

Synthesis of the Copolymer Hydrogel κ -Carrageenan-graft-PAAm: Evaluation of Its Absorbent and Adhesive Properties

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ABSTRACT: κ -Carrageenan-graft-PAAm, a copolymer hydrogel of κ -carrageenan (kC) and acrylamide (AAm), has been synthesized in aqueous medium at \sim pH 7 in the presence of the initiator potassium persulfate (KPS), using microwave irradiation. The reaction conditions were optimized by varying the concentration of AAm and KPS to obtain copolymer hydrogels having different nitrogen contents e.g., %N 6.35, 10.56, and 11.05. It was observed that copolymer hydrogel having %N 11.05 gives superior adhesive properties whereas copolymer hydrogel with %N 10.56 produces superior absorbent properties in the presence of optimized concentrations of AAm (0.87 and 1.1428 mol/L respectively) and KPS (0.022 and 0.0296 mol/L respectively). The product with %N 6.35 is a soft gel (2–5% gel in 1% KCl) exhibiting low gel strength (135 g cm^{-2}). The one with %N 10.56 showed

superior swelling property and maximum swelling was observed in the alkaline pH (22 g/g). The swelling behaviors of the hydrogels were studied at different pHs (pH 1.2–12.5) as well as in 1% aqueous solutions of NaCl, KCl, and CaCl_2 . The 5% dispersion of the hydrogel having %N 11.05 in water had good binding properties with papers, polyethylene sheets, and wood pieces. To evaluate the measure of adhesive property, the viscosity and solid and liquid weights of the applied adhesive were measured. Characterization of the copolymer hydrogels was done by TGA, X-ray diffraction, ^{13}C -NMR, FT-IR, elemental analyses, and rheological studies. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5144–5153, 2006

Key words: κ -carrageenan; copolymer hydrogels; microwave irradiation; adhesive; absorbent; rheology

INTRODUCTION

Super absorbent hydrogels are three-dimensional hydrophilic crosslinked networks, which are able to absorb and retain water, saline, or biological fluids without dissolution many times over their weight.^{1,2} The first industrial superabsorbent hydrogel was synthesized using this method via ceric-induced graft copolymerization of acrylonitrile onto starch followed by crosslinking alkaline hydrolysis of the nitrile groups of the produced graft copolymer.³ Physical and chemical modifications of synthetic or natural polymers have been done with a view to value addition of the same targeting new applications.^{4–8} Because of the large application of starch and cellulose in textile, paper, and food industries, they are being grafted or crosslinked for producing derivatives having different physico-chemical properties.⁹ Ushakov first reported cellulose graft copolymers in 1943.¹⁰

Carrageenan is a seaweed polysaccharide and the backbone of the polymer consists of alternating α -1,3-linked D-galactopyranose and β -1,4-linked 3,6-anhy-

dro-D-galactopyranose (Fig. 1).¹¹ A biopolymer-based super absorbent hydrogel was synthesized through chemical crosslinking graft polymerization of acrylic acid on to κ -carrageenan (kC) in the presence of crosslinking agent (*N,N'*methylene bis acrylamide) and an initiator ammonium persulfate was reported by Pourjavadi et al.¹² Shchipunov¹³ reported a sol-gel biomaterial based on carrageenan and silica. Natural polysaccharides or gums were modified to impart more functional properties.¹⁴ Pourjavadi et al.¹⁵ reported synthesis of carrageenan and sodium alginate based super absorbent hydrogel using vigorous reaction conditions including long duration.

Acrylamide (AAm) is a chemical intermediate used in the production and synthesis of polyacrylamide.¹⁶ These high-molecular-weight polymers can be modified to develop nonionic, anionic, or cationic properties for specific uses. The most important end uses of AAm are in water-soluble polymers as additives for water treatment, enhanced oil recovery, flocculants, paper-making aids, thickeners, soil conditioning agents, sewage and waste treatment, ore processing, and permanent-press fabric.¹⁶ It is also used as gelling agent for explosives, binder in additives, in production of diazo compounds, and for gel chromatography and electrophoresis.^{16,17} Therefore, AAm was used as the grafting

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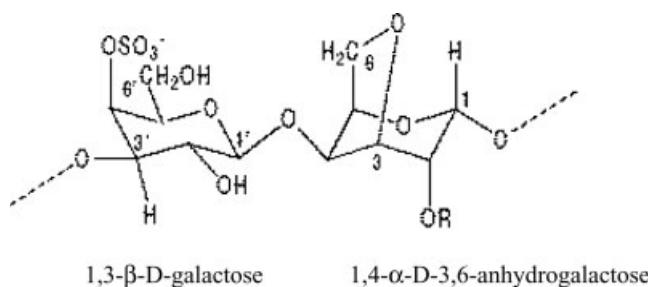


Figure 1 Repeating units of κ -carrageenan.

monomer with κ C, a water soluble biopolymer, with a view to having a copolymer hydrogel with potential utilities. Incidentally, the latter exhibited adhesive properties. A material that is capable of sticking to surfaces of other substances and binding them to one another is called adhesive.¹⁸ Adhesives from vegetable sources are well known; they include natural gums, starch, and starch derivatives. They are commonly used for sizing paper and textiles and for labeling, sealing, and manufacturing paper goods.^{19–21}

In this article we report microwave-induced one-pot route for graft copolymerization of AAm onto κ C initiated by potassium persulfate (KPS). Resultant copolymer hydrogel exhibited adhesive and super absorbent properties.

