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Syntheses and characterisation of graft copolymers of maize starch and methacrylonitrile

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Abstract

Grafting of methacrylonitrile (MAN) onto dried maize starch using ceric ammonium nitrate (CAN) as an initiator has been studied gravimetrically under nitrogen atmosphere in aqueous medium. The percentage grafting is favoured by increasing monomer concentration and reaction time but is affected by higher concentration of initiator and high temperature. No grafting was observed beyond 45°C. The optimum conditions established for grafting were: [CAN] = 0.002 mol/l which was added in molar nitric acid; [MAN] = 0.755 mol/l; reaction time, 180 min; and temperature, 35°C. The graft copolymers were analyzed by infrared spectroscopy and acid hydrolysis. The grafting of methacrylonitrile onto starch does not alter the thermal stability of starch. The crystalline region of starch was also involved in grafting. Scanning electron microscopy showed a thick polymer coating of grafted PMAN on the starch surface. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Methacrylonitrile; Graft copolymerisation; Ceric ammonium nitrate; Characterisation

1. Introduction

Starch is a natural, renewable high polyol, available in plenty and hence very low in cost. Literature survey reveals that grafting of acrylamide (AAm) and acrylonitrile (AN) onto starch has been extensively investigated (Ghosh & Paul, 1986; Hebeish, Bayazeed, El-Alfy & Khalil, 1988; Mehrotra & Ranby, 1977) but with little attention to methyl analogues (Gruber, Alloush, John & Scurz, 1972; Vazquez, Goni, Gurruchaga, Valero & Guzman, 1992a,b). Although Vazquez et al. (1992a,b and Vazquez, Goni, Gurruchaga, Valero & Guzman (1993)) have reported the grafting of methacrylonitrile (MAN) onto starch. In our early work, we found that methacrylamide (MAAm) gets effectively grafted onto maize starch (Athawale, Rathi & Lele, 1998) though the percent grafting efficiency is little less than that for AAm.

Chemical modification of starch via grafting of vinyl monomers is one of the most effective methods to incorporate desirable properties into starch without sacrificing its biodegradable nature. Grafting of vinyl monomers onto various natural polymers such as cellulose, cotton, wool, jute, gelatin has been accomplished by using a range of free radical initiators like AIBN (Gao, Li & Huang, 1995; Mishra, Dogra, Kaur & Sood, 1980), BPO (Mishra et al., 1980), manganic pyrophosphate (Mehrotra & Ranby, 1977) or redox systems like Fenton's reagent (Trimnell, Fanta & Salch, 1996), potassium permanganate–thioacetamide (Eromosele, 1994), potassium monopersulphate–Fe(II) (Giri, Sahoo & Samal, 1990). However, in the present work, due to its unique properties, ceric ammonium nitrate (CAN) has been chosen as an initiator. CAN owes its preferential use as an initiator over other free radical initiators in grafting vinyl monomers onto different polyols, to the simple mechanism of single electron transfer, formation of free radicals on the backbone polymer itself, production of pure graft copolymer and ease of application at ambient temperature in aqueous medium (Mino & Kaizerman, 1958).

In this article, we present the results of a study on grafting of MAN onto maize starch in terms of effect of initiator and monomer concentration, reaction time and temperature using CAN as an initiator. Further, we have examined the effect of grafting on the thermal behaviour and structural aspects of granular starch.

2. Experimental

2.1. Materials

Maize starch (Laxmi Starch Co., India) was dried at

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110°C for about 10 h to remove absorbed moisture/water as it has been experimentally found to be an optimum time for drying to constant weight for starch. Ceric ammonium nitrate (CAN) (AR, J.T. Baker Chemical Co., USA) being hygroscopic in nature was dried in air oven at 110°C for about 6 h. Dried starch as well as CAN were then stored over anhydrous $CaCl_2$ in a desiccator. Methacrylonitrile (MAN) (LR, Sisco-Chem Industries, India) was freed from inhibitor, dried over anhydrous $CaCl_2$ and stored in a refrigerator.

CAN was used as a 0.1 M solution in molar nitric acid (AR, E. Merck, India, Ltd).

2.2. Graft copolymerisation

A mixture of 2 g of dried starch and 70 ml of distilled water was stirred magnetically under N_2 atmosphere to make a uniform slurry. It was then treated with a predetermined quantity of CAN for 10 min to facilitate free radical formation on starch (Fernandez, Casinos & Guzman, 1990; Trimnell et al., 1996). 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 polymerisation proceeded under N_2 blanket, generally for 180 min and at 30°C unless stated otherwise.

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

After 180 min, the reaction mixture was immediately filtered through Whatman filter paper no. 41. The residue was dried in vacuum oven at 70°C. The dry residue was then made free from homopolymer by exhaustive extraction with hot *N*,*N*′-dimethyl formamide for 20–24 h till the supernatant layer showed no precipitation of poly(methacrylonitrile) with water, a precipitant used in the present work. In order to accelerate the filtration, the residue was then treated with excess of water and filtered through preweighed Whatman filter paper No. 41. Finally, the residue was dried in a vacuum oven at 70°C to constant weight. The efficiency of the extraction of the homopolymer was confirmed by subjecting an intimate mixture of pure granular starch and poly(methacrylonitrile) taken in equal weight ratio, to similar exhaustive extraction with hot *N*,*N*′-dimethyl formamide to recover quantitatively granular starch as residue. The absence of any traces of unextracted poly(methacrylonitrile) in this residue was confirmed by infrared (IR) spectroscopy.

