CHARACTERIZATION OF VITRIFIED MALAYSIAN AGROWASTE ASHES AS POTENTIAL RECYCLING MATERIAL

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ABSTRACT

Vitrified materials were made purely using combustion ashes from agricultural based residues (rice husk ashes and palm kernel shell ashes). This vitrified material subjected for further recycling to construction materials. The optimum heat-treatment schedule for the vitrification was 1400°C for 2 h for nucleation and crystal growth and 1050° °C for 1 h for cooling. The properties of the produced samples were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) techniques, Toxicity characteristics leaching procedures (TCLP, physical tests (compressive strength, density, porosity) and thermal tests (differential scanning calorimetry (DSC)). Cristabolite (SiO_2) was formed as a major crystalline phase for rice husk while Cacoxenite and Faujasite were formed in the vitrified palm kernel ashes). The vitrified rice husk samples showed good mechanical properties with a compressive strength of 19.96 MPa, followed by palm kernel shell and coconut shell with 0.78 and 1.37 MPa, respectively. During thermal analysis, glass transition temperature, T_g of brick coconut shell ash greater palm kernel ash and rice husk ash which indicates that the higher vitrified temperature required for the samples. Furthermore, all vitrified agrowaste ashes showed an excellent resistant against leaching of heavy metal ions in water. Toxicity characteristic leaching procedures (TCLP) detected that the amount of heavy metals leached after 18 h at 23°C was well below international regulations. These products appears as a promising solution for the valorization and recycling of these residues because it will make possible to convert them into useful materials with good technology and environmental properties, which allow their potential application as construction materials.

Keyword : *agrowaste, thermal insulator, vitirification*

INTRODUCTION

In Malaysia, more than 2 million tones agricultural waste are produced annually and is either burned or dumped as a waste and are great environment threat, causing damage to the land and the surrounding area in which it is dumped [1]. During the firing process, for instance, for every 1000 kg of paddy milled, about 55 kg of rice husk ash is generated. Despite these advantages, agricultural waste ash contained highly mineral(i.e silica, potassium and magnesium), some are highly porous and lightweight(rice husk ash), with a very high external surface area and extremely low thermal conductivity has been considered for further recycling as potential construction materials [2]. At present, two main uses have been identified, as an insulator in the steel industry and as a pozzolan in the cement industry. However cement-based techniques pose problems of the usage due to weak chemical and physical stability [3]. Particularly, in cases where rice husk ash with high concentrations of alkali chlorides, it is difficult to apply cement-based techniques since the alkali chloride inhibit hydration of cement so that cement matrix cannot be fully solidified or stabilized [4]. Therefore, it is necessary to search for new techniques for treatment of these rice husk ash.

Vitrification is chosen as the most promising solutions among the various available technologies. Vitrification offers advantages upon tremendous volume reduction, effective and durable waste form as the heavy metal ions will be immobilized inside the matrix [5].There are several reports on the vitrification of solid waste [6]. It was demonstrated that formation of glass-ceramic upon melting and quenching can be achieved with the addition bottom ash or glass wastes into fly ash.

This paper reports the production of glass-ceramic and the characteristics of glass-ceramics thus prepared from rice husk ash. The mechanical and thermal properties of the sample were evaluated to identify the recycling possibilities of these glass-ceramics. In addition, the chemical stability also was characterized through Toxicity Characteristic Leaching Procedure (TCLP) to examine the environmental influence.

MATERIALS AND METHODOLOGY

Materials

The fly ash samples used in this study were obtained from local rice husk and palm kernel mill while coconut ash samples from local wet market. 5.0 gram of samples, firstly were dried at 105°C and burned in a furnace at optimum of 1400^{o}C for 2 hours under controlled temperature interval of 100°C per hour. Then, the sample were cooled at room temperature and weighed. The chemical compositions of ash samples were summarized in Table 1. It is clearly shows that the major chemical component in ash samples is SiO_2 which can be used as nucleating agent and rice husk ash (RHA) contained the highest SiO_2 compared to the other agrowaste ashes.