EXPERIMENTAL

Preparation of κ C

Refined κ C used in this study was prepared from dried red seaweed *Kappaphycus alvarezii* (*Euchuema cottonii*) in our lab using the method described by Craigie and Leigh¹¹ and the hot extract was purified by precipitation method using isopropanol (IPA) as a solvent in 1 : 2.5 ratio (v/v). KPS, AAm, IPA, and potassium chloride used were of analytical grade and were purchased from Sigma-Aldrich, Mumbai and Ranbaxy Fine Chemicals, Mohali, India.

Apparatus

LG make domestic microwave oven having temperature range 40–100°C (Magnetrons are set at a frequency of 2450 MHz) [LG Microwave Appliance, Model No. MS-285SD; Korea] was used.

Preparation of κ C-*graft*-PAAm

To a dispersion of κ C (1–2 g) in 35 mL distilled water was added a solution of AAm [2–8 g (0.571–1.1428 mol/L)] in 10 mL distilled water. To this mixture a solution of KPS [0.071–0.4 g (0.00518–0.0296 mol/L)] in 5 mL distilled water was added and was stirred. The

mixture was then irradiated under microwave (60%) for 90–120 s. The mixture turned viscous and turbid white in color. This mixture was then added to IPA (two parts with respect to the reaction mixture, w/w) and was stirred well and allowed to stand for 20 h. The white solid mass that separated out was collected by filtration. The solid samples were washed with 50 mL each of 60% and 80% IPA–water mixture to remove the unreacted homopolymer from the products, followed by washing with 100% IPA to remove the remaining water from the final products. The solid product, κ C-*graft*-PAAm, was then air-dried. The copolymers of κ C-*graft*-PAAm, were prepared using in three different ratios of AAm and KPS, keeping the amount of κ C constant: κ C:AAm:KPS (w/w), 1 : 2.0 : 0.20; 1 : 3.0 : 0.30; and 1 : 4.0 : 0.40; the ratio of AAm:KPS being (in mol/L) 0.0148 : 0.57; 0.87 : 0.022; and 0.0296 : 1.14 respectively].

The κ C-*graft*-PAAm based adhesive was prepared by dissolving the copolymer in water (5% w/w) heating at 90–110°C for 10 min. The κ C-*graft*-PAAm based gel was prepared by dissolving the copolymers with different nitrogen contents in 1% KCl (5% w/w) by heating at 90–110°C; then it was cooled at room temperature and kept overnight at 10°C.

Swelling measurement

An accurately weighed dried amount of powdered copolymer with particle size between 5 and 10 mesh was immersed in the different solutions having pH from 1 to 13, including distilled water and 1% NaCl, KCl, and CaCl₂ solutions, in separate experiments. The swollen gel particles were wipe-dried with tissue paper to remove the adhering water and weighed at regular intervals until equilibrium was reached. Degree of swelling or equilibrium swelling (ES) capacity was calculated using the following equation:

$$ES = [W_s - W_d]/W_d$$

where W_s and W_d are the weights of the swollen and dry material samples, respectively.

Grafting parameters

The grafting parameters e.g., conversion % (C%), grafting efficiency % (E%), grafting % (G%), were determined according to the method described by Liu et al.,²² using the following equations:

$$\text{Grafting percent (G\%)} = (\text{Wt. of poly AAm grafted} / \text{wt. of } \kappa\text{C}) \times 100$$

$$\text{Grafting efficiency (E\%)} = (\text{Wt. of poly AAm grafted} / \text{total wt. of poly AAm}) \times 100$$

TABLE I
Swelling Properties of Copolymer Hydrogels at 35°C

Solution media (pH)	Equilibrium swelling ^a (g/g)			
	kC (%N 0.21)	kC-graft-PAAm copolymers with		
		%N 6.35	%N 10.56	%N 11.05
Water (7.0)	N.S.	8.5 ± 0.05	14.5 ± 0.07	12.7 ± 0.06
Alkaline (12.5)	N.S.	12.6 ± 0.06	22.0 ± 0.06	15.4 ± 0.07
Acidic (1.2)	N.S.	8.0 ± 0.05	14.0 ± 0.05	11.0 ± 0.06
1% NaCl (7.0)	N.S.	8.0 ± 0.07	12.6 ± 0.07	10.3 ± 0.05
1% KCl (7.0)	N.S.	9.0 ± 0.06	13.5 ± 0.06	12.8 ± 0.07
1% CaCl ₂ (7.0)	N.S.	8.5 ± 0.07	12.5 ± 0.06	10.8 ± 0.06

^a Swelling of control kC and different hydrogels were measured with 10-min intervals. Equilibrium swelling values and equilibrium swellings were obtained after 190 min in water, 240 min in alkali, 120 min in acid, and 220 min for salt solutions, respectively; N.S. = no swelling of control kC in solution which turned into viscous dispersion in all media.

