INFLUENCE OF EGGSHELLS CONTENT ON PROPERTIES OF SINTERED GLASS COMPOSITE USING DIRECT SINTERING

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***ABSTRACT**: The purpose of this study is to investigate the influence of eggshells as fillers on the properties of green glass composite and different filler loadings. Green glass-ceramic was prepared using soda lime silicate glass (SLSG), spent bleach earth (SBE), and eggshell (ES). It was believed, by increasing the percentage of weight filler, the properties of the samples will be improved. The filler was divided into two types which are calcined ES and without calcined ES. The eggshell was calcined at 1000°C with 2°C /min and was held for 1 hour to eliminate carbon dioxide in the calcium carbonate compound. The particle size of all materials was approximate <45um. The green glass ceramic was formed using hydraulic dry pressing at a weight fraction of eggshell loading of 3wt%, 6wt%, and 10wt%. The green glass ceramic sintered at constant temperature and heating rates were at 800°C and 2°C /min with a holding time of 1 hour. The green glass ceramic was analyzed in terms of thermal properties by using thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The results indicated the glass transition temperature for SLSG is about 541.27°C, SBE is approximately 680.65°C, and ES is about 432.48°C. These results indicate that as the weight percentage of filler increases, weight loss will be decreased. The FTIR analysis confirmed the presence of hydrogen bonds between calcined eggshells and pure eggshells. The findings concluded that the suitable composition for ES filler loading can be controlled for alternative materials for structural applications.*

KEYWORDS: green glass composite, thermogravimetric analysis (TGA), direct sintering, soda lime silicate glass, spent bleach earth, eggshell

1.0 INTRODUCTION

Recycling has become very important for modern society due to the immense increase in waste and its impact on the environment, human health, and safety. In particular, soda-lime-silica scrap glass, (SLSG) is a non-hazardous waste that mainly derives from packaging applications and is produced in increasing quantities in the world [1]. Soda lime silica glass waste has many advantages to use as a source of SiO2 [2]. Direct sintering of mixtures of inorganic waste including recycled glasses act as fluxes is an important alternative [1]. In this study, SLSG was mixed with spent bleach earth (SBE). Spent bleaching earth (SBE) is the residual adsorbent resulting from the refining process of crude palm oil (CPO) in the cooking oil industry and is categorized as solid waste. Bleaching earth residue is basically the mixture of fresh bleaching earth and CPO's hydrocarbon component. The hydrocarbon component is transformed into coke or charcoal. SBE waste has become a major problem facing the cooking oil industry as a consequence of its growth. Furthermore, about 0.5e1% of bleaching earth (BE) is consumed to produce 60 million tonnes of cooking oil, which all of BE will convert into waste (SBE waste). It is predicted that the production of SBE waste around the world is 600,000 tonnes [3]. This study used eggshell (ES) as filler. Eggshell, which corresponds to about 10 wt% egg, contains about 94 wt% calcium carbonate ($CaCO_3$) in its composition.

Although the ES is not considered hazardous waste, it is inappropriate landfill disposal can result in considerable environmental liabilities due to the large number of eggs produced. Since ES is a calcium carbonate-rich residue, the possibilities of its reuse may include the incorporation in soil for agricultural purposes [4]. This study represents an important contribution to developing new waste management options for this problematic material [5]. This study reports on the effect of eggshells as filler in the SLS glass composite by analyzing the thermal properties, physical observation, and chemical constituents in a compound by FTIR.

