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EFFECT OF GLASS CULLET ON THERMAL PROPERTIES OF KAOLINITE

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Waste compromises environmental preservation as well human health in many countries. Recycling is an alternative that sometimes represents the only economical activity for a significant population in the big cities. Almost 3% of waste materials in Brazil are vitreous. Ceramic production adding waste glass is possible with advantages of costs reduction associated to decrease on firing temperatures and to the raw material itself. At present paper up to 80 mass% of waste glass was added to clay. The sintering temperature decreased linearly and the shrinkage increased with glass content, an effect more pronounced for high glass amount.

Keywords: *clay ceramics, recycling glass, thermal characteristics*

Introduction

The industrial development of many countries brought along it the waste disposal problem, including ambient contamination and health damages. Brazil produces about $64\cdot 10^6$ tons of waste each year, 50% of which is not suitably dumped. Recycling is an important environmental and economical alternative for each material class, mainly for those that do not decompose easily in nature, such as glasses – not decomposed by microbial nor by atmospheric precipitation for thousand years. For ordinary purposes glasses are usually prepared from silica, but currently technological applications, such as in optical fibers, require other compositions, like germanate [1] or fluoride glasses [2]. In Brazil, glass constitutes about 3% of the total waste.

Many researches worldwide are devoted to obtaining products of economical interest using glass waste. Japan, United States, Taiwan and many European countries are attempting the usage of waste glass to partly substitute aggregate of asphalt concrete [3]. Proper usage of contaminated waste glass has also been suggested. Recycling of Cathode Ray Tube glass from computer monitors and television sets, containing lead, has been proposed for foam glass production [4] and in a composite biopolymer-modified concrete, with 30% higher compressive strength than standard concrete [5]. Industrial waste: metallurgical slag, fly-ash, etching refuse, coal ash and glass waste containing chemical contamination has been used to produce glass-ceramics tiles [6]. A process for extracting SiO_2 from waste colored glasses [7], and other based on the usage of glass waste in the production of raw porcelain glazes [8] had been attempted. The effects of up to 10% glass waste addition in porcelain stoneware tiles were researched [9]. Ceramics produced by addition of glass waste had been characterized and resulted in some composition with higher strength, similar thermal conductivity and reduced sintering temperature, compared with ceramics containing only clay minerals [9–12]. Firing temperatures influence the production costs as well the physical properties of the resulting ceramics, also the amount of recycling glass influences the cost of raw materials itself, besides the properties of final ceramics. Therefore, it is important a systematic research on thermal behavior of the mixture of clay with various amounts of glasses, as well as the extent of inclusion acceptable. In the present work, the effects of glass addition, ranging from 0 to 80 mass%, in thermal characteristics of the mixture clay-glass were studied.

Experimental

Materials preparation

Ceramic samples were prepared from commercial clays for ceramists and transparent and domestic colorless cullet. The authors previously investigated raw materials by X-ray diffraction, the clay patterns presented quartz and microcline ($KAlSi_3O_8$) crystalline phases, while the sample of waste glass heated at 900°C/30 min presented nepheline $(K,Na)AlSiO_4$ and microcline phases. The raw materials were milled and sieved to select powders with less than 1180 μm granule diameter.

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For dilatometric measurements the powders were dried, mixed and a mass with addition of 8% of humidity was homogenized in a porcelain jar during 4 min. Cylindrical samples (diameter range of 5.0–5.5 mm) were molded under low pressure. For the other thermal analysis, the mixed powder was used.

Shrinkage was determined from dimensional measurements of green and fired plate bodies with a Mitutoyo caliper.

Ceramics containing 0, 20 and 60 mass% of waste glasses were prepared, in order to run scanning electron microscopy (SEM), in a JEOL 6380LV equipment. The samples were heated at 900°C/30 min, polished and gold was evaporated on them prior to the analysis.

Methods

Differential scanning calorimetry, differential thermal analysis, thermogravimetric and thermomechanical analysis (DSC, DTA, TG and TMA, respectively) were performed in a TA50-H equipment of Shimadzu.

