	6.28

Starch = 2 g, [AA] = 0.2775 mol/L and [CAN] = 0.004 mol/L in 100 mL of distilled water for 180 min.

homopolymer. This was evident from the increase in the viscosity of the reaction medium in which the homopolymer (PAA) was soluble and also from the sticky nature of grafted product unlike the granular product obtained at lower concentration of AA. These homopolymer lumps then progressively hinder the rate of diffusion of monomer molecules to the starch macroradicals, resulting in the gradual decrease in %GE as well as %Add-on.

Needless to say, the starch macroradicals are comparatively immobile and, hence, the grafting efficiency will exclusively depend on the diffusion of monomer molecules in it's vicinity (Khalil *et al.*, 1990).

Effect of reaction temperature

The effect of reaction temperature on the %GE and %Add-on has been shown in Table 3. It can be noted that %GE reaches a maximum of 23.70% at an optimum temperature of 35°C and then decreases steadily with further rise in temperature to reach as low as 6.7% at 55°C.

The increase in %GE up to 35°C was owing to the higher rate of diffusion of monomer molecules to starch macroradicals; however, the decline in %GE beyond 35°C can be explained on the basis of increased rate of homopolymerization. This is also supported by the visual observation that the yellow colour of the starch slurry owing to CAN gradually fades on addition of monomer and the rate of disappearance of colour increases sharply at higher polymerization temperature. Moreover, it is likely that at higher temperature starch undergoes modification of some kind, such as partial hydrolysis in the presence of nitric acid or partial dissolution of the soluble amylose part, and the modified starch thereafter is not as amenable to grafting as the unmodified material.

Table 4. Effect of polymerization time on the grafting of AA onto maize starch

Time (min)	%GE	%Add-on
15	—	—
30	2.65	2.09
60	8.15	7.54
120	12.35	10.99
180	23.70	19.16
240	31.45	23.93
300	33.35	25.01
360	33.65	25.18
420	33.70	25.21

Starch = 2 g, [AA] = 0.2775 mol/L and [CAN] = 0.004 mol/L in 100 mL of distilled water at 35°C.

Table 5. Effect of material-to-liquor ratio on the grafting of AA onto maize starch

Material/liquor	Liquor (mL)	%GE	%Add-on
1:25	100	23.70	19.16
1:20	80	24.35	19.58
1:15	60	25.55	20.35
1:10	40	29.10	22.54
1:05	20	27.85	21.78

Starch = 2 g, [AA] = 0.2775 mol/L and [CAN] = 0.004 mol/L at 35°C for 180 min.

Effect of polymerization time

Table 4 highlights the consistent increase in the rate of grafting from 60 up to 240 min and gradual levelling off thereafter.

The levelling off of %GE is, perhaps, a direct consequence of depletion of monomer available for grafting. The comparatively low yields up to 60 min indicate that there exists some induction period up to which graft copolymerization of AA onto starch does not initiate. The remarkable increase in the rate of grafting is observed beyond 120 min., leading to an optimum %GE of 31.45% at 240 min.

Effect of material-to-liquor ratio

Table 5 exhibits the dependence of %GE and %Add-on on the material-to-liquor ratio. The material-to-liquor ratio was changed by decreasing the quantity of water in the reaction mixture.

It is evident that the decrease in the quantity of liquor favours the rate of grafting. As the quantity of liquor is reduced, the kinetic probability of collision between monomer molecules and starch macroradicals increases resulting in a rise in %GE. The maximum %GE was obtained at material-to-liquor ratio of 1:10. Further decrease in the quantity of liquor led to a decline in %GE, probably because of the restricted movement of the monomer molecules in a relatively small volume of the reaction mixture of 40 mL. In other words, a material-to-liquor ratio of 1:10 is most suitable.

Characterization of graft copolymers

Thermogravimetric analysis

The thermal behaviour of pure and grafted starch is very clearly exhibited by the thermograms and derivatograms (Fig. 2(a) and (b)). Though both pure and grafted starch led to a two-stage weight loss, the onset temperature of decomposition, the maximum decomposition temperature

(T_{max}) and % weight loss for the different stages differ widely.

