Non-ionic surfactant mediated preparation of κ-carrageenan/calcium carbonate biocomposite

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Received 19 December 2011; revised and accepted 14 July 2012

Non-ionic surfactants mediated biocomposites of κ-carrageenan have been prepared by incorporating CaCO₃ particles generated in situ under microwave heating. The CaCO₃ particles generated in presence of a sugar surfactant (SUC-PEO) has near spherical shape in comparison to that prepared in presence of Brij 35. The products have been characterized for their thermal stability, swellability in aqueous medium, crystallinity and microstructures. Reasonable degree of porosity is introduced in the biocomposites by chelating out CaCO₃ particles using EDTA.

Keywords: Composites, Biocomposites, Calcium carbonate, Surfactants, Thermal stability, Swellability, Microstructures, Porosity

Hybrid inorganic/organic materials comprise a new class of functional composites that demonstrate enhanced thermal and mechanical properties due to the synergistic effects resulting from the physical and chemical interactions occurring between the components. There are a number of examples for fabrication of biocomposites using inorganic materials like carbon, graphite, alumina, calcium carbonate, etc., and polylactic acid, polylactides, polymethylmethacrylate, etc., for biomedical applications. The major drawbacks are the toxicity and inferior biodegradability of certain biocomposites. Hence, there is a need for the use of bio-mass derived substrates as a source to prepare biomaterials.

There are many reports for preparation of bio-based materials using very popular natural polymers such as cellulose, starch, chitosan, etc. Seaweeds are also a very good source of various useful chemicals including polysaccharides, and due to advantages such as successful cultivation, cheap, easy harvestings, etc., are viewed as a potential renewable bioresource to prepare various biomaterials. κ-Carrageenan is a water soluble, commercially important phycocolloid extracted from red algae and is used mostly as stabilizers and structure providers in food, ice-cream and pharmaceutical industries. It consists of alternating 1,3-linked α-D-galactopyranose (Gal) and 1,4-linked β-3,6-anhydro-D-galactopyranose (3,6-AGal). Three varieties of carrageenans are known, viz., κ-, τ- and λ-, which differ in the number and position of sulphate groups on the repeating galactopyranose units. κ-Carrageenan has one negative charge per disaccharide unit, while τ- and λ-carrageenans have 2 and 3 negative charges per disaccharide unit respectively. Due to the presence of the negative charges, the carrageenans have an affinity for binding to inorganic cations.

In this study we have prepared biocomposites of carrageenan with CaCO₃ generated in situ by the reaction of calcium acetate and sodium carbonate (Scheme 1) in presence of surfactants instead of

![Scheme 1](image-url)
directly incorporating CaCO₃ particles in the polymer networks. The CaCO₃ particles thus formed were removed by EDTA giving rise to a porous polymer structure. The induction of porosity in the polymer matrix can be considered as one of the many ways to prepare new functional materials based on polysaccharides for possible applications in bio-catalysis, bio-sensing, and bio-separation.

**Experimental**

Refined κ-carrageenan was extracted from *Kappaphycus alvarezii* following the method reported by Craigie & Leigh. The weight average molecular weight (MW) of the polymer was 300,000 Da. Ca(CH₃COO)₂, Na₂CO₃, and Brij 35 were purchased from S D Fine chemicals, Mumbai and the sucrose based surfactant (SUC-PEO) was synthesized following the method described by Prasad et al. All the chemicals were used as received without further purification. Microwave system used was Star-S Microwave Synthesizer, Milestone, Italy.

κ-Carrageenan (1 % w/v; 25 mL) was prepared by dissolving refined κ-carrageenan (κC) powder in boiling distilled water followed by the addition of 2.89 mL (0.7 M) aqueous solution of Ca(CH₃COO)₂ followed by the addition of 3.6 mL of Na₂CO₃ solution (0.5 M) in the presence of ethylene glycol and surfactants (SUC-PEO and Brij 35) under microwave heating at 100 °C for 3 min. The mixture thus obtained was freeze dried to get the biocomposite. In order to study the particle size of CaCO₃ particles in a control experiment, the particles were also generated by mixing A and B under microwave heating at 100 °C for 3 min, in the absence of κ-carrageenan. Although, formation of nano sized CaCO₃ particles has been reported by this method, we were able to prepare CaCO₃ particles having ca. dia. 1-4 µm. It was observed that the CaCO₃ particles formed using the surfactant SUC-PEO was spheroid in shape (Fig. 1a) in comparison to that prepared using Brij 35 (Fig. 1b). The spheroid shape was generated presumably due to the higher degree of hydrophilicity of the sugar surfactant. The biocomposite formed in presence of the sugar

