

M. I. Martín, F. A. López, F. J. Alguacil and M. Romero, Technical characterization of sintered glass-ceramics derived from glass fibers recovered by pyrolysis. *Journal of Materials in Civil Engineering*, 29 (2013) 04014150; doi: 10.1061/(ASCE)MT.1943-5533.0001090

Technical characterization of sintered glass-ceramics derived from glass fibers recovered by pyrolysis

M^a Isabel Martín¹; Félix A. López²; Francisco J. Alguacil²; and Maximina Romero¹

¹ Group of Glass and Ceramic Materials, Department of Construction, Eduardo Torroja Institute for Construction Science (IETcc), CSIC, Serrano Galvache, 4, 28033, Madrid, Spain.

² Recycling Materials Laboratory, Department of Primary Metallurgy and Recycling, National Centre for Metallurgical Research (CENIM), CSIC, Avda. Gregorio del Amo 8, 28040, Madrid, Spain.

E-mail: mromero@ietcc.csic.es

Abstract

Sintered wollastonite-plagioclase glass-ceramics were prepared through crystallization of a parent glass generated by vitrification of pyrolysis residual glass fibers that had been pyrolytically recovered from waste composite materials. A vitrifiable mixture consisting of 95 wt.% glass fiber and 5 wt.% Na₂O was melted at 1450°C to obtain a glass frit. The glass-ceramic materials were produced by a sinter-crystallization process from the powdered glass frit. The effect of firing temperature on the properties of sintered glass-ceramics was investigated. The sintering behaviour of glass-ceramic tiles was evaluated by means of water absorption, apparent porosity and bulk density. In addition, the mineralogical and microstructural characterization of these tiles was carried out using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results from experiments such as water absorption, bending strength, chemical resistance and stain resistance have shown that the developed glass-ceramic materials possess technological properties very suitable for architectural applications.

ASCE Subject Headings: Glass fibers; Recycling; Glass; Ceramics; Construction materials; X-Ray diffraction; Mechanical properties

Author keywords: Pyrolysis residual glass fibers; Glass; Glass-ceramic tiles; X-ray diffraction; Mechanical properties

1. Introduction

Fiberglass is the reinforcement material most commonly used in the manufacture of polymer matrix composites. Fiberglass-reinforced plastics play important roles in high-performance applications in civil, mechanical and biomechanical engineering, as well as in automobile manufacturing and the aeronautical industry. The global production of composite materials increases every year, and output is expected to reach 10.3 Mt in 2015. Approximately 90% of these materials are thermostable composites containing glass fibers as a strengthening constituent. Recycling of fiberglass-reinforced plastics would contribute to the development of sustainable industrial processes. However, recycling these composites is not economically feasible because the fibers recovered possess lower mechanical properties than the virgin fibers, and these fibers are inappropriate for reuse in manufacturing new structural materials. Consequently, most fiberglass-reinforced composite wastes are stored in landfills or are buried. These wastes are usually non-biodegradable and considerable bulky and thus, they produce serious environmental problems. European legislation (EPA Handbook 1992; Höland and Beall 2002; Fernández 2003) limits the amount of these wastes that may be discarded in landfills. The United Kingdom and Germany have gone further by implementing a total ban on dumping these types of waste materials. Thus, the sustainable disposal of composites remains a challenge.

Many technologies have been proposed for recycling thermoset composites: mechanical comminution-based processes (Donald 2012); thermal processes such as combustion, pyrolysis and thermolysis (Kipks et al. 1993; Rübiger et al. 1995; Barbieri et al. 1997); and composite depolymerisation based on chemical processes such as hydrolysis, glycolysis and solvolysis (Barbieri et al. 2001). However, none of these techniques achieves more than partial recovery of the glass fibers.

In recent years, waste vitrification has been considered an attractive alternative for handling different types of municipal and industrial solid wastes (Elliot et al. 1994). The vitrification process can be followed by a thermal treatment that results in the production of glass-ceramics with high mechanical strength and excellent chemical durability (Barbieri et al. 1999; Leroy et al. 2011).