2.0 MATERIALS AND METHODOLOGY

SLS recycled glasses were crushed by using a disc crusher machine (Model Retsch). Then the SLSG powder was milled by using a planetary ball mill for 60 minutes. During the milling, aluminum balls were placed in the ceramic bowl. Then, the powder is sieved using a vibratory sieve shaker to get < 45µm average particle size. The raw SBE has undergone a cleaning process to extract oil using the sonication process. It was then followed by filtration and drying processes in a drying oven for 24 hours until no wet SBE powder was observed. Eggshells were cleaned and dry in a drying oven for 24 hours. Then, the eggshells were crushed using a planetary ball mill for 30 minutes. The eggshell powder was also sieved by using a sieve size of 40μm. Then the eggshells are divided for the calcined process. The calcination process is to eliminate carbon dioxide from the carbon carbonate compound. The temperature involved is at 1000 ºC with a 2 ºC/min heating rate and 1-hour holding time. The particle size distribution for SLSG, SBE, and ES was determined using a particle size analyzer, the Mastersizer 2000 (Malvern, UK Instrument Ltd.) model. The glass transition temperatures (Tg) of SBE, ES, and recycled SLS glass were investigated using a thermogravimetric analysis (TGA) model TA 7000(Q50). The compositions of the GGC composite investigated in this work are shown in Table 1. A different ratio was applied in order to identify the suitable composition with good properties that will be produced [7]. All samples were produced using conventional powder processing methods involving ball milling, pressing, and sintering. 1.5 g of the mixture was pressed into a pellet mold at 17MPa. The obtained green bodies were subjected to sintering treatments using a laboratory electric furnace Carbolite 1300ºC (Carbolite, German) at constant heating rates of 2˚C and constant sintering temperature of 800 ºC and 1 hour of holding time. Fourier transform infrared spectroscopy (FTIR) machine is used to identify chemical constituents in a compound. The samples required to be analyzed are in powder form.

Table 1 Ratio of filler content in green glass ceramic

Sample code	SLSG (wt %)	SBE (wt %)	ES (wt %)
A	65	32	3
B	60	34	6
C	55	36	10

3.0 RESULTS AND DISCUSSION

3.1 Thermal analysis

After the sintering process, the thermal properties of the three types of samples were observed by using thermogravimetric analysis (TGA). TGA is a controlled heating technique used to determine the lost weight mechanism of a sample. Furthermore, it may more helpful than XRD to analyze a complicated matrix and confirm the presence of some phases that are difficult to be identified such as semi-crystalline or amorphous phases. Figure 1 clarifies a comparison between three samples with different weight percentages (wt.%) of filler. Upon heating the glass powder to 1000°C at 10°C /min, the value of T_g was determined from the derivatives weight curve. The curve acted as a reference to the plot intersection of two targets at the start and end point the of T_g curve.

The glass transition temperature of SLSG was determined after extrapolating from the start and end of the transition. The thermograms show that the decomposition of calcium carbonate in three prepared samples occurred in a single step from 400°C onwards as shown in Figure 1.

