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Cathode-Ray Tube panel glass replaces frit in transparent glazes for ceramic tiles

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ABSTRACT

The disposal of Cathode Ray Tubes (CRT) from end-of-life personal computers and TV screens represents a serious problem in electronic-waste management. As an assembly of different materials, finding a use for each of a monitor's parts is a critical step forward a solution. However, the CRT panel is a silicate glass with a relatively high proportion of alkaline and alkaline-earth oxides, for which recycling is a natural task, and the replacement of frit in ceramic glazes arises as an interesting alternative. In this context, we investigated the effect of CRT panel glass in glazes for ceramic tiles based on a comparative analysis. We replaced up to 40 wt% of commercial transparent frit with CRT panel glass in the formulation of one reference slurry. Chemical analyses were conducted by X-ray fluorescence (XRF) and inductively coupled plasma optical emission (ICP-OES) spectrometry. The thermal expansion coefficient and the glass transition and dilatometric softening temperatures were characterized by dilatometry and compared to such properties calculated as a function of composition, using the SciGlass software and database. 20- and 30-min firing cycles were applied in a fast-firing roller kiln, replicating industrial conditions. The samples transparency was measured by spectrophotometry and compared to the colorimetric parameters of a standard glaze. The maximum content of panel glass possible to add in the transparent glaze formulation without affecting the expected properties was 20 wt%, above which transparency decreased due to heterogeneities. The reformulation of a ceramic glaze with waste CRT panel glass was successful, thus suggesting an interesting approach for disposal of other electronic wastes.

1. Introduction

Electronic waste disposal became a serious problem in the last decades when the market in this kind of material increased. Part of such wastes, the Cathode Ray Tubes (CRT) of TV and computer screens have a complex disposal procedure, for comprising different parts, some containing heavy metals, and finding only a few viable recycling alternatives [1,2]. From a global perspective, it is estimated that only 26.75% of the discarded CRTs is recycled, 59% grounded, and 14.75% incinerated [3].

The rapid change in monitor technology has accelerated in recent years the search for large-scale strategies for recycling the CRTs' glass. Among the reported strategies highlights the reuse as raw material for the manufacture of other products. One finds, for example, glass foams for highly-insulating and in microwave applications [4–7], alternative fine aggregates for mortars and concretes [8–10], synthesis of zeolites and nanopowders [11,12], glass-ceramics [13], stoneware tiles [14], and pozzolans for cement clinkers [12] made from CRT glass. In such applications, the immobilization of dangerous elements as heavy metals with minimal environmental and economic implications is an important issue. In the same way, CRT glass is being used as raw material in the production of engobes and ceramic glazes with aesthetic and mechanical properties similar to the standard ones [15–18]. All these efforts are attractive by reducing environmental impacts, saving natural raw materials and energy.

A CRT is composed of three different glasses that are, approximately, 66 wt% panel, 33% funnel, and 1% neck, which represent about 80 wt% of a TV/computer monitor [19]. Among these components, the panel glass contains the highest proportion of alkaline and alkaline-earth oxides, and, hence, has the greatest reuse potential to substitute frit in ceramic glazes. Thus, by using CRT glass in glaze formulations, one may contribute to reducing production time, natural sources of raw materials and energy consumption [20].

Brazil is one of the largest producers and consumer markets of ceramic tiles in the world, second only to China in volume. Its production in 2015 was 899 million square meters [21], while the estimated consumption of frits and derivatives exceeds 500 thousand tons/year. The sector's net income was USD 650 million in 2008 [22]. The

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frit is the most expensive raw material in a conventional transparent glaze slurry, representing 70% of its total mass [23,24]. The production costs correspond to approximately 70% of the total cost of ceramic tiles, of which 15% corresponds to the glaze and 10.5% frit. Therefore, frit represents 7.35% of the total cost of ceramic tiles. Thus, each 10 wt% of frit substituted by a waste glass costing one-third of the frit price represents savings of up to 0.5% of the total cost [25–27]. Note that these are savings in operating costs, so no capital expenditure is required. The only additional operating cost will be sampling to ascertain if the recycled panel continues to meet the expected composition guidelines before use. Therefore, using recycled CRT glass as a raw material to produce glazes and other alternative materials for the ceramic tile industry constitutes a great opportunity.

Schabbach et al. [16] used CRT funnel glass and bottom ash (from municipal solid incinerator) replacing raw materials as olivine and frit in the formulation of an opaque glaze for ceramic tiles, reducing the lead content in the reformulated ceramic glazes. Andreola et al. [18] studied the CRT life cycle mentioning the industrial suitability of using CRT panel glass as a raw material replacing commercial frit in the formulation of a ceramic glaze in the fast single-fired ceramic tile production. They observed a maximum substitution of frit by panel glass of 30 wt% but did not detail the type of commercial glaze and the temperature regime in the industrial process. Thus, the use of CRT panel glass substituting frit in ceramic glazes seems to lack in the technical literature.

In this work, we tested the substitution of a commercial transparent frit by CRT panel glass in the formulation of a standard ceramic glaze for ceramic tiles using fast single-firing conditions similar to that in an industrial process, aiming at valorizing the recycling of CRT waste glass.

