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Synthesis of calcium carbonate in the presence of polymers under ultrasonic waves

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ABSTRACT

Calcium carbonate ($CaCO_3$) was synthesized in the presence of the water-soluble polymers Poly(Vinyl Sulfonic Acid) (PVS) and Carboxymethyl Inulin (CMI) using sonication in aqueous solution medium. We have investigated the effect of the polymers and the amplitude of sonicator on calcium carbonate crystallization. Calcium carbonate crystals synthesized with and without ultrasound were characterized by X-ray diffraction (XRD), Fourier transform infrared spectrometer (FT-IR), scanning electron microscopy (SEM) and particle sizer. A mixture of vaterite and calcite was obtained in the presence of CMI, whereas there was only calcite polymorph in the absence of polymers. Vaterite was obtained with the introduction of PVS. The addition of polymers caused to the change in morphology and polymorph of calcium carbonate. The particle size of calcium carbonate crystals decreased with increasing of sonicator amplitude and polymers concentration. The results showed that the sonicator amplitude and polymers affected the calcium carbonate crystallization.

Keywords: *Calcium carbonate, precipitation, polymorph, vaterite, calcite.*

1. INTRODUCTION

The synthesis of calcium carbonate ($CaCO_3$) has been attracted a great deal of attention in the fields of industrial applications and biomineralization. It is used in industries such as food, paint, wastewater treatment, drug preparation, ink, cosmetics, paper, fillers, plastics, rubber and coating. It also appears in biological systems such as bone and teeth. Many factors –may play a role to control of biomineralization. Although calcium carbonate is the most studied inorganic material, how biomineralization processes affects the morphology of $CaCO_3$ crystals is still a matter of debate [1-5]. As one of the most common biological minerals, calcium carbonate ($CaCO_3$), has three crystalline polymorphs; vaterite, aragonite and calcite, listed in order of increasing stability. Vaterite, which is thermodynamically unstable form of calcium carbonate, can transform easily to calcite [6]. The synthesis of vaterite outside of biological organism has been difficult under ambient conditions. It is difficult to obtain vaterite as a final product. The characteristic properties of calcium carbonate polymorphs are very essential since they can be used to achieve new materials with improved functions. There is a big interest in producing of vaterite. The solubility and dispersion of vaterite are higher than other two $CaCO_3$ polymorphs. Vaterite having lower specific gravity, which would give more volume for same weight, is preferred in paper and plastic industries. Higher luminescence and better refractive index of vaterite increases the quality of paper [7]. Stable vaterite can be useful material for the encapsulation of biomolecules for drug delivery and the formation of biosensor applications [8]. Vaterite having high porous structure can serve as a template for biomolecule incorporation. Vaterite microsphere can be used to augment bone matrix formation [9]. The production of vaterite with various crystal structure and shapes by different methods is an important phenomenon in industrial applications [8-12].

The conditions of synthesis such as concentration of reactants, temperature, aging time, the presence of additives and pH can influence the properties of crystallization of minerals [5, 8]. The interactions between specific molecules have an important role to understand and mimic the process of $CaCO_3$. Soluble additives can be used to mimic the biological formation of calcium carbonate polymorphs [5]. A small amount of additive has a significant influence on the structure and morphology of minerals. Polymers used to inhibit or stabilize the crystal structure act reshaping and directing crystal formation. Therefore, chemical composition, concentration and charge density of polymer are important parameters to control crystallization process [13, 14]. Surfactants and biopolymers play a critical role in polymorph selection [15]. Bis(2-ethylhexyl)sodium sulfate (AOT) [16] and poly(styrenesulfonate) [17] could be used as an additive to control the morphology of vaterite.

