

Synthesis of seaweed polysaccharide-based polyvinylpyrrolidone copolymer with adhesive properties

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ABSTRACT: Polyvinylpyrrolidone (PVP) grafted sulfated polysaccharide of the seaweed *Cystoseira indica* (CI_{sps}) (CI_{sps}-graft-PVP) was synthesized in aqueous medium under microwave irradiation in the presence of potassium persulfate (KPS), as a free radical initiator. Varying the reaction parameters, e.g., concentration of PVP and KPS, reaction time and temperature, optimum grafting condition was identified as the one having the highest grafting ratio (Gr 2.30) and grafting efficiency (Ge 0.92). The grafted copolymer was characterized by FT-IR, ¹³C-NMR and thermo gravimetric analysis (TGA). The 5% (w/v) dispersion of the new material CI_{sps}-graft-PVP in water exhibited comparable binding properties with papers, polyethylene sheets, and wood pieces as against that of a commercial adhesive. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42383.

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INTRODUCTION

In recent years, chemical modification of natural macromolecules has received considerable attention. Polysaccharides of marine origin are unique raw materials as they are abundant in nature, hydrophilic and modifiable biopolymers. They offer tremendous potential for development of alternate materials.^{1–6} Grafting techniques have been widely used to prepare materials especially involving systems in which polysaccharides are used as substrate polymers.^{4,5,7} The polymer that is grafted is expected to be distributed on the backbone of the substrate polymer imparting beneficial effects on both the polymers.

Seaweeds being abundant in the nature are good source of polysaccharides and their use in preparation of grafted materials having biomedical applications may add further value to the seaweeds.⁸ Seaweed polysaccharides are relatively less explored in regard to such modifications. *Cystoseira indica* is a brown algal species containing sulfated polysaccharides consisting of 3-linked fucopyranose residues, as the backbone of the polysaccharide structure.⁹ Many of the copolymers of seaweed polysaccharides reported so far were synthesized by multi-step process involving prolonged reaction time.¹⁰

In an ongoing program of our laboratory on modification and value addition of seaweed polysaccharides for newer applications several reports were published.^{11–19} The sulfated polysaccharide of *Cystoseira indica* (CI_{sps}) was grafted with polyvinylpyrrolidone

(PVP) for the first time. The primary inspiration for generating a sulfated seaweed polysaccharide-based adhesive came from our earlier work on κ -carrageenan-*graft*-PAAm, a copolymer hydrogel.¹⁴ Therefore, it was decided to graft the sulfated polysaccharide of the seaweed *Cystoseira indica* (CI_{sps}) with the water soluble synthetic polymer polyvinyl pyrrolidone (PVP) to generate a new material with possible adhesive properties, which was indeed physically discernible while isolating the reaction product. PVP absorbs water and has multifarious functional applications in the industrial as well as pharmaceuticals domains.^{20–22}

EXPERIMENTAL

Materials

Cystoseira indica (Thivy & Doshi) Mairh was collected from Diu (20°45' N, 70°58'E) on the west coast of India during January, 2008. A herbarium specimen (AL-II-114-03) has been deposited with CSMCRI, Herbarium for future reference. The hot water soluble sulfated polysaccharide (CI_{sps}) was extracted following the method described by Siddhanta *et al.*²³ The products were vacuum dried prior to reaction. Potassium persulfate (KPS), polyvinylpyrrolidone (PVP) (Mw 10,000 Da), isopropanol, used were of analytical grade and were purchased from Sigma-Aldrich, Mumbai and Ranbaxy Chemicals, Mumbai, respectively. Available literature reveals that the majority of such grafting reactions have been attempted in multimode domestic ovens in open vessels, where temperature and pressure of the reaction mixture were not controlled.²⁴ We used here Milestone Start S

(Italy) programmable microwave oven (Model No.: Start S; Terminal T260; Line Voltage 230V; Magnetron S.N. 131528; Frequency 50Hz) was employed for the synthesis. The MW conditions were 1200 W for 1 min, to achieved 90°C temperature and further maintain it for 1.5 min to completion of reaction. This instrument had the programming facility to set a constant temperature and the required reaction time.

