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Crystallization of vaterite and aragonite on chitin whiskers

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Abstract

The need for the possibility of producing calcium carbonate crystals by the evaporation method within five minutes and the growth of different calcium carbonate polymorphs on chitin whiskers within the same time frame at room temperature necessitated these report. Chitin whiskers (CHWs) were used as insoluble substrates, while poly (acrylic) acid (PAA) is used as soluble additive. The crystals were grown in chitin whiskers, Poly (acrylic) acid and CHW/PAA composites. The volume fractions for aragonite, vaterite, and calcite are 0.10, 0.25, and 0.65, respectively, in the absence of chitin whiskers or Poly (acrylic) acid. Calcite and aragonite volume fractions decrease in favour of vaterite when PAA and or CHWs were added. SEM images in the absence of CHWs and PAA shows rhombohedral calcites that display steady and step like plane appearances with an average edge of between 1.3 and 1.4 µm. In the presence of only CHWs, the SEM images show a mixture of ellipsoidal and spherical shape vaterites. The spherical vaterites have smooth, rough, and some irregular surfaces. Rod-like aragonite polymorphs were seen when only PAA was used as the template. In the presence of both PAA and CHWs, the rhombohedral shape showed roughness with irregular faces.

Keywords: Chitin whisker, Calcium carbonate, Calcium, vaterite aragonite, Polymorph, Mole fraction
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Introduction

The process where living organisms produce inorganic/organic hybrids is called biomineralization. The production of these inorganic/organic hybrids under different conditions has received attention from the academic world in recent years. The reason is to study the environmental friendliness of the morphology as well as the mechanical properties to ascertain its applications. The understanding of these hybrids' development processes is still a subject of research. An investigation into the biomimetic synthesis of $CaCO_3$ in the presence of soluble and insoluble additives has been on the increase. Correct usage and proportion of polymer materials can lead to a new hybrid of inorganic or organic materials with different properties and structures. The soluble organic matrix can promote heterogeneous nucleation and suppress homogeneous nucleation (He *et al*., 2009).

Morphological regulation of $CaCO_3$ crystallization using organic templates can likewise lead to the formation of different shapes (Walsh and Mann 1995; Hosoda *et al*., 2001; Park *et al*., 2002; Qi *et al*., 2002; He *et al*., 2009). The polymorphism of $CaCO_3$ crystallized in the presence of chitosan or chitin as substrates and PAA as a soluble matrix show diverse morphologies (Kato and Amamiya 1999; Sugawara and Kato 2000; Hosoda *et al*., 2001; Wada *et al*., 2004; Kotachi *et al*., 2006). Crystallization of $CaCO_3$ in the presence of PAA without any substrate (chitin or chitosan) also produced different polymorphs. The differences in polymorphs were attributed to the concentration of PAA (Dalas and Koutsoukos 1989; He *et al*., 2009), molecular weights (Huang *et al*., 2008), and the temperature of crystallization (Ouheniaa *et al*., 2008). It has been reported that $CaCO_3$ can exist in six different forms. In their decreasing stability, they are calcite, aragonite, and vaterite. The other three are amorphous $CaCO_3$ and two hydrated types. These three can quickly transform into calcite, aragonite, and vaterite (Meldrum 2003; Payne *et al*., 2007).

Different methods of calcium carbonate production have been reported. As stated earlier, the size and morphology of the crystals can be affected by the process or technique used. Wang *et al*. (2013) used a reactor having two reactant precursors in synthesizing calcium carbonate crystals: calcium chloride and sodium carbonate. This technique favoured the precipitation of the three calcium carbonate polymorph that is calcite, vaterite, and aragonite in order of appearance. Using a different method, mixing of calcium chloride and sodium carbonate solutions without any control, vaterite, calcite, and aragonite (in order of appearance) precipitate were observed (Wang *et al*. 2013). Xu *et al*. (2004) attained heterogeneous nucleation of calcium carbonate on a substrate using the gaseous diffusion as against liquid diffusion technique. At lower diffusion time amorphous phase of calcium carbonate was obtained while only calcite and vaterite formed were precipitated after 16 hours of CO_2 diffusion. Other factors that affect nucleation and growth processes of the crystals include; the pH value of the solution, the temperatures of both solutions, and additives.

