Journal of Cleaner Production 69 (2014) 243–249

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Formulation of ceramic engobes with recycled glass using mixture design

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ARTICLE INFO

Article history:
Received 31 May 2013
Received in revised form
22 January 2014
Accepted 22 January 2014
Available online 6 February 2014

Keywords:
Engobe
Recycled glass
Ceramic tiles
Mixture design
Response surface

ABSTRACT

In this work glass frits were fully replaced by recycled glass in engobe compositions. Engobe is an interlayer between glaze and substrate in traditional ceramic tiles. Five ceramic raw materials were used to formulate engobes. Linear shrinkage, water absorption, whiteness, water stain and coefficient of thermal expansion were measured in designed mixtures and described by mathematical models. A statistical analysis enabled describing the engobe properties at a 95% confidence level. A major influence of the raw materials interaction on the engobe properties was determined as a result of the chemical reactions during firing. According to the response surface analysis performed, it was possible to find an area in the triaxial diagram where all properties were optimized.

1. Introduction

The engobe is an interlayer applied on a substrate under the glaze layer which is used in most ceramic tiles, Fig. 1. An engobe is used to opacify the substrate, to attenuate physical-chemical differences, to improve the fitting between the substrate and the glaze, and to reduce the defects on tile surface (Santos et al., 2007). Engobes are formulated from natural raw materials like clays, quartz and feldspars and synthetic raw materials as ceramic frits. A frit is a glass manufactured in a large furnace at high temperatures (around 1500 °C) which is submitted thereafter to a thermal shock to produce irregularly shaped vitreous particles. Hence, this ceramic material is cost intensive and presents some negative impacts on the environment.

In order to reduce the environmental impact of glass residues, the reuse of this solid waste can contribute to reduce and/or avoid its discard, decreasing the use of natural raw materials. Despite the use of recycled glass in ceramic substrates (Bragança and Bergmann, 2005; Raimondo et al., 2007; Bernardo et al., 2009), cement (Ling and Poon, 2012) and glazes (da Silva et al., 2012), few references refer to recycled materials in engobes (Larichkin et al., 2008; Velho and Bernardin, 2011). However, to the best of our knowledge, in no case the ceramic frit was replaced 100% by recycled glass.

Glass wastes can be fully recycled to manufacture new glass products (Tchobanoglous and Kreith, 2002). Nevertheless, some technological constraints hinder the recycling of glasses in ceramic tile production. Generally, ceramic frits used in engobes have a coefficient of thermal expansion between 6 and $7 \cdot 10^{-6}$ °C^{-1}, while recycled glass from containers and flat glass have a coefficient of thermal expansion higher than $9 \cdot 10^{-6}$ °C^{-1}(Navarro, 2003). In this regard, to replace frits by recycled glass in engobes a new formulation is a challenge.

In ceramic materials and processes, statistical tools have been widely used to optimize compositions. The design of experiments (DoE) can help the development of formulations and the interpretation of the results obtained from testing (Cornell, 2002). Statistical techniques applied to DoE have been widely used in various fields such as pharmacology (Cafaggi et al., 2003), food (Kumar et al., 2010) and materials science (Menezes et al., 2008; Correia et al., 2009).

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http://dx.doi.org/10.1016/j.jclepro.2014.01.088
0959-6526/

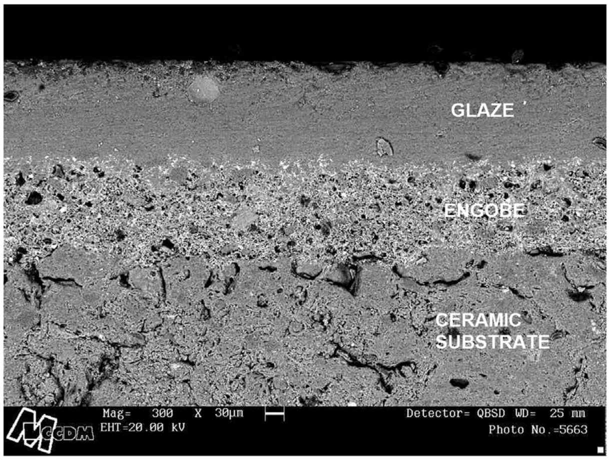

Fig. 1. Microscopic image showing the constitutive layers of ceramic tiles.

Mixture design has been employed as a tool for the optimization of mechanical and esthetical properties of ceramic products, enabling the description of the property under analysis according to the composition. Furthermore, this technique helps to reduce the number of experiments in laboratory. When the processing conditions are kept constant, as sought in the ceramic industry, the final product properties are determined by the combination of raw materials.

Triaxial experimental designs, which can be seen as a special case of DoE with only three variables, have been extensively used to study the properties of ceramic products (Schabbach et al., 2001; Correia et al., 2006). However, the description of the materials properties with only three factors (triaxial designs) can lead to simplistic predictions considering the complexity of ceramic materials, particularly engobes.

