Crystal Structure and Thermal Behaviour of Calcium Monosilicate Derived from Calcined Chicken Eggshell and Rice Husk Ash

Nur Hazlinda Jakfar¹, Khor Shing Fhan¹,², Banjuraizah Johar³, Nur Maizatul Shima Adzali³, Siti Nur Hazwani Mohd. Yunus², and Cheng Ee Meng⁴,⁵

¹Centre of Excellence for Renewable Energy (CERE), Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.
²Faculty of Electrical Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.
³Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.
⁴Advanced Communication Engineering, Centre of Excellence (ACE), Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.
⁵Faculty of Electronic Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.

E-mail: sfkhor@unimap.edu.my

Abstract. This study focuses on the synthesis of synthetic calcium monosilicate ceramic from chicken eggshells and rice husks waste through the mechanochemical route that relatively straightforward without adding any binders. Synthetic calcium monosilicate was mixed using a 1:1 ratio of calcined eggshell and rice husk ash, which both materials known as rich in calcium oxide and silica sources, respectively. The mixed powder was pressed using uniaxial pressing before fired at 1100°C, 1150°C, 1200°C, 1250°C, and 1300°C for 120 minutes with a heating rate of 5°C/min. The XRD spectrum from 1100°C to 1200°C mainly consists of pseudowollastonite (ICSD: 98-005-2576), wollastonite and silicon dioxide phases. However, as the sintering temperature increases, the wollastonite phases was completely transformed into pseudowollastonite, leaving some unreacted silica.

1. Introduction

Calcium monosilicate or calcium silicate is known as wollastonite. It is usually formed by the reaction between calcium carbonate and silica under high heat and pressure, making it a naturally occurring metamorphic mineral [1]. Generally, calcium monosilicate comprises calcium, silica and oxygen with the formula CaSiO₃ or CaO·SiO₂. Theoretically, it contains 48.28% CaO and 51.72% SiO₂ [2]. Calcium silicates or wollastonite crystallise in two normal modifications, either β-wollastonite (parawollastonite) low-temperature phase or α-wollastonite (pseudowollastonite) high-temperature phase. These polymorphic materials have different crystal structure even though both have an identical chemical composition and stoichiometry [3]. According to the CaO-SiO₂ phase diagram, the
amorphous phase is first transformed into β-wollastonite at 870°C and then further transformed into α-wollastonite at 1125°C [4].

Nowadays, the uses of waste are favourable in producing materials, and the same goes for the synthesising of calcium silicate that has significant characteristics and properties as commercial CaSiO₃. Wollastonite can be derived from various raw materials, either from chemical, mineral, or waste precursors. In the present work, calcium oxide (CaO) and silica (SiO₂) sources were derived from waste chicken eggshell and rice husks ash, respectively. From literature, chicken eggshell consists of calcium carbonate (CaCO₃) up to ~94%, and calcium oxide (CaO) can be produced after calcined above 700°C. On the other hand, depending on the ecological origin and combustion conditions of rice husk ash, it can compose up to ~92% of silica sources [5].

Many researchers are studying methods of synthesising calcium silicate. Most of them were using solid-state reaction [6,7,8,9] and wet chemical methods such as sol-gel technique [10-13] and co-precipitation [5,6]. In addition to the conventional method, there are other methods of synthesising fabricated calcium silicate, such as using the hydrothermal method [4,8], microwave synthesis [11,14], and combustion method [10,11]. In addition, the mechanochemical method is a simple, environmentally friendly, solvent-free, and waste-free synthetic that can bring another synthetic calcium silicate. Practically, it is a high-energy milling process that involved repeated mixing and colliding of reactant powder particles in a closed vial of the planetary mill. The solid-state reaction happened due to the kinetic energy transferred from milling balls to the milled powders [6].

This present work attempts to look for the crystal and thermal behaviour of synthetic calcium monosilicate using calcined eggshell (CES) and rice husk ash (RHA) powder as the main ingredients through the mechanochemical method as they are low-cost starting materials and easy to obtain. It is also an attempt to investigate the feasibility of this waste material to be an alternative to synthesise calcium monosilicate that could be used in the industrial field in the future.

2. Experimental Details

2.1 Materials

Chicken eggshells and raw rice husk were used as raw materials. Both materials were cleaned and dried before the calcination process. Rice husks were calcined at temperature 800°C for 2 hours, while raw chicken eggshells were calcined at temperature 900°C for 4 hours at the same heating rate of 10°C/min for both materials. White powder materials were then obtained from both raw materials.