The diffusion method of $CaCO_3$ crystallization on CHWs or chitosan reported by most authors takes hours or days for $CaCO_3$ growth on the substrate (Hosoda *et al*., 2001; Nishimura *et al*., 2008; Yamamoto *et al*., 2010). There is limited literature on the growth of $CaCO_3$ by the evaporation method and within a short period. The need for the possibility of producing $CaCO_3$ by evaporation method within 5 minutes and the growth of different $CaCO_3$ polymorphs on CHWs within the same time frame necessitated the production of $CaCO_3$ crystals. Herein, a report on the formation of $CaCO_3$ crystals/chitin-whisker hybrids using the evaporation method is being presented.

Experimental methodology

Chitin Purification/disintegration

All materials were supplied by Sigma Aldrich UK; these are chitin from shrimps' shell, poly (acrylic acid) Mw of 450,000, HCl, $NaClO_2$, $CaCl_2$, KOH, NaOH and K_2CO_3 all of which are of commercial grades. Chitin purification was carried out as reported by Morin and Dufresne, (2002). Chitin was dispersed into 5wt. % KOH solution, heated for 6 hours at a temperature of 104 °C to remove leftover protein. The resulting suspension was conditioned at ambient temperature overnight under mechanical stirring followed by filtering and washing with distilled water for several times. The crude chitin was bleached with the buffer solution ($NaClO_2$ aqueous containing sodium acetate) for 6 hours at 80 °C under mechanical stirring. The process was done twice and then fully rinsed with water at each stage. The crude chitin was again dispersed in 5 wt % KOH aqueous solution for 48 hours to remove residual chitin protein. This was followed by centrifuging to produce protein-free chitin. The protein-free chitin was dried in the oven at a temperature of 30 °C for up to 24 hours or more.

Acid hydrolysis of chitin

Chitin whiskers were produced by acid hydrolysis, as reported elsewhere (Ofem 2018; Junkasem *et al*., 2010). 5g of dried chitin was mixed with 150 ml of 3N HCl. The solution is heated at 120° C for six hours diluted with distilled water and centrifuged at 8,000 rpm for 10 min. The suspensions were transferred to a dialysis bag and dialyzed in running water for 2 hours after which in distilled water overnight. The dialysis continued for two more days while changing the distilled water every day. The pH level of the suspensions was later adjusted to 3 by adding few drops of HCl acid. The dispersion of chitin whiskers was completed by sonification of 40ml of the suspensions for 5 minutes. The solid content of the chitin whiskers' suspensions was approximately 0.3 wt %.

Crystallization of $CaCO_3$

Preparation of 0.2M $CaCO_3$ crystals is as follows; 0.2M of K_2CO_3 and 0.2M of $CaCl_2$ were mixed at a ratio of 1:1 by volume. The solid precipitates obtained immediately after mixing the two solutions was collected using filtrations, rinsed three times with deionized water. Finally, the $CaCO_3$ precipitates were dried in an oven at 100 °C for 1 hour, resulting in finely grained powders. CHWs, PAA, or CHWs/PAA composite were crystallized calcium carbonate as follows; 5ml of K_2CO_3 and 5ml of $CaCl_2$ were mixed with CHWs, PAA, and PAA/CHWs. CHW/PAA/$CaCO_3$ in the beaker was heated at 30°C for five min. The CHW/PAA/$CaCO_3$ solution was poured in a plastic petri dish and allow to dry in a fume hood and later in oven. The weight fraction of CHWs used was 0.43

Characterizations

Scanning electron microscopy (SEM) images were obtained using a FEM-SEM XL30 field-emission operated at 10 kV. Samples were coated with platinum using the Precision etching coating system, Model 682, to avoid electrical charging during imaging. X-ray diffraction patterns were obtained with an X-ray diffractometer (X'pert PW3710 MPD, Philips) using Cu Kα radiation (λ = 1.54 Å) with an accelerating voltage of 40 kV and a current of 30 mA. The range of the diffraction angle 2θ was from 10 to 60° with 0.02° per step and an exposure time of 5 seconds per step.

