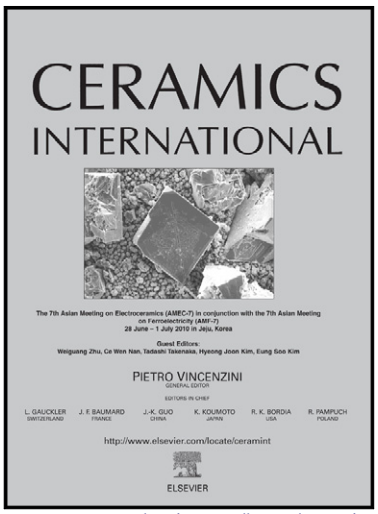

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Design of glass foams with low environmental impact

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Abstract

Glass foams obtained through the end of life fluorescent lamps recycle represent an interesting way for waste prevention and waste management developing potentially commercial products. The aim of the present project is to investigate the possibility to obtain glass foams using fluorescent lamps as glass matrix and egg shells as foaming agent replacing the conventional calcium carbonate. Moreover, the influence of the temperature and the holding time of the foaming process on the apparent density and compressive strength of the obtained materials have been also studied. The experimental work, planned using a Design of Experiment approach has demonstrated that the use of egg shells as foaming agent allows to obtain the same final properties of the glass foams produced by $CaCO_3$, with apparent density and porosity values comparable with the commercial counterparts.

Keywords

glass foams; waste glass; end of life fluorescent lamps; design of experiments.

1. Introduction

Nowadays, increased sensibility to environmental issues together with the orientation towards the reuse of waste materials opens to a wide range of new eco-compatible products. In the field of waste management is strengthened the concept of recovery and improvement of wastes arising from different production for their use in new industrial sectors. This recovery could lead both to economic benefits (in particular with regard to the saving of natural raw materials and energy) and, in some cases, to an improvement of the quality. In this perspective glass foams production represents an excellent opportunity to absorb large quantities of glass waste. Glass foam is generally obtained by the action of a gas-generating agent (foaming agent), which is ground together with the starting waste glass to a finely powder. The mixture of glass powder, foaming agent, and occasionally other mineral agents is then heat treated at a suitable temperature to promote viscous flow sintering and the thermal decomposition or oxidation of the foaming agent. The evolution of gas inside the softened pyroplastic mass of glass leads to a multitude of initially spherical small bubbles, which, under increasing gas pressure, expand to a foam structure of polyhedral cells that, after cooling of the glass, constitute the pores in the glass foam. The properties of finished foamed glass products strongly depend on the type and the quantity of the added foaming agents, on the initial size of the glass particles, and on the firing schedule. The commercial glass foams present low density, typically in the range of 0.1-0.3 $g \cdot cm^{-3}$ and high porosity, typically in the range of 85-95% [1]. They also combine other properties, such as stiffness, compression and fire resistance and chemical inertia, as well as low transport costs [1]. Owing to these characteristics, glass foams can be used for thermal and acoustic insulation, as a valid alternative to polymeric foams, currently employed [2].

The production technology of glass foams is a well-established procedure not only for obtaining products having a unique combination of properties but also for recycling growing quantities of glass waste, in line with Directive 2008/98/EC [3-9]. Glass recycle in glass foams allows energy saving, typically due to low temperature of viscous flow, as well as reduces the need for natural raw materials.

Waste electric and electronic equipment (WEEE) derived glasses are one of the most representative residues in Italy (about 15,000 to 16,000 tons /year) and the main sources of these glasses are R3 Group (TVs and PC monitors) and R5 Group (light sources). Fluorescent lamps (FLs) belong to R5 class corresponding to low-energy lamps and their flow is increasing due to the obliged replacement of the old incandescent lamps, according to Regulation (EC) no. 244/2009. FLs cannot get in a normal waste box or take off to landfill since they often contain hazardous substances as heavy metals, PCB, halogenated substances or ozone-depleting compounds. Moreover, any material recovered from FLs can hardly be reused to produce new electrical and electronic devices.

In Italy the creation of e-waste collection and treatment centres gives the opportunity to have cleaned glassy material useful for an open-loop recycling. Fluorescent lamps are collected in appropriate containers and sent to treatment in dedicated plants. The collection in 2013 was nearly 1,900 ton (Consortium for the recovery and treatment of lighting source equipment -ECOLAMP).

