A CULLET-KAOLIN CERAMIC FROM RECYCLE GLASS

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To my beloved Ayahanda and Bonda: Ahmad Pauzi Mamat and Che Haripah Awg Kechik and to my sweet brothers and sister

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ABSTRACT

A series of ceramic based on (x) Cullet – (70-x) Kaolin – (30) Alumina where $10 \leq x \leq 60$ wt% has successfully been prepared by a solid state reaction. The density has been determined by Archimedes principle while the impact energy has been obtained by Izod Impact Test. The permeability coefficient has been determined by Constant Head Permeability test method using distilled water at pH 7 while their porosity and has been estimated using BET analysis method. The phase occurrence of these ceramic has been determined using X-ray Diffraction (XRD) method before being confirmed by Energy-Dispersive Analysis of X-rays (EDAX). The microstructure and surface morphology have been observed using Scanning Electron Microscopy (SEM) and the existence of water content has been determine using Infrared Spectroscopy (IR) technique. It is found that the bulk density and impact energy is in the range of (1.785 - 2.2817) gcm^{-3} and (2.183 - 6.320) kJm^{-2} respectively, depending on the cullet content. Meanwhile, the permeability coefficient is found to be in the range of ($5.208x10^{-4}$ - $1.812x10^{-4}$) cms^{-1}, decreases as cullet content is increased. The porosity is in the range of (13.34 – 14.5) m^2g and analysis shows that samples with 30-35 wt% of cullet exhibit optimum value. It is also found out that quartz and cristobalite are two major phases that occur in the ceramic while the minor phases are aluminium oxide, devitrite and sodium silicate. The structural morphology in the form of lamellar is observed to aggregate in the matrix with the size become increasingly larger as the kaolin content is increased. An EDX analysis show that the ceramic composition is mainly consists of Si, Al and O with a trace of K, Ca, Na and Pt as minor elements. Meanwhile, the IR Spectroscopy shows that the OH^- content decreases as cullet content is increased

ABSTRAK

Satu siri sampel seramik berdasarkan (X) Kulet – (70-X) Kaolin – 30 Alumina di mana $10 \leq X \leq 60$ peratus berat telah berjaya disediakan dengan kaedah tindakbalas keadaan pepejal. Ketumpatan sampel ditentukan dengan Prinsip Archimedes manakala ujian tenaga hentaman diperolehi melalui Ujian Izod. Keliangan sampel telah ditentukan dengan kaedah analisis BET dan pekali ketelapannya ditentukan dengan menggunakan ujian kepala ketelapan malar. Sementara itu, perubahan fasa sampel ditentukan menggunakan kaedah pembelauan sinar-X (XRD) yang mana turut juga dibuktikan oleh analisis penyebaran tenaga sinar-X(EDAX). Struktur mikro dan morfologi permukaan telah ditentukan dengan menggunakan Mikroskop Pengimbasan Elektron (SEM) dan Spektroskopi Inframerah (IR) telah digunakan untuk menentukan kewujudan kandungan air di dalam sampel. Ketumpatan sampel adalah di dalam julat 1.785 gcm^{-3} hingga 2.2817 gcm^{-3} manakala tenaga hentaman yang menggunakan ujian izod adalah di dalam julat 2.183 KJ/m^2 hingga 6.320 KJ/m^2 bergantung pada kandungan kulet. Pekali ketelapan adalah diantara $5.208x10^{-4}cms^{-1}$ ke $1.812x10^{-4}cms^{-1}$ yang berada dalam tren menurun. Kaedah analisis BET menunjukkan porositi adalah didalam julat $13.34m^2g$ hingga $14.5m^2g$ dan sampel-sampel dengan jisim 30-35 peratus kaca mempunyai keliangan yang optimum. Juga, terdapat dua fasa utama yang dinamakan fasa kuartz dan fasa kristobalite wujud di dalam seramik manakala terdapat juga fasa-fasa minor seperti Aluminium Oksida, "*devitrite*" dan natrium silikat. Morfologi sampel mendedahkan strukturnya adalah berbentuk lamela dengan saiz plat menjadi semakin besar dengan peningkatan kandungan kaolin. Analisis EDX digunakan untuk mengukur komposisi dalam kawasan sampel yang dipilih. Elemen yang banyak dikenalpasti adalah Si, Al dan O dan lain-lain atom seperti K, Ca, Na dan Pt.. Sementara itu, Spektroskopi Inframerah juga digunakan untuk menggambarkan kesan kumpulan OH dalam sampel. Spektroskopi Inframerah menunjukkan bahawa dengan penurunan kumpulan OH, ketelepan akan meningkat.