Synthesis and Purification of the Graft Copolymer

For grafting CI_{sps} (1 g) was first dissolved in 85 mL of distilled water by heating under microwave (MW) irradiation at 90°C for 2 min. To this was added KPS (0.01–0.12 g in 5 mL water) with stirring and was MW-irradiated for 30s, followed by the addition of a solution of PVP (1.0–2.5 g in 10 mL water). The mixture was then irradiated under microwave at a set temperature 90°C. The set temperature 90°C was achieved in 1 min and sustained for remaining 1.5 min to carry out the reaction, while constant stirring when the reaction mixture turned yellowish in color. It was cooled and the product was precipitated in isopropyl alcohol (1 : 2.25, v/v), having isolated the graft copolymer CI_{sps} -graft-PVP by centrifugation at 8000 rpm for 8 min. The unreacted homopolymers PVP was removed from the product by extracting on a Soxhlet extractor with dimethyl formamide (DMF) for 1 h. The product was further washed with isopropyl alcohol and vacuum dried at 50°C for 2 h, which was ground (30–40 mesh) using a mortar and pestle. The unreacted homopolymer was recovered from the extract by evaporating to dryness.

Grafting Parameters

The grafting parameters, i.e., Grafting ratio (Gr), grafting efficiency (Ge), known weight-basis expressions,^{18,19}

$$Gr = W_3 / W_0 \quad (1)$$

$$Ge = W_3 / W_2 \quad (2)$$

$$W_3 = (W_2 - W_1) \quad (3)$$

where W_0 , W_1 , W_2 , and W_3 are the weights of initial substrate, PVP used, the product mixture (i.e., grafted copolymer and unreacted homopolymer), and pure graft copolymer (after washed), respectively.

Weight of Adhesive

Liquid and solid weights of applied adhesive were measured of (CI_{sps} -graft-PVP) using standard method described in ASTM Handbook.^{14,25}

Weight of liquid adhesive:

$$S = [(B_2 - B_1) \times 317.5] / (N \times A) \quad (4)$$

(when B_1 and B_2 are in grams)

where S = Wt. of liquid adhesive applied (expressed in pounds per thousand sq. feet of joint or surface area); B_2 = Wt. of specimen immediately after application of the adhesive; B_1 = Wt. of specimen before applying the adhesive; A = area of test specimen (in sq. inches); and N = number of surfaces spread; and 317.5 = conversion factor.

Weight of solid adhesive:

$$D = [(B_2 - B_1) \times 317.5] / (N \times A) \quad (5)$$

(when B_1 and B_2 are in grams)

where D = Wt. of adhesive solids applied (expressed in pounds per thousand sq. feet of joint or surface area); B_2 = Wt. of the specimen after application of the adhesive and elimination of solvents; B_1 = Wt. of the duplicate uncoated specimen; A = area of test specimen (in sq. inches); and N = number of surfaces spread; and 317.5 = conversion factor.

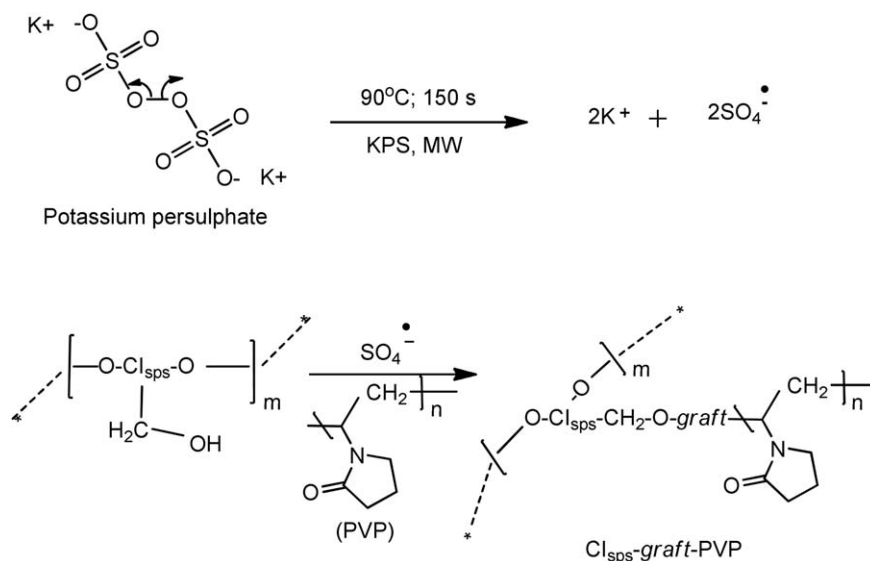
In this experiment two weighed dry pieces of paper, transparency sheets (used in overhead projectors), and wood were taken having measured their surface areas under investigation. Then the 5% (w/v) dispersion of the copolymer adhesive was applied on one of the designated surfaces by uniformly spreading, onto which the other piece without adhesive was placed and pressed to get it stuck. The united pieces were weighed immediately and the weight of the liquid adhesive was calculated as mentioned above. The pieces could not be pulled 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 specimens 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.

