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Polyacrylonitrile-grafted Okra mucilage: A renewable reservoir to polymeric materials

Anuradha Mishra *, Sunita Pal

Department of Chemistry, University Institute of Engineering and Technology, CSJM University, Kanpur 208 024, India

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Abstract

In the present communication, the synthesis and characterization of a polysaccharide-based material is described. Okra mucilage, a water-soluble food grade polysaccharide, was grafted with polyacrylonitrile (PAN) using ceric ammonium nitrate/nitric acid redox initiator for modifying their properties for potential industrial applications. Ceric ion initiated solution polymerization under N_2 atmosphere was found to be an efficient method for the formation of graft copolymers. The effect of variables such as the monomer concentration, initiator concentration, reaction time and temperature on the grafting efficiency (%GE) and percent grafting (PG) was discussed. Evidence of grafting was provided by the characterization of Okra mucilage and its graft copolymers by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) patterns.

Keywords: Polysaccharide; Graft copolymers; FTIR; SEM; DSC; XRD

1. Introduction

In recent years, chemical modification of natural macromolecules has received considerable interest. Polysaccharides of vegetable origin are unique raw materials as they are abundant in nature, widely available in many countries, inexpensive, renewable resources, stable, hydrophilic and modifiable biopolymers. They offer tremendous potential for development of alternate materials (Chauhan, Dhiman, Guleria, & Kaur, 2002; Okieimen, 2003; Sanghi, Bhattacharya, & Singh, 2002; Singh, Tiwari, Tripathi, & Sanghi, 2004a, Singh, Tiwari, Tripathi, & Sanghi, 2004b). Grafting techniques have received considerable attention, especially regarding those systems in which polysaccharides are used as substrate polymers (Gao, Tian, Yu, & Duan, 1994; Singh et al., 2004a, 2004b). An important advantage of graft polymerization is that the grafted polymer chains are held together by chemical bonding, allowing the two polymers to be intimately associated. The polymer that is grafted is expected to be distributed on the backbone of the substrate polymer and also to impart beneficial effects on its properties.

The Ce(IV)-induced graft copolymerization of vinyl monomers onto polysaccharide substrates had been extensively used for their property modification (Fares, 2003; Singh et al., 2000; Yoon, Carr, & Bagley, 1992). We have recently reported the synthesis of polyacrylamide and polyacrylonitrile-grafted copolymers based on mucilage obtained from *Plantago psyllium* husk, *Coccinia indica* fruits and *Tamarindus indica* seeds (Mishra & Bajpai, 2005, 2006; Mishra, Rajani, Agarwal, & Dubey, 2002; Mishra, Rajani, & Gupta, 2003).

In the present communication, we report the synthesis of polyacrylonitrile-grafted copolymers of Okra mucilage (O-g-PAN), which is extracted from the fruits of *Hibiscus esculentus*, and used in food industry as a good emulsifying and foam-stabilizing agent. A solution polymerization technique using CAN/HNO_3 as initiator is reported for

* Corresponding author. Tel.: +91 512 2218330.
E-mail address: anuradha_mishra@rediffmail.com (A. Mishra).

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this synthesis. The influence of reaction time, temperature and concentrations of AN 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

Okra mucilage, an amorphous polysaccharide, is a natural polysaccharide composed of D-galactose, L-rhamnose and L-galacturonic acid. The Okra fruits were thoroughly washed with water, cut into pieces and soaked in distilled water overnight. The mucilage was extracted by filtering through muslin cloth. For deproteinization, it was treated with 0.3 N $Ba(OH)_2$–5% aqueous $ZnSO_4 \cdot 7H_2O$ (Singh, Tiwari, Tripathi, & Sanghi, 2005). Acrylonitrile, ceric ammonium nitrate, hydroquinone, and nitric acid (S.D.Fine-Chem Ltd.) were used as received.

2.1. Preparation of O-g-PAN copolymers

O-g-PAN was synthesized by grafting acrylonitrile (AN) onto Okra mucilage by radical polymerization method in aqueous system using ceric ion/nitric acid redox initiator (Karmakar, Rath, Sastry, & Singh, 1998).