The synthesis of calcium carbonate with pure polymorph and uniform morphology can be promoted ultrasound (US) waves which is a greener method [18]. The use of ultrasound applies sound waves in the range of 16-100 kHz. Ultrasound, which is a source of focused energy, has a potential to increase mass transfer and reduce diffusion barriers. It is used to activate precipitation sites and control crystal growth and morphology. Power is delivered to a solution in ultrasound applications. The formation of small cavities or microbubbles grows and collapses rapidly [19]. The presence of US waves can affect the nucleation of crystals. The particle size, polymorphs and shape of $CaCO_3$ can be changed with US waves [20-25]. Purer products can be obtained under the ultrasound media due to the reduction in quantity in the continuous phase consisting of agglomerates structures. Sonawane et al. [20] found a large reduction in calcium carbonate particle size by increasing of the probe size of sonicator. Wagterveld et al. [25], Stoica-Guzun et al. [11] and Price et al. [24] also synthesized vaterite and calcite with ultrasound waves. Mori et al. [26, 27] has studied ultrasonic homogenizer to prepare vaterite for ink-jet paper. Generally, vaterite-type calcium carbonate is preferred as a coating pigment for ink jet paper instead of silica. High print quality could be obtained with vaterite-coated papers. Quick inward absorption of inks could be promoted with the large hydrophilicity of vaterite [26, 27]. The effect of sonication on the precipitation rate of $CaCO_3$ was tested by Nishida [28]. The precipitation rate of calcium carbonate was proportional to intensity of ultrasound and horn tip diameter. Neither the morphology nor the size of the calcium carbonate crystals formed were found to be affected by the ultrasonic irradiation [28]. López-Periago et al. [29] produced precipitated calcium carbonate (PCC) with the combination of supercritical carbon dioxide (scCO2) and ultrasonic agitation. The conversion to $CaCO_3$ increased from 50 wt% without agitation, to 65 wt% with mechanical stirring, and 89 wt% with sonication in their study. Many authors have investigated the effect of ultrasound on the crystallization of calcium carbonate, but the results are not clear [30-33]. To the best of our knowledge, the effect of ultrasound on the crystallization of calcium carbonate in the presence of polymers has not yet been reported.

The aim of this work was to synthesize calcium carbonate crystals with different structure in the presence of polymer poly(vinyl sulfonic acid) (PVS) and carboxymethyl inulin (CMI) at spontaneous crystallization under ultrasound waves. The results showed that polymers and ultrasonic irradiation has played a big role to control the morphology, crystal size and polymorph of calcium carbonate. The presence of sulfonic groups and carboxyl groups on polymers could stabilize the vaterite structure. Ultrasound waves caused to reduce the particle size of calcium carbonate. The narrower particle size distribution was obtained under ultrasound waves. Different polymorphs have been carefully obtained, yielding new information on the effect of ultrasound on the precipitation of $CaCO_3$ from solution.

2. EXPERIMENTAL SECTION

Calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) (reagent grade) were from Merck. Poly(vinyl sulfonic acid) (PVS) of 5000 MW was from Aldrich. Carboxymethyl inulin (CMI) of 3022 MW (CMI-20) was from thermPhos, Switzerland as Dequest DPB-116AB (where AB = 20 for CMI-20). The AB number also indicates the degree of substitution (DS). DS is defined as the average number of carboxylate moieties per fructose unit (for CMI-20, DS = 2.0).

The experiments were conducted in a 0.5 dm^3 water-jacketed reactor providing a constant-temperature at 25 ± 3 ºC. The total molar concentration of calcium was 100 mM with calcium/carbonate molar ratio of 1. Calcium carbonate was always precipitated by mixing 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 polymer solution were quickly poured into the reactor. Ultrasound was applied for 1 minute by use of an ultrasound horn into the reaction. The crystallization 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 polymer concentration was ranged 0.25 g/L to 0.50 g/L. Precipitated crystals were kept in mother liquor for 1 day and were washed with distilled water several times. The obtained $CaCO_3$ particles were filtered through a 0.2 μm cellulose nitrate membrane filter, dried at 100 ºC for 24 h. The results were determined from at least three separate experiments and only the average values were reported. The reproducibility of this approach was 4-5%.