Characterization

Grafted product was characterized by FT-IR using a Perkin-Elmer Spectrum GX FT-IR system, by taking 2.0 mg of sample in 600 mg KBr. All spectra were average of two counts with 10 scans each and a resolution of 5 cm^{-1} . ^{13}C NMR spectrum (noise-decoupled) was recorded on a Bruker Ultrashield Spectrometer, Switzerland at 125 MHz. Sample (30 mg/mL) was dissolved in D_2O and DMSO (5 : 1). The deuterated d_6 -DMSO was used as an internal locking standard and spectrum was recorded at 70°C. The TGA of the parent polysaccharide (10 mg) and its graft copolymer (11.4 mg) were carried out on a Mettler Toledo, TGA/SDTA 851° system, Switzerland, using a temperature program 30–600°C at a heating rate 10°C min^{-1} in an air atmosphere. Total nitrogen was estimated by Kjeldahl method on a KEL PLUS-KES 201 Digestion unit attached to a KEL PLUS-CLASSIC DX Distillation unit (M/s PELICAN equipments, Chennai, India). The molar mass (weight average molecular mass, M_w ; number average molecular mass, M_n and polydispersity index, PDI) of the CI_{sps} and grafted copolymer CI_{sps} -graft-PVP; (500 ppm solution in 0.1 M Na_2NO_3 at 45°C) were determined by gel permeable chromatography (GPC, Waters alliance HPLC, with Waters 2695 separation modules and 2414 refractive index detector, USA). The apparent viscosity was measured on a Brookfield DV-II + Pro viscometer with spindle number SC-18 and at 60 rpm. Measurements were done in triplicate in each experiment.

RESULTS AND DISCUSSION

A proposed mechanism for the grafting reaction of PVP onto CI_{sps} is schematically presented subsequently (Scheme 1; cf. Ref. [8]). Potassium persulfate (free radical initiator) forms sulfate anion radical under microwave conditions. The sulfate anion radical coupled the alkyl chain end of PVP radical with CI_{sps} presumably with its pendant $-CH_2-OH$ forming $-CH_2-O^{\bullet}$, possibly at C-6 of the pyranose carbohydrate rings of the



Scheme 1. Schematic presentation of the proposed mechanism of grafting reaction of PVP onto Cl_{sps} .

heteropolysaccharides affording Cl_{sps} -graft-PVP. Similar observations on the reaction involving C-6 carbon of galactopyranose polymer was reported earlier in the literature (see ^{13}C NMR data subsequently).^{26,27}

Optimization of Grafting Parameters

In the present investigation the optimum values of the various parameters of the reaction were; $W_0 = 1$ g; $W_1 = 2$ g; $W_2 = 2.50$ g and $W_3 = (2.50 - 0.20)$ g = 2.30 g [unreacted homopolymer (PVP) was 0.20 g]. The grafting parameters calculated for the product were as follows; $Gr = 2.30 (\pm 0.045)$; $Ge = 0.92 (\pm 0.055)$

PVP was grafted on to the polysaccharide Cl_{sps} in a homogeneous solution. Since the polymerization variables affected the grafting parameters and homopolymer quantity, certain critical parameters were investigated to identify the optimum condition for obtaining graft copolymer with minimum degradation of the parent polysaccharide.

