Communications in Science and Technology 9(1) (2024) 192–198

COMMUNICATIONS IN
SCIENCE AND TECHNOLOGY
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# Development of $CaCO_3$ novel morphology through crystal lattice modification assisted by sulfate incorporation and vibration

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*Article history:*
Received: 24 April 2024 / Received in revised form: 25 June 2024 / Accepted: 28 June 2024

## Abstract

$CaCO_3$ has long been used as a filler to increase many properties of the material. The filler commonly consists of inexpensive materials that replace some volume of the more expensive materials, which can reduce the cost of the final product. $CaCO_3$ morphology that can be used as filler depends on the filler's function, such as filler for paper, paint, rubber, or composite. A filler for composite materials is needed to increase interfacing interactions between the particulate fillers and the matrix. So, the particulate in a broader shape will be the best choice to function for such filler. In this research, in an attempt to increase the interfacing interaction, $CaCO_3$ morphology was modified in such a way through crystal lattice modification assisted by sulfate incorporation and vibration. SEM analysis was implemented, and showed that the research successfully produced novel morphology in branchy-like polymorphs. FTIR analysis also proved that the crystal lattice has been modified. The morphology in branchy-like polymorph is supposed to increase interfacing interaction between $CaCO_3$ as the filler and the matrix. The methods are also supposed to be implemented as the research is scaled up to commercial scale.

*Keywords:* CaCO3, crystal; incorporation; modification; morphology; sulfate

## 1. Introduction

In the current research, a novel morphology of $CaCO_3$ was developed to form a new particular shape to increase its surface contact when $CaCO_3$ is functioned as the particulate filler of composite materials. It has been known that the mechanical properties of the composite are determined by interfacing interactions between the particles and the matrix [1,2]. In the composite material study, precipitated calcium carbonate (PCC) is commonly used as filler and added to the matrix to improve the mechanical properties of the composites [2,3]. To clarify, the current research discussions do not delve into the influence of $CaCO_3$ novel morphology on the mechanical strength of the composite material. Instead, the focus is on developing PCC with a novel morphology suitable for use as a filler

The filler typically is an inexpensive material that replaces some volume of more expensive materials, thereby reducing the cost of the final product [4]. The morphology of $CaCO_3$ used as filler depends on the intended function of the filler, such as in paper, paint, rubber, and composite materials. This research emphasizes the production of fillers for composites with better interfacing interactions between particulate fillers and the matrix. Thus, particles with broader shapes will be the best choice.

PCC with the specific polymorph could be synthesized at room temperature in that the process parameters could effectively control the morphology [5]. Such processing also influences the polymorphic formation, growth mechanism, nucleation, shape, and size of the crystal. However, limited reports could be found in the literature concerning the crystallization behavior and kinetic analysis of $CaCO_3$ focused on morphology development. Correspondingly, there is a lack of investigation for agglomeration, instability of morphology, and the design of the reactor in the engineering scale-up [6]. However, data on crystallization kinetics, nucleation, crystal growth, and agglomerations, which may not be readily available are necessary for controlling $CaCO_3$ characteristics and reactor design.

Many researchers have already conducted research in the development of $CaCO_3$ morphology. Li et al. revealed in their report that the formation of $CaCO_3$ with the addition of 20 mM magnesium can produce vaterite on a coarse surface [7]. Toshiki et al, also reported that they controlled $CaCO_3$ morphology using electrolysis under 0.4 ampere of direct current and treated by ice cooling, to be vaterite in hexagonal polymorph [8]. In previous research, the author also

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https://doi.org/10.21924/cst.9.1.2024.1426

investigated the formation of $CaCO_3$ under the influence of formic acid in 5 ppm and vibration at 6 Hz. The result was $CaCO_3$ new morphology in hexagonal thin plate vaterite [9]. However, such particulates (from the research of Li, Toshiki, and Mangestiyono) may still cannot help to increase the interfacing interaction between the particulate filler and the matrix due to the geometrical aspect in which the surface is less comprehensive.