Results/Discussions

Scanning Electron Microscopy Morphology

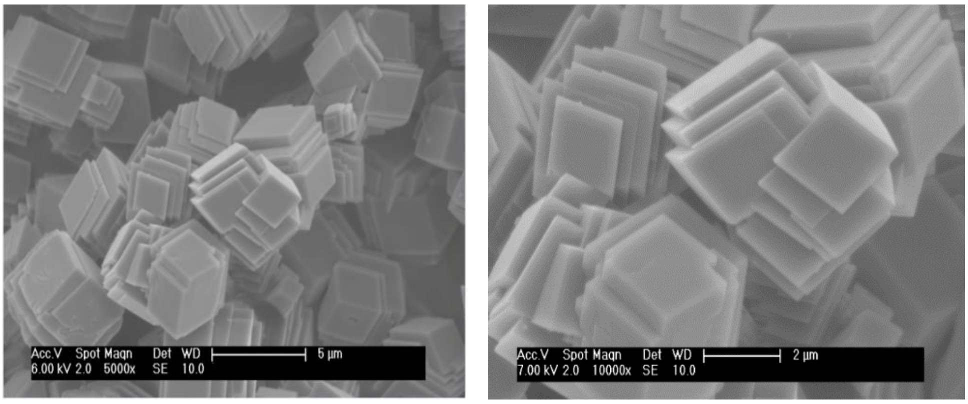
Figure 1 shows the SEM images of $CaCO_3$ precipitate synthesized without poly(acrylic acid) at different magnifications. From the figure, rhombohedral calcite $CaCO_3$

polymorphs were formed. The calcite displays steady and step like plane appearances and has an average edge of between 1.3 and 1.4 µm. The contour of the rhombohedral calcite seems to be similar. Similarities in the calcite structure have been reported (Shivakumara *et al*., 2006; Huang *et al*., 2008; Ouheniaa *et al*., 2008). The method of $CaCO_3$ crystallization, to a large extent, exhibited different polymorphs. Shivakumar *et al.* (2006) reported the role pH played on the types of polymorphs formed when $CaCl_2$ and $NaCO_3$ were mixed. A mixture of vaterite and calcite was obtained when the pH value was ~5. At a pH of 7-7.5, only calcite was observed. No precipitate of $CaCO_3$ was observed outside this range (5-7.5). Ouhenia *et al.* (2008) obtained a mixture of calcite and vaterite when $CaCl_2$ and K_2C0_3 as substrates were used. The pH value was not stated.

Figure 2 shows the SEM images of $CaCO_3$ precipitate synthesized with chitin at different magnifications. The SEM images show a mixture of ellipsoidal and spherical shape vaterites. The spherical vaterites have smooth, rough, and some irregular surfaces. Depending on the method of $\mathrm{CaCO_3}$ crystallization, different authors have reported different polymorphs when $\mathrm{CaCO_3}$ is grown on chitin or its derivative chitosan. Another major factor that determines the polymorph growth on chitin or its derivative is the pH value of the solution. FTIR spectroscopy, and X-ray diffraction measurement shows that calcite was formed when $\mathrm{CaCO_3}$/chitin-whisker was exposed to ammonium carbonate vapour (Yamamoto *et al*., 2010). Calcite crystals were found to be deposited when calcium nitrate, sodium bicarbonate, and potassium nitrate solutions at a pH of 8.50 were mixed at 25°C (Manoli *et al*., 1997)

Figure 3 shows SEM images of $CaCO_3$ in the presence of PAA. The SEM images show two different morphologies; aragonite rods of $CaCO_3$ aligned parallel to each other, and aggregate or clusters of grains or spherical lump of vaterite are equally seen. Contrary to the observation here, calcite has been grown on a porphyrin monolayer system containing PAA as a soluble agent [Xu *et al*., 1998]. In another report, aragonite and vaterite crystals were observed on a poly (vinyl alcohol) substrate with PAA and poly (glutamic acid), respectively (Hosoda 2003). Planar films made of orientated crystal grains of calcite on a glass substrate using a binary PAA system have been produced (Kotachi *et al*., 2004). Irrespective of the temperature (10-35 °C) and molecular weight calcite have been grown on PAA (Kotachi *et al*., 2006). When $CO_2$was bubbled into supersaturated calcium bicarbonate solution and stirred for 5 hours at 30 °C, no crystallization was observed (Kato *et al*., 1998). Temperature played a significant rule in the volume fraction of the polymorph precipitated when $\mathrm{CaCl_2}$ and $\mathrm{K_2CO_3}$ solutions were mixed (Ouheniaa *et al*., 2008). At 25°C with or without PAA, a mixture of calcite and vaterite were observed with calcite having 0.71 fractions, reducing to 0.49 when PAA was added. At 50 and 80°C with or without PAA, all three polymorphs were observed. The fraction of calcite dropped from 0.47 at 50°C without PAA to 0.087 at 80°C at the presence of PAA while that of aragonite increased from 0.07 to 0.89 at 80°C. At 25°C, calcite polymorph is being favoured while vaterite is dominant at 50°C. The molecular weight of poly(acrylic acid) (PAA) did not have any effect on the morphology of $\mathrm{CaCO_3}$ precipitation when the double jet method was used for crystallization. Irrespective of the additional time, spherical vaterite particles (3 to 4 µm) for all the samples were predominant (Huang *et al*., 2008). The above analysis is an indication that except on control measures using the same substrates with different methods of crystallization will grow different polymorph.