Glass-ceramics are produced from parent glasses by sequential thermal processes involving controlled crystallisation that results in one or more crystalline phases (Martín et al. 2011). Developed in the 1950s, the earliest glass-ceramics were produced by a conventional glass route

with subsequent crystallisation – usually two heat treatments to generate nuclei followed by a crystal growth stage. Recently, the sintering method has become a technically viable route for manufacturing glass-ceramics. Glass-ceramics find a wide variety of uses in different technological fields, including architecture (Höland and Beall 2002). The most important glass-ceramic for architectural applications is Neoparies[®]. Wollastonite glass-ceramic is manufactured on a large scale as a building material for interior and exterior walls. Large, flat and large, curved sheets of the material are also produced for constructing facades. Furthermore, glass-ceramics for exterior applications are manufactured in different colours and textures. Neoparies[®] glass ceramics is highly resistant to weathering, has a negligible water absorption rate, is harder and 30% lighter than natural stone, is easily shaped and is not affected by common chemical agents (Höland and Beall 2002; <http://www.negb.co.jp/en/product/01/01.html>). This paper aims to describe the development of glass-ceramics from glass fibers that have been pyrolytically recovered from waste composite materials. These glass-ceramic materials possess technological properties that are good for architectural applications.

2. Materials and methods

2.1. Recovery of glass fibers and glass-ceramic preparation

The glass-ceramics were synthesised through crystallization of a parent glass (hereafter referred to as PGF glass) generated by vitrification residual glass fibers recovered by pyrolysis from waste composite material. The waste composite was a fiberglass-reinforced polyester (PGF) produced by POLIFIBRA, S.A. (Guadalajara, Spain). POLIFIBRA's PGF is composed of unsaturated polyester resin (32.8 wt.% orthophthalic polymer resin, 1.2 wt.% styrene monomer, 1.2 wt.% Zn stearate and 0.3 wt.% organic catalyst) and 64.5 wt.% type E glass fiber.

The PGFs were heated for 3 h at 550°C in a 9.6 dm³ pyrolytic reactor equipped with an electric heating system and a gas condenser. Typical batch used approximately 4 kg of PFG pieces measuring 12 x 4 cm². The products obtained in this type of pyrolysis are complex organic compounds (oils), non-condensable gases, and glass fiber (López et al. 2012a,b). The yields of oils (23.9 wt.%) and fibers (68.1 wt.%) were determined with respect to the initial PGF

weights. The gas yields (8 wt.%) were determined by subtracting the initial PGF weights from the combined weights of the oils and fibers.

Prior to use, the recovered fibers (97 wt.% glass fiber and 3 wt.% residual organic matter) were milled and then were sieved to a particle size <250 μm . Na_2O (as Na_2CO_3) was incorporated at 5 wt.% into the PGF glass formulation to facilitate melting. The 95 wt.% glass fiber and 5 wt.% Na_2O batches were mixed for 30 minutes in a blender (TURBULA) to obtain homogeneity. Each batch was transferred to an aluminosilicate crucible, placed in an electric furnace and then heated $10^\circ\text{C}/\text{min}$ to 1450°C . After holding for 120 minutes at the melting temperature, the melt was quenched by pouring into water, producing a glass frit.

The chemical composition of the recovered glass fiber and the synthesised PGF glass was determined by X-ray fluorescence (XRF) (Bruker model S8 Tiger with a tungsten tube, LiF-crystal analyser and 4-kW generator). B_2O_3 content was determined by inductively coupled plasma spectroscopy with an emission spectrometer (ICP-OES) (Varian 725-ES ICP Optical Emission Spectrometer).

Previous studies have shown that PGF glass devitrifies through a surface crystallization mechanism (López et al. 2012a; Martín et al. 2014); therefore, the most appropriate method for manufacturing glass-ceramic materials from the PGF glass frit should be a sinter-crystallization process, i.e., one that involves sintering and then crystallization (Donald, 2010).

The PGF glass frits were ground (BIOMETAL RETSCH PM, 100 ball mill at 400 rpm) and then sieved to a 80-100 μm particle size. Distilled water (2 wt %) was sprayed onto the powders to moisten. The moistened powders were then shaped into rectangular glass tiles (55 mm x 20 mm x 4 mm) by uniaxial pressing (Perkin Elmer) at 60 MPa in a steel die. To evaluate the effect of temperature on the technological properties of end glass-ceramics, tiles were treated at different temperatures (850-1100°C) for 20 minutes. After treatment, the samples were taken out of the oven and air cooled to room temperature.

2.2. Glass-ceramic characterization

Crystalline phase development after the different thermal treatments was studied by X-ray diffraction (XRD) (Philips model X 'PERT MPD) using Ni-filtered $\text{Cu-K}\alpha$ radiation operating at 30 mA and 50 kV. Data were recorded in the $3-75^\circ$ 2θ range. A step size of 0.019732° and a step rate of 0.5 s per step were employed.

