# Hydrogel-Forming Agar-*graft*-PVP and κ-Carrageenan-*graft*-PVP Blends: Rapid Synthesis and Characterization

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**ABSTRACT:** Grafting of agar and κ-carrageenan with polyvinylpyrrolidone (PVP, average molecular weight 10,000 D) in an aqueous medium at a pH of about 7 produced agar-*graft*-PVP and κ-carrageenan-*graft*-PVP blends capable of forming hydrogels. The reaction was carried out with microwave irradiation in the presence of a water-soluble initiator, potassium persulfate. Optimum microwave irradiation conditions for obtaining hydrogels of the grafted products were achieved. The structural characteristics and thermal stability of the grafted blends were studied by Fourier transform infrared, $^{13}$C-NMR, and thermogravimetric analyses. Appearance of new IR bands at 1661, 1465, and 1426 cm$^{-1}$ in the grafted products indicated the insertion of PVP into the polysaccharide structure. Powder X-ray diffraction studies revealed the enhanced crystallinity in the products compared to in the control polysaccharides as well as PVP. Agar and κ-carrageenan were grafted to a considerable degree, with 62.5 E % and 125 G % for agar-*graft*-PVP and 65.5 E % and 131 G % for κ-carrageenan-*graft*-PVP. Optical micrographs of the grafted blends indicated considerable changes in the morphology of the agar and the κ-carrageenan, substantiating the X-ray diffraction data. A plausible mechanism for the crosslinking of PVP to agar and κ-carrageenan is proposed. These hydrogels exhibited enhanced water-holding capacity despite weaker gel strength than that in the respective control polysaccharides.  J Appl Polym Sci 102: 3654–3663, 2006

**Key words:** hydrogels; blends; morphology; polysaccharides; modification

## INTRODUCTION

Grafting is one of the popular ways of modifying polysaccharides. Grafting reaction in cellulose has been found to be of considerable interest. This method allows the attachment of chemically different side chains to a polymer molecule. The reaction mechanism is principally the same as that of synthesis of polymers.[1–2]

In recent times microwave irradiation techniques have occupied an important position in grafting-type modification reactions because of their simplicity and rapidity. Hydrolyses of starch and plant seed gums have been achieved readily with microwave irradiation under very mild reaction conditions.[3–5] Synthesis of alkyl glycosides and graft copolymerization of acrylic acid with starch has been efficiently carried out with microwave irradiation.[6,7] Microwave-promoted methylation of plant polysaccharides was reported by Singh and coworkers.[8] Recently, natural polymers have been receiving a great deal of attention because of their biodegradability and availability at low cost. Several published studies investigated modification of natural polymers such as starch, chitosan cellulose, gelatin, and dextrin by blending, crosslinking with synthetic polymers to form well-characterized hydrogels.[9–14] It was observed that these natural polymers could enhance the viscoelastic properties of synthetic polymers.[15] A wide range of biomedical, agricultural, and industrial applications of hydrogels have been explored, including wound dressing, controlled-release systems, separation membranes, and biomedical uses.[16–22] Controlled drug delivery from injectable biodegradable triblock copolymer was reported by Young et al.[23] Hydrogel formation by photo-induced crosslinking of poly(isopropyl acrylamide) copolymers also was reported.[24]

Agar (**1**) and κ-carrageenan (**2**) are seaweed polysaccharides that chemically consist of alternating 3-*O*-linked β-D-galactopyranose and 4-*O*-linked 3,6-anhydro-α-L-galactopyranose and 3-*O*-linked β-D-galactopyranose and 4-*O*-linked 3,6-anhydro-α-D-galactopyranose, respectively.[25] Abad et al. studied the formation and properties of radiation-synthesized PVP-kappa carrageenan hydrogel blends, using γ-radiation for the preparation of the hydrogel blends.[26] Their reported results proved the presence of a network structure in which kappa carrageenan was physically entangled in the crosslinked PVP (SIPN).

As part of an ongoing program of modifying seaweed polysaccharides for newer applications,[27,28] we

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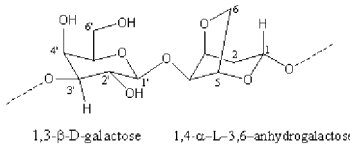



**Structure 1** Repeating dimeric unit of agar.

report here the synthesis of agar-*graft*-PVP and κ-carrageenan-*graft*-PVP blends by a novel method, that is, microwave irradiation in the presence of a water-soluble redox initiator, potassium persulfate, which enabled the formation of the desired products in a shorter duration (120 s) and resulted in grafted products that were more crystalline than the control polysaccharides. The microwave irradiation conditions were also optimized in order to produce grafted products capable of forming hydrogels in water. The physicochemical and rheological properties of the hydrogels were studied and were compared with control agar and κ-carrageenan. Formation of the grafted products was confirmed by IR, X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and thermal studies. Because such hydrogels are not as strong and have more spreadability (i.e., more gel thinning) and more water-holding capability, they are potentially useful in moisturizer formulations and active carriers of drugs. The use of blended PVP with agar in hydrogel dressings has also been reported.[29]

## EXPERIMENTAL

### Materials

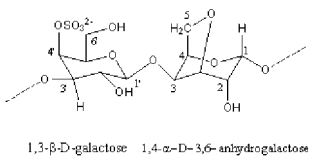
The agar and κ-carrageenan used in this experiment were Oxoid Agar No. 1 (Oxoid, Basingstoke, Hampshire, England, UK; Lot/Ch.-B: 810501-2) and carrageenan kappa Type III; (Sigma, C-1263), respectively. The analytical-grade potassium persulfate and polyvinylpyrrolidone ($M_r$ 10,000 Da) used in this work were procured from Sigma-Aldrich (Mumbai, India).

### Apparatus

An LG kitchen microwave oven with a temperature range of 40°C–100°C was used (magnetrons were set at a frequency of 2450 MHz).

