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Facile preparation of *Chaetomorpha antennina* based porous polysaccharide–PMMA hybrid material by radical polymerization under microwave irradiation

Gayatri Prasad · Kamalesh Prasad · Ramavatar Meena · A. K. Siddhanta

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Abstract A hybrid material was prepared from the hot water soluble sulphated polysaccharide of the green seaweed *Chaetomorpha antennina* (CM_{sps}) and polymethyl methacrylate (PMMA) by radical polymerization in aqueous medium under microwave irradiation. An insoluble material was formed with the progress of the polymerization. The product was characterized by the IR spectrum and elemental analysis, as well as by acid hydrolysis followed by mass spectrum of the hydrolysate of the hybrid CM_{sps}–PMMA for confirming the insertion of PMMA. Comprehensive characterization of the product included TGA, XRD, ESI-MS and BET surface analysis. The hybrid material was porous, and formed gel in water–DMSO mixture. It had the crystallinity index of 0.122, and had BET pore diameter of 3.71 nm, a size which is far larger than the molecular diameters of common natural gases and zeolites (0.5–1.0 nm). This material may be useful in the domain of certain adsorption and catalytic applications.

Introduction

Hybrid materials from natural and synthetic polymers are being extensively investigated in recent times [1, 2]. Grafting of synthetic polymers on to polysaccharides such as dexrtran, starch, chitin, amylose and carrageenan have been reported by several authors [3–9]. Natural polymers such as starch, chitosan, cellulose, carrageenan, dextrin, etc. were blended or cross linked with synthetic polymers to form hydrogels [10–14]; other reports included formation of IPN materials with synthetic materials [15, 16].

Sulphated polysaccharide extracted from *Chaetomorpha antennina* (CM_{sps}) of Indian waters is reported to consist of 4-linked arabinose, 4- and 3- linked galactose and 4-linked rhamnose residues [17]. Polymethylmethacrylate (PMMA) is a very important macromolecule and it is useful in diverse applications, e.g., in preparing conducting gels, in micro chips, in enzyme immobilization, bone cement and as micro/nano-electromechanical systems (MEMS/NEMS) in biological applications [18–23]. Although there are some reports of preparation of hybrid material from some seaweed polysaccharides, this particular seaweed polysaccharide has not been harnessed for the preparation of any materials so far. We report herein the facile preparation of a new CM_{sps}–PMMA porous hybrid material by radical polymerization of the polysaccharide with methyl methacrylate monomer using microwave irradiation.

Experimental

Materials

Chaetomorpha antennina (Bory) Kuetz was collected from Diu (20°45′ N, 70°58′E) in west coast of India on 30 April 2005. A herbarium specimen (AL-II-70-01) has been deposited with the CSMCRI, Herbarium. The hot water soluble sulphated polysaccharide was extracted following the method described by Siddhanta et al. [24]. The polysaccharide was vacuum dried prior to reaction. Potassium persulphate, methyl methacrylate, isopropanol, toluene used were of analytical grade and were purchased from

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G. Prasad · K. Prasad · R. Meena · A. K. Siddhanta (✉)
Marine Biotechnology and Ecology Discipline, Central Salt & Marine Chemicals Research Institute, Council of Scientific & Industrial Research, Gijubhai Badheka Marg, Bhavnagar, Gujarat 364 002, India
e-mail: aks@csmcri.org

Sigma-Aldrich, Mumbai, and Ranbaxy Chemicals, Mumbai, respectively.

Preparation of the hybrid material CM_{sps}–PMMA

A MILESTONE -START *S* microwave lab station for synthesis was used (fixed frequency of 2,450 MHz) over set temperature parameters to prepare the hybrid material CM_{sps}–PMMA. This instrument has the programming facility to set the constant temperature and required reaction time.