![Fig. 1—SEM micrographs of CaCO₃ particles prepared in presence of (a) SUC-PEO, and, (b) Brij 35.](image-url)
surfactant was subjected to detailed characterization. The SEM micrograph of the surface of the corresponding \( \kappa \text{C/CaCO}_3 \) biocomposite is shown in Fig. 2. An irregular distribution of \( \text{CaCO}_3 \) particles can be seen on the surface of the composite. It was observed that the diameter of the \( \text{CaCO}_3 \) particles present on the surface was in the range of 200 - 500 nm, which were smaller in size in comparison to the control particles prepared without using the \( \kappa \)-carrageenan solution (1- 4 \( \mu \)m), indicating the role of carrageenan on the size of the particles. It should further be noted that the morphology of the \( \text{CaCO}_3 \) particles present on the carrageenan biocomposite surface were also different in comparison to Fig. 1a. The EDTA treatment further chelates out the \( \text{CaCO}_3 \) particles (white spots), but the chelation was not complete due to the presence of \( \text{SO}_3^2- \) groups at C-4 position of \( \kappa \)-carrageenan and hence only thinly scattered footprints of pores can be seen (Fig. 3). Furthermore, the removal of irregular clustered shaped \( \text{CaCO}_3 \) particles gave rise to a relatively more unevenly porous surface morphology. However, pores can be clearly seen in the SEM micrographs of cross section of the biocomposite, indicating the degree of penetration of \( \text{CaCO}_3 \) particles inside the three dimensional network of the polysaccharide (Fig. 4). The dimensions of the pores were in the range of 200 - 300 nm. Since the polysaccharide has large three dimensional structures the porosity developed was not enough to penetrate the complete structure, instead it is formed on the surface and the sub-surface as shown in Scheme 1. The apparently meandering porous structure was further supported by the low surface area found.
in the BET analysis (Fig. 5 & Supplementary data Table S1). Generally, for inorganic porous material, the surface area is quite high due to relatively greater adsorption of N\textsubscript{2}. The EDTA treatment of the physical mixture of \kappaC and CaCO\textsubscript{3} completely chelates out CaCO\textsubscript{3} and no cross-sectional porous structure was observed in the SEM micrographs for the samples. Chelating out of CaCO\textsubscript{3} from the composite by EDTA, which is well known chelating agent for Ca\textsuperscript{2+}, further confirms presence of CaCO\textsubscript{3} particles in the biocomposite. The cross-sectional SEM picture of the physical mixture of \kappa-carrageenan and CaCO\textsubscript{3} after chelating out Ca\textsuperscript{2+} by EDTA did not show any white particles confirming chelation of Ca\textsuperscript{2+} by EDTA from polysaccharide matrices (Supplementary data Fig. S1).

In order to study the effect of CaCO\textsubscript{3} on the thermal properties of \kappa-carrageenan in the biocomposite, the TGA of the biocomposite along with pure \kappaC and physical mixture of \kappa-carrageenan and CaCO\textsubscript{3} (P\textsubscript{mix}) was performed (Fig. 6). About 3-12 \% moisture was observed for pure \kappaC and P\textsubscript{mix}, while on the other hand the biocomposite shows distinctly lower moisture (2 - 4 \%) indicating binding of CaCO\textsubscript{3} particles with the \kappaC resulting in decrease of moisture sensitivity of the composite. It was also observed that between 100 °C and 200 °C the decomposition of the biocomposite remained to 4 \%, in contrast to that of pure \kappaC and P\textsubscript{mix}, where the decomposition was 14 \% and 12 \% respectively, representing higher thermal stability of the composite in comparison to the other samples under investigation. Furthermore, there was 30 \% thermal decomposition of the biocomposite beyond 240 °C in comparison to 35 \% and 45 \% of P\textsubscript{mix} and pure \kappaC respectively, indicating binding of CaCO\textsubscript{3} with \kappaC further supports the SEM observations discussed above. Figure 7 shows the XRD patterns of the biocomposite along with these of pure \kappaC and CaCO\textsubscript{3} synthesized herein. Characteristics peaks for CaCO\textsubscript{3} can be seen at 2\theta values of 24° and 30°, which are also present in the biocomposite, indicating the presence of CaCO\textsubscript{3} particles in the composite. On the other hand, pure \kappaC shows an amorphous behavior with a sharp peak at 42° due to the presence of potassium ion\textsuperscript{9}. It is interesting to note that, the potassium peak was absent in the biocomposite, presumably due to the ionic exchange between Na\textsuperscript{+} (formed as CH\textsubscript{3}COONa during reaction of Ca(CH\textsubscript{3}COO)\textsubscript{2} and Na\textsubscript{2}CO\textsubscript{3}) and K\textsuperscript{+} further, supporting the labile nature of the potassium observed previously\textsuperscript{9}. In addition to this, the ash obtained from the biocomposite showed presence of Ca\textsuperscript{2+} by inductively coupled plasma mass spectrometry (data not shown) further confirming presence of CaCO\textsubscript{3} particles in the biocomposite. The absence of other less intense crystalline peaks of CaCO\textsubscript{3} in the biocomposite is probably due to the overwhelming amorphous structure of the polysaccharide.

Substantial decrease in the swellability (48 \%) in water of the biocomposite was observed as compared with that of pure \kappaC, indicating insertion of CaCO\textsubscript{3} particles inside the polysaccharide network affecting the three dimensional swelling phenomenon (Fig. 8). It can be seen from Fig. 8 that pure \kappaC is almost...
totally dispersed in water after 20 min of residency, while the biocomposite is not dispersed completely and was isolable from the media. Low swellable biocomposites are important in the applications in the domain of water purification. In the present study preparation and characterisation of sugar surfactant (SUC-PEO) mediated CaCO₃ impregnated biocomposite based on κ-carrageenan has been described. The CaCO₃ particles inside the biocomposite are spheroid in shape. This biocomposite is thermally more stable and less aqueous swellable than κ-carrageenan. A reasonable degree of porosity is introduced in the biocomposite by chelating out CaCO₃ particles. Such biocomposites may find applications in catalysis and adsorption chemistry wherein their biodegradability will be a welcome attribute.

**Supplementary data**

Supplementary data associated with this article, viz., Table S1 and Fig. S1, are available in the electronic form at http://www.niscair.res.in/jinfo/iJCA/iJCA 51A(08) 1085-1089_Suppl Data.pdf.

**Acknowledgement**

Department of Science & Technology, GOI, New Delhi, India, is gratefully acknowledged for financial support (FAST track young scientist project to KP). SK acknowledges Ministry of Earth Sciences, GOI, New Delhi, India, for the award of Senior Research Fellowship (MoES/9-DS/6/2007-PC IV; dated March 5, 2008).

**References**