On the Characterization of Grafted and Ungrafted Starch, Amylose, and Amylopectin

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ABSTRACT: Graft copolymers of polyacrylamide with starch, amylose, and amylopectin have been synthesized using ceric-ion-induced redox initiation technique. The polymers were characterized using different instrumental techniques like thermal, XRD, SEM, IR, NMR, and elemental analysis. The results indicated that there is a substantial amount of grafting with minimum formation of homopolyacrylamide. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1795–1810, 1998

INTRODUCTION

It has been observed recently that the grafted polysaccharides[1] circumvent several deficiencies of polysaccharides and synthetic polymers like polyacrylamide in causing turbulent drag reduction and flocculation. Polysaccharides, in general, are shear-stable but easily biodegradable and cause drag reduction and flocculation at high concentration. On the other hand, polyacrylamide is very effective as a turbulent drag-reducing and flocculating agent, but it does not have required shear stability. When polyacrylamide branches are grafted on polysaccharides like starch, amylose, xanthan gum, guar gum, and carboxymethyl cellulose, one can have a large number of graft copolymers[2–5] with varying number and length of grafted chains. In general, it has been observed that the graft copolymers having fewer but longer branches are fairly shear-stable[6] drag-reducing and flocculating agents.[7] Recently, extensive investigation has been carried out in the authors' laboratory on the flocculation characteristics of graft copolymers of starch and its constituents (amylose and amylopectin) with polyacrylamide. It has been observed that polyacrylamide-grafted amylopectin performs the best as a flocculating agent,[8,9] particularly for industrial effluents. This has been attributed to the fact that the dangling polyacrylamide chains on rigid and branched amylopectin have better approachability to the colloidal particles in the effluents. In our previous articles, we have reported the flocculation characteristics of grafted and ungrafted starch family for various kinds of synthetic[10] and industrial effluents.[8,9] In this article, we report the characterization of the grafted and ungrafted starch, amylose, and amylopectin by various techniques like thermal analysis, X-ray diffraction, scanning electron microscopy, infrared nuclear magnetic resonance, and elemental analysis. Further proof of grafting by enzyme hydrolysis in a series of graft copolymers of amylopectin and polyacrylamide is reported in our next article.

MATERIALS

Amylopectin (from corn) was purchased from Sigma Chemical Company, USA. Acrylamide was purchased from E. Merck, Germany. Ceric ammonium nitrate (CAN) was obtained from Loba Chemie, Bombay, India. Acetone and hydroquinone were supplied by s. d. Fine Chemicals, India. Sodium nitrate was supplied by E. Merck, Bombay, India. All the chemicals received were used as such without further purification.

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Table I Details of Synthesis Parameters of the Graft Copolymers

Sl. No.	Polymer	(Moles of AGU)[a]	AM (Mol)	CAN (Mol × 10^4)	% Conversion[b]	[η] (dL/g)
I	Ap-*g*-PAM 5	0.0154	0.21	0.5016	70.8	11.38
II	Ap-*g*-PAM 1	0.0154	0.21	1.003	87.6	10.61
III	Ap-*g*-PAM 6	0.0154	0.21	1.5048	88.13	9.76
IV	Ap-*g*-PAM 2	0.0154	0.21	2.006	90.95	6.95
V	Ap-*g*-PAM 3	0.0154	0.28	1.003	77.8	9.93
VI	Ap-*g*-PAM 4	0.0154	0.14	1.003	84.1	7.46
VII	Ap-*g*-PAM 7	0.006	0.28	1.003	78.4	11.68
VIII	Ap-*g*-PAM 8	0.006	0.35	1.003	81.6	11.67
IX	St-*g*-PAM	0.0154	0.14	1.003	89.33	6.85
X	Am-*g*-PAM	0.0154	0.14	1.003	72.38	7.46

[a] Calculated on the basis of anhydroglucose units (AGU). 1 Mol of AGU = 162 g.

[b] %Conversion was calculated from the following relation: % Conversion = (wt of graft copolymer − wt of polysaccharide)/wt of acrylamide monomer.

SYNTHESIS

All the graft copolymers (those of starch–amylose–amylopectin with polyacrylamide) were synthesized[11,12] by ceric-ion-induced solution polymerization method. The details of synthesis and separation of graft copolymers have been discussed in our previous article. The synthesis parameters of graft copolymers are summarized in Table I.

CHARACTERIZATION

Elemental Analysis

The elemental analysis of all the samples, namely, starch, amylose, amylopectin, and the graft copolymers was done using a Carlo Erba 1108 Elemental Analyzer. The estimation of only three elements, that is, carbon, hydrogen, and nitrogen, was done. The facility was availed from the Regional Sophisticated Instrumentation Centre (RSIC) at The Central Drug Research Institute (CDRI), Lucknow, India.

Study of Natural Aging

The following test was carried out to test the natural aging characteristics of amylopectin and one of its graft copolymers. The time of flow of a 0.3% solution of amylopectin was measured in the capillary viscometer (CS/S: 0.00527) at 27 ± 0.1°C, every 20 days from the date of preparation of the solution. The solution of amylopectin was made in distilled water, and it was kept stoppered in a volumetric flask under ambient conditions. The relative viscosity, η_{rel}, was calculated as the ratio of t, the flow time of amylopectin solution, and t_0, the flow time of distilled water at the temperature of measurement, as specified above. In case of the graft copolymer, a similar method was followed. Graph of η_{rel} versus time in days was plotted to study the natural degradation of amylopectin and the backbone in the graft copolymer.

Infrared Spectra

The infrared (IR) spectra of starch, amylose, amylopectin, polyacrylamide and the graft copolymers (Ap-*g*-PAM 3, St-*g*-PAM, and Am-*g*-PAM) were recorded in solid state using a KBr dispersion method in the transmittance mode. All the polymers as well as the KBr were properly dried in a vacuum oven and were preserved in a desiccator. The IR spectra were recorded with a Perkin–Elmer 630 IR spectrophotometer in the range of 4000–400 cm^{-1}. A uniform resolution of 3.2 cm^{-1} was maintained in all cases. In the case of Ap-*g*-PAM, the IR spectra was also recorded after complete hydrolysis of the graft copolymer with the enzyme α-amylase.

NMR Spectra

Both ^1H and ^{13}C nuclear magnetic resonance (^1H-NMR and ^{13}C-NMR) of Ap-*g*-PAM 4 were recorded in D_2O solution. A homogeneous gel of about 20 mg/mL of the polymer was prepared in D_2O. Dioxane was used as the reference. NMR

