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Biodegradable graft copolymers of fenugreek mucilage and polyacrylamide: A renewable reservoir to biomaterials

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Abstract

Polyacrylamide-grafted-fenugreek mucilage (Fen-*g*-PAM) copolymers were synthesized by grafting acrylamide (AM) onto fenugreek mucilage (Fen) backbone by ceric ion initiated solution polymerization technique under nitrogen atmosphere. A total of 19 copolymer samples were prepared by varying the concentrations of AM and ceric ammonium nitrate (CAN), reaction time and temperature. The variation in reaction parameters affected the percent grafting (PG), grafting efficiency (%GE) and intrinsic viscosity of the copolymer samples. The copolymers were characterized by FTIR, scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and viscosity measurements. The prepared copolymers were partially soluble in water and completely soluble in 1 N NaOH aqueous solution. These graft copolymers have also been tested for their biodegradability.

Keywords: Biodegradable; Mucilage; Graft copolymer; TGA; SEM; XRD

1. 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, chemical, mechanical and rheological properties of materials (Dalman, Puskar, & Marganitis, 2003). Incorporation of vinyl monomers onto the backbone of natural polysaccharide helps in improving some original properties of polysaccharides and also allows the product copolymers to show novel functionality (Singh et al., 2000; Teramoto & Nishio, 2003). Graft copolymers of AM have received much attention because of their increased industrial potential. The most important applications of AM graft 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 mud (Schiller & Suen, 1956; Swift, 1957).

Out of several grafting techniques reported in the literature (Battard & Trigear, 1976; Ceresa, 1973), ceric ion initiated method has been used extensively (Athawale & Rathi, 1997; Mino, Kaiserman, & Rasmussen, 1959). Singh et al. has prepared a large number of graft copolymers of AM with polysaccharides such as guar gum, xanthan gum, sodium alginate, carboxymethyl cellulose and starch using ceric ion/HNO_3 acid as redox initiation (Singh et al., 2000). We have recently reported the synthesis of polyacrylamide and polyacrylonitrile grafted copolymers of mucilage obtained from food grade polysaccharides (Mishra & Bajpai, 2005; Mishra, Rajani, & Dubey, 2002a; Mishra, Rajani, & Gupta, 2003).

Fenugreek seeds are used as condiment in Indian food and have some medicinal uses. Fenugreek seeds contain a high percentage of mucilage. Although it does not dissolve in water, mucilage forms a thick, gooey mass when exposed to fluids. In the present communication, we report the synthesis of polyacrylamide-grafted copolymers of Fenugreek mucilage (Fen-*g*-PAM). 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. Grafted copolymers were characterized by FTIR, SEM, DSC and XRD.

2. Experimental

Fenugreek (Trigonella *foenum-graecum*) mucilage, an amorphous polysaccharide consists of D-galactose and D-mannose in 1:1 and 1:1.2 ratio (El-Molla, Abdel Rehman,

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& El-Taloath1998). Extraction of the milled seeds with hot water yields a thick mucilaginous solution. For deproteinization, it was treated with solution of 0.3 N $Ba(OH)_2$–5% aqueous $ZnSO_4 \cdot 7H_2O$ (Singh, Tiwari, Tripathi, & Sanghi, 2005). Acrylamide, ceric ammonium nitrate (CAN), hydroquinone, nitric acid (SD, Fine-Chem Ltd, India) were used as received.

The Fen-*g*-PAM copolymer samples have been synthesized by varying the concentrations of AM and CAN in the reaction mixture by radical polymerization method using ceric ion/nitric acid redox initiator in aqueous medium (Agrawal, Rajani, & Mishra, 2001; Mishra, Rajani, & Dubey, 2002b). One gram of Fenugreek mucilage was slurried with 200 mL of distilled water in an Erlenmeyer flask at room temperature. The required amount of acrylamide monomer was dissolved in distilled water (100 mL) in other flask and then it was added to the Fen solution. The mixture of solutions was stirred with magnetic stirrer for 1 h. The flask was then sealed with septum stopper. Nitrogen gas was then flushed into the solution through hypodermic needle. 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 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 at 30 °C by immersing the flask in constant temperature bath. The reaction was continued for 24 h with occasional stirring, 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 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 %GE 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:

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

2.1. Characterization and analysis

The structure of Fenugreek mucilage and Fen-*g*-PAM was determined by Fourier Transform (FT) IR spectrum (Brucker Vector 22 spectrophotometer) using KBr pellets. Scanning electron micrographs (SEM) of pure and the grafted copolymer were obtained on JEOL, JSM-840 SEM. The sample in the form of films were mounted on the specimen stabs and coated with gold ion by sputtering method. The micrographs were taken at a magnification of 1500. The thermograms of the Fenugreek mucilage and Fen-*g*-PAM were obtained by using thermal gravimetric analyzer (TGA V5.1A Dupont 2100) under nitrogen atmosphere at a heating rate of 20 °C per minute. X-ray diffraction patterns off powder sample of pure and grafted copolymer were obtained at ambient condition on X-ray diffractometer model ISO-Debyflux-2002. The viscosity of the polysaccharide and grafted copolymer samples in distilled water was measured by Ostwald's viscometer.

3. Results and discussion

The most important feature of the ceric ion initiated polymerization technique is that the oxidation proceeds via single electron transfer with the formation of free radicals on reducing agent. In this system the free radical is produced on the Fen (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 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 case of low ceric ion concentration and vice versa. This method of grafting yields substantially pure graft copolymer since the free radicals are produced exclusively on the backbone. The detailed mechanism proposed for the synthesis of Fen-*g*-PAM is same as described elsewhere for other polysaccharide based grafted copolymers of acrylamide (Mishra, Rajani, & Dubey, 2002a).

4. Influence of reaction parameters

4.1. Effect of monomer concentration

The effect of monomer concentration on percent grafting and grafting efficiency is shown in Table 1. As the monomer concentration increased from 0.07 to 0.35 mol, the percent grafting (PG) and percent grafting efficiency (%GE) increased up to 0.21 mol [AM] but with further increase in AM concentration, the PG and %GE decreased. The increase in %GE and PG was expected with increase in AM concentration due to the availability of AM monomer with respect to polysaccharide macroradicals, leading to 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 decrease in GE (Fares, 2003).

4.2. Effect of initiator (CAN) concentration

On increasing the concentration of CAN from 0.02×10^{-3} to 0.05×10^{-3} mol both %GE and PG increased (Table 1) due to increase in the free radicals on polysaccharide chains. The falling off of %GE and PG at higher CAN concentration (0.10×10^{-3}) is a well-known phenomenon and ascribed to

Table 1
Effect of monomer and initiator concentrations on PG and %GE

Sample no.	AM (mol)	Ce (IV) × 10^3 (mol)	Percent grafting (%)	Grafting efficiency (%)	Intrinsic viscosity (η_{int})
1.	0.07	0.02	20.31	42.13	1.90
2.	0.07	0.05	30.12	50.83	2.20
3.	0.07	0.10	22.69	45.95	2.10
4.	0.14	0.02	35.22	52.31	2.61
5.	0.14	0.05	45.80	75.00	3.40
6.	0.14	0.10	39.16	65.70	3.12
7.	0.21	0.02	44.32	62.91	3.25
8.	0.21	0.05	62.10	80.49	4.30
9.	0.21	0.10	48.00	69.22	4.10
10.	0.35	0.02	31.15	41.12	2.42
11.	0.35	0.05	51.27	51.27	3.17
12.	0.35	0.10	43.69	43.69	2.93

Temperature = 30 °C; time = 24 h; mucilage = 1.0 g.

the increasing participation of the ceric ions in the termination of the growing grafted chains (Yao & Tang, 1992).

4.3. Effect of reaction temperature

PG and %GE both increased on varying the reaction temperature from 20 to 30 °C as shown in Table 2. The increase in %GE and PG with increasing temperature was expected due to the increased diffusion rate of monomer and initiator and consequently raised rate of grafting (Gao, Tian, Yu, & Duan, 1994) but decreased %GE and PG observed with increase in temperature beyond 30 °C might be attributed to faster rate of termination and more homopolymerization at higher temperature.