The percentage grafting (%PG) and grafting efficiency (%GE) were calculated from the relation (Athawale & Lele, 1998; Athawale & Rathi, 1996; Eromosele, 1994; Shukla & Sharma, 1987).

$$\%\mathrm{PG} = 100(W_2 - W_1)/W_1$$

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

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

2.3. 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 heating rate of 20°C/min.

2.4. Infrared spectral analysis

The IR spectra of grafted and ungrafted starch were run as KBr pellets on Shimadzu FTIR 4200 spectrophotometer in the frequency range of 4000–400 cm^{-1}.

2.5. X-ray diffraction studies

The wide angle X-ray diffraction (XRD) studies were carried out using a Phillips diffractometer (Model PW 1820) with copper as target material. The voltage, the current and the wavelength of the X-ray source were 40 kV, 30 mA and 0.154060–0.154438 nm, respectively. The representative graft copolymer sample and pure granular maize starch were scanned on XRD between 5 and 80°.

2.6. Scanning electron microscopy

The surface morphology of polymer samples was studied using a scanning electron microscope (SEM) of Cameca (France) model SU 30. 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. The micrographs were taken at magnification of 700, 1000 and 1500 using 20 kV accelerating voltage.

3. Results and discussion

All graft copolymer samples were pale yellow and hard. It is well known that DMSO is a good solvent for pure starch and poly(methacrylonitrile), however, the grafted starch only swells but does not dissolve in DMSO even after a considerably long period of time. The graft copolymers also are insoluble in *N*,*N*′-dimethyl formamide, cyclohexane and acetone, which are solvents for poly(methacrylonitrile). The insolubility of these copolymers may be the result of cross-linking due to chain combination of the growing ends of grafted chains. Grafted samples did not fully gelatinise when heated in water, which is consistent with cross-linking.

3.1. Evidence for grafting

3.1.1. Gravimetric estimation

The graft copolymerisation was followed gravimetrically. The increase in weight of the residue for each copolymerisation reaction, over that of the corresponding control reaction, indicates possible grafting.

3.1.2. Infrared spectroscopy

The IR spectra of pure granular starch and representative

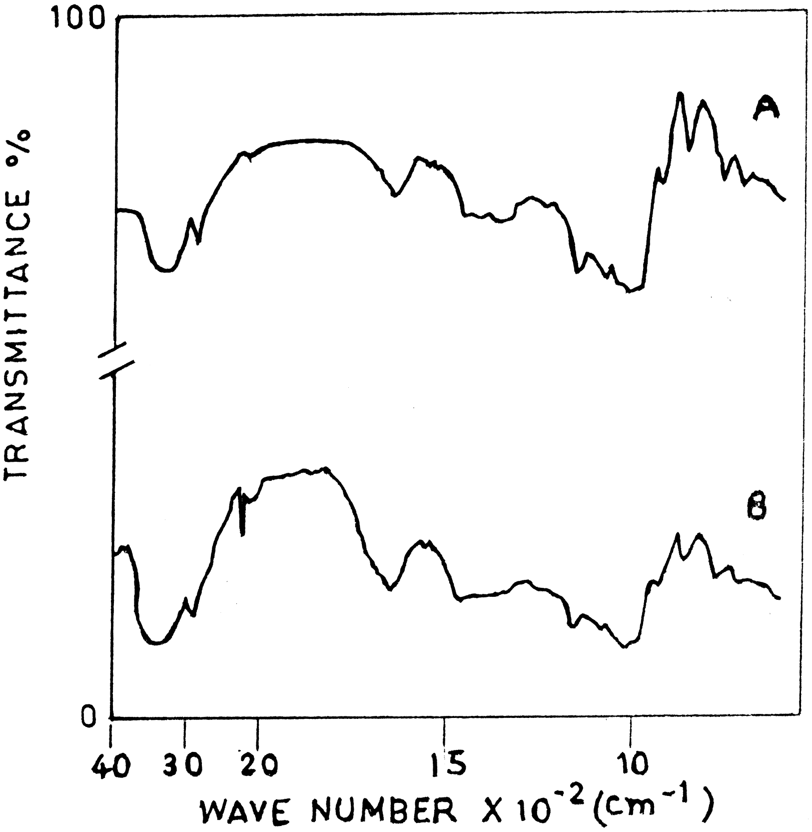

Fig. 1. IR spectra of (a) pure starch and (b) grafted starch.