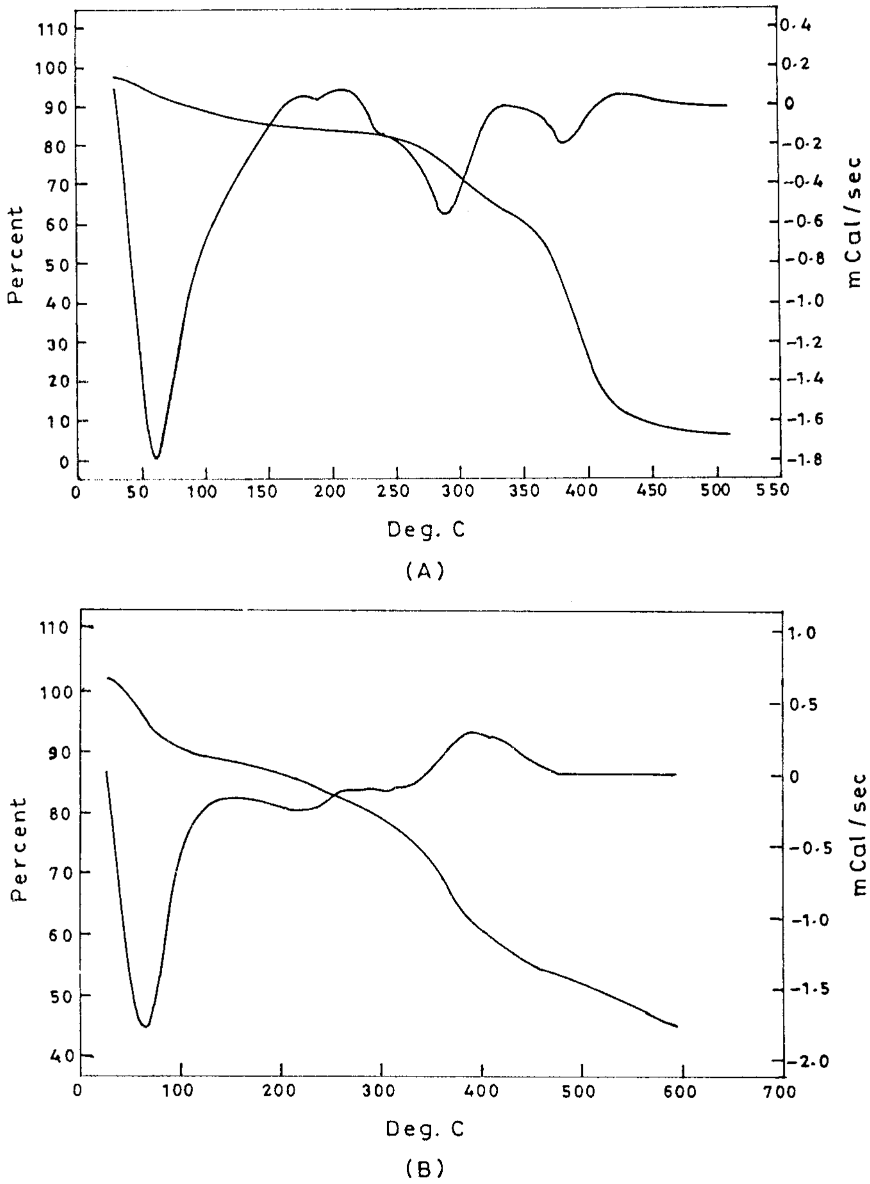


Figure 1 Original thermal curves of (A) Ap-*g*-PAM 1 and (B) Ap-*g*-PAM 3 as obtained by the recorder.

spectra were recorded with a Bruker–Superkon 200 MHz NMR spectrophotometer.

Thermal Analysis

The thermal analysis of all the samples were carried out with Stanton Redcroft (STA 625) Thermal Analyzer. Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the samples were performed up to a temperature of 600°C, starting from room temperature in an atmosphere of nitrogen. The heating rate was uniform in all cases at 10 deg/min.

During the thermal analysis, both the TGA and DSC curves of each of the polymers were obtained in a single printout. But the scales (both along X- and Y-axes) of the plots in each case were different from the other. For example, Figure 1 shows the original thermal curves of two graft copolymers (Ap-*g*-PAM 1 and Ap-*g*-PAM 3). It can be observed that not only the temperature axes are of different scales but also the Y-axes as well in both cases. Thus, in the case of TGA curves, the percent axis (along the ordinate) of Ap-*g*-PAM 1 is from 0-110; whereas, in the case of Ap-*g*-PAM 3, it

Table II Results of Elemental Analysis

Polymer	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Starch	39.31	6.36	Negligible
Amylose	39.43	6.49	Negligible
Amylopectin	39.2	5.9	Negligible
Ap-*g*-PAM 1	43.13	6.93	15.12
Ap-*g*-PAM 2	44.37	7.7	15.5
Ap-*g*-PAM 3	44.45	7.55	16.08
Ap-*g*-PAM 4	43.25	7.83	14.23
Ap-*g*-PAM 5	43.29	6.78	15.65
Ap-*g*-PAM 6	43.6	6.65	15.47
Ap-*g*-PAM 7	43.67	6.73	16.58
Ap-*g*-PAM 8	44.95	7.17	16.92
St-*g*-PAM	43.29	7.8	14.31
Ap-*g*-PAM	43.16	7.92	14.18

is from 40-110. Similarly, for the DSC curves the enthalpy (mCals/s) variation is from −1.8 to 0.4 in the case of Ap-*g*-PAM 1; whereas the same has a variation of −2.0 to 1.0. The aim was to make a comparative assessment of the TGA as well as DSC curves of different polymers separately. This was not possible with such a wide variation in the scales. Thus, all the original curves were redrawn to a uniform scale taking sufficient number of points on the curves. The redrawn curves and the comparison among different polymers is shown in the section under results and discussion.

X-ray diffractometry

X-ray diffractograms of all the polymers in powder form were recorded with a Philips (PW 1840) X-ray diffractometer using Mo K_α radiation. The scattering angle (2θ) was varied from 10–45°.

Scanning Electron Microscopy

Amylopectin could not be analyzed in scanning electron microscopy (SEM) in the original powder form. Hence, it was dissolved in distilled water, precipitated in acetone, and vacuum-dried before submitting for SEM. In the case of graft copolymers, small granules after sieving the pulverized samples were submitted. The samples were gold-coated, and magnifications of 200–300 times were obtained. CAM SCAN SERIES-2 (Cambridge Scanning Company, UK) was used for the above study.

RESULTS AND DISCUSSION

Synthesis

Table I shows the synthesis details of the graft copolymers based on starch, amylose, and amylopectin. With amylopectin, a series of eight graft copolymers were synthesized. In the case of the first four graft copolymers (sl. no. I–IV), a variation in the catalyst concentration was effected, keeping the moles of amylopectin and acrylamide constant. The second set of four graft copolymers (sl. no. V–VIII) was synthesized at a fixed catalyst concentration with variation in the moles of acrylamide. The mechanism of ceric ion action involves the formation of a chelate complex[13] that decompose to generate free radical sites on the polysaccharide backbone. These active free radical sites in the presence of acrylic monomers generate graft copolymers. Following a simplistic approach, the number of free radical sites generated should be proportional to the concentration of ceric ion. In other words, the length of the grafted chains at a fixed monomer concentration should be the longest in the case of the lowest ceric ion concentration and vice versa. This trend is clearly observed in case of graft copolymers I to IV. The variation in the length of grafted chains produces gradually decreasing intrinsic viscosity values that can be explained in terms of variation in the number and length of polyacrylamide chains.

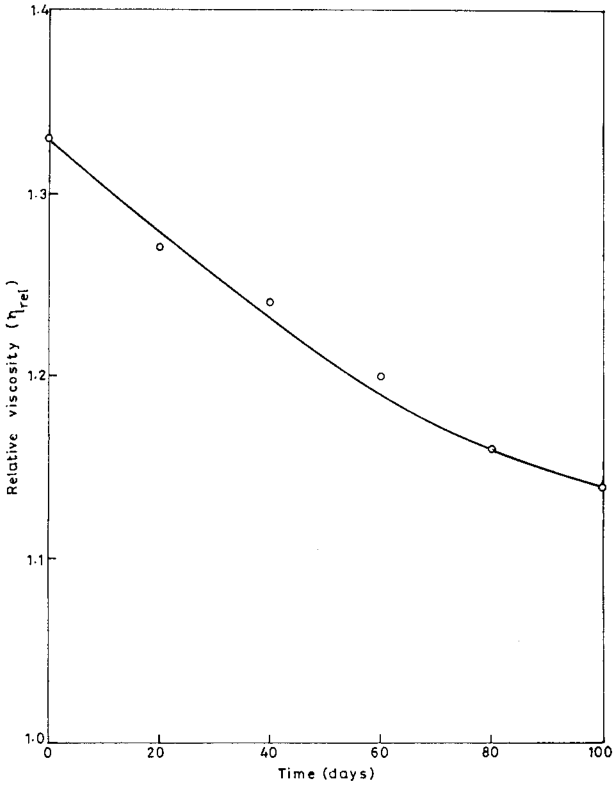


Figure 2 The study of natural aging of amylopectin: variation of relative viscosity with time.