Effect of the Ratio of PVP to Polysaccharide

The influence of the ratio of PVP to Cl_{sps} on the grafting parameters was studied. It was found that “Gr” and “Ge” reached a maximum value when the ratio of PVP to polysaccharide was 2 : 1 (w/w) and then decreased gradually (Figure 1). In the absence of the water soluble initiator the reaction did not take place at all. In presence of the initiator in the aqueous solution of polysaccharide when the PVP to polysaccharide ratio increased then Cl_{sps} -graft-PVP could play the role of self-emulsifier so as to absorb more monomers (PVP) on the polysaccharide surface, which subsequently enhanced the rate of the graft reaction thereby sharply increasing Gr and Ge till the PVP to polysaccharide reaches 2 : 1. When the ratio of PVP was higher which led to the acceleration of chain transfer reaction as a result Ge decreased gradually.¹³

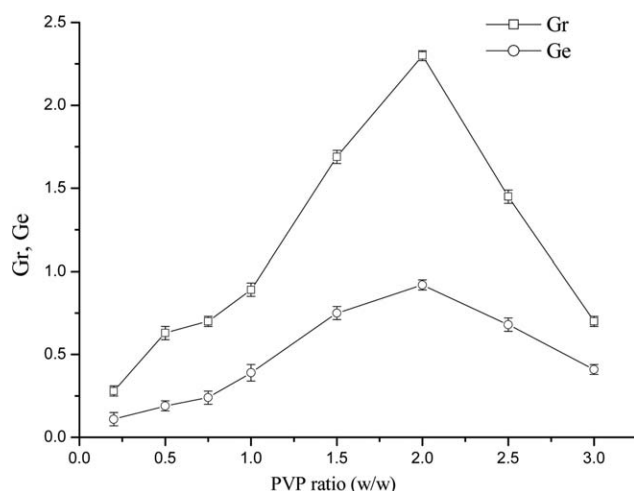


Figure 1. Effect of PVP concentration (w/w) on grafting parameters.

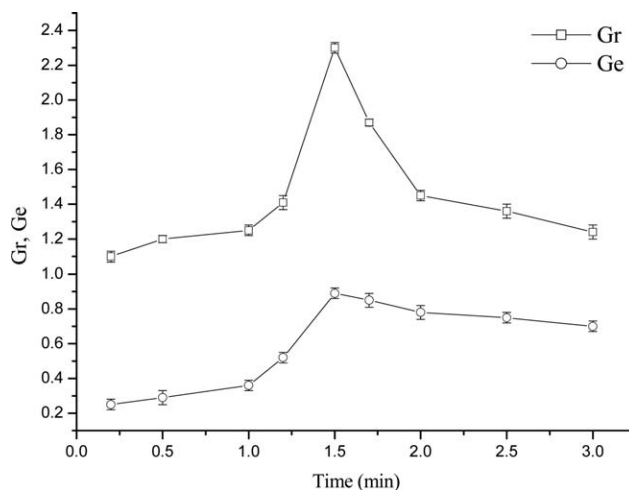


Figure 2. Effect of reaction time duration on grafting parameters.

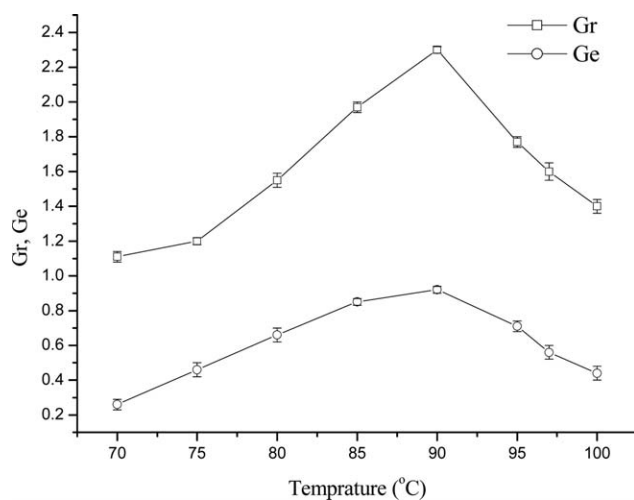


Figure 3. Effect of reaction temperature on grafting parameters.