Conversion percent (C%) = (Total wt. of poly AAm/
wt. of AAm charged) × 100

Weight of adhesive

Liquid and solid weights of applied adhesive were measured using standard method described in ASTM Handbook.¹⁸

Weight of liquid adhesive:

$$S = [(W_2 - W_1) \times 317.5] / (N \times A) \text{ (when } W_1 \text{ and } W_2 \text{ are in grams)}$$

where, S = Wt. of liquid adhesive applied (expressed in pounds per thousand sq. feet of joint or surface area); W_2 = Wt. of specimen immediately after application of the adhesive; W_1 = Wt. of specimen before applying the adhesive; A = area of test specimen (in sq. inches); N = number of surfaces spread; and 317.5 = conversion factor.

Weight of solid adhesive:

$$D = [(W_2 - W_1) \times 317.5] / (N \times A) \text{ (when } W_1 \text{ and } W_2 \text{ are in grams)}$$

where, D = Wt. of adhesive solids applied (expressed in pounds per thousand sq. feet of joint or surface area); W_2 = Wt. of the specimen after application of the adhesive and elimination of solvents; W_1 = Wt. of the duplicate uncoated specimen; A = area of test specimen (in sq. inches); N = number of surfaces spread; and 317.5 = conversion factor.

In this experiment two weighed pieces of paper, transparency sheet, and wood were taken having measured their surface areas under investigation. Then the 5% dispersion of the copolymer adhesive (with %N 11.05) was applied on one of the designated surfaces by uniformly spreading, onto which the other piece without adhesive was placed and stuck. The united pieces were weighed immediately and the weight of the liquid adhesive was calculated as mentioned above. The pieces could not be taken apart after 1 h of application. The united pieces were air dried at 30°C for 20 h, followed by at 50°C for 4 h when the weight of the specimen remained constant. The above experiment was repeated with a standard adhesive available in the market (Fevicol, Pidilite Industries, Mumbai, India), using specimens with identical size and surface areas.

TABLE II
Properties of kC-graft-PAAm Copolymer Hydrogels

Sample ^a	Apparent viscosity (in cP at 80°C)	pH (at 80°C)	Gel strength (g/cm ²) at 30°C	Gelling temperature (°C)	Melting temperature (°C)
kC (in 5% KCl)	1100 ± 7.4	7.3 ± 0.07	> 1400	71 ± 0.54	> 100 ± 0.57
kC-graft-PAAm ^b gel (in 1% KCl)	65 ± 0.75	6.8 ± 0.05	135 ± 3.3	28 ± 0.45	65 ± 0.67
kC-graft-PAAm ^c gel (in 1% KCl)	69 ± 0.75	6.5 ± 0.06	120 ± 5.4	22 ± 0.54	58 ± 0.62
kC-graft-PAAm ^d gel (in 1% KCl)	74 ± 0.54	6.2 ± 0.05	< 100 ± 5.4	19 ± 0.54	55 ± 0.54

^a Measured in 5% sol-gel.

^b %N = 6.35.

^c %N = 10.56.

^d %N = 11.05.

TABLE III
Effect of %N on the Grafting Parameters

Grafting parameter	%N content		
	%N 6.35	%N 10.56	%N 11.05
G%	170 \pm 0.67	272 \pm 0.51	320 \pm 0.77
E%	87.8 \pm 0.60	97.8 \pm 0.62	98.5 \pm 0.50
C%	76.0 \pm 0.53	90 \pm 0.67	80.0 \pm 0.60

Characterization

The analytical characterizations of the copolymer were done as follows: IR spectra in KBr on a Perkin-Elmer Spectrum GX, FT-IR System (USA); X-ray diffractions studies on a Philips X'pert MPD X-ray powder diffractometer using $2\theta = 5^\circ$ to 60° ; optical micrographs were recorded on an optical microscope of Olympus model SZH 10, Japan, with $70\times$ magnification; elemental analyses on a Perkin-Elmer-2400, CHNS/O Analyser; thermal analysis on a TGA Toledo Mettler TGA system, Switzerland; and rheological measurements on a RS1 Rheometer (HAAKE Instruments, Karlsruhe, Germany). Cone/plate geometries (60 mm diameter, 1° rad angle) were selected for rheological measurements in solutions taking 1 mL sol on to the plate of the rheometer, for measurements in the sol and gels, prepared from two hydrogels (i.e., hydrogels with, %N = 6.35 and 11.05) and the results were compared with those of control kC (1% gel in 1% KCl). Viscosities at varying shear rates were studied at 25°C . Oscillation measurements were carried out in controlled deformation mode with 0.05% strain and plate/plate geometry (35 mm diameter) was used. The temperature was maintained using the DC50 water circulator. Rheological data presented are means of three replicate measurements. Under the given experimental conditions no syneresis or slippage of gel was observed, as there was no abrupt decrease in G' values. The apparent viscosity was measured on a Brookfield Viscometer (Synchrolectric Viscometer, Stoughton, MA 02072). Spindle No. 1 and rpm 60 were used for measuring the apparent viscosity. The gel strength (g/cm^2) was measured using a Nikkansui-type gel tester (Kiya Seisakusho, Tokyo, Japan). In this study the gelling and melting temperatures were measured according the method described by Craigie and Leigh.¹¹ For measurement of gelling temperature, 10 mL 1% sol of kC and κ -carrageenan-*graft*-PAAm in 1% KCl were allowed to cool gradually