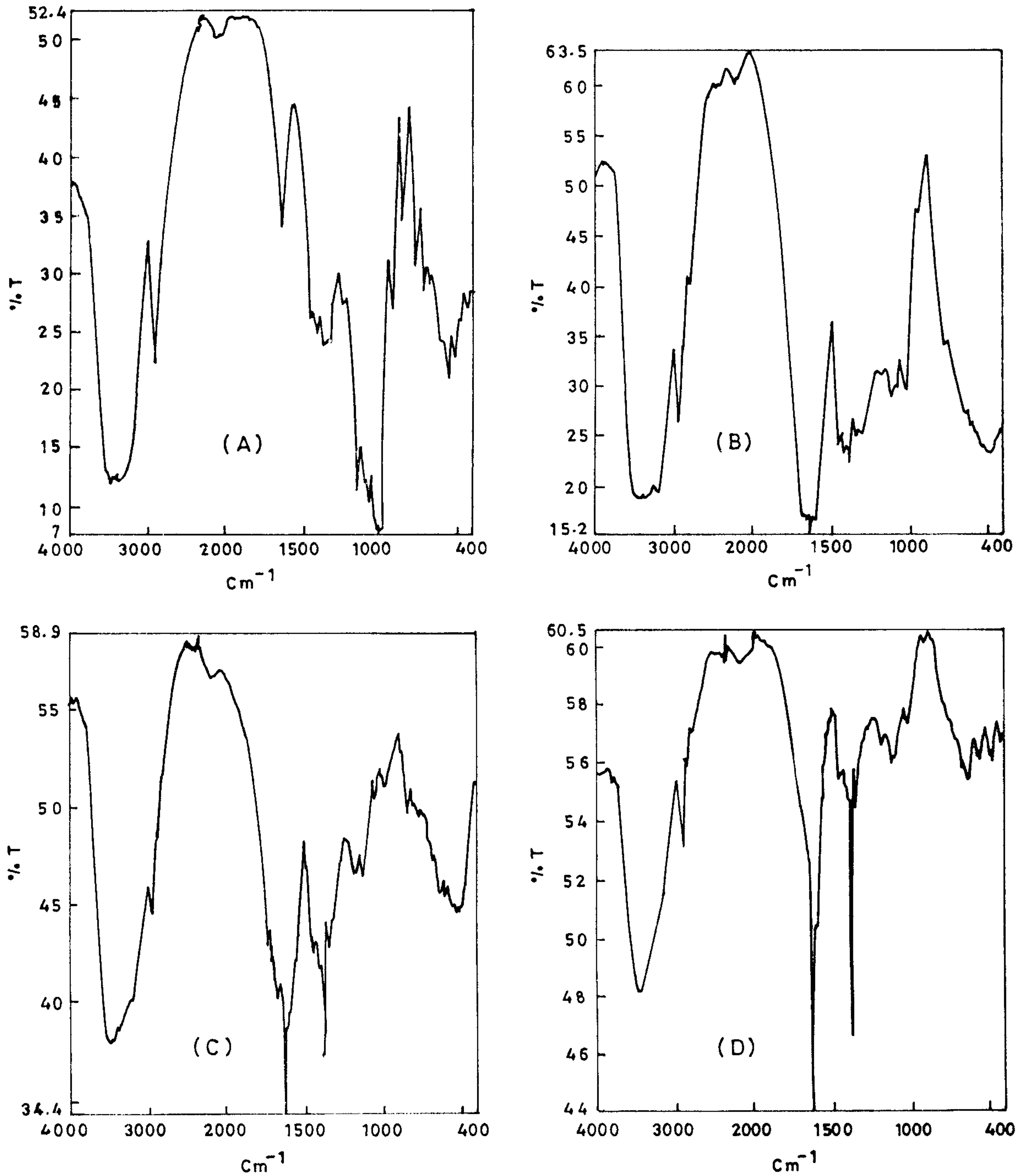


Figure 3 IR spectra of (A) amylopectin, (B) Ap-*g*-PAM 3, (C) polyacrylamide, and (D) Ap-*g*-PAM 3 after hydrolysis with α-amylase.

Similarly, there is a decrease in the intrinsic viscosity between V and VI, which could be due to short branches because of lower acrylamide concentration in case of latter. In the case of VII and VIII, a deliberate attempt was made to use a very high molar concentration of acrylamide to see the impact of the length of grafted chains on the intrinsic viscosity. Interestingly, the intrinsic viscosity values of VII and VIII are similar, which seems anomalous. This indicates that at a very high molar concentration of acrylic monomers, there may be a higher percentage conversion to homopolymer, and the resulting intrinsic viscosity might be the reflection of the mixture of homo-

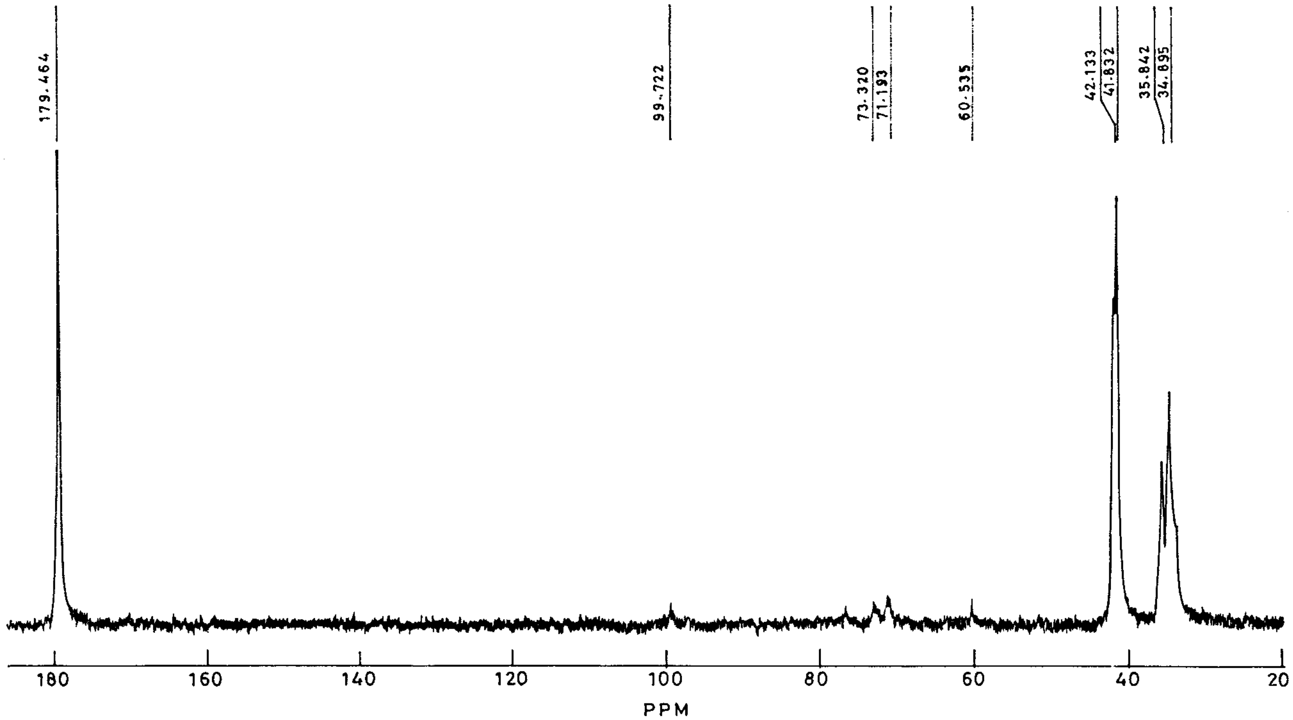


Figure 4 ^{13}C-NMR of Ap-*g*-PAM 4.

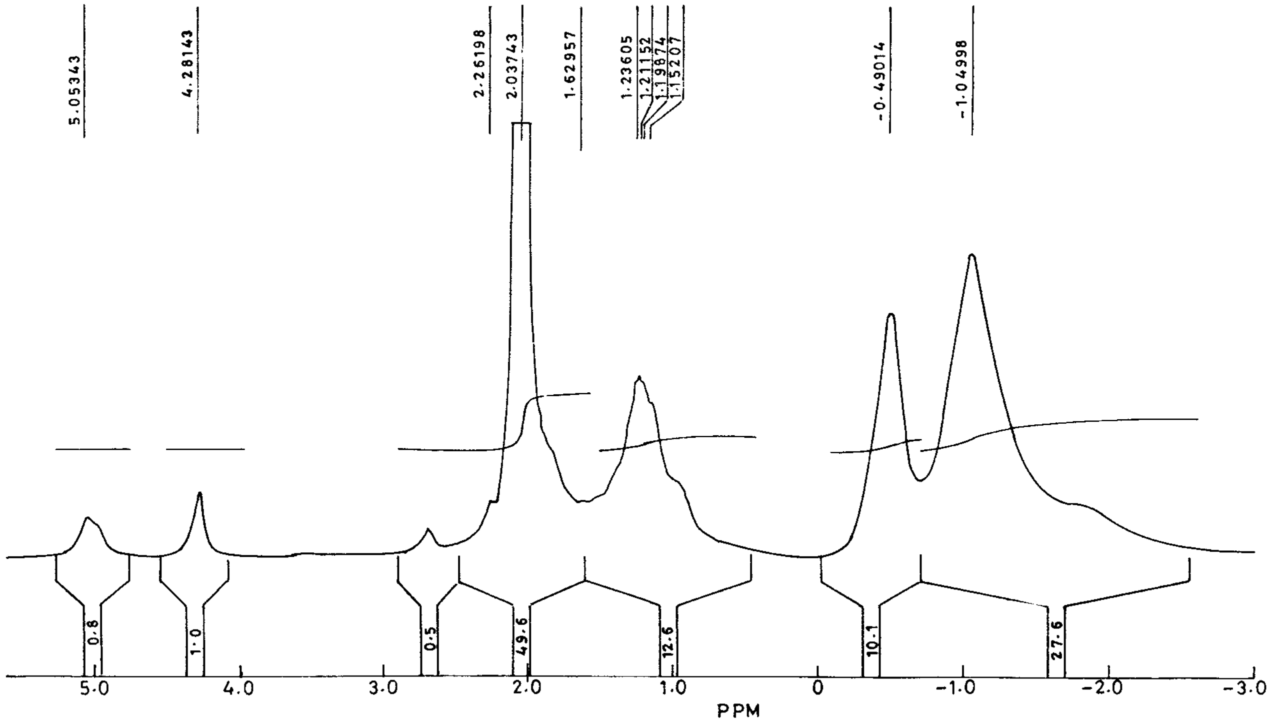


Figure 5 ^{1}H-NMR spectrum of Ap-*g*-PAM 4.