### Grafting and treatment of blend

Grafting was carried out in 100-mL narrow-mouthed conical flasks. One gram of polysaccharide (agar or κ-carrageenan) was first dissolved in 100 mL of distilled water, followed by the addition of 0.01 g (0.00037 mol/L) of potassium persulfate. Then 2.0 g [0.002 mol/L] of PVP was added to the reaction mixture, which was microwave-irradiated for 120 s with constant stirring. The reaction mixture turned yellowish; it was cooled and precipitated in isopropyl alcohol [1 : 2.25 (v/v)], followed by centrifugation at 8000 rpm for 3 min. The yellowish precipitate thus obtained was vacuum-dried. The grafted blends were found to form gel in water. Grafting parameters, such as conversion percentage, grafting efficiency, and grafting percentage, were determined as described by Bajpai et al.[30]




**Structure 2** Repeating dimeric unit of κ-carrageenan.

### Characterization of agar-*graft*-PVP and κ-carrageenan-*graft*-PVP blends

Agar-*graft*-PVP and κ-carrageenan-*graft*-PVP were characterized by Fourier transform infrared (FTIR) analysis on a Perkin-Elmer Spectrum GX FTIR system (USA) by taking 10.0 mg of sample in 600 mg of KBr. All spectra are an average of two counts with 10 scans each and a resolution of 5 $cm^{-1}$. The $^{13}$C-NMR spectrum (noise-decoupled) was recorded on a Bruker Advance DPX 200 Spectrometer (Switzerland) at 50 MHz. A sample (50 mg/mL) was dissolved in $D_2O$, and the spectrum was recorded at 70°C with 9279 accumulations, a pulse of 5.9 μs, an acquisition time of 1.245 s, and a relaxation delay of 6 μs using DMSO (δ39.5) as an internal standard.

Thermogravimetric analysis (TGA) of agar (4.34 mg) and its grafted blend (4.41 mg) and of κ-carrageenan (4.50 mg) and its grafted blend (4.81 mg) was carried out on a Mettler Toledo TGA system (Switzerland), using a temperature program going from 30°C to 600°C at a heating rate of 10°C/min in an air atmosphere. Powder X-ray diffractions were recorded on a Philips X'pert MPD X-ray powder diffractometer using $2\theta = 5°–60°$. For optical rotation measurements, polysaccharides and their grafted blends (0.025 g) were dissolved in distilled water (100 mL), and specific rotation was measured at 589 nm at 45°C on a Rudolph DigiPol-781 Polarimeter (Rudolph Instruments Inc., Denville, NJ). Optical micrographs were recorded on an Olympus optical microscope model SZH 10 (Japan) at 70× magnification.

Dynamic rheological measurements were done on a rheometer (RS1, HAAKE Instruments, Karlsruhe, Germany). The measuring geometry selected for measurements in solutions was a cone/plate (60 mm diameter, 1° rad angle), putting 1 mL of sol on the peltier of the rheometer for measurements at 45°C. Viscosity at varying shear rates was studied at 45°C. Oscillation was measured in a controlled deformation mode with 0.05% strain and plate/plate geometry (35 mm diameter) at 25°C. Temperature was maintained using a

**TABLE I**
**Physical Properties of Agar-*graft*-PVP and κ-Carrageenan-*graft*-PVP Hydrogels**

| Properties | Apparent viscosity (cP) at 80°C[a] | pH (80°C) | Gel strength ($g/cm^2$) at 20°C[b] | Gelling $T$ (°C) (3.0% w/v) | Melting $T$ (°C) (3.0% w/v) |
|---|---|---|---|---|---|
| Control agar sol/gel (3.0 % w/v) | 57 | 6.9 | 1440 | 40 | 84 |
| Agar-*graft*-PVP sol/gel (3.0% w/v) | 25 | 7.2 | 250 | 37 | 74 |
| Control κ-carrageenan sol/gel (3.0% w/v in 1% KCl) | 69 | 7.0 | 890 | 37 | 80 |
| κ-Carrageenan-*graft*-PVP sol/gel (3.0% w/v in 1% KCl) | 47 | 7.4 | 410 | 35 | 75 |

[a] Viscosity was measured in a 1.5% (w/v) concentration at 80°C.
[b] Gel strength was measured in a 1.5% (w/v) gel at 20°C.

DC50 water circulator. For measurements at higher temperature, the outer surfaces of the samples were covered with silicon oil to avoid loss from evaporation. The 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 not an abrupt decrease in $G'$ values.[31]

Intrinsic viscosity [η] was determined at 32°C using an Ostwald viscometer with a flow time of 2.11 min for 1*M* NaCl, for which sols of the samples were prepared in 1*M* NaCl at a concentration of 0.02%–0.14% (w/v).

The pH was measured with a model 535 pH meter from Systronics Scientific Instruments (India). Gelling and melting temperatures of the agar gel in the mixtures in the presence of various fatty acids were measured as described by Craigie and Leigh.[32] Gel strength ($g/cm^2$) was measured using a Nikkansui-type gel tester (Kiya Seisakusho Ltd., Tokyo, Japan). Measurements were performed on a 1.5% (w/v) agar solution in water and 1% κ-carrageenan in 1% KCl (previously cured overnight at 10°C), using a solid cylindrical plunger 1.127 cm in diameter.[33] Apparent viscosity was measured at a temperature of 80°C using a Brookfield Viscometer (Synchrolectric Viscometer, Stoughton, MA) with spindle no. 1 at 60 rpm.

### Syneresis index

The amount of water exuded from the gel samples after standing for a certain period of time was determined and quantified using a modified method as described by Fiszman and Duran.[34] Approximately 10 g of hot 1.5% (w/w) polysaccharide and polysaccharide-*g*-PVP blends was poured into test tubes (21 mm in diameter) and allowed to gel at room temperature (32°C–33°C), and then kept at 5°C for 24 h. The initial weight of the gel was measured before being placed on dry Whatman (No. 1) filter paper. The weight of the gel was again measured 2 h after placement on the filter paper, and loss of water from the gel was then calculated. The syneresis index values of the gel samples were taken as the difference between the initial weight of the gel and its final weight after 2 h. This value indicates the water-holding capacity of the gels. The extent of syneresis was estimated by the amount of water, $\Delta w$, separated from the gel phase. The degree of syneresis was estimated by $\Delta w/w_o$, where $w_o$ is the initial weight of the gel. All measurements were done in triplicates.