and a thermometer was placed in the sol. The temperature at which the thermometer was fixed to the gel was noted. For melting temperature, the gel was heated on a water bath and one iron ball (~ 1 g of weight) was placed on the surface of the gel. The temperature at which the ball touched the bottom of the tube was noted.

¹³C-NMR studies

¹³C-NMR spectrum (noise-decoupled) was recorded on a Bruker Advance DPX 200 Spectrometer, Switzerland, at 50 MHz. Sample (50 mg/mL) was dissolved in D₂O and spectrum was recorded at 70°C with 9279 accumulations, pulse 5.9 μs , acquisition time 1.015 s, and relaxation delay 6 μs using DMSO ($\sim \delta$ 39.5) as internal standard.

RESULTS AND DISCUSSION

Solubility and swelling

In the solubility measurement we observed that the parent polysaccharide kC was soluble in cold water and gets degraded in acidic solutions while the samples of the copolymer kC-*graft*-PAAm are not soluble in water, acidic and alkaline solutions, hexane, dichloromethane, or CCl₄ at ambient temperature. It was observed that the grafted copolymer swells in water, acid and alkaline solutions, but no swelling was observed in organic solvents. Thus grafting hampers solubility or dispersibility of kC, making the backbone less hydrophilic compared with the parent kC. On the other hand grafting of the hydrophilic PAAm moiety on the kC backbone makes the copolymer capable of undergoing extensive inter and intra hydrogen bonding in water, resulting in improved networking arrangement manifesting the swelling capacity.

The copolymer samples had increased swelling capacity, the highest being with the copolymer having %N 10.56 at pH 12.5 (Table I). This may be attributed to an increase in the diffusion of AAm molecules into the polysaccharide backbones resulting in an increase in swelling capacity; and the higher AAm content enhances the hydrophilicity of the hydrogels. However, the copolymer with 11.05% N showed a decrease in swelling possibly because of the increase in viscosity and hydrodynamic volume of the polymer chain. The

TABLE IV
Elemental Composition of κ -Carrageenan and kC-*graft*-PAAm Copolymers

Elements (%)	κ -Carrageenan	AAm : KPS		
		0.57 : 0.0148	0.87 : 0.022	1.14 : 0.0296
C	35.80 \pm 0.07	37.76 \pm 0.07	38.90 \pm 0.05	41.94 \pm 0.07
H	6.40 \pm 0.074	5.76 \pm 0.074	7.10 \pm 0.02	7.60 \pm 0.023
N	0.21 \pm 0.004	6.35 \pm 0.02	10.56 \pm 0.07	11.05 \pm 0.074

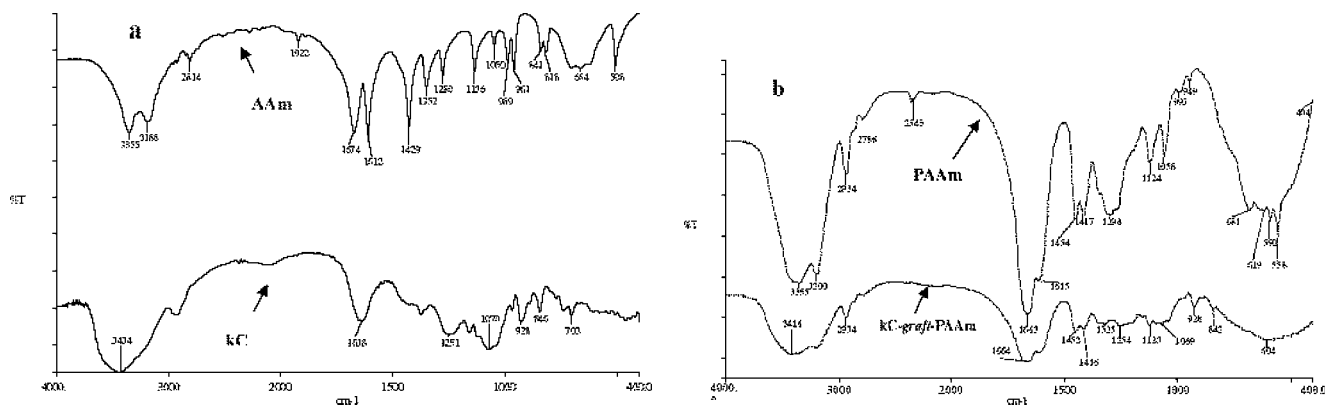


Figure 2 FTIR spectra of (a) AAm and kC, and (b) PAAM and kC-graft-PAAM.