Table 2
Effect of reaction temperature on PG and %GE

Sample no.	AM (mol)	Ce (IV) × 10^3 (mol)	Percent grafting (%)	Grafting efficiency (%)	Temperature (°C)
1	0.21	0.05	41.00	54.37	20
2	0.21	0.05	62.10	80.49	30
3	0.21	0.05	31.24	43.26	40
4	0.21	0.05	27.63	35.72	50

Time = 24 h; mucilage = 1.0 g.

Table 3
Effect of reaction time on PG and %GE

Sample no.	AM (mol)	Ce (IV) × 10^3 (mol)	Percent grafting (%)	Grafting efficiency (%)	Time (h)
1	0.21	0.05	00.00	00.00	1
2	0.21	0.05	30.42	32.40	2
3	0.21	0.05	38.96	51.26	4
4	0.21	0.05	56.13	72.37	20
5	0.21	0.05	62.10	80.49	24

Temperature = 30 °C; mucilage = 1.0 g.

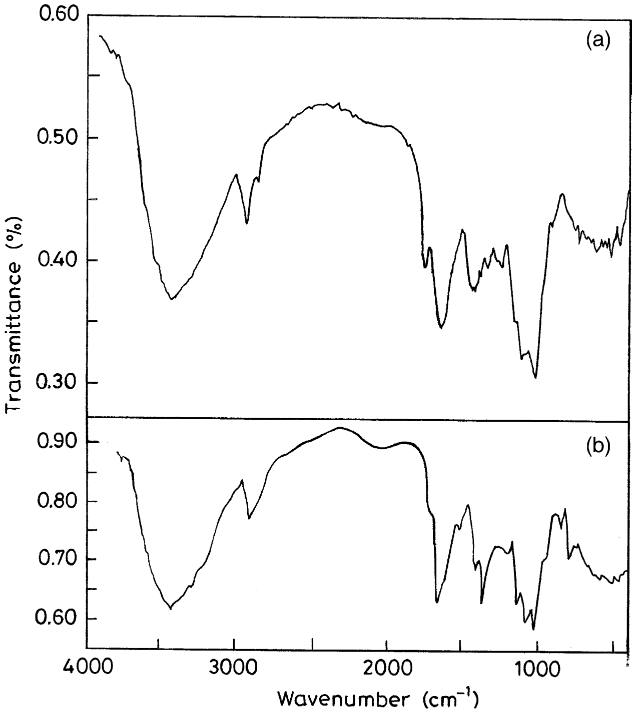

Fig. 1. FTIR spectra of Fen (a) and Fen-*g*-PAM (b).

4.4. Effect of reaction time

The effect of time on %GE and PG is shown in Table 3. The percent grafting as well as grafting efficiency increased with

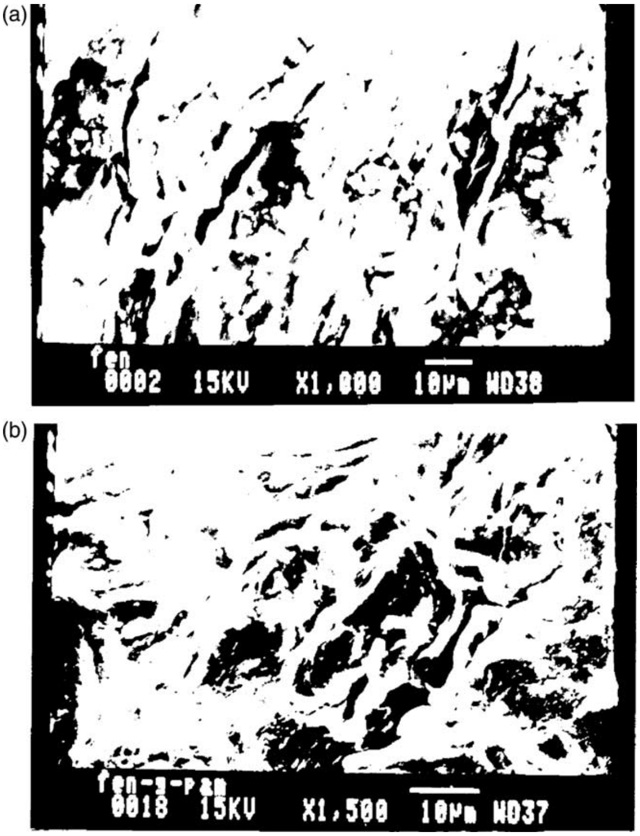

Fig. 2. Scanning electron micrographs of (a) Fen and (b) Fen-*g*-PAM.

increasing the reaction time. This agrees with the earlier observation with free radical initiated polymerization. (Sudhakar, Srinivasan, Joseph, & Santappa, 1981).