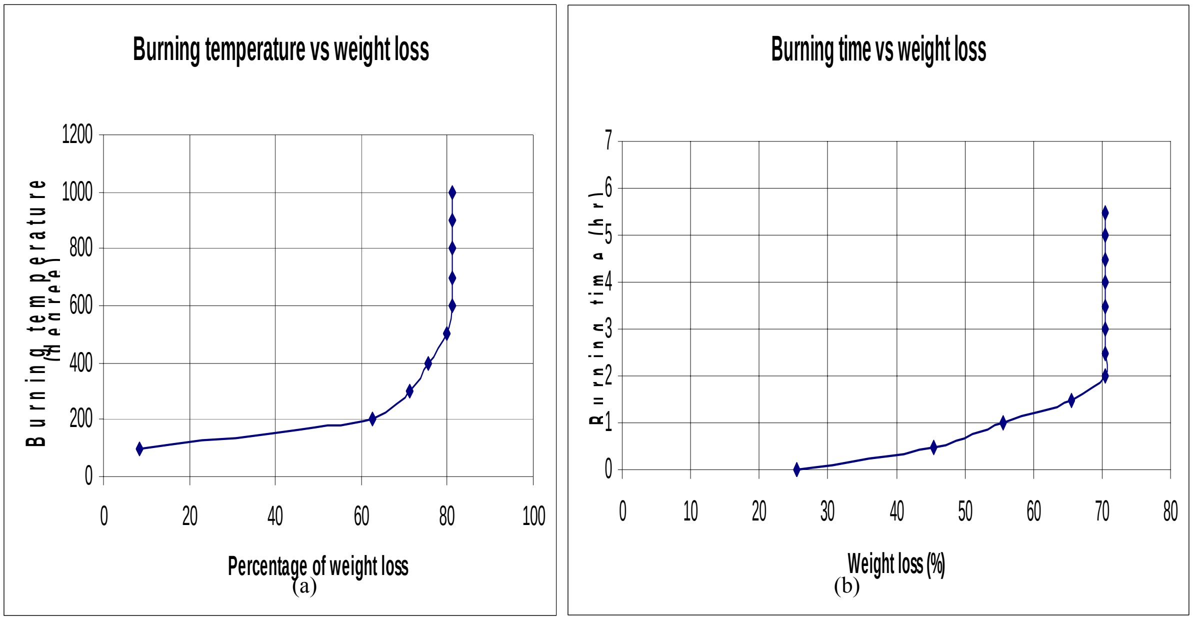
Table 1 Composition of as-received ashes of rice husk, coconut shell and palm kernel shell

Compound	Percentage (%)	
	Rice husk	Palm kernel shell
SiO_2	89.57	31.73
Al_2O_3	1.32	3.46
Fe_2O_3	1.43	1.78
P_2O_5	1.04	2.57
CaO	0.77	20.27
TiO_2	1.01	12.39
MgO	0.76	1.01
Na_2O	1.15	1.38
K_2O	1.65	1.51
Cl	1.3	0.08
MnO	-	1.27
C	-	12.55

Heat treatment and Vitrification method

Temperature and duration of heat treatment for the nucleation and crystal growth is the most important parameter for vitrification process. For the determination of the most convenient and economical temperature required for conversion rice husk to rice husk ash, losses on ignition (LOI) tests were performed and the results as shown in Figure 1. The graph revealed that the optimum burning time and temperature were 2 hours and 500°C, respectively. Loss in weight represents the quantity of unburned carbon present in the material and is often as good indication of how it will affect the air content [7].

