PRELIMINARY INVESTIGATION ON THE PHYSICAL PROPERTIES AND MORPHOLOGICAL OF SINTERED COCKLE SHELL/RECYCLED SODA LIME SILICATE COMPOSITE

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ABSTRACT: The effect of treatment condition cockle shell (CS) on physical properties, phases and morphology behaviour of CS filler/recycled soda lime silicate glass (rSLSG) composite were investigated. The CS filler was prepared at drying condition and calcined at temperature of 800 °C and 1000 °C before subjected to the direct sintering process. The crystalline phases present in the treated samples of CS fller and composite were identified by X-ray diffraction (RIGAKU MINIFLEX II) and was observed that CaO fully precipitated when the calcination temperature was increased to 1000 °C and quartz phases predominate at high volume glass content. The tested samples were characterized using Fourier transform infrared spectroscopy (FTIR) and confirmed hydrogen bond affected densification of CS/rSLSG composite. This composite was tested using physical testing and results revealed that the average of porosity, water absorption, and bulk density was a function of calcination temperatures. Scanning electron microscope shows observation on CS filler revealed that the treatment condition led the phase separation of the cluster interconnected before the skeleton crystals shape formed at 1000 °C. The findings concluded that the suitable composition for CS filler loading was 30 wt.% and can be controlled for building material applications.

KEYWORDS: *Cockle Shell; Glass Waste Composite; Soda Lime Silicate; Calcination; Physical Properties*

1.0 INTRODUCTION

Recycled materials have been applied numerous in structural applications such as building materials [1]. Building materials are characterized by their physical properties as well as can be indirectly assessed by the determination of microstructural for the utilization of secondary raw materials such as recycled soda lime silicate glass.

The soda lime silicate glass (SLSG) waste usage has embarked due to the awareness in environmentally friendly and unique behavior of the glass [2]. The unique behavior of glass is it can be recycled many times without loosening its strength and adaptability in different technique and shape of fabrication [3-4]. The usage of recycled soda lime silicate glass (rSLSG) which contain with quartz phase has attracted researchers study on the fabrication of glass ceramic or so-called green glass-ceramics composite [5]. Research from Wahab et al. [5] stated that quartz is classified as glass network formers and known as silicate mineral that applied for construction material.

Cockle shell (CS) is one of the most waste shells that consist of calcium carbonate ($CaCO_3$) and a feature of cockle shell can be indicated to the variation and polymorphism of colors [6] which was white color due to element presence between cockle shells contained higher amount of carbon and calcium [7]. CS are ideal to be produced with high purity calcium carbonate ($CaCO_3$) solid from shell wastes and have been applied because contain the highest source of biogenic $CaCO_3$ [8]. This element of $CaCO_3$ through process calcination to transformed to CaO [9] which is very important for structural applications since it attributed the improvement in strength in structure and thermal stability. Since this has shown improvement of the properties such as non-hazardous waste and exhibited low firing shrinkage with 1.14% and flexural strength which within the acceptable limit for building materials [10], it also has great potentially to be serving as a purely structural member as it can change physical properties as well as improve mechanical properties of glass composite. However, if the temperature processing such as calcination and sintering temperature uncontrolled main issues will be raised is lack of densification due to the porosity [11-12].

The porosity influenced by processing temperature and consequently on the physical behavior of recycled glass using cockle shells was not reported in any literature data for building materials. Thus there is a gap of knowledge regarding the study on preparation CS/rSLSG

composite by controlling preliminary condition of preparation of cockle shells that can lead to achieve the good properties of low porosity, low water absorption and high density with respect to the formation of phases and observation on the microstructure. The present study is focused on investigating the effect of preparation condition of CS filler on physical properties of the CS/rSLSG composite. Correlation between the physical properties and crystalline phases is supported by microstructural analysis after the single step of a sintering process.

