



Morphology modification in freshly Precipitated Calcium Carbonate particles using surfactant-polymer template



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ABSTRACT

Morphology study of synthesized Precipitated Calcium Carbonate (PCC) is done using calcined dolomite (CaO.MgO). These PCC nano-composites were fabricated at ambient temperature using surfactant-polymer template: cationic surfactant cetyltrimethylammonium bromide (CTAB) with different polymers *viz.*, polyvinyl alcohol (PVA), polyvinyl acetate (PVAc) and polyethylene glycol (PEG). In this work, we report the systematic characterization of the modified crystals using these templates by spectral, diffraction, scattering and microscopy techniques. Results obtained provide a reasonable explanation to the influence of the polarity of the polymer on to the templated nucleation where the inclusion of such molecules within the crystal lattice of the host growing crystal influences the overall crystal morphology. Scattering measurements further confirms and compliments the structural changes occupying in calcium carbonate particles with our microscopic findings.

1. Introduction

Dimension of CaCO₃ particles ranging in nanometer to micrometer scale hold an important class of materials because of their distinctive structural, optical and surface properties which promote them widely in the arena of industrial applications [1]. Precipitated Calcium Carbonate (PCC) occurs in three crystalline polymorphs: calcite, aragonite and vaterite [2]. Out of which the former is thermodynamically most stable and industrially important polymorph of CaCO₃ while aragonite is moderately stable and the vaterite is the least [3]. Amorphous calcium carbonate (ACC) is unsteady at initial stage of PCC formation and further transforms into a composition of crystalline calcium carbonates with several beautiful morphologies *viz.*, rhombic calcite, needle-like aragonite, spherical/flower-like vaterite and tetrahedral dolomite. However these resultant polymorphs of crystalline CaCO₃ are pH, and temperature dependent [4].

Reported studies have revealed that the properties of CaCO₃ particles get greatly influenced and controlled in the presence of functional organic additives/modifiers if present in the crystallizing solution. Following early demonstrations of crystal growth by oriented assembly, this subject was extended to persuade the crystallization process by selective adsorption on crystal surface, and thereby altering the overall crystal morphology and/or the crystallizing phase [5]. Self-assemblies of molecules like polymers, surfactants, surfactant/polymer mixed systems and other organic additives are mentioned to be employed to explore the aggregation-based crystallization with better

mechanical properties. In particular, use of polymer-surfactant supra-molecular mixtures as template in designing and modifying the morphology, nucleation, growth and polymorphs of CaCO₃ offer an excellent opportunity for tailoring the crystal aggregates and thus tune the physico-chemical and mechanical properties which has become an intense field of research interest [6,7].

In this article we look critically to understand the formation of different morphologies of CaCO₃ using sodium carbonate and calcium chloride through precipitation reaction at controlled temperature. In order to tailor made the morphology using surfactant-polymer templates; we have chosen cationic surfactant CTAB with several polymers varying in the degree of polarity *viz.*, polyvinyl alcohol (PVA), polyethylene glycol (PEG), and polyvinyl acetate (PVAc). Here PVA being atactic material is water soluble and exhibit crystallinity while PEG is polyether crystalline compound and PVAc is an aliphatic rubbery synthetic polymer having poor water solubility. It was observed that the surfactant-polymer template interacts with the nascent growing CaCO₃ crystals very specifically and thus the templated nucleation of the desired Precipitated Calcium Carbonate (PCC) results due to the inclusion of small molecules within the crystal lattice of the host growing crystal, thereby controlling the crystallization mechanism and ultimately influencing the morphology. We have performed a systematic characterization to validate the correct synthesis, nucleation and morphology of nanostructures crystals.

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2. Experimental section

2.1. Materials

Cetyltrimethylammonium bromide (CTAB) (purity > 99.5%), Polyvinyl glycol (PEG), Polyvinylalcohol (PVA), Polyvinylacetate (PVAc) were of analytical grade.

2.2. Synthesis

2.2.1. Preparation of calcium succrate from dolomite

The calcium succrate solution which is used to synthesize PCC is prepared by the addition of 10 g calcined dolomite ($\text{CaO} \cdot \text{MgO}$) to 1 M sucrose solution (100 mL). During this synthesis, the MgO component of calcined dolomite gets precipitated out in unreacted form while the CaO transmute into dissolved calcium succrate solution which is collected by filtration [8,9].

2.2.2. Synthesis of Precipitated Calcium Carbonate (PCC)

Polymers viz, PVA, PEG and PVAc were used with CTAB to prepare the surfactant-polymer templates in which solution containing 1.3 mM CTAB and 1 g/L polymer concentration are mixed to prepare 80 mL solution. The mixture was stirred for 1 h to form the surfactant-polymer template. Further equal volume of calcium succrate and sodium carbonate solutions (concentration 1 M each) were poured simultaneously to the template solution to form the desired PCC. The reaction mixture was further stirred for 30 min and allowed to settle down for 24 h. The precipitated product was filtered with vacuum filter, washed several times with distilled water and placed in oven at 50 °C for 30 min to dry. The product was then grounded well and thoroughly mixed to powdered form.