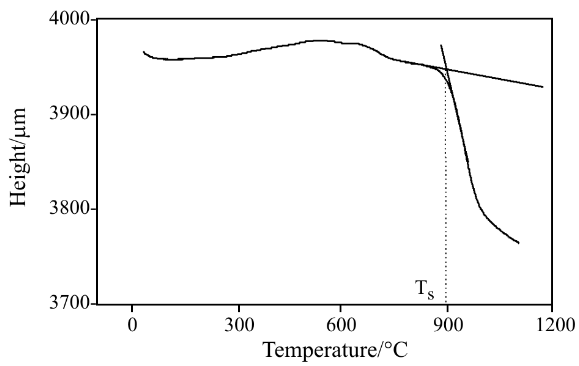

Fig. 1 Dilatometric curve of sample with 20% of glass

The dilatometric curves were obtained on TMA under nitrogen gas flux, heating rate of 10°C min^{-1} and load of 4.41 kPa. The sintering temperature (T_s) was determined, as the temperature of intersection of two tangents: at baseline before shrinking and at descending slope as can be seen in the Fig. 1 for a sample with 20% of cullet addition.

Results and discussion

TG curves, Fig. 2, for severe glass amounts, presented three regions with accentuate mass loss, near 50, 238 and 450°C, the temperature onset varying only slightly on glass content. However, the mass loss percentage decreases linearly with glass amount, see Fig. 3 in which the mass losses dependence on glass content were calculated at 238 and 450°C, from the curves of Fig. 2. Then, at these temperatures there is no chemical interaction between clay and glass, the

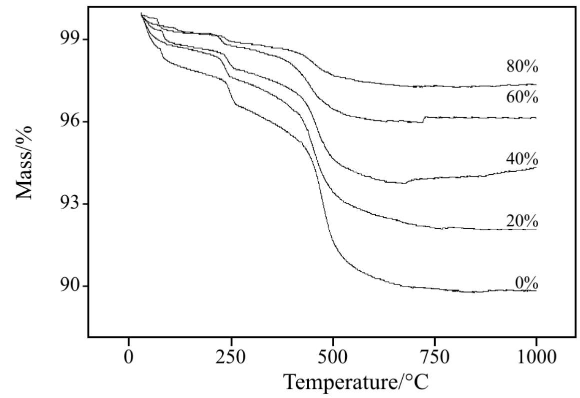

Fig. 2 TG curves of samples with various glass contents

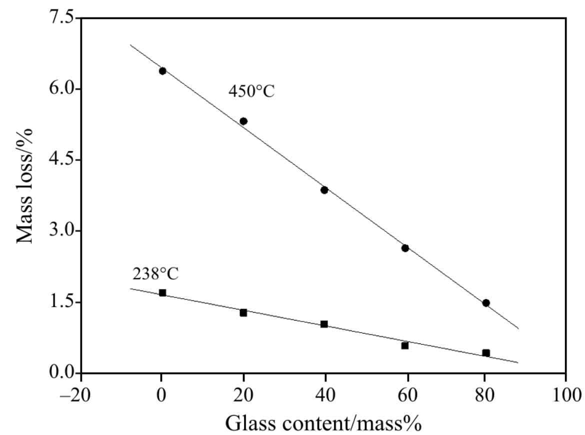

Fig. 3 Mass loss of samples with various glass contents at approximately 238 and 450°C

mass losses are due only to clay water losses, due the total melting of clay mineral into the glassy matrix.

DSC curves presented three endothermic peaks near 50, 250 and 480°C, Fig. 4, for samples with different glass content, related to free water evaporation, to surface bound water evaporation and to lamellar clay water evaporation, respectively. Therefore, the areas of the peaks are smaller as the clay amounts decrease, in accordance with TG results. The peak temperatures depend not only on the bound energy of clay-glass but also on the water vapor pressure inside the pores. The vapor pressure in the sample:

- Increases with clay amount due to the increasing rate of water liberation by clay grain to the pores or interstitial sites between grains. Therefore, the peak temperature tends to decrease with glass content.
- Varies with powder packing, depending on how the material is prepared before measurement. Packing condition is difficult to reproduce and affects the peak location, sometimes masking the tendency mentioned in the previous item.