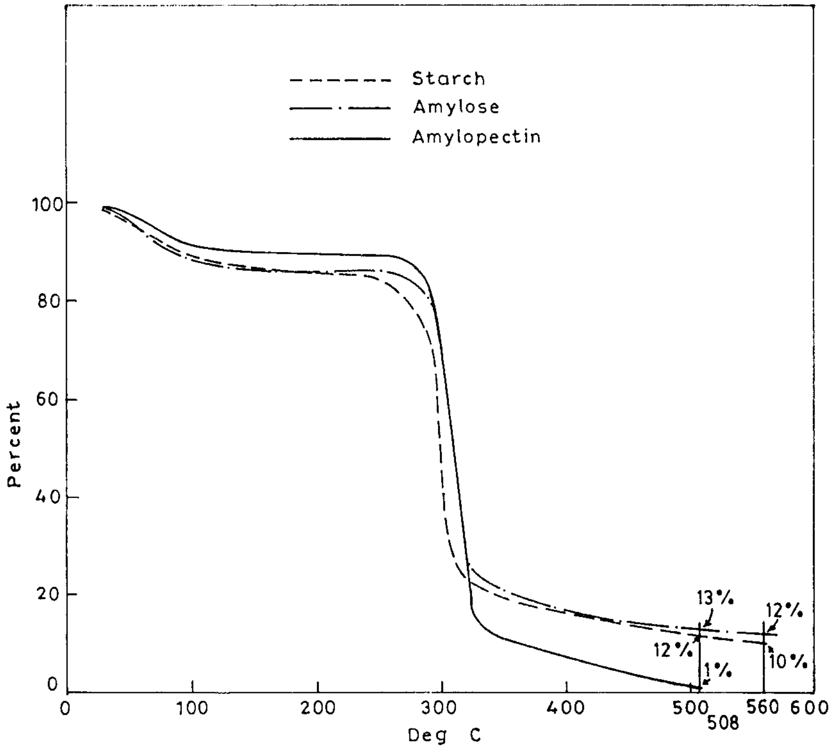


Figure 6 TGA curves of starch, amylose, and amylopectin.

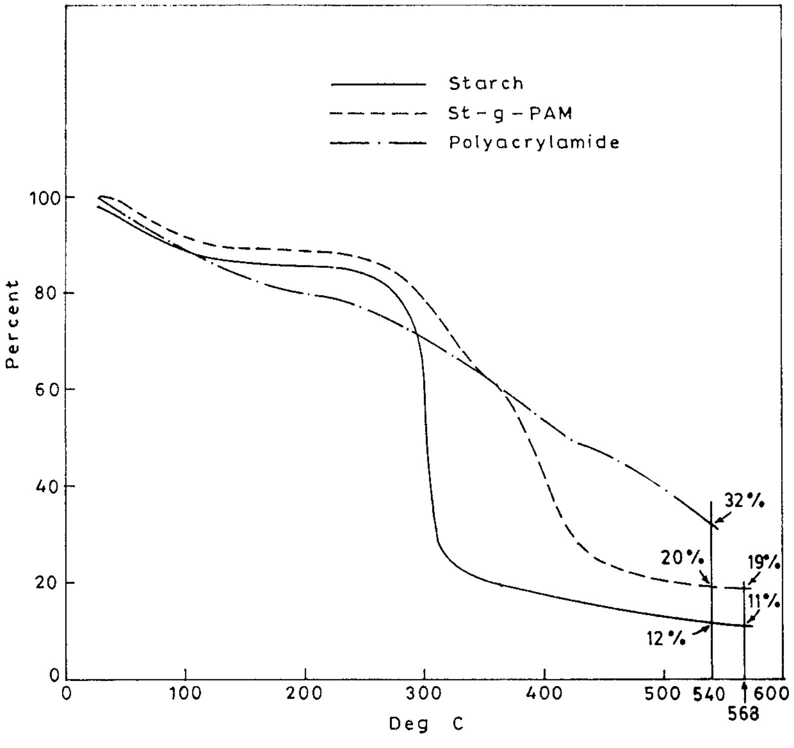


Figure 7 TGA curves of starch, St-*g*-PAM, and polyacrylamide.

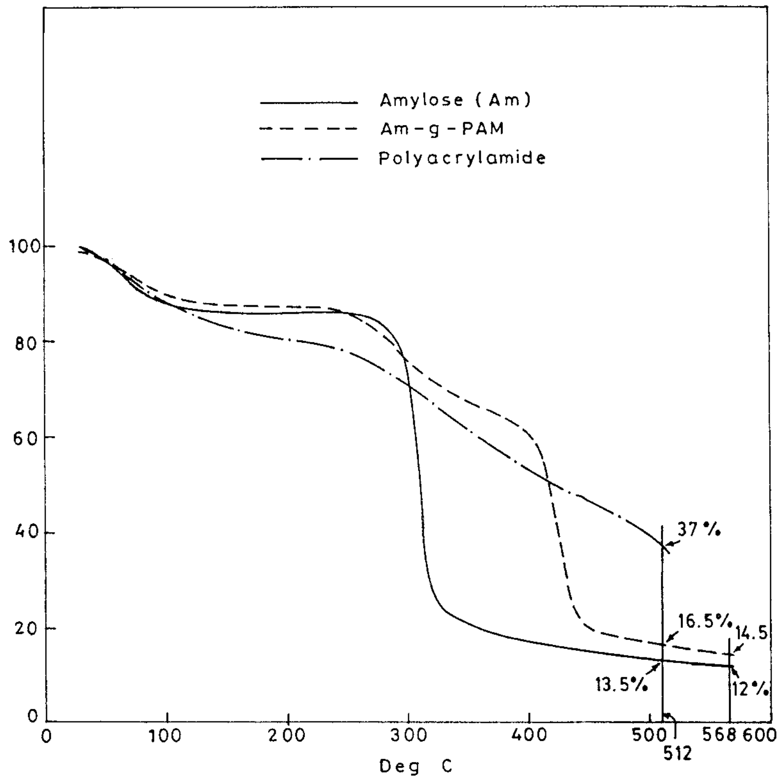


Figure 8 TGA curves of amylose, Am-*g*-PAM, and polyacrylamide.

and graft copolymers. It may be emphasized that there could be some amount of homopolymer formed at a low acrylamide concentration, but the percentage conversion to homopolymer is probably higher at higher monomer concentration in the reaction feed. This observation also qualitatively agrees with the experimental findings of Owen and Shen,[14] who have observed that a

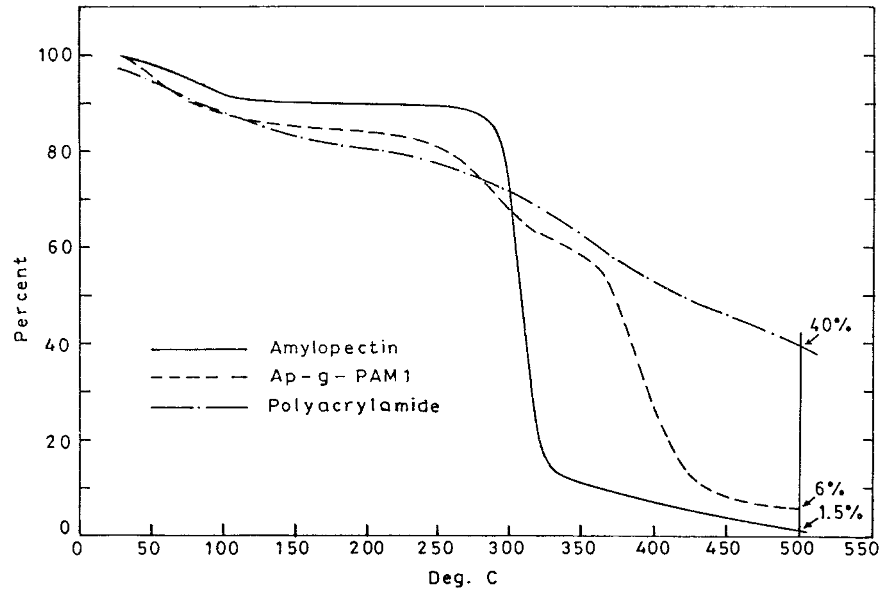


Figure 9 TGA curves of amylopectin, Ap-*g*-PAM 1, and polyacrylamide.

