Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Graft Copolymerization of Polyacrylamide onto Tamarind Mucilage

Anuradha Mishra[a]; Malvika Bajpai[a]
[a] Department of Chemistry, University Institute of Engineering and Technology, CSJM University, Kanpur, India

To cite this Article Mishra, Anuradha and Bajpai, Malvika(2006) 'Graft Copolymerization of Polyacrylamide onto Tamarind Mucilage', Journal of Macromolecular Science, Part A, 43: 2, 315 — 326
To link to this Article: DOI: 10.1080/10601320500437243
URL: http://dx.doi.org/10.1080/10601320500437243

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:315–326, 2006

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320500437243

Graft Copolymerization of Polyacrylamide onto Tamarind Mucilage

ANURADHA MISHRA AND MALVIKA BAJPAI

Department of Chemistry, University Institute of Engineering and Technology, CSJM University, Kanpur, India

In the present communication, grafting of acrylamide onto a water-soluble food grade polysaccharide, Tamarind mucilage, initiated by ceric ion in aqueous medium has been studied under N_2 atmosphere. A ceric ion initiated solution polymerization technique was found to be satisfactory for the formation of copolymer. The effect of monomer concentration, initiator concentration, reaction time, and temperature in terms of grafting efficiency (%GE) and percent of grafting (PG) have been investigated. The graft copolymers were characterized by FTIR, scanning electron microscope (SEM), differential scanning calorimetry (DSC), thermo gravimetric analyzer (TGA), and biodegradation studies.

Keywords polysaccharide, graft copolymers, FTIR, SEM, DSC, TGA

Introduction

The preparation and applications of functional polymers is one of the most important research areas in polymer science. Incorporation of specific functional groups into polymers influences the physical, mechanical, and rheological properties of materials. Incorporation of vinyl monomers on to the backbone of natural polysaccharide helps in improving some original properties of polysaccharides and also allows the product copolymers to show novel functionality (1, 2). Graft copolymers of acrylamides have received much attention because of their increased industrial potential. The most important applications of acrylamide grafted copolymers are those associated with drug delivery systems, flocculation and settling of aqueous suspension, paper treating resins and as gelling and stabilizing agent for soils and muds.

Out of several grafting techniques reported in the literature (3, 4) ceric ion initiated method has been used extensively (5, 6). Singh et al. (1) have prepared a large number of graft copolymers of acrylamide with polysaccharides such as guar gum, xanthan gum, sodium alginate, carboxymethyl cellulose, and starch using ceric ion/HNO_3 acid as redox initiation. We have recently reported the synthesis of polyacrylamide and polyacrylonitrile-grafted copolymers based on mucilage obtained from *Plantago psyllium* husk (7, 8).

Received March 2005; Accepted June 2005.
Address correspondence to Anuradha Mishra, Department of Chemistry, University Institute of Engineering and Technology, CSJM University, Kanpur 208 024, India. E-mail: anuradha_mishra@rediffmail.com

In the present communication, synthesis of graft copolymer of acrylamide (AM) onto Tamarind mucilage (Tam-g-PAM) is reported using a cericion-initiated solution polymerization technique. The influence of reaction time, temperature, and concentrations of AM and CAN in the reaction mixture on percent grafting is studied by preparing different samples. The prepared samples were characterized by FTIR, SEM, TGA, and biodegradation studies.

Experimental

Tamarind mucilage, an amorphous polysaccharide extracted from the seeds of *Tamarindus indica* consists of D-glucose, D-xylose, and D-galactose in 3 : 2 : 1 ratio. Extraction of the milled seeds with hot water yields a thick mucilaginous solution. For deproteinization, it was treated with 0.3 N Ba $(OH)_2$—5% aqueous $ZnSO_4 \cdot 7H_2O$ (9). Acrylamide, ceric ammonium nitrate, hydroquinone, nitric acid (S. D. Fine-Chem., Ltd.) were used as received.

Preparation of TAM-G-PAM Copolymers

Tam-g-PAM was synthesized by grafting acrylamide (AM) onto Tamarind mucilage by radical polymerization method in aqueous system using ceric ion/nitric acid redox initiator (10).

