# THE EFFECT OF COLOURING AGENT ($Fe_2O_3$) ON THE PHYSICAL AND MECHANICAL PROPERTIES OF GLASS CERAMIC PRODUCED BY RECYCLING WASTE GLASS

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**MASTER OF SCIENCE**

**IN MANUFACTURING ENGINEERING**

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# Faculty of Manufacturing Engineering

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**NUR FARIZAN BINTI AYOOB**

**A thesis submitted in fulfilment of the requirements for the degree of Master of Science of Manufacturing Engineering**

**Faculty of Manufacturing Engineering**

**UNIVERSITI TEKNIKAL MALAYSIA MELAKA**

**2013**

# DECLARATION

I declare that this thesis entitle "The effect of colouring agent ($Fe_2O_3$) on the physical and mechanical properties of glass ceramic produced by recycling waste glass" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not currently submitted in candidature of any other degree.

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| Signature | : | ........................................................ |
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**ABSTRACT**

Large volume of waste glass (e.g. bottles, jars and windowpanes) is being generated and discarded daily and this is likely to increase considerably in the future. Thus, efforts to reduce such wastes by recycling which give benefit to the economy and sustaining the environment are needed. In this research, waste glass is utilized as raw material for the production of glass ceramic material (GCM) via sinter crystallization route. Basically, the main aspiration is to maximise the utilization of waste glass amount; as to enhance recycling effort. Two types of waste soda lime glass (SLG) that are non-coloured and green coloured is utilised as the main raw material during the batch formulation. Optimization of processing parameters (batch composition and sintering temperature) is carried out as an attempt to produce high quality sintered GCM. The glass were milled and sieved to < 75 μm and mixed with ball clay. Similar ball clay content is add into different type of waste glass according to the ratio of SLG to ball clay of 95: 05 wt. %, 90: 10 wt. % and 85 :15 wt. %. The batch mixtures were then uniaxial pressed and sintered at 800 ºC, 825 ºC and 850 ºC with holding time of one hour. The GCM properties were then compared between those produced using non-coloured and green coloured SLG in order to evaluate the effect of colouring agent ($Fe_2O_3$) on the GCM produced. It was observed that the colour of the GCM produced from non-coloured SLG is brownish while GCM produced from green coloured SLG is slightly pale green. The main crystalline phase in both GCM (identified using X-ray diffraction analysis) is wollastonite ($CaSiO_3$). Microstructure analysis conducted using scanning electron microscope (SEM) reveals the presence of needle-like crystals of wollastonite indicating that crystallization take place during the sintering. The optimum properties of non-coloured SLG is produced with smaller ball clay content (10 wt. %) compared to green coloured SLG (15 wt. %). The physical properties (determined thru ASTM C373) of the optimized GCM produced from non-coloured SLG and green coloured SLG are 0.69 % of porosity, 1.92 g/cm$^3$ of bulk density, 0.36 % of water absorption; and 1.96 % of porosity, 2.69 g/cm$^3$ of bulk density, 0.73 % of water absorption; respectively. Meanwhile, the optimized mechanical properties of Vickers microhardness and modulus of rupture (determine thru ISO 10545-4) is (580 $HV_{0.5}$, 39 MPa) for non-coloured SLG and (510 $HV_{0.5}$, 44 MPa) for green coloured SLG. In conclusion, there were not extremely difference between non-coloured and green coloured SLG being utilized in GCM. The used of both glasses as raw material is able to positively produced good physical and mechanical properties of GCM as results of a modification of their sintering behaviour.

