Synthesis and Characterization of Polyacrylamide Grafted Copolymers of Kundoor Mucilage

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ABSTRACT: In the present research, grafting of acrylamide monomer onto a water-soluble food grade polysaccharide, Kundoor mucilage, initiated by ceric ion in aqueous medium has been studied under N_2 atmosphere. Ceric ion initiated solution polymerization 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 per- cent of grafting (%PG), have been investigated. The graft copolymers were characterized by FTIR, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and X-ray diffraction (XRD). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1186–1191, 2005

Key words: DSC; FTIR; graft copolymers; polysaccharide; synthesis; XRD

INTRODUCTION

Natural polymers are widely used as flocculants for various wastewater treatments. Homopolymers suffer from various drawbacks, such as a shear instability, uncontrolled biodegradability, and various inefficiencies. These shortcomings may be overcome by developing copolymers based on efficient, but shear degradable, acrylic polymer and stable polysaccharides. It is observed that grafting of shear degradable polymers onto rigid polysaccharide backbone provides fairly shear stable systems.[1] The improvement of natural polymers, such as starch,[2–4] cellulose,[5,6] and wool,[7] by grafting other monomers has found considerable interest in the literature and industry due to combinatorial properties of both natural and synthetic polymers.

The water-soluble tendency of polyacrylamide under nearly all conditions has made it possible to form graft copolymers with other monomers easily. By further reaction at the amide function, one can convert many of the polymers into polyelectrolytes. Water-soluble polymeric flocculants are of considerable importance in colloidal science and in various industrial solid-liquid separation operations, such as drilling fluid, water treatment, mineral processing, and papermaking. Acrylamide polymers are approved for use as coagulant aids in potable water treatment.[8]

Various methods of graft copolymerization have been reported in the literature.[9–12] The Ce (IV) induced graft copolymerization of vinyl monomers onto polysaccharide substrate is a widely used process for property modification of naturally occurring polymers[13,14] due to the simple mechanism of electron transfer and low activation energy.[15] Singh and coworkers[16] have prepared a large number of graft copolymers of AM with polysaccharides, such as guar gum, xanthan gum, carboxylic methylcellulose, and starch, using ceric ion/HNO_3 acid [CAN] as redox initiator.

In the present article, synthesis of a graft copolymer of AM onto Kundoor mucilage is reported using a ceric-ion-initiated solution polymerization technique. The influence of reaction time, temperature, and concentrations of AM and CAN in the reaction mixture on % grafting is studied by preparing different samples. The prepared samples were characterized by FTIR, SEM, DSC, and X-ray diffraction patterns.

EXPERIMENTAL

Coccinia *indica* plants are cultivated throughout the Indian subcontinent and also grow wild in thickets and wasteland. The fruits cost around 8 Kg per $. They have considerable medicinal value and are used for the treatment of diabetes, skin disorders, jaundice, intermittent fever, asthma, cough, and bronchitis. To extract the mucilage from the fruits, they were thoroughly washed with water, cut into pieces, and soaked in distilled water overnight. The mucilaginous extract was filtered through muslin cloth. It was pre-

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TABLE I
Effect of Monomer and Initiator Concentrations on %PG and %GE

Sample no.	AM (mols)	Ce (IV) $\times 10^3$ (mols)	Percent grafting	Grafting efficiency %
1	0.07	0.05	39.75	85.16
2	0.07	0.10	54.40	78.20
3	0.07	0.15	46.68	89.76
4	0.14	0.05	63.38	64.76
5	0.14	0.10	68.60	95.20
6	0.14	0.15	26.74	75.50
7	0.21	0.05	39.23	77.70
8	0.21	0.10	52.50	81.09
9	0.21	0.15	41.91	75.20
10	0.30	0.05	33.82	72.28
11	0.30	0.10	43.31	65.53
12	0.30	0.15	32.27	49.97

Temperature = 30°C; Mucilage = 1.0 g.

cipitated from the extract by addition of alcohol. The precipitate was washed with acetone 2 to 3 times and finally dried by keeping in an oven at 40°C for 24 h. The crude mucilage was purified by barium complexing.[17] The purified mucilage is easily soluble in cold water. The mucilage extracted from the Kundoor fruits is rich in pectin. Sugars present are D-Glucose and D-galacturonic acid.[18,19]

Acrylamide, ceric ammonium nitrate, hydroquinone, and nitric acid (S.D.Fine-Chem Ltd.) were used as received.