Effect of Reaction Time

The influence of the reaction time on grafting parameters is illustrated in Figure 2. The Gr and Ge increased up to 1.5 min and decreased beyond that. This phenomenon may be explained on the basis of pH of the reaction mixture. The initiator produces hydrogen and hydroxyl free radicals. Simultaneously, it produces hydroxyl or alkoxy radicals on polysaccharide (Cl_{sps}). The sulfate

free radicals generated from KPS absorbed the hydrogen radical resulting in the formation of sulfuric acid. The pH of the reaction mixture was about neutral (pH = 6.6) up to 1.5 min may be due to formation of sulfuric acid and KOH in equal amounts. After that the pH decreased and so did the Gr and Ge as a result of degradation of the parent polymer in acidic pH. When the reaction was extended up to 3 min the pH of reaction mixture

Table I. Physicochemical Properties of the Polysaccharide (Cl_{sps}) and the Graft Copolymer

Samples	Apparent viscosity (cP) at 30°C (\pm SD) ^{a,b}	Total nitrogen (%) ^a (\pm SD)	M_w (kDa)	M_n (kDa)	PDI, M_w/M_n
Cl_{sps}	6.2 ± 2.5	0.84 ± 0.1	320.2	88.15	3.63
Cl_{sps} -graft-PVP	74.5 ± 3.5	6.04 ± 0.2	560.0	123.0	4.55

^aData presented are mean of triplicate measurements (\pm SD).

^bViscosity was measured in a 2% (w/v) concentration at 30°C.

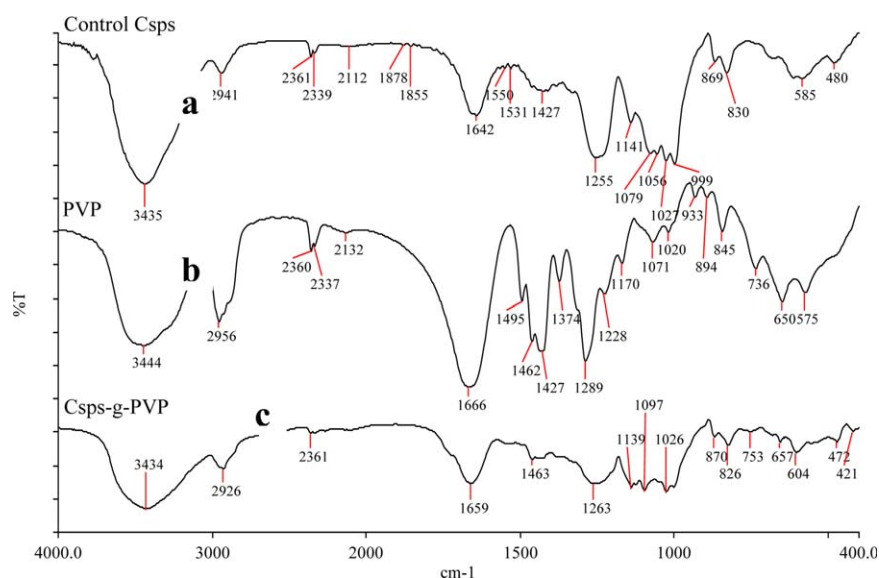


Figure 5. FT-IR spectra of (a) Cl_{sps} , (b) PVP, and (c) Cl_{sps} -graft-PVP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