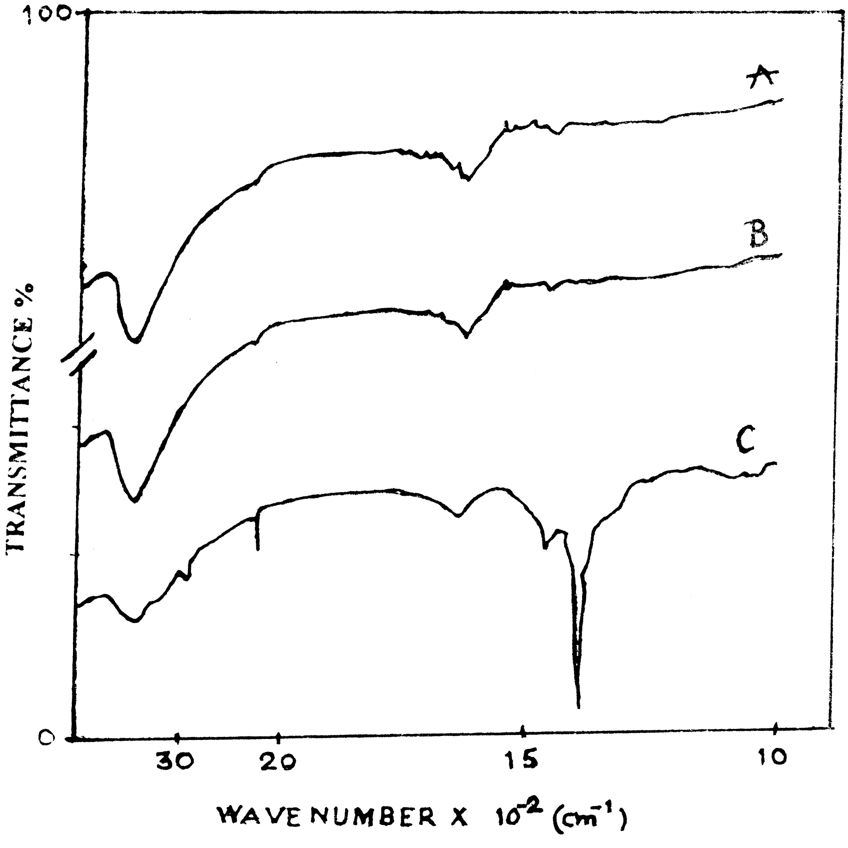

Fig. 2. IR spectra of (a) hydrolysed graft copolymer, (b) hydrolysed poly(methacrylonitrile) and (c) poly(methacrylonitrile).

Table 1
Effect of initiator concentration on the grafting of methacrylonitrile onto maize starch (reaction conditions: starch, 2.0 g and [MAN] = 0.377 mol/l in 100 ml of distilled water at 30°C for 180 min)

[CAN] (mol/l)	%GE	%PG
0.0005	0	0
0.0010	7.0	7.0
0.0020	38.5	38.5
0.0040	29.1	29.1
0.0060	25.2	25.2
0.0080	15.2	15.2

graft copolymer samples, contained a broad band at 3600–3400 cm^{-1} due to –OH stretching frequency of anhydroglucose units (AGU) (Fig. 1a and b). All the grafted samples showed an additional sharp absorption band at 2237 cm^{-1} (Fig. 1b) due to –CN stretching indicating the occurrence of grafting of MAN onto starch.

3.1.3. Acid hydrolysis

Starch on acid hydrolysis, transforms to glucose which is soluble in water and does not precipitate with methanol. In order to illustrate the behaviour of graft copolymer towards acid hydrolysis, in the present study, a representative sample of graft copolymer with %PG = 77.9 was chosen for this treatment as it was grafted to sufficiently higher level. The grafted sample (0.2 g) was subjected to acid hydrolysis by refluxing it with 100 ml of 0.5 M HCl for 120 min. After cooling, when the whole solution was poured in excess of methanol, the precipitate of hydrolyzed grafted starch was obtained. The IR spectrum of the precipitate so obtained is shown in Fig. 2a.

It is known that nitrile group on hydrolysis with strong and hot acid tranforms to amide and acid group. Fig. 2b and c shows the IR spectra of the hydrolyzed PMAN and of pure homopolymer of methacrylonitrile (PMAN), respectively. It can be further noted that the IR spectrum of the hydrolyzed graft copolymer (Fig. 2a) matches exactly with that of hydrolyzed PMAN (Fig. 2b) and thereby indicates the existence of grafting, assuming all homopolymer had been extracted.

3.2. Effect of initiator concentration

Table 1 shows the effect of [CAN] on the grafting of MAN onto maize starch. It should be noted that, both, %GE and %PG have identical values in this set as the weight of starch and MAN as well were equal. It is clear that there exists a critical concentration of ceric ion (0.002 mol/l) up to which both the grafting efficiency (%GE) as well as the percentage grafting (%PG) increase and decrease thereafter. The initial increase in %GE can be attributed to the increasing number of free radical sites on the starch backbone at which the monomer can be grafted. However, the decrease in %GE at higher concentration of CAN may be attributed to (i) the termination of the growing grafted chains by excess ceric ions (Shukla & Sharma, 1987), (ii) primary radical termination i.e. the reaction of the free radicals on the starch backbone with excess of ceric ions to produce oxidised starch which is incapable of initiating polymerisation.

At higher concentration of CAN, it was noticed that the initial yellow colour due to excess CAN disappeared only after 45 min of addition of monomer. This observation indicates that the excess [CAN] is used up in initiating homopolymerisation but with a long induction period in case of MAN as against that of MAAm and AAm (Athawale et al., 1998; Mino & Kaizerman, 1958).