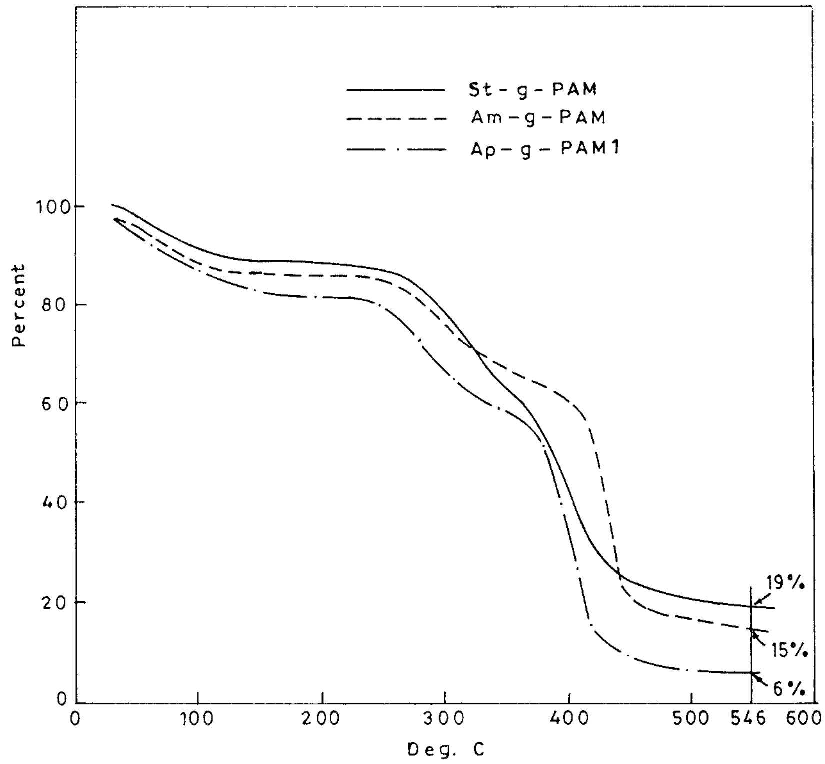


Figure 10 TGA curves of St-*g*-PAM, Am-*g*-PAM, and Ap-*g*-PAM 1.

monomer concentration of greater than 2.0*M* encourages homopolymer formation. In our case, the concentration of monomer is much smaller than 2.0*M*. Hence, the possibility of homopolymer formation is very very less.

In a separate study,[15] we have established the formation of graft copolymers by a combined use of viscometry and enzyme hydrolysis, without the separation of homopolymers. Moreover, Ungeheur, Brostow, and Singh have convincingly demonstrated by rheological techniques that under the conditions prescribed by Owen and Shen,[14] there is little or no homopolymer formation. It may be noted that little conversion to homopolymer in this case cannot be ruled out. However, since the homopolymer and the graft copolymer are water soluble, it was difficult to separate one from the other, except with the help of HPLC.

Elemental Analysis

The results of elemental analysis of starch, amylose, amylopectin, and all the graft copolymers are presented in Table II.

Starch, amylose, and amylopectin do not show any significant presence of nitrogen. The negligible amount of nitrogen observed may be because of the trace quantities of unisolated proteins present in the polysaccharides. It is observed that there is a considerable percentage of nitrogen in the graft copolymers, which can be accounted to the presence of the grafted polyacrylamide chains. In the series of graft copolymers based on amylopectin, the variation in the nitrogen content, although not much, is significant in the case of Ap-*g*-PAM 3, Ap-*g*-PAM 7, and Ap-*g*-PAM 8 compared to the other graft copolymers. The higher percentage of nitrogen may be due to the increased polyacrylamide content in the graft copolymer because of higher moles of acrylamide in the reaction feed (Table I). Among other graft copolymers, Ap-*g*-PAM 4 has the smallest nitrogen percentage, which is again evident from the lowest amount of acrylamide in the reaction feed compared to other graft copolymers in the series.

Natural Aging

The variation of relative viscosity of amylopectin solution with time (in days) is shown in Figure 2. It is evident that amylopectin does, in fact, degrade appreciably over a period of 100 days. But the study of relative viscosity of its graft copolymer (Ap-*g*-PAM 1) with polyacrylamide (not

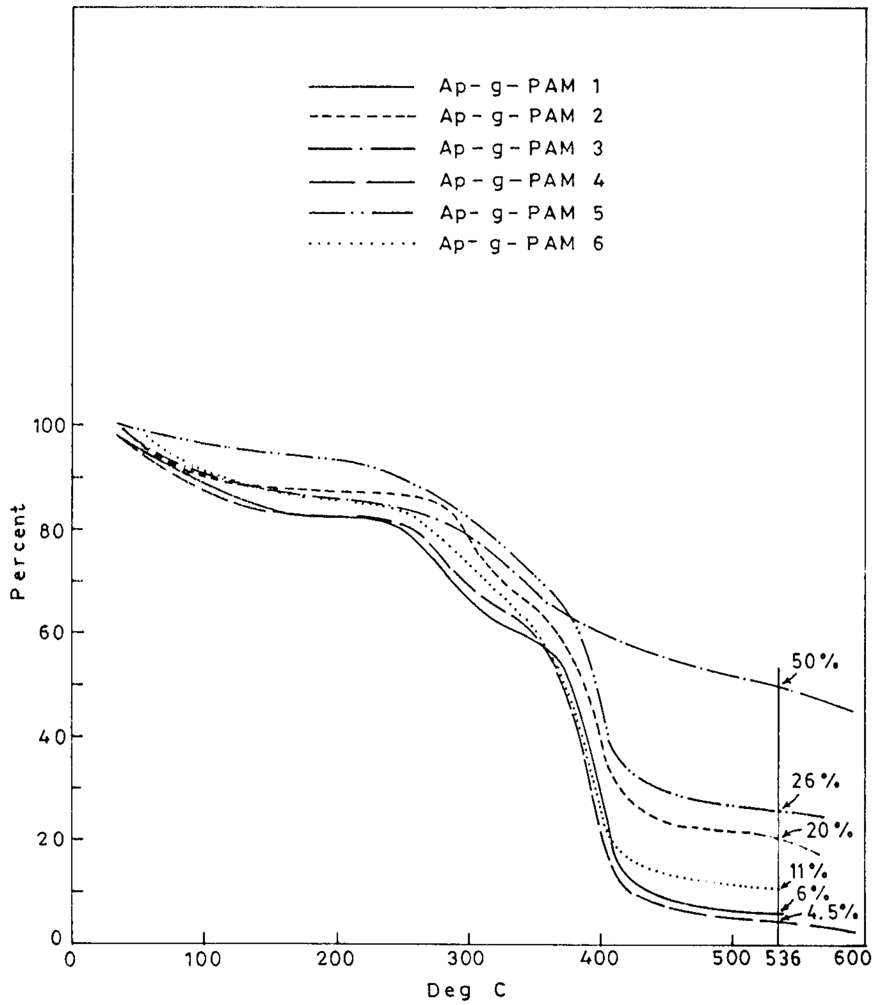


Figure 11 TGA curves of amylopectin-based graft copolymers (Ap-*g*-PAM 1 to Ap-*g*-PAM 6).

shown in the figure) over the same period did not indicate degradation to any significant extent. This could be due to the alteration in the structure of amylopectin as a result of grafting and the enhanced percentage of the synthetic content in the graft copolymer which is not suitable as a food for bacteria.[16]

IR Spectra

The IR spectra of amylopectin, polyacrylamide, Ap-*g*-PAM 3, and Ap-*g*-PAM 3 (after treatment with α-amylase) are presented in Figure 3. IR spectra of starch and amylose have not been shown because the three spectra of amylopectin, starch, and amylose have similar absorptions. For a similar reason, the IR spectra of St-*g*-PAM and Am-*g*-PAM have not been shown. The presence of a strong absorption characteristic of $>C{=}O$ stretching, which is absent in amylopectin is a proof of grafting. Hydrolysis of Ap-*g*-PAM with α-amylase destroys the amylopectin backbone in the graft copolymer, and a mixture of polyacrylamide chains is obtained. It is observed from Figure 3 that there is a strong similarity between the IR spectra of polyacrylamide (commercial product) and the one obtained from hydrolysis of graft copolymer with α-amylase. This is a further proof of grafting.