The reaction was carried out in a 100 mL narrow-mouth conical flask. CM_{sps} (1 g w/v, 3.22 mmol as per repeating arabinopyranose–galactopyranose repeating unit, the molecular weight was ca. 1.12×10^5 D) was first dissolved in 100 mL of distilled water followed by the addition of methyl methacrylate (3.10–7.76 per mole equivalents of CM_{sps}) and 0.00037 mol/L of potassium persulphate. The mixture was then irradiated under microwave at set temperature 100 °C. The set temperature 100 °C was achieved in 1 min and sustained for remaining 1.5 min to carry out our reaction. The used microwave instrument has inbuilt magnetic stirrer and the reaction mixture was continuously stirred throughout the course of reaction. The reaction mixture turned milky white, presumably due to the polymerization of MMA to PMMA, which was first cooled and the product was precipitated in isopropyl alcohol (1:2.25, v/v), followed by centrifugation at 8000 rpm for 3 min. The off-white precipitate was collected and air dried. The unreacted homopolymer (PMMA) was extracted from the product by Soxhlet extraction with toluene for 1 h. The product was further washed with isopropyl alcohol and vacuum dried. The toluene was evaporated and weight of unreacted PMMA was calculated. The hydrogel of the hybrid material was prepared in DMSO–water mixture (1:5 v/v) by heating at ca. 80 °C. The product obtained by using CM_{sps}/MMA as 1:6.20 was solid in nature, very stable unlike those obtained using the proportions 1:3.09 and 1:4.68, which were not solid and was heterogeneous as observed under microscope. The yield of the product obtained with 1:6.46 (CM_{sps}/MMA) was low. Hence the product obtained by the optimized molar ratio (1:6.20) of CM_{sps} and MMA was used for further characterization. The schematic pathway for the formation of the material is shown in Fig. 1.

Preparation of a physical mixture of CM_{sps} with PMMA

To a viscous solution of CM_{sps} (1 g) in 50 mL water, MMA was added in a molar ratio of 1:6.20 and the mixture was heated under microwave irradiation for 150 s followed by isolation as described above.

Characterization

Grafted hybrid product was characterized by FT-IR using a Perkin-Elmer Spectrum GX FT-IR system, by taking 10.0 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}. The TGA of the parent polysaccharide (10 mg) and its hybrid material (11.4 mg) were carried out on a Mettler Toledo, TGA/SDTA 851^e system, using a

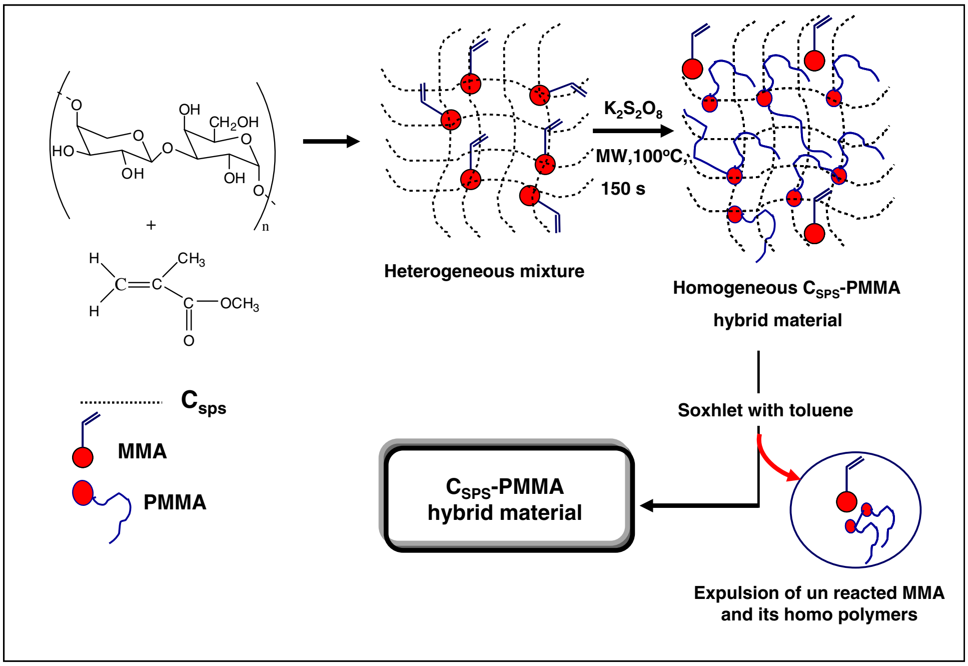


Fig. 1 Schematic presentation of the formation of CM_{sps}–PMMA hybrid material by free radical polymerization