A ceramic engobe must present suitable values in key properties such as linear shrinkage (LS), water absorption (WA), tonality, whiteness expressed as lightness, L*, according to the CIELAB color space (Schanda, 2007), water stain (WS), expressed as color difference, ΔE*, according to the CIELAB color space (Witt, 2007) and the coefficient of thermal expansion (CTE).

Table 1
Mixture design with five factors.

Formulation	Clay	Feldspar	Recycled glass	Quartz	Zircon
1	40.0	40.0	20.0	0.0	0.0
2	10.0	40.0	10.0	40.0	0.0
3	40.0	40.0	10.0	10.0	0.0
4	40.0	40.0	10.0	0.0	10.0
5	40.0	20.0	40.0	0.0	0.0
6	40.0	0.0	40.0	20.0	0.0
7	20.0	0.0	40.0	40.0	0.0
8	10.0	10.0	40.0	40.0	0.0
9	40.0	20.0	10.0	0.0	30.0
10	40.0	0.0	10.0	20.0	30.0
11	10.0	40.0	10.0	10.0	30.0
12	20.0	40.0	10.0	0.0	30.0
13	10.0	10.0	10.0	40.0	30.0
14	20.0	0.0	10.0	40.0	30.0
15	10.0	40.0	20.0	30.0	0.0
16	10.0	20.0	40.0	30.0	0.0
17	20.0	30.0	10.0	40.0	0.0
18	40.0	30.0	10.0	20.0	0.0
19	20.0	40.0	20.0	0.0	20.0
20	10.0	40.0	20.0	10.0	20.0
21a	24.5	25.0	19.5	19.5	11.5
21b	24.5	25.0	19.5	19.5	11.5

Table 2
Restrictions in contents of raw materials.

Raw material	Minimum value (wt%)	Maximum value (wt%)
Clay	10.0	40.0
Feldspar	0.0	40.0
Recycled glass	10.0	40.0
Quartz	0.0	40.0
Zircon	0.0	30.0

Table 3
Chemical analysis (wt%) of the raw materials as measured by XRF.

Raw material	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	ZrO_2	TiO_2	Fe_2O_3	LoI
Quartz	98.0	0.2	–	–	0.8	–	–	<0.1	<0.1	0.9
Zircon	32.5	0.9	–	–	–	–	66.2	0.1	<0.1	0.3
Feldspar	66.2	18.7	2.9	11.4	0.2	<0.1	–	<0.1	0.1	0.5
Recycled glass	70.4	1.3	14.2	0.3	8.9	3.9	–	<0.1	0.4	0.6
Clay	42.4	35.1	0.1	1.1	–	0.2	–	1.2	1.1	17.8

In this work, those properties were investigated and a comparison to a currently used engobe was done. Some properties were measured in a standard engobe composition and taken as target values, which include LS = 3.9%, WA = 15.0%, L* = 90.02, ΔE* = 2.5 and CTE = $8.0 \cdot 10^{-6}\ ^{\circ}C^{-1}$.

According to a previous study (Dal Bó et al., 2011), LS and CTE are properties of ceramic tiles to be adjusted to decrease the stresses between the layers during the cooling step. The residual stresses after firing can promote some defects in ceramic tiles such as curvature and deformation (Cantavella et al., 2000; Melchiades et al., 2000). Therefore, the characterization of those properties represents an important support to industrial processes. Water stains are associated to some engobe characteristics (Melchiades et al., 2002), and may be expressed in terms of tonality difference between the dry and wet engobe (ΔE*) (Quinteiro et al., 2010). Moreover, the chromatic coordinate L*, which expresses the whiteness of the engobe, must be also taken into account particularly when the ceramic glaze is transparent (Melchiades et al., 2002).

Thus, the aim of this work is replacing frits by recycled glass in ceramic engobes. A design of experiments is performed and response surfaces are build to analyze relevant properties of engobes as a function of the composition.

2. Experimental

2.1. Engobe formulation and sample preparation

For the mixture design five factors corresponding to five raw materials were applied, resulting in 21 formulations and one genuine replica (central point or centroid). The software Statistica 7.0 (Statsoft) was used to assist the design and the analysis of the experiments. Some restrictions on raw materials content were imposed according to industrial practice.

Table 1 presents the mixture design matrix, i.e., the composition of each formulation, showing the content (wt%) of the raw materials selected.

Engobe raw materials were obtained from a local ceramic industry (Endeka, Mogi Guaçu, SP, Brazil). Recycled glass was obtained from a recycling company (Masfix, São Paulo, SP, Brazil).

Table 2 and Equations (1)–(3) are related to the restrictions regarding the raw materials content (wt%).