Preparation of Ku-g-PAM copolymer

Ku-g-PAM was synthesized by grafting acrylamide (AM) onto purified Kundoor mucilage by the radical polymerization method in an aqueous system using ceric ion/nitric acid redox initiator.[20]

The following procedure was adopted in carrying out the reactions. One gram of Kundoor mucilage was dissolved in distilled water (200 mL) in an Erlenmeyer flask. The flask was then sealed with a septum stopper and flushed with nitrogen for 20 min. The required amount of AM solution, prepared in 100 mL distilled water, was 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 $1N$ 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 at 20°C by immersing the flask in a constant temperature bath. The reaction mixture was stirred occasionally; the reaction was continued for 4 h and then terminated by injecting 0.5 mL of saturated aqueous hydroquinone solution.

The reaction product was precipitated in excess 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 a vacuum oven at 40°C. The % grafting was calculated by the equation

$$\%\text{Grafting} = \frac{\text{Weight of Polymer Grafted}}{\text{Weight of Kundoor Mucilage}} \times 100$$

The % efficiency was calculated by the equation

$$\%\text{Efficiency} = \frac{\text{Weight of Polymer Grafted}}{\text{Weight of Polymer Grafted} + \text{Weight of Homopolymer Formed}} \times 100$$

The structure of Kundoor mucilage and Ku-g-PAM was determined from Fourier Transform (FT) IR spectra (Brucker Vector 22 spectrophotometer) using KBr pellets. Scanning electron micrographs (SEM) and thermograms of pure and the grafted copolymer were obtained on a JEOL JSM-840 SEM. The samples, in the form of films, were mounted on the specimen stubs and coated with gold ion by the sputtering method. The micrographs were taken at a magnification of 1500. The thermograms of the Kundoor mucilage and Ku-g-PAM were obtained by using differential scanning calorimetry (DSC) by a METTLER TA4000 SYSTEM under nitrogen atmosphere at a heating rate of 20°C per minute. X-ray diffraction patterns of powder samples of pure mucilage and grafted copolymer were obtained at ambient conditions on an X-ray diffractometer, model Iso-Debyflux-2002 (Rich and Scifert), using Cu K$\propto$ radiation.

RESULTS AND DISCUSSION

Influence of reaction parameters

The results are summarized in Tables I–III.

TABLE II
Effect of Reaction Time on %PG and %GE

Sample no.	AM (mols)	Ce (IV) $\times 10^3$ (mols)	Percent grafting	Grafting efficiency %	Time (hours)
1	0.14	0.10	32.00	84.20	1
2	0.14	0.10	44.00	93.70	2
3	0.14	0.10	52.00	95.48	4
4	0.14	0.10	68.60	95.20	24

Temperature = 30°C; Mucilage = 1.0 g.

TABLE III
Effect of Reaction Temperature on %PG and %GE

Sample no.	AM (mols)	Ce (IV) × 10³ (mols)	Percent grafting	Grafting efficiency	Temperature (°C)
1	0.14	0.10	29.56	76.28	20
2	0.14	0.10	32.00	84.20	30
3	0.14	0.10	44.86	76.20	40
4	0.14	0.10	58.00	95.60	50

Time = 1 hour; Temperature = 30°C; Mucilage = 1.0 g.

Effect of monomer concentration

The effect of monomer concentration on percent grafting and grafting efficiency is shown in Table I. The initial increase in %PG and %GE was followed by a decrease at higher monomer concentrations. As the monomer concentration increases (0.07 mol to 0.14 mol), the percent grafting (%PG) and percent grafting efficiency (%GE) increases; but with further increase in AM concentration from 0.21 mol to 0.30 mol, the %PG and %GE decrease. The increase of %GE and %PG is expected with 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 decline in %GE and %PG may 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.[21]

Effect of initiator (CAN) concentration

On increasing the concentration of the initiator, that is, CAN, from $0.05 × 10^3$ moles to $0.10 × 10^3$ moles, both %GE and %PG increase due to an increase (Table I) in the free radicals on polysaccharide chains. The falling off of %GE and %PG at higher CAN concentration $(0.15 × 10^3)$ is a well-known phenomenon and is ascribed to the increasing participation of the ceric ion in the termination of the growing grafted chains.[22]

Effect of time

On increasing the reaction time, percent grafting as well as grafting efficiency increase, as shown in Table II. This agrees with the earlier observation with free radical initiated polymerization.[23]

Effect of reaction temperature

Reaction temperature is an important reaction condition in the graft copolymerization. The effect of temperature on percent grafting and grafting efficiency is shown in Table III. 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 the monomer and the initiator and the raised rate of grafting.[24]