The following procedure has been adopted in carrying out the reactions. One gram of Tamarind mucilage was dissolved in distilled water (200 mL) in an Erlenmeyer flask. The flask was then sealed with septum stopper and flushed with nitrogen for 20 min. The required amount of AM solution prepared in 100 mL distilled water was then added into the solution through the stopper by a hypodermic syringe with constant stirring. The solution was stirred for 30 min while being bubbled with nitrogen. The required amount of ceric ion solution (in ^{1}N HNO_3) was injected through the stopper by a hypodermic syringe. The nitrogen flushing was continued for another 20 min; then the needles were taken out, and the flask was further sealed with teflon tape. The reaction temperature was maintained by immersing the flask in a constant temperature bath. The reaction was continued for 24 h with occasional stirring unless stated otherwise, and then terminated by injecting 0.5 mL of saturated aqueous hydroquinone solution.

The reaction product was precipitated in excess of isopropanol and filtered through a sintered glass filter. The precipitate was again slurried in acetone followed by filtration and finally the precipitate was dried in vacuum oven at 40°C. The % grafting was calculated by the equation:

$$\% \text{ Grafting} = \frac{\text{Weight of polymer grafted}}{\text{Weight of pure mucilage}} \times 100$$

The % efficiency was calculated by the equation:

$$\% \text{ Efficiency} = \frac{\text{Weight of polymer grafted}}{\text{weight of polymer grafted} + \text{weight of homopolymer formed}} \times 100$$

Characterization and Analysis

The structure of Tamarind mucilage and Tam-g-PAM was determined by Fourier transform (FT) IR spectrum (Brucker Vector 22 spectrophotometer) using KBr pellets. Scanning electron micrographs (SEM) and thermograms of the pure and grafted copolymer were obtained on JEOL, JSM-840 SEM. The samples in the form of films were mounted on the specimen stabs and coated with gold ion by a sputtering method. The micrographs were taken at a magnification of 1500. The thermograms of the Tamarind mucilage and Tam-g-PAM were obtained by using a thermal gravimetric analyzer (TGA) by TGA V5.1A Dupont 2100 under nitrogen atmosphere at a heating rate of 20°C per minute and DSC scans by METTLER TA4000 SYSTEM. The viscosity of the polysaccharide and grafted copolymer samples in distilled water was measured by a Ostwald's viscometer.

Results and Discussion

Ceric ion initiated polymerization technique was used for the synthesis of Tam-g-PAM and the results are summarized in Table 1. The most important feature of the oxidation with ceric ion is that it proceeds via a single electron transfer with the formation of free radicals on reducing agent. In this system, the free radical is produced on the TAM (substrate backbone), which in the presence of acrylamide, initiates polymerization to produce a graft copolymer. The number of free radical sites so generated should be

Table 1
Details of graft reaction

Sample no.	Moles of acrylamide (AM)	Moles of Ce IV $\times 10^3$	Percentage grafting (%)	Grafting efficiency (%)	Time (h)	Temperature (°C)
1	0.05	0.05	41.60	73.90	24	30
2	0.05	0.10	45.40	77.60	24	30
3	0.05	0.15	52.80	75.70	24	30
4	0.07	0.05	47.72	72.96	24	30
5	0.07	0.10	52.00	86.60	24	30
6	0.07	0.15	66.24	79.92	24	30
7	0.14	0.05	30.86	62.80	24	30
8	0.14	0.10	35.76	66.51	24	30
9	0.14	0.15	38.92	60.90	24	30
10	0.21	0.05	29.43	61.40	24	30
11	0.21	0.10	34.00	66.66	24	30
12	0.21	0.15	36.25	59.9	24	30
13	0.07	0.15	59.57	63.81	24	20
14	0.07	0.15	62.30	78.50	24	40
15	0.07	0.15	52.4	72.90	24	50
16	0.07	0.15	40.75	76.88	1	30
17	0.07	0.15	42.80	63.81	2	30
18	0.07	0.15	52.67	78.26	4	30

proportional to the concentration of ceric ions. In other words, the length of the grafted chains at a fixed monomer concentration should be largest in the case of low ceric ion concentration and vice versa. This method of grafting yields a substantially pure graft copolymer since the free radicals are produced exclusively on the backbone. The detailed mechanism proposed for the synthesis of Tam-g-PAM is the same as described elsewhere for other polysaccharide based grafted copolymers of acrylamide (7).