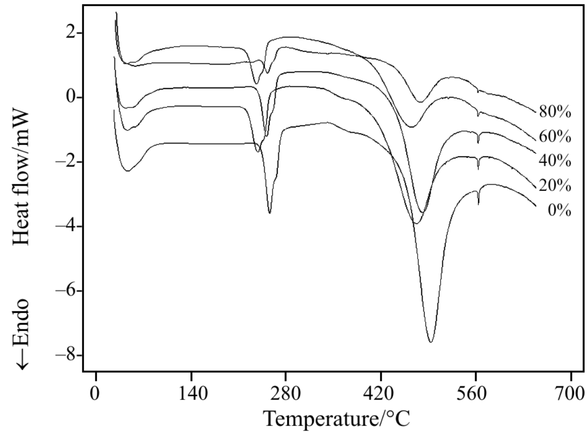

Fig. 4 DSC curves of samples with various glass contents

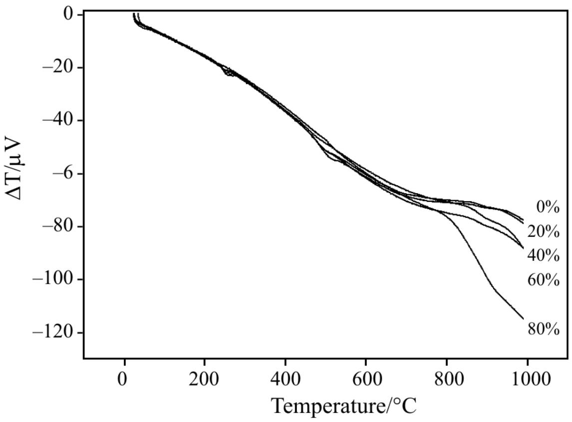

Fig. 5 DTA curves of samples with various glass contents

There was a fourth thin small endothermic peak near 570°C, Fig. 4, corresponding to a quartz polymorphic transition.

Above 700°C, DTA curves presented large exothermic peaks, Fig. 5. The peaks became higher and occurred at lower temperature with increasing glass content; they correspond to recrystallization during sintering process.

The sintering onset temperature decreases with increasing glass amounts, as can be observed on TMA curves, Fig. 6. Besides it, the shrinkage intensity of the samples during sintering is higher as the glass amounts

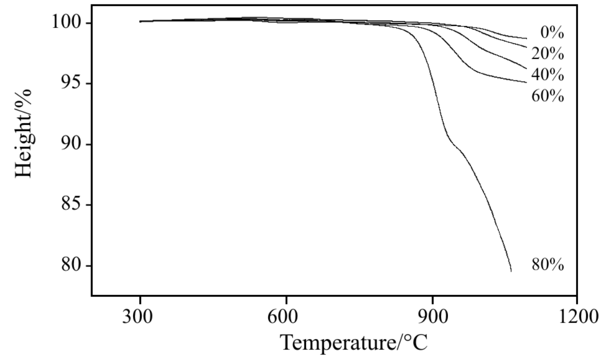

Fig. 6 TMA curves of samples with various glass contents

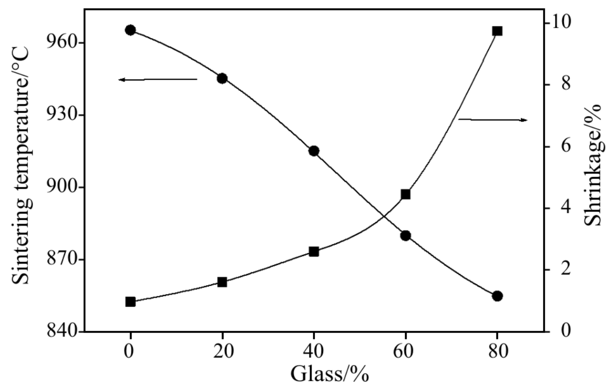

Fig. 7 Shrinkage and sintering temperature dependence on glass content

increased, Fig. 7. The sample containing 80% of glass and heated above 1000°C resulted in transparent glass.