The glass-ceramics microstructures were examined by field emission scanning electron microscopy (FESEM) (HITACHI model S-4800) operating at 20 kV. To study porosity, FESEM specimens were ground with silicon carbide paper and water and then polished using 6, 3 and 1 μm diamond pastes. The polished surfaces were etched for 10 s in a 5 vol.% HF solution, washed ultrasonically with distilled water and ethyl alcohol and then dried. Additional SEM specimens were prepared from freshly fractured glass-ceramic surfaces. For enhancing SEM observations, all samples were Au-Pd coated using a Balzers SCD 050 sputter.

The sintering behaviour of the glass-ceramic tiles was evaluated by linear shrinkage, water absorption, apparent porosity and bulk density. The water absorption was measured according to ISO 10545-3:1997 (International Organization for Standardization (ISO) 1997. ISO 10545-3), which involved drying the test specimens to constant mass and boiling in distilled water for 2 h. Then tiles should be left cooling for four hours immersed in water. The water absorption coefficient, E (wt.%), was calculated by the equation:

$$E = [m_2 - m_1/m_1] \times 100 \quad (1)$$

where m_1 and m_2 are the masses (g) of dry and wet specimen, respectively.

The apparent porosity and the bulk density were measured according to ASTM C373-88:1999 (American Society of Testing and Materials (ASTM) 1999. C373-88), which involved drying the test specimens to constant mass (D), boiling in distilled water for 5 h and then soaking for an additional 24 h at room temperature. The test was performed on ten representative specimens. After immersion, the suspended mass (S) of each specimen and their saturated mass (M) were determined. The apparent porosity, P (%), expresses the relationship of the open pore volume to the specimen's exterior volume and was calculated as follows:

$$P = [(M - D)/V] \times 100 \quad (2)$$

where V (cm^3) is the exterior volume ($V = M - S$).

The bulk density, B (g/cm^3), of a specimen was calculated by dividing its dry mass by its exterior volume, including pores:

$$B = [D/V] \quad (3)$$

Bending strength, BS (MPa), was measured for ten specimens at each sinter temperature according to EN 843-1:2006 (European Norm (EN) EN 843-1) in an electronic universal tester

(Servosis model ME-402/01). BS tests were carried out using a three point flexural test technique with a span of 32 mm and a crosshead speed of 1 mm/min.

Finally, chemical and stain resistance were evaluated according to ISO 10545-13:1997 (International Organization for Standardization (ISO) 1997. ISO 10545-13) and ISO 10545-14:1997 (International Organization for Standardization (ISO) 1997. ISO 10545-14), respectively. The aqueous solutions used for determining chemical resistance were a household cleaning product (ammonium chloride 100 g/L), a swimming pool salt (sodium hypochlorite 20 mg/L), and acids and bases (hydrochloric acid 3 and 18% (v/v), citric acid 100 g/L, lactic acid 5% (v/v), and potassium hydroxide 30 and 100 g/L). The test specimens were dried to constant mass, immersed vertically a depth of 25 mm for 12 days at room temperature, soaked in running water for 5 days, boiled in tap water for 30 min and finally dried at 110°C. After drying, the test samples were examined to detect changes on the exposed surfaces, e.g., changes in colour, reflection, surface texture and brilliance. This test was carried out on five representative specimens for each test solution.

The reagents used for determining stain resistance were green stain agent (Cr_2O_3) in light oil, iodine (alcoholic solution 13 g/L) and olive oil. Test specimens were dried to constant mass, and then, their surfaces were exposed to a staining agent for 24 hours. Afterward, the specimens were subjected to defined cleaning methods and were finally inspected for visual changes. The tests were performed on five representative samples for each staining agent.

3. Results and discussion

Table 1 shows the chemical composition of both the pyrolytically recovered glass fiber and the PGF glass. They consist mainly of SiO_2 , CaO and Al_2O_3 , with B_2O_3 being the most abundant trace component. In the PGF glass, higher concentrations of Na_2O are found because of its 5 wt.% inclusion in the glass formulation.

Fig. 1 shows the sintered glass-ceramic tiles after firing for 20 minutes at different temperatures within 850-1100°C. The green glass compacts show good sintering behaviour throughout the different temperatures and result in compact tiles without apparent defects such as bumps, depressions, cracks or undulations. The figure also illustrates that tile colour undergoes an important change with increasing temperature. The tile fired at 850°C appears greenish brown, but the tiles fired at higher temperatures appear pinkish-white. For the glass

ceramic produced at 850°C, the PGF glass exhibits a greenish-brown, which is due to the action of iron oxide present in its composition.