2.2 Preparation of calcium monosilicate, CaSiO₃

Calcined powder of chicken eggshell and rice husks with the chemical formula of CaO and SiO₂ was mixed in a closed agate vial with a stoichiometric 1:1 molar ratio using the mechanochemical method. Two respective powders were dried mill in a high-energy planetary mill (Planetary Monomill Pulverisette 6 Classic line) for 10 hours at 300 rpm with the agate ball to powder ratio of 1:10 gram. Next, the milled powders without binder were pressed at 12 Mpa for 5 minutes under a uniaxial hydraulic press to form pellets. These pellets were sintered at different sintering temperatures (1100°C, 1150°C, 1200°C, 1250°C, and 1300°C) in an air atmosphere with 2 hours soaking time and 5°C/min heating rate.

2.3 Experimental Analysis

Thermogravimetric and differential thermal analysis (TGA-DTA) was carried out for raw chicken eggshell and rice husk up to 900°C at a heating rate of 10°C/min in an air atmosphere by using TG 209 F3 Tarsus model while the pre-sintered mixed powder was analysed using Rigaku TG-DTA 8120 model up to 1400°C with 10°C/min heating rate in air. The phase identification of pre-sintered powder and sintered sample at various temperatures were characterised by X-ray diffraction measurement (Bruker D2 Phase Model) and Xpert Highscore Plus software. This X-ray diffraction measurement
operated from 10° to 90° 2θ at a scan speed of 2° 2θ/min and a step size 0.02° with CuKα radiation (Kα = 1.5406 nm) at 10 mA and 30 kV.

3. Result and Discussion

3.1 Thermal behaviour of raw materials and pre-sintered powder

The thermal stability of rice husk was ascertained using thermogravimetric analysis (TGA)/ differential thermal analysis (DTA), as shown in figure 1. The thermal degradation of rice husk is manifested in three main stages. The first stage starts below 100°C as a drying region where moisture and light volatiles are released. The second stage is pyrolysis between 250°C and 400°C, and the third stage is decomposition at high temperature. The weight loss in the first stage of thermal degradation of rice husk is about 6%, mainly due to the loss of moisture. This finding was supported by the appearance of an endothermic peak of DTA, indicating that energy was absorbed during the volatilisation of moisture from the rice husk surface [15]. The second decomposition stage with ~47% weight loss corresponded to the complete pyrolysis of hemicellulose and cellulose. The second stage is active pyrolysis because most of the main components of rice husk were decomposed and cause a significant total weight loss. For this reason, rapid degradation is seen in Figure 1. The third stage shows a slow degradation due to a regular continuity of lignin decomposition and other high molecular weight components [16]. Among the three components of rice husk (hemicellulose, cellulose, and lignin), hemicellulose is the easiest to be pyrolysed, followed by cellulose, and lignin is the most difficult to decompose [17].

![Graph of (i) thermal gravimetric analysis (TGA) and (ii) differential thermal analysis (DTA) for raw rice husks.](image)

Figure 1. Graph of (i) thermal gravimetric analysis (TGA) and (ii) differential thermal analysis (DTA) for raw rice husks.

Thermal analysis of the chicken eggshell was performed to determine the optimum calcination temperature. Thermal gravimetric analysis (TGA)/Differential thermal analysis (DTA) result of the eggshell was shown in Figure 2. The TGA/DTA curve showed thermal stability up to 600°C with a mass loss of 5%, referring to volatile material. The decomposition process occurs in a single step with a defined temperature between 600°C and 750°C, with a weight loss of ~43%. This is equivalent to the CO₂ molecules released to the environment from the structure of eggshell. The reaction can be represented as

\[
\text{CaCO}_3 (s) \xrightarrow{\text{heat}} \text{CO}_2 (g) + \text{CaO} (s). \tag{1}
\]
Figure 2. Graph of (i) thermal gravimetric analysis (TGA) and (ii) differential thermal analysis (DTA) for raw chicken eggshells.

Figure 3 shows the thermal gravimetric analysis (TGA)/Differential thermal analysis (DTA) result for the mixture of RHA and CES after milling. The figure clearly illustrates the weight loss of the mixture between 20°C and 1400°C. The first weight loss started before 100°C may be due to removing moisture and bounded water molecules [9]. The next weight loss approximate 15% is observed in the range of 450°C to 700°C. As reported by S.K Hossain and FHG Leite et al., it may be due to the dehydration of portlandite (Ca(OH)₂) that most probably formed due to the moistening of CES. This is confirmed with endothermic peaks on the DTA curve at the same temperature range. In addition, the existence of exothermic peaks around 1300°C is detected due to the formation of calcium silicates [9, 18]. Weight losses around 800°C showed the optimal stabilisation of beta calcium silicate.

Figure 3. Graph of (i) thermal gravimetric analysis (TGA) and (ii) differential thermal analysis (DTA) for the mixture of RHA and CES after milling.
3.2 Phase analysis of sintered samples at various temperatures.