In a different research, authors also investigated the formation of $CaCO_3$ under the incorporation of sulfate and assisted by vibration [10]. In this research, the fraction of $CO_3/SO_4$ was set as 50/50 Wt%. Those two anions and calcium cations were inserted into the flask simultaneously. This experiment showed the novel morphology in needle-hexagonal as the merger between orthorhombic and hexagonal crystal lattice. $CaSO_4$ owns the needle-like polymorph, and $CaCO_3$ owns the hexagonal polymorph. Based on the author, this particle is suitable for use as a filler for composite materials. However, the gap is still found in this experiment because only a quarter of crystals have a novel morphology.

On the other hand, the authors would like that most of the crystals can be modified. This finding inspired the authors to research how lattice modification can be implemented better. So, in this work, the author incorporated $CaSO_4$ with $CaCO_3$ crystal lattice in a certain way, so the novel morphology has resulted in at most. The incorporation of the crystal lattice of $CaSO_4$ in orthorhombic form and $CaCO_3$ in rhombohedral and triclinic forms is capable of generating novel morphologies. Therefore, the purpose of this project is to cover the methods to produce a new habit $CaCO_3$ crystalline that is appropriate as a particulate filler of composite materials. Furthermore, the process can also be implemented when the research is scaled up from laboratory to commercial scale.

## 2. Materials and Methods

### 2.1. Material

$CaCl_2.2H_2O$, $Na_2CO_3$, and $Na_2SO_4$ powder in analytical grade were supplied by Merck. The solvent was doubled distilled water provided by PT. Brataco Indonesia. In this research, calcium and carbonate have been functioned as the crystal former otherwise sulfate was a lattice modification reagent. The calcium concentration was defined in accordance to the experimental design, while the carbonate and sulfate solutions were adjusted stoichiometrically to match calcium. The reaction was expected to occur according to the equation (1).

$$CaCl_2 + Na_2CO_3 + Na_2SO_4 \rightarrow CaCO_3 + CaSO_4 + 2NaCl \quad (1)$$

The solution was prepared by dissolving the powder into the solvent and then was filtrated two times by filter paper 0.22µm micropore. Then, it was stored separately in plastic vessels and covered to protect from the dirt material and other impurities.

### 2.2. Experimental set up

This study involved four experiments performed at ambient temperature. The parameters of the experiments are listed in Table 1. Ca concentration was set in 0.5 M for all experiments otherwise carbonate and sulfate anions were set in their stoichiometry to the calcium solution. The composition of $CO_3$ with $SO_4$ was set in any fractions i.e.: 100/0; 40/60; 50/50 and 60/40 Wt%. So, in experiment A, 500 ml Ca and 500 ml $CO_3$ solution were inserted into the flask without sulfate. In experiment B, 500 ml Ca and 200 ml $SO_4$ solution were inserted into the flask, and 300 ml $CO_3$ solution was put in 10 minutes later. In experiment C, 500 ml Ca and 250 ml $SO_4$ solution were inserted into the flask, and 250 ml $CO_3$ solution was put in 10 minutes later. In experiment D, 500 ml Ca and 300 ml $SO_4$ solution were inserted into the flask, and 200 ml $CO_3$ solution was put in 10 minutes later.

Table 1. Experiments parameter

| Experiments | Concentration (M) | | | $CO_3/SO_4$ Fraction |
|---|---|---|---|---|
| | Ca | $CO_3$ | $SO_4$ | Wt% |
| A | 0.50 | 0.50 | - | 100/0 |
| B | 0.50 | 0.30 | 0.20 | 60/40 |
| C | 0.50 | 0.25 | 0.25 | 50/50 |
| D | 0.50 | 0.20 | 0.30 | 40/60 |

The diversity between sulfate and carbonate fractions was expected to produce their differences in ionic strength concerning novel morphology generation. The difference time of the insertion between $CO_3$ and $SO_4$ in ten minutes was supposed that $CaSO_4$ lattice could be generated earlier. Therefore, $CaCO_3$ lattice modification could be well done.

### 2.3. Experimental rig

The rig as depicted in Fig.1 consisted of the computer program, electrical motor, vibrator table, and 2,000 ml of Erlenmayer flask. The computer program was used to control the vibration frequency at 8.00 Hz. The trajectory was in a 3 mm, horizontal direction. To operate the rig (for experiments B, C, and D), carbonate and sulfate solution was firstly inserted along the flask with the volume as defined and listed in Table 1. Then, vibration was operated. In this step, the interaction between calcium and sulfate ions has already started and the $CaSO_4$ crystals lattice started to form even though the nucleation has not occurred yet. Ten minutes later, the carbonate solution was inserted into a flask. The duration of each experiment was set at 40 minutes to ensure that the crystal habit remained or did not transform to the next phase. Regarding this point, a filtering flask and a vacuum pump should be employed to collect the crystals and proceed with the drying process. This step should be applied to the wet crystals immediately.