3.3. Effect of monomer concentration

Table 2 exhibits the effect of MAN concentration on the grafting parameters. The %GE increases from as low as 19.3% at [MAN] of 0.188 mol/l to as high as 48.7% at monomer concentration of 0.755 mol/l but further increase in monomer concentration results in decline in %GE. It is well known that the grafting reaction system is heterogeneous and the overall rate of reactions depends on the rate of

Table 2
Effect of monomer concentration on the grafting of methacrylonitrile onto maize starch (reaction conditions: starch, 2.0 g and [CAN] = 0.002 mol/l in 100 ml of distilled water at 30°C for 180 min)

[MAN] (mol/l)	%GE	%PG
0.188	19.3	9.7
0.377	38.5	38.5
0.755	48.7	97.3
1.132	42.4	127.1
1.509	19.5	77.9

Table 3
Effect of polymerisation time on the grafting of methacrylonitrile onto maize starch (reaction conditions: starch, 2.0 g; [CAN] = 0.002 mol/l and [MAN] = 0.755 mol/l in 100 ml of distilled water at 30°C)

Time (min)	% GE	% PG
60	3.8	7.7
120	18.5	36.9
180	48.7	97.3
240	50.0	99.9
300	52.6	105.2

Table 4
Effect of reaction temperature on the grafting of methacrylonitrile onto maize starch (reaction conditions: starch, 2.0 g; [CAN] = 0.002 mol/l and [MAN] = 0.755 mol/l in 100 ml of distilled water for 180 min)

T (°C)	%GE	%PG
30	48.7	97.3
35	50.1	100.1
40	29.4	58.8
45	3.4	6.8
50	0	0

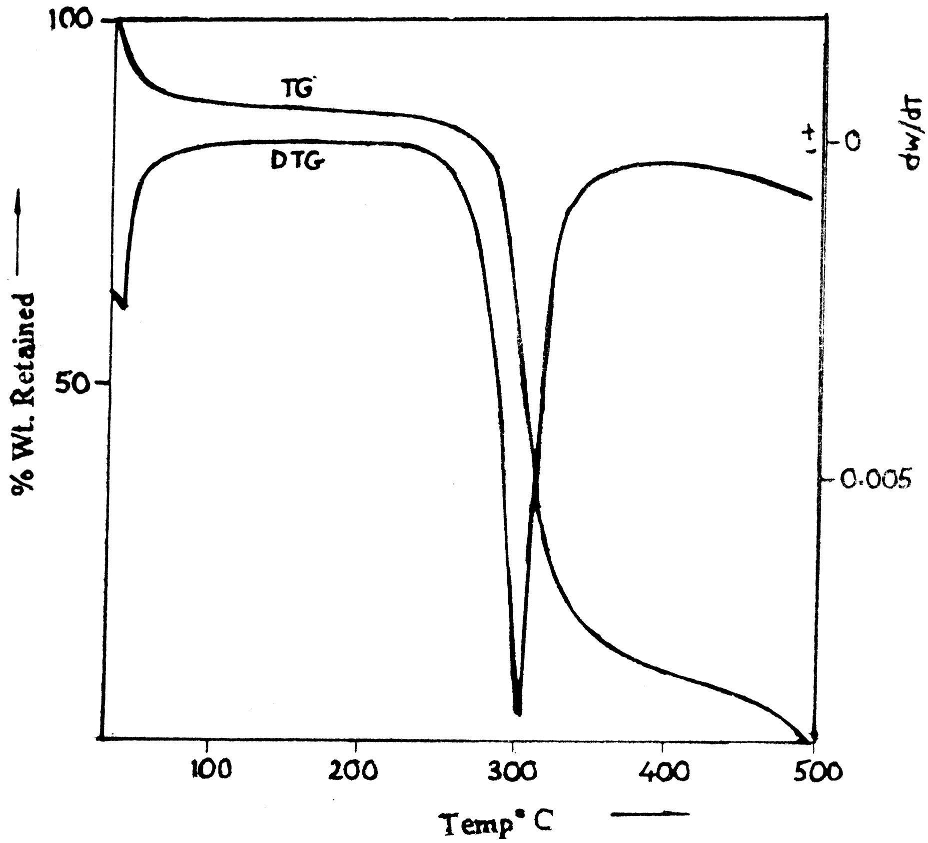

Fig. 3. Primary thermogram and derivatogram for pure granular maize starch.