Table 1. Chemical composition (wt.%) of the glass fiber recovered by pyrolysis and the PGF glass

Oxide	Pyrolysis residual glass fiber	PGF glass
SiO ₂	55.00	52.86
CaO	22.90	20.36
Al ₂ O ₃	13.90	13.95
B ₂ O ₃	6.35	6.03
Na ₂ O	0.79	5.82
MgO	0.34	0.24
K ₂ O	0.29	0.24
Fe ₂ O ₃	0.23	0.25
TiO ₂	0.12	0.20
SrO	0.11	0.02
ZrO ₂	0.01	0.02

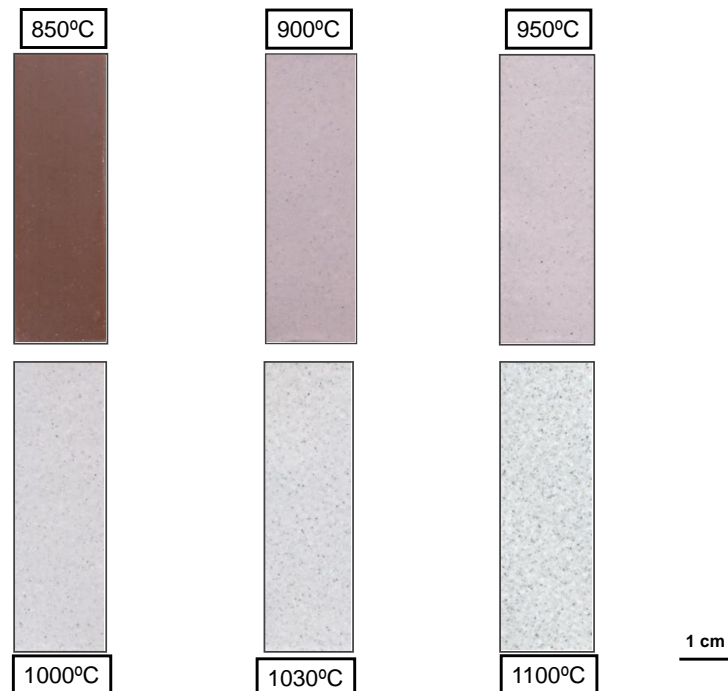


Fig. 1. Appearance of the glass-ceramic tiles obtained at 850-1100°C for 20 minutes.

The Fe_2O_3 leads to a brown colour. However, if the Fe ions are dissolved in the molten glass as a divalent FeO, they give rise to a green colour. When the glass composition includes a high proportion of alkaline oxides, such as PGF glass, Fe_2O_3 is chemically reduced to FeO in the oxidising atmosphere (Matthes 1990). The colour change observed after heat treatment is most likely due to the incorporation of iron oxide in the crystalline phases formed because of the devitrification of the glass.

Table 2 lists the results of linear shrinkage, water absorption, open porosity and bulk density calculations. After firing, glass particles achieve a high degree of sintering, as evinced by the exceptionally low open porosity and water absorption values

Table 2. Linear shrinkage and technological properties of the glass-ceramic materials obtained at different temperatures (time = 20 minutes)

Sintering temperature T (°C)	Linear shrinkage		Water absorption		Open porosity		Bulk density	
	LS (%)		E (wt.%)		P (%)		B (g/cm ³)	
	Value	SD	Value (x10 ⁻³)	SD (x10 ⁻⁵)	Value (x10 ⁻²)	SD (x10 ⁻⁴)	Value (x10 ⁻³)	SD
850°C	13.26±0.26		0.7±1.4		0.2±1.0		2.60±8.8	
900°C	14.97±0.11		4.3±1.3		1.1±2.4		2.61±2.4	
950°C	15.17±0.33		5.3±1.5		1.4±1.0		2.62±3.6	
1000°C	15.12±0.22		2.5±4.2		1.4±7.7		2.62±2.6	
1030°C	15.20±0.37		6.9±1.6		2.2±2.3		2.61±2.4	
1100°C	14.25±0.20		5.1±2.1		1.3±4.0		2.58±10.0	

Fig. 2 presents the XRD patterns of tiles fired at 850 and 1000°C for 20 minutes. The absence of crystallization peaks in the 850°C diffractogram implies that glass compacts fired at 850°C maintain their amorphous nature. These results indicate that sintering ends before crystal growth begins, which is desirable for a sinter-crystallization process.