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LIST OF SYMBOLS AND ABREVIATIONS

SiO_2	Silicon Oxide
CaO	Calcium Oxide
Na_2O	Sodium Oxide
Al_2O_3	Aluminium Oxide
MgO	Magnesium Oxide
K_2O	Potassium Oxide
Fe_2O_3	Iron Oxide
H_2O	Water
Cr_2O_3	Chromium Oxide
Pt	Platinum
Na	Sodium
Ca	Calcium
Al	Aluminium
O	Oxygen
Si	Silicon
K	Potassium
Cu	Copper
OH^-	Hydroxyl
O_2^-	Oxygen ion
H^+	Hydrogen ion
$[Si_2O_5]_2^-$	Silicon Pentoxide ion
$Al_2Si_2O_5(OH)_4$	Kaolinite

$Mg_3(Si_2O_5)_2(OH)_2$	Talc
$KAl_3Si_3O_{10}(OH)_2$	Muscovite
KBr	Potassium bromide
FTIR	Fourier Transform Infrared
XRF	X-ray Fluorescence
EDAX	Energy Dispersive Analysis of X-ray
SEM	Scanning Electron Microscope
BET	Brunauer-Emnett-Teller
XRD	X-ray Diffraction
ASTM	American Standard Testing Material
PoP	Plaster of Paris
ICDD	International Centre for Diffraction Data
mL	Milliliter
cm	Centimeter
cm^2	Centimeter square
K	Kelvin
nm	Nanometer
α	Alfa
β	Beta
γ	Gamma
ρ	Density
θ	Theta
Å	Angstrom
°C	Degree Celsius
M	Molar
m	Mass
V	Volume
μm	Micrometer
g/cm^3	Gram per Centimeter cubic
ft-lb/in	Pound per Inch
J/cm	Joule per Centimeter
m^2/kg	Meter square per Kilogram
P/P_o	Pressure difference

J/m^2	Joule per Meter square
g/mol	Gram per Mol

CHAPTER 1

INTRODUCTION

1.1 Problem Overview

Nowadays, people have becoming more aware on the global wastes issues. It is reported that over 15,000 tons of waste has been produced every day. Approximately ten percent(10%) municipal refuse is glass, most of which is in the form of discarded containers from beverages, food products and the like (Duane A. Mosch, 1998). The quantities are very huge and urged steps need to be taken to reduce the increasing quantity of waste. The clock is ticking and it is only a matter of time before the space to dispose of them is run out. Much waste glass are dumped in landfill sites but in many countries there are a limited number of suitable sites and furthermore this disposal method is generally considered to be environmentally unfriendly. Because of the undesirability of dumping, the direct costs to the waste producer (handling, transport costs, etc.) are in many cases significantly increased by government taxes. A consequence of these environmental and financial considerations is that there is a growing demand for wastes to be re-used or recycled. Thus re-use of cullet for the production of ceramics is a promising development.

Recycling had attracted a great interest as a major way to reduce wastes. Recycling reduces pollution and as well as saves energy. In the developed countries, a growing interest in conservation of via recycling has led to an increasing in the recovery of solid wastes including glass, some of which is re-melted and some had turn wastes into something useful such as ceramic.