X-ray diffraction analysis of the $CaCO_3$ crystals was carried out by means of PanalyticalX'pert Pro PW 3040/60 powder diffractometer operating with Cu Kα radiation in operating at 40mA and 45 kV. The 2θ range was from 5° to 90° at scan rate of 0.026° $step^{-1}$. The samples were also tested by FT-IR spectral analysis. The samples were analyzed using a Bruker Alpha-P in the 4000 – 400cm^{-1} region at a resolution of 4cm^{-1}. The samples crystal morphology was analyzed by scanning electron microscopy (FEI-Philips, XL 30 ESEM-FEG). We investigated the particle-size distribution of the powders by Laser particle sizer Fritsch Analysette 22-Compact, which measures materials in the particle size range from 0.3 to 300 μm.

3. RESULTS SECTION

The experimental conditions were given in Table 1 with the sample names carrying the information of synthesis conditions. The first number in the code of samples indicates polymer concentration (g/L). The capital letter shows the species of polymer used in the experiments. The second number coming after letter shows the amplitude of sonicator (%). For instance, while 0.25VS38 denotes sample synthesized in the presence of 0.25 g/L of polymer PVS at 38% of sonicator amplitude, 0.25C38 shows sample synthesized in the presence of 0.25 g/L of polymer CMI at 38% of sonicator amplitude.

Table 1. Experimental conditions of $CaCO_3$ crystals obtained at 25 ºC

Sample Code	CMI (g/L)	PVS (g/L)	Amplitude %
*NP1	0	0	25
*NP2	0	0	50
0.25C25	0.25	-	25
0.25C38	0.25	-	38
0.25C50	0.25	-	50
0.50C25	0.50	-	25
0.50C38	0.50	-	38
0.50C50	0.50	-	50
0.25VS25	-	0.25	25
0.25VS38	-	0.25	38
0.25VS50	-	0.25	50
0.50VS25	-	0.50	25
0.50VS38	-	0.50	38
0.50VS50	-	0.50	50

*NP: no-polymer

3.1. XRD and FT-IR analysis of the calcium carbonate crystals.

Figure 1 shows the X-ray diffraction pattern of the crystals obtained in the absence and presence of polymers. The characteristic peaks of calcite at 2θ of 29.4^{o}, 35.9^{o} and 39.5^{o} which are corresponding to (104), (110) and (113) crystallographic planes of calcite were observed in the absence of polymers [4, 5, 14]. The main characteristic peaks of vaterite at 2θ of 24.92°,26.99° and 32.78° correspond to the (110), (112) and (114) crystallographic planes, respectively [4]. The formation of vaterite peak were observed in the presence of PVS and CMI. The mixture of calcite and vaterite peaks were observed in the presence of CMI. The intensity of peak at 29.4^{o} which belongs to calcite decreased with the introduction of CMI. The characteristic peak of calcite at 29.4^{o} disappeared when PVS was used as additive. PVS which is a polyelectrolyte having negatively charged sulfonate groups induced the formation of unstable phase of vaterite. PVS showed stronger modification ability for calcium carbonate crystallization. It is known that the addition of additive can be used to control the morphology of crystals [34-37]. Nagaraja et. al [8] studied the crystallization of calcium carbonate in the presence of PVS and PVS stabilized the particles in solution as the vaterite polymorph. It was stated that the incorporation of PVS into the crystallization caused to a decrease in nucleation growth rate of calcium carbonate. The surface charge density of $CaCO_3$ increased by adding polymer and the electrostatic repulsion between particles prevented the agglomeration of particles. This high surface charge prevented the transformation of vaterite to calcite [8].