2.3. Instrumentation

The morphologies of PCC products were examined using several physico-chemical techniques. Fourier Transform Infrared Spectroscopy (FT-IR) of PCC products was recorded on FT-IR SHIMADZU-8400S. X-Ray Diffraction (XRD) analysis was recorded using an XTRA powder X-ray diffractometer (XRD-BD111915-Rigiku) with Cu-K α radiation ($\lambda=1.54178 \text{ \AA}$) at $0.02^\circ \text{ s}^{-1}$ scanning rate in the 2θ range 20–80° where the samples were directly deposited on a collodion-coated copper grid. Field emission scanning electron microscopy (FE-SEM) captured the images of the CaCO_3 morphologies at an applied accelerating voltage of 10 kV using a Hitachi S-3400N field emission microscope. The particle size distribution of surfactant-polymer templates were obtained by Malvern Zetasizer Nano (Malvern, UK) Dynamic light scattering (DLS) instrument where a vertically polarized light of 514.5 nm wavelength from Argon LASER was used as the incident beam and the measurements were conducted at a scattering angle 90°.

3. Results and discussion

3.1. Characterization

Fig. 1a shows the FT-IR spectra of synthesized PCC products. The characteristic absorption bands observed at 711–713 cm^{-1} , 872–875 cm^{-1} and 2515 cm^{-1} revealed the presence of calcite [10,11]. Additional peaks at 1462 cm^{-1} and 2515 cm^{-1} confirmed the formation of calcite crystals. Weak bands observed at 2872 and 2951 cm^{-1} represented asymmetric and symmetric methyl and ethylene C–H stretching respectively indicating the strong association of surfactant molecules with calcite crystals. Absorption peak at 3301 cm^{-1} indicated the probable O–H stretching due to the presence of alcohol group while the peak around 1794 cm^{-1} ascribed the stretching vibration of C=O bond. Like the FT-IR data, the typical XRD patterns obtained for the various fabricated surfactant-polymer templates at $2\theta=29.4$, 29.5, and

30 (Fig. 1b) inferred the presence of higher amount of calcite form while peaks at $2\theta=48.32$, 48.52, 48.66, 48.68 and 48.88 exhibited the presence of vaterite phase.

Fig. 1c presents particle size distribution of surfactant-polymer complexes obtained by DLS which is a hydrodynamic quantity that may differ from the actual size as the particles carry charges on their surfaces depending on their degree of polarity [12,13]. PEG is polar than PVA and PVAc. Consequently there lies somewhat difference in

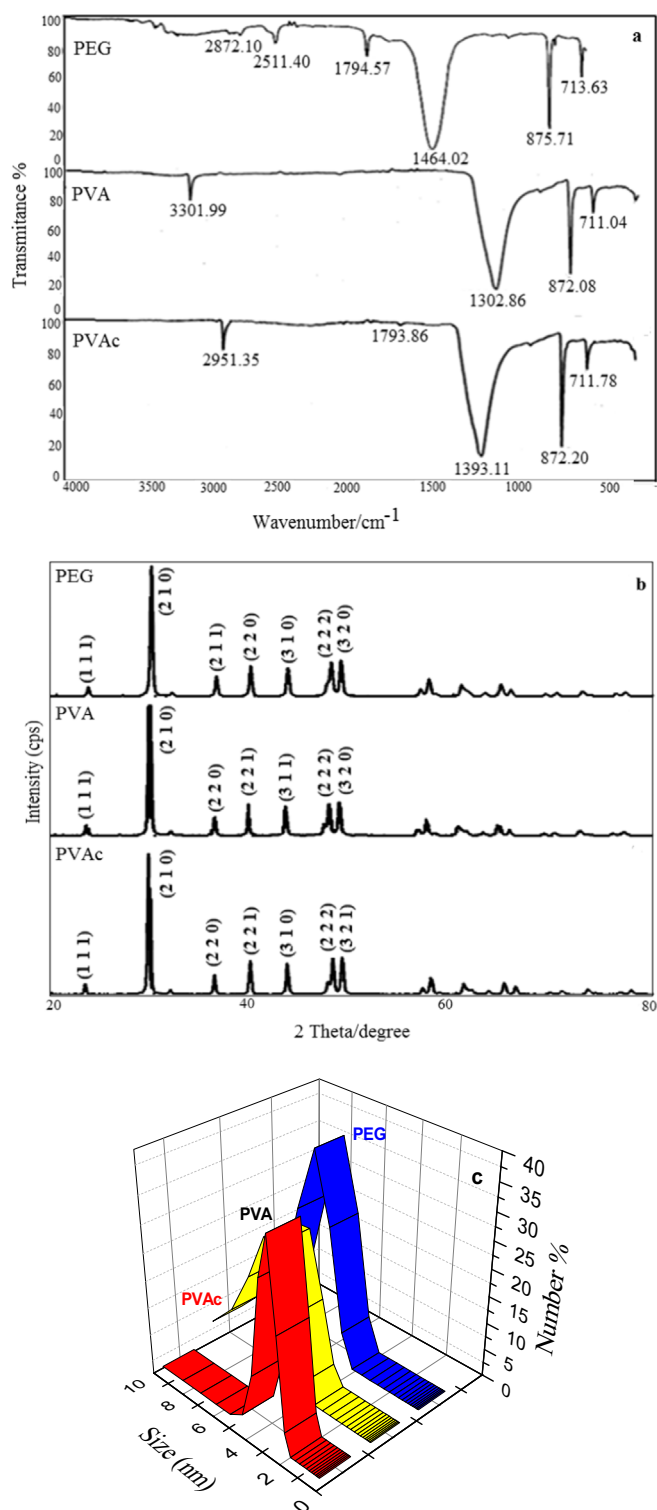


Fig. 1. (a) Spectral (b) diffraction and (c) scattering analysis of CTAB modified PCC product in presence of various polymeric templates.

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