temperature program 30–600 °C at a heating rate of 10 °C min^{-1} in an air atmosphere. Powder X-ray diffractions were measured on a Philips X'pert MPD X-ray Powder Diffractometer using $2\theta = 5$–$60°$. For optical rotation measurements polysaccharides and its grafted product (0.2 g) was dissolved in distilled water (100 mL) and specific rotation was measured at 589 nm at 30 °C on a Rudolph Digi pol-781 Polarimeter (Rudolph Instruments Inc, NJ, USA). The specific surface area, pore volume and pore size distribution of the samples were determined from N_2 adsorption–desorption isotherms at 77.54 K using volumetric equation adsorption equipment (ASAP 2010, MicroMetrics, NH), using BET and BJH models. The dried samples were mounted on a sample holder and coated with gold for SEM analysis using a scanning electron microscope (Model Carl-Zeiss Leo VP 1430) at an accelerating voltage of 20 kV. ESI-MS experiments were performed on a Q-Tof micro YA-260 (Micromass, USA) tandem quadruple-orthogonal Tof instrument, fitted with a lock spray source using Waters Mass Lynx Version 4.0 software. Circular dichroism (CD) spectra were recorded on a JASCO model J-815 CD Spectrometer, in the range 190–250 nm using sample concentration of ca. 0.8 mg/mL (800 ppm). Molar ellipticity values, (θ) are reported in units of deg cm^2 dmol^{-1}. All measurements were performed at room temperature using 1.0 cm quartz cells.

ESI-MS and MS/MS experiments were carried out with synthesized PMMA as well as with that extracted from the hydrolyzed hybrid material using an electro spray positive mode (ES^+). PMMA standard for comparison was synthesized by polymerizing MMA in water in the presence of KPS with microwave irradiation for 10 s. The hybrid material was hydrolyzed in 70% aqueous sulphuric acid for 1 h at 80 °C. The PMMA was then extracted in toluene; the toluene extract was evaporated to dryness. Finally both the PMMA samples were dissolved in methanol by sonication prior to mass spectra recording. These experiments were done to confirm that the hybrid material actually consisted of PMMA. The microwave lab station (Milestone, START-S) was used to synthesize the hybrid material, which used a specific fixed frequency of 2,450 MHz (2.45 GHz).

Results and discussion

Preparation of $\mathrm{CM_{sps}}$–PMMA hybrid material

The hybrid material prepared using $\mathrm{CM_{sps}}$ and MMA in molar ratio 1:6.20 was obtained in 91% yield followed by 66%, 53% and 42% yields from 1:4.68, 1:3.09 and 1:6.46 molar ratios, respectively. This material was subjected to FT-IR; appearance of carbonyl band at 1732 cm^{-1} (ester carbonyl stretching) indicated the presence of PMMA in the material. The physical mixture of the polysaccharide and PMMA after Soxhlet extraction with toluene yielded only the polysaccharide as the whole lot of PMMA present was extracted (IR). This lends support to the formation of the hybrid product. Apart from the carbonyl band, appearance of the characteristic IR bands at 829, 753, 996 cm^{-1} (β-skeletal bending of basic carbohydrate moieties) in the hybrid material indicated that during the reaction the polysaccharide did not get decomposed (Fig. 2).

The PMMA was extracted and subjected to ESI-MS and MS/MS. The electro spray ionization mass spectra (ESI-MS^+) of PMMA were dominated by doubly charged ions, with relatively lower abundance of singly charged ions [25] (Fig. 3). The ESI-MS fragmentation patterns for synthesized PMMA and PMMA extracted from the hydrolyzed hybrid material were similar confirming the presence of PMMA in material. The ESI-MS/MS fragmentation of *m/z* at 223.2370 of synthesized PMMA was similar to that with PMMA extracted from hydrolyzed hybrid material at *m/z* 223.25.