Here, lamps are disassembled and the components are separated and reclaimed. The recovery can be done through two different technologies: end cut, or crush and sieve. In the second method, used in particular in Italy, the fluorescent tubes are crushed and the materials are separated into glass, metal and fluorescent powders; a distillation process is additionally applied on fluorescent powders in order to extract the mercury fraction [10]. The amount of glass recovered, corresponding to the 80 % of the total

weight of the recovered lamps, is approximately 1,500 ton/year and it is classified as a non hazardous waste (code: EWC 19 12 05). Thus, it became evident the big opportunity, for several industries (operating in different sectors), to exploit that waste as a secondary raw material [10].

In an industrial perspective, where huge amounts of materials are produced, a potential mix of the fluorescent lamps with others waste glasses can be proposed. As an example, the waste glasses fraction derived from discarded glass bottles can be interesting for their chemical composition and they are estimated in 160,000 ton/year (excluding those addressed to the glassware industry). From an environmental legislation point of view this is possible since after reclaim processes they become non-dangerous residues. However, a deeper knowledge of both chemical nature and thermal properties of the mixed glasses is necessary in order to evaluate its effective reliability, which, in all likelihood will however need to be evaluated on a case to case basis.
The production of egg shells, mainly derived from the food industries, is estimated in Italy to be approximately 250,000 t per year [11]. The amounts of the generated waste, as well as the cost associated to the waste disposal, have encouraged the community to find alternative solutions for their recycling (in an improved economical and environmental perspective). Basically, egg shell is potentially a valuable material for numerous branches of the industry, but one of the most important aspects is related to the fact that it is considered one of the best natural sources of calcium carbonate ($CaCO_3$). Thus, its use in this framework can significantly reduce the environmental impact caused by the strong decreasing of the limestone reserves, which represent a non- renewable natural source. The present work exactly focuses on this key perspective.

This study is focused on the design of low environmental impact glass foams. Generally, in the glass foams design perspective several factors can be considered to

tailor materials with ad hoc properties, as previously discussed. Then, the study of the role of each factor on the final properties of these materials becomes fundamental.

To this reason, Design of Experiments (DoE) is used in this study to investigate how the type of foaming agent, the foaming temperature and the holding time influence the density and the compressive strength of the obtained foam glasses.

Glass cullet coming from EOL fluorescent lamps treatment has been used as glassy matrix, considering the composition of this glass, which makes it a good candidate to obtain manufactures at relative low temperatures. Egg shells, separately collected as waste from alimentary local industry, have been selected as foaming agent because they are constituted by 95 wt% of $CaCO_3$, in turn known to produce, by decomposition, CO_2 gas as pore former. The use of egg shells represents an important economic advantage, since the costs of glass foams are also affected by the type of the used foaming agents [3].

It s worth noting that the glass foams obtained in this work, show physical and mechanical properties comparable to commercial products opening to possible environmentally sustainable technological applications

2. Experimental procedure

2.1 Materials and method

For this study, FLs glass cullet coming from three representative treatment plants located in the North of Italy have been mixed together and finely ground in an alumina jar for 30 minutes in order to prepare the glass matrix. Subsequently, 5 wt% of foaming agent in the form of calcium carbonate or egg shells has been added to the glass powder and pellets (diameter of 40 mm and thickness of 5 mm) of raw materials have been prepared by uniaxial pressing (40MPa). The amount of foaming agent has been chosen considering the results reported in previous works [1, 12-14]. The obtained green

samples have been dried at 110°C overnight, thereafter a heat treatment at 700-800°C in air for 14-45 minutes has been applied, in order to obtain the foam glasses. The experiments have been performed according the Run Order reported in Table 1.

The pellets have been inserted in furnace directly at the foaming temperature, considering previous studies in which a fast heating is suggested to promote a finer microstructure [13].

