Agar/sodium alginate-\textit{graft}-polyacrylonitrile, a stable hydrogel system

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Polyacrylonitrile grafted agar/sodium alginate (Agar/Na-Alg-\textit{graft}-PAN) has been synthesized in aqueous medium under reflux conditions in the presence of potassium persulphate as a free radical initiator. By varying the reaction parameters, e.g., concentrations of acrylonitrile monomer and $\text{K}_2\text{S}_2\text{O}_8$, reaction time and temperature, the optimum grafting conditions have been identified as that having the highest grafting ratio (Gr 1.87), total conversion (Ct 1.05) and grafting efficiency (Ge 0.89). The blend and grafted products have been characterized by FT-IR, X-ray diffraction, differential scanning calorimeter and scanning electron microscopy. The swelling capacity of Agar/Na-Alg-\textit{graft}-PAN is found to be 8.5 g/g at pH 1.2 and the swelled material is stable for over 24 h. This copolymer hydrogel system may be exploited in various applications utilizing its swelling properties and stability.

Keywords: Polymers, Graft polymers, Copolymers, Biopolymers, Alginates, Polyacrylonitriles, Hydrogels

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Agar is a seaweed polysaccharide and chemically consists of alternating 3-O-linked D-galactopyranose and 4-O-linked 3,6-anhydro-L-galactopyranose. Alginates are linear anionic polysaccharides of (1,4)-linked $\alpha$-guluronic acid and $\beta$-D-mannuronic acid residues. Both biopolymers are biodegradable and are used in the adhesive, food, cosmetics and pharmaceuticals industries. Sodium alginates obtainable from Indian seaweeds are of low viscosity, which limits their applications.

Modification of natural polymers by grafting technique is a promising method for the preparation of new materials. This method enables one to introduce special properties and widen the field of the potential applications. Acrylonitrile has been grafted onto various natural and modified polysaccharides (e.g., gum arabic, gum tragacanth, xanthan gum, sodium alginate, chitosan, sodium carboxymethyl cellulose, hydroxy-ethyl cellulose, methyl cellulose) by using the ceric-carbohydrate redox initiating system. Under the ongoing program of our laboratory on value addition of seaweed and seaweed polysaccharides, we have reported different stable hydrogel systems with improved properties.

We report herein a one-pot synthesis by graft copolymerization of acrylonitrile (AN) onto the blend of agar and sodium alginate (Agar/Na-Alg) in presence of the initiator, potassium persulphate. The grafted product has better swelling properties and stability in aqueous media of pH 1.2, 7.0 and 12.5. To our knowledge, this is the first report of grafting of PAN onto the agar-sodium alginate blend.

Materials and Methods

Agar and sodium alginate used herein were extracted from seaweeds, viz., Gelidiella acerosa and Sargassum tenerrimum, growing in Indian waters. The agar and alginate were extracted following the methods reported in the literature. The manuronic acid to guluronic acid ratio (M/G ratio) of sodium alginate used in this study was 0.37 and the weight average molecular weight of agar was $2.65 \times 10^5$ Dalton. Potassium persulfate (KPS; AR grade), a water-soluble initiator, and acrylonitrile (AN) AR grade were purchased from SD Fine Chemicals, Mumbai.

Agar and Na-Alg blend were prepared by mixing agar and Na-Alg in 1:3 (w/w) ratios, as described in our previous work.

For grafting, the blend (1 g) was dissolved in 85 mL distilled water by heating for 2 min. To this was added KPS (0.01–0.08 g in 5 mL water) with stirring followed by addition of a solution of AN (1.0–2.5 g in 10 mL water). The reaction mixture was heated under reflux conditions at 70 °C for 5h with constant stirring,
cooled to room temperature to make the gel, cut into small pieces and dehydrated with IPA to isolate the solid graft copolymer (Agar/Na-Alg graft-PAN). The solid product was filtered through a nylon cloth under reduced pressure and unreacted acrylonitrile homopolymer (PAN) was removed from the product by washing with dimethyl formamide (DMF) and aqueous methanol. Finally it was washed with pure methanol. The unreacted homopolymer (PAN) was recovered from the washings by evaporating to dryness. The grafted copolymer was dried at 50 °C for 2 h, and ground (30–40 mesh) using a mortar and pestle.

