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Characterization of $CaCO_3$ Polymorphs Prepared from Waste Eggshell

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ABSTRACT

The chicken eggshell was firstly prepared by crushing and then calcining in air at different temperatures from 200 to 1300 °C for 4 hours at an interval of 100 °C. From the X-ray diffraction pattern (XRD) results, this initial phase of powdered chicken eggshell was exclusively identified as calcite of $CaCO_3$. Heating to 1100-1300 °C this calcite was completely changed into calcium oxide (CaO). The phase transformation of this CaO was studied by keeping the samples in air at room temperature for 6 months. In the results, after one day incubation, CaO phase was changed slowly to portlandite ($Ca(OH)_2$) phase due to its reaction with humidity in the air. In addition, after 7 days, the CaO was completely transformed into $Ca(OH)_2$. Then after 9 days, partial $Ca(OH)_2$ phase was later combined with CO_2 and transformed into calcite phase. Then 21 days and 3 months, it was simultaneously changed to vaterite and aragonite, respectively. These corresponded phases were verified with Fourier transform infrared spectroscopy (FT-IR) method with the correct crystallized absorption peaks. Moreover, these validated data of the phase transformation of $CaCO_3$ were assured by the Rietveld refinement method.

Key words: Calcium Carbonate, Phase Transformation, Calcite, Eggshells

INTRODUCTION

Calcium carbonate ($CaCO_3$) is a common mineral in nature and it has the properties of high melting temperature, low vapor pressure, and thermodynamic stability in the presence of carbon as well as high alkalinity, thus it has long been considered to be used as the raw materials for high temperature ceramics (such as crucible and ceramic filter), refractories and metallurgical accessories (such as refining slag and tundish covering powder) [2]. $CaCO_3$ polymorphs consist of three main crystal structures; calcite, vaterite and aragonite. Calcite, stable form of them at room temperature and atmospheric pressure, has been used as fillers in the industries of plastics, rubber, as a fixed controller in the manufacture of steel, iron and so forth [12,13]. Vaterite has been used as pigments in coating colors for high-grade ink-jet papers. vaterite is one of the alternative candidates for the coating pigments of ink-jet paper [4]. Aragonite has been used as fillers for the improvement of the mechanical properties of paper and applied in composite biomedical material because it is denser than calcite, and it is enabled to integrate, resolve and replace by bone [1,8]. On the other hand, $CaCO_3$ is widely used in health and dietary. It is widely used medicinally as an inexpensive dietary calcium supplement or antacid [11].

The chicken eggshell is a complex and highly structured calcite of $CaCO_3$. It consists of calcium carbonate (94%), calcium phosphate (1%) and organic matter (4%). Chicken eggshell, the waste from food industries, may be developed to use as a source of $CaCO_3$ in the future because it has high content of calcium and can be easily procured. Thus in this study, the effect of the temperature and interaction each sample in air at room temperature on phase transformation of chicken eggshell was investigated. The prepared samples were characterized by X-ray diffraction (XRD), Rietveld refinements dna Fourier transform infrared analysis (FT-IR). We expected that the results of this work may lead to the better understand the phase transformation of chicken eggshells and their possible applications on some products.

Materials and Methods

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Sample Preparation:

The eggs were obtained from Charoen Pokphand Foods, (CPF) public company limited, Bangkok, Thailand. The eggs were removed their membranes and washed with distilled water to remove impurities. The shells were dry in air for a few days and then were ground into fine powder. To prepare calcium oxide (CaO) powder, these powdered eggshells were calcined at the range from 200 to 1300 ^{o}C for 4 h with a rate of 5 ^{o}C/min. Finally, the CaO samples was kept in air at room temperature for 6 months to investigate the phase transformation of obtained CaO powders.

Sample Characterization:

The crystal structures of samples ware identified by X-ray diffractometer (XRD) (model- PW-1830). These analyses were carried out on powdered samples by a Philips diffractometer using monochromatized CuK$_{\alpha}$ radiation. The X-ray tube was operated at 30 kV and 25 mA. The powders were scanned in the 2θ range of 10-60° with a scanning speed of 5°/min. Then phase fraction was refined by the Rietveld method using FULL PROF SUITE-2000 software program .The function group of powders was obtained by FT–IR measured at room temperature cover the range from 400-4000 cm^{-1} using FT-IR spectrometer (Perkin Elmer model 2000) with KBr pellet technique.