Influence of Reaction Parameters

Effect of Monomer Concentration. The effect of monomer concentration on percent grafting and grafting efficiency is shown in Figure 1. As the monomer concentration increased from 0.05 moles to 0.21 moles, the percent grafting (PG) and percent grafting efficiency (%GE) increased up to 0.07 moles [AM], but with a further increase in AM concentration, the PG and %GE decreased. The increase of %GE and PG was expected with an increase in AM concentration due to the availability of AM monomer with respect to polysaccharide macroradicals, leading to a larger possibility of grafting, but the decrease in GE and PG might be due to the formation of homopolymers. These homopolymers successfully hinder the rate of penetration of monomer molecules to the polysaccharide free radicals, resulting in a decrease in GE (11).

Effect of Initiator (CAN) Concentration

The effect of the initiator concentration [CAN] on percent grafting and grafting efficiency is shown in Figure 2. As the initiator concentration increased from 0.05×10^{-3} moles to 0.15×10^{-3} moles, the increase in percent grafting was observed throughout,

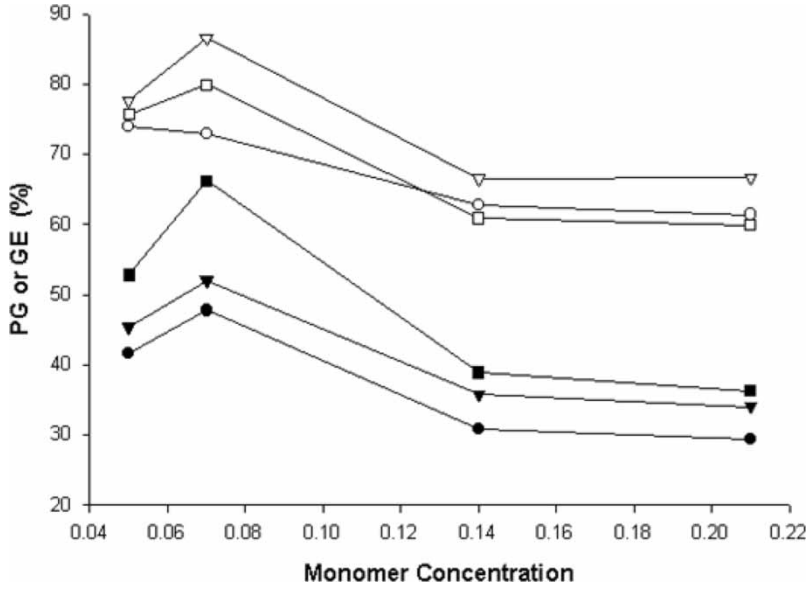

Figure 1. Effect of monomer (AM) concentration on PG and GE; (●) PG, (○) GE with CAN concentration 0.05×10^{-3} moles/L; (▼) PG, (▽) GE with CAN concentration 0.10×10^{-3} moles/L; (■) PG, (□) GE with CAN concentration 0.15×10^{-3} moles/L.

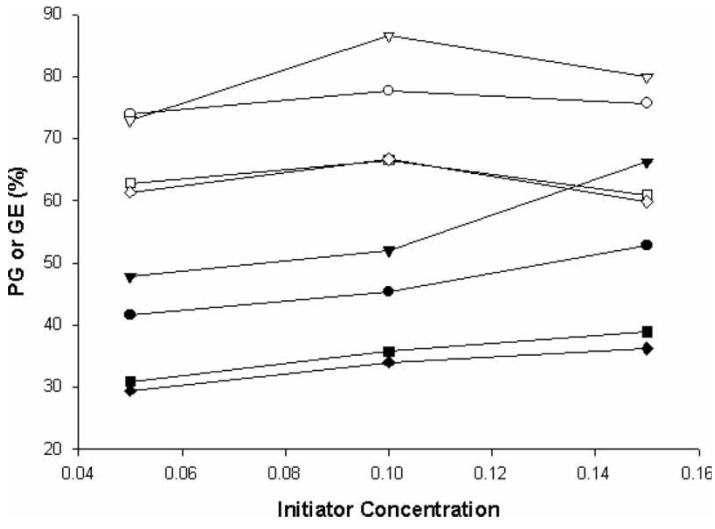

Figure 2. Effect of initiator (CAN) concentration on PG and GE; (●) PG, (○) GE with AM concentration 0.05 moles/L; (▼) PG, (▽) GE with concentration 0.07 moles/L; (■) PG, (□) GE with concentration 0.24 moles/L; (◆) PG, (◇) GE with concentration 0.20 moles/L.

but %GE has its maximum at 0.10×10^{-3} moles [CAN]. It seemed that [CAN] beyond 0.10×10^{-3} moles, both initiator radicals and radicals formed at mucilage are wasted by recombination and other termination processes (12) and in increasing the rate of homopolymerization (13).