Pure starch shows a characteristic three-step thermogram, wherein the major weight loss (75.5%) occurs in the second step within the temperature range of 233–368°C. The derivatogram gives the T_{max} 309°C. The third stage of decomposition is rather slow and results in about 11% weight loss up to 495°C.

In case of grafted starch (%GE = 25.21), the onset temperature of decomposition for the second step was as low as 133°C as against 233°C for that of pure starch. The last two steps for starch-graft-AA are continuous and can be made out clearly only from the derivatogram. It is evident from Table 6 that the grafted starch is thermally less stable than the pure starch.

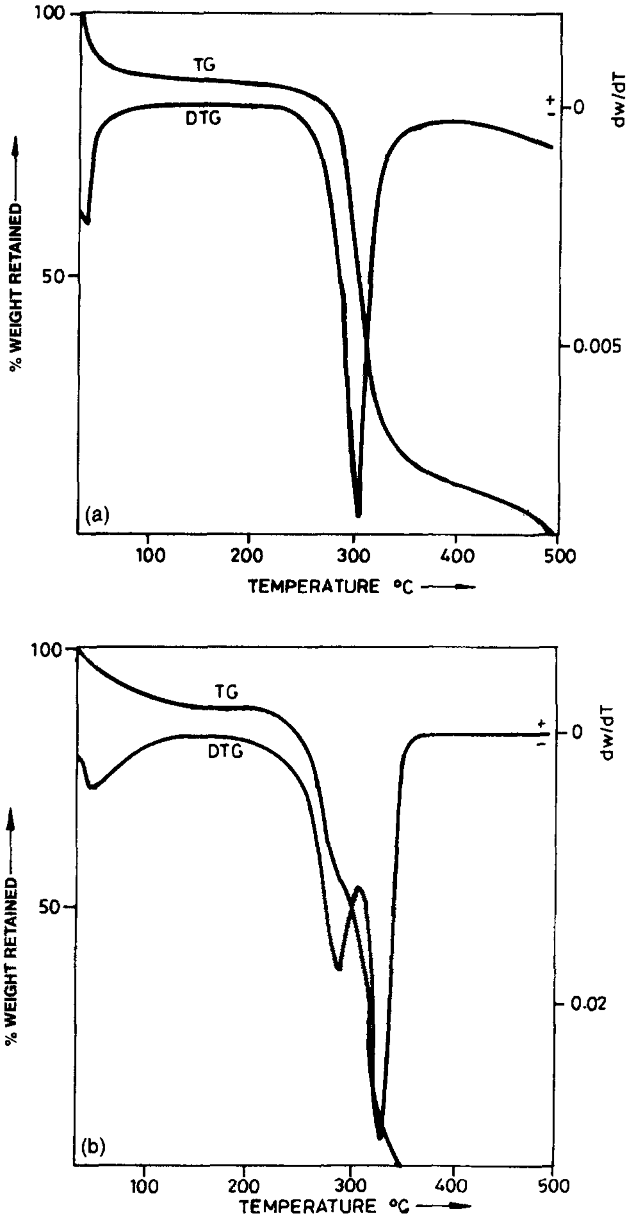

Fig. 2. (a) TGA and DTG thermograms of pure starch. (b) Representative TGA and DTG thermograms of starch-g-acrylic acid (%Add-on = 25.21).

Table 6. Thermal decomposition data of starch and graft copolymer

Substance	Number of stages	Temperature range (°C)	T_{max} (°C)	% weight loss
Starch	1	37–100	42	11.8
	2	233–417	308	75.5
	3	417–495	495	10.6
Graft copolymer	1	35–133	46	10.5
	2	133–303	287	43.6
	3	333–352	324	45.7:

X-ray diffraction studies

Starch granules are semi-crystalline in nature. The crystallinity is essentially owing to the amylopectin fraction. The areas of crystallinity comprise about 20–25% of the total volume of the starch granules (Swinkles, 1985). Fig. 3(a) shows a diffraction pattern of pure granular maize starch. The low counts (only up to 800) indicate that starch has very low crystallinity. On grafting, the count rate of pure granular starch was further reduced (Fig. 3(b)). It can, therefore, be inferred that along with the amorphous region, the crystalline region of the granular starch is also involved in grafting (Gao *et al.*, 1994).