Results and Discussions

The XRD patterns of chicken eggshells before and after calcining in the air at difference temperatures for 4 h are shown in Fig. 1. The initial phase of them was identified as calcite of $CaCO_3$ according to the JCPDS file no. 82-1690. No other crystalline types were detected in the calcining temperature up to 600 ^{o}C. As shown at temperature ranges of 700-1000 ^{o}C, XRD peaks of calcite phase decreased while the new peaks of lime (CaO) phase increased corresponding to JCPDS 48-fine no. 48-1467. Heating to 1100-1300 ^{o}C this calcite was completely changed into CaO. The chemical reaction is given by equation1 [10]:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

For certainty of the complete transformation of CaO, thus in present work the temperature of 1300 °C for 4 h was selected in order to prepare CaO powders. The phase transformation of this CaO was studied by keeping each sample in air at room temperature for 6 months as shown in Fig. 2. After one day incubation, CaO phase was changed slowly to portlandite ($Ca(OH)_2$) phase corresponding to JCPDS file no. 72-0156 due to its reaction with humidity in the air. With increasing time, the intensity of CaO decreased as the intensity of new peak increased. As shown in Fig. 2, At 7 days the CaO was completely transformed into $Ca(OH)_2$ as following equation 2 [7]:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

Then after 9 days, partial $Ca(OH)_2$ phase was later combined with CO_2 and transformed into calcite of $CaCO_3$. After 21 days and 6 months, it was more changed to vaterite and aragonite of them, respectively. (JCPDS file no. 33-0268 for vaterite and JCPDS file no. 33-0*** for aragonite). It was found that all phase of $CaCO_3$ increased as $Ca(OH)_2$ decreased. $Ca(OH)_2$ transform into $CaCO_3$ was give by following equation 3 [7]:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (3)$$

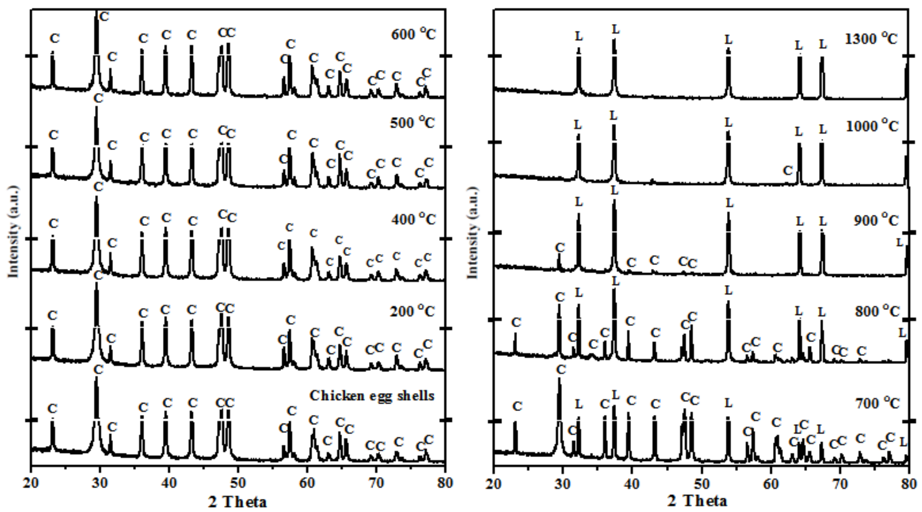

Fig. 1: X-ray diffraction patterns of chicken eggshells before and after heating at various temperatures, the peaks are marked by symbol; C : calcite, L : lime.