Effect of Reaction Temperature

PG and %GE both increased on varying the reaction temperature from 20 to 30°C as shown in Figure 3. The increase in %GE and PG with increasing temperature was expected due to the increased diffusion rate of the monomer and initiator and consequently, raised the rate of grafting (14), but decreased %GE and PG observed with an increase in temperature beyond 30°C might be attributed to a faster rate of termination and more homopolymerization at a higher temperature.

Effect of Reaction Time

The effect of time on GE and PG is shown in Figure 4. The percentage grafting, as well as grafting efficiency, increased with increasing the reaction time. This agrees with the earlier observation with free radical initiated polymerization (12).

Characterization of Graft Copolymer

Infra Red (IR) Spectrum. The FTIR spectra of ungrafted mucilage and Tam-g-PAM (PG = 66.24) are shown in Figure 5. The FTIR spectrum of Tam-g-PAM is different from that of Tamarind mucilage by showing characteristic peaks at 1665.4 cm^{-1} of –C═O of amide, at 1527.3 cm^{-1} of –NH bending, at 1383.1 cm^{-1} of –CN stretching, at 1283.5 cm^{-1} of –C–C–N asymmetric. Moreover, the broadening and shifting of the band coming after 3000 cm^{-1} towards slightly higher wave number in Tam-g-PAM, as

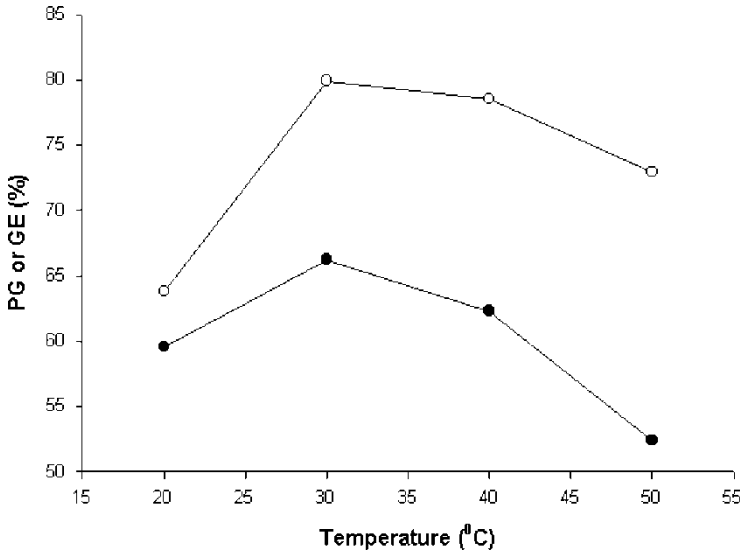

Figure 3. Effect of reaction temperature on (●) percentage grafting and (○) grafting efficiency.

compared to that of pure mucilage, was also expected due to the overlapping of –NH of amide and –OH of mucilage.

Scanning Electron Microscopy (SEM)

The SEM technique is considered to be one of the best techniques to study the surface topology of different kinds of polymers. A comparative study of the scanning electron micrographs of ungrafted mucilage and Tam-g-PAM (Figure 6) is used as supportive

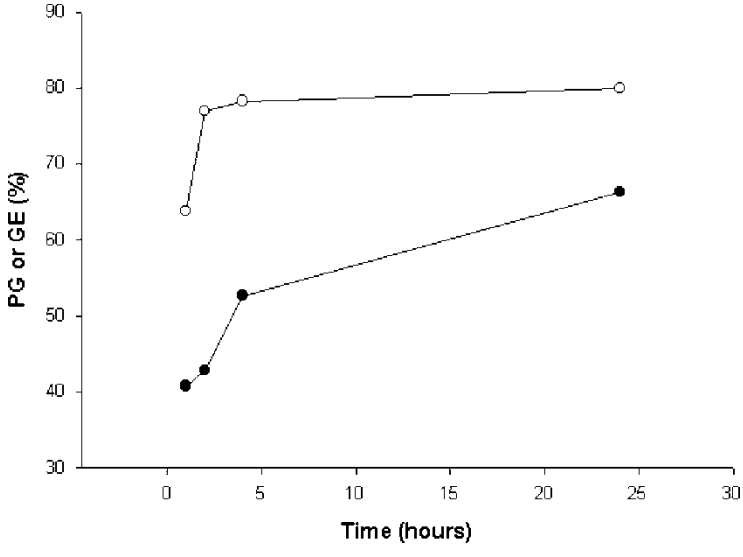

Figure 4. Effect of reaction time on (●) percentage grafting and (○) grafting efficiency.