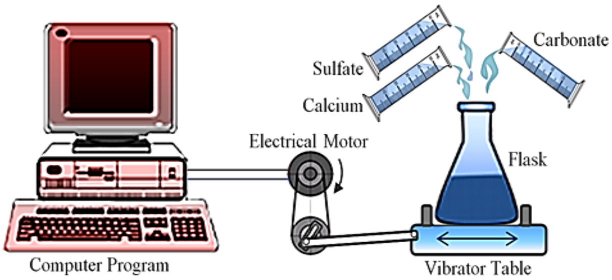


Fig. 1. Experimental rig

## 3. Results and Discussion

### 3.1. Mass deposition

Four experiments of morphological study under the influence of sulfate incorporation on $CaCO_3$ formation were conducted. After weighing the dry precipitant with Ohauss AR 2140 analytical balance, the deposition data were listed in Table 2. Mass deposition showed a decrease from experiment A to experiment D. The situation was caused by the transition of $CO_3/SO_4$ fraction in 100/0; 60/40; 50/50, and 40/60 Wt%. This was certainly caused by two reasons: the decrease of $CO_3$ fraction and the increase of $SO_4$ fraction. This finding is congruent with the research of Cong & Sheikholeslami in which they revealed that the sulfate weakened the formation of $CaCO_3$ [11].

Table 2. Mass deposition

| Experiment | Deposition (gr) |
|---|---|
| A | 3.6482 |
| B | 2.4416 |
| C | 2.2624 |
| D | 2.0033 |

Pingitore revealed that sulfate substitutes for carbonate in the calcite structure when sulfate is present in the solution [12]. In addition, other researchers revealed that adding sulfate to calcite could reduce its thermodynamic stability, which may lead to an increase in its solubility [6,13]. The mass deposition will therefore decrease primarily due to the increasing solubility in this reaction. The condition could be deduced that $CaCO_3$ crystallization process has been retarded as the presence of sulfate. As the process needed longer time, crystal modification opportunities are getting widely open.

### 3.2. Phases Identification and Quantification

Samples of four experiments were analyzed through XRD to identify and quantify the phases. The data were then listed in Table 3. The data exhibited that calcite decreased as the level of sulfate increased. Such situation showed an agreement with the report of Fernandez et al. revealing that the increased sulfate concentration promoted the precipitation of vaterite instead of calcite due to the stabilization of vaterite by sulfate incorporation [6]. The PHREEQC operation also revealed predictions regarding the saturation index (SI) of calcite, which decreased from 1.72 to 1.65, 1.62, and 1.60 for experiments A, B, C, and D. The incorporation of sulfate into calcite decreased its thermodynamic stability, potentially leading to increase solubility [13]. The increasing solubility in these experiments would be the main reason of why the calcite phase decreased.

The domination of vaterite in these experiments may also occur for other reasons. As the reaction was conducted in 40 minutes only, an opportunity to transform in such duration was assumed to lack time still. The sequence of vaterite formation has been promoted by Rodriguez-Blanco et al., which was initiated from ACC and was then crystallized to vaterite [14]. The temperature set at the ambient was also a matter which made vaterit not transfer to the next phase [15]. This will be an advantage for crystals modification.

In experiment C, only gypsum was produced with a sulfate fraction of 50%. In experiment D, a sulfate fraction of 60 Wt% produced gypsum and bassanite. However, sulfate was not significantly incorporated into the structure and did not affect the stability of ACC significantly [16]

Table 3. Phases identification and quantification.

| Exp. | Phases Quantification (Wt%) | | | |
|---|---|---|---|---|
| | Calcite | Vaterite | Gypsum | Bassanite |
| A | 25.45 | 74.55 | | |
| B | 18.69 | 81.31 | | |
| C | 16.64 | 78.80 | 4.56 | |
| D | 12.59 | 76.45 | 3.71 | 7.25 |