In Malaysia itself, experts believed a landfill exist can last 10 years longer if Malaysians do recycled their 50% of waste. As examples, the residents of Johor Bahru itself generate 1300 tons of waste every day and it will take only 3 days to fill the entire length of the Johor Causeway with this amount of waste. "**Currently, our country needs to spend RM400 mil just to manage these wastes. We can use these savings on other development projects. Recycling can also reduce our need to extract new economic resources while the industry itself can generate business opportunities and jobs,**"(Abdullah, 2003). If compared to other developed countries, where the recycling rate is about 30% to 47%, Malaysia is falling behind. There is not enough number of recycling centers and the practice is not widespread. Also, despite the recycling program being implemented three years ago, it had only managed a recycling rate of around 3% (Abdullah, 2003). Table 1.1 demonstrates roughly solid waste generated by Malaysians.

Table 1.1 : Breakdown of solid waste created by Malaysians in 2003 (Abdullah, 2003)

Types of Waste Materials	**Weight (%)**
Paper	27
Steel	3.9
Glass	3.7
Plastic	16.4
Others	12.5

To encourage recycling and minimize waste, there are national regulations and legislated guidelines being implemented in reinforcing environmental protection measures. There is a great interest in finding alternative technological options capablity, at the same time, to convert a waste product into a new marketable material. The transformation recycle glass (cullet) by wet forming process appears a promising solution because it is able to convert, at relatively low cost, simple chemical compositions into useful materials with good technological properties.

Cullet waste glass (Holloway, 1973) means the broken bottle. It is a special terminology used in glass industry. This word probably derived from the French word, *collet*, as collat. In those days of hand-pressed glass, it refers to the portion of glass cut off from the article which will be discarded or remelted later, the shape of which looked like a collar. Cullet has been used in glass container manufacturing industry since the earliest days of glass making for the purpose of assisting melting and saving raw materials consumption (Owen-Broadway, 1994). It has been reported that for every 60% of cullet used, 30% of fuel energy may be saved (Sahar *et al*., 2003)

Cullet is commonly used in various manufacturing activities, (for example glass reforming or melting additives for ceramics), mainly due to its low softening temperature. The Italian production of cullet in the year 2005 was around 106 tons. Great importance must be given to the colour of cullet while proposing its reuse for the production of ceramics, in particular light colour products require colourless cullet (Asquini *et al.*, 2008).

Collection of cullet is much depending on the willingness of the glass industry to collect and to process them. There are several reasons why cullet has to be recycled. It has been known that sand is natural resources that highly contained with up 70%-90% of silica which is the main component for glass production. If all the glass industries are simultaneously using this material, the chance is the tarnishing of environment in every part of the world. Every day, tonnages of bottles and containers are being produce and marketed. If this glasses are not being recycle, then the abundance of cullet are being dumped somewhere. This activity would require some space. It has been known that for every 1 ton of glass container, it requires about 3 meter square of space. If this happen and the space factor is very crucial, then the space could be waste in term of profit and economics.

This product would be firing in the furnace to obtain a solid sample. Generally all the steps, since raw material preparation, drying conditions and firing cycle are going to have a strong influence in the product qualities. The firing cycle influence is related to the kind of furnace, firing atmosphere, maximum temperature and soaking time. All these parameters are related to quality and cost of the products. Because all of these parameters, firing temperature is set to $1000^{o}C$ and 30 minutes soaking time. Although cullet-kaolin has been previously fabricated, very little information concerning on the microstructure and permeation rate of ceramic. Therefore this study has the significant importance and the result will be presented and discussed with respect to cullet content.

Ceramics is well known material and has been given an increasing attention for their successful applications in bioceramics (Engin, 1999), catalyst supports (Ismagilov, 1997), hot gases filter (Jo, 1997), liquid food production (Bennasar, 1982), sensors (Burgraaf, 1996), and membrane reactors (Coronas, 1994). Glass cullet (GC) is classified, in the European Waste Catalogue. In the present research a recycle glass containing SiO_2, CaO, Na_2O, Al_2O_3 as most abundant components and minimal amounts of MgO, K_2O and Fe_2O_3 was used (Maschio *et al*., 2009).