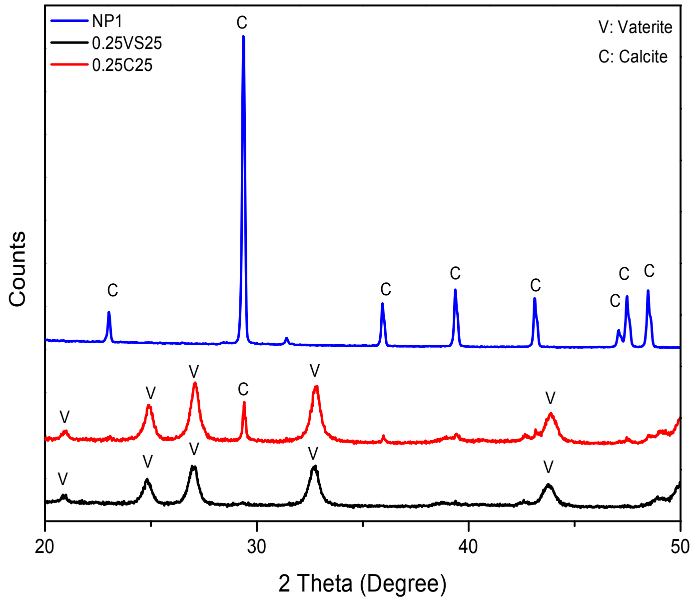


Figure 1. XRD analysis of obtained $CaCO_3$ crystals.

The effects of hyperbranched polyesters with sulfonic acid (BT21-SO_3H) and carboxylic acid groups (BT21-COOH) on calcium carbonate crystallization were studied by Meng et. al [38]. The mixture of calcite and vaterite was obtained in the presence of BT21-COOH. Spherical vaterite was produced in the presence of BT21-SO_3H.

The presence of vaterite and calcite was also confirmed by FT-IR analysis. In Figure 2, vibrational bands at about 875 and 712 cm^{-1} can be attributed to the *v2* and *v4* modes of calcite [39]. The formation of vaterite was further confirmed with the absorption bands at about 875 (*v2* mode) and 744 cm-1 (*v4* mode) [12] in FT-IR spectrum obtained in the presence of polymers (Figure 2). These results obtained by FT-IR spectrums are in agreement with those obtained by XRD patterns. The bands at about 1632 cm^{-1} is attributed to the C=O stretching (Figure 2a). In Figure 2a, the bands at 1036 cm^{-1} and 933 cm^{-1} correspond to C-O-C stretching. The peaks at 1598 cm^{-1} and 1423 cm^{-1} can be attributed to antisymmetric and symmetric stretching modes of the carboxylate group (-COO−). They are a strong proof for the addition of carboxymethyl groups to inulin [40, 41]. The infrared peak at ~1191 cm^{-1} indicates the S=O=S symmetric vibration of the sulfonic group for PVS [42].