## ABSTRAK

Jumlah sisa kaca yang dihasilkan dan dibuang setiap hari adalah besar dan ini mungkin akan meningkat dengan ketara pada masa akan datang. Oleh itu, usaha untuk mengurangkan bahan buangan itu diperlukan dengan cara mengitar semula bahan tersebut. Dalam kajian ini, sisa kaca digunakan sebagai bahan mentah untuk menghasilkan kaca seramik (GCM) melalui penghabluran persinteran. Pada asasnya, aspirasi utama adalah untuk memaksimumkan penggunaan amaun sisa kaca bagi meningkatkan usaha kitar semula. Dua jenis sisa soda kapur kaca digunakan iaitu kaca yang tidak berwarna dan kaca berwarna hijau sebagai bahan mentah utama dalam pengubalan komposisi. Pengoptimuman parameter pemprosesan (pengubalan komposisi dan suhu pensinteran) dijalankan sebagai usaha untuk menghasilkan GCM yang berkualiti tinggi. Kaca telah dikisar dan diayak < 75 µm dan dicampur dengan bebola tanah liat. Jumlah tanah liat yang sama dimasukkan ke dalam sisa kaca yang berbeza mengikut nisbah peratus berat soda kapur kaca dan bebola tanah liat iaitu 95:05, 90:10 dan 85:15. Setelah itu, campuran ditekankan dengan menggunakan kaedah penekanan dan disinter pada suhu 800°C, 825 °C dan 850 °C. Sifat-sifat GCM yang dihasilkan oleh kaca tidak berwarna dan kaca berwarna hijau kemudiannya dibandingkan untuk menilai kesan agen perwarna keatas kaca seramik yang dihasilkan. Diperhatikan bahawa GCM yang dihasilkan oleh kaca tidak berwarna menjadi keperangan manakala GCM dihasilkan dari kaca berwarna hijau menjadi sedikit hijau pucat. Fasa hablur utama dalam kedua-dua GCM (yang dikenalpasti melalui kaedah pembelauan sinar-X) adalah wollastonite ($CaSiO_3$). Analisa mikrostruktur yang dijalankan menggunakan imbasan electron (SEM) menunjukkan kehadiran kristal seperti jejarum terhasil. Sifat-sifat optimum bagi GCM dihasilkan oleh kaca tidak berwarna dapat dihasilkan dengan kandungan jumlah berat bebola tanah liat yang rendah (10 %) berbanding dengan kaca berwarna hijau (15 %). Sifat fizikal (ditentukan melalui ASTM C373) yang optimum dikecapi oleh GCM daripada kaca tidak berwarna dan kaca berwarna hijau masing-masing adalah 0.69 % keliangan, 1.92 g/cm$^3$ daripada ketumpatan pukal, 0.36 % daripada penyerapan air; dan 1.96 % keliangan, 2.69 g/cm$^3$ ketumpatan pukal, 0.73 % daripada penyerapan air. Sementara itu, sifat-sifat optimum mekanikal bagi kekerasan dan modulus kepecahan (menentukan melalui ISO 10.545-4) adalah (580 $HV_{0.5}$, 39 MPa) untuk kaca tidak berwarna dan (510 $HV_{0.5}$, 44 MPa) untuk kaca berwarna hijau. Kesimpulannya,tiada perbezaan ketara terhadap pengunaan kaca tidak berwarna dan kaca berwarna hijau dalam menghasilkan GCM. Kedua-dua kaca yang digunakan sebagai bahan mentah menunjukkan sifat yang positif dari segi fizikal dan mekanikal terhadap GCM

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# CHAPTER 1

# INTRODUCTION

## 1.1 Research background

Nowadays, there is a great concern regarding to the increasing amount of the industrial wastes such as plastic, glasses and grogs. The disposal of these wastes is one of the issues that have received a lot of attention and a high demand for the safety of the environment. In the developed countries, growing interest in conservation of resources and ecological preservation has led to an increase in the recovery of solid wastes. One technique used to reduce such wastes is by recycling which is not only benefits to the environment but also to the economy. Recycling processes became more importantly due to impressive increase in the production of wastes and growing the attention to environmental safeguard (Raimondo *et. al.* 2007).