swelling of copolymers decreased in salt solutions compared to that in the alkali solution. This decrease in swelling capacity can be explained on the basis of "charge screening effect" as described by Pourjavadi et al.¹⁵

Physicochemical properties

Physical properties of the grafted copolymer kC-graft-PAAM having different nitrogen contents and those of control kC are given in Table II. It has been observed that apparent viscosity of the copolymer hydrosol increased with increase in %N. The one with %N 11.05

exhibited greatest apparent viscosity (74 cP) at 5% concentration in water at 80°C. The increase in apparent viscosity with the increase in the %N of the products could be explained on the basis of stiffness and the increase in the hydrodynamic volume of the copolymers in the presence of high PAAM or %N.^{15,22} Gel strength of the copolymer hydrogels decreased from 135 g/cm² for 5% hydrogel with %N 6.35 to < 100 g/cm² for 5% hydrogel with %N 11.05. Corresponding decrement in the gelling and melting temperature of the hydrogels were also observed (Table II). It was also observed that all the copolymer samples did not gel in absence of KCl. The gel formation in the presence of KCl indicates that the parent polysaccharide is present in the copolymer network. The gel strength decreased with increasing %N values in the copolymers, and this may be due to the decrease in the quantity of parent polysaccharide which is actually responsible for the gel network formation in presence of KCl. Copolymer samples also showed increase in %N with increasing concentration of AAm in the grafting reaction. A similar observation was reported by Sharma et al.¹⁴

TABLE V
¹³C-NMR Data (in ppm) Observed for Parent Polysaccharide, PAAM, and Copolymer with %N 10.56

Compound	δ (ppm) ^a	Assignment
κ-Carrageenan	61.4 (61.0)	C-6'
	68.7 (69.2)	C-6
	69.4 (69.3)	C-5
	69.8 (69.5)	C-2
	76.1 (76.5)	C-5'
	77.1 (78.0)	C-4
	80.1 (78.9)	C-3
	98.2 (94.9)	C-1
	102.4 (102.2)	C-1'
	PAAM	36.54
42.63		-CH
kC-graft-PAAM (with %N 10.56)	180.18	-CONH ₂
	35.69	-CH ₂ of PAAM
	43.66	-CH of PAAM
	62.34	C-6'
	70.76	C-6
	71.11	C-5
	75.11	C-2
	75.85	C-5'
	77.85	C-4
	79.29	C-3
80.26	C-3' (cf. Ref. 24)	
96.41	C-1	
103.56	C-1'	
180.72	-CONH ₂ of PAAM	

^a Values in parentheses are quoted from Ref. 23.

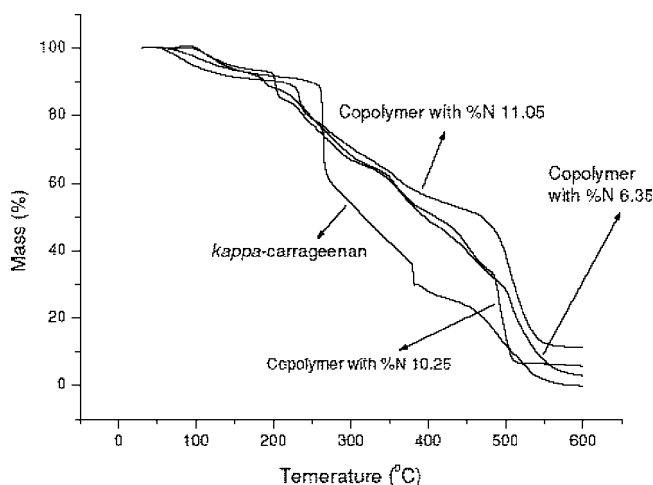


Figure 3 TGA thermograms for kC and different copolymers with %N 6.35, 10.56, and 11.05.

Grafting parameters and effect of monomer concentration

The weights of unreacted AAm monomer that were recovered from the reaction mixture were 0.27, 0.22, and 0.75 g for κ C-*graft*-PAAm having %N = 6.35, 10.56, and 11.05 respectively. The data of *G*%, *E*%, and *C*% are given in Table III. The relative increase in %N and %G of the copolymers was significant when the concentration of AAm increased from 0.57 to 0.87 mol/L. These parameters did not change significantly on further increase in the concentration of AAm from 0.87 to 1.14 mol/L. The general increasing pattern was also observed with %E and %C, albeit in smaller extent, except for a decrease in %C when the concentration of AAm was 1.14 mol/L (Table III). It may be due to the fact that when AAm and KPS are present in higher concentration, there are higher chances of generation of active free radical sites on the κ C backbone, which would give higher yield of grafted product (higher *C*%, *G*%, and *E*% values) as reported in the literature.^{15,23}

In presence of the initiator in the aqueous solution of κ C if the AAm to polysaccharide ratio increased then κ C-*graft*-PAAm could play the role of self emulsifier so as to absorb more monomers (AAm) on the polymer (κ C) surface, which subsequently enhanced the rate of the grafting reaction, thereby sharply increasing *C*%, *G*%, and *E*% values.⁸ It was observed that in the absence of the water-soluble initiator the reaction did not take place at all.