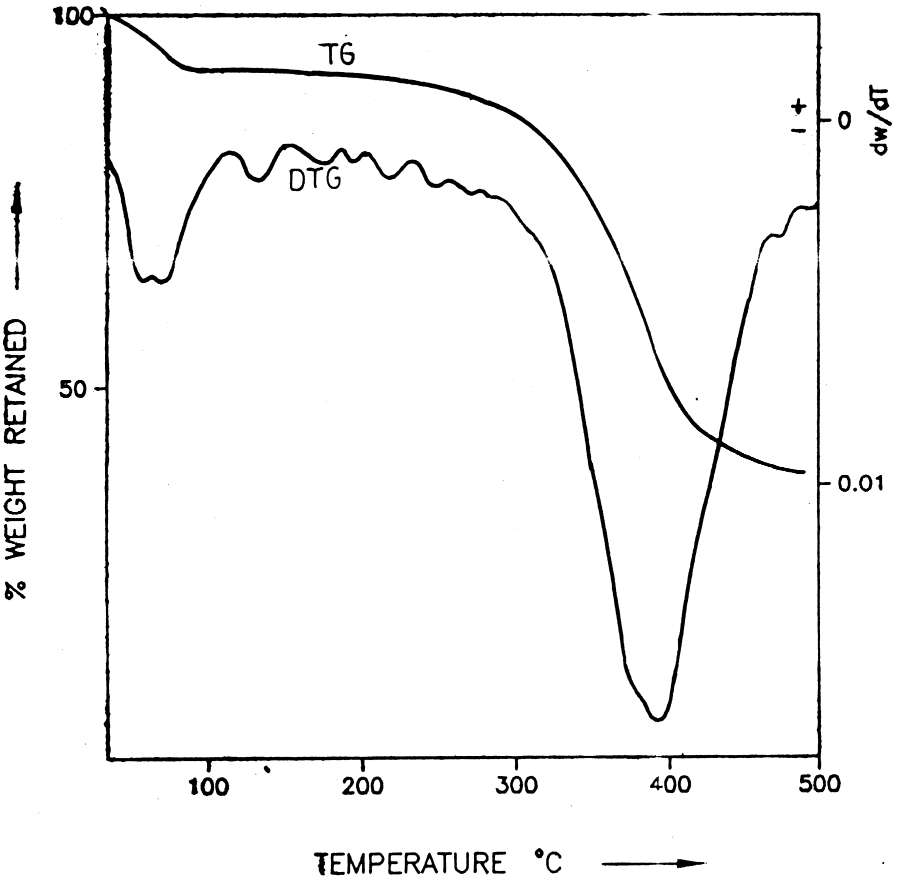

Fig. 4. Primary thermogram and derivatogram for poly(methacrylonitrile).

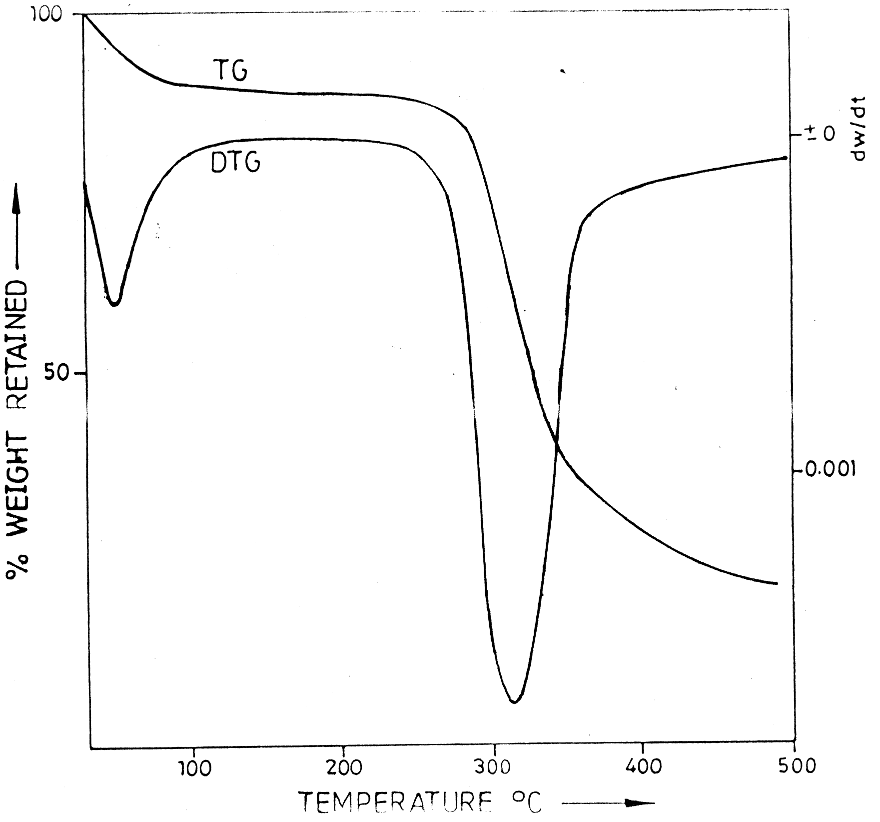

Fig. 5. Primary thermogram and derivatogram for grafted starch with %PG = 9.7.