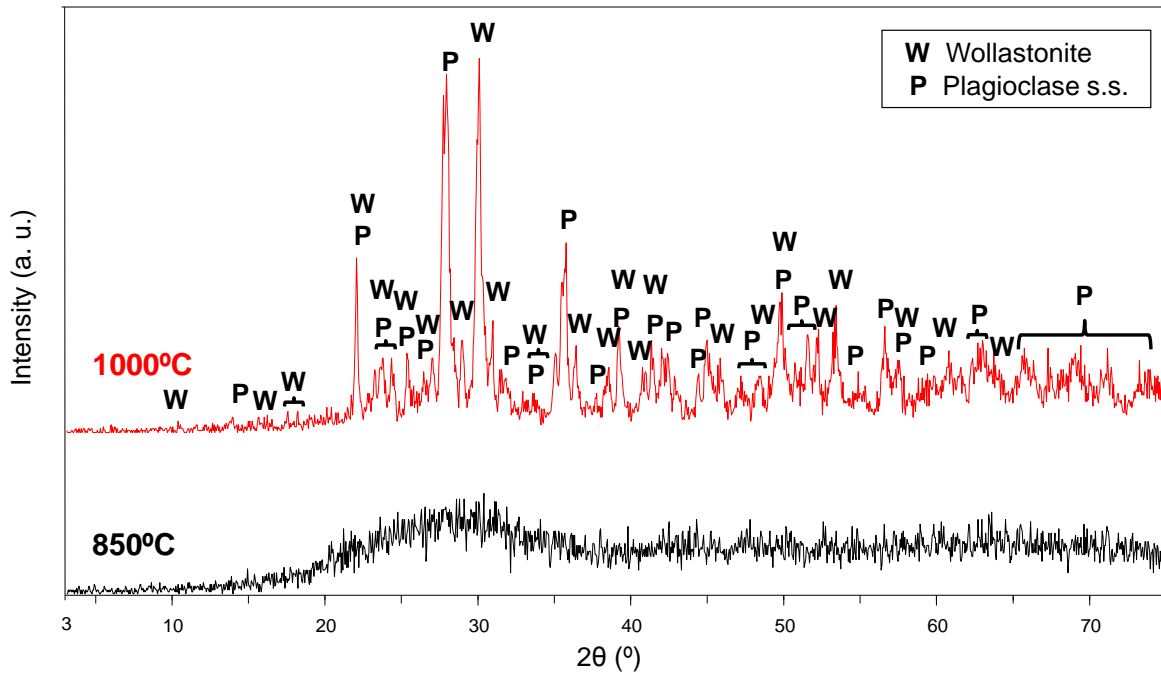


Fig. 2. X-ray diffraction patterns of the glass-ceramics produced after thermal treatment at 850°C/20 min and 1000°C/20 min.

All the synthesised glass-ceramic tiles exhibit water absorption values lower than $7.0 \times 10^{-3}\%$, comparable to Neoparies[®] glass-ceramic (water absorption degree of 0.0%) (<http://www.negb.co.jp/en/product/01/01.html>). Using the European Standard EN 14411:2003 (European Norm (EN) 2003 EN 1441), these PGF glass-derived tiles fall under the BIa group classification, which comprise dry-pressed ceramics with water absorption coefficients (E) \leq 0.5%. FESEM also showed changes in porosity accompanying changes in firing temperature.

Fig. 3 shows low magnification FESEM images of glass compacts heat treated at different temperatures (850-1100°C) for 20 minutes. The images reveal a homogeneous microstructure free of internal defects such as laminations or cracks. At 850°C, some open porosity is observed, which consists of interconnected and elongated pores producing small channels along the glass particles' boundaries. At 900°C, the open porosity slightly lowers, and from 950 to 1100°C, closed porosity consisting of rounded pores becomes increasingly observable.