Here, anhydrite as the part of $CaSO_4$ phase was not formed. Anhydrite formation actually needs high temperature and ionic strength [17]. These experiments conducted at the ambient temperature still required more energy. In this experiment, although sulfate may not exist in the structure of $CaCO_3$ species, an increase in sulfate concentration may lead to $CaSO_4$ precipitation. This finding agrees with the publication of Dydo [18]. Therefore, gypsum and bassanite were present. The present gypsum and bassanite also decreased the quantity of vaterite and calcite as some of the calcium cations reacted with the sulfate anions. In this case, sulfate also could not suppress ACC from collaborating in forming $CaSO_4$ in anhydrate phase because PHREEQC has predicted that its saturation index (SI) was $\leq 1$ [19]. Thus, the absence of anhydrite was explained. In such situation which the crystals growth have been retarded, crystals modification attained better opportunities.

### 3.3. Morphological study

In this section, eight photomicrographs of the sample are depicted in Fig. 2. Figures on the left side describe the crystals from experiments A, B, C, and D, otherwise the right side describes the enlargement of selected crystals. As shown in Fig. 2-a1, many crystals existed in rhombohedral and spherical-like polymorphs. Rhombohedral is the polymorph of calcite and the spherical like is the polymorph of vaterite which those two polymorphs are shown in normal habit as the reaction underwent without any impurities. The photomicrographs also exhibited that aragonite was not formed at all. The data were relevant to the XRD data as listed in Table 3. In this experiment aragonite was not identified and vaterite dominated the phases in 74.5% otherwise calcite in only 25.45%. Referring to the scale line of the micrograph, it could be assessed that the dimension of the crystal was around 15μm in diameter or diagonally. The size of all crystals was also identified as almost similar or in uniformity. This was caused by the nucleation process that underwent more intensively than the crystal growth. According to kinetic studies of calcium carbonate crystallization, a higher level of supersaturation produced smaller particles as the nucleation was more sensitive than the growth [20].

Fig. 2-a2 shows the higher magnification of the selected

crystal from the same experiment. The morphology showed a spherical shape commonly exhibited by a normal vaterite. In the route of the formation of vaterite, spirulitic vaterite was initiated by the formation of ACC [21]. The vaterite formation started from aggregates ACC in ± 15 Å transform to the least stable vaterite. The ACC dissolved and continued to form the vaterite spheres through homogeneous nucleation, and nanoparticles of vaterite crystalline began to grow [22]. The first vaterite particles that formed below 70 seconds had initial diameters of 9 nm. Hence, the process was continued by fast aggregation to form nano sized polycrystalline spheres [23].

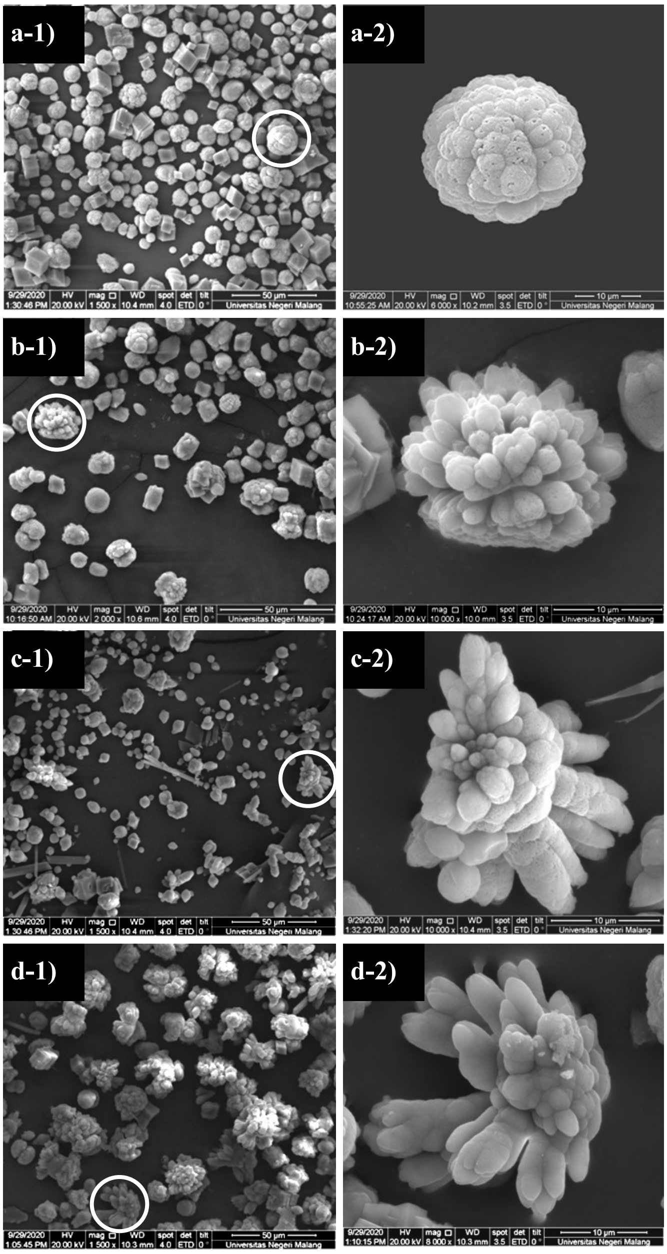
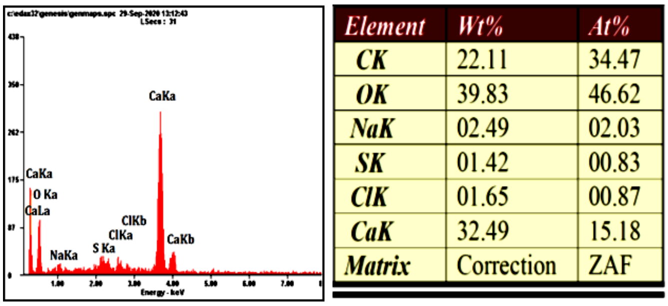