The following procedure has been adopted in carrying out the reactions. One gram of Okra 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. Then the required amount of AN solution was added into the solution through the stopper by 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 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 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 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. O-g-PAN, in each case, was separated from PAN (homopolymer) by pouring the reaction mixtures into a large quantity of dimethyl formamide (DMF) for 24 h. 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

$$\%\ \text{Efficiency} = \{\text{Weight of Polymer Grafted}/(\text{Weight of Polymer Grafted} + \text{Weight of Homopolymers Formed})\} \times 100.$$

2.2. Characterization and analysis

The structure of Okra mucilage and O-g-PAN 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 by sputtering method. The micrographs were taken at a magnification of 2000. The thermograms of the Okra mucilage and O-g-PAN were obtained by using differential scanning calorimetry (DSC) by METTLER TA4000 SYSTEM under nitrogen atmosphere at a heating rate of 20 °C per minute. X-ray diffraction (XRD) was carried out on Iso Debyflux-2002 (Rich and Scifert) X-ray powder diffractometer.

3. Results and discussion

The most important feature of the ceric ion initiated polymerization technique for grafting vinyl monomers is that it proceeds via single electron transfer with the formation of free radicals on reducing agent. This method of grafting yields substantially pure graft copolymer since the free radicals are produced exclusively on the backbone. In this system, the free radical is produced on the Okra mucilage (substrate backbone), which in the presence of acrylonitrile, initiates polymerization to produce a graft copolymer. The length of the grafted chains at a fixed monomer concentration is proportional to the number of free radical sites so generated, i.e., the length of the grafted chains should be largest in case of low ceric ion concentration and vice-versa. The detailed mechanism proposed for the synthesis of O-g-PAN is same as described elsewhere for other polysaccharide-based grafted copolymers of acrylonitrile (Mishra et al., 2003).

3.1. Influence of reaction parameters

3.1.1. 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 0.14 to 0.50 mol, the percent grafting (PG) and percent grafting efficiency (%GE) increased up to 0.23 mol [AN] but with further increase in AN concentration, the PG and %GE decreased. The PG and %GE increased with increase in AN concentration up to a certain level but beyond this it showed decline in %GE and PG with increase in its concentration. This might be due to the formation of homopolymers that

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

Sample No.	AN (mol)	$[Ce(IV)] \times 10^3$ (mol)	Percent grafting (%)	Grafting efficiency (%)
1	0.14	0.75	24.6	76.77
2	0.14	1.00	32.8	83.93
3	0.14	1.50	36.7	87.28
4	0.14	2.00	39.4	90.36
5	0.14	2.50	29.8	85.76
6	0.23	0.75	36.8	86.14
7	0.23	1.00	42.4	88.92
8	0.23	1.50	56.9	95.14
9	0.23	2.00	68.5	97.10
10	0.23	2.50	38.4	92.26
11	0.50	0.75	28.1	81.87
12	0.50	1.00	38.3	86.80
13	0.50	1.50	39.9	90.45
14	0.50	2.00	43.5	91.38
15	0.50	2.50	37.7	89.82

Temperature, 30 °C; time, 2 h; mucilage, 1.0 g.

successfully hinder the rate of penetration of monomer molecules to the polysaccharide-free radicals, resulting in decrease in %GE and PG (Fares, 2003; Sudhakar, Srinivasan, Joseph, & Santappa, 1981).

3.1.2. Effect of initiator (CAN) concentration

On increasing the concentration of initiator, i.e., CAN from 0.75×10^{-3} to 2.0×10^{-3} mol, both %GE and PG increased due to increase (Table 1) in the number of free radicals on polysaccharide chains. The falling off of %GE and PG at higher CAN concentration (2.5×10^{-3}) is a well-known phenomenon and ascribed to the increasing participation of the ceric ion in the termination of the growing grafted chains (Yao & Tang, 1992).

3.1.3. Effect of reaction temperature

Reaction temperature is an important reaction condition in the graft copolymerization. The effect of temperature on PG and %GE is shown in Table 2. PG and %GE both increased on varying the reaction temperature from 20 to 50 °C. The increase in %GE and PG with increasing temperature may be due to the increased diffusion rate of monomer and initiator and raised rate of grafting (Shukla & Srivastava, 2003).

3.1.4. Effect of reaction time

The effect of time on %GE and PG is shown in Table 3. The PG as well as %GE increased with increasing the reaction time up to 2 h and then a decline in both PG and %GE was seen.

Table 2
Effect of reaction time on PG and %GE

Sample No.	AN (mol)	$[Ce(IV)] \times 10^3$ (mol)	Percent grafting (%)	Grafting efficiency (%)	Time (h)
1	0.23	2.0	59.6	93.32	1
2	0.23	2.0	68.5	97.10	2
3	0.23	2.0	51.4	91.52	3
4	0.23	2.0	46.8	88.73	4
5	0.23	2.0	42.3	87.03	24

Temperature, 30 °C; mucilage, 1.0 g.