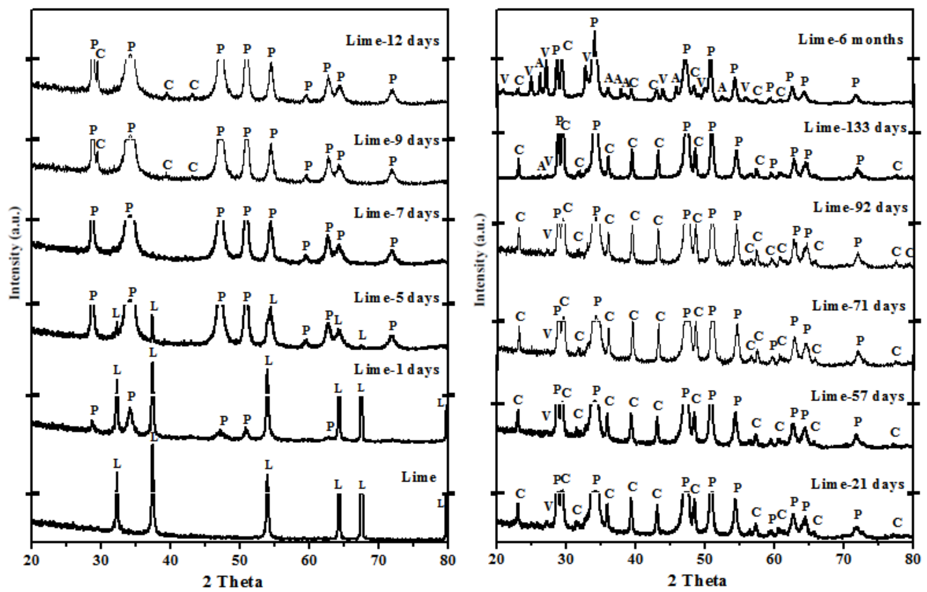

Fig. 2: X-ray diffraction patterns of lime after keeping in air at room temperature, the peak are marked by symbol; C : calcite, L : lime, P : portlandite, V : vaterite, A : aragonite.

In our study, the Rietveld refinement was used as the simplest tool to verify exact structure of $CaCO_3$ and to quantify the phase transformation from calcite to lime, lime to portlandite and portlandite to calcite, vaterite and aragonite. Using this method, we analyzed the structural compositions of chicken eggshells qualitatively and quantitatively by fitting the experimental powder XRD profiles with respect to corresponding structural parameters (i.e. lattice parameters, atomic coordinates) and instrumental parameters (i.e. zero-point and profile parameters). By taking the structure information established from the single-crystal X-ray diffraction, the crystal structure of calcite is trigonal with space group $R\bar{3}c$, lime is cubic with space group Fm3m, portlandite is hexagonal with space group $P\text{-}3m1$, vaterite is hexagonal with space group $P63/mmc$ and aragonite is orthorhombic with space group $Pmcn$, respectively. A summery of the refined lattice parameters and phase fractions of chicken eggshells upon heat treatment and lime from chicken eggshells keep in the air are reported in Table 1 and Table 2, respectively. As seen in Table 1 and Table 2, it should be point out that the refinement shows that the structural transformation of calcite to lime, lime to portlandite and portlandite to calcite, vaterite and aragonite. The results show that the calcite phase started to occur when portlandite was kept in the air at 9 days. The vaterite and aragonite phase began to be observed at 21 days and 3 months, respectively. All phase of calcium carbonate increased with portalandite decreased.

Table 1: Relevant crystallographic data for chicken eggshells transform to lime, established from powder X-ray diffraction refinements.

Samples	Phase	Phase fraction	Cell parameter (Å)			V($Å^3$)
			a	b	c	
Eggshells	Calcite	1.00	4.92989	4.92989	16.87526	410.133
200	Calcite	1.00	4.93443	4.93443	16.88003	411.005
300	Calcite	1.00	4.93984	4.93984	16.89499	412.272
400	Calcite	1.00	4.94603	4.94603	16.89941	413.414
500	Calcite	1.00	4.94689	4.94689	16.90087	413.593
600	Calcite	1.00	4.94742	4.94742	16.92008	414.152
700	Calcite	0.84	4.95237	4.95237	16.94444	415.579
	Lime	0.16	4.77265	4.77265	4.772650	108.712
800	Calcite	0.04	4.96439	4.96439	16.91952	416.984
	Lime	0.96	4.77131	4.77131	4.771310	108.621
900	Calcite	0.02	4.93285	4.93285	17.01298	413.977
	Lime	0.98	4.77095	4.77095	4.770950	108.596
1000	Calcite	0.01	4.95124	4.95124	17.02153	417.279
	Lime	0.99	4.77006	4.77006	4.770060	108.535
1100	Lime	1.00	4.77135	4.77135	4.771350	108.624
1200	Lime	1.00	4.76934	4.76934	4.769340	108.486
1300	Lime	1.00	4.76831	4.76831	4.768310	108.416