2.0 METHODOLOGY

The cockle shells (CS) have cleaned from dirt and impurities via purification process before filtration process. CS was then dried under sunlight for two (2) days. The preparation of cockle shell powder starts by crushing shells into small parts and then followed with the pulverizing process. Powdered shell then sieved using siever shaker to obtain required particle size which was approximate to 75 μm determined using particle size analyzer, Mastersizer 2000 Malvern Instrument Ltd model. This size was set to compliment and standardized with size glass particles that have been studied [2] for analysis purpose. One container of the cockle shell powder was dried at 100 °C for 24 hours in drying oven and another container of the cockle shell powder was calcined at two different temperatures which were 800 °C and 1000 °C [8] with a heating rate of 10 °C/min for 4 hours. All calcined powder was kept in close container together with silica gel to avoid the reaction with carbon dioxide and humidity before being used. rSLSG was sieved using vibratory sieve shaker to get 75 μm average particle size. Throughout the study, this composition was a variety from literature [9] as shown in Table 1. This composition has selected for its suitability in forming glass ceramic. These samples called as green bodies were produced via several steps consist of ball milling, pushing and heat treatment. Pressure at 30 MPa was used to press 3.2 g of the mixture into a mold of dimension 18 mm x 18 mm x 4 mm. All of samples pressed were subjected to direct sintering treatments via laboratory electric furnace Carbolite 1300 model at fixed for both heating rate 2°C and sintering temperature of 800 °C for 1 hour dwelling time. The selection of the sintering temperature was based on respective DTA curve from

of dimension 18 mm x 18 mm x 4 mm. All of samples pressed were subjected to direct sintering treatments via laboratory electric furnace Carbolite 1300 model at fixed for both heating rate 2°C and sintering temperature of 800 °C for 1 hour dwelling time. The selection of the sintering temperature was based on respective DTA curve from previous study [2]. An observation on physical sample sintered will be recorded. The physical analysis of water absorption, bulk density, shrinkage and apparent porosity were determined according to ASTM C373. Sample underwent FT-IR analysis to investigate the unknown materials present in the sample. The precipitation of crystalline phase was conducted using X-ray diffraction (RIGAKU Model MINIFLEX II) operating at 30 kV and 15 mA with Cu Kα radiation. The detector was scanned in the range of 2θ angle from 10° to 80°. The appeared crystalline phases were compared with ICDD and X'Pert Highscore software to analyze the data. The observation of microstructural was conducted for gold coated samples under scanning electron microscopy (SEM) (Model: EVO 50 Carl Zeiss SMT).

Table 1: Batch composition of SLSG/cockle shell [9]

Code	Composition (wt%)	
	SLSG	Cockle Shell
A	70	30
B	60	40
C	50	50

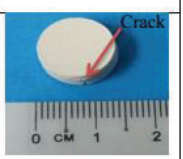
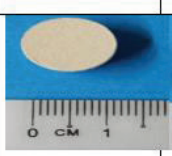
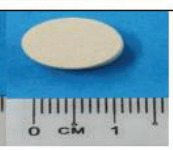
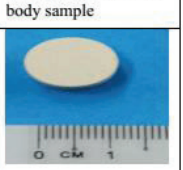
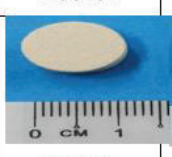
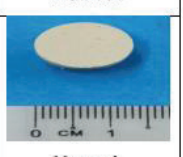
3.0 RESULTS AND DISCUSSION

3.1 Physical Properties

Table 2 shows the visible changes in sample appearance after sintering by visual inspection and expected that when cockle shell (CS) is treated, one of the compositions provides shape and colour responses. The colour of sample C is more whitish compared to sample A which related to the amount addition of CS filler as previously reported in [6-7]. A slightly changes occurred on all samples that were subjected to a single step sintering at a different condition which is a condition of drying and calcination at 800 °C and 1000 °C, respectively. These calcination temperatures in the range 800 °C and 1000 °C are suggested by the [8] to

allow the organic content been removed which can cause molecules of water absorption affects the densification of the ceramic bodies during sintering. All sintered sample that has been calcined to give a better result and there is no presence of crack been observed through visual observation. However, samples without calcination and inclusion of wt.% of CS filler increased from 30 wt.%, resultant in an initiation of crack within sample B and C.

Table 2: Effect of composition and condition on physical appearance of cockle shells/SLSG composite

Composition / Process	A (30 wt. %)	B (40 wt. %)	C (50 wt. %)
With drying			
	No crack	Crack at the edge	Crack at the middle of body sample
Calcination (800ºC)			
	No crack	No crack	No crack
Calcination (1000ºC)			
	No crack	No crack	No crack

Samples B and C were observed to have crack at the edge and center of sample, respectively. Such behaviour was expected because the absorption water molecules still entrapped and shown from hydrogen bond in Figure 1. Figure 1 shows FTIR result revealed for cockle shell filler at different condition of treatment. The IR spectra for the dried cockle shell shows that the weak band at 1788 cm ^{1}. It coincides to C=O bonds from carbonate that presence in the chemical composition of the cockle shell. The two bands at 1478 cm and 863 cm are attributes to the C-O bending and stretching modes of calcium carbonate [8]. The presence of peak at 3641 cm ^{1} for calcination at 800 °C and 1000 °C is due to OH bonding in formed during adsorption of water by CaO. It was also reported [8] that varying a number of cockle shells in the

composition more than 30 wt.% will produce visible changes in the appearance. For all investigated batches, only 30%wt CS filler at all condition represents good appearance. Therefore, based on the observation of physical changes, it was concluded that a 30 wt.% of cockle shells filler represented the most appropriate to be used and was chosen for further investigation.