NMR Spectra

Figure 4 shows the ^{13}C-NMR of Ap-*g*-PAM 4. It is observed that distinct peaks occur for different carbons in the graft copolymer. The position of absorption[17] for the carbonyl group of polyacryl-

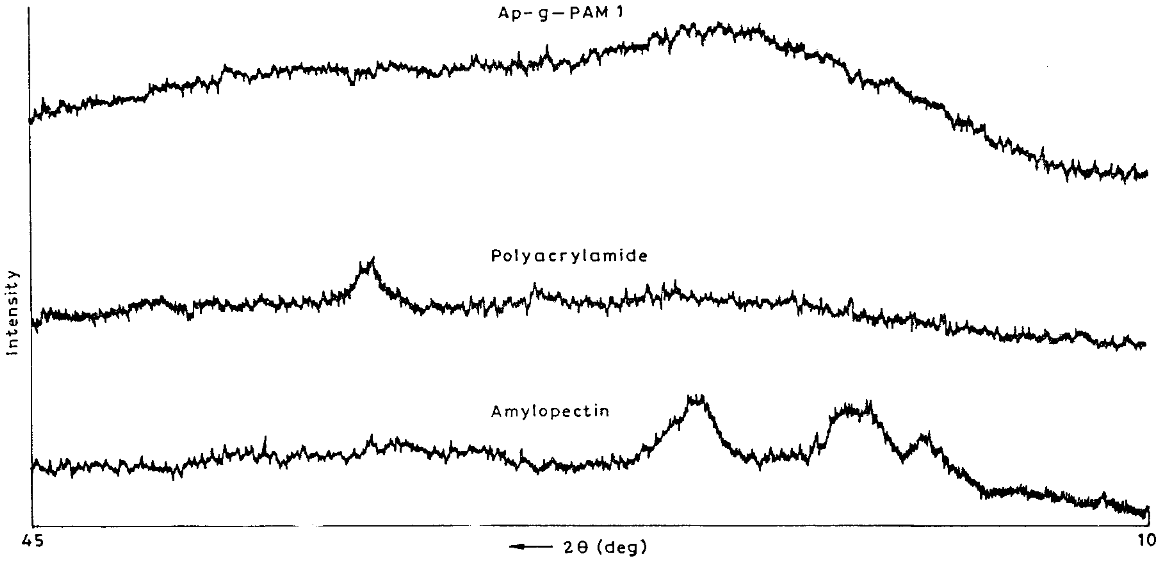


Figure 12 X-ray diffractograms of amylopectin, polyacrylamide, and Ap-*g*-PAM 1.

amide chains occurs at 179.464 ppm, whereas those for the —CH_2—CH— group occur as doublets at δ-values of 34.895, 35.842, 41.832, and 42.133 ppm. The carbons of the anhydroglucose units occur as small peaks at δ-values of 60.535, 71.193, 73.320, and 99.722 ppm. One of the essential characteristics of an NMR spectrum is the proportionality of area under the peaks to the concentration of respective nuclei in the sample. If we compare the relative amount of starting components before carrying the grafting reaction, it is observed that the amount of amylopectin in the graft copolymer should be quite low compared to polyacrylamide in the grafted product. Proportionately, the amount of amylopectin will be still lower in the sample (≃ 20 mg/mL) taken for NMR study. The spectra show that the area under the peak for $\rangle$C=O is maximum followed by that under the —CH_2—CH— group. In contrast, the area of the peaks for anhydroglucose units is quite low. It may be noted that it was difficult to increase the concentration of samples in NMR because of instrumental difficulties. Figure 5 shows the ^1H NMR spectrum of the same graft copolymer. The protons of the anhydroglucose units absorb in the range of δ 1.0–3.0 ppm. On the other hand, the protons of the amide groups occur in the range of δ 0.0 to −2.0 ppm. The protons of the —CH_2—CH— group occur in the range of δ 4.0–5.0 ppm. In contrast to the ^{13}C-NMR spectrum, the peaks in this case sweep larger area because of the relative abundance of respective protons (^{13}C isotope has a very low natural abundance of 1.01% only). The protons of —CO—NH_2— groups occur at a lower field strength compared to those in the —CH_2—CH— group.

Thermogravimetric Analysis

Figure 6 shows the TGA curves of starch, amylose, and amylopectin. It can be observed that each of the curves has four distinct regions: I, up to 100°C; II, 100–260°C; III, 260–325°C; and IV, 325–560°C. The initial weight loss of the polysaccharides may be due to the presence of small amount of moisture in the samples. There is virtually no weight loss in the second region until a temperature of 260°C is attained. Starting from 260°C, there is a sharp fall in the weight percent of the polymers, which is complete by the end of a narrow temperature range of about 65°C. This weight loss might be due to the loss of the abundant hydroxyl groups on the polysaccharides in the form of water. Thereafter, the nature of curves in case of starch and amylose remain almost same (10 wt % residue in the case of starch and 12% in the case of amylose at a temperature of 560°C). But amylopectin is almost completely degraded before a temperature of 520°C is attained (1 wt % residue at 508°C). It may be noted that amylopectin has a higher thermal stability (as evident from a lower wt % loss) compared to starch and amylose up to a temperature of 260°C. But beyond 325°C, the relative stability is reversed. In the third region, starch degrades earlier than both amylose and amylopectin.

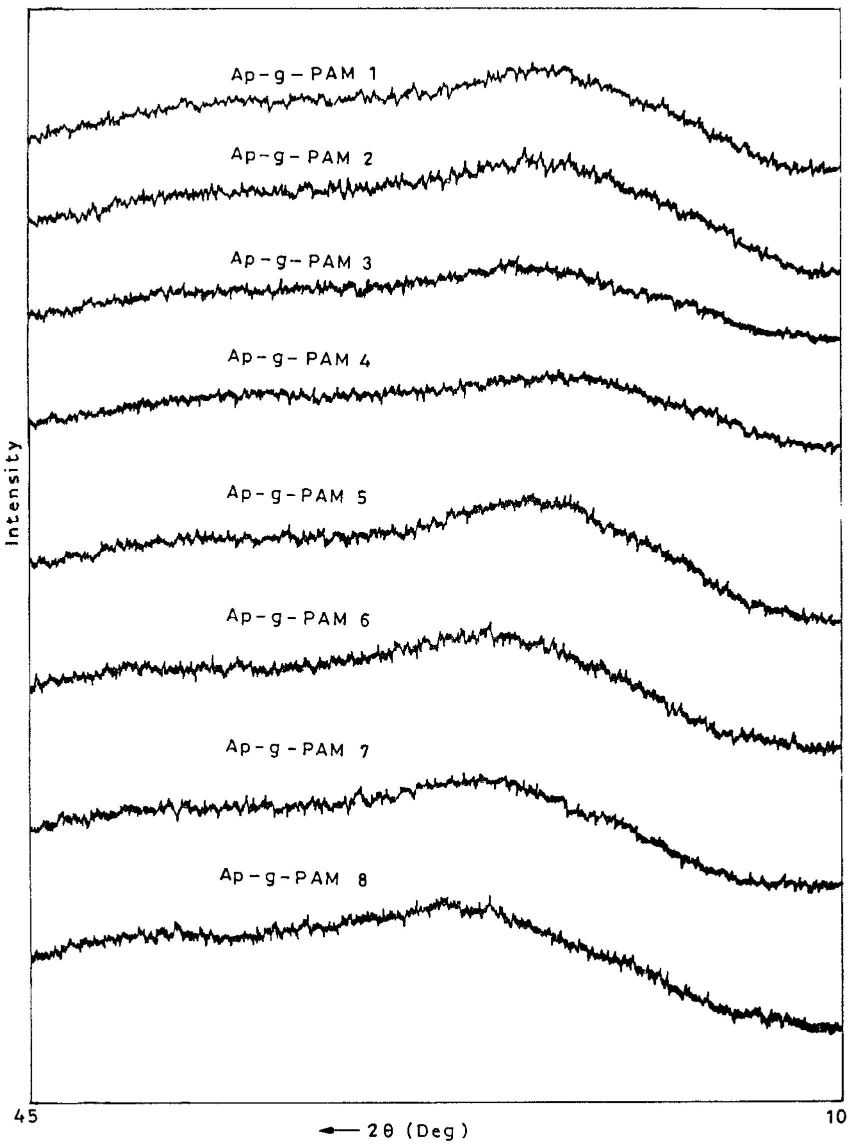
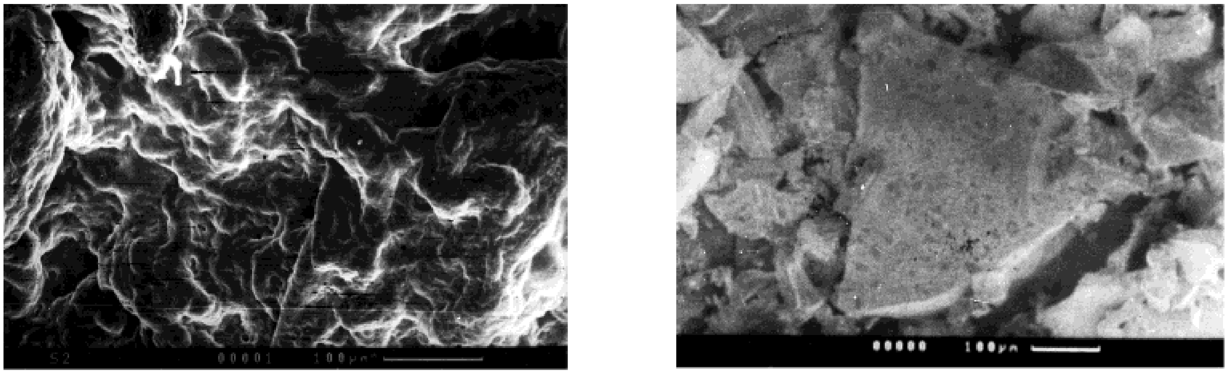