### Water absorption

The water-holding capacity of the polysaccharides and their grafted blends was measured by soaking the samples in water and measuring the weight gain in regular intervals as described by Park et al.[35]

## RESULTS AND DISCUSSION

### Physicochemical properties

The physical properties of the polysaccharide-*g*-PVP blend sol and gel and a comparison with those of the control agar sol and gel are given in Table I. It was observed that the apparent viscosity of the 3% (w/v) agar-*graft*-PVP sol had decreased to 25 cP from the 57 cP exhibited by the 3% agar sol. Similarly, the κ-carrageenan-*graft*-PVP sol in 1% KCl showed an apparent viscosity of 47 cP as against the 69 cP of the control

**TABLE II**
**Degree of Syneresis of Agar Gel and Agar-*graft*-PVP Hydrogel**

| Sample | Initial weight, $w_0$ (g) | Final weight (g) | Syneresis ($\Delta w$) | Degree of syneresis ($\Delta w/w_0$) |
|---|---|---|---|---|
| Control agar | 10.74 | 9.41 | 1.33 | 0.1230 |
| Agar-*graft*-PVP hydrogel | 10.26 | 9.16 | 1.10 | 0.1072 |
| Control κ-carrageenan | 10.32 | 9.09 | 1.23 | 0.119 |
| κ-Carrageenan-*graft*-PVP hydrogel | 11.8 | 10.6 | 1.20 | 0.1016 |

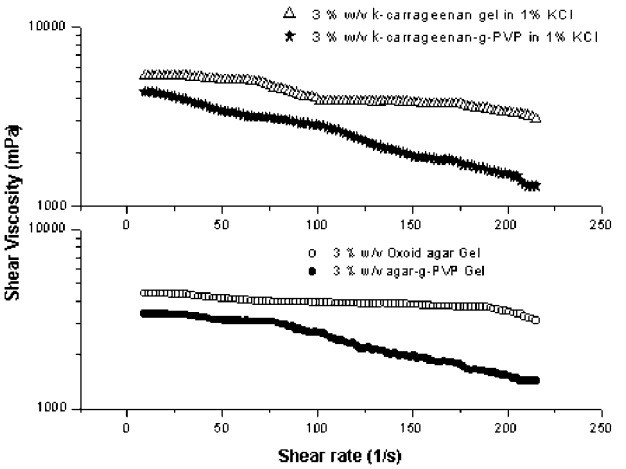



**Figure 1** Gel thinning behavior of 3% agar-*g*-PVP and κ-carrageenan-*graft*-PVP hydrogels versus the corresponding 3% control polysaccharides.

κ-carrageenan sol in 1% KCl. The gel strength of the grafted blend hydrogels decreased to 250 g/cm$^2$ for the agar-*graft*-PVP and to 410 g/cm$^2$ for the κ-carrageenan-*graft*-PVP in 1% KCl. Similar reductions in the gelling and melting temperatures of the hydrogels were also observed. All these properties indicated that the agar and κ-carrageenan-*graft*-PVP hydrogels had become weaker relative to the corresponding control polysaccharide gels.

### Grafting parameters under optimized conditions

The yield of agar-*graft*-PVP was 2.25 g; total conversion percentage, C% [(total weight of polymerized PVP/weight of PVP charged) × 100 = 2.25 − ½], was 62.5%; grafting efficiency, E% [(weight of PVP grafted/total weight of PVP) × 100 = 2.25 − ½], was 62.5%; and grafting percentage, G% [(weight of PVP grafted/weight of polysaccharide) = 2.25 − 1/1], was 125%.

κ-Carrageenan-*graft*-PVP yield was 2.31 g, and C%, E%, and G% were 65.5%, 65.5%, and 131%, respectively.

### Optimization of parameters for polysaccharide-*g*-PVP hydrogel formation

All the parameters—polysaccharide-to-PVP ratio, duration of microwave irradiation, concentration of initiator, and temperature of reaction—were optimized to achieve optimum G%, E%, and C% values, which formed hydrogels of the grafted blends in water. On varying the initiator concentration from 0.001% ($3 \times 10^{-5}$ mol/L) to 0.15% (0.0055 mol/L), it was observed that a 0.06% concentration of KPS produced a maximum yield at the grafting parameter values, but no hydrogel was formed. To obtain a product that formed hydrogel, the following optimized combination of parameters was employed: polysaccharide–PVP ratio, 1:2; duration of microwave irradiation, 120 s; temperature of reaction, 95°C; and KPS concentration, 0.01% (w/v) (0.00037 mol/L).

### Syneresis

The extent of syneresis, as determined by measuring the degree of syneresis of the polysaccharide gels and the polysaccharide-*g*-PVP blends, is given in Table II. It was observed that polysaccharide-*g*-PVP had less syneresis at 3% (w/v) concentration, indicating the grafted blends had greater water-holding capacity compared with that of the control polysaccharide. For carrageenan-*graft*-PVP the gel was prepared in 1% KCl.