The morphologies of the calcium carbonate crystals grown on Chitin/PAA, as observed by SEM (figure 4) shows a mixture of disc-shaped platelets vaterite and smaller aggregates of calcite rhombohedral. Trances of aragonite can be seen. It has been reported by Munro and McGrath, [Munro and McGrath 2012 30] that chitin-aragonite materials can be made by reacetylating chitosan templates to chitin prior to exposure of the chitosan templates to combined mineralization process in the presence of PAA solution. The complex between chitin and PAA prompts predominance of aragonite compared with vaterite prevalence in the case of the PAA-chitosan complex (Munro and McGrath 2013). The preparation of thin films of calcium carbonate crystals on solid matrixes (cellulose, chitosan, and chitin) in the presence of poly (acrylic acid) have been reported (Hosoda *et al.*, 2001). Thin films grown on chitin and cellulose consist of only calcite, while those produced on chitosan are mainly of vaterite. The polymorphs of $CaCO_3$ crystals developed on chitosan films were dependent on the concentrations of poly(acrylic acid) in the solution, while the higher molecular weight of PAA indicates the deposition of crystals films polymorphs that are less stable on these polymer matrixes. A gel matrix of chitin was formed by acid hydrolysis (Yamamoto *et al.*, 2010). Ammonium carbonate vapour was slowly diffused into a calcium chloride solution containing the gel and poly (acrylic acid). Raman spectra identified the spherical $CaCO_3$ as calcite. Wada *et al.*, (2004); Kotachi *et al.*, (2006) and He *et al.*, (2009) reported the formation of vaterite and or aragonite when $CaCO_3$ grown on chitin or its derivative chitosan in the presence of Poly(acrylic acid).



A B

Figure 1: $CaCO_3$ without PAA at different magnifications

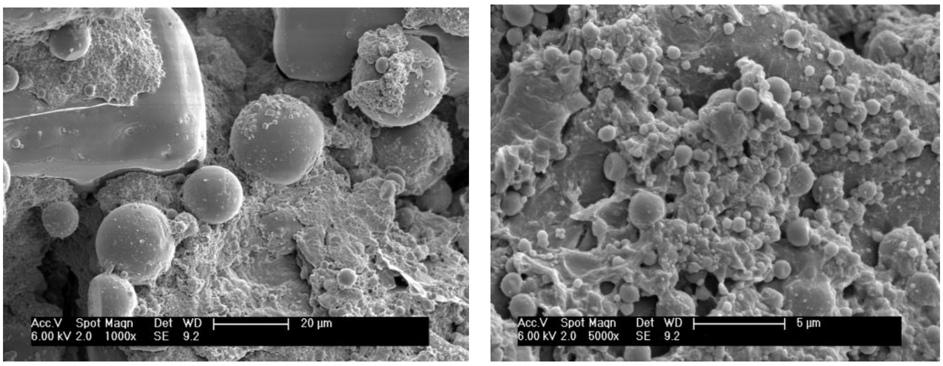


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Figure 2: $CaCO_3$ with CHWs at different magnifications

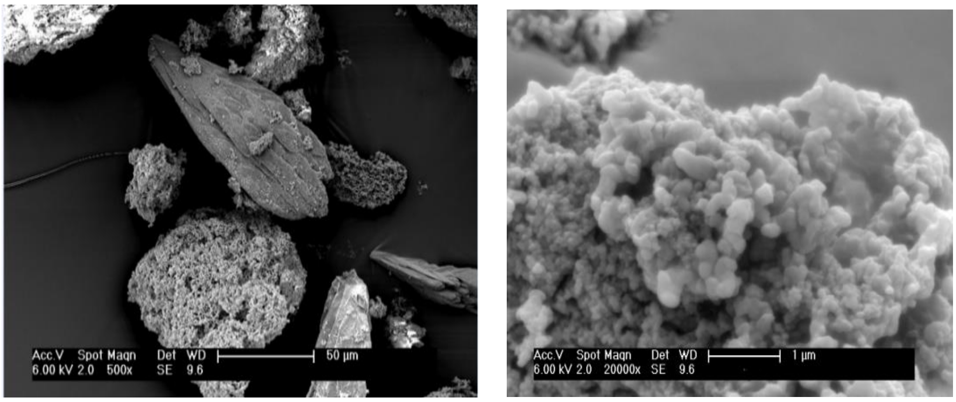

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Figure 3: $CaCO_3$ /45KPAA without chitin at different magnifications