Characterization of graft copolymers

Infrared (IR) spectrum

IR spectra of pure Kundoor mucilage (Fig. 1a) and its graft copolymer, Ku-g-PAM (Fig. 1b) having %PG = 68.60, are compared to confirm grafting. It is observed that the IR spectrum of Ku-g-PAM shows additional peaks at 1670 cm^{-1} of -C = O of amide, at 1543 cm^{-1} of -NH bending, at 1383 cm^{-1} of –CN stretching, at 1237.67 cm^{-1} of –C-C-N asymmetric, and a broad out of plane-NH band between 800 and 600 cm^{-1}. Moreover, the broadening and shifting of the band towards higher wave number, from 3311 cm^{-1} in pure mucilage to 3419 cm^{-1} in Ku-g-PAM, is 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 (Figs. 2a and 2b) of purified
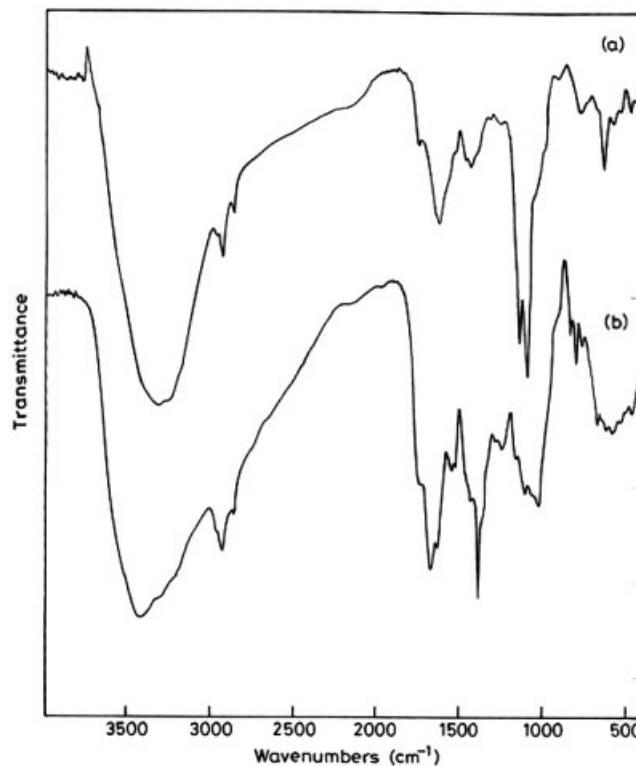

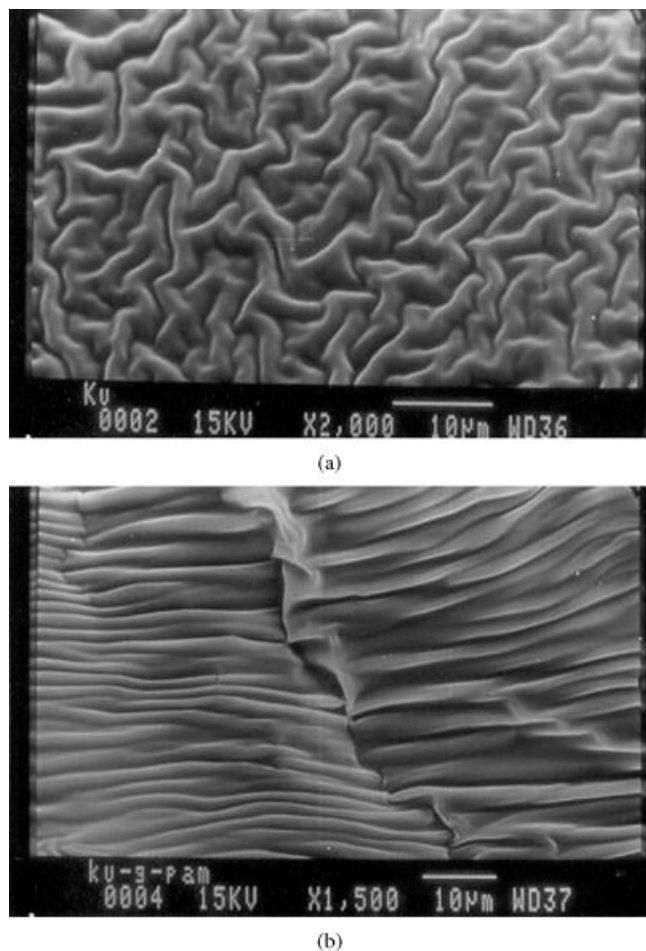**Figure 1** IR spectra of (a) Kundoor mucilage and (b) Ku-g-PAM.