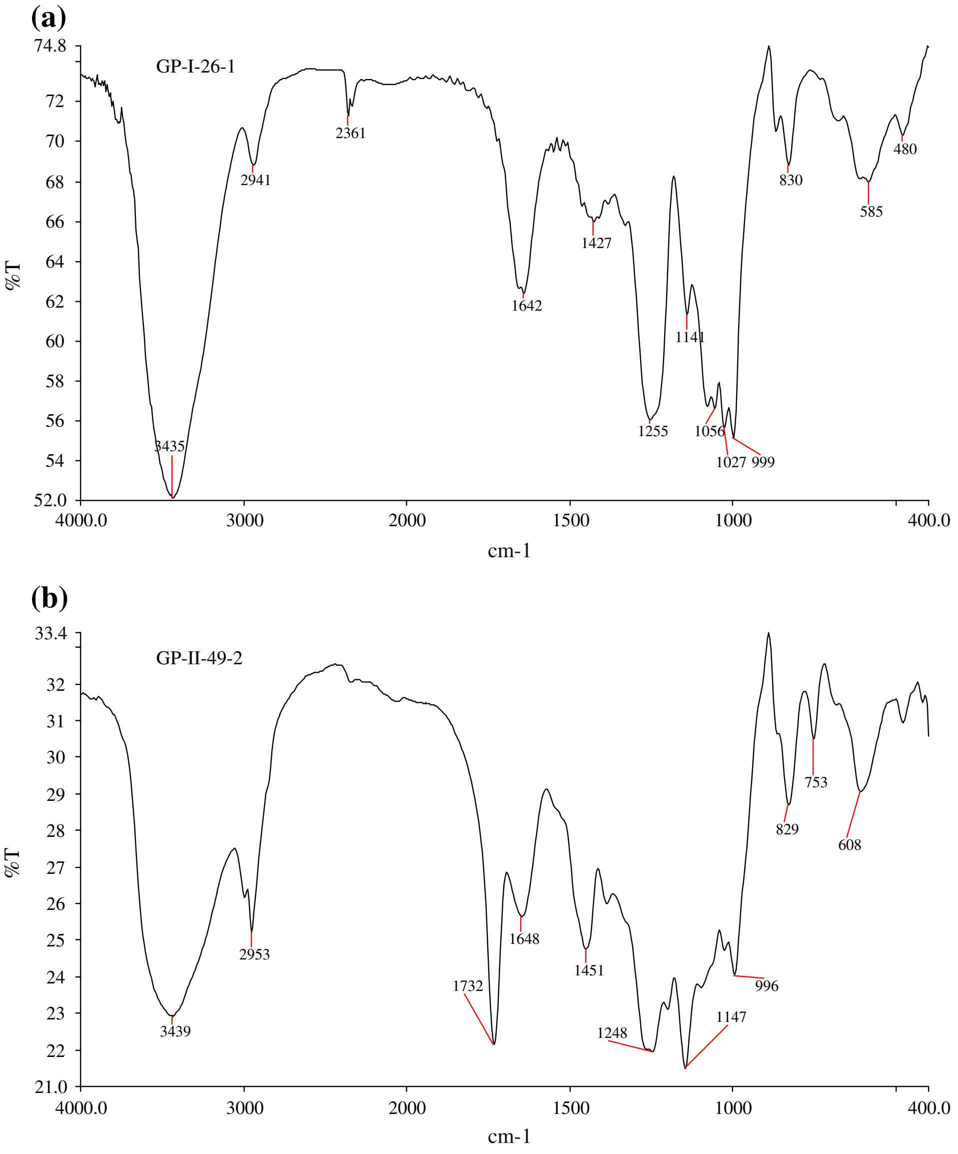
Thermal analysis

The thermograms of $\mathrm{CM_{sps}}$, hybrid material and the physical mixture of $\mathrm{CM_{sps}}$ and PMMA are shown in the Fig. 5a, b and c, respectively. In case of the hybrid material the degradation took place in two steps. The major weight loss took place in the temperature range 220–455 °C (60%; Fig. 4b). The initial weight loss (ca 10%) may be due to the loss of bound water. On the other hand, for the parent polysaccharide ($\mathrm{CM_{sps}}$) significant mass loss took place at 210–450 °C (80%; Fig. 4a), which is different from that of the hybrid material, similarly physical mixture showed a different major weight loss pattern (Fig. 4c). It is evident that PMMA has indeed influenced the thermal property of the hybrid material indicating thereby the formation of a new compound with altogether different structure [cf. 26]. Expectedly the thermogram of hybrid material (Fig. 4b) traced a middle path between the parent polysaccharide ($\mathrm{CM_{sps}}$) and the physical mixture, indicating thereby that the thermal stability of hybrid is more than the parent polysaccharide and less than the physical mixture which virtually is PMMA.