For vitrified samples preparation, 5.0 g of agricultural wastes (rice husk and palm kernel shell) ash samples were undergone heat treatment at 500^{o}C for 1 hour using carbolite furnace, Model Vecstar. Heat treatment is to ensure total water loss. Then, treated sample was heated at a heating rate of 10^{o}C min^{-1} in refractory alumina crucibles up to 1400^{o}C. The melted sample was poured into a pre-heated brass cylindrical mould immediately transferred into electrical muffle furnace for annealing process at 500^{o}C for 1 hour. Later, the sample was cooled at room temperature inside the furnace. After annealing, the sample was cut into several partitions by using diamond disk (ATA Brilliant 221). The prepared sample then were characterize for mechanical and physical test (compressive strength, porosity, density), thermal analysis (DSC) and chemical test and phase analyses (TCLP, SEM, XRD) and in order to recycling possibilities on the properties examined.



(a) (b)

Figure 1: (a) Burning temperature ; (b) burning time of the agricultural waste samples

Properties Characterizations

Several techniques were used to assess the mechanical and physical properties of the glass-ceramics. The compressive test was measured by using Sinetron 6500 equipment. The sample with dimension 15 X 12.5 X 0.2 mm was prepared for this compressive test. This equipment pressed the sample until it break and crack. The maximum force was used to crack the sample was recorded. The other physical characterizations were obtained based on standardized tests and laboratory procedures. The apparent porosity was determined according to ASTM C 134/95, apparent density according to ASTM C 773/88. The hardness was analyzed by the Vickers indentation method. Vickers hardness was measured with a load of 15 g and loading time of 60 s. The apparent porosity was determined according to ASTM C 134/95, apparent density according to ASTM C 773/88.

For XRD analysis, the powder was taken to detect the presence of crystalline phase or structure. XRD was performed in a Rigaku diffractometer (model RAD IIA) at room temperature with CuKα radiation. SEM (Leo, 435 VP) was used to examine the morphology of the powders. Before SEM analysis, the samples were grinded to be powder form. Then, the powder was put on the film as a one piece of layer.

Glass transition (Tg) and Crystallization (Tc) temperatures were determined from differential scanning calorimetry (DSC) thermograms. Thermal analyses were performed at a heating rate of 20 °C/min in air atmosphere with nitrogen gas flowrate of 50ml/min. Leaching of heavy metal ions from glass-ceramics in water was estimated by the toxicity characteristics leaching procedure (TCLP) method of the US Environmental protection Agency (EPA).

RESULTS AND DISCUSSION

SEM and X-ray diffraction (XRD) Analyses

Microscopic observation shows particle shape and structure variations in all vitrified ashes. As shown in Figure 1, SEM analysis of RHA reveals particles that presence of crystalline grains which may indicated by the formation of the white color mineral. The crystals were formed randomly in the microstructure and show some agglomeration. This may due to many pores in the structure of RHA. On the contrary, different structures were observed for palm kernel shell ash sample (see Figures 2) where only minor crystalline grains were formed. Their structure quite inhomogeneous and also contains rough and porous surface. All these structures were compared with commercial brick as shown in Figure 3.