Figure 2 Scanning electron micrographs of (a) Kundoor mucilage and (b) Ku-g-PAM.

Kundoor and Ku-g-PAM (% PG = 68.60) are used as supportive evidence for grafting. A considerable amount of grafted polymer is deposited on the pure mucilage and it appears to have a different structure from the pure mucilage.[22] The fringed-micelle structure is evident in Figure 2(a), whereas the micrograph of Ku-g-PAM shows lamellar structure. The oriented layers in the graft copolymer structure can be probably attributed to hydrogen bondings between PAM and mucilage chains.

Differential scanning calorimetry (DSC)

The DSC scans of pure mucilage [Fig. 3(a)] and grafted copolymer [Fig. 3(b)] (% PG = 68.60) show 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°C and 250°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.

X-ray diffraction analysis (XRD)

The X-ray diffraction patterns of pure mucilage and Ku-g-PAM (% PG = 68.60) at room temperature from $2\theta = 10°$ to $70°$ (error range of 2θ is 0.01 to 0.31) are shown in Figures 4(a) and 4(b). The mucilage Figure 4a shows, like all other natural polymers, partial crystalline nature. Figure 4(b), the XRD pattern of Ku-g-PAM, is quite different from that of pure mucilage. The 2θ and d values observed in both cases are different. This constitutes primary evidence that a different
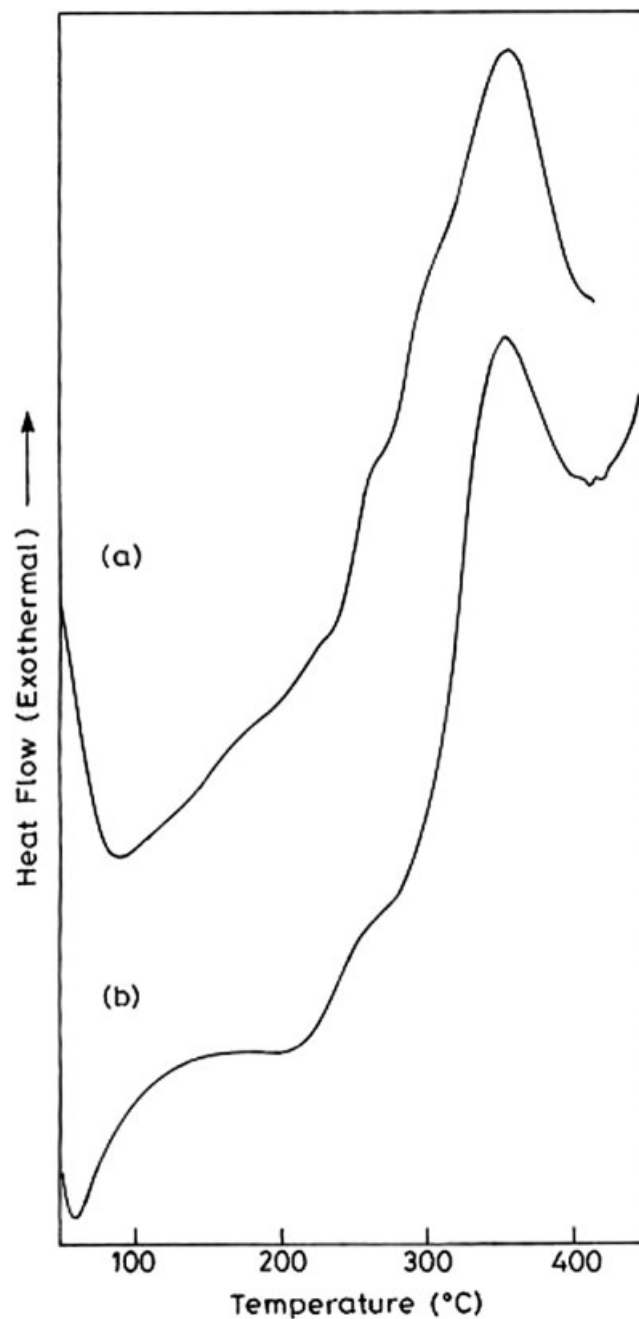