The sintering temperature decreases almost linearly with glass content, while the shrinkage increases faster for samples with 60% or more of cullet. The shrinkage behavior is coherent with the fact that porosity decreases drastically when glass phase become predominant.

In pictures obtained by SEM, Fig. 8, we can observe that silica grains are broadly present in ceramics containing 0 and 20% of glass, but at higher content, as 60%, it reacts with glass, providing higher structural as well as compositional homogeneity, as well as intense porous production.

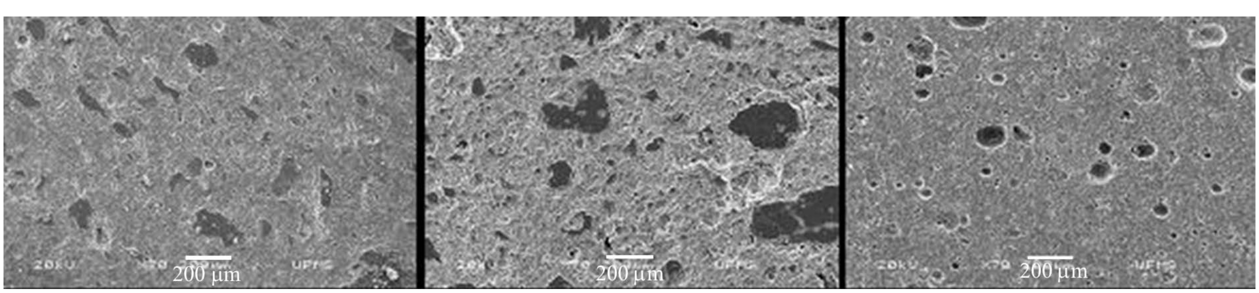

Fig. 8 SEM micrographs for samples with 0, 20 and 60% of glass cullet, from left to right

Conclusions

The ceramic sintering temperature decreased linearly with the amount of waste glass addition. This recycling process hold two advantages: waste glass is a low-price material available in every city, and the ceramic firing temperatures can decrease as well as the energetic costs of the production.

The shrinkage increased with cullet content, an effect more pronounced for additions above 60%. Recycling presents environmental interest, reducing dumping problems in the cities and for ceramics preparation yet colored waste glasses are acceptable.

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References

1 S. Grujić, N. Blagojević, M. Tošić, V. Živanović and B. Božović, J. Therm. Anal. Cal., 83 (2006) 463.
2 J. R. J. Delben, A. A. S. T. Delben, K. Miazato, S. L. Oliveira and Y. Messaddeq, J. Therm. Anal. Cal., 75 (2004) 637.
3 N. Su and J. S. Chen, Resources, Conservation Recycling, 35 (2002) 259.
4 F. Mear, P. Yot, M. Cambom and A. M. Ribes, Adv. Appl. Ceram., 104 (2005) 123.
5 D. Kim, I. G. Petrisor and T. F. Yen, J. Air Waste Manage. Assoc., 55 (2005) 961.
6 R. Cindims, I. Rozenstrauha, L. Berzina, L, Bossert and M. Bucker, Resources, Conservation Recycling, 29 (2000) 285.
7 H. Mori, J. Ceram. Soc. Jpn., 111 (2003) 376.
8 S. Zafirovski, K. Davkova, S. Pocev and S. Bagoevski, Glass Technol., 41 (2000) 199.
9 M. Francesco, D. Michele and G. Guia, Euro Ceramics VII – Key Eng. Mater., 206 (2002) 851.
10 B. H. Kim, J. H. An, Y. H. Yun, B. Kang, B. Jeon, Y. S. Jeon and K. S. Hwang, J. Ceram. Proc. Res., 5 (2004) 140.
11 V. A. Leshina and A. L. Pivnev, Glass Ceram., 59 (2002) 356.
12 V. Balkyavichus, C. Valyukyavichus, A. Shpokauskas, A. Laukaitis and F. Pyatrikaitis, Glass Ceram., 60 (2003) 179.

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