Glass has been widely used for many years in various applications and had become a very important industrial material in ceramic industry (Loryuenyong *et. al.* 2009). As a result, a large volume of waste glass is being generated and discarded daily and this is likely to increase considerably in the future. Most of the available waste glass is from containers having different colours. When the glass colours get mixed, it becomes unsuitable for use as new containers and are then sent to landfill unless alternative method of recycling is adopted (Limbachiya *et. al.* 2012). In the last decades, several research works have been conducted to evaluate and investigate the potential of using waste glass in new glass ceramic production. In fact, waste glasses are readily incorporated as alternative ceramic raw material or fluxing agent in stoneware tiles, bricks and concrete (Matteucci *et. al.* 2002; Luz and Ribeiro 2007; Hwang *et. al.* 2006; Andreola *et. al.* 2008; Limbachiya *et. al.* 2012). Hwang *et. al.* 2006 claimed in his work that a lowering softening point material is potentially capable of reducing the sintering temperature of clay products through a chemical reaction with the clay. Waste glasses can be used as a potential fluxing agent to help lowering sintering temperature of clay bodies. The utilization of waste glasses could then be an alternative way to save energy in the production process and to reduce manufacturing cost. In addition, used in small amounts of waste glass (up to 5 wt. %), can improving the densification process, resulting in higher density, less water absorption and lower the amount of porosity (Andreola *et al.* 2008). Luz and Ribeiro (2007) also indicated that the waste glass powder was an efficient fluxing agent in ceramic mixtures for the manufacture of porcelain stoneware tiles by accelerating the densification process. The results showed good mechanical and physical properties with small amounts of glass powder addition.

Sinter crystallisation of glass powder compacts is an alternative processing route of producing strong and fully dense glass ceramics from waste glasses, recently (Bernardo *et. al.* 2010). The technology relies on the viscous flow sintering of fine glass powders with concurrent crystallisation, in turn due to a surface mechanism (Hölland and Beal 2002). The process allows very short processing cycles on the basis of a short single step sintering at the glass crystallisation temperature accompanied by rapid heating and cooling. The advantages of this method are essentially that it does not require high investment and it is suitable for the production of small quantities of articles of complicated shapes. Commercial examples of using sinter crystallisation are wollastonite- based “Neoparies”, developed in Japan since 1970s. Recently, sintered glass ceramic materials were produced using natural raw material such as clay as well as using different industrial wastes such as incinerator fly ash and coal fly ash. However, not much attention has been paid to the sintered glass ceramic materials produced from coloured waste glass.

## 1.2 Problem statement

Over the last decades, industrial development has generated large amount of waste. Due to rapid change, waste products are always increasingly expected to be great. In Malaysia, glass waste represent 18, 000 tons per day and the amount of these wastes will increased day by day due to ever growing use of glass products (Ismail 2004; Chiew 2005). This one of the problem that will raise social and environmental concerns and adequate management and recycling of waste glass is gathering social interest (Park *et. al.* 2004). Therefore, many investigations have been addressed to reuse waste glass to manufacture ceramic-like glassy products (Brown *et. al.* 1982).

From the recent research, the reuse of different waste glasses (such as TV/PC cathodic tube and screen glasses; structural glass walls; glass containers) has been investigated so that these waste glasses became a commercial alternative to traditional raw materials in ceramic bodies (Loryuenyong *et. al.* 2009; Karamberi and Moutsatsou 2005; Raimondo *et. al.* 2007). The use of waste glasses in the production of building materials has been successfully pursued since it can reduce the consumption of natural resources and the cost of waste disposal. According to Raimondo *et. al.* (2007) being the glass one of the predominant constituent of vitrified ceramic bodies where the large amount of liquid phase (50-65 %) developed during sintering process. Glassy materials may introduce into porcelain stoneware bodies without modifying significantly the manufacture cycle.

However, since waste glasses contain of variable chemical composition, their utilization cannot be easily molded. From previous researchers, Hwang *et. al.* (2006) proved that scrap glass was able to be utilized in clay products but also benefits in reducing sintering temperatures. Other than that, Dondi *et. al.* (2009) claimed that waste glasses from PC monitors and TV sets were feasible in the manufacturing of clay bricks and roof tiles. It is also showed that such waste behave as plasticity, reducing agent in unfired clay bodies and sintering promoter during sintering. In additions of waste glass however should be kept between 2 to 4 wt. % depending on the characteristics of clay bodies, to prevent deleterious effects on final products. In this research, the main objective was to investigate the feasibility of using waste glass from glass container in the manufacture of glass ceramic material. The effects of sintering temperature and ball clay addition were discussed in terms of physical-mechanical properties and microstructure.