Elemental analysis

The average values of C, H, N percentages in the copolymers and those of κ C are given in Table IV. It was observed that the %N increased with increasing amount of AAm.

FTIR spectrum of the super water absorbent

The FTIR spectra were recorded with the grafted copolymer with %N 10.56, PAAm, AAm, and κ C

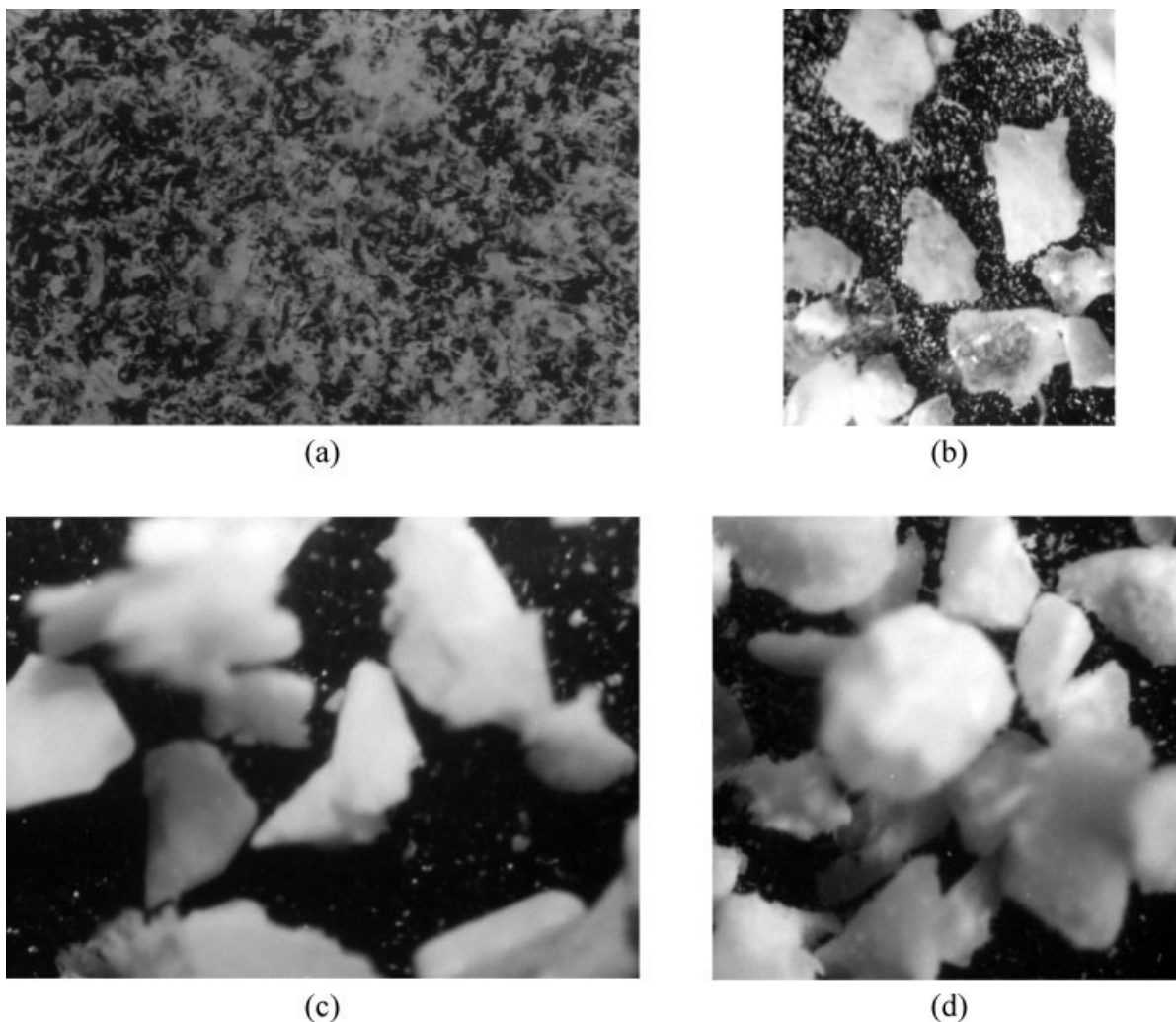


Figure 4 Optical micrographs of the κ C (a), AAm (b), and different copolymer hydrogels with %N 6.35 (c) and %N 10.56 (d).

TABLE VI
Liquid and Solid Weights of Copolymer Adhesive (5% Dispersion of kC-graft-PAAm with %N 11.05) and Standard Adhesive (Fevicol)

Specimens	Liquid and solid weight of adhesives (in pound per thousand square feet of surface area)			
	kC-graft-PAAm (%N 11.05)		Fevicol	
	Liquid weight	Solid weight	Liquid weight	Solid weight
Paper sheets	6.55 ± 0.059	1.82 ± 0.059	7.22 ± 0.069	2.56 ± 0.068
Transparency sheets	4.01 ± 0.045	2.1 ± 0.059	4.2 ± 0.059	1.6 ± 0.059
Wood blocks	16.92 ± 0.059	4.7 ± 0.068	18.6 ± 0.055	4.8 ± 0.055

[Figs. 2(a and b)]. The spectrum of the copolymer showed the presence of PAAm, having an absorption band at 1664 cm^{-1} for (C=O stretching and at 1452 cm^{-1} for C—N stretching. Presence of the C-4 sulfate band at 842 cm^{-1} in IR of kC,²³ as well as a less intense band at 3416 cm^{-1} , compared to parent kC, appeared for OH group in the copolymer, indicating that grafting took place on OH group, rather than on the sulfate moiety.