The grafted product was characterized by FT-IR analysis on a Perkin-Elmer Spectrum GX FT-IR system (USA) in KBr pellets (10.0 mg sample per 600 mg KBr). All spectra were an average of two counts with 10 scans each and a resolution of 5 cm

Powder X-ray diffractions were recorded on a Philips X'pert MPD X-ray powder diffractometer with Cu-Kα radiation (30–40 mesh) using powdered samples having a magnification, using powdered samples having particle size between 20-30 μm under identical conditions. In this study, gelling and melting temperatures of copolymer gels were measured as described by Craigie and Leigh

The grafting parameters i.e., total conversion (Ct), Grafting ratio (Gr), grafting efficiency (Ge), add-on (Ad) and homopolymer content (Hp) were determined according to the known weight-basis expressions

where W_o, W_1, W_2 and W_3 are the weights of initial substrate, monomer used, the product mixture (i.e., graft copolymer and unreacted PAN) and pure graft copolymer (after DMF washed) respectively.

A weighed sample of dried parent agar polysaccharide, blend polysaccharides and Agar/Na-Alg-graft-PAN copolymers with particle size between 30 and 40 mesh were immersed in aqueous medium of selected, pH i.e., 1.2, 7.0 and 12.5, in separate experiments. Equilibrium swelling (ES) capacity was calculated as described in our previous reports using Eq. (6),

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

Results and Discussion

In the present investigation the optimum values of the various parameters of the reaction were: W_o = 1 g; W_1 = 2 g; W_2 = 2.11 g and W_3 = (2.11-0.24) g =1.87 g (unreacted homopolymer (PAN) was 0.24 g). The grafting parameters calculated for the product were as follows: Ct = 1.05 (± 0.012); Gr = 1.87 (± 0.041); Ge = 0.89 (± 0.055); Ad = 0.46 (± 0.033); Hp = 0.11 (± 0.0008). These data indicate that PAN was grafted on to the polysaccharide blend. Optimization of the reaction conditions, e.g., effects of monomer concentration, reaction temperature, reaction time and initiator concentration was also carried out after detailed study

A plausible mechanism for the formation of the graft copolymer is proposed in Scheme 1. The physical properties of agar, sodium alginate, Agar/Na-Alg blend and Agar/Na-Alg-graft-PAN copolymer are given in (Table 1). The viscosity of agar, sodium alginate, Agar/Na-Alg blend and Agar/Na-Alg-graft-PAN were 55.0 ± 0.55 cP, 26.0 ± 0.45 cP, 38.0 ± 0.50 cP and 63.0 ± 0.51 cP respectively at 80 °C temperature, indicating that the grafted copolymer has the greatest viscosity (Table 1).

Gel strength of the gel sample prepared from grafted copolymer was significantly lower than that of the parent blend. The gel strength of copolymer gel sample and parent blend gel sample were 110 g cm

and 180 g cm

respectively (Table 1). Similarly, the gelling and melting temperatures of the copolymer gel
Table 1—Physicochemical properties of the blend polysaccharide and the graft copolymer hydrogels

<table>
<thead>
<tr>
<th>Samples</th>
<th>Equil. swelling (^a) (g/g) (^a) at pH=1.2</th>
<th>Equil. swelling (^a) (g/g) (^a) at pH=7.0</th>
<th>Equil. swelling (^a) (g/g) (^a) at pH=12.5</th>
<th>Apparent viscosity at 80ºC (cP)(^{ab})</th>
<th>pH at 60ºC</th>
<th>Gel strength (g/cm(^2)) (^{ab})</th>
<th>Gelling temp. (ºC) (^{ab})</th>
<th>Melting temp. (ºC) (^{ab})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agar</td>
<td>6.0 ± 0.54</td>
<td>5.0 ± 0.46</td>
<td>5.0 ± 0.43</td>
<td>55 ± 0.55</td>
<td>6.9</td>
<td>800 ± 7.2</td>
<td>41 ± 0.52</td>
<td>84 ± 0.48</td>
</tr>
<tr>
<td>Na-Alg</td>
<td>NA(^c)</td>
<td>NA(^c)</td>
<td>NA(^c)</td>
<td>26 ± 0.45</td>
<td>7.0</td>
<td>NA(^c)</td>
<td>NA(^c)</td>
<td>NA(^c)</td>
</tr>
<tr>
<td>Agar/Na-Alg blend (1:3 w/w)(^d)</td>
<td>14 ± 0.55</td>
<td>10 ± 0.54</td>
<td>8.5 ± 0.45</td>
<td>38 ± 0.50</td>
<td>6.2</td>
<td>180 ± 4.5</td>
<td>28 ± 0.55</td>
<td>69 ± 0.52</td>
</tr>
<tr>
<td>Agar/Na-Alg-graft-PAN (1:2 w/w)(^d)</td>
<td>8.5 ± 0.45</td>
<td>7.2 ± 0.45</td>
<td>6.5 ± 0.5</td>
<td>63 ± 0.51</td>
<td>6.7</td>
<td>110 ± 6.3</td>
<td>25 ± 0.45</td>
<td>61 ± 0.55</td>
</tr>
</tbody>
</table>