To further understand the phase transformation of samples, the FT-IR spectra of chicken eggshells before and after calcining at different temperatures are shown in Fig 3. The spectrum of chicken eggshells before heated yields a common feature of calcite where the signal positions and their assignments for the CO_3^{2-}. From our results, the signals at about 712, 875 and 1427 cm^{-1} can be observed for calcite [3,9]. Heated chicken eggshells started to loss carbonate above 600 °C and relative intensities of CO_3^{2-} band clearly decreased from 700 to 1300 °C. The present of small vibration bands of CO_3^{2-} (1427 cm^{-1}) molecules at 1300 °C indicates that the transformation of calcite to CaO is not entirely completed. The absorption bands around 3400–3600 cm^{-1} arise from stretching vibration of water molecules [6].The signals of water molecules decreased with increasing temperature and disappeared at 900 °C. The spectra observed at about 3000-2400 cm^{-1} are attributed to C-H stretching mode. At this point, it decreased slowly with an increasing temperature and disappeared completely at 1100 °C. The formatted ions at 1100 °C is due to thermal reactions on surfaces containing C=O chemical species where protons are available [6].

Table 2: Relevant crystallographic data for lime of chicken eggshells transform to calcium carbonate, established from powder X-ray diffraction refinements.

Samples	Phase	Phase fraction	Cell parameter (Å)			V(Å^3)
			a	b	c	
Lime	Lime	1.00	4.76831	4.76831	4.76831	108.416
Lime-1day	Lime	0.86	4.76897	4.76897	4.76897	108.461
	Portlandite	0.14	3.56580	3.56580	4.88326	62.0903
Lime-5days	Lime	0.20	4.76584	4.76584	4.76584	108.248
	Portlandite	0.80	3.55789	3.55789	4.87244	61.6782
Lime-7days	Portlandite	1.00	3.55754	3.55754	4.87432	61.6898
Lime-9days	Portlandite	0.99	3.55968	3.55968	4.87942	61.8287
	Calcite	0.01	4.97388	4.97388	16.95758	419.522
Lime-12days	Portlandite	0.98	3.56001	3.56001	4.87556	61.7912
	Calcite	0.02	4.96151	4.96151	16.88147	415.564
Lime-15days	Portlandite	0.95	3.55991	3.55991	4.87786	61.8169
	Calcite	0.05	4.96313	4.96313	16.9006	416.307
Lime-21days	Portlandite	0.93	3.55926	3.55926	4.8777	61.7923
	Calcite	0.06	4.95794	4.95794	16.90947	415.654
	Vaterite	0.01	4.13000	4.13000	8.49000	144.813
Lime-36days	Portlandite	0.73	3.55814	3.55814	4.87393	61.7057
	Calcite	0.08	4.96724	4.96724	16.90623	417.135
	Vaterite	0.19	4.13026	4.13026	8.49748	144.959
Lime-43days	Portlandite	0.69	3.55768	3.55768	4.87879	61.7513
	Calcite	0.09	4.95782	4.95782	16.90558	415.539
	Vaterite	0.22	4.13528	4.13528	8.49886	145.335
Lime-57days	Portlandite	0.66	3.55677	3.55677	4.87886	61.7206
	Calcite	0.10	4.95895	4.95895	16.90832	415.796
	Vaterite	0.24	4.13499	4.13499	8.52175	145.706
Lime-71days	Portlandite	0.63	3.55828	3.55828	4.87793	61.7612
	Calcite	0.11	4.95961	4.95961	16.90809	415.901
	Vaterite	0.26	4.13486	4.13486	8.52327	145.723
Lime-92days	Portlandite	0.59	3.55712	3.55712	4.87895	61.7339
	Calcite	0.12	4.95774	4.95774	16.90693	415.559
	Vaterite	0.29	4.13017	4.13017	8.49859	144.972
Lime-133days	Portlandite	0.44	3.56111	3.56111	4.87332	61.8010
	Calcite	0.13	4.95931	4.95931	16.90726	415.829
	Vaterite	0.31	4.13353	4.13353	8.52526	145.663
	Aragonite	0.12	4.96230	7.96800	5.74390	227.112
Lime-6Months	Portlandite	0.06	3.55799	3.55799	4.8793	61.7685
	Calcite	0.16	4.95797	4.95797	16.90639	415.584
	Vaterite	0.42	4.13508	4.13508	8.49994	145.339
	Aragonite	0.36	4.95500	7.96100	5.73600	226.267

The spectra of the CaO before and after keeping in the air at room temperature are shown in Fig. 4. At 1 day, the signal at 3641 cm^{-1} assigned to OH^- began to appear and become stronger with keep in the air increasing time. The absorption bands around 3400–3600 cm^{-1} arise from stretching vibration of water molecules [6]. These results correspond to the XRD result for $Ca(OH)_2$. At 9 days, the spectrum of calcite (875 cm^{-1}) began to appear and become to stronger with increasing time. At 21 days, the spectra of new signals at 745 and 875 cm^{-1} assigned to vaterite began to appear. On the other hand, CaO from chicken eggshells keep in the air for longer time than 6 months had polymorph of $CaCO_3$ (calcite, vaterite and aragonite). These results corresponding to the XRD result for polymorph of them.