Figure 4 shows the XRD pattern of the mixed powder of CaO\(\cdot\)SiO\(_2\) after milling for 10 hours. The mixture presence of portlandite (Ca(OH)\(_2\)) on most of the peaks with some cristobalite beta high (SiO\(_2\)) phases, matching to ICSD file no 98-004-6213 and 98-06-1839, respectively. The portlandite phases were detected at most peaks while the presence of cristobalite beta high, SiO\(_2\) was detected at angle 21.729° and 59.371°. Phase formation in the XRD pattern was in line with the raw material used. The portlandite is probably formed by adsorption of moisture from the atmosphere by calcium oxide, CaO due to its hygroscopic behaviour [5]. However, calcium silicates (CaSiO\(_3\)) phases that expected to exist after the milling process are not successfully present as it has not been identified in the XRD pattern below. The mechanochemical method tends to mix the SiO\(_2\)-CaO powder only without having any reaction.

The XRD pattern for sintered mixed powder at temperature 1100°C, 1150°C, 1200°C, 1250°C, and 1300°C is shown in Figure 5. The formation of pseudowollastonite phase (ICSD 98-005-2576) is present in all sintering temperatures along with traces of unreacted silica at \(2\theta\) within 21° – 23°. In this work, the pseudowollastonite phase was formed at 1100°C, which is lower than the 1125°C reported in [4]. Besides, it can be seen that the peaks at 20 of 25° – 30° at temperature 1100°C, 1150°C, and 1200°C belong to wollastonite 1A (ICSD 98-004-6164) with different percentages of composition. The sample that sintered above 1200°C did not show any wollastonite phase and disappeared after sintered at 1250°C and 1300°C, forming a complete pseudowollastonite phase with monoclinic modification (space group 15, C 1 2/c 1) and some unreacted SiO\(_2\) that related to an excess of SiO\(_2\) in the initial system of the stoichiometric ratio.
Figure 5. XRD pattern of sintered samples at different sintering temperatures.

4. Conclusion
This study reveals the crystal and thermal behaviour of mixed chicken eggshell and rice husk ash waste used to synthesise calcium monosilicate as a component of ceramic products. According to the empirical results of phase analysis, the pre-sintered synthetic calcium monosilicate powder does not show any calcium silicate phases from the mechanochemical method. However, the weight loss of the powder starts at about 450°C, and there is an endothermic peak on the DTA curve, indicating a reaction between the two mixed powders. In addition, the XRD results at various sintering temperatures showed that pseudowollastonite, wollastonite phases, and unreacted silica were formed starting from 1100°C.

References
[1] S H Abd El Rahim, A A Melegy and E M A Hamzawy 2017 Inter. Ceram. 66 232-236.
[2] H H Beheri, K R Mohamed and G T El-Bassyouni 2013 Mater. Des. 44 461-468.
[3] H Ismail, R Shamsuddin, M A Abdul Hamid and R Awang 2016 J. Aust. Ceram. Soc. 52 163-174.
[4] T Nuchnapa, K Tunchanoke, K Supawinee, K Ruksapong and S Anuvat 2011 J. Sol-Gel Sci. Technol. 58 33-41.
[5] S K S Hossain and P K Roy 2018 J. Asian Ceram. Soc 6 289-298.
[6] S P Singh and K Basudeb 2011 NJGC, 1 (2) 49-52.
[7] H Wang, J Chen, W Yang, S Feng, H Ma, G Jia and S Xu 2012 J. Eur. Ceram. Soc. 32 (3) 541-545.
[8] P Rimruthai, C Napat, P Pusit, and P Ratchadaporn 2015 Adv Mat Res 1103 1-7.
[9] F H G Leite, T F Almeida, R T Faria and J N F Holanda 2017 Ceram. Int. 43 (5) 4674-4679.
[10] U Anjaneyulu, K Sivasankar and S Sasikumar 2013 Trans. Indian Ceram. Soc. 72 (4) 260.
[11] L Rvindra, V Venugopal and S Sasikumar 2013 Combust. Sci. Technol. 185.
[12] C C Chen, C C Ho, S Y Lin and S J Ding 2015 Ceram. Int. 41 (4) 5445-5453.
[13] O Mohammed, S Majid and A M Elham 2014 *Int. J. Eng. Technol.* 4 426-429.
[14] S Vichaphund, M Kitiwan, D Atong and P Thavornitti 2011 *J. Eur. Ceram. Soc.* 31 (14) 2435-2440.
[15] X Yao, K Xu and Y Liang 2016 *Bioresources* 11 (4) 10549-10564.
[16] S El-Sayed 2019 *Engineering in Agriculture, Environment and Food* 12 (4) 460-469.
[17] H Wang, S Xu, S Lu, S Zhao and B Wang 2009 *Ceram. Int.* 35 (7) 2715-2718.
[18] S K S Hossain and P K Roy 2019 *Bol. Soc. Esp. Ceram.* 58 (6) 274-284.

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