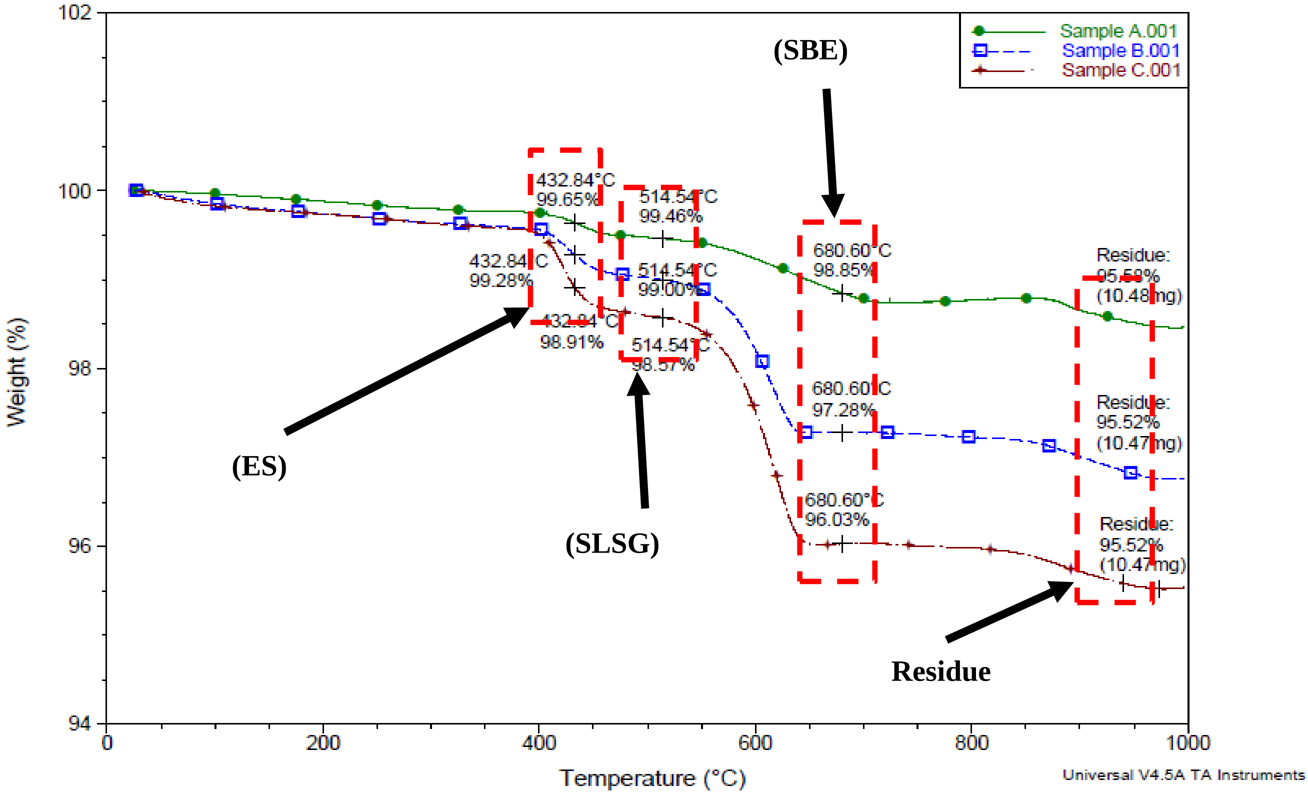

Figure 1: TGA curve of ES (a) 3wt%, (b) 6wt%, (c) 10wt%

Table 2: Percentage of weight loss at Tg in samples

Sample code	Percentage of weight loss (%)		
	ES	SLSG	SBE
A	99.65	99.46	98.85
B	99.28	99.00	97.28
C	98.91	98.57	96.03

Figure 1 shows the TGA curves of three samples. The weight loss of the three samples starting near 54°C is related to the physically adsorbed water released from the sample. With the increased temperature up to nearly 400°C, the glass transition temperature (T_g) of ES was determined at 432.84°C. As the temperature increase up to 550°C, T_g of SLSG was determined at 514.54°C. The value found for SLSG in literature is 514°C [6, 7]. With the increased temperature near 700 °C, T_g of SBE was determined at 680.60°C as shown in Figure 1. When the glass reaches its highest densification from approximately 600°C, the glass expansion occurs up to 1000°C due to viscous liquid phase formation. Based on Figure 1, the glass continues gradually decreasing from 1000°C onwards. Moreover, between 400°C to 700°C, the thermogram plot indicates the percentage of weight loss decreased, suggesting the gases originating from the sintered samples were released during the heating [8]. As shown in Figure 1, the TGA pattern of calcined eggshells as filler showed three distinct stages of weight loss. ES at a temperature between 409.93°C and 438.21°C, while SLSG is below 600°C and SBE below 700°C. The first stage is the glass transition temperature of ES. It can be attributed to the CaO phase starting to soften. The second stage exhibited the major weight loss at 514.54°C represented by SLSG, corresponding to 99.65 wt.% was due to the change of the SLSG phase from solid to semi-solid. The third stage indicates weight loss to 98.91 wt.% of SBE which can be attributed to the loss of organic compounds.

A summary of the percentage of weight loss results is shown in Table 2. The table shows different percentages of weight losses over constant temperature ranges.

Generally, there are three stages of weight loss in the TGA curves related to thermal dehydration or decomposition of different phases for each material formed in sintering samples. The first stage represents by ES which falls at 432.84°C. In stage two, 500°C to 520°C, it is clearly seen that the TGA curves of SLSG exhibit a low percentage of weight loss compared to ES which has a high rate of percentage weight loss, 99.65 %. The third stage represents by SBE at 680.60°C which falls between 650°C to 700°C, and has 96.85%, percentage of weight loss corresponding to the decomposition of eggshell.

The residue is where the sample is fully burned. Sample A is fully burned at 13.25mg where the percentage of weight loss is 99.73%. On the other hand, Sample B is fully burned at 9.125 mg where the percentage of weight loss is 69.25%. For Sample C, the residue value is 10.39 mg (73.69%). To summarize, the weight loss of the three samples due to physically absorbed water and organic matter that had been burnt off was approximately 95.52 °C below 1000°C. The result of TGA is important because the choice of a particular method depends on the properties of raw materials, the melting temperature, and size requirements [1].

As shown in Figure 1 and Table 2 above, high loading of eggshells as filler decreased the percentage of weight loss during a fire in TGA. The lowest weight percentage is contributed by sample C with 10wt% of filler. Also, there was a significant weight loss of calcined ES of about 99.65 % from 400 °C to 433°C at a peak of 432.84°C in the TGA curve, which may have been due to the decomposition of CaO [9]. These results could be confirmed by the FTIR results in Figures 4 and 5.