The mean particle size of the glass powder has been determined by light scattering technique (Fraunhofer optical model, Malvern, Mastersizer 2000). The chemical composition of the glass has been obtained by X-Ray fluorescence (XRF, Thermo ARL ADVANT' XP+) and inductively coupled plasma (ICP) analysis. The X-Ray powder diffraction analysis (XRD) has been performed by using a powder diffractometer (PW 3710, Philips) in the 5-80° 2θ range to confirm the vitreous nature of the sample. The thermal behavior of the glass has been analyzed by Differential Thermal Analysis (DSC 404, Netzsch) and Hot-Stage Microscope (HSM) (Model Misura, Expert System Solutions, Modena, Italy). For all the experimental characterization the glass has been milled in a mortar to a fine powder (< 38 μm). Particularly, for the HSM analysis the glass powder has been compacted to obtain small cylinders (1 mm of diameter and 3 mm of height) by uniaxial pressing and subjected to a heat treatment from 20°C to 1400°C with a heating rate of 20°C/min. Moreover, the viscosity–temperature curve of the glass has been obtained by using the Vogel-Fulcher-Tamman (VFT) [15, 16, 17] equation (eq. 1) considering three characteristic points: sintering ($\log \eta = 10$) and softening ($\log \eta = 6$) from the hot stage microscopy and the glass transition point ($\log \eta = 13$) determined from the differential thermal analysis.

$$\log \eta = A + B / (T-T_0) \qquad \text{eq. 1}$$

where A, B and T_0 are the constant parameters of equation.

The calcite and waste egg shells foaming agents have been both characterized in a previous work [18]. Only the grain size distribution, after a grinding process of 5 minutes, and the thermal analysis has been conducted in this work to complete the characterization of the foaming agents. The granulometry of both powders have been measured by using the light scattering technique while the thermal analysis has been performed through TG/DTA (Netzsch STA 409) with a heating rate of 20°C/min, in order to evaluate the temperature at which the gas-generation occurs.

The obtained glass foams have been characterized by means of apparent density (ρ_a) absolute density (ρ_{as}) and compressive strength. In detail, ρ_a has been estimated by an envelope density analyzer (GeoPyc 1360, Micromeritics) using a dry-flow medium; while ρ_{as} has been determined by gas (He) pycnometer (AccyPy1330, Micromeritic). Samples "ad hoc" have been prepared for the tests: cube pieces (1x1x1cm^3) for ρ_a and powders (≈ 10 gr) below 26 μm for ρ_{as} [19]. The collected data correspond to the average of 5 samples.

Small blocks of about 10 mm x 10 mm x 8 mm have been cut from larger samples and used for compressive testing (by means of Instron 1121 UTS, Instron, Danvers, MA) with a cross-head speed of 1 mm/min. Each data point represents the average of 5 to 10 individual tests.

The measured data have been analyzed using a statistical approach in order to evaluate all their possible correlations with the input factors (or experimental conditions).

The glass foams presenting lowest density and the best compressive strength have been analyzed by scanning electron microscopy (SEM) and X-Ray diffraction in order to give detailed information on their microstructure strictly related to the final properties.

Finally, the porosity (P) in the foam volume has been calculated from the apparent and absolute densities according to eq. 2:

$$P_{total}\ (\%) = (1 - (\rho_a/\rho_{as}))\ 100 \qquad \text{eq. 2}$$

2.2 Experimental design

In the present work an organized approach has been pursued in order to develop glass foams through the reuse of EOL fluorescent lamps glass and egg shells as alternative foaming agent. The study has been planned using the Design of Experiment (DoE) method; particularly, a 2^k full factorial design has been applied. Three different input factors: temperature, holding time and type of the foaming agent have been varied during the experimental work and their effect on both ρ_a and compressive strength of the foam glass have been investigated. Particularly, the temperature has been varied between 700°C and 800°C, based on the thermal properties of the raw materials but also considering the results obtained from the preliminary tests, which indicated 800°C as the maximum temperature to avoid the uncontrolled swelling of the pores and thus the collapse of the foam structure. The time has been changed between 15 and 45 minutes considering the well-defined dependence of the two studied properties on the duration of the heat treatment [1, 13]. Finally, two types of foaming agents (calcium carbonate or egg shells) have been chosen with the aim to explore the possibility to replace the conventional foaming agent (calcium carbonate) with an alternative one (egg shells) already tested in a different system [18, 20]

The experiments conducted in this work included center point and their replications, as reported in Table 1. The data obtained for apparent density (ρ_a) and mechanical strength have been analyzed using the Analysis of Variance (ANOVA) [21, 22].