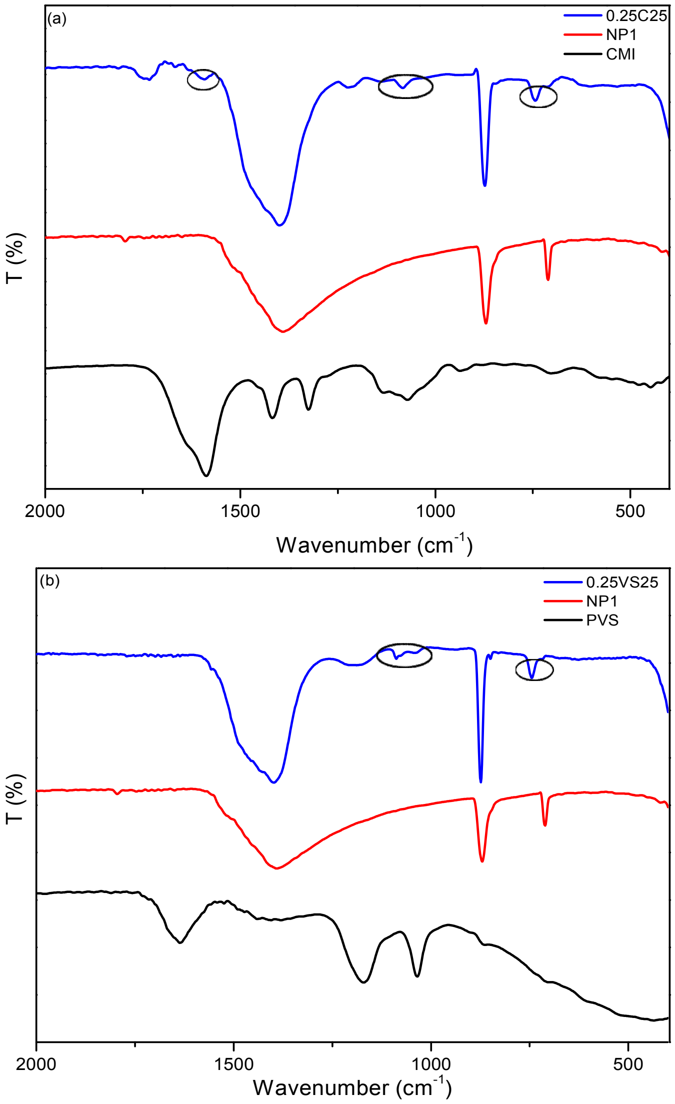


Figure 2. FT-IR spectra of $CaCO_3$ crystals obtained at 25 ^{o}C.

The main parameter to alter the polymorph of $CaCO_3$ is the selection of polymers under this condition. The phase of vaterite was obtained in the presence of PVS, while CMI has led to the mixture of calcite and vaterite. It is clear that PVS was effectively induced the formation of vaterite in all experimental conditions. Polar functional groups such as $–CO_2H$, $–PO_3H$, $–SO_3H$ can alter the crystallization mechanism of $CaCO_3$ [43]. The change in morphology or structure of crystals occurs due to the growth rates in the distinct crystallographic directions [43]. Vaterite which is unstable form of calcium carbonate can easily transform into calcite in water, so it is much rarer as a geologic mineral or biomineral. Synthetic vaterite can be produced in template-directed or additive-assisted conditions [44]. There are big difficulties in obtaining vaterite with large, pure, single crystals, so vaterite has been elusive for almost a century [45]. The studies on the control of vaterite has been limited, especially studies related with US waves.

3.2. SEM analysis of the calcium carbonate crystals.

To visualize the effect of process conditions such as the types of polymers, polymers concentration and the amplitude of sonicator, on particle size and morphology, scanning electron microscopic images (SEM) were used for all the samples. The morphology of the $CaCO_3$ crystals from SEM investigation was given in Figure 3. The SEM shows a visible change in the morphology and phase of the calcium carbonate crystals with the introduction of polymers. In the absence of polymers, the crystal shape of the calcite formed was the typical rhombohedral which is a common shape of calcite consists of (104) faces. It has the lowest surface energy and it is the most stable face of calcium carbonate [5]. We have analyzed the particle size of $CaCO_3$ from SEM micrographs. The dimensions of minimum of 50 crystals in each sample were measured from SEM photomicrographs. The mean crystal size of rhombohedral shapes was 3.8 µm and 3.6 µm for NP1 and NP2, respectively. While the common shape of calcite was rhombohedral (Figure 3a), the mixture of vaterite and calcite obtained when CMI was used as additive (Figure 3b). Especially, the precipitate consisted of a mixture of typical spherical vaterite and prolate spheroid calcite in the presence of CMI. Prolate spheroid calcite was also observed by using of EDTA [46]. The strong interaction of CMI with calcium carbonate could cause to a change in the morphology of calcite. The formation of rhombohedral shape which is characteristic shape of calcite was blocked due to the strong interaction. The observed changes in the morphology of calcium carbonate indicate that the polymers affect the nucleation and crystal growth of the calcite and vaterite. The relative strength of the interaction between CMI-calcite and CMI-vaterite may explain our results. According to our results, CMI binds more strongly to the surfaces of calcite than vaterite. Therefore, the morphology of calcite crystals was altered by using of CMI. The crystal growth of calcium carbonate was suppressed by the strong interaction between polymer and $CaCO_3$. Hence a mixture of calcite and vaterite obtained in the presence of CMI. As the calcite growth rate decreases due to biopolymer poisoning, the formation of vaterite was promoted with addition of CMI. The incorporation of polymers into the reaction dramatically change the nucleation of calcium carbonate.