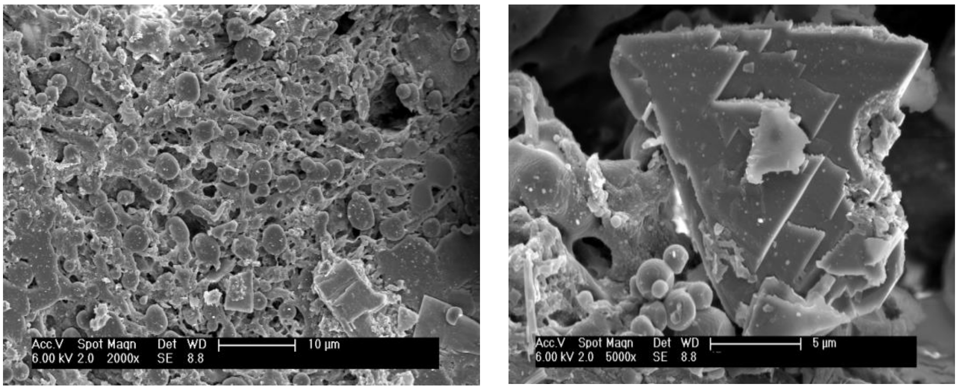

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Figure 4: $CaCO_3$/450PAA/CHWs at different magnifications

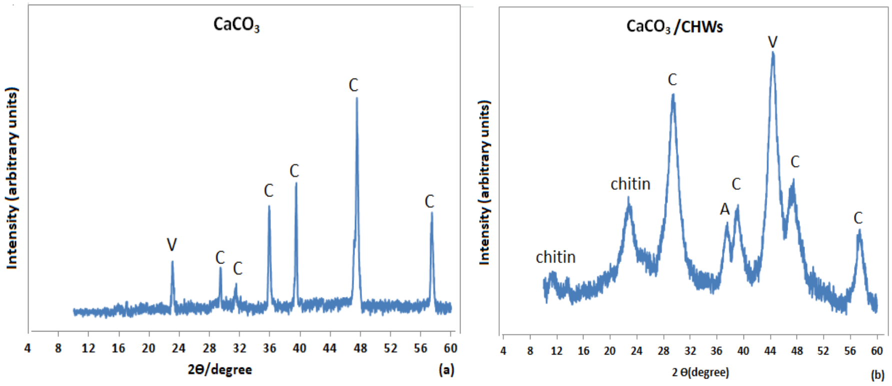
XRD characterizations

The XRD patterns of $CaCO_3$, $CaCO_3$/Chitin, $CaCO_3$/PAA, and CHWs/PAA/$CaCO_3$ prepared at 30 °C are presented in figure 5. For $CaCO_3$ without chitin or PAA, calcite peaks are predominant, with only one peak for vaterite appearing at around 23.9°(101). Peaks at 29.4° (104), 31.5° (006), 35.9° (110), 39.4° (113), 47. 5°(018) and 57.4°(221) were assigned to calcite.

In the presence of chitin, $CaCO_3$ growth shows the presence of all three polymorphs with calcite peaks dominating. A sharp peak at 22.8° assigned to the crystalline peak of chitin was observed. For calcite, the peaks are 29.4° (104), 39.03° (113), 47.3° (018) and 57.4° (122) while 37.4° (112) and 44.4° (300) are for aragonite and vaterite respectively. The presence of a 22.8° peak for chitin is a confirmation of interaction at the interface between chitin and $CaCO_3$.

$CaCO_3$ growth in the presence of PAA shows that all three polymorphs are present; with aragonite having the strongest peak at 33.1 ° (012) other peaks for aragonites are 26.8° (111), 33.1° (012), 42.5° (220) and 50.6° (132). Vaterites peaks were observed at 24.5° (110), 32. 6° (102), 34.6° (121) and 55.8° (113). The only calcite peak observed is at 47.5° (018).