3. Results

3.1 Chemical and mineralogical analyses

The chemical and mineralogical analyses have been performed on the glass material. The XRD pattern (not here shown) presents a broad band (20-40° 2θ) typical of

amorphous material. The XRF chemical analysis reported in Table 2 reveals the soda-lime nature of the glass and the abundant presence of alkali oxides with respect to alkaline-earth ones underlines its stability toward crystallization.

The low concentration of both PbO and BaO (confirmed by the most accurate ICP-AES atomic emission spectroscopy technique and added in the Table 2) in the glass is seen as a favorable sign for glass foams with limited hazardousness. The chemical stability is supported by the same processing strategy: in fact, the low temperatures associated to the use of a calcite-containing waste, and the absence of reducing agents (SiC or TiN) decrease the risk of heavy metals reduction upon the foaming process of EOL fluorescent lamp glass.

The chemical resistance of the glass has been effectively verified, applying leaching tests in water for 1 day, accordingly to EN 12457 regulation (European norm EN 12457 ‘‘Characterisation of waste-Leaching-Compliance test for leaching of granular waste materials and sludges”). As reported in Table 2, the leachable metals in the test solution, determined by ICP-AES, fall within limit values set by regulation for non-dangerous waste; only Sb is actually above the limits for inert materials, to be disposed in landfills without any recommendation.

Our approach has some analogies with that applied in the literature [1] to heavy metal containing glasses such as those from dismantled Cathode Ray Tubes (CRTs). Panel glass (a barium–strontium glass) and mixtures of panel glass and funnel and neck glasses (these last belonging to lead silicate glasses family with a PbO content around 20 -50 wt%, respectively), have been successfully foamed by addition of $CaCO_3$ and firing at low temperature. Some preliminary chemical tests (acid attack) demonstrated that the heavy metal release of the foams was negligible and, above all, independent on the chemical formulation (ratio of panel/-lead-rich glass) of the glass cullet employed. Therefore, the foaming of CRT glasses by $CaCO_3$ thermal decomposition appears to be

a promising way of treating heavy metal containing glasses, since foaming does not depend on oxidation/reduction processes, which could cause the precipitation of metallic colloids by reduction of easily reducible oxides like PbO.

3.2 Particle size analysis

As mentioned above the granulometry of the materials involved in the glass foams production, covers an important role [12], indeed it is well known that similar particle size distribution of the raw materials promotes homogeneous microstructure of the foam glasses [1, 23].

In Figure 1, the cumulative and frequency curves of glass size particles, after the grinding process, are illustrated. From the cumulative curve, the percentage of particles below or above a defined value as well as the amount of materials between two values can be obtained, while from the frequency one the range of particle size can be evaluated. The cumulative curve shows that the glass powder is constituted by particles with size less than 100 µm and from this curve the D10, D50 and D100 values have been obtained (Table 3). The frequency curve exhibits a bimodal distribution, with two peaks at 5 µm and 21 µm and with the 100% of the total distribution below 120 µm.

The particles size distributions of $CaCO_3$ and egg shells are similar to the glass one.

In Table 4, the particle size of all the materials involved in the glass foams production is reported.

3.3 Differential thermal analysis (DTA) and termogravimetric analysis (TG)

The TG/DTA analysis (not reported) has been performed for both glass matrix and egg shells. In the first case the analysis allowed to determine the glass transition temperature (T_g) of the glass which approximately resulted 520°C, and this value has been used to draw the viscosity-temperature curve, as previously reported. For the egg shells it has

been possible to analyse the temperature at which the material starts to release the gas necessary for the foaming process. The results show a strong weight loss between 700-850°C, which is the temperature range chosen for the construction of the experimental plan.

3.4 Hot stage microscope (HSM)

The viscosity and the selected foaming temperature are directly correlated, and the last one should be chosen considering the maximum foam stability, which is controlled by viscosity [24].

Figure 2 shows the hot stage microscopy (HSM) results. HSM analyzes the behaviour of the glass during the thermal process, allowing the estimation of the characteristic temperatures in terms of sintering (the grains sintering starts), softening (the sample is plastic), sphere (the sample still posses a surface tension which contrasts the gravity force) and hemisphere (the glassy material collapses) at which a certain viscosity is associated. In Figure 3, the viscosity-temperature curve is illustrated.