X-ray diffraction analysis

The X-ray diffraction patterns of the parent polysaccharide ($\mathrm{CM_{sps}}$) and its hybrid material are shown in Fig. 5. The X-ray diffraction pattern of $\mathrm{CM_{sps}}$ showed that it was amorphous in nature, but the hybrid material with PMMA exhibited three distinct sharp peaks (at $2\theta = 28.14°$, $29.83°$ and $31.16°$). This indicated that the polysaccharide was substantially modified imparting enhanced crystallinity in the hybrid material. Enhanced crystallinity suggested ordered molecular arrangement [8]. The crystallinity index

Fig. 2 FT-IR spectra of **a** CM_{sps} and **b** CM_{sps}–PMMA hybrid material



(C.I.) of the grafted product was determined using the following equation described by Herman and Weidinger [27].

$$\text{C.I.} = \text{Area of crystalline Peak}/[\text{Area of crystalline peak} + \text{Area of amorphous peak}]$$

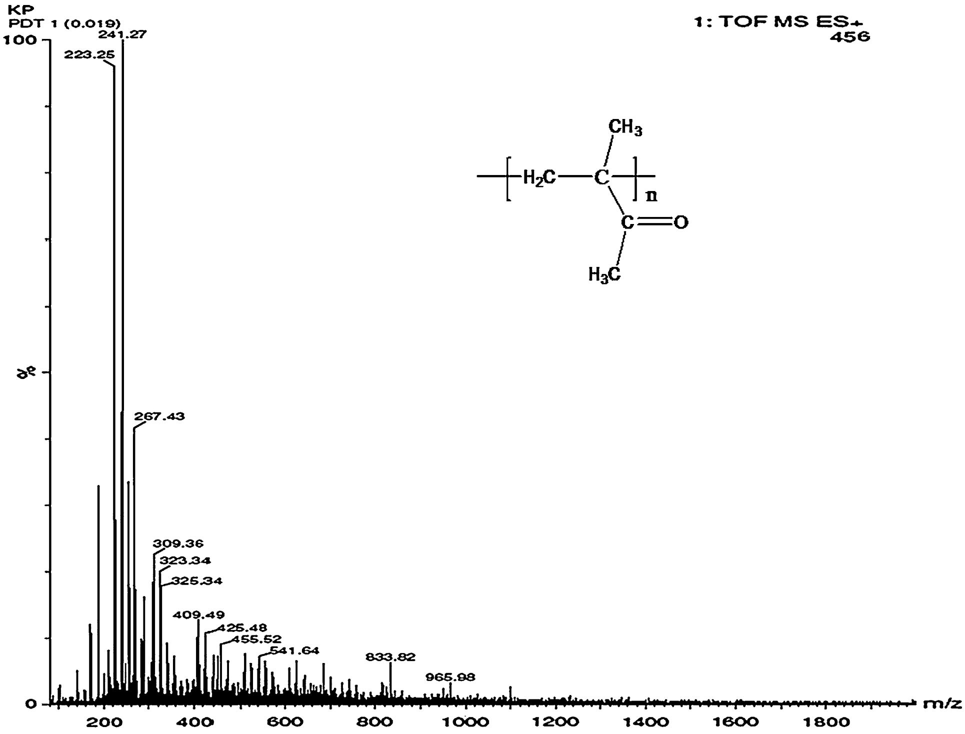
The C.I. value calculated for the hybrid material was 0.122 and the control polysaccharide was amorphous (Fig. 5). This suggests that, the polymerization reaction has brought about reorganization in the symmetry profiles of the parent polysaccharide inducing orderliness in the molecular architecture.