### Water absorption experiment

To measure the water-holding capacity of the grafted products, dry samples (2 g) were soaked in water, and the weight gained by the samples was monitored and

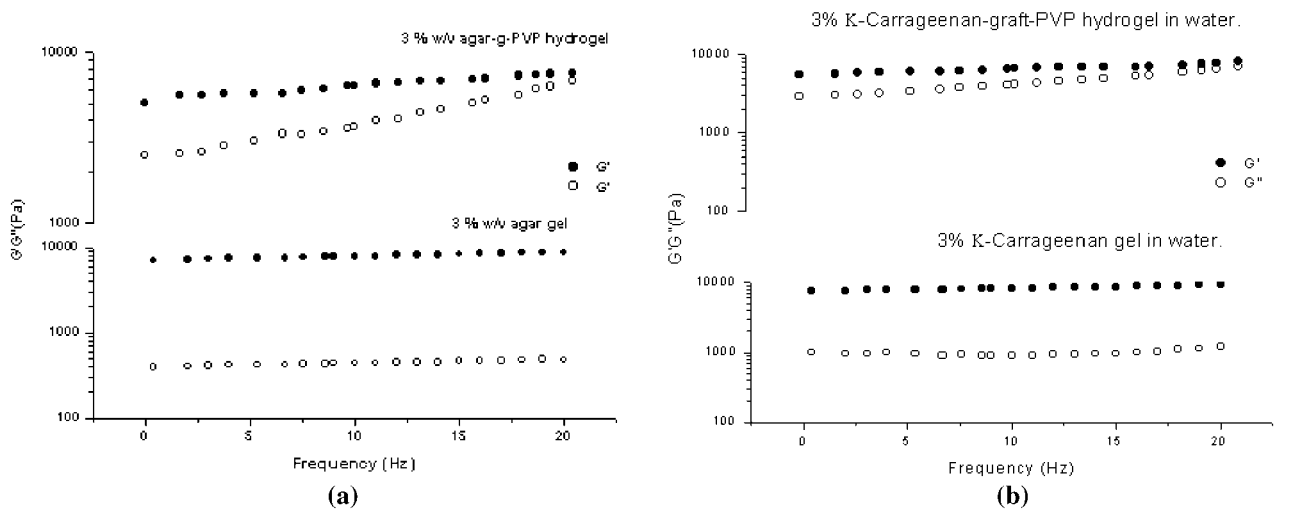



**Figure 2** Viscoelastic behavior of (a) agar and agar-*graft*-PVP and (b) κ-carrageenan and κ-carrageenan-*graft*-PVP.

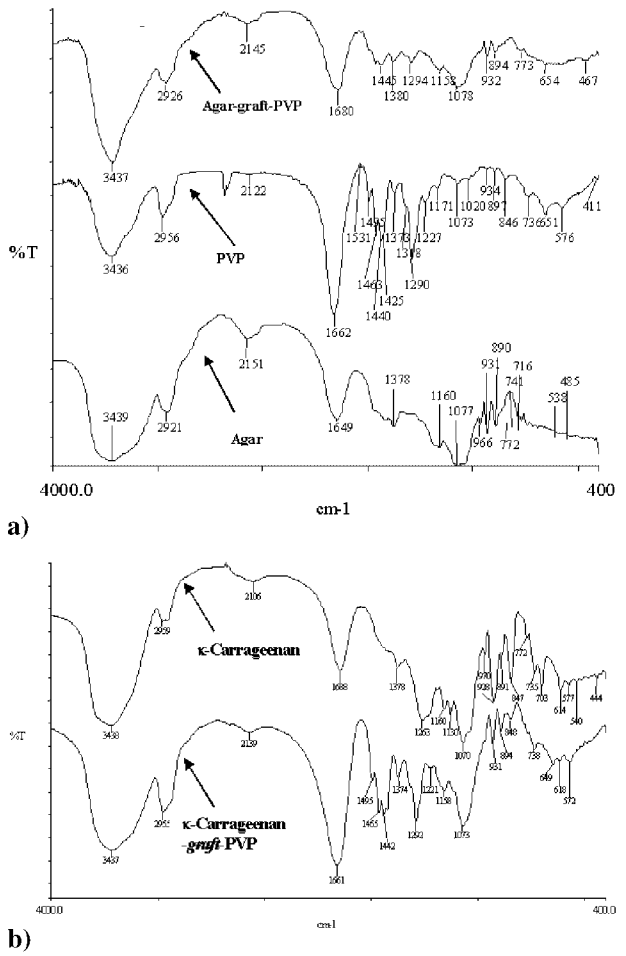



**Figure 3** FTIR spectra of (a) agar, agar-*graft*-PVP, and PVP and (b) κ-carrageenan and κ-carrageenan-*graft*-PVP grafted blend.

recorded at regular intervals (0.5–10 min). It was observed that the agar-*graft*-PVP had a greater water-holding capacity (8.5 g/g) than did the control agar (5 g/g); similarly, the κ-carrageenan-*graft*-PVP had a greater water-holding capacity (9.6 g/g) than the control κ-carrageenan (4.1 g/g).

## Dynamic viscous behavior

### Flow behavior

Shear viscosity was measured using the applied shear rate. It was observed that the gel-thinning property of the polysaccharide-*g*-PVP was greater than that of the control polysaccharide gels. This indicated that PVP had induced more gel-thinning behavior in both the agar and carrageenan gels. The corresponding mechanical spectra are depicted in Figure 1.

### Dynamic viscoelasticity

The frequency dependence of G′ and G″ for the polysaccharides and polysaccharide-*graft*-PVP blends are shown in Figure 2(a,b). Both moduli decreased for the hydrogels of the agar-*graft*-PVP blends and became more frequency dependent, that is, they tended to be more liquidlike under an applied strain of 0.01%.[36]