The melting temperature is around 1050°C as expected, due to the high alkali oxide content (detected from the chemical analysis) which makes it a low melting glass. For the foaming process the relation between the temperatures measured by HSM and corresponding viscosities permits to identify the optimal range for the heating treatments [25]. Important information derive by the sintering (682°C) and the softening (826°C) temperatures considering that in this work, the foaming process is induced by the thermal decomposition of the foaming agents. Different studies reported in literature demonstrated that the optimum foaming point is attributed to the temperature at which the foaming agent evolves gas while the glassy phase has a viscosity between 10^6-10^7 Pa s (between the sintering and softening point).

For this reason, considering that the decomposition temperatures of $CaCO_3$ and egg shells are approximately comprised between 600-700°C and 700-850°C respectively, and the softening point of the glass is ≈ 826°C the temperature range has been chosen between 700-800°C. 800°C has been selected as the maximum temperature also considering the results of preliminary tests at 850°C for 10 minutes which reveals an uncontrollable foaming behavior.

3.5 Design of Experiments (DoE) analysis

The analysed data are reported in Table 4. The results of the ANOVA analysis for the apparent density (ρ_a) and the compressive strength are illustrated in Tables 6 and 7. The *F-values* related to the regression model significance test are higher than one with p-values approaching to zero. This means that the linear models are statistically significant in a confidence interval of 95%. The *lack of fit* tests show low F-values and p-values higher than 0.05, in both the cases, suggesting that the variance related to the model error and the variance associated to the replicate one, are close to each others and there is not lack of fit related to the pure error. By default the analysis separates the curvature effect from that caused by lack of fit and for both the properties a significant curvature has been observed. However, the overall results obtained through the ANOVA analysis, also in term of model parameters (Table 5), suggest that the linear models can be confidently used to describe the relationships between the selected input factors and the foam glass properties, even if curvatures in the data were observed, thus suggesting the need of more complex model to ensure an appropriate prediction, which is however far from the main screening objective of the present work.

The central point is not of particular interest in this study considering that the same ρ_a value associated to better mechanical properties can be obtained by selecting a different experimental region.

The residuals are normally distributed (not reported) and for this reason it is possible to move towards the model interpretation (coefficient analysis) reported in Table 6. The analysis of the ρ_a data reveals that temperature, time and the interaction factor (time x temperature) are significant, while the type of foaming agent does not produce any variation. In detail, an increase of the temperature (maintaining the time constant, or viceversa) produces a decrease of the ρ_a value. The effect of the interaction factor on the studied density can be instead easily described through the plot illustrated in Figure 4. Particularly, a strong variation in ρ_a can be observed working at 700°C but changing the time from 15 to 45 minutes, while using a temperature of 800°C the ρ_a value is less affected by the time change. The highest value of the ρ_a is reached at 700°C for 15 minutes while the lower one can be obtained working at 700°C for 45 minutes and at 800°C for 45 or 15 minutes. The coefficients analysis for the compression strength suggests that temperature and time contribute to a change in the final ρ_a of the foam glass and an increase of these two factors decreases the mechanical properties. Particular mention need to be devoted to the non significant effect of the type of foaming agent (calcium carbonate and egg shells) which suggests that the introduction of a recovery material as foaming agent can be considered an alternative way to the natural one to obtain an entirely recycled material without any lost in the material performances.

4. Discussion

The control of the process parameters covers an important role in view of the obtaining glass foams with specific properties [12]. The DoE analysis has confirmed the significant role of the temperature and time for both the measured properties according to literature, moreover it was highlighted the influence of the interaction term (time x temperature) only for the apparent density response.

The variation of the final properties as a function of the process parameters can be explained as a function of the viscosity of the glass system or kinetic decomposition of the foaming agent [1, 13].

According to the literature, an optimum thermal treatment is realized when the foaming agent releases gas while the glassy phase has a viscosity between 10^6-10^7 Pa s, allowing the formation of a homogeneous porous structure [18]. In the present work, by increasing the temperature of the foaming process (and keeping constant the time) the ρ_a tends to decrease. Comparing the structure obtained at 800°C and 700°C with an holding time of 45 minutes (Figure 5), it is possible to observe that the foam glass obtained at higher temperature presents a inhomogeneous structure with pores of large dimensions and an increase of the number of channel connecting the pores.