In another study soda-lime float or container glass was introduced, in replacement of soda feldspar in typical porcelain stoneware bodies (up to 10 wt.%) that underwent a laboratory simulation of tile making process, with a technological and compositional characterization of both fired and unfired tiles. Soda-lime glass had no significant effect on semi-finished products, but it influenced remarkably the firing behaviour, increasing shrinkage and closed porosity, decreasing open porosity and bulk density, and lowering mechanical and tribological performances (Jiann-Yang Hwang, 2006).

A new ceramic materials can be produce by adding a recycle glass(cullet) as part in new materials as reported elsewhere (Luz, 2007; Maschio *et al*., 2009). For example, the resulting ceramics with porous surfaces applicable for filter application, tile, brick, etc can be formed. In some cases a kaolin ($Al_2O_3.2SiO_2.2H_2O$) powder can be employed as a starting material. The detailed sequence of chemical reactions during the sintering of kaolin bodies is very complicated, depending on the compositions of raw materials, characteristics of powders, and fabrication conditions. Commonly used kaolin powder containing a small amount of quartz, then by adding recycle glass (cullet) which acts as fluxing agent (Bragança & Bergmann, 2004) and alumina to increase the strength (Sahar *et al.*, 2003), a new ceramic can be formed.

1.2 Problem Statement

This research is meant to reduce the problem of waste glass. A large amount of waste glass has already affected the environment and an urged steps must be taken to encounter the problem. Also, these large amounts of waste glass will require a lot of space to store them and thus the space value would be wasted. This research will encounter such problems by turning them into a new ceramic product. In this research, recycle glass will be mixed with kaolin to produce ceramic with attractive properties. By doing so, not only new ceramic will be formed but more important is that the problems stated before can be solved.

1.3 Aim of the Project

The aim of this work is to study the possibility of the use of glass powder waste (cullet), in ceramic mixtures, for manufacturing of new ceramic material namely Cullet-Kaolin ceramic. Cullet powder when incorporated into a mixture of kaolin and alumina has a good potential as a new fluxing agent in replacement of traditional feldspar and open possibility to obtain a porous microstructure during sintering. This project will stress on the effect of cullet on ceramic. Thus a suitable combination of cullet, kaolin and alumina would be determined. The effects due to the use of cullet powder is investigated in laboratory experiments and discussed in terms of cullet level and physical–mechanical properties (Luz, 2007). Therefore, the use of cullet as part of the composition would likely to reduce this effect and thus conserve the energy resources.

1.4 Objective of Study

The main objectives of this research are ;

i. To prepare a new ceramic material samples based on mixtures of cullet-kaolin ceramic materials.
ii. To determine the physical properties such as density and impact energy of the sample.
iii. To determine the permeability coefficient of the sample.
iv. To investigate the sample surface morphology.
v. To study the phase changes in the sample at different cullet level.
vi. To determine the specific surface area and particle size of the sample.
vii. To analyse the composition of the sample.

1.5 Scope of Study

To achieve the objectives that have been listed, the scope of research is outlined.

i. Preparations of new Cullet-Kaolin ceramic based on (X) Recycle Glass – (70-X) Kaolin – 30 Alumina where $10 \leq X \leq 60$ weight percent.
ii. Determination of density using Archimedes Principle and Impact energy using Izod Test.
iii. Determination of permeability coefficient using Constant Head Permeability test.
iv. Determination of sample morphology using Scanning Electron Microscope.
v. Determination of phase changes using X-Ray Diffraction.
vi. Determination of Specific Surface Area and particle size using BET (Brunauer-Emmet-Teller).
vii. Determination of composition of sample using Energy dispersive X-Ray analysis.
viii. Determination of OH-group

1.6 Significance of the Study

In the fast growing field of ceramic material, there are lots of their applications in this modern world such as tiles, filter water, kitchenware and toiletries. Because of this useful application, a new Cullet-Kaolin ceramic probably could be use in one this application. Furthermore, this ceramic is one of the ways to preserve and avoid natural resources such as silica and clay from tarnishing forever.