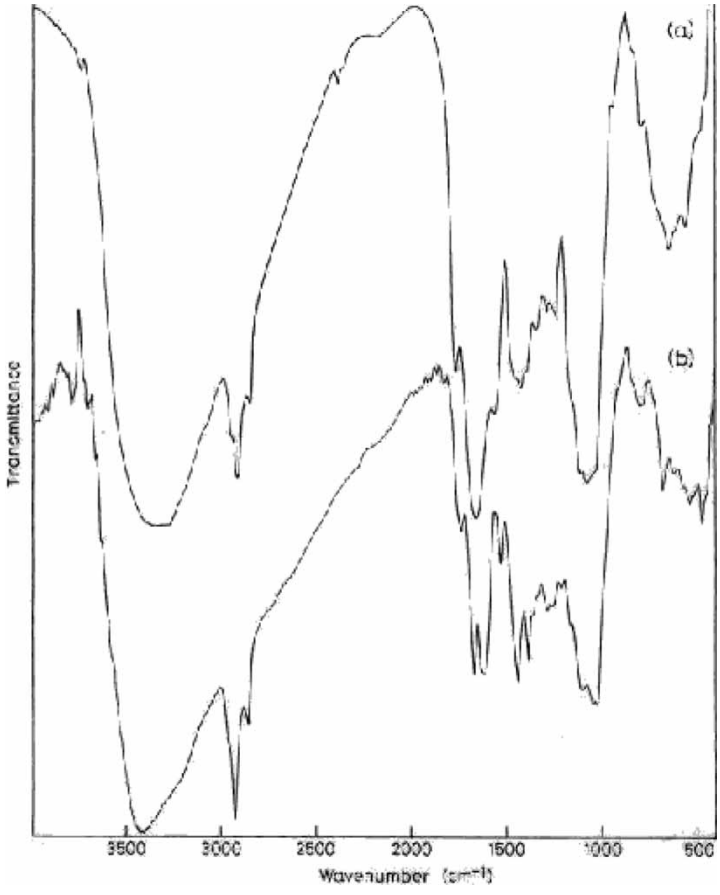

Figure 5. IR spectra of (a) Tamarind mucilage and (b) TAM-g-PAM.

evidence for grafting. The morphology of the surface of pure Tamarind mucilage is different than that of its grafted copolymer i.e., Tam-g-PAM. A considerable amount of grafted polymer is deposited, which appears to have a different structure from the pure mucilage (14).

Differential Scanning Calorimetry (DSC)

Different exothermic patterns can be clearly seen in the DSC scans of pure (Figure 7) and grafted copolymer (PG = 66.24), which proved that grafting had indeed taken place. The difference in the exotherms indicated that the crosslinking reactions occurring in the region between 50°C and 250°C were different for pure mucilage and grafted copolymer. Even the pattern for moisture loss up to 100°C was different in both scans.

Thermogravimetric Analysis (TGA)

The TGA thermograms of ungrafted mucilage and Tam-g-PAM copolymer (PG = 66.24) are shown in Figure 8. The grafting of polyacrylamide chains in mucilage does not