The inhomogeneity can be attributed to the fact that at 800°C the viscosity of the glass is lower with respect to the viscosity at 700°C and close to the softening temperature (826°C, $\eta = 10^{5.3}$ Pa s), so that the gas expansion is hardly controllable [26]. The material treated at 700°C for 15 minutes shows a high ρ_a probably due to an incomplete decomposition of the foaming agents associated to a low viscosity of the glass matrix at this temperature, which does not promote the gas release, while at 800°C for 15 minutes the viscosity is enough to allow the pores formation. The same ρ_a trend is obtained by increasing the holding time and by keeping constant the temperature. The ρ_a tends to decrease due to the gas release, thus leading to the production of more or larger pores [1, 13, 14].

For a better explanation of the role of the process conditions on the ρ_a it is more interesting to consider and to discuss the effect of the interaction factor (temperature x time). Figure 6 illustrates that the variation of the ρ_a as a function of the time is stronger at 700°C with respect to 800°C. This behaviour can be associated to the fact that a heat treatment performed at 700°C for 15 minutes is not adequate to obtain completely

foamed samples. At this temperature the glass viscosity is close to $10^{7.1}$ Pa s, thus more time is required to induce a complete foaming process. At 800°C, an holding time of 15 minutes is enough to promote the pores formation but it is important to underline that the ρ_a values at 15 and 45 minutes are close to each other while the mechanical properties significantly decrease, suggesting that an increase of the holding time produces the coalescence of the existing pores producing larger ones as previously mentioned.

The compressive strength of the obtained foam glass materials decreases, increasing both the holding time and temperature (Figure 7). This trend can be associated to the formation of pores and lightweight materials but also to a coalescence of pores as previously discussed.

The samples obtained at 700°C for 45 minutes and at 800°C for 15 minutes using egg shells as foaming agent have been characterized also in terms of porosity, scanning electron microscope (SEM) and X-Ray diffraction (XRD).

In Figure 8, it is possible to observe that the samples show a non completely homogeneous microstructure, where the larger pores are separated by walls containing other smaller pores (<100 μm). The porosity of the samples of interest is illustrated in Table 7. The porosity results can be discussed considering the compressive strength values since it is well known that the compressive strength depends on the structure and the density of the foam glass [27].

Indeed, the sample obtained at 700°C for 45 minutes presents higher values of porosity and compressive strength (*ca.* 2 MPa) with respect to that obtained at 800°C for 15 minutes (*ca.* 1 MPa). This result can be associated to the fact that the microstructure of the first sample is more homogeneous and the pores are smaller with respect to the sample obtained at 800°C for 15 minutes.

The X-Ray powder diffraction reveals that all the glass foamed are mainly vitreous and only some peaks related to calcium carbonate have been detected (the spectrum is not reported).

5. Conclusions

The results obtained and discussed in this paper lead to the following conclusions:

- Egg shells proved to be a good alternative to conventional additives for the production of glass foams; in particular, egg shells may replace $CaCO_3$ of mineral origin; this implies an advantage in both saving of natural resources and reusing of waste.
- EOL fluorescent lamp glass provides additional advantages, since it represents a form of inorganic waste and its characteristic temperatures are compatible with the foaming by decomposition of $CaCO_3$, of mineral or natural (egg shell) origin; the foaming occurs at temperatures (700-800°C) well below those employed for commercial glass foams from oxidation of C-containing compounds in common soda-lime glass;
- The foaming temperature/foaming time combinations have been studied with a DoE approach; optimized combinations (e.g. 700°C for 45 min) led to foams with a good microstructural homogeneity and a compressive strength (ca. 2 MPa, with an apparent density of ca. 0.4 g cm^{-3}) comparable to that of commercial foams.

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Figure captions

Figure 1. Cumulative and frequency curves of glass powder after grinding process

Figure 2. Hot stage microscope (HSM) images of the EOL fluorescent glass cullet

Figure 3. Viscosity versus temperature for the EOL fluorescent glass cullet

Figure 4. Effect of the interaction term (time x temperature) on the apparent density (ρ_a)

Figure 5. Glass foams obtained using egg shells as foaming agents at a) 700°C 45 minutes, b) 800°C 45 minutes and c) 800°C 15 minutes

Figure 6. 3D Contour plot of the interaction term (time x temperature) for the apparent density (ρ_a)