Our purpose was to assess some of the main aspects of the technical viability of substituting frit by the discarded CRT panel glass. We used different amounts of CRT panel glass replacing a commercial frit in the formulation of the transparent glaze. We experimentally characterized the glass transition and softening temperatures, and the thermal expansion coefficient (TEC) of the obtained materials and compared the results with the same properties calculated as a function of composition using empirical models and the SciGlass software and glass-property database. We also measured the transparency of the studied glazes applied on the traditional ceramic substrates and compared it with the standard material.

2. Experimental

We decided to use only CRT panel glass because it represents 66% (a relatively high proportion) of the total weight of a discarded kinescope, and for it is easy to disassemble and clean. The CRT panel glass came from a polychromatic LG monitor manufactured in 2008. The standard glaze utilized for comparison was prepared using a fast-firing transparent frit supplied by a regional company. The chemical composition of the panel glass and commercial frit was determined by X-ray fluorescence (XRF) spectroscopy (PANalytical Axios Advanced XRF spectrometer). The boron concentration in the transparent frit was measured by inductively coupled plasma optical emission spectrometry (ICP-OES), using a SPECTRO ARCOS FHS12 spectrometer.

Ceramic suspensions were prepared with 70 wt% solid concentration and 1.7 g/cm^3 density, using the glaze slurry formulation described in Table 1. The partial substitutions of frit for CRT panel glass were 10, 20, 30 and 40 wt%. The ceramic suspension was ground in an alumina ball mill until less than 5 wt% retained in a 325 mesh sieve (45 µm mesh size).

The glaze suspensions were applied manually on the surface of unfired ceramic substrates, previously engobed and supplied by a local company, producing glaze layers approximately 0.3-mm thick. Green bands were previously painted on the top of the white engobe to facilitate visual evaluation of transparency. Fig. 1 shows a ceramic substrate on which the standard glaze was applied, along with the test formulation to facilitate comparison.

Table 1
Raw material proportions for glaze slurry formulation.

Raw material	Slurry	
	wt%	vol%
Frit	65.5 ± 0.01	42.5 ± 0.003
Kaolin	4.2 ± 0.01	2.7 ± 0.003
Dispersant (TPF-Na)	0.1 ± 0.01	0.1 ± 0.003
Binder (CMC)	0.1 ± 0.01	0.2 ± 0.010
Water	30.0 ± 0.01	54.5 ± 0.010

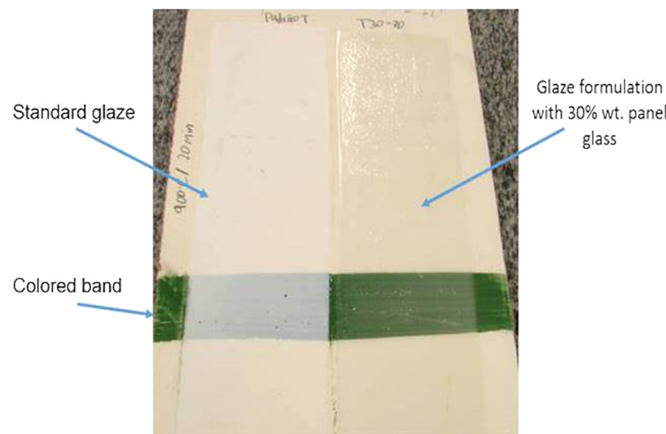

Fig. 1. The unfired ceramic substrate with the applied green band; test and standard glaze layers on engobe.

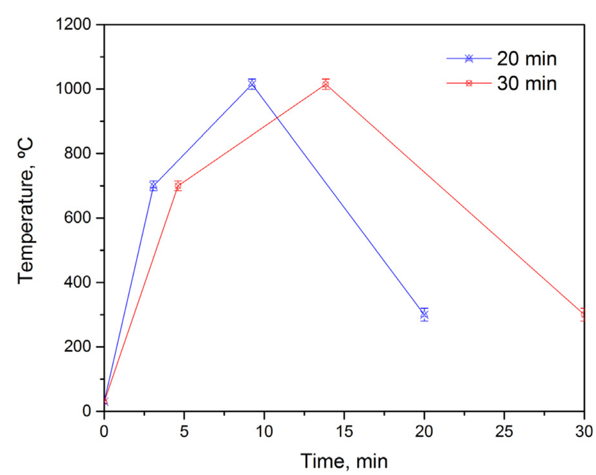

Fig. 2. The temperature as a function of time for different firing cycles (20 and 30 min).

The glazed substrates underwent 20 or 30-min firing cycles in a rapid firing roller kiln (Inti, FTU1300) at a maximum temperature of 1015 °C. Fig. 2 illustrates the temperature profile used, with temperature curves as a function of time, and heating and cooling rates defined by the cycle time. A firing cycle of approximately 20 min appropriately simulates the firing program currently adopted by the ceramic tile industry in Brazil. Firing parameters were defined according to the water absorption grade BIIb (between 6% and 10%) established for ceramic tile flooring market [28].

Glaze specimens for dilatometry were produced by drying suspensions and sintering them in a ceramic mold under the already mentioned conditions. Sample blocks were cut into cylindrical bars 5 mm in