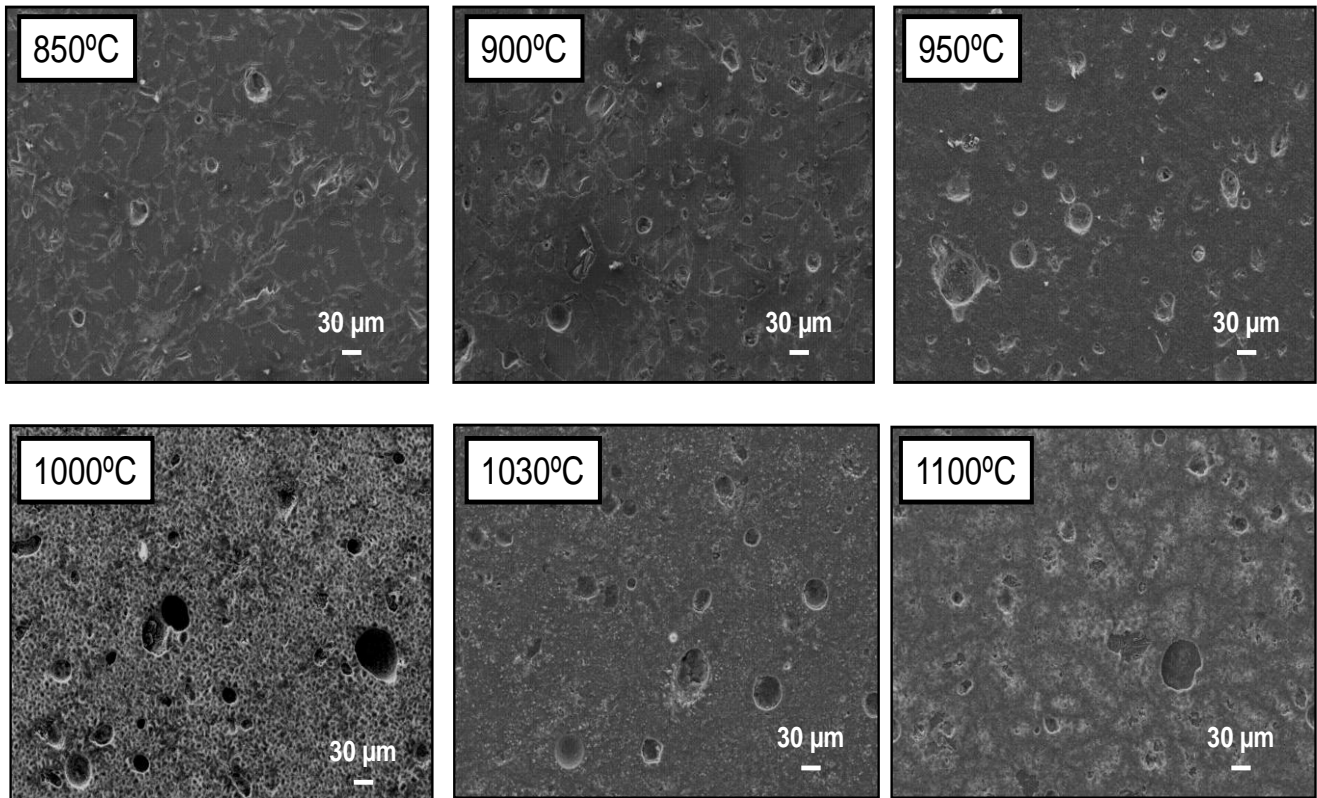


Fig. 3. a) Secondary electron images of samples heat treated at different temperatures (850-1100°C) for 20 minutes.

Fig. 4 shows the trend of changes in bending strength with firing temperature. BS increases with temperature up to approximately 1030°C because of both high sinterisation and crystalline-phase development. At firing temperatures above 1030°C, however, increased closed porosity decreases BS. Nevertheless, all the glass-ceramics show bending strength values considerably higher than 35 MPa - the minimum strength for classification under the BIa group by the European Standard EN 14411. Moreover, all the glass-ceramics exhibit a bending strength higher than 41 MPa, the value reported for Neoparies[®] (<http://www.negb.co.jp/en/product/01/01.html>).