3.2 Fourier transform infrared spectroscopy (FTIR) analysis

The visual inspection is shown below in Figure 2 (without calcined eggshells) and Figure 3 (with calcined eggshells). The ratio of the composition is still the same but the type of eggshells as filler is different. Figure 2 illustrates that the sintered samples were bloated as compared to Figure 3. This is due to a fraction of the gaseous products generated being trapped within the pores of samples and this effect has been reported by [8]. On the other hand, samples without calcined eggshells [10] as filler have a high tendency to expand compared to the shape of sintered sample in Figure 3. These results indicate that the gases released in which the glass is relatively dense will be partially retained on the glass matrix and will cause its expansion. Based on the result in Figure 3, the height of sintered samples was increased as high filler loading increased. The high amount of calcium oxide has associated with the presence of calcium carbonate, which is the main component of the waste eggshell confirmed by FTIR results.

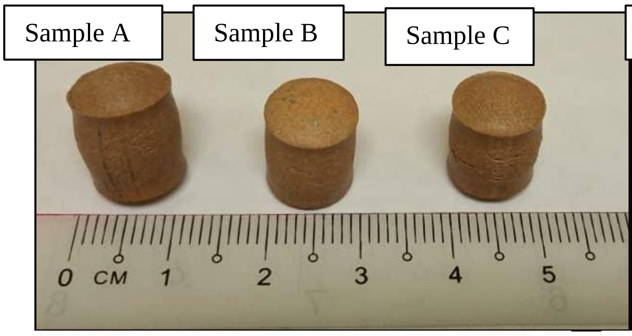

Figure 2: Sample without calcined eggshell (in the form of CaC)

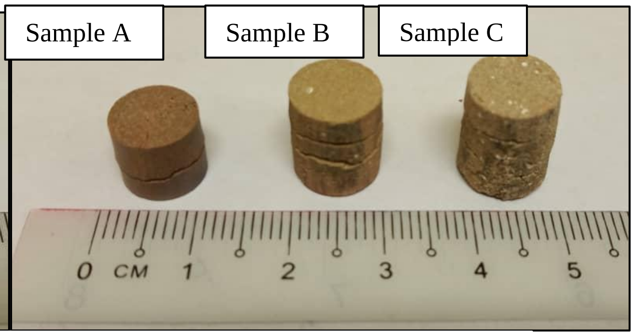

Figure 3: Sample with calcined eggshell (in the form of CaO)

Calcine temperature for this study was constant which was 1000ºC with a 2ºC /min heating rate and 1-hour holding time. This temperature was selected based on a study conducted by [11]. The study reported the temperature of 900°C was then suitable for use as the calcination temperature to ensure complete conversion to CaO. This could be due to the fact that the calcined eggshell exhibited smaller particle size and appeared more macro-pore volume than the calcined commercially available calcium carbonate. As result, the calcined eggshells provided a higher exposed surface for the surface reaction of CO_2. The application of CaO is basically based on the reaction stated in Equation 1.

$$CaO + CaO_2 \leftrightarrow CaCO_3 \quad \Delta H = -171.2 \text{ kJ } mol^{-1} \quad \text{(Eq.1)}$$