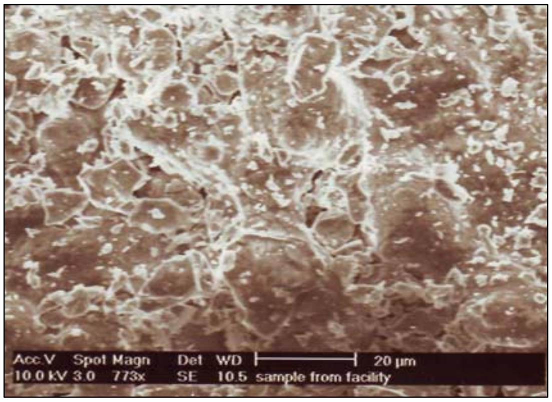


Figure 1: SEM of Vitrified Rice Husk Ash

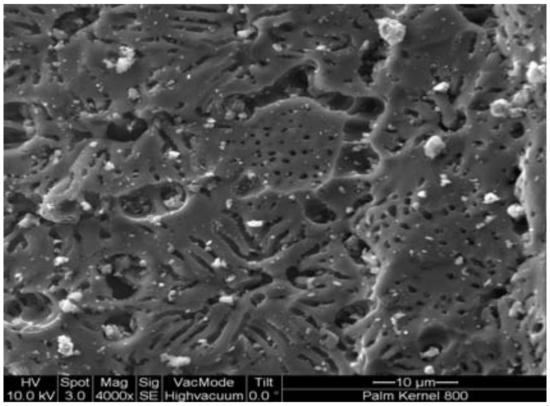


Figure 2: SEM of Vitrified Palm Kernel Ash

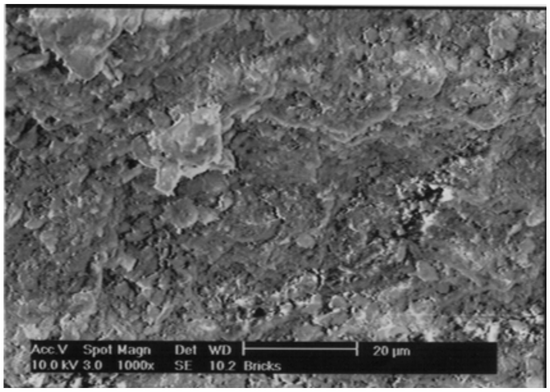


Figure 3: SEM of Commercial Brick

Silica is the most important minerals for bricks due to the fact that as construction material must have strong hardness properties. XRD analysis as shown in Figures 5 (a-c) revealed that the presence of silica in the form of cristabolite and quartz as the major component contributed to the crystalline phase formed in the vitrified samples. This was indicated by a broad peak between 20^o and 25^o. In rice husk ash (RHA), the silica is present in the form of cristabolite. While for PKS ash and CS ash silica is present in three types of phases; cristabolite, tridymite and quartz. According to Bronzeoak [8], quartz transforms to tridymite and the cristabolite with increasing temperature. In addition, other minerals that exist in palm kernel shell and coconut shell are Faujasite nickel-m dichlorbenzene and Cacoxenite. These minerals are the minerals exist from the result of bricks.