Table 3
Effect of reaction temperature on PG and %GE

Sample No.	AM (mol)	$[Ce(IV)] \times 10^3$ (mol)	Percent grafting (%)	Grafting efficiency (%)	Temperature (°C)
1	0.23	2.0	32.86	85.97	20
2	0.23	2.0	68.50	97.10	30
3	0.23	2.0	70.40	97.23	40
4	0.23	2.0	74.60	97.79	50

Time, 2 h; mucilage, 1.0 g.

3.2. Characterization of graft copolymer

3.2.1. Infrared (IR) spectrum

The FTIR spectra of ungrafted mucilage and O-g-PAN (PG = 68.50) are shown in Figs. 1 and 2. The FTIR spectrum of O-g-PAN is different from that of Okra mucilage by showing additional peak at 2198 cm^{-1}, characteristic of –C≡N. The shifting of –OH band towards higher wavelength in O-g-PAN shows the loss of secondary association between the pendant groups of pure mucilage due to insertion of PAN chains.

3.2.2. 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 [Fig. 3(a)] and O-g-PAN [Fig. 3(b)] is used as a supportive evidence for grafting. The morphology of the surface of pure Okra mucilage is different than that of its grafted copolymer,

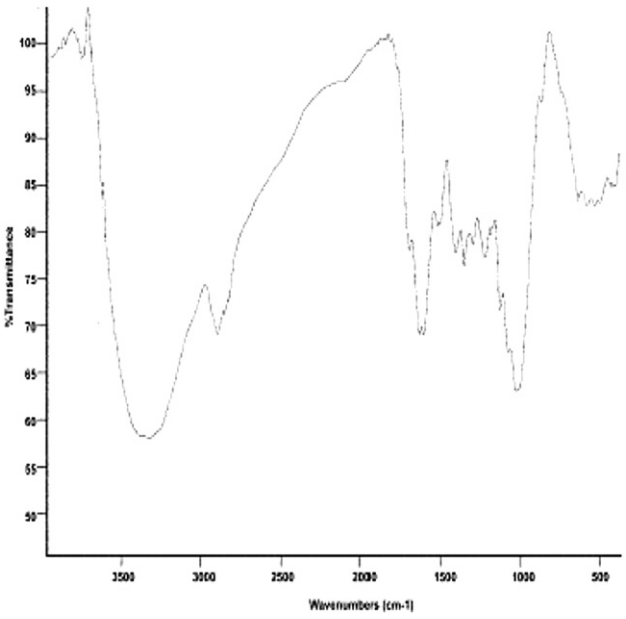

Fig. 1. IR spectrum of Okra mucilage.

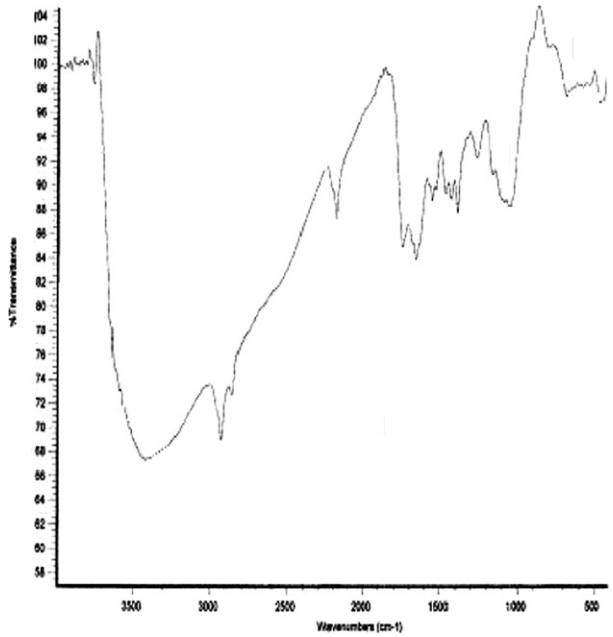

Fig. 2. IR spectrum of O-g-PAN.