In the presence of chitin and PAA (figure 5 (d)), vaterite has the strongest peak at 32.4° (102) among the three polymorphs with three other peaks at 24.9° (110),34.8° (121) and 39.5° (122). Only one calcite peak at 29.5° (104) and three peaks at 42.9° (220), 45.8° (221) and 51.8° (140) for aragonite. The molecular weight of PAA used here is 450000, while the temperature of crystallization is 30°C. Different polymorphs of $CaCO_3$ crystallized in the presence of PAA as a soluble additive and chitin or chitosan as substrates have been was found to form different morphologies, as explained above (Kato and Amamiya 1999; Sugawara and Kato 2000; Hosoda *et al.*, 2001; Wada *et al.*, 2004; Kotachi *et al.*, 2006). The absence of chitin and or chitosan in the presence of PAA equally produced different polymorphs. The difference in $CaCO_3$ polymorph precipitate with or without chitin or chitosan has been attributed to the temperature of crystallization (Dalas and Koutsoukos 1989; Huang *et al.*, 2008; Ouheniaa *et al.*, 2008; He *et al.*, 2009).



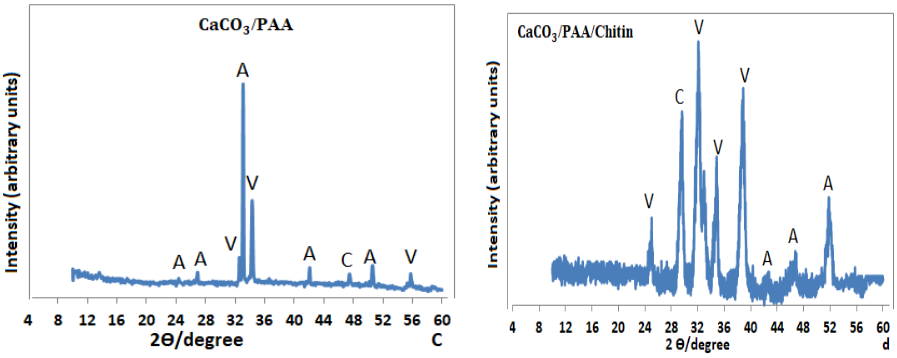


Figure 5: XRD pattern of CaCO$_3$ in the absence of PAA and chitin (a), in the presence of only chitin (b), the presence of only PAA (c) and in the presence of chitin and PAA (d)

Kontoyannis and Vagenas (2000) reported a modified X-ray calibration line for the determination of molar fraction for calcite, vaterite, and aragonite. The three equations are used here to determine the mole fraction of each polymorph. These equations are;

$$f_A = \frac{3.157x\, I_A^{221}}{I_C^{104} + 3.157x\, I_A^{221} + 7.691x\, I_V^{110}} \qquad 1$$

$$f_A = \frac{f_A x\, I_C^{104}}{3.157x\, I_A^{221}} \qquad 2$$

$$f_V = 1 - f_C - f_A \qquad 3$$

Where f_A, f_C, and f_V are the fractions for aragonite, calcite and vaterite respectively and I_C^{104}, I_V^{110} and I_A^{221} and are the intensity of calcite, vaterite, and aragonite at the indicated planes respectively. The mole fractions for calcite and other polymorphs are presented in figure 6.

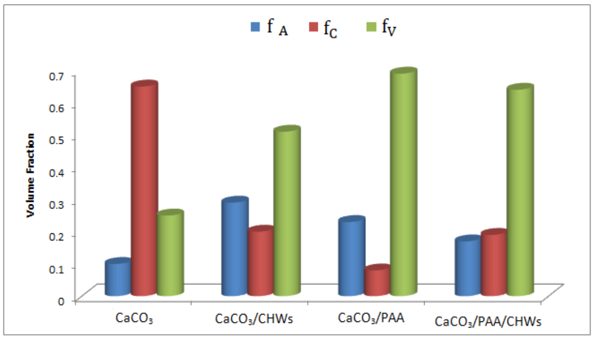


Figure 6: The volume fraction of Calcite f_C, vaterite f_V and aragonite f_A mole fractions bases on Kontoyannis and Vagenas equations

From figure 6, the calcite fraction yielded 0.65. The growth fraction of calcite in the absence of additive has been reported to be between 0.71 and 0.98 (Ouheniaa *et al*., 2008; Tang *et al*., 2008). The addition of PAA and or chitin whiskers had reduced the calcite fraction to 0.08, that is in the presence of PAA only. Under ambient conditions, calcite is the most thermodynamically stable CaCO$_3$ polymorph. When the supersaturation of calcite is increased in the presence of a soluble or insoluble additive, it can convert to vaterite or aragonite (Tang *et al*., 2008). A three-stage mechanism of crystallization of calcite has been proposed by Cai *et al.*, (2007). These are the formation of an unstable phase, the transformation of the unstable phase to a metastable phase, and the development of the stable phase. These three stages were abridged by Choi and Kuroda, (2012) to two; rapid crystallization of amorphous calcium carbonate (ACC) to vaterite and the transformation of vaterite into calcite. The transformation rate, according to Rodrigues-Blanco *et al*. (2011), is ten times slower than the crystallization step. The growth of CaCO$_3$ crystals in the presence of CHWs reduced calcite fraction from 0.65 to 0.19 and to 0.08 in the presence of PAA. The reduction is an indication that both polymers may be acting as inhibitors (Tang *et al*., 2008).