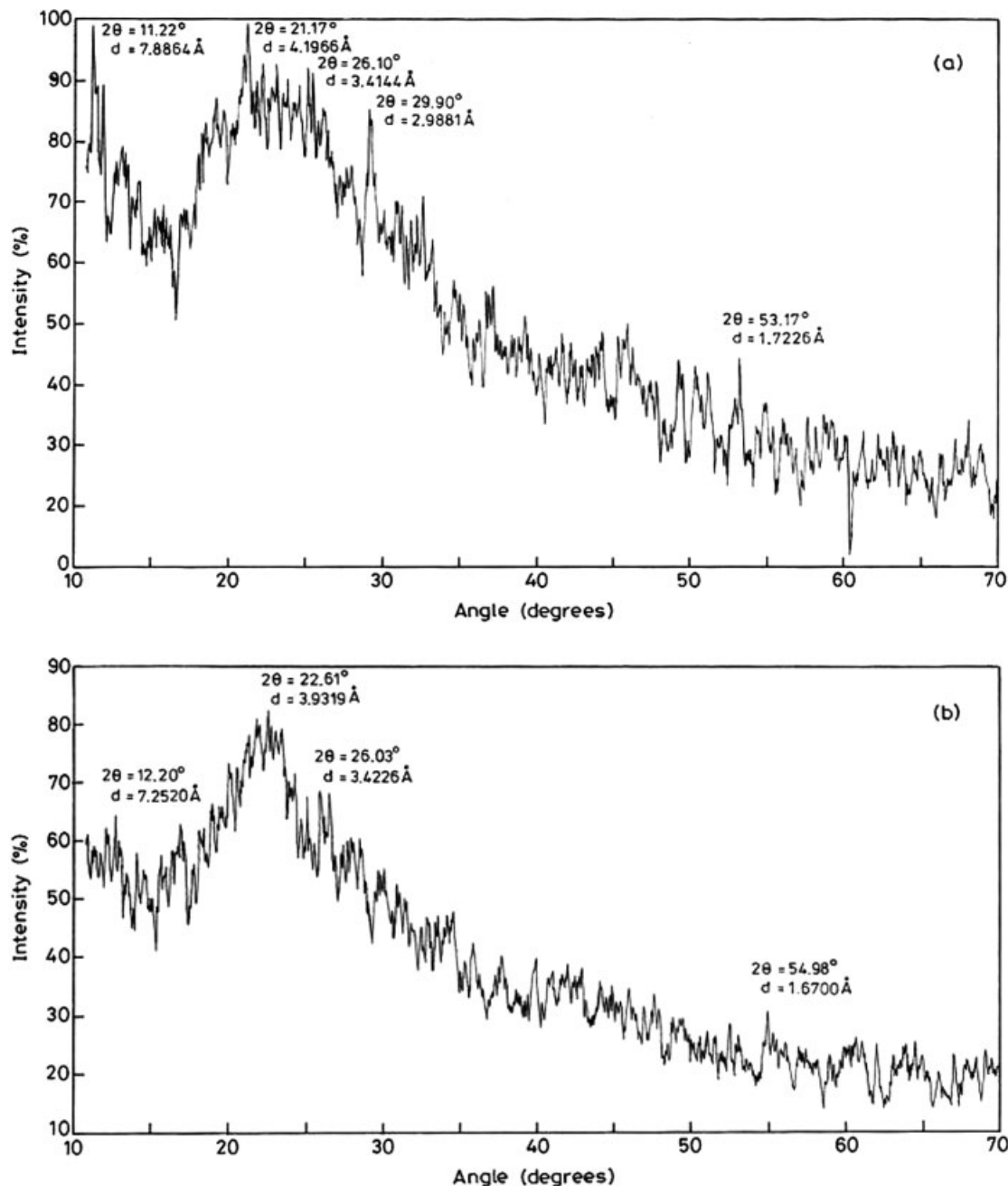**Figure 3** DSC scans of (a) Kundoor mucilage and (b) Ku-g-PAM.

Figure 4 XRD patterns of (a) Kundoor mucilage and (b) Ku-g-PAM.

solid phase was formed after grafting[25] and the grafting causes destruction of the crystalline nature of the mucilage.[15]

CONCLUSIONS

Grafting of Kundoor mucilage to prepare its acrylamide-grafted copolymers has been done successfully by using a CAN/HNO$_3$ redox initiator system. The maximum percent grafting and grafting efficiency was obtained when acrylamide and CAN concentrations in the reaction mixture were 0.14 mol and 0.10×10^{-3}

moles. Various analytical techniques, such as FTIR, SEM, DSC, and XRD patterns, confirmed the grafting of acrylamide onto the mucilage chains.

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