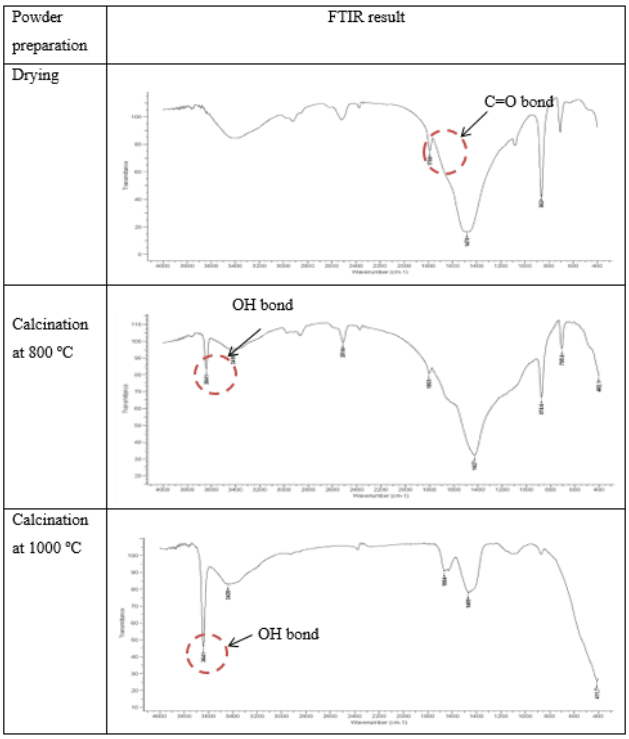
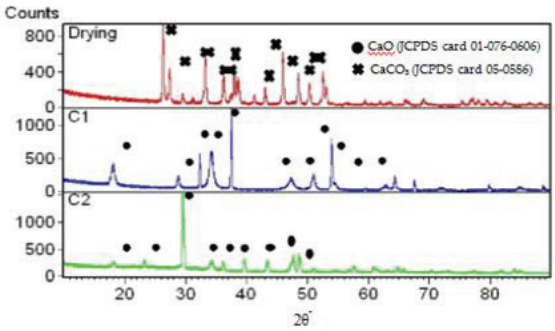


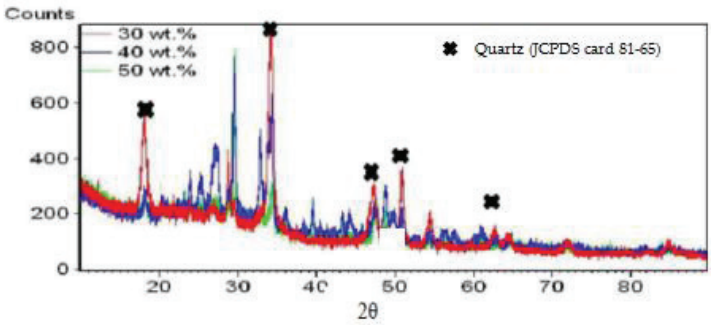
Figure 1: Comparison of FTIR spectrum in response to condition treatment for cockle shell filler

Referring to the diffractogram of the sample CS filler in Figure 2(a), it was found that the predominant crystalline phase at 800 °C and 1000 °C was calcium oxide, CaO (JCPDS card 01-076-0606). The amount of peaks is higher in sample A than those indicated in sample B and C which can be correlated with the $CaCO_3$ (JCPDS card 05-0586) content of the CS filler. Sample C shows distinct peaks compared to sample B and A indicating that the composition in CS filler is transforming to CaO which corresponds to an increased carbon content and reduced carbonates as compared to sample A [8] and it was also reported in [9] that cockle shell was fully crystallized. XRD result for sintered glass waste composite was

shown in Figure 2(b). The distinct peak at 36.14 ° of 2θ indicated the presence of a quartz (JCPDS card 81-65) solid solution with a high intensity. It can be observed the quartz phase is identified due to major composition of in both of cockle shell and glass. Quartz phase presence with high intensity at all sample observed at diffraction peak between 20° and 40°. This result is in same agreement by research from [2, 5] stated that the intensity of this reflection slightly increased with increased glass content which high quartz was formed.