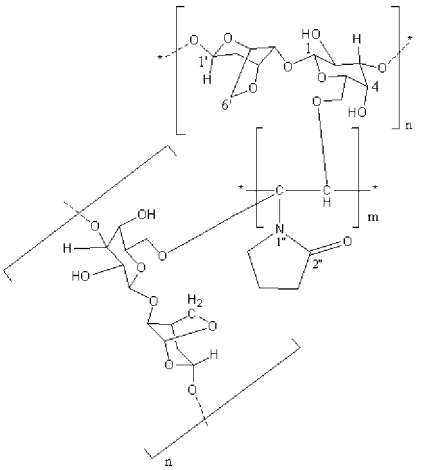
### IR spectral studies

Sample spectra of agar, PVP, and agar-*graft*-PVP are shown in Figure 3(a), and those of κ-carrageenan and κ-carrageenan-*graft*-PVP are shown in Figure 3(b). The major bands of agar and κ-carrageenan and the corresponding grafted products are given in Table III. The FTIR spectra of the agar-*graft*-PVP and κ-carrageenan-*graft*-PVP showed a distinct carbonyl band at around 1700 $cm^{-1}$. Figure 3(a,b) clearly shows that the grafted products contained the functional groups of PVP, agar, and κ-carrageenan. The carbonyl group from PVP and all the major functional groups of agar and κ-carrageenan were present in these grafted products. Irradiation of agar and κ-carrageenan resulted in the formation of radicals on the carrageenan chain, and these sites of radical formation become the points of initiation for side chains with PVP. Sites where free radicals form in PVP have already been studied using pulse radiolysis.[37]

Characteristic IR bands at 773, 894, and 932 because of 3,6-anydro-β-galactose skeletal bending in agar and carrageenan,[38,39] which were observed for the grafted blends, indicated the backbone configuration remained unaltered during the grafting reaction. The area under the —OH band in the agar was 46,497.45% of transmittance (in $cm^{-1}$); on the other hand, the area under the —OH band in the agar-*graft*-PVP was 30,121.22% of transmittance (in $cm^{-1}$).[40] Similarly, the

**TABLE III**
**FTIR Band Positions for κ-Carrageenan**

| Structure | Absorption ($cm^{-1}$) | Functional group |
|---|---|---|
| **1** | 1646 | Polymer-bound water |
| | 1378 | Methylene group |
| | 1263 | Covalent sulfate |
| | 1070 | Glycosidic linkage |
| | 928 | 3,6-Anhydro-D-galactose |
| **2** | 847 | D-Galactose-4-sulfate |
| | 1655 | Polymer-bound water |
| | 1378 | Methylene group |
| | 1043 | Glycosidic linkage |
| | 930 | 3,6-Anhydro-D-galactose |
| **3** | 1680 | Carbonyl group |
| | 1374 | Methylene group |
| | 1158 | —C—O—C— group |
| | 1073 | Glycosidic linkage |
| | 931 | 3,6-Anhydro-D-galactose |
| **4** | 1688 | Carbonyl group |
| | 1373 | Methylene group |
| | 1293 | —C—O—C— group |
| | 1067 | Glycosidic linkage |
| | 928 | 3,6-Anhydro-D-galactose |
| | 844 | D-Galactose-4-sulfate |

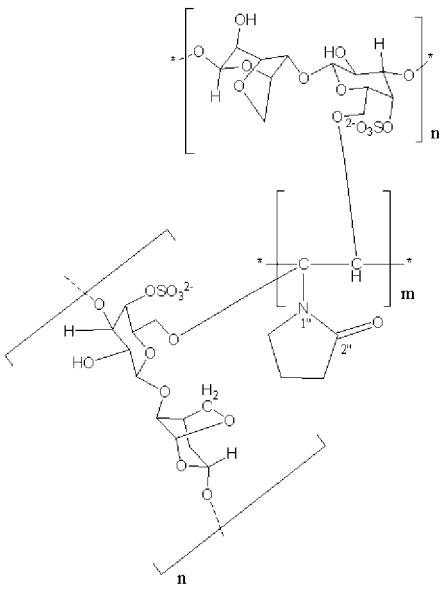


**Structure 3** Agar-*graft*-PVP blend.

observed area under the —OH band was 33,440.91% of transmittance (in $cm^{-1}$) in the carrageenan and 26,744.13% of transmittance (in $cm^{-1}$) in the carrageenan-*graft*-PVP. The relatively lower transmittance intensity values of the —OH stretching frequency in the grafted blends in comparison to those of the control polysaccharides suggests the grafting might have occurred with the —OH groups of the polysaccharides.[40] The presence of a band at 844 $cm^{-1}$ in the κ-carrageenan-*graft*-PVP, which was a result of a C-4 sulfate, indicates the grafting reaction might have occurred with the —OH of the κ-carrageenan.

## $^{13}$C-NMR studies

The $^{13}$C-NMR resonances of (**1**) control agar, (**2**) κ-carrageenan, (**3**) agar-*graft*-PVP, and (**4**) κ-carrageenan-*graft*-PVP and their probable assignments are given in



**Structure 4** κ-Carrageenan-*graft*-PVP.

**TABLE IV**
**$^{13}$C-NMR Data for Control Agar (1) and κ-Carrageenan (2)**

| Compound | δ (ppm)[a] | Assignment |
|---|---|---|
| **1** | 69.8 (69.1) | C-6 |
| | 61.4 (61.1) | C-6′ |
| | 69.4 (69.9) | C-2′ |
| | 75.3 (75.3) | C-5 |
| | 75.6 (75.0) | C-5′ |
| | 68.7 (68.4) | C-4′ |
| | 77.3 (77.0) | C-4 |
| | 80.1 (79.8) | C-3 |
| | 82.2 (81.9) | C-3′ |
| | 98.2 (97.9) | C-1 |
| | 102.4 (102.1) | C-1′ |
| | 112.1 | Not assigned |
| **2** | 98.2 (94.9) | C-1 |
| | 102.4 (102.2) | C-1′ |
| | 77.1 (78.0) | C-4 |
| | 80.1 (78.9) | C-3 |
| | 76.1 (76.5) | C-5′ |
| | 69.4 (69.3) | C-5 |
| | 68.7 (69.2) | C-6 |
| | 61.4 (61.0) | C-6′ |
| | 69.8 (69.5) | C-2 |

[a] Values in parentheses were reported by Usov[41] for agarose and κ-carrageenan.

