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The effect of ultrasonication on calcium carbonate crystallization in the presence of biopolymer

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ABSTRACT

Synthesis of calcium carbonate ($CaCO_3$) was carried out using sonication in aqueous solution medium. The effect of the probe immersion depth (PID) and the amplitude of sonicator on calcium carbonate crystallization were studied in the absence and presence of biopolymer, carboxymethyl inulin (CMI). Calcium carbonate crystals synthesized with and without ultrasound were compared. X-ray diffraction (XRD) analysis showed that calcium carbonate obtained in the presence of biopolymer was a mixture of calcite and vaterite whereas there was only calcite polymorph in the absence of biopolymer. In the presence of biopolymer, the relative fraction of vaterite increased with the application of sonication process. The higher amplitude resulted in the higher relative vaterite fraction. The results showed that the probe immersion depth and the amplitude affected the morphology of calcium carbonate.

1. Introduction

The synthesis of inorganic particle has been attracted a great deal of attention in many research areas. Calcium carbonate is the most widely inorganic minerals. It is used in many industrial applications such as rubber, plastics, coating, cosmetic, pharmaceuticals, food, ceramic etc. It also appears in many mineralized tissues in biological systems. Calcium carbonate has three crystalline polymorphs: calcite, aragonite and vaterite [1–6]. Calcite and vaterite can be produced from aqueous solution at room temperature whereas aragonite can be obtained at high temperatures [7]. Polymorphs having different crystal structures have an important role in industrial applications due to differences in their properties, so morphology and crystal structure are essential parameters for industrial applications [1,2].

The synthesis condition of calcium carbonate can influence the properties of calcium carbonate such as particle shape, particle size and morphology. The ultrasound (US) process is a promising and greener method to synthesis of $CaCO_3$. A narrow particle size of calcium carbonate can be obtained with application of US process [4,8,9]. In addition, the nucleation of crystals can be affected by the presence of US waves. Particle size and shape can be changed by varying the US process conditions [5,9]. Different polymorphs can be synthesized by applying US waves [5]. Sonawane et al. [4] has investigated calcite using sonochemical carbonization method. They obtained only calcite polymorph in their studies. Kojima et al. [7] has also investigated the effect of frequency and amplitude on the morphological of vaterite at high supersaturation without additives. Synthetic conditions such as temperature, pH and supersaturation in liquid reaction were found the most important parameter to control the morphology and polymorph of $CaCO_3$.

In this work we have studied calcium carbonate crystallization by using US in the presence of biopolymer with low amplitude at low supersaturation. The effect of the US process conditions on the formation of calcium carbonate crystals was investigated. Ultrasound amplitude and PID were investigated in the absence and presence of biopolymer, carboxymethyl inulin. CMI is a biodegradable, environmentally friendly polysaccharide-based polycarboxylate [1–3,10]. CMI was chosen as a biopolymer because the biodegradability and non-toxicity of CMI allows a wide application possibility in industries. Various polymorphs have been carefully obtained, yielding new information on the effect of ultrasound on the precipitation of $CaCO_3$ from solution.

2. Experimental

Calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) (reagent grade) were from Merck. CMI of 3022 molecular weight (MW) (CMI-20) was from thermPhos, Switzerland as Dequest DPB-116AB (where AB=20 for CMI-20). The number AB also indicates the degree of substitution (DS). DS is defined as the average number of carboxylate moieties per fructose unit (DS=2.0).

The experiments were conducted in a 0.5 dm^3 water-jacketed reactor providing a constant-temperature at 25 ± 0.1 °C. The total molar concentration of calcium was 100 mmol with calcium/carbonate molar ratio of 1. Calcium carbonate was always precipitated by mixing

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equal volumes (100 cm^3) of $CaCl_2$ and Na_2CO_3 solutions. Reaction solution was prepared by adding calcium solution to the reactor first. Sodium carbonate solution and inhibitor solution were quickly poured into the reactor. The experiments were carried out under either US waves or magnetic stirring at 400 rpm. The above reaction solution was subjected to sonication (Sonics Vibra Cell, 20 kHz and 13 mm with threaded end and replaceable tip probe) at room temperature. The amplitude value was ranged 25% to 50% whereas PID was varied from 1 cm to 2 cm below the liquid surface. The obtained $CaCO_3$ particles were filtered through a 0.2 μm cellulose nitrate membrane filter, dried at 100 °C for 24 h.

3. Results and discussions

Samples were coded to include the information about the synthesis conditions. The first number in the code of samples indicates the sonicator amplitude (%). The second number coming after dash shows the biopolymer concentration (g/L), the last number shows the probe immersion depth (cm). While S0-0/0 denotes sample synthesized without US waves in the absence of biopolymer without the probe immersion depth, S25-0.5/1 denotes sample synthesized with 25% of US waves in the presence of 0.5 g/L biopolymer with 1 cm of probe immersion depth (Table 1).