Glass container is generally available in non-coloured, amber and green in colour. The colour in glass is obtained by addition of colouring agent that is homogeneously distributed (Dalbey and Purser 1996). Taking into consideration on the effect of colouring agent present in the glass on properties of glass ceramic material, this research has been focused on the use of non-coloured and green coloured soda lime glass (SLG) as a component of glass ceramic material as raw material. In order to evaluate the effect of colouring agent on glass ceramic material, properties of glass ceramic material produced from green coloured SLG was compared with glass ceramic material produced from non-coloured SLG.

## 1.3 Aims of investigation

There are several aims that need to be achieved in this research:

i. To determine the effect of sintering temperature and ball clay content on the physical and mechanical properties of glass ceramic material produced from non-coloured and green coloured soda lime glass.

ii. To compare the physical and mechanical properties of glass ceramic material produced utilizing non-coloured and green coloured soda lime glass.

iii. To evaluate the effect of colouring agent ($Fe_2O_3$) on the physical and mechanical properties of glass ceramic material.

## 1.4 Scope of work

Scope of work is to study the effect of colouring agent ($Fe_2O_3$) on the physical and mechanical properties of glass ceramic material (GCM) produced from waste glass. Two types of soda lime glass (SLG) is used which are non-coloured and green coloured SLG. The effect on sintering temperature and ball clay content on the physical and mechanical properties of GCM also is studied. The forming process is by common ceramic technique of using uniaxial pressing method. The process of producing GCM starts by preparing glass powder as raw material to be used. The powders were prepared by crushing bottles using hammer, milled with milling machine and sieved until they passed through 75 µm sieve. The process continue by mixing glass powder with ball clay with ratio of 95:5 wt. %, 90:10 wt. % and 85:15 wt. %. Then, the mixture powder gently pressed in a die and sintered at three different temperatures of 800 ºC, 825 ºC and 850 ºC.

At the end of this study, the products were characterized by x-ray diffraction (XRD) for phase crystal structure determination, field-emission scanning electron microscope (FE-SEM) for morphology observation and energy dispersive x-ray (EDX) for determination element presence in sintered GCM. Furthermore, other properties such as microhardness, three point bending strength, linear shrinkage, porosity, water absorption and bulk density were also investigated.

## 1.5 Thesis contents

This thesis consists of 6 chapters including the introduction, literature review, methodology, results, discussion, conclusion and recommendations. Chapter 1 briefs introduction of this research and explain on the research objectives. The scope of work on the research also include in this chapter. Chapter 2 on literature review provides the background information and brief description of glass ceramic produce from waste glass. A detailed review on the process and properties of glass ceramic from previous research are also included. Chapter 3 briefs the experimental methods employed throughout this study, including preparation of glass powders, forming of glass ceramic material (GCM), material characterization, physical analysis and mechanical analysis. Chapter 4 explain on the results obtained in this study. The results involve raw material characterization, physical properties, mechanical properties, phase analysis and microstructural characterization for both non-coloured and green coloured glass. Chapter 5 discuss on the effect of sintering temperature and clay addition on GCM. The effect of colouring agent on the properties of GCM produced from waste glass is also discussed in this chapter. Lastly, chapter 6 give the conclusions on the entire work carried out and the recommendations for future work.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

This chapter explains the background of waste glasses recycling and processing method used to produce glass ceramic material (GCM). Detail review from previous study on GCM produced from waste glasses in terms of its physical properties, mechanical properties and microstructure characterization are also been discussed.