**TABLE V**
**$^{13}$C-NMR Data for Agar-*graft*-PVP (3) and κ-Carrageenan-*graft*-PVP (4)**

| Compound | δ (ppm)[a,b] | Assignment |
|---|---|---|
| **3** | 179.1 (172.6) | C-2″ of PVP moiety |
| | 32.4 (36.8) | C-3″ of PVP moiety |
| | 18.6 (16.6) | C-4″ of PVP moiety |
| | 140.6 | Not assigned |
| | 102.6 (102.4) | C-1′ |
| | 98.8 (98.2) | C-1 |
| | 80.8 (80.1) | C-3 |
| | 76.3 (75.6) | C-5 |
| | 70.4 (69.4) | C-2′ |
| | 69.3 (69.8) | C-6 |
| | 61.9 (61.4) | C-6′ |
| | 77.6 (77.0) | C-4 |
| **4** | 177.9 (172.6) | C-2″ of PVP moiety |
| | 32.3 (36.8) | C-3″ of PVP moiety |
| | 18.7 (16.6) | C-4″ of PVP moiety |
| | 140.5 | Not assigned |
| | 103.2 (102.4) | C-1′ |
| | 98.6 (98.2) | C-1 |
| | 82.9 (80.1) | C-3 |
| | 80.4 (80.6) | C-5 |
| | 77.5 (77.1) | C-4 |
| | 75.9 (76.1) | C-5′ |
| | 70.4 (69.8) | C-2 |
| | 62.2 (61.4) | C-6′ |

[a] δ Values in parentheses are those estimated for the simulated α-methylpropyl pyrrolidone obtained by using ChemDraw Ultra Version 7.0 software (CambridgeSoft Corporation, Cambridge, MA).

[b] δ Values in parentheses are those of the control polysaccharides used in the study (see Table III).

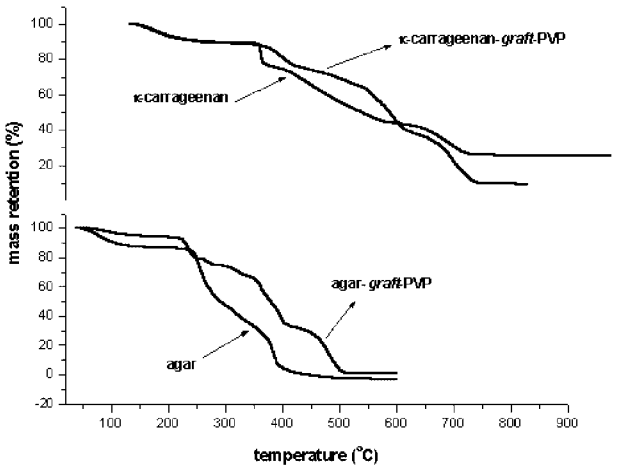



**Figure 4** TGA profiles of agar, κ-carrageenan, and agar-*graft*-PVP and κ-carrageenan-*graft*-PVP blends.

Tables IV and V. The probable assignments of the control polysaccharides that is, the agar and carrageenan used in this study, were made by comparing the observed δ values reported in the literature.[41] The assignments of the PVP moiety in **3** and **4** were done by comparing the estimated δ values obtained from the simulated structure of α-methylpropyl pyrrolidone [δ172.6 (C-2′), 36.8 (C-3′), 16.6 (C-4′), 37.8 (C-5′), 48.8 (α-C), 29.2 (β-C)] using ChemDraw Ultra Version 7.0 software (CambridgeSoft Corporation, Cambridge, MA). The presence of the $^{13}$C-NMR resonances of the 3,6-anhydrogalactose moiety in both the agar-*graft*-PVP and the κ-carrageenan-*graft*-PVP indicated the backbone of the polysaccharides was not degraded during the reaction.

## Thermal analysis (TGA)

Thermogravimetric analysis showed the process of mass loss occurred in three steps for the agar-*graft*-PVP but in only two steps for the agar. Mass loss of agar was approximately 15%–30% at temperatures in the range of 208°C–259.2°C and 68%–100% at temperatures in the range of 354.6°C–422.0°C. Mass loss of the grafted blend was 7%–21% at temperatures in the range of 193.8°C–274.2°C, 53%–70% at temperatures in the range of 391.7°C–436.9°C, and 92%–100% at temperatures in the range of 490.6–533.0°C. Mass loss of κ-carrageenan occurred in a three-step process. During the first stage, at temperatures from 75°C to 89°C, mass loss was 8%–10%; in the second stage, at temperatures from 208°C to 231°C, there was loss of another 10%–25% of mass; and in the final stage, observed in the temperature range of 448°C–558°C, mass loss was approximately 50%–75%. κ-Carrageenan-*graft*-PVP also had three distinct stages of mass loss: about 20% mass loss at 250°C, followed by 60%–100% mass loss in the temperature range of 420°C–500°C. In addition, the different crossover temperatures of the thermograms of the agar- and carrageenan-grafted blends with those of their respective polysaccharides indicated that grafting of PVP affected the thermal behavior of the polysaccharides in various ways (Fig. 4). TGA of physical mixtures of agar and carrageenan with PVP in a 1 : 2 ratio showed that for the physical mixture of agar and PVP there was only one step of mass loss, 60%–80% mass loss occurring in the temperature range of 391°C–479°C, but that for the physical mixture of κ-carrageenan and PVP, there were two steps of mass loss, 10%–20% mass loss in the temperature range of 175°C–290°C and 50%–60% mass loss in the temperature range of 565°C–725°C.