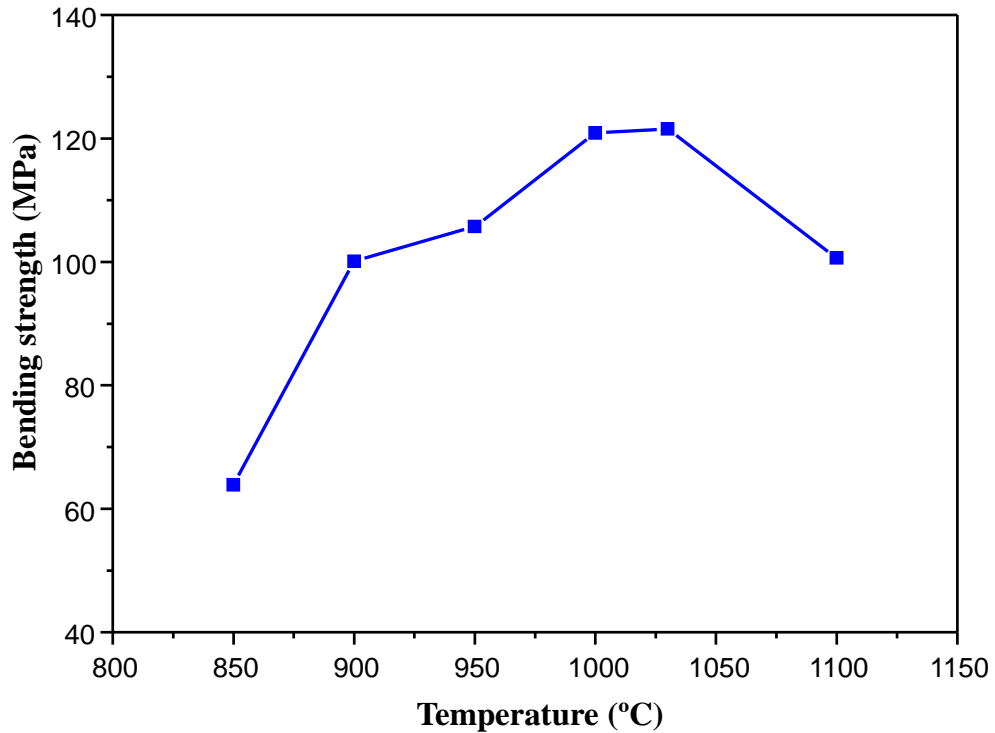


Fig. 4. Bending strength (MPa) as function of heating temperature in the 850-1100°C interval.

Table 3 lists the BS values for the glass-ceramic materials produced from different wastes that have been reported previously. Glass-ceramics sintered in the 1000-1030°C range exhibit the highest bending strength values (122 MPa). In fact, except the material obtained by firing at 850°C, all sintered glass-ceramics derived from PGF glass show strength values above 100 MPa, which are exceeded in Table 3 only by glass-ceramics made from MSW incinerator fly ash (BS=127 MPa) (Park and Heo 2002).

Table 3. Bending strength of different glass-ceramic materials made from various wastes

Waste	Thermal treatment (temperature/time)	Bending strength BS (MPa)
Coal ashes (Leroy et al. 2011)	870°C/120min	67.02±13.32
MSW incinerator fly ash (Park and Heo 2002)	720°C/90min+870°C/600min	127
MSW incinerators bottom ashes (Appendino et al. 2004)	950°C/60min	61
Mixtures of wastes(panel glass, lime and mining residues) (Bernardo et al. 2007)	930°C/60min	77.7±8.6
Marine sediments (Romero et al. 2008)	1125°C/60min	22
Water quenching-induced cracked-glass (Zhou and Wang 2008)	860°C/60min+1080°C/90min	45.60
Mixtures of wastes (soda-lime glass, lime and mining residues) (Bernardo et al. 2008)	960°C/30min	96.5±10.6
Red mud (Bernardo et al. 2009)	900°C/30min	89.6±22.6
Volcanic ash and waste glass (Vu et al. 2008)	815°C /10min	9.58±0.2
Blast furnace slag (Zhao et al. 2012)	780°C/30min+960°C/90min	45.8
Waste glass and coal fly ash (Yoon et al. in press)	1050°C/60min	94.1
Rice husk ask (Martín et al. 2013)	900°C/40min	39±3
Pyrolysis residual glass fibers (Present paper)	1000-1030°C/20min	122±9

Fig. 5 shows the microstructure of a glass-ceramic produced with a 1000°C firing temperature for 20 minutes. The high flexural strength of glass-ceramics from PGF glass most likely results from its microstructure, which is composed of a dense network of tightly interlocked, wollastonite and plagioclase crystals.

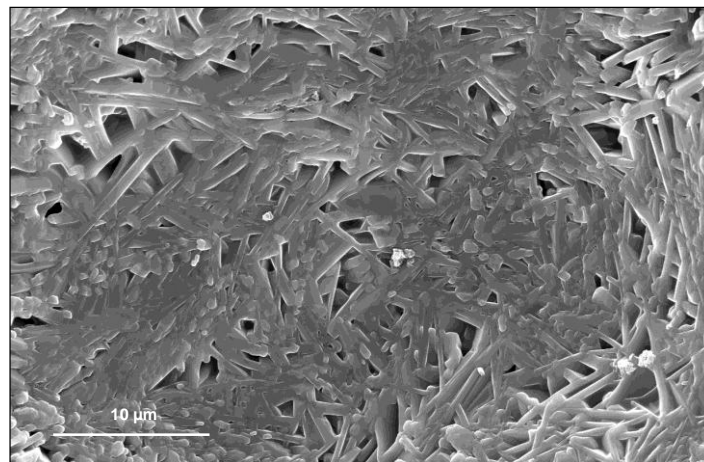


Fig. 5. Secondary electron images (3000x) of samples after thermal treatment at 1000°C for 20 min.