## 2.2 Waste glass

In recent years, there have been numerous issue regarding landfills due to intensifying amount of the solid waste generation and human population as well. In Malaysia, the amount of waste disposed by 23 million people is 18, 000 tons per day or an average of 800 grams for each individual. Figure 2.1 show the percentage of solid wastes that can be breakdown into different types which consists of food waste (47 %), paper (15 %), plastic (14 %), wood (4 %), iron (4 %), glass (3 %), textiles (3 %), others (10 %) and has continued to demonstrate an increasing trend (Utusan Malaysia 2004). Glass waste represents 900 tons per day and the amount of these wastes has increased over the recent years due to an ever growing use of glass products. Moreover, landfilling can cause major environmental problems because the glass is not biodegradable material which is not an environmental-friendly practice (Limbachiya *et. al.* 2012). Thus, many investigations have been addressed to reduce such wastes by recycling which is not only benefit to the economy but also make them reasonably safe for the environment.

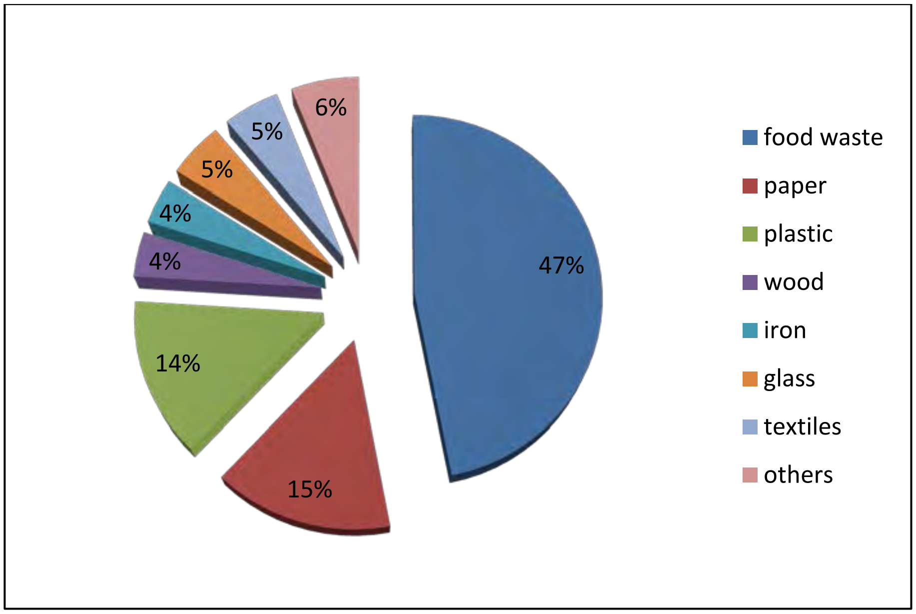


Figure 2.1 Breakdown of solid waste in Malaysia (Utusan Malaysia 2004)

### 2.2.1 Recycling of waste glass

In the near future the development of new recycling technologies is getting more important and the recycling of by-products and industrial waste materials will dramatically increase. Recycling is the process which waste materials are diverted from the waste stream. They are sorted and used to produce new materials. Glass is 100 % recyclable material with high performances and unique aesthetic properties, which make it suitable for wide spread uses. Non-coloured, green and brown bottle wine, beer, all glass jars, spread and sauce bottles can be recycled. Other possible wastes from glass industries are refractory scraps from which glass facilities can also be recycled. Usually, the container glasses, tableware and flat glass are termed as soda lime glasses. The crystal tableware, TV screens and display screen equipment are from lead glasses while glass fibers, wool insulation, and ovenware and thermo flasks are produced from borosilicate glasses (Isa 2008).

In Malaysia, there are three glass bottle manufacturers and they produce 600 tonnes of new bottles daily. However, only 10 % of these bottles will eventually go back to the factories and be reused to make new ones (Chiew 2005). In foreign countries much effort has been taken to recycle waste glass bottles. A bottle recovery system, through which empty bottles previously containing alcoholic beverages, refreshing beverages, condiments, milk and others are collected, washed and reused, has already been practiced. Moreover, broken bottles and bottles previously containing chemicals, cosmetics are melted down to be reused or crushed and turned into paving material, block material, glass marble and glass tile (Park *et. al.* 2004). However, only negligible proportions of the total used bottles are actually currently being recycled. Therefore, many investigations have been conducted to evaluate and investigate the potential of using waste glass in ceramic industries.