Figure 13 X-ray diffractograms of amylopectin-based graft copolymers (Ap-*g*-PAM 1 to Ap-*g*-PAM 8).

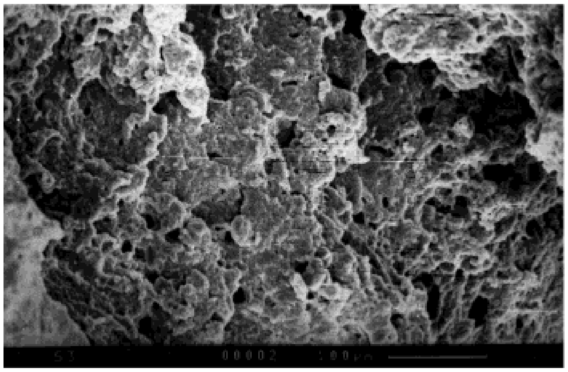
Figure 7 compares the TGA curves of St-*g*-PAM with those of starch and polyacrylamide. The TGA curve for polyacrylamide shows a characteristic pattern distinctly different from the base polysaccharides. After the initial loss of weight because of some probable moisture, there is a continuous loss of weight with temperature without any significantly sharp slope. But it still retains a considerable weight percent (32% at 540°C). This is due to a high cohesive energy density per backbone chain atom in case of polyamides, which is about 7.3 times that of CH_2.[18]

It is observed that grafting of polyacrylamide onto starch not only increases the thermal stability of starch, but also the characteristic TGA pattern of both starch and polyacrylamide is changed drastically (Fig. 7). Almost a similar behavior is observed when the TGA curve of Am-*g*-PAM is compared with amylose and polyacrylamide (Fig. 8). Here, both amylose and Am-*g*-PAM appear to have similar thermal stability up to about 300°C, beyond which amylose degrades. But Am-*g*-PAM continues to maintain a higher weight percent of about 60% until 420°C before a sharp degradation brings down the same close to that of amylose. Interestingly, a different trend is observed when the TGA curve of Ap-*g*-PAM is compared with amylopec-

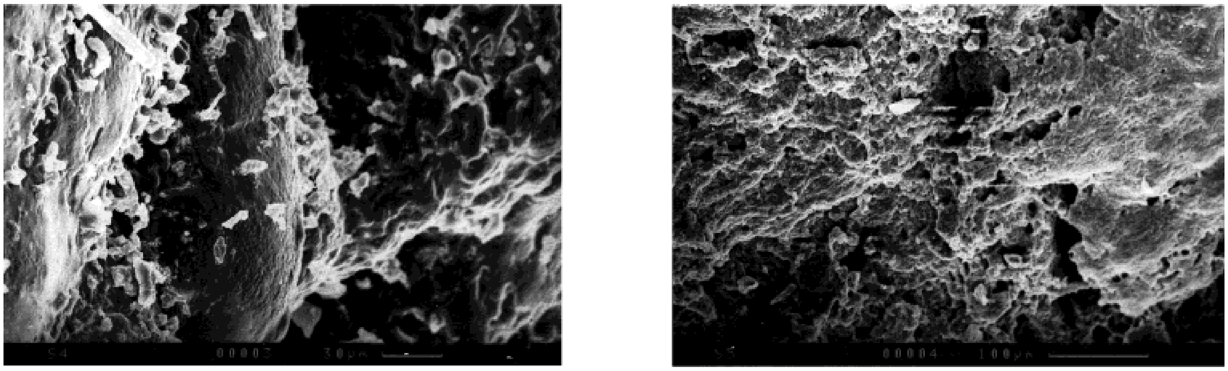


I. Amylopectin

II. Polyacrylamide



III. Ap-g-PAM 1



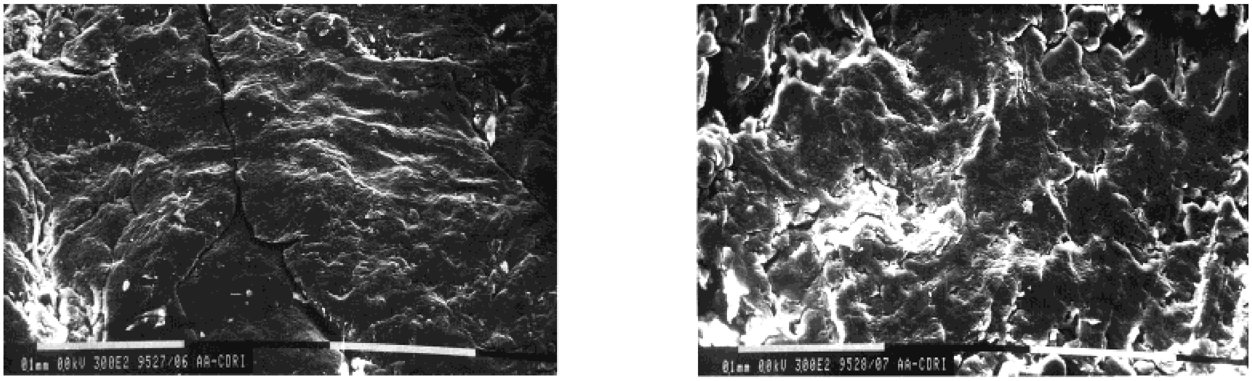
IV. Ap-g-PAM 2

V. Ap-g-PAM 3

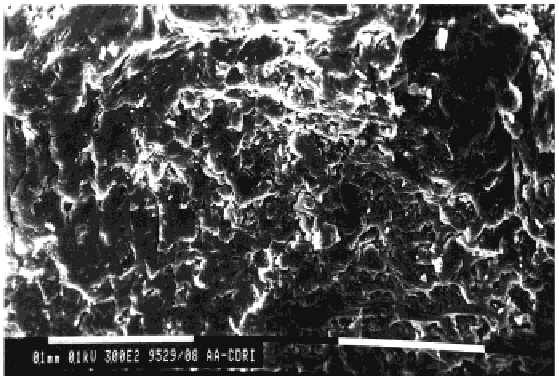
Figure 14 Scanning electron micrographs of amylopectin, polyacrylamide, and the eight graft copolymers based on the two (Ap-*g*-PAM 1 to Ap-*g*-PAM 8).

tin and polyacrylamide (Fig. 9). Here, amylopectin maintains a higher thermal stability than both its graft copolymer and polyacrylamide for a temperature up to about 275°C before dehydration occurs in it. On the other hand, the graft copolymer maintains a weight percent of about 60% until about 375°C. Comparison among the TGA curves of the graft copolymers of starch, amylose, and amylopectin is shown in Fig. 10. All the curves show similar degradation pattern, but St-*g*-PAM has a higher weight percent left (19% at 546°C), followed by Am-*g*-PAM (15% at 546°C) and Ap-*g*-PAM (6% at 546°C).