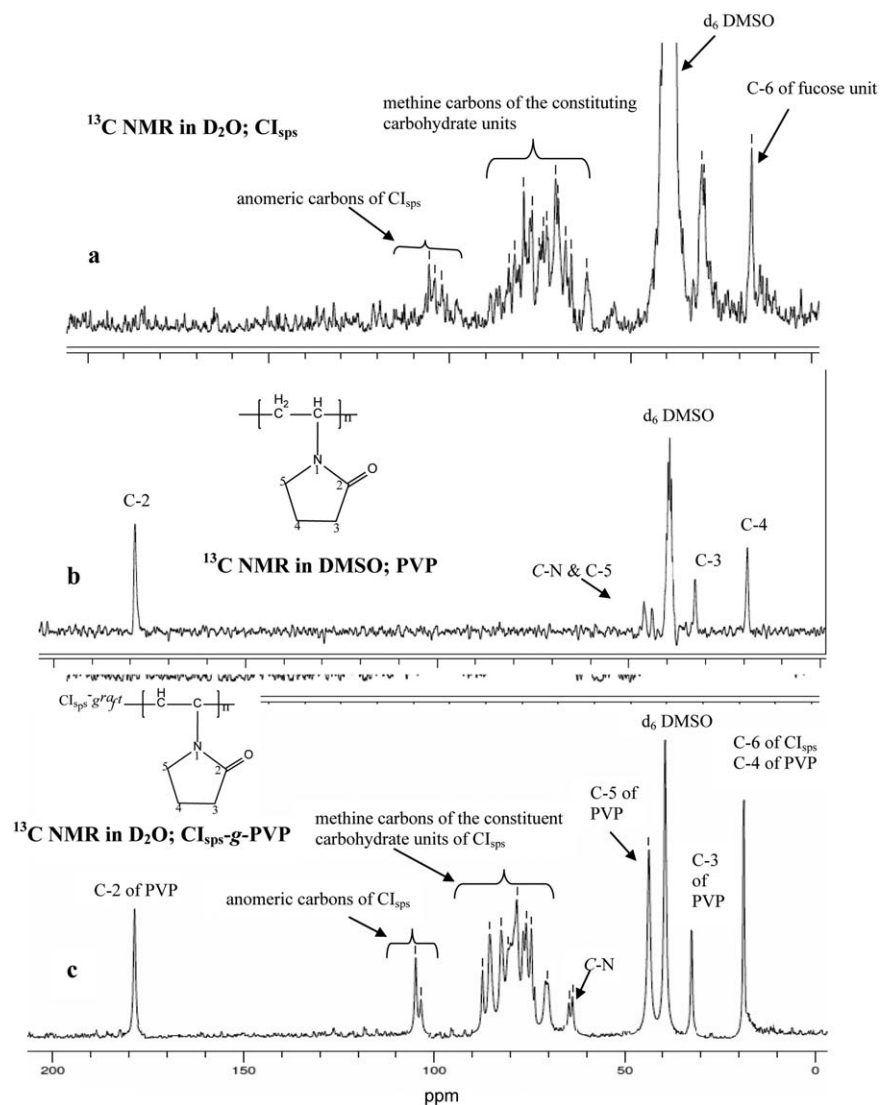


Figure 6. ^{13}C -NMR spectra of (a) Cl_{sps} , (b) PVP, and (c) Cl_{sps} -graft-PVP.

was acidic ($\text{pH} = 2.1$) and subsequently it lowered the Gr and Ge may be due to degradation of parent polysaccharide (Cl_{sps}). Similar observation was registered in the earlier report.⁸

Effect of Reaction Temperature

When the other reaction conditions were constant (microwave irradiation time duration 1.5 min, polysaccharide to PVP = 1 : 2), the grafting parameters at various temperatures were studied. In accordance with the general rule of radical polymerization, Ge increased and then it got leveled off (Figure 3). In this type of microwave induced reactions at 2450 MHz microwave frequency, the molecular rotation was affected without disturbing the molecular structure, increasing the reaction temperature and reaction rate. With further increase in temperature, excessive molecular vibration led to the destruction of the polymer chain and as a result products with lower Ge and Gr values were obtained. In this study, no product was obtained in the reactions that were carried out at temperatures less than 70°C . The reaction temperature was optimized to be 90°C . The weight-average molecular

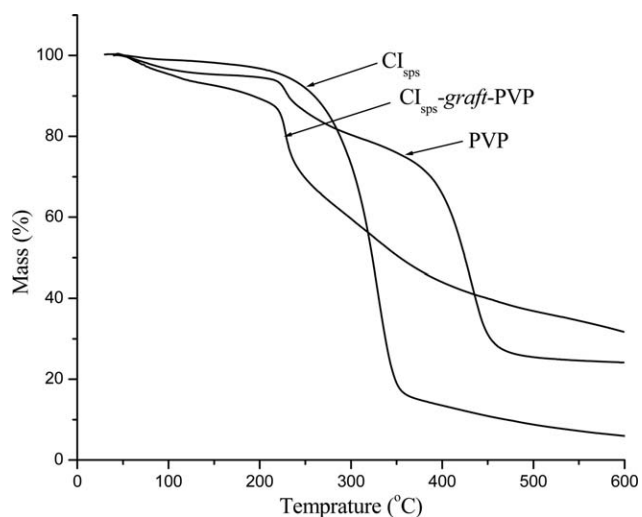


Figure 7. Thermogravimetric analysis (TGA) profile for PVP, control Cl_{sps} , and Cl_{sps} -graft-PVP.