SEM observation also shows that PVS led to the formation of uniform morphology for spherical vaterite (Figure 3c). These results are consistent with the XRD and FTIR results that are confirming the effect of polymer. Spherical vaterite was also obtained in the presence of (EO)20–(PO)72–(EO)20 [47] and a carboxylateterminated dendrimer [48]. The blocking of the crystal surface by CMI or PVS may prevent the phase transformation of vaterite to calcite. The adsorption of carboxylic or sulfonic groups on vaterite was explained by Meng et. al [38]. The sonicator amplitude has not affected the morphology of calcium carbonate neither in the presence nor in the absence of polymer.

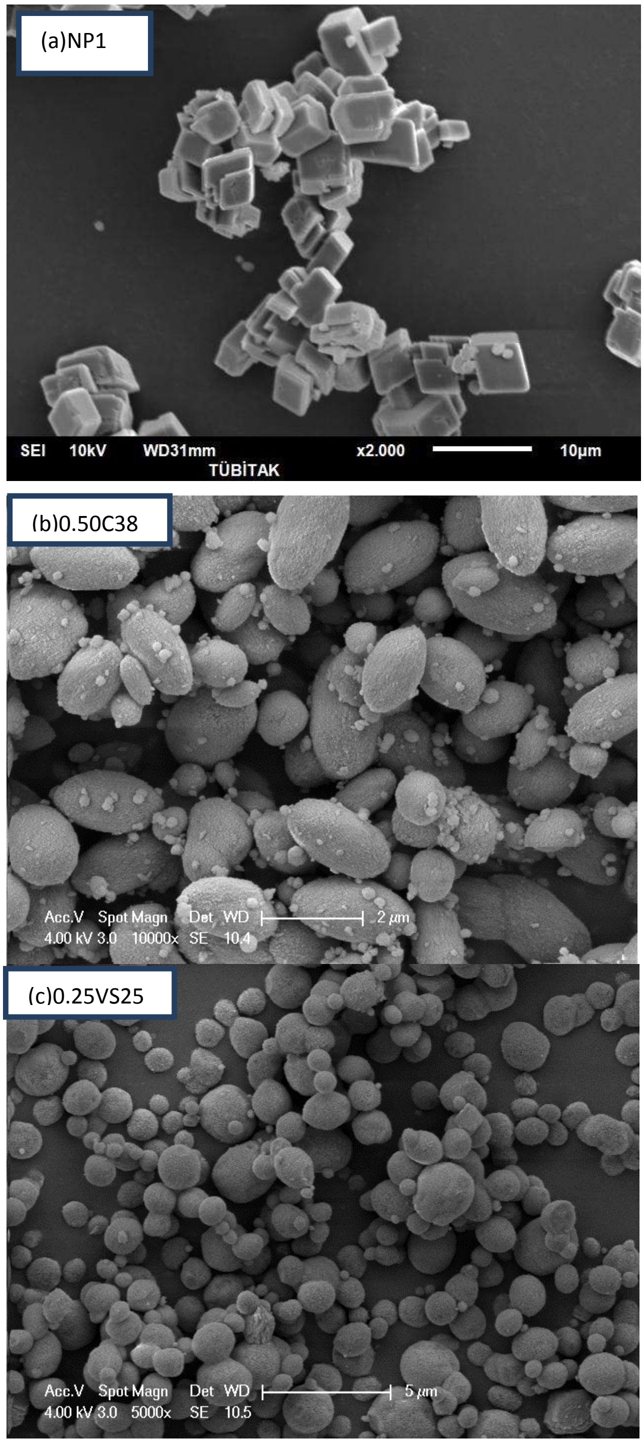
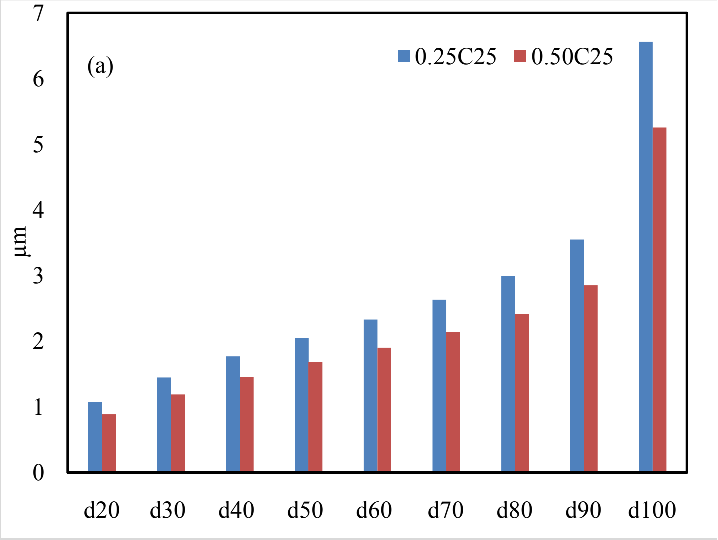