¹³C-NMR studies

The ¹³C-NMR resonances of kC, PAAm, and κ-carrageenan-graft-PAAm and their probable assignments are given in Table V. The assignments of the parent polysaccharide (kC) that was used in this study, was done by comparing the observed δ-values (61.4, 68.7, 69.4, 69.8, 76.1, 77.1, 80.1, 98.2, and 102.4 ppm) reported in the literature.^{24,25} The assignments of carbons of the PAAm moiety in the copolymer kC-graft-PAAm were done by comparing the δ-values obtained from the PAAm spectrum (Table V). The δ-values of PAAm carbons in the copolymer (35.69, 43.66, and 180.72 ppm), however, remained marginally affected compared to those of pure PAAm (36.54, 42.63, and 180.18 ppm). Presence of the 3,6-anhydrogalactopyranose as well as galactopyranose moieties of the repeating unit of parent kC in the copolymer was indicated by the corresponding ¹³C-NMR resonances. A small downfield shift of all the backbone carbons of the polysaccharide in the copolymer in comparison to those of the parent kC was observed, except for C-1 carbon showing upfield shift of 1.81 ppm in the copolymer (Table V). This may have been due to the introduction of the PAAm moiety onto the polysaccharide, which is expected.

Thermal analysis

Thermogravimetric analysis (TGA) of kC and the grafted copolymers (kC-graft-PAAm) are shown in Figure 3. The TGA of kC shows mass loss in stages. The first stage ranges between 40°C and 105°C corresponding to 7–9% mass loss. This is presumably due to the loss of adsorbed and bound water molecules. The sec-

ond stage of the weight loss starts at 190°C and that continued up to 260°C during which there were 20–22% of mass loss followed by up to 455°C showing 100% mass loss. The thermograms of the grafted products indicate that they are more thermally stable than kC, and their thermal stability to be in the order (%N values) 11.05 > 10.56 > 6.35 and are different from that of kC. It was observed that the mass losses in all the copolymers also took place in stages.

X-ray diffraction analysis

The X-ray diffraction experiments of kC, AAm, and graft copolymers of kC-graft-PAAm were carried out. The diffraction patterns of kC and kC-graft-PAAm are not significantly different. The samples of pure kC showed no clear sharp or narrow peaks; the profile appeared to be a signature of amorphous compound showing two less intense and an intense (at $2\theta = 28.53^\circ$) noisy bumps in addition to a feeble bump $\sim 2\theta = 8^\circ$. In the copolymers with %N 6.35, 10.56, and 11.05, the intense bump appeared at slightly higher 2θ values e.g., 29.57° , 30.52° , and 30.99° respectively, the bump below $2\theta = 10^\circ$, however, did not appear in the copolymers. In the copolymer with %N 6.35 four additional peaks appeared at 2θ values of 9.07° , 22.09° , 35.79° and 43.31° . In the copolymers with %N 10.56 and 11.05 two

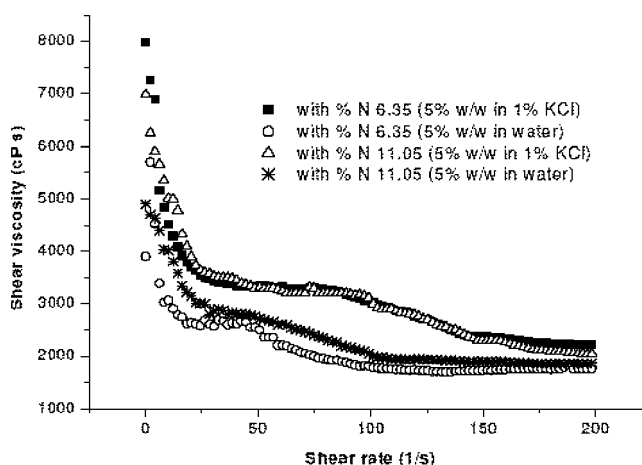


Figure 5 Dynamic viscosity of the copolymers with %N 6.35 and %N 11.05 in absence and presence of KCl.