Table II. Liquid and Solid Weight of Copolymer Adhesive (5% Dispersion of CI_{sps} -graft-PVP) and Standard Adhesive (Fevicol)

Specimens	Liquid and solid weight of adhesives (in pound per thousand square feet of surface area)			
	CI_{sps} -graft-PVP		Fevicol	
	Liquid weight	Solid weight	Liquid weight	Solid weight
Paper sheets	6.25 ± 0.058	1.50 ± 0.080	7.25 ± 0.067	2.57 ± 0.072
Transparency sheets	4.0 ± 0.073	1.5 ± 0.058	4.3 ± 0.063	1.6 ± 0.069
Wood blocks	15.7 ± 0.057	4.5 ± 0.065	18.5 ± 0.055	4.8 ± 0.060

Data presented are mean of triplicate measurements (±SD).

weight (M_w) for CI_{sps} -graft-PVP was measured as 560 kDa at optimized reaction conditions. When the reaction temperature was increased up to 100°C, the weight-average molecular weight (M_w) for CI_{sps} -graft-PVP was measured as 80 kDa.

Effect of Initiator Concentration on Grafting Parameters

Potassium persulfate (KPS) was added in the range 0.007–0.10 g in the reaction mixture (100 mL). Gr and Ge increased with increasing concentration of KPS up to 0.02 (w/w; Figure 4) decreasing thereafter with increasing KPS as reported in the literature.²³ At higher concentrations, KPS underwent induced decomposition, leading to a decrease in the radical concentration. The reaction did not take place in the absence of KPS.

Physical Properties

Total nitrogen content of CI_{sps} -graft-PVP which was prepared under optimum reaction conditions was determined and shown in Table I. The nitrogen contents in CI_{sps} and CI_{sps} -graft-PVP were 0.84 ± 0.1 and 6.04 ± 0.2%, respectively, the higher percentage of nitrogen in the grafted product indicated the insertion of PVP.

Apparent viscosities of the grafted copolymer CI_{sps} -graft-PVP and the parent polysaccharide (CI_{sps}) were measured in distilled water (Table I). The CI_{sps} revealed values of apparent viscosities (6.2 ± 2.5 cP) at ambient temperature, while the CI_{sps} -graft-PVP was increasing the apparent viscosity 74.5 ± 3.5 cP (Table I). This finding reflects the increase in the molecular weight of the grafted polysaccharide relative to the parent polysaccharide.

The weight-average molecular weight (M_w) for CI_{sps} -graft-PVP was measured as 560 kDa ($M_w/M_n = 4.55$). This value represented an increase from the initial M_w of CI_{sps} 320.2 kDa, $M_w/M_n = 3.63$). The high polydispersity indices indicated branched, nonhomogeneous structures for the polysaccharide as well as for the grafted copolymer unlike synthetic polymers (Table I).

FT-IR Spectrum

The grafting was confirmed by comparing the IR spectrum of CI_{sps} with that of the grafted products and the results obtained are shown in Figure 5.

Characteristic IR bands at 753, 826, and 870 cm^{-1} for β -skeletal bending of basic carbohydrate moieties in the copolymer indicated that during grafting reaction the polysaccharide did not get decomposed, cf. Refs. [29–32 (Figure 5)]. Appearance of new IR band of carbonyl group (PVP) at 1659 cm^{-1} and additional bands at 1463, 1426, 1370, and 1263 cm^{-1} in the grafted product indicated the insertion of PVP onto the polysaccharide

structure. The broad band at 3435 cm^{-1} was due to stretching of –OH group of CI_{sps} .

¹³C NMR

The ¹³C NMR spectra of CI_{sps} , PVP and CI_{sps} -graft-PVP are depicted in Figure 6. Probable assignments of the carbon resonances were done by comparison of the chemical shifts with the reported values.^{13,30–34} Inspection of the ¹³C NMR spectra revealed a significant clarity of signals in CI_{sps} -graft-PVP as opposed the parent heteropolysaccharides CI_{sps} . This indicated that insertion of PVP caused considerable anisotropy in the polysaccharide molecule showing up clearer signals of anomeric carbons in the product, to mention one, as opposed the parent polysaccharide. There was a downfield shift of C-6 carbon of the pyranose carbohydrate ring of CI_{sps} moiety in the product to 18.8 ppm from 16.5 ppm for that in the parent polysaccharide CI_{sps} . This indicated that presumably in all likelihood the grafting reaction took place on the pendant C-6 carbon of the carbohydrate pyranose ring (see proposed mechanism above; cf. Refs. [26,27]).