(a)



(b)

Figure 2: XRD patterns of (a) calcination condition for cockle shell filler and (b) sample CS/SLSG sintered at different loading of CS filler

Figure 3 shows linear shrinkage of CS/rSLSG composite as a function of the condition of CS powder preparation and composition of CS filler loading. As the weight percentage of CS loading was decreased, the percentage of shrinkage was increased after the sintering for all condition which reflects an increase in volume glass phases as supported by Figure 2(b). Sample A represents the highest value of linear shrinkage due to high SLSG powder volume compared to sample B and C which expected the presence of high quartz causes the viscosity of viscous flow high during the sintering process. This viscous attributed to the gases

entrapped which finding in same agreement with [11]. Additional works by Pontikes et al. [12] reported that the sintered sample contained the higher mixture of glasses exhibited high shrinkage compared to the high clay content of a glass-ceramic sample.

As shown in Figure 4, the apparent porosity and water absorption for sample A, B and C is a function of the cockle shell loading. It was noticed that the porosity and water absorption is directly proportional to filler loading. The porosity and water soaking up increase with increasing CS loading. Sample shows the lowest percentage of porosity and water absorption which is 3.62 % and 1.48 %, respectively. The lowest percentage of porosity is shown in sample A which has high glass powder volume in the mixture resulting viscosity of the phase. An excellent flow of viscous liquid phase can decrease the porosity towards the open pores. The volume of the glass powder affects the porosity percentage through the viscous flow. These results are in same agreement by research from Juoi et al. [3] who stated that good flow of viscous liquid phase obtained from high volume of glass powder and sintering effect.

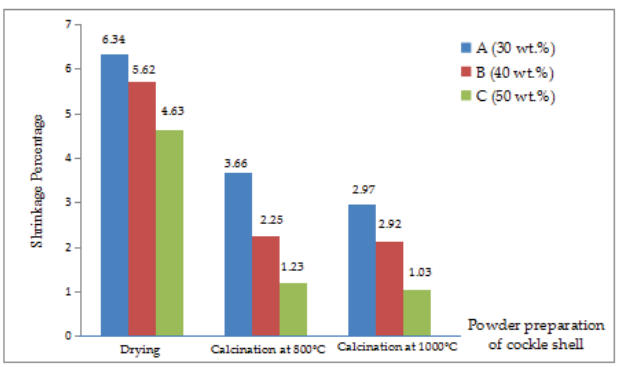


Figure 3: Percentage of linear shrinkage at different loading with different powder preparation of CS filler

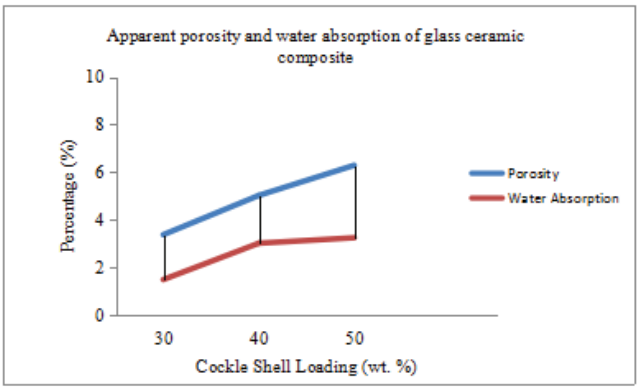


Figure 4: Percentage of apparent porosity and water absorption at different loading of CS filler

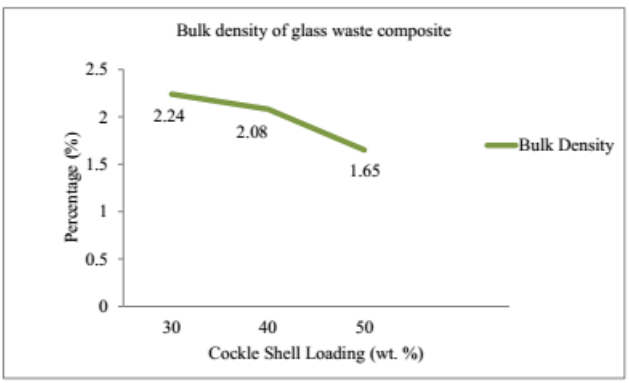


Figure 5: Densities of the CS/SLSG composite at different loading of CS filler

In this study, the density profile only focused on drying condition since the results between the calcined samples exhibited no major differences with average results of bulk densities. The bulk density in Figure 5 shows a decreasing trend as the CS loading increases. As expected, the highest value of the bulk density was observed in sample A which is 2.24 g/cm^3. This finding may be attributed to the proportional relationship between the proportion of major crystal phase as summarized in Figure 2. The densities gradually decrease as the CS loading increases. This trend could be supported by features morphology in Figure 6 where the micrograph of CS was discerned have high pore attribute. Hence, the density of high wt.% of CS filler was low as compared to the composition with high recycled SLSG content. The porosity and water absorption results were inversely proportional to density. This indicates that the density of this composite is proportional to the developed microstructure.