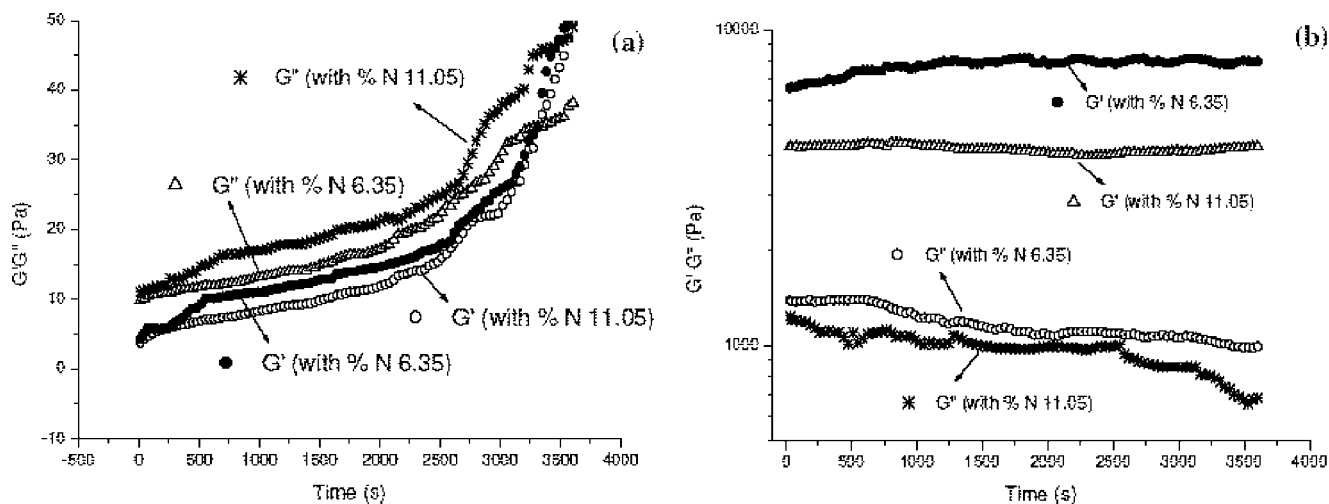


Figure 6 Storage and loss moduli versus time for copolymers with %N 6.35 and %N 11.05 in absence (a) and presence of KCl (b).

such additional peaks appeared at $\sim 2\theta$ values of 16.23° , 43.42° . The X-ray diffraction pattern of AAm showed its crystalline nature having sharp peaks at $\sim 2\theta$ values of 11.99° , 24.08° , and 28.58° . It can be concluded that considerable modification of the polysaccharide has taken place, leading to a change in molecular association in the copolymers when compared with kC and AAm. Xiao et al. reported that the X-ray diffraction pattern of PAAm is amorphous, having a very weak broad shaped one,²⁶ which is apparently masked by the strong bumps of that of kC in the copolymers.

Morphology

Optical micrographs of the copolymer were taken with $70\times$ magnifications and compared with kC [Fig. 4(a–d)]. These images revealed that the morphology of kC got modified significantly in the copolymers. The optical micrograph of the parent polymer kC appeared fibrous in nature, while those of grafted copolymers appeared to have definite shapes akin to rectangular and/or spheroid geometries. It was also observed that the shapes appeared more spheroidal in the copolymer with higher %N. This reaffirms the enhancement of organized molecular arrangements in the copolymer as indicated by the X-ray diffractogram discussed above.

Adhesive property

A comparison of the liquid and solid weights of the copolymer adhesive (kC-*graft*-PAAm with %N 11.05) and Fevicol are shown in Table VI. It appears that the efficacy of the copolymer adhesive is comparable with that of the standard adhesive in about same usage level (cf. solid weight of the adhesives).

Rheological properties

Variations of dynamic viscosity with shear rate for sol and gel samples prepared from the copolymer with %N 6.35 and 11.05 (5% w/w sols or gels) are shown in Figure 5. It was observed that the sol and gel samples showed gel-thinning behavior throughout the shear rate range studied. The result obtained in this study was similar to that reported by Harry-O'Kuru et al.²⁷ The stability of modulus during storage at 25°C was investigated and is depicted in Figures 6(a) and 6(b). The storage modulus values of the 5% sol (without KCl) and gel (in 1% KCl) samples were obtained from copolymers having %N 6.35 and 11.05. It was observed that the G'' values for gel samples increased with increment of time, indicating absence of syneresis in the gel samples at 5% concentration as described by Ross-Murphy.²⁸ This observation shows the stability of the gel samples under stress for a long duration. The G' values for 5% gel of the copolymer with %N 6.35 was higher than that of the one with %N 11.05. Moreover, in case of 5% hydrogel sols (without KCl), the modulus exhibited a reverse trend i.e., $G'' > G'$ value and after storage for long duration, values of G' increased and G'' decreased slightly.

CONCLUSIONS

A rapid method of synthesizing copolymers of kC and AAm using microwave irradiations has been described. The maximum water absorbency (22 g/g) was achieved in the copolymer with %N 10.56, under the optimized reaction conditions with specific w/w ratios of kC:AAm:KPS, while highest adhesive property was observed with the copolymer having %N 11.05. The adhesive property was evaluated with wood blocks, paper and transparency sheets, and was

found to be comparable with an adhesive (Fevicol) available in the market. That the copolymer was formed with kC and PAAm was assessed from the physicochemical, thermal, and rheological properties and FTIR and ^{13}C -NMR spectra. The changes in the molecular association in the copolymers were observed from the X-ray diffractograms and optical micrographs.

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