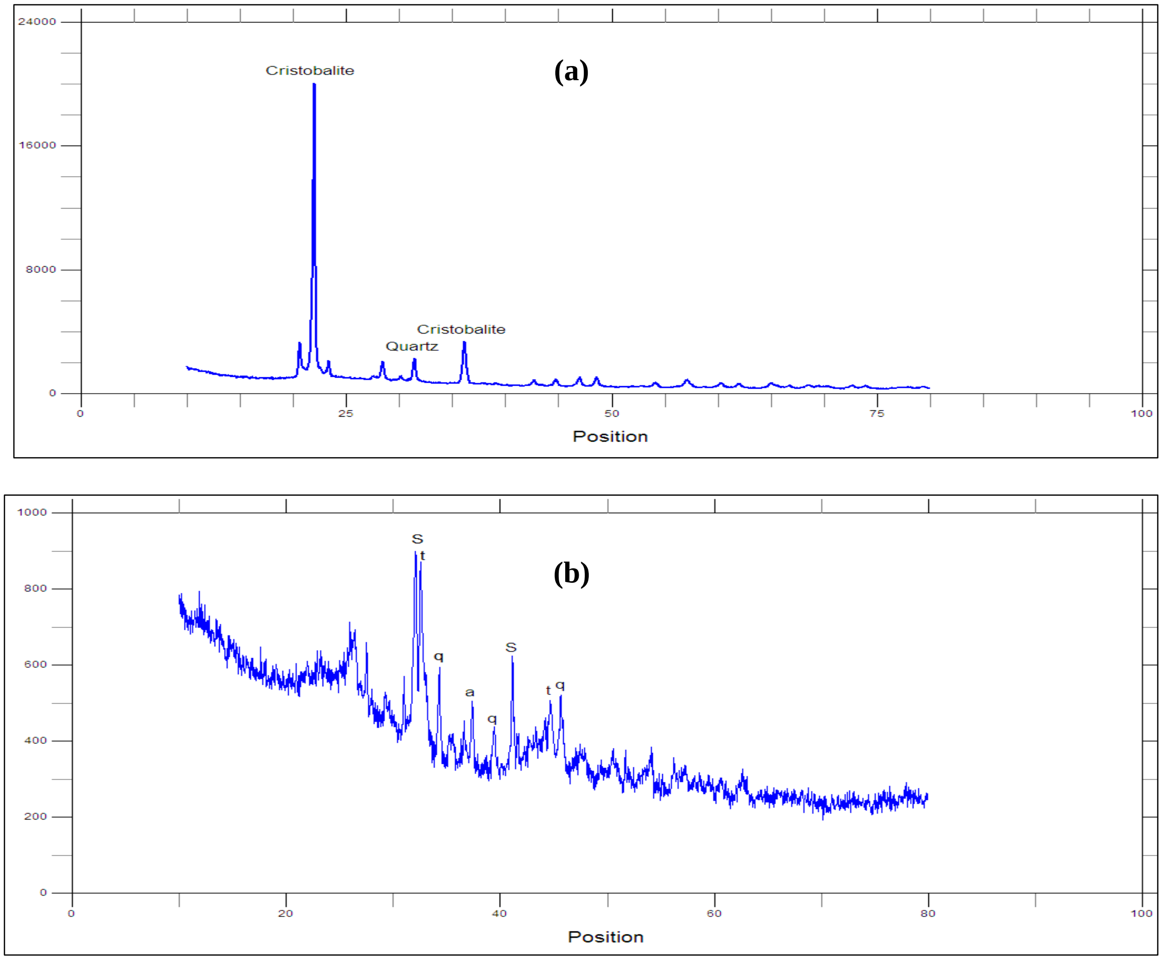


Figure 5: X-ray diffraction pattern of a) rice husk ash and b) palm kernel shell ash

Mechanical properties

Table 2 compares properties of commercial bricks and vitrified samples prepared in this study. As can be seen in Table 2, rice husk ash (RHA) gave the most comparable properties with the commercial brick sample in particular mechanical properties such as compressive strength (10% different). Compressive strength of vtrified rice husk ash (RHA) was 19.96 MPa, which is however lower to those of clay bricks (28.5 MPa) [3]. In addition, some of the properties of vitrified rice husk ash such as thermal conductivity are better than these of commercial brick. This is due to the fact that the higher percentage of apparent porosity of the vitrified RHA samples. Both porosity and water absorption correlated with each other [4]. Porous refractories have air trapped in their pores and it will act as non-heat conducting material [9]. The amount of the entrapped air increases with porosity of the refractory and hence its thermal conductivity decreases [4].

Thermal properties

As shown in Figure 6, thermal gravimetric analysis of the ash powder reveals weight loss in the range of 90 to 250^{o}C for most of the ash powders. The maximum weight loss loses up to 17 wt% between 90°C and 150^{o}C. This could be due to volatilization of unburned carbon and other organic matter present due to incomplete combustion as well as SiO_2 present in agricultural waste ash samples. On the contrary, in case of rice husk ash the weight loss is insignificant. This can be attributed to the fact that rice husk comprises primarily of silica with negligible amounts of volatile oxides. During thermal analysis, glass transition temperature, T_g of brick palm kernel ash greater than rice husk ash which indicates that the higher vitrified temperature required for the samples (see table 3).