5. Characterization of graft copolymer

5.1. Infra red (IR) spectrum

The FTIR spectrum of purified fenugreek mucilage (Fig. 1a) shows characteristic peaks of –OH between 3509 and 3150 cm^{-1}, ether linkage at 1455–1400 cm^{-1}, –CH stretching between 2923 and 2854 cm^{-1}, –CO stretching at 1018 cm^{-1} and –CH_3 at 2923 cm^{-1}. It is observed that FTIR spectrum (Fig. 1b) of Fen-*g*-PAM (sample no. 5) is different from that of pure mucilage by showing a new small peak of –CO of amide at 1670.30 cm^{-1}, at 1383.1 cm^{-1} of –CN stretching, between 1224 and 1151 cm^{-1} of –C–C–N asymmetric and out of plane –NH band at 800–600 cm^{-1}. The broadening of the band coming after 3000 cm^{-1} in Fen-*g*-PAM as compared to that of pure mucilage was also expected due to the overlapping of –NH (amide) and –OH (mucilage) bands.

5.2. Scanning electron microscopy (SEM)

A comparative study of the scanning electron micrographs (Fig. 2a and b) of purified Fen and Fen-*g*-PAM (sample no. 8) is used as supportive evidence for grafting which indicated that grafting had indeed taken place. A considerable amount of grafted polymer is deposited (Fig. 2b), which appears to have a different structure from the pure mucilage (Fig. 2a) (Yao & Tang, 1992).