### 2.2.2 Process of recycling waste glass

Generally, the process of recycling glass starts by glass being collected and taken to a processor where it is separated of different types of glass and sorted by colour. But for glass waste such as window pane, light bulbs and Pyrex cookware are not taken because the chemical composition of these kind of glass are much different than the glass that they use as cullet (Elliott 2010). After that, the process continues by rinsing and crushing. The glass then were mixed with sand, soda ash and lime and heated to extremely high temperature above 1000 ºC where the glass will liquefied into a liquefied state. Then, the liquefied glass is poured into molds and cooled slowly to increase its strength. The new glass containers are then shipped out to be used and sold (Recycle 2012). Figure 2.2 described the life cycle of glass container.

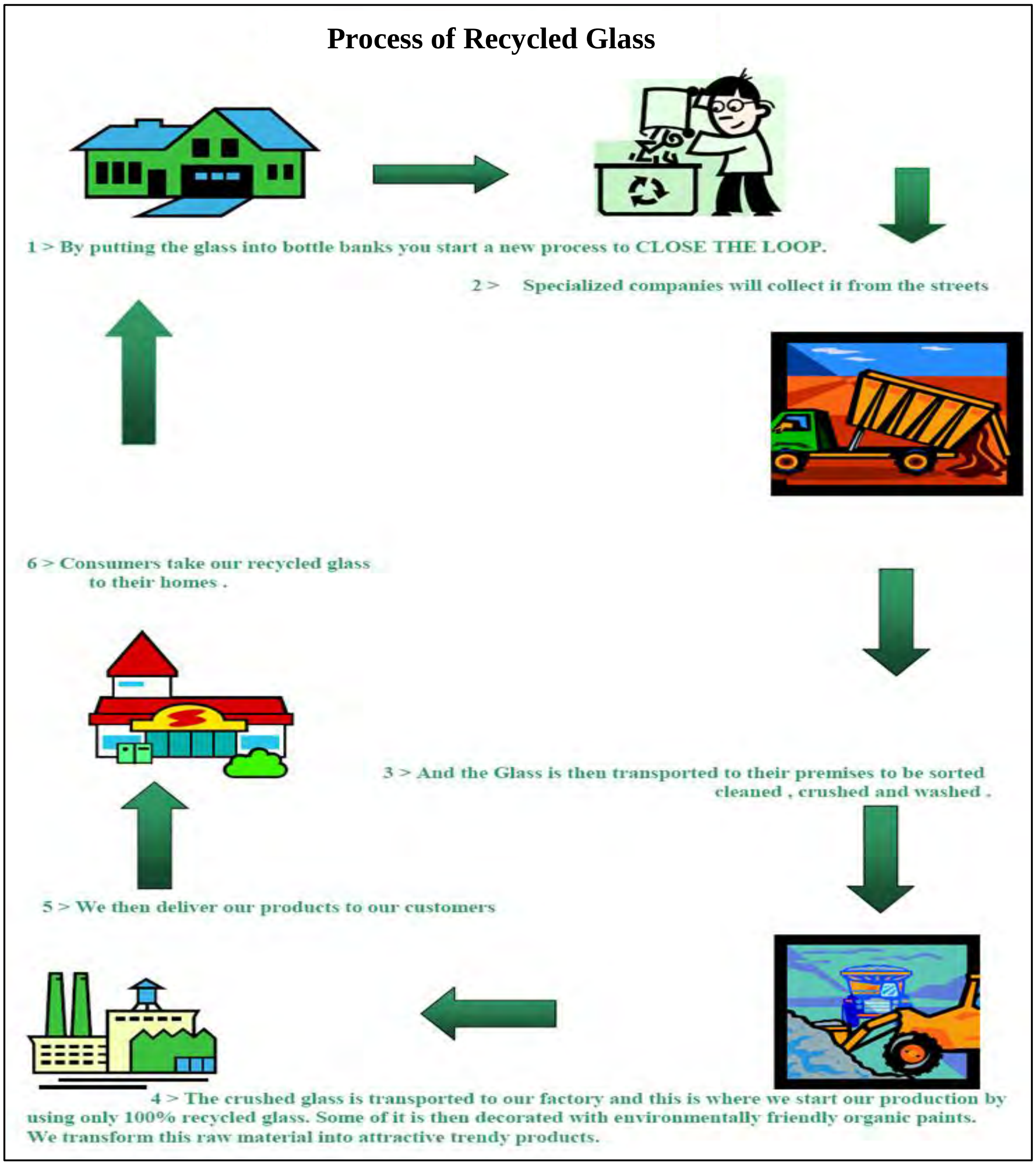


Figure 2.2 Life cycle of glass container (Recycle 2012)

Most of the available waste glass is from containers having different colour. When the glass colours get mixed, it becomes unsuitable for use as new containers and are then sent to landfill unless alternative method recycling is adopted. A growing interest in using waste glass in glass ceramic fabrication has emerged throughout the last decades offering valuable and efficient alternative recycling method (Limbachiya *e. al.* 2012). Conventional method of producing glass ceramic consumes large amounts of energy which also affect the total manufacturing cost, thus new methods to reduce the amount of energy required will give benefit to ceramic industry (Matteucci *et. al.* 2002; Luz and Ribeiro 2007). Hwang *et. al.* 2006 claimed in his work that a lowering softening point material is potentially capable of reducing the sintering temperature of clay products through a chemical reaction with the clay. Soda lime glasses typically soften from 500 °C to 745 °C (Alger 1997). This softening behavior causes articles formed from fine glass powder to vitrify by viscous-phase sintering at temperature lower than usually required to crystallize glass ceramic products which usually above 1000 °C. Therefore, the literature on fabrication of glass ceramics from soda lime glass in different mixtures of ball clay, quartz-feldspathic sand, fly ashes and other wastes have been carried by several researches where it could be beneficial for the development of cheap building material (Karamberi and Moutsatsou 2005; Hwang *et. al.* 2006; Bernardo *et. al.* 2010; Matteucci *et. al.* 2002).