Fig. 2. $CaCO_3$ morphology of the sample from: (a) Experiment A, (b). Experiment B, (c). Experiment C and (d). Experiment D

Fig. 2-b1 describes the photomicrograph of the sample from the experiment B. In this Figure, calcite and vaterite existed normally but were also accompanied by the new habit crystal due to the sulfate incorporation. This crystal was selected and is depicted in Fig. 2-b2 in higher magnification to indicate the change more evident. In this experiment, carbonate and sulfate solution were inserted into the flask and 10 minutes later carbonate solution was inserted in. In the first 10 minutes, the reaction between carbonate and sulfate was initiated, and firstly, $CaSO_4$ lattice crystal was formed, which has been proven by FTIR analysis. In the following sequence, incorporation between $CaSO_4$ and $CaCO_3$crystal lattice was performed, which resulted in a new habit crystal of $CaCO_3$. The proof and the mechanism of this process will be discussed elsewhere. The SEM photomicrograph of the sample showed that $CaCO_3$ crystals have already been modified. Many branches existed on the crystals' surface and were quite different from the habit as shown in Fig. 2-a2. The habit of the branches could be clearly stated in its cross-section that had a circular shape and this habit is usually owned by vaterite. As the XRD data listed in Table 3 depicted only two phases that existed in experiment B, i.e. calcite and vaterite, it could be assumed that the phase of the branches was vaterite. This novel morphology emerged from the incorporation of $CaSO_4$ polymorphs in needle-like shapes and vaterite in spherical forms.

This finding appeared to be consistent with the work of Chong and Sheikholeslami, who discovered that the cross-link between two types of pure crystal structures could result in composite precipitants including the hexagonal crystal of $CaCO_3$ interlinked by the needle shape of $CaSO_4$ [11]. However, other researchers have not observed the $CaCO_3$ crystalline habit in branches-like polymorphs, and the author expected that this discrepancy will spark interest in the discussion.



| *Element* | *Wt%* | *At%* |
|---|---|---|
| *CK* | 22.11 | 34.47 |
| *OK* | 39.83 | 46.62 |
| *NaK* | 02.49 | 02.03 |
| *SK* | 01.42 | 00.83 |
| *ClK* | 01.65 | 00.87 |
| *CaK* | 32.49 | 15.18 |
| *Matrix* | Correction | ZAF |

Fig. 3. SEM-EDS analysis of the sample from experiment D

Experiments C and D also produced a branchy-like crystal habit. Although experiment C produced more branches of such crystalline, experiment D produced almost entirely. The phenomenon was affected by the carbonate-sulfate fraction difference. The fraction of experiment C at 50/50 Wt% and experiment D at 40/60 Wt%. This meant that increasing the sulfate fraction from 40 to 60 Wt% affected the formation of crystal in branchy-like polymorph, similar to a significant increase. The incorporation of $CaSO_4$ and $CaCO_3$ crystal lattice appeared to reach the best conditions, as evidenced by the formation of new morphology when the fraction was set to 40/60 Wt%. Based on this finding, the author concluded that such a carbonate-sulfate fraction was the best option.