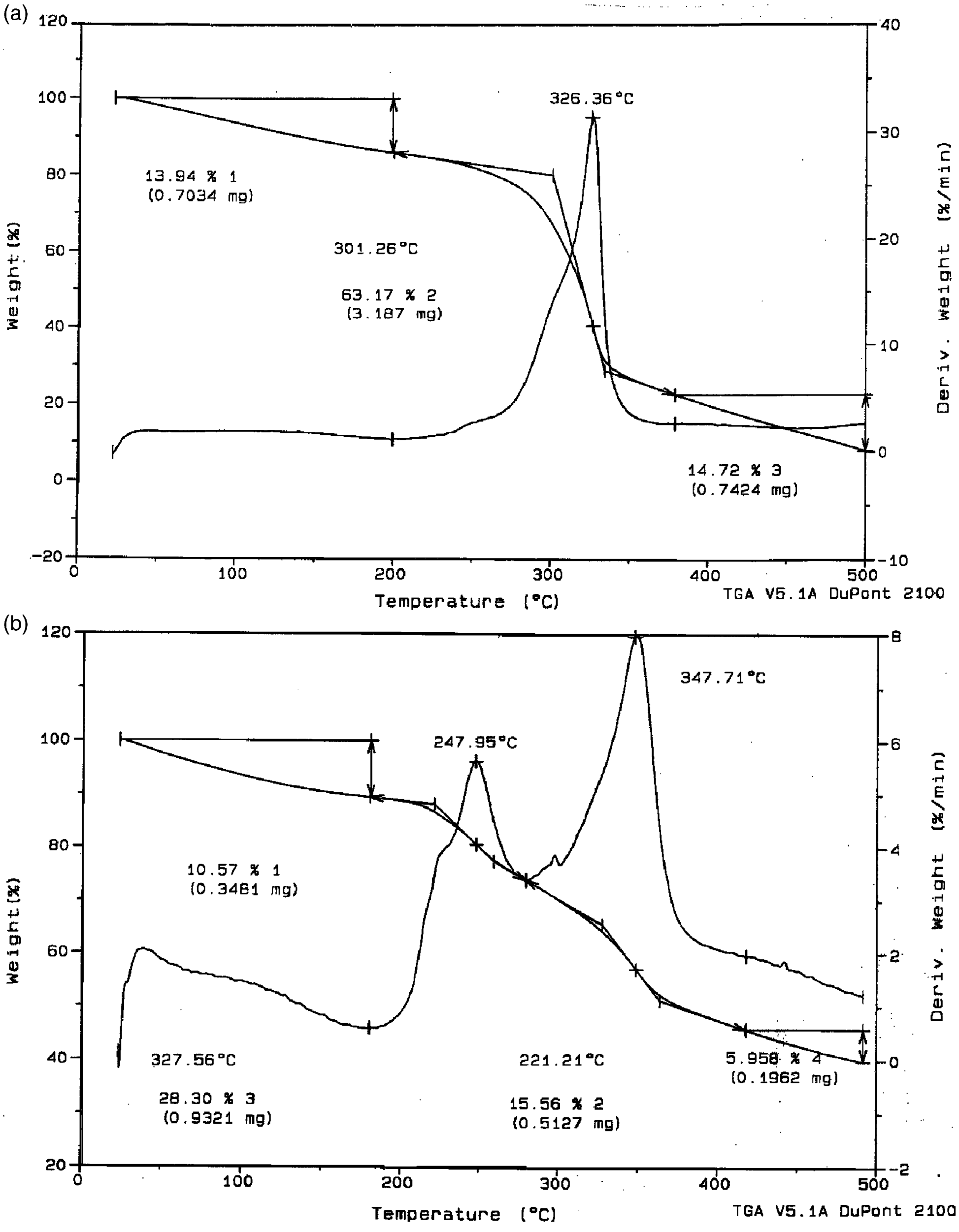

Fig. 3. TGA thermograms of (a) Fen mucilage and (b) Fen-*g*-PAM.

5.3. Thermogravimetric analysis (TGA)

The TGA thermograms of Fen and Fen-*g*-PAM copolymer (sample no. 8) are shown in Fig. 3a and b, respectively. The grafting of polyacrylamide chains in mucilage contributed more stability towards temperature and the difference in thermal decomposition behavior of the mucilage and copolymer can be clearly noticed in the thermograms. The percent weight loss with increasing temperature was almost equal up to 300 °C but beyond this temperature it was slower in case of Fen-*g*-PAM, as compared to that of Fen. In case of Fen, single stage decomposition was observed with the onset of major weight loss at 200 °C (T_o) and $T_{max}=326.36$ °C, whereas in Fen-*g*-PAM, two stage decomposition was observed with $T_o=181$ °C and $T_{max}=247.95$ and 347.73 °C. The percentage weight loss with an increase in temperature in both the cases is summarized in Table 4.

5.4. X-ray diffraction analysis

The X-ray diffraction patterns of pure mucilage and Fen-*g*-PAM (sample no. 8) at room temperature from $2\theta=5°$ to 70° (error range of 2θ is 0.01–0.31) are shown in Fig.4a and b. The mucilage Fig.4a shows, like all other natural polymers, partial crystalline nature. Fig.4b, the XRD pattern of Fen-*g*-PAM also shows a partially crystalline nature but is quite different from that of pure mucilage. The 2θ and d values observed in both the cases are different. This constitutes primary evidence that a different solid phase was formed.

5.5. Viscosity measurements

The viscosity measurements taken for the Fen and Fen-*g*-PAM copolymer samples are given in Table 1. The variation in concentration of CAN affected the percentage grafting and viscosity of the grafted samples. It was observed that η_{int} of Fen-*g*-PAM copolymers decreased with initiator concentration (Yao & Tang, 1992).

Table 4
Percent weight loss of fenugreek mucilage and Fen-*g*-PAM on varying the temperature

Substance	Temperature range (°C)	T_{max} (°C)	% Weight loss
Pure mucilage	0–200	–	3.6
	200–250	–	17.1
	250–300	–	20.0
	300–350	326.36	57.4
	350–400	–	76.0
	400–500		80.2
	Above 500		Not studied
Fen-*g*-PAM	0–200	–	7.10
	200–250	–	10.0
	250–300	247.95	21.1
	300–350	347.73	44.2
	350–400	–	49.0
	400–500	–	56.0
	Above 500		Not studied