Circular dichroism

The CD spectra of non-modified CM_{sps}, were in the entirely negative region (peak 194.5 nm, (θ) −282.46 and trough 199 nm, (θ) −1562.66). However, CM_{sps}-*graft*-PMMA showed a mixed pattern having positive and negative bands (peak 197.9 nm, [θ] +10.07 and trough 201.9 nm, [θ] −32.5).

If the ratio of peak height to trough depth in CD spectrum were <1, overall composition of any compound will show negative CD spectrum (i.e., peak/trough <1). When the spectrum crosses the baseline, then the overall composition shows entirely positive spectrum (i.e., peak/trough >1) [28–30]. The use of the peak-to-trough analysis has been gainfully used to describe conformational changes that occur within polymers or modified polymers with varied chain lengths [31]. The presence of molecules or substance in parent compound, able to induce conformational changes in the polymeric chain under appropriate physical conditions, leads to a more or less pronounced change in the mol. ellipticity versus wavelength [30]. The peak-to-trough analyses were observed for CM_{sps} (0.81),

Fig. 3 ESI-MS spectra of PMMA extracted from the hybrid material



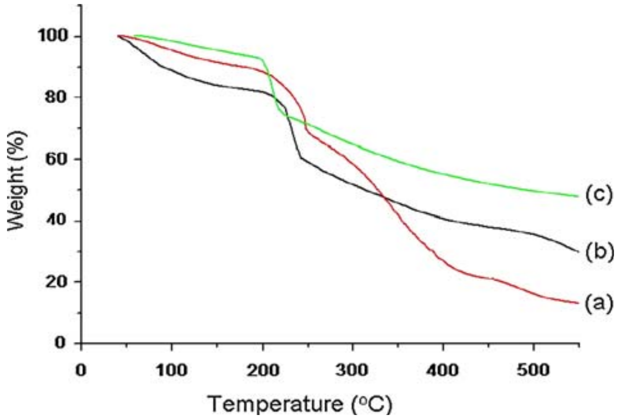


Fig. 4 TGA thermograms of (*a*) CM_{sps}, (*b*) CM_{sps}–PMMA hybrid material and (*c*) physical mixture of CM_{sps} and PMMA

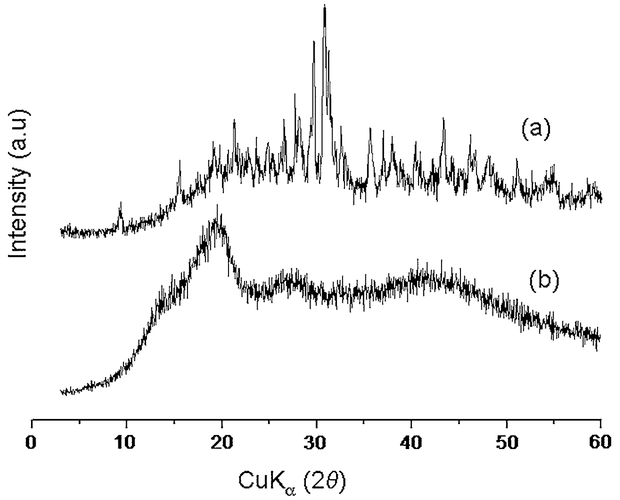


Fig. 5 XRD profile of (*a*) CM_{sps}–PMMA hybrid material and (*b*) CM_{sps}

i.e., peak/trough <1, whereas for CM_{sps}–PMMA (1.23), i.e., peak/trough >1. The CD spectrum and the peak-to-trough analysis indicated a reversal of chiroptical profiles that took place after insertion of PMMA onto the parent polysaccharides leading to alteration of symmetry elements. The overall chiral configurations of the parent polysaccharides have been deduced to be L for CM_{sps} by virtue of peak/trough ratios in the CD spectra [28–30].