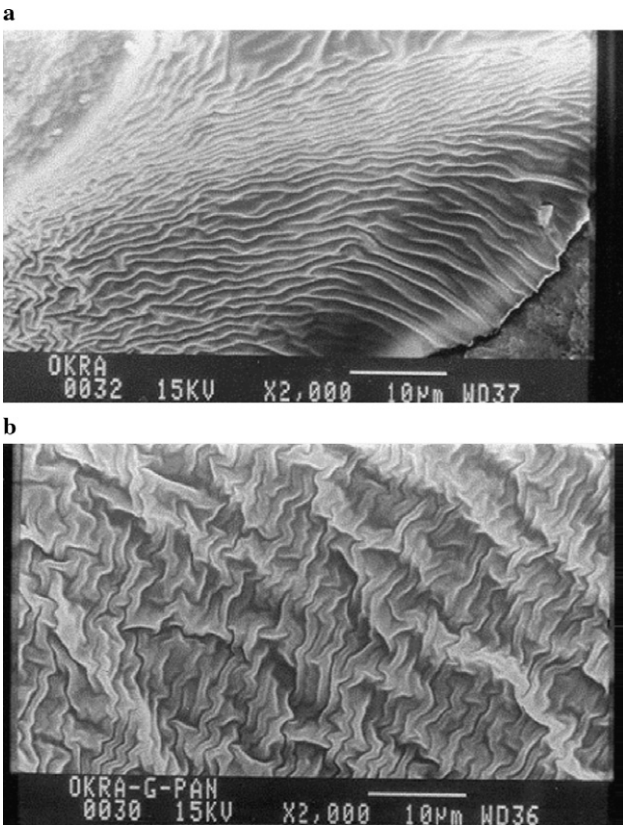

Fig. 3. Scanning electron micrographs of (a) Okra mucilage and (b) O-g-PAN.

i.e., O-g-PAN (PG = 68.50). A considerable amount of grafted polymer is deposited, which appears to have a different structure from the pure mucilage (Gao et al., 1994). In Fig. 3a, the lamellar structure is evident for ungrafted mucilage. The oriented layers indicate its regular structure, which can be due to hydrogen bonding between the pendant groups whereas micrograph of O-g-PAN does not show (Fig. 3b) lamellar structure confirming the breakage of secondary bonding between the pendant groups of pure mucilage as indicated in IR spectrum.

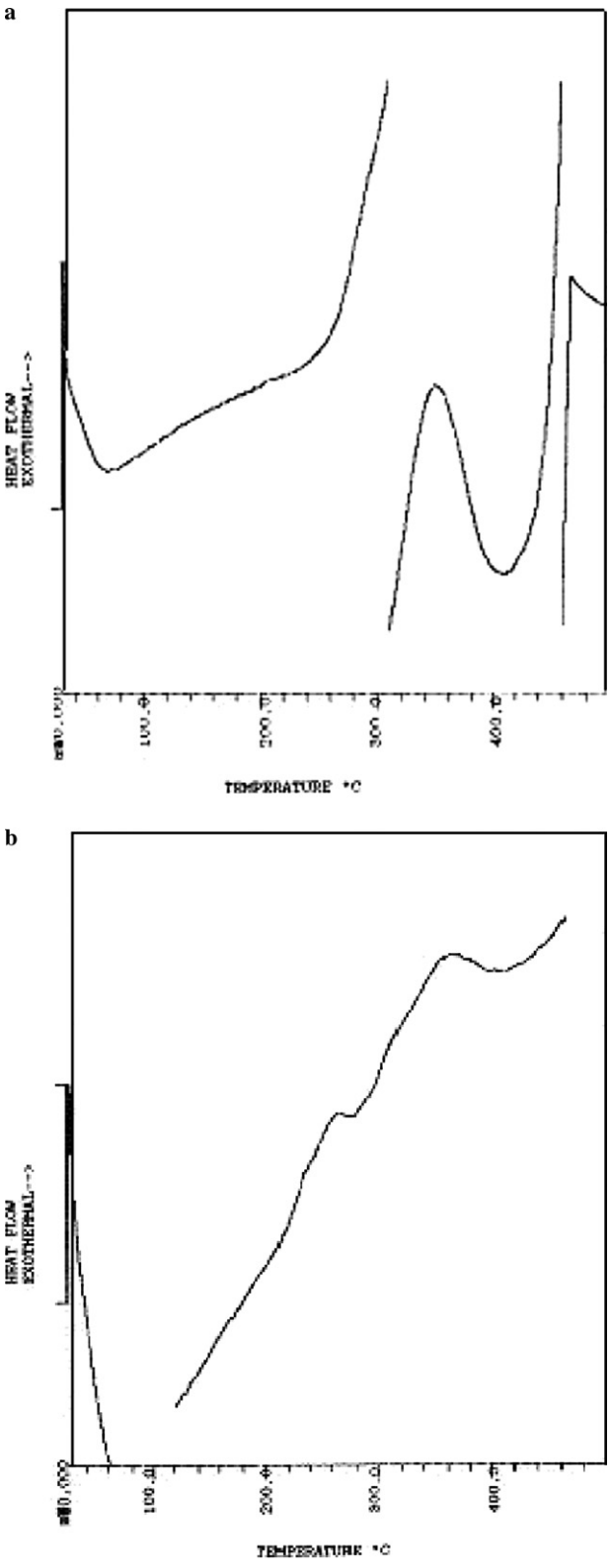

Fig. 4. DSC Scans of (a) Okra mucilage and (b) O-g-PAN.