Scanning electron microscopy (SEM)

SEM is the correct technique to study the surface topography of spherulites of size ranging between 0.1 and 10 μm, such as maize starch granules. The scanning electron micrograph of a pure starch sample (Fig. 4(a)) exhibits it's granular structure. The electron micrographs of the graft copolymer (Fig. 4(b) and (c)) show a variation in morphology also distinguishable from the pure starch. It

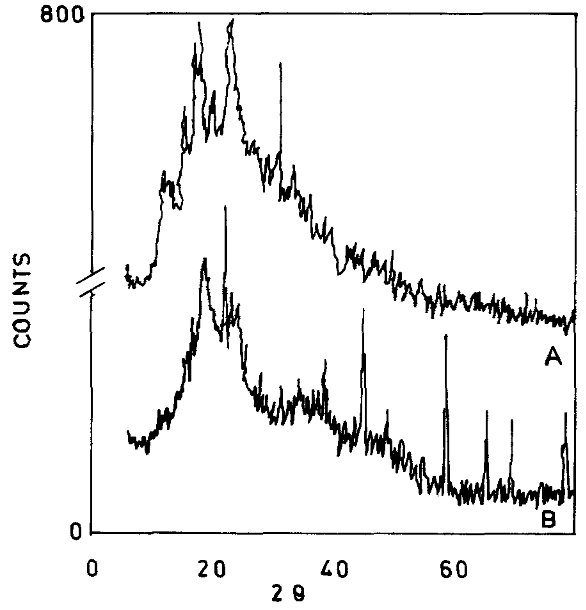

Fig. 3. X-ray diffraction pattern of pure starch and graft copolymer (%Add-on = 25.21).

Table 7. Water absorbency values of N-SPAA

Monomer/starch	Initial quantity of solvent (mL)		
	80	60	40
0.50	20	60	15
1.00	30	90	35
1.50	70	140	45
2.00	100	200	60

Starch (2 g) gelatinized at 75°C for 30 min; reacted with AA (1.0, 2.0, 3.0 or 4.0 g, respectively) and 0.004 mol/L of CAN at 30°C for 120 min; pH of the final product adjusted to 8.

can be seen that individual granules of starch remain largely intact during the grafting process and the grafted synthetic polymer chain surrounds and agglomerates individual granules of the starch (Trimnell *et al.*, 1996).

Water absorbency values of N-SPAA

Tables 7 and 8 give the water absorbency values of hydrogels (N-SPAA). These tables also exhibit the effect of various parameters such as monomer-to-starch ratio (M/S), quantity of solvent and pH of the final product on the water absorbency values.

It can be noted that, in general, with increase in monomer-to-starch ratio the water absorbency value increases. It is well-known that the properties of hydrogels strongly depend on the initial degree of dilution of monomers, hence, in the present work this effect was studied by varying the quantity of solvent in the reaction mixture. As expected, the reduction in the quantity of solvent from 80 to 60 mL resulted in a rise in water absorption by hydrogels. This may be owing to the formation of a better and continuous network between grafted chains of PAA which helps in retention of water. But, the drastic decrease in absorption on reducing the quantity of solvent further to 40 mL is probably because of the formation of tiny lumps of starch gelatinization under the present experimental conditions.

There was a remarkable increase in water absorption by hydrogels when the pH of the final products was adjusted to 10 instead of mildly alkaline pH 8.

CONCLUSIONS

(1) The maximum %GE and %Add-on for the graft copolymerization of acrylic acid onto granular maize starch are 33.35% and 25%, respectively (Table 4). The increase in the polymerization time has a positive effect on the grafting parameters.