Morphology by SEM and N_2 adsorption–desorption isotherms

The SEM image of the polysaccharide and the product is shown in Fig. 6. In the hybrid, PMMA has canopied the polysaccharide and presented a different morphology (Fig 6b). It is of interest to note that the presence of some pores in the hybrid material had average diameter of 110–150 nm (shown in oval). The pore diameter and surface area was further calculated by the studies employing N_2 adsorption–desorption isotherms using BET and BJH models (Table 1). It can be seen from the table that the hybrid material has significantly low surface area and pore diameter in comparison with those of the polysaccharide indicating formation of material having different molecular arrangements due to graft-polymerization. Presence of

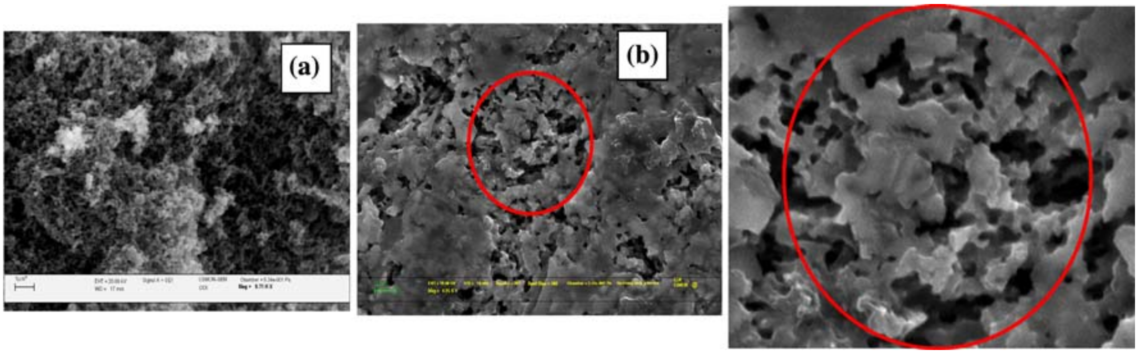


Fig. 6 SEM image of **a** CM_{sps} and **b** CM_{sps}–PMMA hybrid material [pores are shown in oval in (**b**)]

Table 1 Surface area and pore diameters of CM_{sps} and CM_{sps}–PMMA

Sample	Surface area (m^2/g)			Pore diameter (nm)		
	BET	BJH adsorption	BJH desorption	BET	BJH adsorption	BJH desorption
CM_{sps}	8.47	3.41	6.41	9.23	64.15	35.01
CM_{sps}–PMMA hybrid material	1.96	1.14	2.04	3.71	6.674	3.807

the pores of diameter 3.71 nm (BET), 6.674 nm (BJH-adsorption) and 3.807 nm (BJH-desorption), further supports the formation of the porous hybrid material. Lowering the surface area of the hybrid material in comparison to the control polysaccharide indicates the role of PMMA to form material with different property.

It may be noted that the BET pore diameter of the hybrid material 3.71 nm (Table 1), which is far larger than the molecular diameter of common natural gases and adsorbents, such as oxygen (0.29 nm), nitrogen (0.31 nm), CO_2 (0.28–0.34 nm), NO_x gases (<0.5–1.0 nm), preferred zeolites (0.5–1.0 nm) [32], CH_4 (0.29–0.38 nm) [33, 34]. Therefore, this porous hybrid material which is crystalline and has large pore diameter may be of potential utility.

Conclusion

A rapid and water-based synthesis of a porous hybrid material consisting of sulphated polysaccharide of the green seaweed *Chaetomorpha antennina* and polymethyl methacrylate has been achieved using microwave irradiation for effecting radical polymerization. The analytical data of the hybrid, e.g., IR spectrum, thermal analysis, circular dichroism, X-diffraction and SEM imaging as well as the mass fragmentation analysis of the hydrolyzed product confirmed that the product was composed of the polysaccharide and polymethyl methacrylate. Furthermore, the hybrid material has shown enhanced crystallinity (C.I. 0.122), forms weak gel in water-DMSO (5:1) and was partially hydrophobic, compared to the amorphous parent polysaccharide (CM_{sps}). The large pore diameter of the material coupled with its crystallinity makes it a likely candidate to be harnessed in the domain of certain adsorption and catalytic applications.