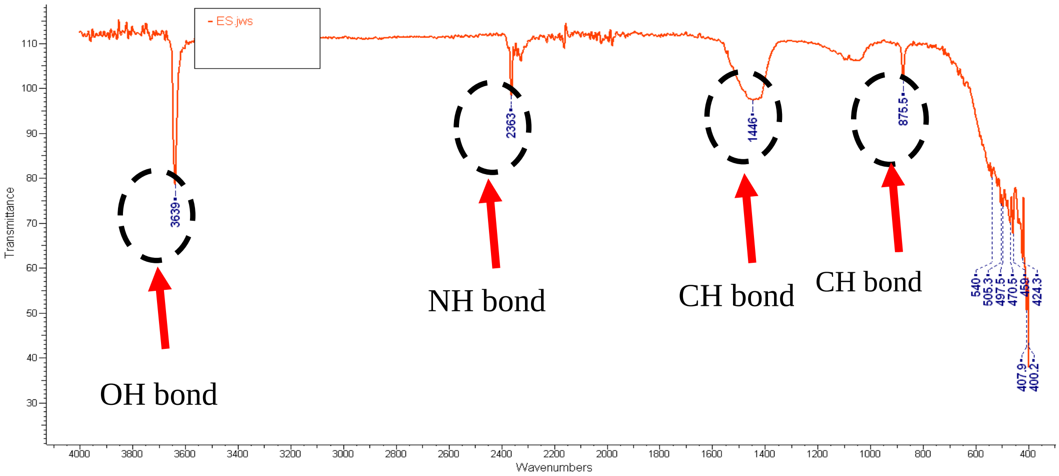

Figure 4: FTIR result for calcined eggshell

The usefulness of qualitative analysis from the characteristic frequencies provides information to identify chemical constituents in a compound. Figure 4 shows the IR spectra of the calcined eggshell. The presence of the broad peak at the band at 3639 cm^{-1} as a result of OH in Ca$(OH)_2$ formed during the adsorption of water by CaO. The weak band at 2363 cm^{-1} corresponds to NH bonds. Well-defined infrared bands at 1446 and 875 cm^{-1} are characteristic of the CH bond.

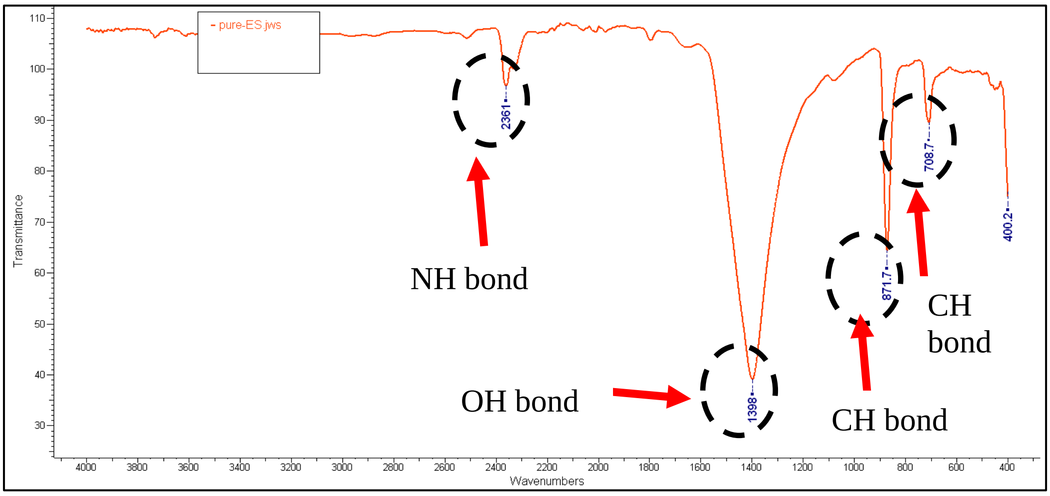

Figure 5: FTIR result for pure eggshell

Figure 5 reveals several bands from 400 cm^{-1} to 4000 cm^{-1}. The band aspect of the FTIR spectra of pure eggshells shows the difference between the FTIR calcined eggshell powder (Figure 4).

As shown in Figure 5, the presence of the peak at 2361 cm^{-1} corresponds to NH bonds. The strong bond of OH was found at a peak of 1398 cm^{-1}. The weak band at 871 and 708 cm^{-1} corresponds to CH bonds.

4.0 CONCLUSION

The influence of eggshell contents on green glass ceramic was investigated. The glass transition temperature is important for sintering temperature. Besides that, the high loading of eggshells as filler decreased the percentage of weight loss during the fire in TGA. The presence of carbon dioxide in the filler also affected the properties, shape, and color of the sintered sample. Carbon dioxide present in sintered sample caused the sample to be bloated. The heating rate is not caused by the color of the sample change but by the ratio of filler content itself. The physical observation is related to the calcination process of the filler. FTIR analysis showed a difference between calcined eggshells and pure eggshells. From this study, using calcined eggshell as the filler has the ability to avoid sintered samples from becoming bloated. This is because the pure eggshell powder has undergone a calcination process to release carbon dioxide gas. Therefore, it is believed that sintered samples become bloated due to carbon dioxide gas because it has a high potential to make the samples expand. The usefulness of qualitative analysis from the characteristic frequencies provides information to identify chemical constituents in a compound. FTIR analysis confirmed the presence of hydrogen bonds between calcined eggshell and pure eggshell. The findings concluded that the suitable composition for ES filler loading can be controlled for alternative materials for structural applications. These findings encourage further investigation into different weight percentages of filler and the thermal property also its microscopy.

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