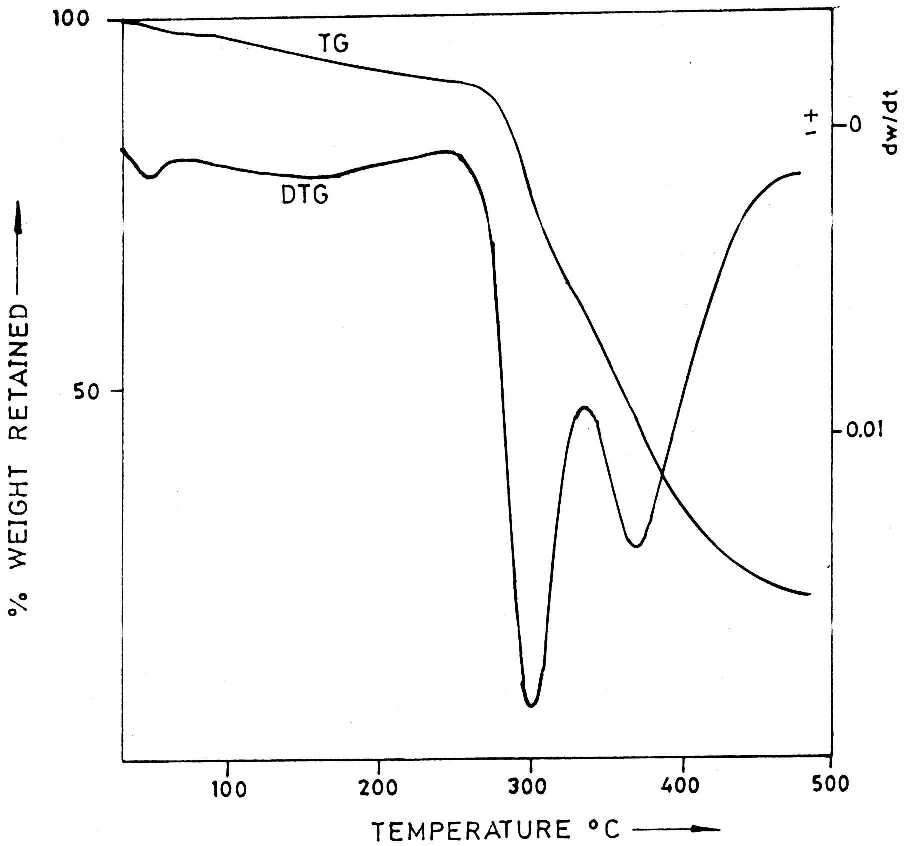

Fig. 6. Primary thermogram and derivatogram for grafted starch with %PG = 77.9.

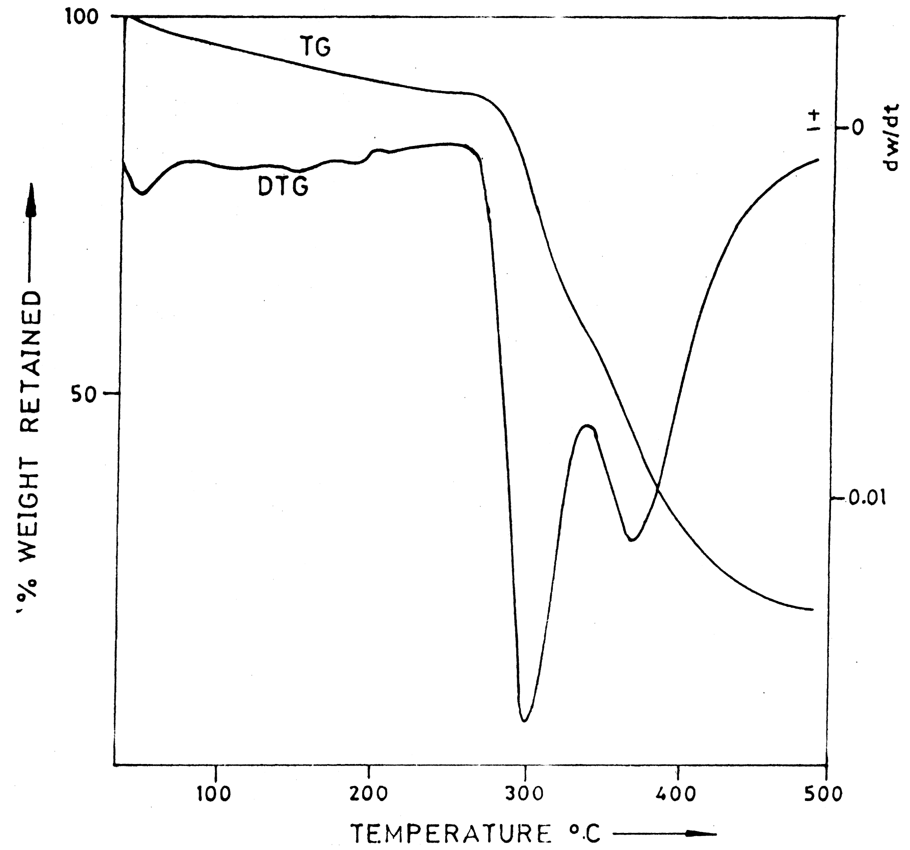

Fig. 7. Primary thermogram and derivatogram for grafted starch with %PG = 97.3.

supply of monomer to the substrate (Vazquez et al., 1992a,b). The present grafting system is a heterogeneous one when MAN concentration exceeds approximately 2.8% in the reaction medium. Obviously, the initial increase in the grafting yield is due to increasing supply of monomers to the starch macroradicals, however, the decline in %GE at higher [MAN] can be ascribed to the chain transfer to excess monomer molecules in the vicinity of growing ends of grafted chains (Gao, Tian, Yu & Duan, 1994). Moreover, the large amount of homopolymer deposits blocks the way of monomer molecules to the starch macroradicals resulting in further decrease in graft yield. Nevertheless, the optimum concentration of MAN in the present experiments is found to be 0.755 mol/l.

3.4. Effect of polymerisation time

Table 3 illustrates the effect of polymerisation time on the grafting of MAN onto granular maize starch. Although grafting begins slowly registering only 3.8%GE at the end of 60 min, the rate of grafting increases rapidly with time reaching an optimum %GE of 48.7% within 180 min and then it levels off.

The %GE is a measure of the propagation of graft copolymerisation reaction as it tells us about the percent of

Table 5
Thermal decomposition data of starch and graft copolymers

Substance	Initial temperature for different stages of decomposition (°C)			Corresponding T_{max} (°C)			Respective %wt. losses			Residue %wt. at 496°C
	1	2	3	1	2	3	1	2	3	
Starch	37	233	420	42	308	495	12	76	11	[1]
Poly(methacrylonitrile)	30	258	–	67	382	–	9	53	–	[38]
Graft copolymer										
%PG = 9.7	37	230	–	51	310	–	10	68	–	[22]
%PG = 77.9	35	245	338	51	301	369	8	28	34	[30]
%PG = 97.3	37	242	340	49	301	371	9	30	34	[27]