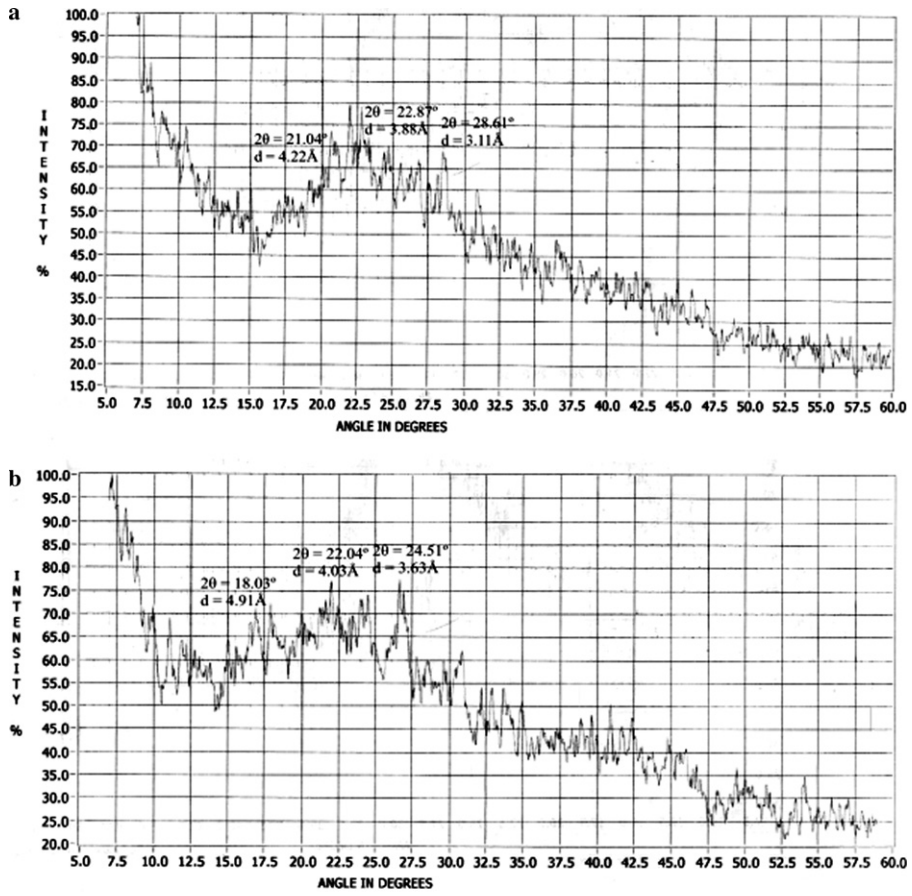

Fig. 5. XRD pattern of (a) Okra mucilage and (b) O-g-PAN.

3.2.3. Differential scanning calorimetry (DSC)

The DSC scans of pure mucilage (Fig. 4a) and grafted copolymer (PG = 68.50) (Fig. 4b) are showing different exothermic patterns which proves that grafting has indeed taken place. The difference in the exotherms indicates that the crosslinking reactions occurring in the region between 50 and 400 °C are different for pure mucilage and grafted copolymer. Even the pattern for moisture loss up to 100 °C is different in both the scans.

3.2.4. X-ray diffraction (XRD)

Fig. 5a and b are the results of X-ray differaction analysis of pure mucilage and grafted copolymer (PG = 68.50), respectively, at room temperature from $2\theta = 7.5°$ to 60° (error range of 2θ is 0.01–0.31). The XRD patterns for mucilage as well as for O-g-PAN do not show any sharp crystalline peak. The difference observed for 2θ and d values in both the cases constitutes primary evidence that a different solid phase was formed after grafting (Huang, Allen, & Tonelli, 1999).

4. Conclusions

Grafting of polyacrylonitrile onto Okra mucilage, a polysaccharide of vegetable origin, offers a new polymeric material with properties that can be exploited industrially. Grafting only improves the properties of mucilage by introducing more reactive sites and without making any change in the molecular mobility of chelating groups of polysaccharide. A redox initiator system of CAN/HNO_3 was efficiently used to graft PAN onto the mucilage. The remarkable variation in extent of grafting was seen with the variation in the concentrations of monomer and initiator and reaction time and temperature. Various analytical techniques such as FTIR, SEM, DSC and XRD patterns confirmed grafting of acrylonitrile onto mucilage chains.

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