## 2.3 Glass

Glass has been used for centuries where the Egyptians were the first to use glass containers in the fifteenth century BC. However, the first fully automated bottle making machine was developed on 1903 in Ohio, USA. The "glass" term points out a highly transparent material produced by melting a mixture of materials such as silica, soda ash and $CaCO_3$ at high temperature followed by cooling during which solidification occurs without crystallization (Callister 2003). It is an amorphous with non crystalline solid material. Furthermore, glasses are typically brittle and optically transparent. Glass has a wide range of applications and uses depending on its source of raw materials. There are several commercial glasses used nowadays which are soda lime glass, lead glass, borosilicate glass and others. Table 2.1 shows the composition of several common glass materials and their characteristics.

Table 2.1 Compositions and characteristics of commercial glasses (Callister 2003)

| | Composition (wt. %) | | | | | | |
|---|---|---|---|---|---|---|---|
| Glass Type | $SiO_2$ | $Na_2O$ | CaO | $Al_2O_3$ | $B_2O_3$ | Other | Characteristics |
| Fused silica | > 99.5 | | | | | | High melting temperature, very low coefficient expansion |
| Vycor | 96 | | | | 4 | | Thermally shock and chemically resistant |
| Borosilicate | 81 | 3.5 | | 2.5 | 13 | | Thermally shock and chemically resistant |
| **Soda Lime** | **74** | **16** | **5** | **1** | | **4 MgO** | **Low melting temperature, easily worked and durable** |
| Fiberglass | 55 | | 16 | 15 | 10 | 4 MgO | Easily drawn into fibers |
| Optical flint | 54 | 1 | | | | 37 PbO, 8 $K_2O$ | High density and high index of refraction |
| Glass ceramic | 43.5 | 14 | | 30 | 5.5 | 6.5 $TiO_2$, 0.5 $As_2O_3$ | Easily fabricated,strong and resists thermal shock |

In this research, the work is focused on the possibility of recycling soda lime glass from glass container wastes. A typical soda lime glass consists of 70 wt. % $SiO_2$ (silica)