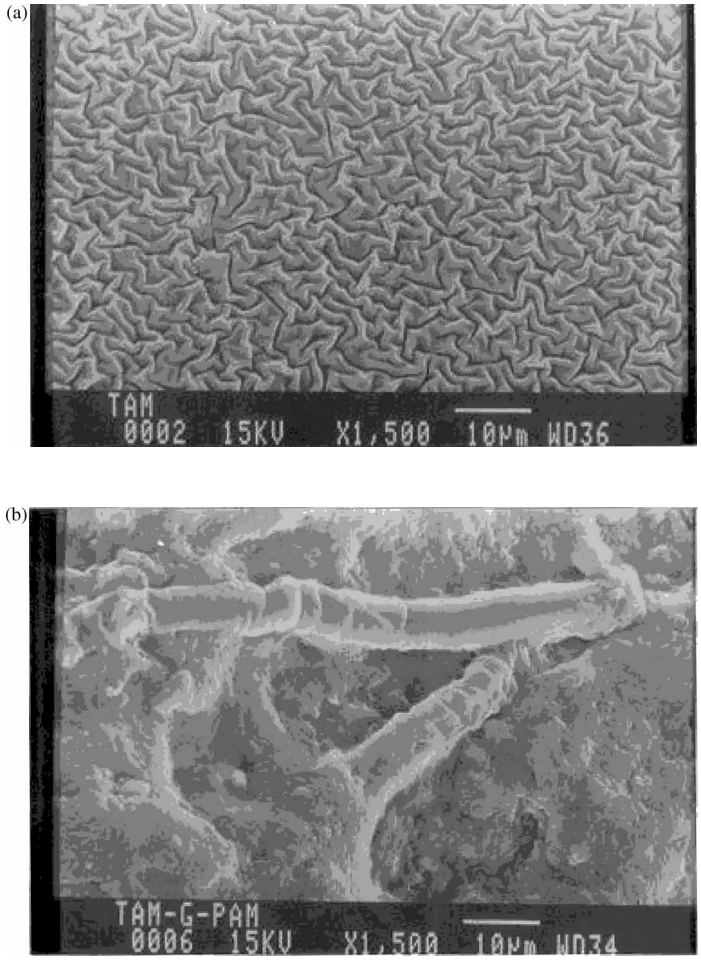

Figure 6. Scanning electron micrographs of (a) Tamarind mucilage and (b) TAM-g-PAM.

contribute more stability towards temperature. But the difference in thermal decomposition behavior of the mucilage and copolymer can be clearly noticed. In both cases, one-stage decomposition was observed with the onset of a major weight loss at 200°C and $T_{max} = 296.88$°C in ungrafted mucilage and at 198°C and $T_{max} = 250.88$°C in the grafted sample. The % weight loss with an increase in temperature in both cases is summarized in Table 2. The % weight loss with increasing temperature is slower in the case of Tam-g-PAM as compared to that of Tam mucilage.

Biodegradation Study

The viscosity of solution as a function of time is taken as the criterion for study of biodegradation (15). Ungrafted mucilage and Tam-g-Pam copolymer samples were tested for their biodegradability. In each experiment, 0.1 g of polymer was dissolved in 100 mL distilled water and viscosity measurements were performed using Ostwald's viscometer over a time period of 8 days. All measurements were carried out at room

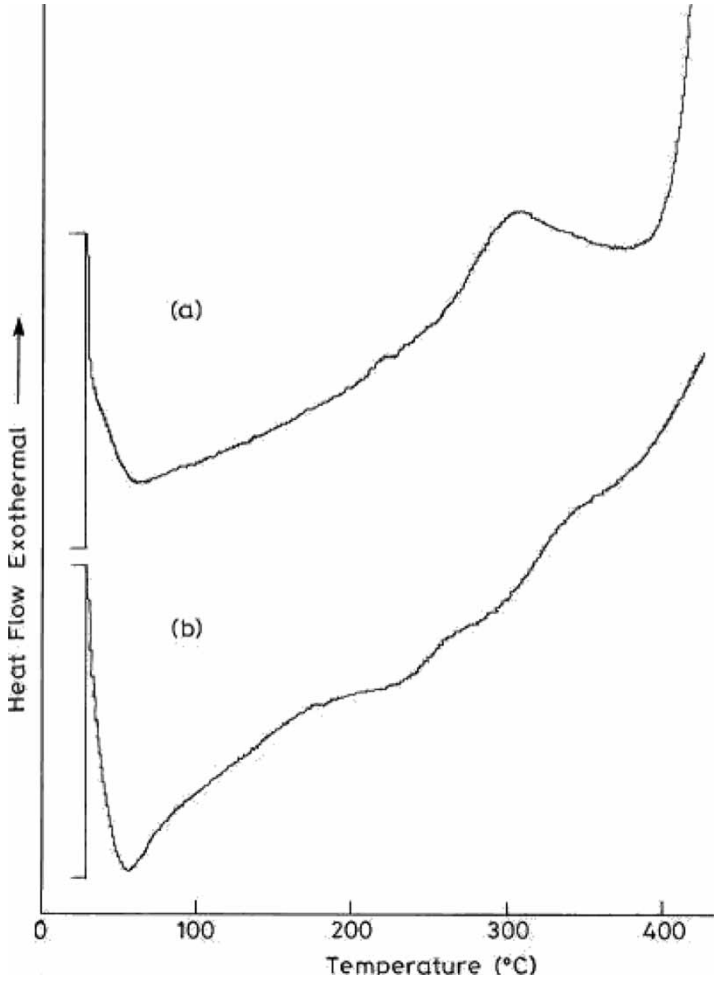

Figure 7. DSC scans of (a) Tamarind mucilage and (b) TAM-g-PAM.