## X-ray diffraction analysis

The X-ray diffraction profiles of the agar, PVP, and agar-*graft*-PVP blends and of the κ-carrageenan

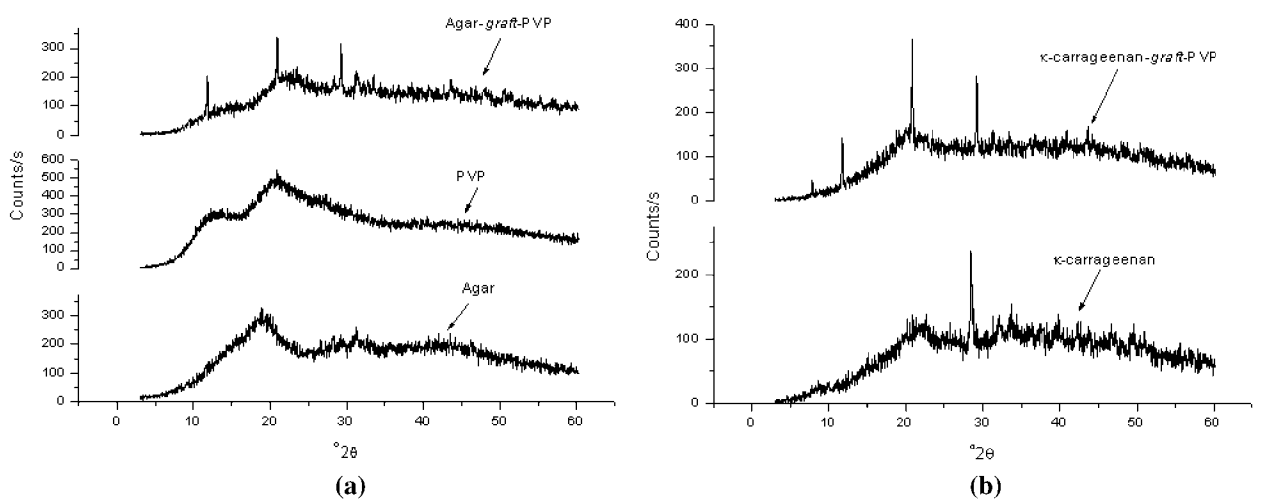



**Figure 5** Powder X-ray diffraction spectra of (a) agar, PVP, and agar-*graft*-PVP and (b) κ-carrageenan and κ-carrageenan-*graft*-PVP.

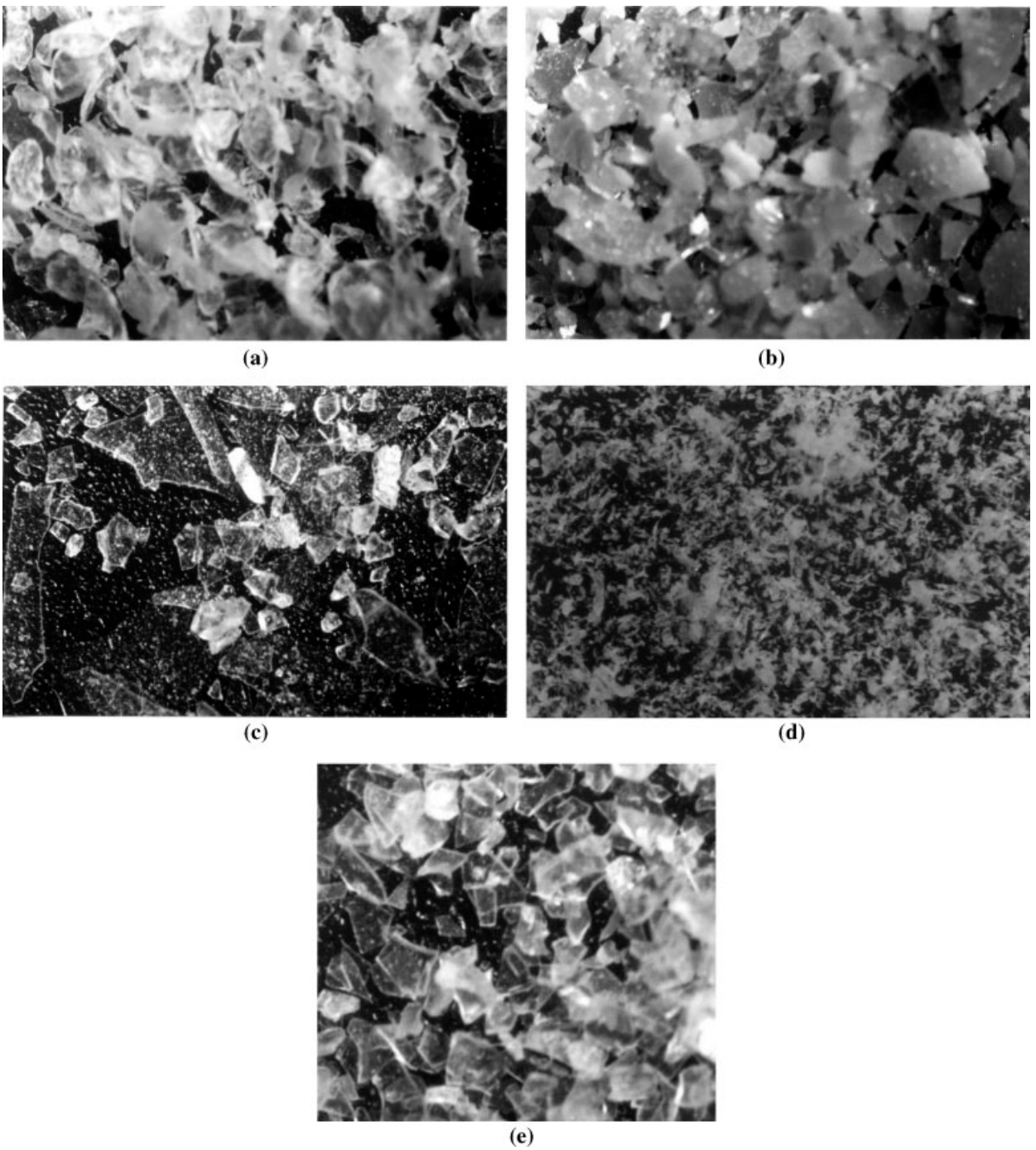



**Figure 6** Optical micrographs of (a) agar, (b) PVP, (c) agar-*graft*-PVP blend, (d) κ-carrageenan, and (e) κ-carrageenan-*graft*-PVP blend.