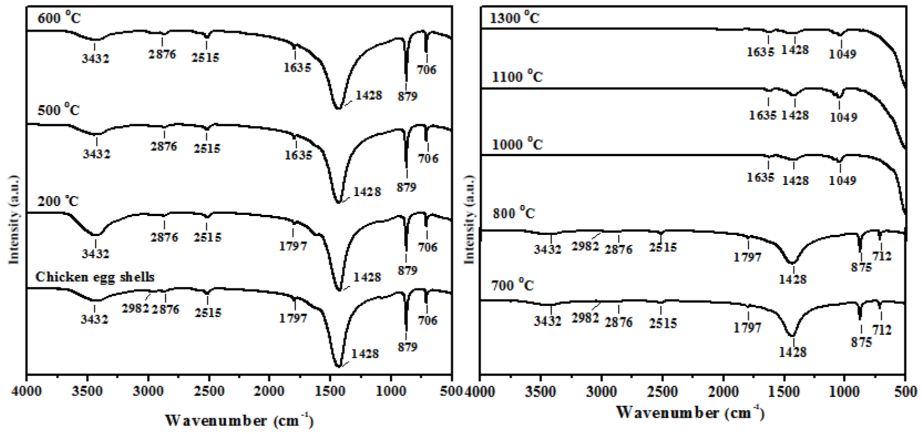

Fig. 3: FT-IR spectra of chicken eggshells before and after heating at various temperatures.

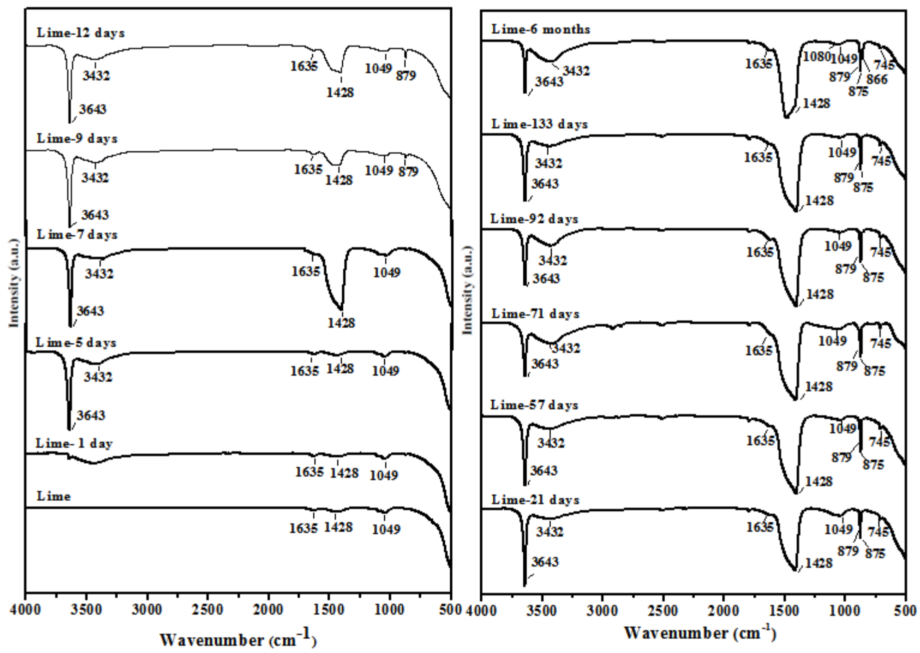

Fig. 4: FT-IR spectra of chicken eggshells after heating at 1300 °C and keep in air at room temperature.

Conclusion:

In the present investigation, we successfully prepared various phases of $CaCO_3$ obtained from eggshells. CaO powders were obtained by calcining chicken eggshells at 1300 ^{o}C for 4 h. The phase transformation of this CaO was studied by keeping the samples in air at room temperature for 6 months. After 7 days, the CaO was completely transformed into $Ca(OH)_2$. The results show that the calcite phase start to occur after portlandite was kept in the air at 9 days. The vaterite and aragonite phase beginning to be observed at 21 days and 3 months, respectively.

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