¹³C NMR signals of CI_{sps} (125 MHz, D₂O, d₆-DMSO as internal standard; δ ppm): 103.4; 104.8; 105.68 [anomeric carbons of CI_{sps}]; 67.92, 69.95, 70.67, 73.15, 74.19, 75.56, 77.17, 77.78, 79.45, 81.98, 83.64 [methine carbons of the constituting carbohydrate units of CI_{sps}]; 62.02, 66.34 [C-6 of carbohydrate units of CI_{sps}]; 16.5 [C-6 of fucose unit of CI_{sps}].

¹³C NMR signals of PVP (125 MHz, d₆ –DMSO; δ ppm): 44.11 [C-N of PVP]; 176.91 [C-2 of PVP]; 32.80 [C-3 of PVP]; 19.18 [C-4 of PVP]; 46.14 [C-5 of PVP].

¹³C NMR signals of CI_{sps} -graft-PVP (125 MHz, D₂O, d₆-DMSO as IS; δ ppm): 104.8, 103.4 [anomeric carbons of CI_{sps}]; 70.18, 74.49, 75.85, 78.33, 80.53, 82.40 [methine carbons of the constituent carbohydrate units of CI_{sps}]; 63.71, 64.65 [C-6 of carbohydrate units of CI_{sps}]; 18.79 [C-6 of fucose unit of CI_{sps}]; 85.40 [C-N of PVP]; 176.58 [C-2 of PVP]; 32.46 [C-3 of PVP]; 18.79 [C-4 of PVP]; 43.66 [C-5 of PVP].

Thermal Analysis

The TGA thermograms of CI_{sps} and the grafted product are shown in Figure 7. In case of the grafted product CI_{sps} -graft-PVP mass loss took place in three stages, ca.13% between 47 and 217°C, 55% between 220 and 260°C and finally ca. 70% mass loss observed up to 600°C. The initial mass loss (ca. 10%) was presumably due to the loss of water (moisture) bound to the

polysaccharide.³⁵ Nonmodified CI_{sps} significant mass loss took place at 230–360°C (85%; Figure 7) and finally ca. 95% mass loss was observed up to 600°C. The TGA profile suggested that the weight loss of grafted product was smaller but it began to degrade at a lower temperature, confirming that the grafting took place.

Adhesive Property of CI_{sps}-graft-PVP

An adhesive is a material used for holding two surfaces together, which must wet and adhere to the surfaces developing strength after it has been applied, while remaining stable. Polysaccharides with adhesive properties have been eminently reviewed by Smith³⁶ with an accent on biological adhesives.

The PVP grafted product exhibited adhesive property which was determined by comparison of the liquid and solid weights of the copolymer adhesive (CI_{sps}-graft-PVP) and Fevicol (Table II). It appears that the efficacy of the copolymer adhesive was comparable with that of the standard adhesive Fevicol in the same usage level (i.e., solid weight of the adhesives).²⁵ Similar effect was reported by Meena *et al.*¹⁴ using κ -carrageenan-graft-PAAm exhibiting adhesive property. Smith and Stewart *et al.* have opined that adhesion in biological systems arises out of electrostatic interactions between polyanions (sulfated polysaccharides) and participating polycations and or divalent calcium and magnesium ions, which “could bring together the polymers in a complex network consisting of fiber-rich regions and dilute aqueous intervening regions” cf. Refs. [36,37]. This would throw some light on the manifestation of the adhesive functionality of CI_{sps}-graft-PVP, involving the polyanionic nature of CI_{sps} (sulfated) as well as the water absorbing properties of the latter and PVP moieties.

CONCLUSION

Hetropoysaccharides of *Cystoseira indica* (CI_{sps}) containing seven sugar residues were chemically modified by grafting with synthetic polymers for the first time. The grafted product was thermally more stable than the parent polysaccharide. The PVP grafted product exhibited adhesive property comparable to that of a commercially available one. This provides an example of a value added seaweed polysaccharide with potential utility.

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