and κ-carrageenan-*graft*-PVP blends are shown in Figure 5(a,b), respectively. From a comparison of the diffraction patterns, we observed that: (1) there was no sharp or narrow peak for the control agar and PVP, indicating an amorphous nature; (2) the agar-*graft*-PVP had three sharp peaks, at $2\theta = 11.82^\circ$, $20.9^\circ$, and $29.28^\circ$, and three peaks of relatively lesser intensity, at $2\theta = 31.28^\circ$, $33.47^\circ$, and $43.53^\circ$; (3) the control κ-carrageenan had only one sharp peak, at $2\theta = 29.12^\circ$; and (4) the κ-carrageenan-*graft*-PVP had four intense peaks at $2\theta = 8.0^\circ$, $12.27^\circ$, $20.71^\circ$, and $29.12^\circ$. The crystallinity indices (CIs) of the control and grafted blends were determined using the following equation described by Herman and Weidinger[42]:

$$\text{CI} = \text{area of crystalline peak}/(\text{area of crystalline peak} + \text{area of amorphous peak}).$$

The CIs calculated for the control κ-carrageenan, the κ-carrageenan-*graft*-PVP, and the agar-*graft*-PVP were 0.0284, 0.0490, and 0.0410, respectively. The control agar and PVP were found to be amorphous [Fig. 5(a,b)]. All these observations indicate an alteration in molecular association in the grafted blends leading to enhanced crystallinity compared to the respective polysaccharides [Fig. 5(b)].

It was observed that powder XRD of the physical mixture of agar and PVP (1 : 2) and carrageenan and PVP (1 : 2) had amorphous profiles. It is well known that formation of junction zones during double helix formation in gel provides strength to the gel.[43] Because of the crosslinked PVP in the grafted products, the formation of the junction zones presumably was disturbed, resulting in weaker network formation in its gel. The increase in crystallinity indicates a more ordered structure of the grafted products relative to their respective control polysaccharides. The increase in crystallinity and decrease in gel strength may have resulted from the slight decrease in the molecular weight of the grafted products (intrinsic viscosity was measured as 570.23 mL/g for agar, 526.7 mL/g for agar-*graft*-PVP, 452.12 mL/g for κ-carrageenan, and 405.8 mL/g for κ-carrageenan-*graft*-PVP).

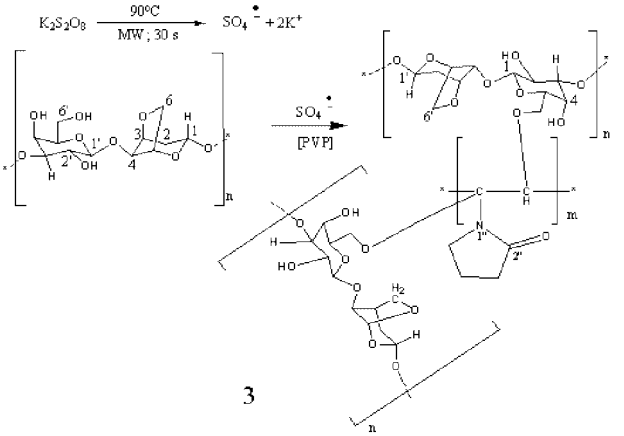
The values for the specific optical rotation, $[\alpha]_{589}$[45] (c 0.025, $H_2O$), of agar-*graft*-PVP and κ-carrageenan-*graft*-PVP were 24° and 31°, respectively; whereas those of the control agar and κ-carrageenan under the same conditions were −22.6° and 73.5°, respectively. These values indicate the formation of new optically active compounds.

## Morphology

Optical micrographs of the grafted blends were taken at a 70× magnification and compared with the control polysaccharides [Fig. 6(a,b)]. The grafted blends appeared glassy in the micrographs, indicating an obvious modification of the polysaccharide morphology, as revealed in the XRD profiles.

## Proposed mechanism of graft crosslinking

The above results indicate that PVP was grafted on the polysaccharides. Crosslinking and grafting of PVP onto the backbone of κ-carrageenan and agar were carried out in an aqueous medium using KPS as a free-radical initiator and PVP as a crosslinking agent. The proposed mechanism by which this crosslinking grafting process occurs is illustrated in Scheme 1 for the formation of agar-*graft*-PVP blend (**3**). Following the same mechanism, κ-carrageenan-*graft*-PVP blend (**4**) would be formed. The sulfate anion radical that would be produced as a result of thermal decomposition of KPS in the presence of microwave irradiation would abstract




**Scheme 1** Proposed mechanism of the formation of agar-*graft*-PVP blend (**3**).

hydrogen from the hydroxy group of agar and κ-carrageenan to form the corresponding alkoxy radicals on the C-6′ of the polysaccharide. Then the resulting macroradicals would initiate grafting of PVP. During the propagation step a free radical thus formed would combine with a free radical of PVP (on —CH —$CH_2$—). Because the crosslinking agent, PVP, would be present in the reaction mixture, a three-dimensional network would result.[44] The mechanism of crosslinked graft copolymerization of acrylic acid on κ-carrageenan in the presence of ammonium with persulfate as a free-radical initiator and *N*,*N*′=methylene bisacrylamide was discussed by Pourjavadi et al., who described the formation of alkoxy radicals in the presence of a redox initiator on the C-6 carbon atom of polysaccharide.[45] Formation of free radicals in the presence of different free radicals on gelatin and the formation of gelatin-*graft*-*N*-vinylpyrrolidone were also reported.[46]

## CONCLUSIONS

Modification of seaweed polysaccharides with various substrates employing graft copolymerization results in hydrophobization of the polysaccharides.[38] In the present investigation we developed a one-pot method of achieving a hydrogel-forming material with PVP exhibiting enhanced water-holding capacity and crystallinity. Therefore, employing this method, it is possible to prepare seaweed polysaccharide–based products suitable for targeted applications by judiciously selecting the graft substrates. The seaweed polysaccharide–based graft blends reported here may be of potential utility in biomedicine, in tissue engineering, in agriculture as water retainer, in microbiology, and in pharmaceuticals as hydrogel dressings. These hydrogels may also be useful as a substitute for collagen-based materials of animal origin.

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