Figure 7. 3D Contour plot for compression strength

Figure 8. SEM micrographs of the samples foamed with egg shells and heat treated at a) 700°C for 45 minutes and b) 800°C for 15 minutes

Tables

Table 1. Experimental design

Table 2. Mean chemical composition of the three glasses from EOL fluorescent lamps by XRF and ICP analyses

Table 3. Characteristic diameters of the used materials

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Table 6. Estimated coefficients

Table 7. Absolute density (ρ_a) and Total Porosity (%) of the egg-shells containing glass foams

Table 1. Experimental design

Run Order	Temperature (°C)	Time (minutes)	Type of foaming agent
1	800	45	egg shells
2	750	30	$CaCO_3$
3	700	45	egg shells
4	750	30	$CaCO_3$
5	750	30	egg shells
6	750	30	$CaCO_3$
7	700	45	egg shells
8	800	15	egg shells
9	700	45	$CaCO_3$
10	800	45	egg shells
11	750	30	egg shells
12	700	45	$CaCO_3$
13	700	15	$CaCO_3$
14	700	15	egg shells
15	700	15	egg shells
16	800	45	$CaCO_3$
17	700	15	$CaCO_3$
18	800	45	$CaCO_3$
19	800	15	$CaCO_3$
20	800	15	$CaCO_3$
21	800	15	egg shells
22	750	30	egg shells

Table 2. Mean chemical composition of the three glasses from EOL fluorescent lamps by XRF and ICP analyses

Oxide	wt%
SiO_2	67.90
Na_2O	17.50
CaO	5.09
MgO	2.96
Al_2O_3	2.26
K_2O	1.60
BaO	0.94 (0.95*)
PbO	0.78 (0.78*)
Fe_2O_3	0.08
Sb_2O_3	0.08
SrO	0.07
TiO_2, SO_3, P_2O_5 et al.	0.74

XRF error ± 0.1 wt%; ICP error ± 0.05 wt%

Table 3. Characteristic diameters of the used materials

	Glass mix (μm)	$CaCO_3$ (μm)	Egg shells (μm)
D10	1.9	1.3	3
D50	9	5	13
D90	40	26	50
D100	120	84	320

Table 4. Analyzed data

RUN	Apparent density (g cm^{-3})	Compressive strength (MPa)
1	0.37	0.29
2	0.39	0.94
3	0.38	2.07
4	0.4	1.1
5	0.43	1.16
6	0.38	1.04
7	0.31	2.13
8	0.43	0.99
9	0.5	2.77
10	0.29	0.3
11	0.48	0.94
12	0.37	2.69
13	2.2	13.02
14	2.36	8.29
15	2.08	11.03
16	0.24	0.14
17	1.8	10.04
18	0.25	0.35
19	0.38	1.55
20	0.45	1.53
21	0.31	1.04
22	0.42	0.95

Table 5. Analysis of variance (ANOVA) results

	Sum of Squares	Mean Square	F-Value	p-value
Apparent density (g/cm^3)				
Model	9.25125	3.08375	243.5105	< 0.0001
Curvature	0.624594	0.624594	49.3215	< 0.0001
Residual	0.215283	0.012664		
Lack of Fit	0.070017	0.014003	1.156769	0.3843
	R-Squared	Adj R-Squared	Pred R-Squared	
	0.98	0.97	0.96	
Compressive strength (MPa)				
Model	5.638198	2.819099	327.8934	< 0.0001
Curvature	0.22824	0.22824	26.54696	< 0.0001
Residual	0.154757	0.008598		
Lack of Fit	0.066347	0.011058	1.500876	0.2584
	R-Squared	Adj R-Squared	Pred R-Squared	
	0.97	0.97	0.96	

Table 6. Estimated coefficients

	Estimated coefficient	95% CI Low	95% CI High
Apparent density (g/cm^3)			
Factor			
Intercept	0.795	0.735644	0.854356
A-Temperature	-0.455	-0.51436	-0.39564
B-Time	-0.45625	-0.51561	-0.39689
AB	0.40375	0.344394	0.463106
Center Point	-0.37833	-0.49199	-0.26468
Compressive strength (MPa)			
Factor			
Intercept	0.236514	0.187812	0.285215
A-Temperature	-0.48434	-0.53304	-0.43564
B-Time	-0.34323	-0.39193	-0.29453
Center Point	-0.2287	-0.32196	-0.13545