Figure 3. SEM photographs of obtained $CaCO_3$ crystals (a) NP1, (b) 0.50C38 and (c) 0.25VS25.

3.3. Particle size analysis of the calcium carbonate crystals.

Fritsch Analysette 22 Compact was used to measure particle size and the size distribution of samples. This analysis gives us a possibility to observe small changes in the contribution of components to a mixture in a predictable manner [49]. . The concentration of polymers and the value of sonicator amplitude were varied in order to understand how particle size and morphology would be affected. Figure 4 shows the numerical data obtained from particle size for $CaCO_3$ crystals obtained in the presence of polymers at 25% of sonicator amplitude.



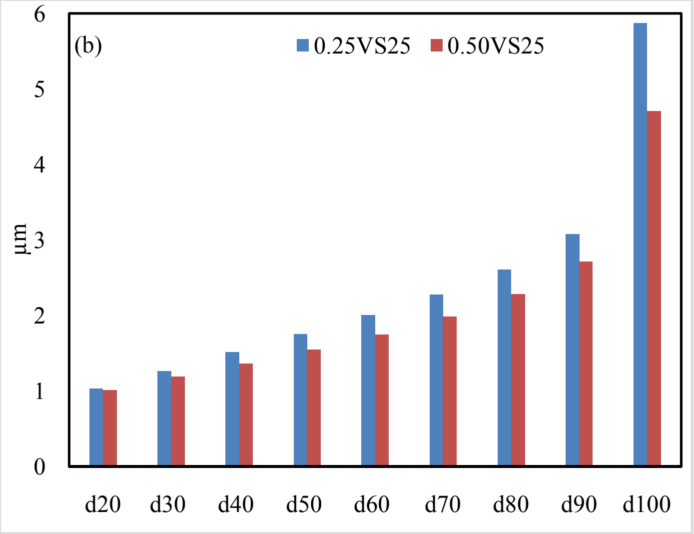


Figure 4. Numerical data obtained from particle size for $CaCO_3$ crystals obtained at 25% of sonicator amplitude in the presence of (a) CMI and (b) PVS.