SEM-EDS also investigated the elements to check the composition of C, O, and Ca (Fig. 3). The data were found from the sample of experiment D. The composition was shown in general as they are the atomic former of the $CaCO_3$ crystals. However, the presence of sulfate, even at a meager degree (01.42Wt %), did not match the author's thinking.

Earlier, the author deduced that the branchy-like polymorph was entirely vaterite, but why was sulfate still present? Authors deduced that may sulfate in $SO_4$ or $Na_2SO_4$ was trapped in the crystals as the sulfate was inserted into the flask earlier than carbonate. The attraction between sulfate and calcium underwent slowly; otherwise, carbonate and calcium ions were more tenacious. Therefore, may sulfate was trapped in the $CaCO_3$ crystal. This reason may be relevant to understanding the presence of sulfate in crystals.

### *3.4. FTIR Analysis*

Fourier Transform Infrared (FTIR) analysis was operated to study the process of crystal lattice modification. The samples of experiments A, C, and D were chosen to analyze by FTIR and the spectra as depicted in Fig. 4. In the spectra of the sample from experiment A (denoted as blue line), bands of 713 and 1,082 $cm^{-1}$ existed that were assigned as the asymmetric bending of calcite [24,25,26,27,28]. If those spectra were compared to the spectra from experiment C, the intensity of those spectra decreased. Spectrum 713 $cm^{-1}$ almost could not identified because its intensity was very little. This spectra was similar to the phase quantification data in which calcite decreased from 25.45 to only 16.64 Wt%. So, the phenomenon showed the consistency of the data of every analysis. Here, the retardation of crystals growth also pointed out and supposed could be help for crystals modification opportunities.

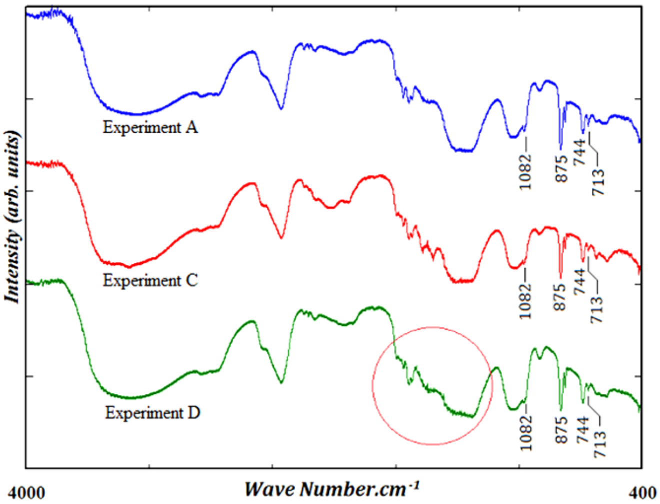


Fig. 4. FTIR analysis of three sample

In the spectra of the sample from experiment D, the peak of 744 and 875 $Cm^{-1}$ existed and were assigned as the asymmetric bending of vaterite [29]. In an experiment under the presence of sulfate, the intensity of those peaks increased. The phenomenon agreed with the phase quantification data in which vaterite was identified larger. The decrease of calcite and the increase of vaterite as the presence of sulfate have been discussed in the quantification section. Normally, vaterite should be transferred to the calcite phase at ambient temperature after several minutes, but it does not happen in the reaction influenced by sulfate. This finding is relevant to the research of Chong dan Sheikoleslami [11]. In their work, they revealed that the presence of sulfate could also decrease the growth of $CaCO_3$ and vaterite remained stable. Fernandez et al. also stated that the influence of sulfate on the formation of the vaterite could stabilize the vaterite [6].