Table 8. Water absorbency values of N-SPAA

Monomer/starch	Initial quantity of solvent (mL)		
	80	60	40
0.50	40	100	30
1.00	60	170	35
1.50	85	250	60
2.00	130	260	70

Starch (2 g) gelatinized at 75°C for 30 min reacted with AA (1.0, 2.0, 3.0 or 4.0 g, respectively) and 0.004 mol/L of CAN at 30°C for 120 min; pH of the final product adjusted to 10.

The optimum conditions for an effective grafting of acrylic acid onto 2.0 g of maize starch have been worked out as follows:

[CAN] = 0.004 mol/L in molar HNO_3;
[AA] = 0.2775 mol/L;
reaction temperature = 35°C;
polymerization time = 240 min.;
material-to-liquor ratio = 1:10.

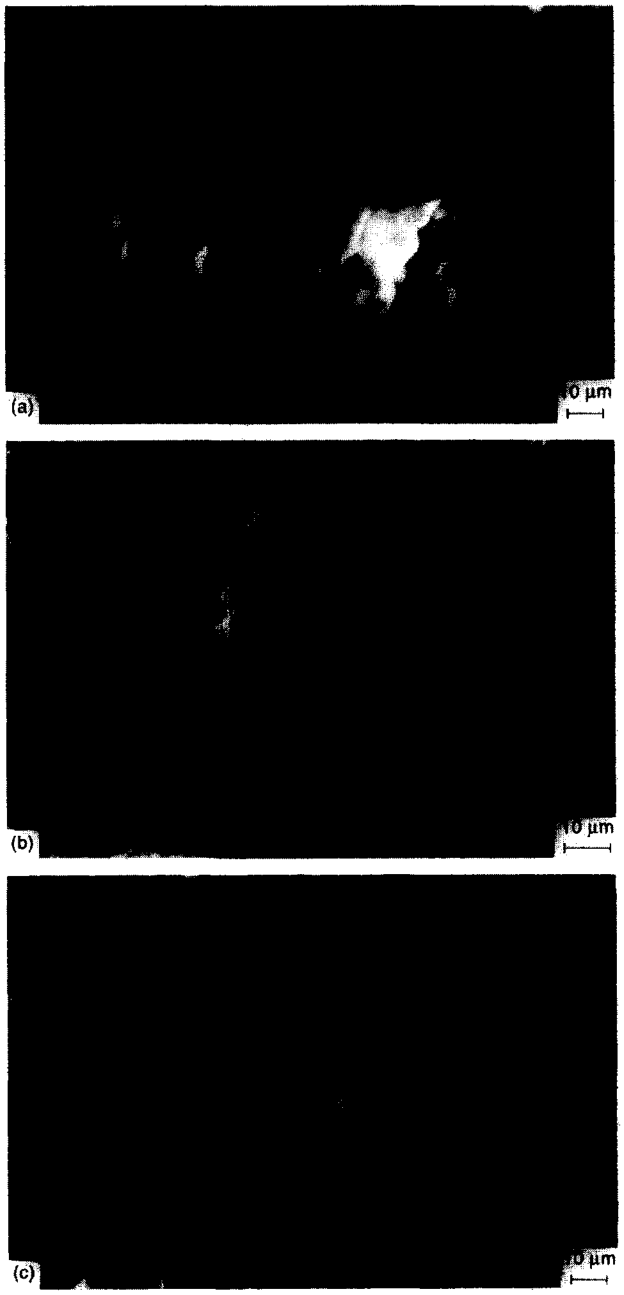

Fig. 4. SEM photographs of: (a) pure starch (magnification 1000); and (b) graft copolymer (%Add-on = 25.21) at magnification 700; and (c) at magnification 1000.

(2) The maximum absorbency value obtained in the present work is 250 g/g of N-SPAA at monomer to starch ratio of 1.5 and quantity of solvent 60 mL, when the pH of the final product was adjusted to 10. Based on the water absorbency values obtained in the present work, it can be positively argued that neutralized graft copolymers of AA onto gelatinized maize starch can yield excellent hydrogels.

(3) X-ray diffraction studies show that the crystallinity of the starch reduces on grafting. As can be seen from the thermal analysis, grafting of acrylic acid onto maize starch reduces it's thermal stability. SEM reveals that grafting is purely a surface phenomenon.

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