3.2 Morphological Analysis

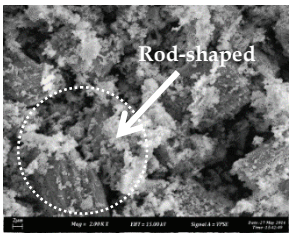
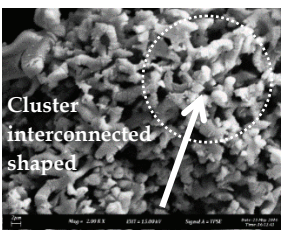
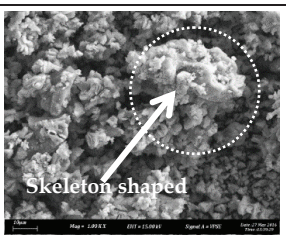
The apparent morphologies of dried and calcined cockle shell were examined by SEM as shown in Table 3. The particles of powder prepared from drying process showed were irregular, rod-shaped and undulated. Many pores and pits distributed over the surface. The pores and pits are randomly form one place to another place. The microstructure of cockle shell filler is changed from irregularly to a porous surface for both powders of calcination at 800 °C and 1000 °C.

Porous structure was built from agglomeration of particles. The morphologies of calcined cockle shell powder at 800 °C were a cluster of interconnected structure and bonded together as aggregates. For calcination temperature at 1000 °C, the cluster of interconnected start to disappear and the shape skeleton formed clearly and porously becomes wider. It can be seen that the calcination process attributes to the porous microstructure which represents rod-shaped, cluster interconnected and skeleton shape. Later shape shows a better indication of dense surface and reduction of pores. This could be explained by the composite calcined at 800 °C and 1000 °C. It should be noticeable that size of contour of the cockle shell sample was changing. This may affect the observed XRD data shows the presence of the difference in intensity of XRD peaks between the samples. The obtained results suggested that type of calcination affected the characteristics of the $CaCO_3$ powder sample. Based on the results in Table 2, the glass composite sample with added of 30 wt.% of cockle shell was considered for microstructure analysis as shown in Figure 6.

It can be observed the microstructure of 30 wt.% of cockle shell sample shows more crystal due to high glass volume. This implies the volume glass induced the crystallization. Besides, it shows least pores and dense surface. This result is in same agreement by research from Juoi et al. [3] who reported that addition of 30 wt.% bottom slag filler loading produces least pores and higher dense even surface compared to other reinforced glass waste composite. This can be concluded that the increasing composition of filler loading attribute to increasing pores and decreasing in a dense surface. The image of SEM results proves that the glass composite sample with a high volume of glass able to produced promising physical properties which resultant shape and appearance are

still remained due to crystal phase present. It also supports sample with added of 30 wt.% of CS has more crystal phase gives less porosity.

Table 3: Morphologies of dried and calcined CS powder

Powder Preparation Condition	Micrograph (at magnification of 2.00KX)
Drying	
Calcination at 800°C	
Calcination at 1000°C	

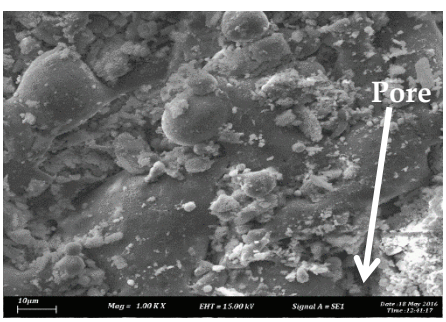


Figure 6: Micrograph of morphology of CS/rSLSG composite

4.0 CONCLUSION

The CS/rSLSG composite was successfully characterized using SEM, FTIR, XRD and tested for physical properties. This study showed that different condition of preparation powder CS and the weight percentage of CS loading generate significantly different values in physical properties. The calcination temperatures were strongly correlated with the microstructure where SEM observation exhibited that the CS powder had cluster interconnected and skeleton crystals shape which is expected to have better physical properties as compared to rod-like crystals accompanied with results from XRD and FTIR analysis. Moreover, these results encourage further investigation into the application of glass ceramic composite in building materials.

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