The spectra showed more little peaks emerge between 1,373 and 1,764 $Cm^{-1}$ bands (encircled) identified as the adsorption of crystal lattice modification [29,30]. FTIR analysis also informed that a band of 1444.68 $Cm^{-1}$ emerged and was assigned as stretching vibration of $CaSO_4$ lattice mode [30]. The existence of these peaks made it evident that the crystals lattice have been modified. Also, it supported the morphology data in which the crystal polymorph has been modified from a normal shape to a branchy-like polymorph.

### *3.5. XRD analysis*

Fig. 5 shows the XRD spectra from three experiments. Experiment A, experiment C and experiment D denoted in a blue line, red line and green line respectively. In this spectra, vaterite existed in nine peaks; otherwise, calcite existed only in three peaks, and aragonite was absent. Miller indices also completed all of peaks. The relative intensity of calcite (1 0 4) decreased from 100 to 91 % and decreased again to 55.68 % as the effect of sulfate incorporation in 50 and 60 Wt%. In experiment D, vaterite (1 1 3), (1 1 6), and (3 0 1) decreased their relative intensity, otherwise vaterite (1 0 4) and (1 0 2) increased significantly. The decrease of calcite that has been shown in XRD spectra due to the increase of sulfate and the absence of aragonite was caused by the temperature set at the ambient. This finding showed the consistency of the all data and proved that the data were really true as the experiments were conducted carefully.

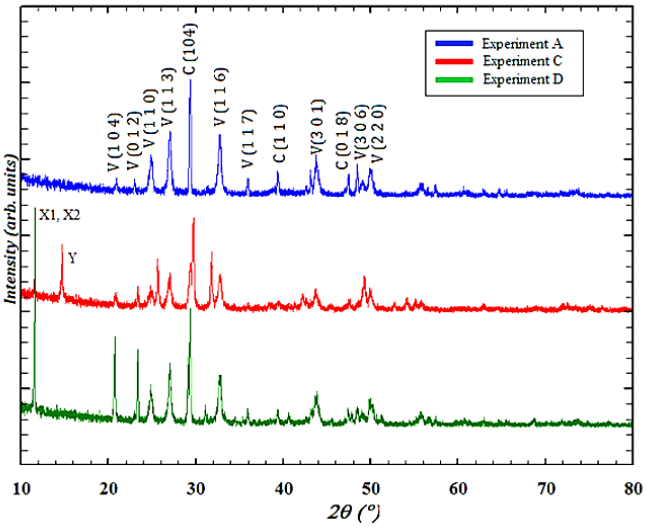


Fig. 5. XRD spectra of three different sample

In XRD spectra, two peaks emerged in the red line's graph (experiment C) at the position of 11.63° with a relative intensity of 60.72% and at the position of 14.70° with a relative intensity of 100 %. Authors assigned those peaks as X1 and Y peaks as the peaks were not recognized by AMCSD data. The unknown peak also appeared in the sample of experiment D at the position of 11.63° (2θ) and in relative intensity 100% and was assigned as X2 peak. This peak was also not recognized by AMCSD data.

Those X1, X2, and Y peaks have been checked by the reference AMCSD of calcite (00-005-05860), aragonite (00-041-1475), and vaterite (01-072-0506) [31], but the matching was not found at all. Concerning the morphological data, the undetected peaks were inferred to be the representation of the new habit morphology.

Table 4. Summary of XRD data of peaks X1, X2, and Y

| Peak | Position (°) | Height (counts) | FWHM (2Θ) | d-Spacing (Å) | Relative Intensity (%) |
|---|---|---|---|---|---|
| X1 | 11.6329 | 230.49 | 0.0787 | 7.6072 | 100.00 |
| X2 | 11.6011 | 527.78 | 0.0984 | 7.6280 | 100.00 |
| X3 | 14.708 | 139.96 | 0.0984 | 6.0229 | 60.72 |

To understand better these X1, X2, and Y peaks may still need further investigation. Therefore, the data of those peaks are summarized and listed in Table 4. The author expects that other researchers can assess those peaks well.

### *3.6. The steps of branchy-like polymorph formation*

In step one, the $CaSO_4$ lattice in orthorhombic was generated through the insertion of sulfate solution along with calcium solution into the flask. Vibration in planar trajectory was set at 8 Hz, and expected to contribute the mechanical energy, which is helpful for ionic collision [32]. In this step, lattice crystals in orthorhombic started to form. The formation of the lattice have been detected by FTIR analysis at a peak of 1444.68 $Cm^{-1}$ [30]. Currently, the lattice is still empty and has not been filled by $CaSO_4$ crystals. It has been known that the nucleation time of $CaSO_4$ needs to be around 31 minutes [10,33].