Table 2: Physical properties analysis

Properties	Feedstock		
	Rice husk	Palm kernel shell	Commercial Bricks[10]
Bulk density (g/cm3)	0.61	0.78	1.85
Apparent porosity (%)	79.7	25.9	53.9
Moisture content (%)	62.22	57.2	62.22
Water absorption (%)	37.41	19.75	13.5
Thermal conductivity(W m^{-1} K)	0.15	0.97	1.04
Compressive strength (MPa)	19.90	0.78	28.5

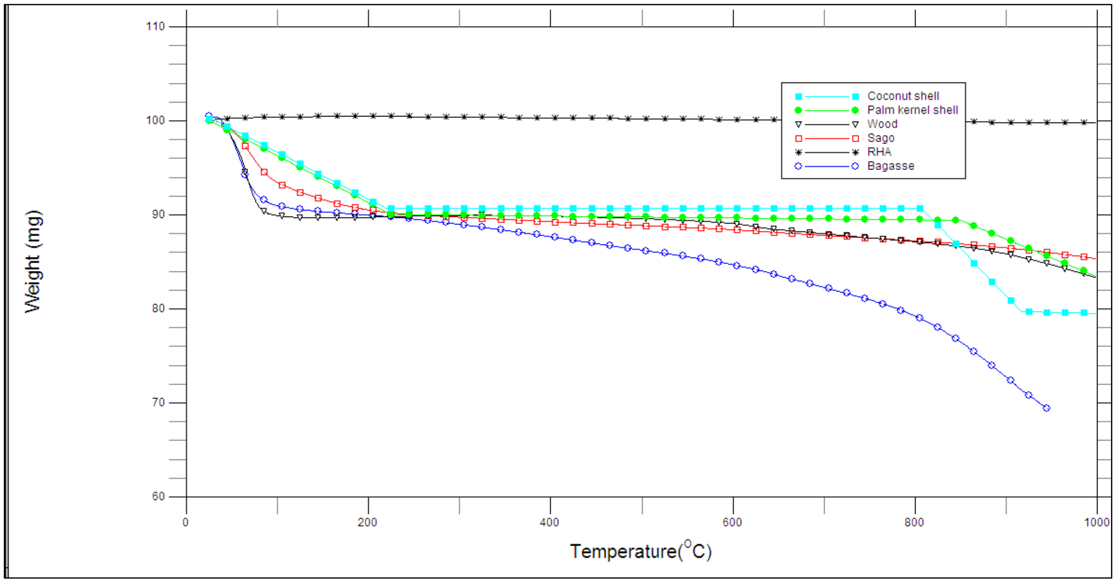


Figure 6: TGA analysis of ash powder.

Table 3 Nucleation and crystallization temperature for vitrified samples

Sample	Nucleation temperature (Tg) °C	Crystallization Temperature (Tc)°C
Rice Husk	98	100
Palm kernel shell	100	200.34
Clay bricks	nd	566.34

**nd-not detected*

TCLP test

Ash samples from combustion may contains high concentrations of heavy metals and still remain in the vitrified materials. Therefore, the chemical stability of the glass-ceramics must be evaluated to access the environmental safety of these recycled substances. The American EPA's toxicity characteristic and leaching procedure (TCLP) was used to examine the chemical stability of these in terms of leaching of heavy metal ions (Table 4). All other heavy metal ions were also incorporated inside these materials which proved that these new recycled materials are environmentally sustainable.

Table 4: Toxicity characteristic leaching procedure (TCLP) test (ppm in wt)

Heavy metals	Rice husk ash	Palm kernel shell	Limit [11]
Cd	0.084	0.099	1.0
Cr	0.702	0.069	1.75
Cu	0.962	0.108	100
Pb	0.149	0.215	0.25
Ni	0.083	0.058	100

CONCLUSION

In general, vitrified samples prepared using raw rice husk ash showed good mechanical properties with a compressive strength of 19.96 MPa and thermal conductivity less than 1.0 W m^{-1} K made this material suitable to be recycled as construction materials (i.e. thermal insulator bricks). While for other vitrified samples from raw palm kernel ash and coconut shell ash with different properties may be suitable for other applications. However, some additives should be added to enhance their properties. Furthermore, in all cases, the chemical stability estimated by TCLP proved that heavy metal ions formed chemically stable bonds with vitrified matrices. In summary, the formation of a vitrified product from agricultural waste ashes appears as a promising solution for the valorization and recycling of these residues because it will make possible to convert them into useful materials with good technology and environmental properties [10].

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