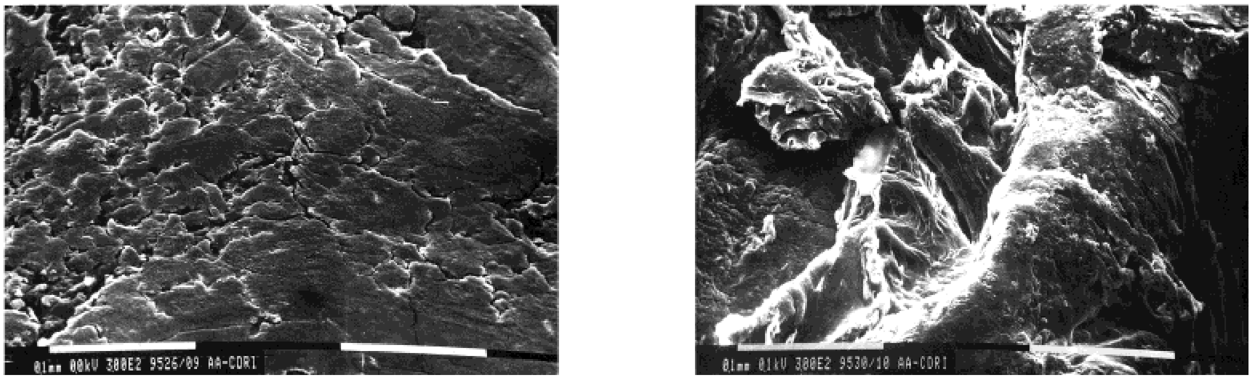
Lastly, Figure 11 compares the TGA curves of the series of six graft copolymers of amylopectin



VI. Ap-g-PAM 4 VII. Ap-g-PAM 5



VIII. Ap-g-PAM 6



IX. Ap-g-PAM 7 X. Ap-g-PAM 8

Figure 14 (*Continued from the previous page*)

and polyacrylamide. The characteristic patterns of degradation of graft copolymers resembles those of St-*g*-PAM and Am-*g*-PAM. But an important observation is the different percent weight for each graft copolymer remaining at a temperature of 536°C. Ap-*g*-PAM 3 is found to retain the highest percent weight (50%), followed by Ap-*g*-PAM 5 (26%), Ap-*g*-PAM 2 (20%), Ap-*g*-PAM 6 (11%), Ap-*g*-PAM 1 (6%), and Ap-*g*-PAM 4 (4.5%). If this feature of the graft copolymers is compared with the synthetic parameters in Table I, it is found that the wt % left at the highest common temperature (536°C) is dependent on the amount of polyacrylamide contained in it. Thus, Ap-*g*-PAM 4 having the lowest acrylamide concentration in the reaction feed has the lowest percent weight (4.5%).

The general conclusion thus arrived from the TGA results is that grafting of polyacrylamide enhances the thermal stability of polysaccharides (Ap-*g*-PAM is found to be an exception). Among a series of graft copolymers, the one with the highest proportion of polyacrylamide in it has the highest thermal stability.

X-ray Diffractometry

Figure 12 shows the X-ray diffractograms of amylopectin, polyacrylamide, and Ap-*g*-PAM. In the case of amylopectin crystallinity peaks are observed, which may be due to crystallization in the branched chains. Polyacrylamide does not show any peak due to crystallinity. The absence of crystallinity peaks in the case of Ap-*g*-PAM may be due to the disruption of crystalline structure by the grafted polyacrylamide chains. Similar trends were observed in case of St-*g*-PAM and Am-*g*-PAM). Figure 13 shows the X-ray diffractograms of all the eight graft copolymers based on amylopectin and polyacrylamide. It is evident from the diffraction patterns that the disruption caused in crystallinity in amylopectin is maximum in those graft copolymers, which have higher polyacrylamide content.

Scanning Electron Micrographs

Figure 1 shows the scanning electron micrographs of amylopectin, polyacrylamide, and the series of eight amylopectin-based graft copolymers. A careful examination of the micrographs reveals a large difference in the morphological appearance of the polymers. Polyacrylamide has a granular structure, which is changed drastically when grafted onto amylopectin. This, once again, is indicative of grafting.

CONCLUSION

The aim of this study was to prove the occurrence of grafting by various techniques. Variation in the synthetic parameters results in a series of graft copolymers with variation in the number and length of polyacrylamide chains that result in different intrinsic viscosities. Study of natural aging proves that the graft copolymers are less susceptible to degradation because of the presence of synthetic polyacrylamide chains as compared to virgin polysaccharide. Study of IR spectra, especially of the graft copolymers (before and after hydrolysis with α-amylase), provides a strong proof of grafting. Both ^{13}C- as well as ^{1}H-NMR also support the formation of graft copolymers. TGA results show different thermal decomposition patterns for the virgin polysaccharides as well as the graft copolymers. Of interest is the variation in the TGA pattern, when one compares the series of graft copolymers based on amylopectin. X-ray diffraction (XRD) patterns show the presence of crystallinity in the polysaccharides, which disappears on grafting of polyacrylamide due to disruption in original crystalline structure. Morphological variation of graft copolymers, polysaccharides, and polyacrylamide also support the above conclusion.

REFERENCES

1. G. F. Fanta and W. M. Doane, in *Modified Starches: Properties and Uses,* O. B. Wurzburg, Ed., CRC Press, Boca Raton, 1986, Chap. 10, p. 149.
2. S. R. Deshmukh and R. P. Singh, *J. Appl. Polym. Sci.,* **33,** 1963 (1987).
3. S. R. Deshmukh, K. Sudhakar, and R. P. Singh, *J. Appl. Polym. Sci.,* **43,** 1091 (1991).
4. S. R. Deshmukh and R. P. Singh, *J. Appl. Polym. Sci.,* **32,** 6163 (1986).
5. S. R. Deshmukh, Ph. D. thesis, IIT, Kharagpur, India, 1986.
6. S. Ungeheur, H. W. Bewersdorff, and R. P. Singh, "Turbulent Drag Reduction Effectiveness and Shear Stability of Xanthan-Gum-Based Graft Copolymers"; *J. Appl. Polym. Sci.,* **37,** 2933 (1989).
7. R. P. Singh, in *Polymers and Other Advanced Materials: Emerging Technologies and Business Opportunities,* P. N. Prasad, J. E. Mark, and T. J. Fai, Eds., Plenum Press, New York, 1995, p. 227.
8. S. K. Rath and R. P. Singh, "Flocculation Characteristics of Grafted and Ungrafted Starch, Amylose and Amylopectin," *J. Appl. Polym. Sci.,* **66,** 1721 (1997).
9. S. K. Rath and R. P. Singh, *Colloids Surf. A: Physicochem. Eng. Aspects,* **139,** 129 (1998).
10. N. C. Karmakar, S. K. Rath, B. S. Sastry, and R. P. Singh, to appear.
11. G. Mino and S. Kaizerman, "A New Method for the Preparation of Graft Copolymers. Polymerization Initiated by Ceric Ion Redox Systems"; *J. Polym. Sci.,* **31,** 242 (1958).

12. G. P. Karmakar, Ph.D. thesis, IIT, Kharagpur, India, 1984.
13. H. L. Hinz and D. C. Johnson, "The Mechanism of Oxidation of Cyclic Alcohols"; *J. Org. Chem.,* **32,** 556 (1967).
14. D. R. Owen and T. C. Shen, in *Structure Solubility Relationships in Polymers,* F. W. Harris and R. B. Seymour, Eds., Academic Press, New York, 1977, pp. 245–258.
15. S. K. Rath and R. P. Singh, to appear.
16. R. P. Singh, *Proceedings of the National Seminar on Recycling and Plastics Waste Management,* CIPET, Chennai, India, 24–26 Sept., 1997, p. 261.
17. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., Wiley, New York, 1981.
18. B. Wunderlich, in *Thermal Characterization of Polymer Materials,* Edith A. Turi, Ed., Academic Press, New York, 1981, Chap. 2.