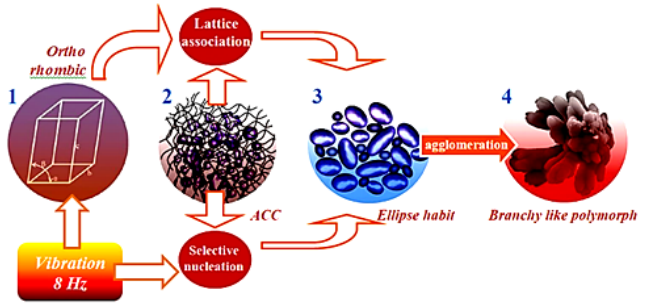


Fig. 6. The steps of branchy-like polymorph formation

In step two, the carbonate solution was inserted into the flask 10 minutes later, under calcium concentration in 0.5 M and assisted by vibration. In 70 seconds, ACC was tenaciously formed and immediately transformed into ACC aggregates. As ACC had a magnitude of approximately 15 $Å^3$ and a $CaSO_4$ lattice of 303.58 $Å^3$, ACC easily molded into a $CaSO_4$ lattice [14]. This stage was critical as the $CaSO_4$ and $CaCO_3$'s incorporation of lattice has just begun. The molding process may need an additional energy. For that reason, mechanical vibration in planar trajectory was given. Based on the previous research, a vibration frequency of 8 Hz will be the best choice [32]. Excessive energy may damage the crystals and stirring potentially destroys crystal lattice; therefore, it should be avoided.

In step three, ACC aggregates were transformed into ellipse-like polymorphs, suspected to undergo two mechanisms. First, ACC aggregates were incorporated with $CaSO_4$ lattice in a needle-like polymorph, which resulted in a new habit crystal in an ellipse-like polymorph. FTIR has proven the evident of lattice modification as the presence band was in the range of 1,373 to 1,764 $Cm^{-1}$ [24, 25, 26]. SEM photomicrograph also proved this evidence, which seems clear in Fig. 2-c1. Second, the formation of the ellipse habit might be undergone through selective nucleation, and the crystal grew on a particular side. Those two alternatives were possible. ACC has been known be easily molded to a broad variety of crystal shapes. Therefore, this ACC characteristic potentially enables the adjustment of the formation of a new crystal habit.

Step four involved the agglomeration of crystals into elliptical-like polymorphs, forming new crystal habits resembling branched structures. Agglomeration occurred through the ellipse-like polymorph's tip, and it was also able to be reassembled at the other tip. As a result, the crystal's habit may resemble the branch. The vibration direction may also be the reason for the branches to only have one direction or non-random directions as shown in Fig. 2-c2 and Fig. 2-d2.

## 4. Conclusion

The experiment of sulfate incorporation in $CaCO_3$ formation respecting morphological study has been successfully conducted. New habit crystals in branchy-like polymorph have been produced based on the incorporation of $CaSO_4$ and $CaCO_3$ lattice and assisted by the vibration. This $CaCO_3$ novel morphology is expected suitable be functioned as a particulate filler of composite materials. The formation of branches like polymorph can be explained in four steps, i.e. the formation of orthorhombic lattice, incorporation between orthorhombic with spherical-like polymorph, the formation of ellipse habit, and agglomeration. Ellipse habit formation was formed into two mechanisms, i.e. incorporation between ACC aggregates with $CaSO_4$ lattice and through selective nucleation in which the crystal grew on a certain side. Because of the existence of the new habit crystal, three peaks could not be identified by XRD analysis. The peaks did not match the reference data of AMCSD for calcite (00-005-05860), aragonite (00-041-1475), and vaterite (01-072-0506). Therefore, those three peaks were labeled as X1, X2, and Y and summarized in a table that may get the attention of other researchers to investigate. This method of the formation $CaCO_3$ novel morphology in branchy-like polymorph could be implemented as the research is scaled up to commercial scale.

## Acknowledgment

The funding of this research was supported by Diponegoro University, Semarang, Indonesia with the number of grants: 233-41/UN7.6.1/PP/2021.

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