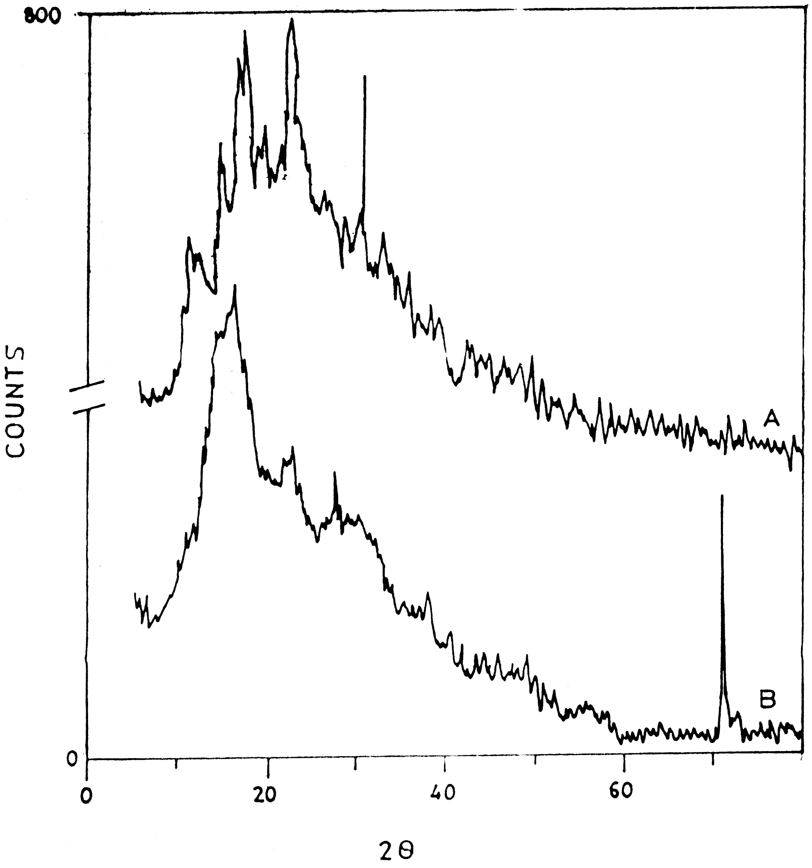

Fig. 8. Wide angle X-ray diffraction pattern of (a) granular maize starch and (b) grafted starch with %PG = 77.9.

synthetic polymer in the graft copolymer. The initial low value of %GE shows slow propagation which gets accelerated with time. The levelling off of the grafting rate after 180 min can be rationalised on the basis of progressive consumption of the monomer and initiator with time (Shukla & Sharma, 1987).

3.5. Effect of reaction temperature

The %GE and %PG for the grafting of MAN onto maize starch are tabulated in Table 4. As the present study was confined to the granular maize starch, the reaction temperature was not allowed to cross the lower level of the gelatinisation temperature range (62°C). Initially, %GE increases with increase in temperature up to 35°C probably due to the enhanced diffusion of monomer molecules to the macroradical sites but further increasing the temperature results in decrease in graft yield. This is expected as the chain transfer reactions with higher activation energy are favoured at high temperatures and in most of the cases they contribute nothing to the grafting (Mishra et al., 1980). It is also likely that at higher temperature there is an increase in the rate of oxidation of starch (Patil & Fanta, 1993). Acrylonitrile shows similar behaviour when grafted onto starch with benzoyl peroxide as an initiator (Mishra, Dogra, Kaur & Sood, 1979).

3.6. Characterisation of graft copolymers

3.6.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Figs. 3–7 show the primary thermograms and derivatograms for the pure and grafted starch with varying %PG which is the preferred grafting parameter to be considered for TGA studies as it reflects the percentage of synthetic polymer grafted onto pure starch.

Pure starch (Fig. 3) shows a characteristic three-step thermogram. The initial slight loss in weight, is merely due to evaporation of absorbed moisture. The rapid decomposition occurs in the second stage resulting in the major weight loss of 76% (Table 5). The derivatogram clearly exhibits the temperature for maximum decomposition for this stage as 309°C. The final stage of decomposition is due to formation and evaporation of some volatile compounds hence is rather slow and results in about 11% weight loss. Similar thermal behaviour is observed for cellulose (Saikia, Tosh, Goswami & Ghosh, 1996).

Poly(methacrylonitrile) (PMAN) shows two stage decomposition pattern (Fig. 4). Obviously the first stage (30–107°C) is due to dehydration showing about 9% weight loss, while about 53% weight loss occurs in the second stage