temperature. Figure 9 represents the result of a biodegradability study of Tam and Tam-g-Pam, respectively. It shows the plots of intrinsic viscosity (η_{int}) vs. time in days. It is apparent from the plots that in the case of ungrafted mucilage, degradation started after two days and was almost completed within seven days. The values of the intrinsic viscosity were 3.20 dL/g and 0.8 dL/g on the first and sixth day, respectively. In the case of Tam-g-PAM, the values of intrinsic viscosity were 6.58 dL/g and 3.16 dL/g on the first and seventh days, respectively. This indicated that the biodegradable character of the mucilage did not change by grafting synthetic polymer chains. Although the grafted copolymer seemed to have a slower rate of biodegradation than that of ungrafted mucilage.

Conclusions

Grafting of Tamarind mucilage has been done successfully by using the CAN/HNO_3 redox initiator system. Biodegradability studies show a minor difference in time

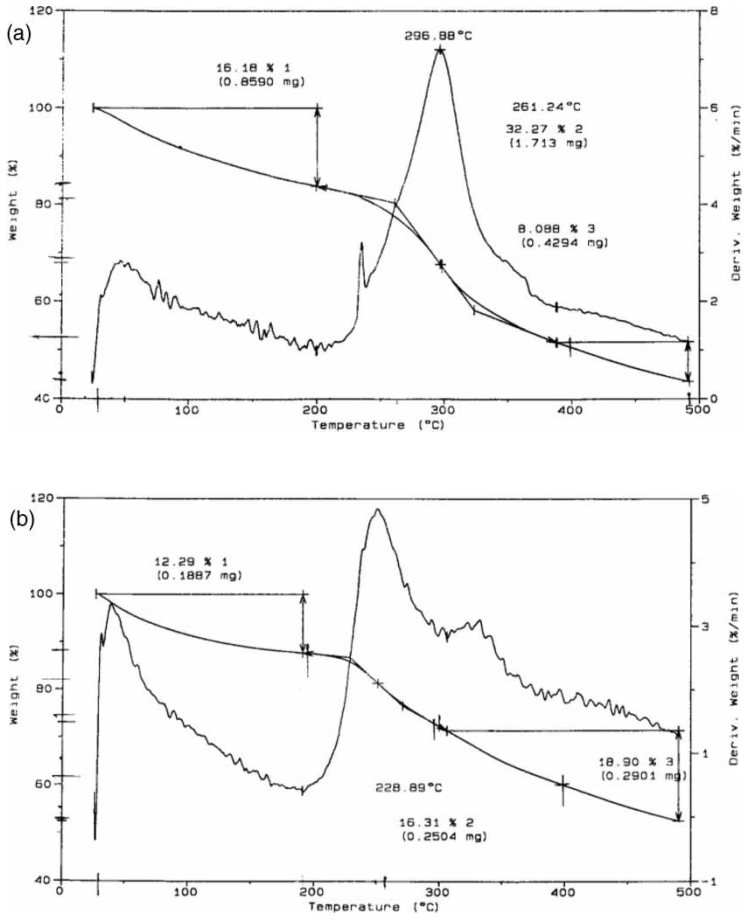

Figure 8. TGA thermograms of (a) Tamarind Mucilage and (b) TAM-g- PAM.