Conclusion

PAA and chitin whiskers have been used as templates to induce crystals of CaCO$_3$ particles. Rhombohedral calcite was seen in the absence of CHWs and PAA. The calcite displays stable and stair-like plane appearances with an average edge of between 1.3 and 1.4 µm. A mixture of ellipsoidal and spherical shape vaterites was observed in the presence of CHWs. The spherical vaterites have smooth, rough, and some irregular surfaces. Aragonite rods of $CaCO_3$ aligned parallel to each other, and aggregate or clusters of grains or spherical lump of vaterite are seen when PAA alone was used as a template. The morphologies of $CaCO_3$ crystals grown on PAA/Chitin as show a mixture of disc-shaped platelets vaterite with small aggregates of calcite rhombohedral. Trances of aragonite can be seen. Calcite fraction reduced from 0.65 in the absence of PAA and CHWs to 0.08 in the presence of PAA in favour of vaterite, which stood at 0.69 while aragonite grown made an improvement to 0.29 in the presence of CHWs.

References

Cai, Z. G., Jiang, G. J., Qin, S. M., Lin, P. B., Tao, M. and S. Z. Zheng (2007). Investigation of scale inhibition mechanisms based on the effect of scale inhibitor on calcium carbonate crystal forms. Science in China B: Chemistry, 50: 114-120.

Choi, K. and K. Kuroda (2012). Polymorph Control of Calcium Carbonate on the Surface of Mesoporous Silica. Crystal Growth and Design, 12, 887-893.

Dalas, E. and P. G. Koutsoukos, (1989). The crystallization of vaterite on cholesterol. Journal of Colloidal Interface Science, 127: 273-280.

He, L., Xue, R. and R. Song (2009). Formation of calcium carbonate films on chitosan substrates in the presence of poly (acrylic) acid. Journal of Solid State Chemistry, 182: 1082-1087.

Hosoda N. and T. Kato (2001). Thin-Film Formation of Calcium Carbonate Crystals: Effects of Functional Groups of Matrix Polymers. Chemical Materials, 13: 688-693.

Hosoda, N., Sugawara, A. and T. Kato (2003). Template effect of crystalline Poly (vinyl alcohol) for selective formation of aragonite and vaterite $CaCO_3$ thin films. Macromolecules, 36: 6449-6452.

Huang, S., Naka, K. and Y. Chuj, (2008). Effect of molecular weights of poly(acrylic) acid on crystallization of calcium carbonate by delayed addition method. Polymer Journal, 40, 154-162.

Junkasem, J., Rujiravanit, R., Grady, B. P. and B. Supaphol (2010). X-Ray Diffraction and Dynamic Mechanical Analyses of α-Chitin Whisker-Reinforced Poly (vinyl alcohol) Nanocomposite Nanofibers. Polymer International, 59, 85-91.

Kato, T. and T. Amamiya (1999). A new approach to organic/inorganic composites. Thin film coating of CaCO3 on chitin fibre in the presence of acid-rich macromolecules. Chemistry letters, 199-200.

Kato, T., Suzuki, T., Amamiya, T., Irie, T. and M. Komiyama (1998). Effects of macromolecules on the crystallization of $CaCO_3$ the formation of organic/inorganic composites. Supramolecular Science, 5: 411-415.

Kontoyannis, C. G. and N. V. Vagenas (2000). Calcium carbonate phase analysis using XRD and FT-Raman Spectroscopy. Analyst, 125, 251-255.

Kotachi, A., Miura, T. and H. Imai (2004). Morphological Evaluation and Film Formation with Iso-Oriented Calcite Crystals Using Binary Poly(Acrylic Acid) Chemical Materials, 16, 3191-3196.

Kotachi, A., Miura, T. and I. Hiroaki (2006). Polymorph Control of Calcium Carbonate Films in a Poly(acrylic) acid-Chitosan System. Journal of Crystal Growth and Design, 6, 1636-1641.