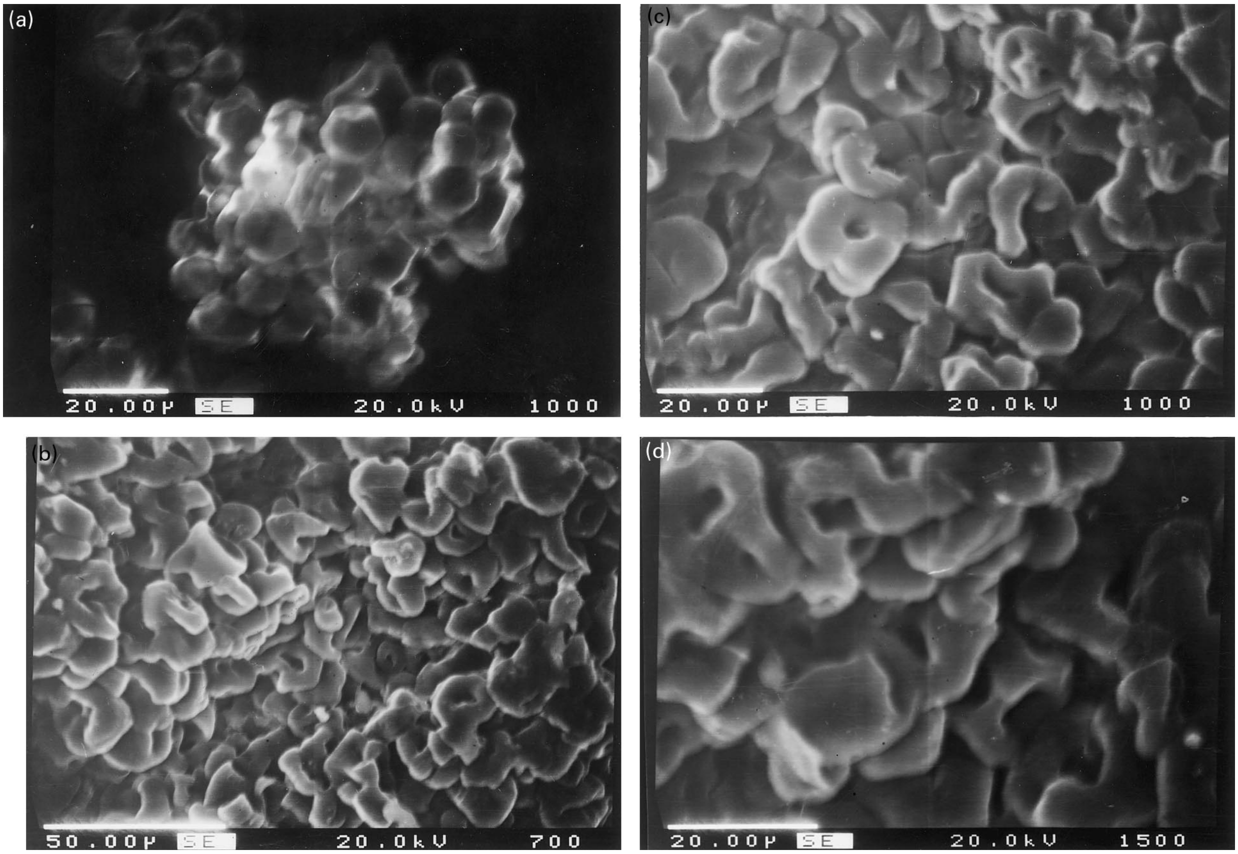

Fig. 9. SEM photographs of (a) granular maize starch at magnification 1000 and of grafted starch with %PG = 77.9, (b) at magnification 700 × , (c) at magnification 1000 × , and (d) at magnification 1500 × .

of decomposition in the temperature range of 259–492°C. The char yield of 38% is obtained at 496°C.

As far as the first stage of weight loss (dehydration) is concerned, the samples of grafted starch show insignificant change in their behaviour over the pure starch sample (Figs. 5–7).

However, for all the grafted samples, the initial decomposition temperature for the second stage of decomposition lies almost between that of pure starch and PMAN (Table 5). The third stage of decomposition is quite significant for the grafted samples with high %PG. The graft copolymer samples with higher %PG decompose rather slowly (Table 5) up to 496°C. The residue at 496°C may be mainly due to grafted PMAN.

It can be concluded that grafting of methacrylonitrile onto starch does not significantly alter the thermal stability of starch.

3.6.2. X-ray diffraction studies

Starch granules are semi-crystalline in nature. The crystallinity is essentially due to amylopectin fraction. The areas of crystallinity comprise about 20–25% of the total volume of the starch granule (Swinkles, 1985). The wide angle X-ray diffraction pattern of pure granular maize starch (Fig. 8a) comprises four more or less sharp peaks with low counts merely up to 800 between 2θ values of 10–30°, which on drying and grafting, appears to have compressed into a broad smoothened peak thereby altering the crystallinity of pure granular starch (Fig. 8b). It can therefore, be inferred that along with the amorphous region, the crystalline region of the granular starch is also involved in grafting.

3.6.3. Scanning electron microscopy

SEM is the right technique used for direct observation of microstructure of spherulites of size in the range between 0.1–10 μm like maize starch granules. The electron micrographs of pure starch (Fig. 9a) samples clearly exhibit its granular structure. A change in contour of the granules on grafting and the thick polymeric coating on their surface, obviously of grafted poly(methacrylonitrile), are seen in Fig. 9b–d. It can be seen that individual granules of starch have joined through these surface coatings, during grafting process.

4. Conclusions

- Ceric ammonium nitrate can effectively initiate graft copolymerisation of MAN onto granular starch at

ambient temperature. The maximum %GE and %PG obtained are 52.6 (Table 3) and 127.0 (Table 2), respectively.
- The %GE and %PG can be adjusted by varying the reaction parameters. The optimum conditions worked out on the basis of present work are as follows:

  [CAN] = 0.002 mol/l;
  [MAN] = 0.755 mol/l;
  reaction time, 180 min;
  polymerisation temperature, 35°C.

- The grafting of methacrylonitrile onto starch, does not significantly alter the thermal stability of starch.
- Along with amorphous region, the crystalline region of starch is also involved in grafting.
- The grafted starch forms a thick layer over individual starch granules.

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