The glass-ceramic density resulting from different firing temperatures is practically identical (mean value: 2.60 g/cm³). The densities of the wollastonite and plagioclase crystalline phases are as 2.84 and 2.68 g/cm³, respectively (<http://www.webmineral.com/data/Wollastonite-1A.shtml>; <http://www.webmineral.com/data/Plagioclase.shtml>). The material resulting after the thermal treatment at 850°C for 20 min is mainly amorphous as denoted by its DRX pattern (Fig. 2). The theoretical density of this material, calculated by the Appen method (EPA Handbook 1992) from its chemical composition (Table 1) is 2.66 g/cm³, which is slightly higher than the mean value of 2.60 g/cm³ experimentally calculated. This divergence likely results from the presence of closed porosity (Fig. 3), which is not taken in account in the determination of bulk density.

Finally, Table 4 shows the classification of the glass-ceramic tiles based on the chemical resistance test according to EN ISO 10545-13. All synthesised glass-ceramic tiles reached the highest “A” classification, indicating that the test solutions produce no visible effects on the tiles.

Table 4. Chemical-resistance classification, according to ISO 10545-13, of the glass-ceramic tiles sintered at the 850-1100°C interval for 20 minutes

Ammonium chloride 100 g/L	Sodium hypochlorite 20 mg/L	Hydrochloric acid 3% (v/v)	Citric acid 100 g/L	Potassium hydroxide 30 g/L	Hydrochloric acid 18% (v/v)	Lactic acid 5% (v/v)	Potassium hydroxide 100 g/L
Class UA	Class UA	Class ULA	Class ULA	Class ULA	Class UHA	Class UHA	Class UHA

Table 5 compiles the results of the stain resistance test according to EN ISO 10545-14. Notably, each sintered glass-ceramic tile obtained the highest rating (5) for iodine and olive oil agents. Exposure to running water for 5 minutes and then wiping with a damp cloth is sufficient for cleaning these tiles. The tiles exposed to the green staining agent required hand cleaning with a commercial product at pH 6.5 to 7.5, thereby resulting in a score of 4.

Table 5. Resistance-to-stain classification, according to ISO 10545-14, of the glass-ceramic tiles sintered at the 850-1100°C interval for 20 minutes

Green stains agent in light oil	Iodine (alcoholic solution 13 g/L)	Olive oil
4	5	5

Conclusions

This study demonstrates the feasibility of obtaining wollastonite-plagioclase glass-ceramics through crystallisation of a parent glass made from glass fibers pyrolytically recovered from waste composites materials. Water absorption values lower than $\leq 0.5\%$, which is characteristic of highly sintered ceramics, classify these tiles into European Standard EN 14411's BIa group. Overall, the sintered glass-ceramics, produced at different firing temperatures, show bending strength values higher than 100 MPa, greater than that of the commercial glass-ceramic Neoparies[®]. The greatest bending strength values (121.49 MPa) are obtained by a firing temperature of 1030°C for 20 minutes. The tiles produced in this study do not show any visual effects from exposure to the chemical agents in ISO 10545-13, and all tiles are easily cleaned with water or commercial products at pH 6.5 to 7.5 after exposure to the staining agents in EN ISO 10545-14.

In conclusion, the glass-ceramic developed in this research possess technological properties very suitable for both indoor and outdoor architectural applications. Their most advantageous properties are high flexural strength, high resistance to weathering and a zero water absorption rate.

Moreover, environmental benefits such as reduced raw material consumption and use of landfills would be achieved with this technology by using residual glass fibers from waste composites materials as main raw material to produce glass-ceramic materials with architectural applications.

Acknowledgments

Dr. M.I. Martín thanks the Spanish National Research Council (CSIC), co-financed by the European Social Fund Operational Programme 2007-2013 Adaptability and Employment Multiregional, for the contract JAE-Doc_08-00032. The authors also thank IRICA from University of Castilla-La Mancha (Spain) for their experimental assistance with XRD.

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