Küther, J., Seshadri, R. and W. Tremel (1998). Crystallization of Calcite Spherules around Designer Nuclei. Angewandte Chemie International Edition, 37: 3044-3047.

Manoli, F., Koutsopoulos, S. and E. Dalas (1997). Crystallization of calcite on chitin. Crystal Growth, 182, 116-124.

Meldrum, F. C. (2003). Calcium carbonate in bio mineralization and biomimetic chemistry. International Materials Reviews, 48, 187-224.

Morin, A. and A. Dufresne (2002). Nanocomposites of Chitin Whiskers from Riftia Tubes and Poly(caprolactone). Macromolecules, 35, 2190-2199.

Munro, N. H. and K. M. McGrath (2013). How important is polyelectrolyte complex formation in biomimetic mineralisation? Manipulatio via alcohol addition. Dalton Transaction, 42: 8259-8269.

Munro, N. H. and K. M. McGrath (2012). Biomimetic approach to forming chitin/aragonite composites. Chemical Communication, 48, 4716-4718.

Nishimura, T., Ito, T., Yamamoto, Y., Yoshio, M. and T. Kato (2008). Macroscopically Ordered Polymer/CaCO3 Hybrids Prepared by Using a Liquid-Crystalline Template. Angewandte Chemie International Edition, 47, 2800-2803.

Ofem, M. I. (2018). Deformation of microfibrillated chitin film and composites. Journal of Material Science, 53, 8666-8675.

Ouheniaa, S., Chateigner, D., Belkhira, M., Guilmeaub, E. and E. Kraussb (2008). Synthesis of calcium carbonate polymorphs in the presence of poly(acrylic) acid. Crystal Growth, 310:2832-2841.

Park, R. J. and F. C. Meldrum (2002). Synthesis of Single Crystals of Calcite with Complex Morphologies. Advanced Materials, 14:1167-1169.

Payne, R., Heppenstall-Butler, M. M. F. and M. Butler, (2007). Formation of Thin Calcium Carbonate Films on Chitosan Biopolymer Substrates. Crystal Growth and Design, 7, 1262-1276

Qi, J., Li, J. and J. Ma (2002). Biomimetic morphogenesis of calcium carbonate in mixed solutions of surfactants and double-hydrophilic block copolymer. Advanced Materials, 14, 300-303.

Rodriguez-Blanco, J. D., Shaw, S. and L. G. Benning (2011). The kinetics and mechanisms of amorphous calcium carbonate (ACC) crystallization to calcite, via vaterite. Nanoscale, 3, 265-271.

Shivkumara, C., Singh, P., Gupta, A. and M. S. Hegde, (2006). Synthesis of vaterite CaCO3 by direct precipitation using glycine and L-alanine as directing agent. Materials Research Bulletin, 41, 1455-1460.

Sugawara, A. and T. Kato (2000). Aragonite $CaCO_3$ thin-film formation by cooperation of Mg^{2+} and organic polymer matrices. Chemical Communications, 487-488.

Tang, Y., Yang, W., Yin, X., Liu, Y., Yin, P. and J. Wang, (2008). Investigation of $CaCO_3$ scale inhibition by PAA, ATMP and PAPEMP. Desalination, 228, 55-60.

Wada, N., Suda, S., Kanamura, K. and T. Umegaki (2004). Formation of thin calcium carbonate films with aragonite and vaterite forms coexisting with poly(acrylic) acids and chitosan membranes. Journal of Colloidal Interface Science, 277, 167-174.

Walsh, D. and S. Mann (1995). Fabrication of hollow porous shells of calcium carbonate from self-organizing media. Nature, 377: 320-323.

Wang, H., Huang, W. and Y. Han (2013). Diffusion-reaction compromises the polymorphs of precipitated calcium carbonate. Particuology, 11, 301-308.

Yamamoto, Y., Nishimura, T., Saito, T. and T. Kato (2010). $CaCO_3$/chitin-whisker hybrids: formation of $CaCO_3$ crystals in chitin-based liquid-crystalline suspension. Polymer Journal, 42, 583–586.

Xu, X., Han, J. T. and K. Cho (2004). Formation of Amorphous Calcium Carbonate Thin Films and Their Role in Bio mineralization. Chemical Materials, 16, 1740-1746.

Xu, G., Yao, N., Aksay, I. A. and J. T. Groves (1998). Biomimetic Synthesis of Macroscopic-Scale Calcium Carbonate Thin Films. Evidence for a Multistep Assembly Process. Journal of Am. Chem. Soc., 120, 11977-11985.