Table 2
Percent weight loss of Tam and Tam-g-Pam on varying the temperature

Substance	Temperature range (°C)	T_{max} (°C)	% Weight loss
Pure mucilage	0–200	—	16.18
	200–300	296.88	31.76
	300–400	—	48.33
	400–500	—	56.29
	Above 500	—	Not studied
Tam-g-PAM	0–200	—	13.1
	200–300	228.89	17.65
	300–400	—	38.05
	400–500	—	47.5
	Above 500	—	Not studied

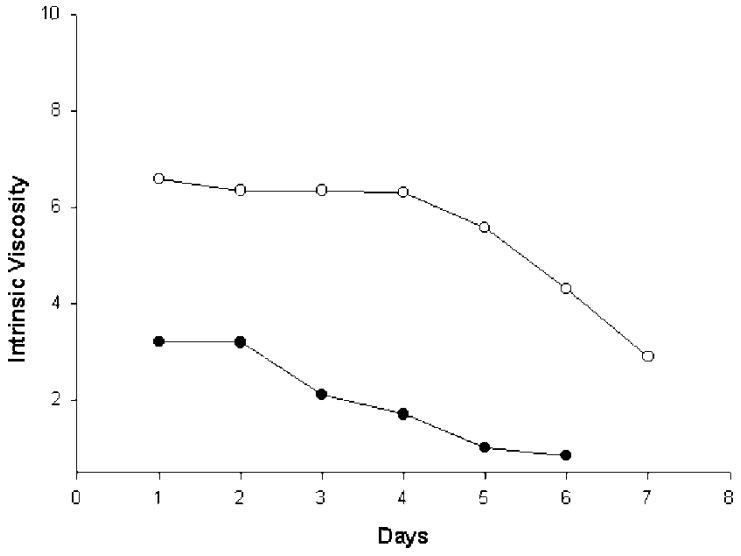

Figure 9. Plots of intrinsic viscosity vs. time in days; (●) Pure TAM and (○) TAM-g-Pam.

duration taken for complete degradation of natural and grafted copolymers. Therefore, it can be concluded that the introduction of AM onto the backbone of natural polysaccharide only improves its properties with little influence on its biodegradable nature. Grafting was ascertained by infrared spectroscopy, scanning electron microscopy, differential scanning calorimetry, and thermo-gravimetric analysis.

Acknowledgement

The authors are grateful to the University Grants Commission, New Delhi for financial support of this study (Project No. F.12-133/2001 (SR-1)].

References

1. Singh, R.P., Tripathy, T., Karmakar, G.P., Rath, S.K., Karmakar, N.C., Pandey, S.R., Kannan, K., Jain, S.K., and Lan, N.T. (2000) *Current Sci.*, 78 (7): 798–803.
2. Fanta, G.F., Burr, C.R., Russell, C.R., and Rist, C.E. (1969) *J. Appl. Polym. Sci.*, 13: 133–140.
3. Ceresa, R.J. (1973) *Block and Graft Copolymers*; Wiley: New York; Vol. 1.
4. Battard, H.A.J. and Trigear, G.W. (1976) *Graft Copolymers*; Wiley Interscience: New York.
5. Yoon, K.J., Carr, M.E., and Bagley, E.B. (1992) *J. Appl. Polym. Sci.*, 45: 1093–1100.
6. Chauhan, G.S., Bhatt, S.S., Kaur, I., Singha, A.S., and Kaith, B.S. (2000) *Polym. Degrad. Stability*, 69: 261–265.
7. Mishra, A., Rajani, S., Agarwal, M., and Dubey, R. (2002) *Poly. Bull.*, 48: 439–444.
8. Mishra, A., Rajani, S., and Gupta, R. (2003) *Colloid Polym. Sci.*, 281: 187–189.
9. Singh, V., Tiwari, A., Tripathi, D.N., and Sanghi, R. (2005) *Biomacromolecules*, 6: 453–456.
10. Karmakar, N.C., Rath, S.K., Sastry, B.S., and Singh, R.P. (1998) *J. Appl. Polym. Sci.*, 52: 1165–1172.

11. Fares, M.M. (2003) *J. Polym. Mater.*, 20: 75–82.
12. Sudhakar, D., Srinivasan, K.S.V., Joseph, K.T., and Santappa, M. (1981) *Polymer*, 22: 491–493.
13. Shukla, S.K. and Srivastava, D. (2003) *J. Polym. Mat.*, 20: 207–212.
14. Gao, J.-P., Tian, R.-C., Yu, J.-G., and Duan, M.-L. (1994) *J. Appl. Polym. Sci.*, 53: 1091–1102.
15. Owen, D.R. and Shen, T.C. (1977) *The Effect of Acrylamide Graft Copolymerization on the Solubility and Viscosity of Several Polysaccharides, in Structure Solubility Relationship in Polymers*; Harris, F.W. and Seymour, R.W., eds.; Academic Press: New York.