X-ray diffraction, Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM) were used in order to characterize the synthesized $CaCO_3$ crystals. X-ray diffraction analysis was carried out by means of Panalytical X'pert Pro PW 3040/60 powder diffractometer operating with Cu *K*α radiation in operating at 40 mA and 45 kV. The 2θ range was from 5° to 90° at scan rate of 0.026° $step^{-1}$. The ratios of the different polymorphs were determined by semi-quantitative analysis of the XRD results using the Rietveld method with HighScore Plus software (Table 1). The samples were analyzed using FT-IR spectral analysis (Bruker Alpha-P) in the 4000–400 cm^{-1} region at a resolution of 4 cm^{-1}. The morphology of crystals was analyzed by scanning electron microscopy (JEOL JSM 6335F and JSM 6510LV). The specific surface area (SSA) of the $CaCO_3$ crystals was determined by nitrogen sorption isotherms according to the multiple-point BET (Brunauer, Emmett and Teller) method using a continuous flow apparatus (COSTECH Kelvin Sorptometer 1042). Calcium carbonate samples were first outgassed at 80 °C. The nitrogen adsorption isotherm has been performed by additions of gaseous nitrogen to the tube containing the sample at 77 K.

Table 1
Synthesis conditions and the relative fraction of $CaCO_3$ crystals obtained at 25 °C.

Sample code	[CMI] (g/L)	Amplitude (%)	PID (cm)	Relative calcite fraction (%)	Relative vaterite fraction (%)
S0-0/0	0	–	–	100	0
S25-0/1	0	25	1	100	0
S50-0/1	0	50	1	100	0
S25-0/2	0	25	2	100	0
S50-0/2	0	50	2	100	0
S0-0.5/0	0.5	–	–	46.97	53.03
S25-0.5/1	0.5	25	1	36.42	63.58
S50-0.5/1	0.5	50	1	13.90	86.10
S25-0.5/2	0.5	25	2	43.13	56.87
S50-0.5/2	0.5	50	2	18.33	81.67

The addition of additive is a general method which is used to control the morphology of crystals [11–13]. Fig. 1 shows XRD diagram of obtained crystals in the absence and presence of CMI. The XRD pattern (Fig. 1) indicates two crystalline polymorphs, calcite and vaterite. We observed the characteristic peaks of calcite at 2θ of 29.4°, 35.9° and 39.5° which are corresponding to (1 0 4), (1 1 0) and (1 1 3) crystallographic planes of calcite [1–3]. The characteristic peaks of calcite were observed not only in the presence (Fig. 1b) but also in the absence of the biopolymer (Fig. 1a). The introduction of CMI biopolymer caused the formation of a new absorption peak presented vaterite form. The diffraction peaks at 24.92°, 26.99° and 32.78°, which were obtained only in the presence of CMI, proved the existence of vaterite [1,2]. The diffraction peaks of the crystals can be indexed as the (1 1 0), (1 1 2) and (1 1 4) reflection of vaterite at 24.92°, 26.99° and 32.78°, respectively [1]. The addition of CMI caused the changes in calcium carbonate polymorphs, probably due to its strong specific interaction with calcium carbonate [1–3].

In order to investigate the influence of the ultrasound, precipitations were carried out over two ranges of ultrasound amplitudes (25% and 50%). With the increasing of the sonicator amplitude, the intensity of peak at ~29.4° decreased. It is clear that the proportion of vaterite formed was higher when higher amplitude was used. On the other hand, the intensity of characteristic peak of vaterite at ~24.9° increased (Fig. 1). These results indicated that the amount of vaterite was proportional with the sonicator amplitude. Similar results were obtained at all PID's (Table 1). The formation of vaterite, which is an unstable phase, was effectively induced by ultrasonic waves. The control of the formation of polymorph by chancing the amplitude was observed by other research groups. It was reported that aragonite could be

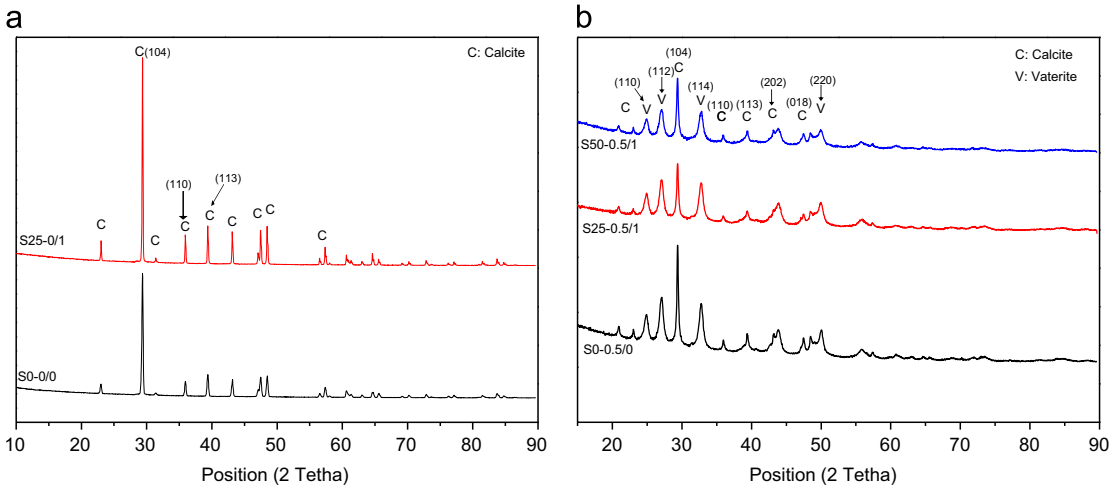

Fig. 1. XRD analysis of obtained calcium carbonate crystals (a) in the absence of biopolymer, and (b) in the presence of biopolymer at 25 °C.