\(^a\) Mean of triplicate measurements ± SD; \(^b\) Measurements in 1.5 wt% sol/gel; \(^c\) NA = not applicable; \(^d\) w/w = weight by weight.
sample were also less than that of the parent blend gel sample (Table 1). The lowering of gel strength of the copolymer hydrogel was presumably due to the fact that the -OH groups, which take part in network formation through hydrogen bonding in the hydrogel, become part of new ether linkages that are formed with PAN (Scheme 1). This results in weak network formation in the hydrogel having still weaker gel strength, which is also associated with lower gel melting temperature.

The swelling capacity of the Agar/Na-Alg-graft-PAN was lower in all pH media as compared to that of parent polysaccharide blend at pH 1.2, 7.0 and 12.5. The swelling capacities of the copolymer hydrogel were 8.5 ± 0.45, 7.2 ± 0.45 and 6.5 ± 0.5 g/g at these pHs respectively, while those of parent polysaccharide blend were 14.0 ± 0.55, 10.0 ± 0.54 and 8.5 ± 0.45 in acidic (pH 1.2), neutral and alkaline media (pH 12.5), respectively (Table 1). It may be noted that one of the blend components is agar which is acid labile, while the grafted copolymer is stable beyond 24 h in acidic as well as the other pHs studied. The blend swelled and got dispersed after 12 h at all pHs studied. The relatively lower swelling in the copolymer hydrogel may be due to the grafting of blend with hydrophobic PAN moieties.

FT-IR spectra of grafted blend, PAN, blend and parent polysaccharides are presented in Fig. 1. The existence of a sharp intense peak at 2245 cm\(^{-1}\) for
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Fig. 3—DSC curve of (a) Agar/Na-Alg blend, (b) polyacrylonitril (PAN), and, (c) Agar/Na-Alg- graft-PAN.

Fig. 4—SEM images of (a) agar, (b) Na-Alg, (c) PAN, (d) Agar/Na-Alg blend, and, (e) graft copolymer.
(C=N-) stretching vibration in the IR spectra of the graft copolymers is definite evidence of grafting. This absorption band arises from the stretching vibration mode of the nitrile groups and at 1454 cm\(^{-1}\) for C-N stretching (Fig. 1). Characteristic IR bands at 777, 890, and 931 due to 3,6-anhydro-\(\beta\)-galactose skeletal bending in agar\(^{20,21}\), which were also observed for the blend and grafted product, indicate that the backbone configuration remained unaltered during the grafting reaction.

The X-ray diffraction pattern of PAN, Agar/Na-Alg blend and Agar/Na-Alg-graft-PAN are shown in Fig. 2. The XRD patterns showed that the parent blend and PAN were amorphous and crystalline in nature, respectively (Fig. 2), while one intense peak appears in copolymer indicates enhanced crystallinity of the modified blend (Fig. 2).

The results of DSC study confirm the grafting of the blend with PAN (Fig. 3). The enthalpy of melting \((\Delta H)\) was calculated by integrating the areas of the exothermic and endothermic peaks. The blend polysaccharide shows two endothermic peaks (Fig. 3a) indicating that it is amorphous in nature. Polyacrylonitrile exhibits 94% crystallinity while the grafted copolymer blend shows 38% crystallinity due to the insertion of crystalline PAN on to the blend\(^{12,13}\).

The SEM images of the graft copolymer confirm grafting when compared to those of parent polysaccharides, PAN, blend and grafted product (Fig 4). The SEM image of the grafted product shows a surface morphology having an integrated and convoluted floral structure. This is distinctly different from the images of the parent ungrafted blend and also of the individual base component polymers, each of which shows surface morphology of a segregated system with discrete form.

Conclusions
In the present study, readily water-soluble sodium alginate, a non-gelling seaweed polysaccharide, has been converted into a stable copolymer hydrogel through blending with agar and grafting the blend with acrylonitrile. This hydrogel is stable in aqueous media over a wide range of pH (pH 1.2, 7.0 and 12.5). The unmodified blend swells and is dispersed after 12 h in all pH studied while the grafted copolymer is not dispersed even after 24 h. The copolymer hydrogel will be useful in newer applications especially due to its resilience to acidic pH medium.

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References