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References

1. Crescenzi V, Paradossi G, Desideri P, Dentini M, Cavalieri F, Honici E (1997) Polym Gels Netw 5:225
2. Kaneko Y, Kadokawa J (2005) Chem Rec 5:36
3. Hoffmann H, Kästner U, Dönges R, Ehrler R (1996) Polym Gels Netw 4:509
4. Kobayashi K, Tsuchida A, Usui T, Akaike T (1997) Macromolecule 30:2016
5. Van Dijk-Wolthuis WNE, Kettenen-Vanden Bosch JJ, Van der Kerkvan Hoof A, Hennink WE (1977) Macromolecules 30:3411
6. Kaneko Y, Beppu K, Kadokawa J (2008) Macromol Chem Phys 209:1037
7. Kadokawa J, Nakamura Y, Sasaki Y, Kaneko Y, Nishikawa T (2008) Polym Bull 60:57
8. Prasad K, Meena R, Siddhanta AK (2006) J Appl Polym Sci 101:161
9. Meena R, Prasad K, Siddhanta AK (2006) J Appl polym Sci 102:5144
10. Kennedy JP, Fenyvesi G, Keszler B, Rosenthal KS (2003) ACS Symp Ser ACS Washington 833:290
11. Lee YM, Kimt SH, Kimt SJ (1996) Polymer 37:5897
12. Hwang D, Damodaran S (1996) J Appl Polym Sci 62:1285
13. Prasad K, Mehta G, Meena R, Siddhanta AK (2006) J Appl Polym Sci 102:3654

14. Ramaraj B, Radhakrishnan G (1994) J Appl Polym Sci 52:837
15. Cerrai P, Guerra GD, Tricoli M, Maltinti S, Barbani N, Petarca L (1996) Macromol Chem Phys 197:3567
16. Chavasit V, Kienzle-Sterzer C, Torres JA (1988) Polym Bull 19:223
17. Rao EV, Ramana KS (1991) Carbohydr Res 217:163
18. Sharma JP, Sekhon SS (2006) Mater Sci Eng B 129:104
19. Liu D, Zhou X, Zhong R, Nannan Y, Chang G, Xiong W, Mei X, Lin B (2006) Talanta 68:616
20. Li S, Hu J, Liu B (2004) Biosystems 77:25
21. Kim SB, Kim YJ, Yoon TL, Park SA, Cho IH, Kim EJ, Kim IA, Shin J-W (2004) Biomaterials 25:5715
22. Stańczyk M (2005) J Biomech 38:1397
23. Tambe NS, Bhushan B (2005) Ultramicroscopy 105:238
24. Siddhanta AK, Goswami AM, Ramavat BK, Mody KH, Mairh OP (2001) Indian J Mar Sci 30:166
25. Jackson AT, Slade SE, Scrivens JH (2004) Int J Mass Spectrom 238:265
26. Murakami M, Kaneko Y, Kadokawa J (2007) Carbohydr Polym 69:378
27. Herman PH, Weidinger A (1948) J Appl Phys 19:491
28. Morris ER, Rees DA, Sanderson GR, Thom D (1975) Chem Soc Perkin Trans 2:1418
29. Morris ER, Rees DA, Thom D (1980) Carbohydr Res 81:305
30. Dentini M, Rinaldi G, Barbetta A, Risica D, Skjak-Bræk G (2006) Carbohydr Polym 63:519
31. McReynolds KD, Gervay-Hague J (2000) Tetrahedron Asymmetry 11:337
32. Yuejin Li, Armor JN (1992) US Patent 5149512
33. Sloan ED (1998) Energy Fuels 12:191
34. Szotak R (1993) Technical Report OSTI, ID-6776784, Georgia Tech Res Institute, Atlanta, GA, USA (www.osti.gov/energycitations)