We have had similar tendency at all values of sonicator amplitude in the presence of polymers. The results show that the increasing of polymer concentration resulted in a decrease of particle size. The value of d_{50} decreased from 2.049 µm to 1.681 µm when the concentration of CMI increased from 0.25 g/L to 0.50 g/L at 25% of sonicator amplitude. PVS caused to produce calcium carbonate crystals with smaller size. The values of d_{50} were measured 2.049 µm and 1.757 µm for 0.25C25 and 0.25VS25, respectively. For the same polymer concentration and same sonicator amplitude, all samples obtained in the presence of PVS were smaller than crystals synthesized in the presence of CMI. It is clear that the concentration of polymer and polymer type strongly affected the particle size. The higher is the polymer concentration the smaller are the particles.

Figure 5 shows the median diameter of $CaCO_3$ obtained in the presence of polymers. The minimum particle size was obtained at maximum sonicator amplitude for polymers. It is clear that the sonicator amplitude have played an important role to decrease the particle size. In addition, PVS had stronger effect on particle size than CMI.

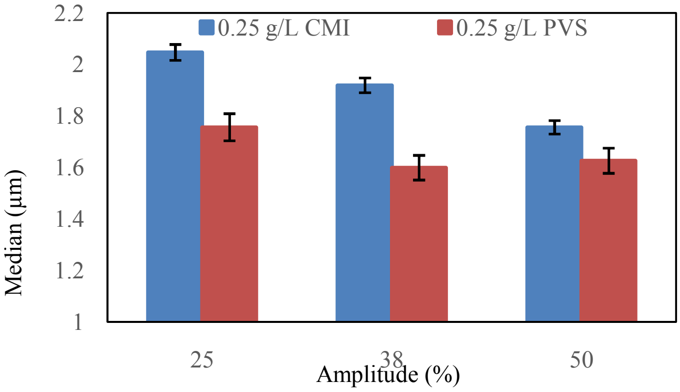


Figure 5. Median diameter for calcium carbonate crystals.

The results obtained from SEM were compatible with particle sizer. We have previously reported the effect of the polymer on $CaCO_3$ crystallization with using magnetic stirring [5]. In the absence of polymer, we obtained pure rhombohedral calcite. The mixture of vaterite-calcite was obtained in the presence of polymer with magnetic stirring. The particle size of $CaCO_3$ crystals obtained in the form of rhombohedral was app. 5.79 x 5.05 µm. In this study, the particle size decreased with using ultrasound. Ultrasound wave could lead to the reduction of particle size by breaking the bridges between crystals that form agglomerates. The effect of sonication on particle size was similar with the studies in literature [33, -50].

4. CONCLUSIONS

In conclusion, we have showed an easy method to synthesize calcium carbonate. We have managed to synthesize $CaCO_3$ particles with different polymorph and morphology in a short time. $CaCO_3$ crystals having small particle size were obtained by applying ultrasound waves in the presence of polymers. The particle size of crystals decreased with increasing of sonicator amplitude. The smaller particles of calcium carbonate were obtained by using ultrasound wave. The data obtained from SEM, XRD and FTIR confirmed the change in calcium carbonate crystallization. The nucleation and growth of $CaCO_3$ were controlled by altering the polymer concentration, the types of polymer and the sonicator amplitude, with result that the morphology of crystals obtained from rhombohedral to spherical shape. Both CMI and PVS exhibited strong modification in $CaCO_3$ crystallization, especially remarkable polymorph control ability. Whereas pure calcite phase obtained in the absence of polymers, calcite-vaterite mixture was the most favored composition in the presence of CMI. Vaterite phase obtained when we used PVS as additive. PVS stabilized the particles as vaterite. The main parameters for the formation of selective polymorph of $CaCO_3$ were the types of polymer and polymer concentration under these conditions. Increasing polymers concentration provided smaller particle size and narrower size distribution. Especially, the particle size decreased with increasing PVS concentration and the amplitude of sonicator. PVS was more effective than CMI on calcium carbonate crystallization.

It is clear that the types of polymer, polymer concentration and ultrasound have affected the morphology, the structure and particle size of $CaCO_3$. The obtained results might be helpful in selecting the operating conditions to produce specific calcium carbonate crystals.

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6. ACKNOWLEDGEMENTS

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