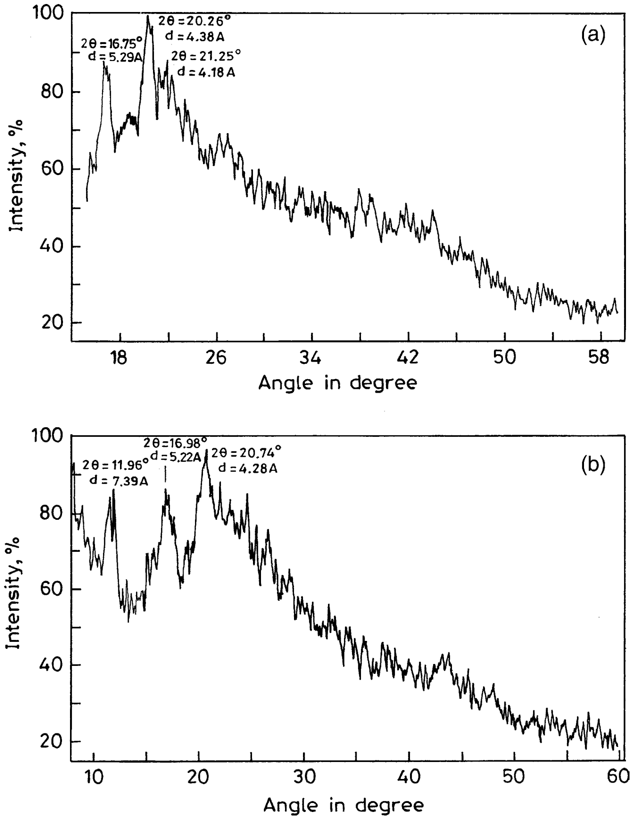

Fig. 4. XRD scans of (a) Fen and (b) Fen-*g*-PAM.

5.6. Biodegradation studies

The viscosity of solution (in 1 N NaOH) as a function of time is taken as the criterion for study of biodegradation. Fen and Fen-*g*-PAM copolymer samples were tested for their biodegradability. In each experiment, 0.1 g of polymer was dissolved in 100 mL of 1 N NaOH solution and viscosity measurements were performed using Ostwald's viscometer over a time period of 10 days. All the measurements were carried out at room temperature. The plots of intrinsic viscosity (η_{int}) vs time (Fig. 5) were used to study the biodegradation of

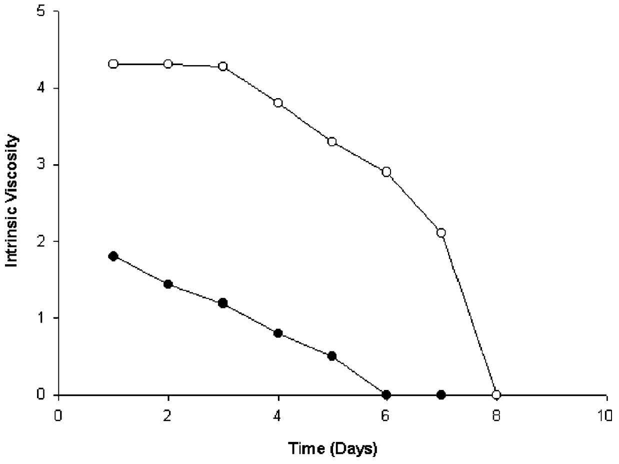

Fig. 5. Plots of intrinsic viscosity vs time in days (●) Fen and (○) Fen-*g*-PAM.

Fen and Fen-*g*-PAM. It is apparent from the plots that Fen starts degrading after day one and gets completely degraded on day four, whereas Fen-*g*-PAM starts degrading from day three and gets completely degraded on day seven. The time taken for the complete biodegradation of both natural and grafted copolymer samples is almost the same.

6. Conclusions

The Fen-*g*-PAM copolymers were successfully synthesized using ceric ion initiated redox method. The percent grafting increased on increasing the monomer (AM) and decreased with initiator (CAN) concentration in the reaction mixture. FTIR, scanning electron microscopy, biodegradability studies and viscosity measurements proved that grafting indeed had taken place. Thermal properties of the copolymers seemed to be much better than that of pure mucilage. Biodegradability studies showed a minor difference in the length of time taken for complete degradation of Fen and Fen-*g*-PAM. Therefore, it can be concluded that the introduction of AM onto the backbone of natural polysaccharide only improves its properties without affecting its biodegradable nature.

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