Table 7. Absolute density (ρ_{as}) and Total Porosity (%) of the egg-shells containing glass foams

T (°C)	time (minutes)	Absolute density (g/cm^3)	Porosity (%)
700	45	2.44	87.3
800	15	2.46	81.7

Figure 1

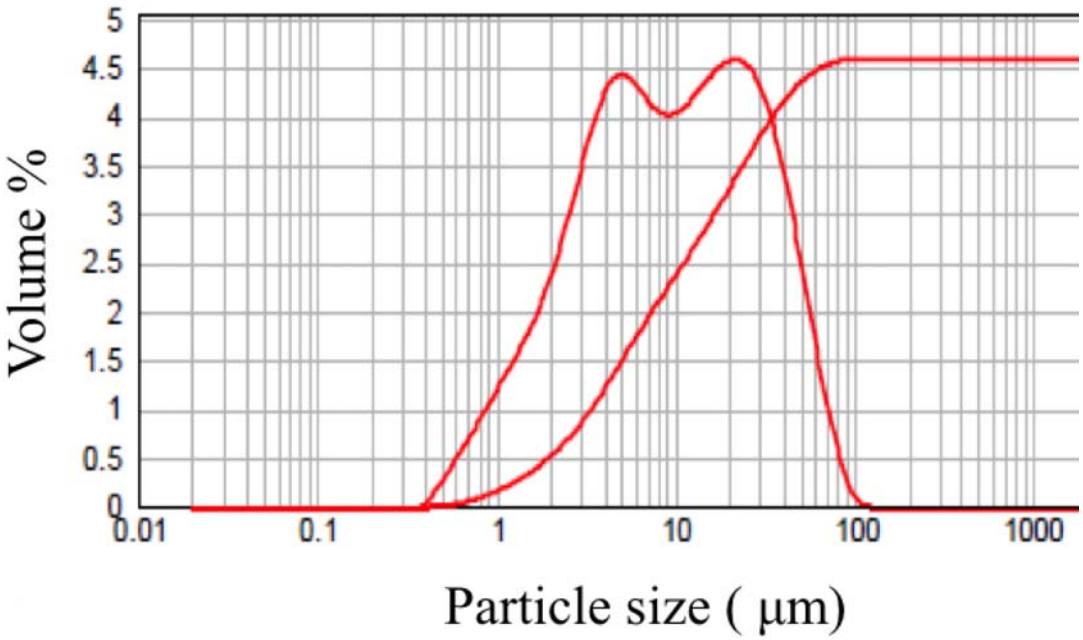


Figure 2

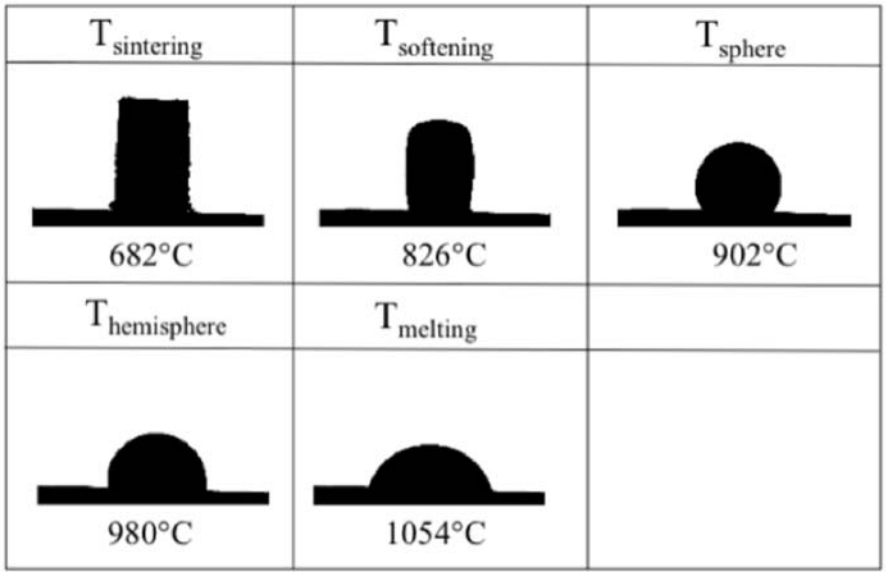
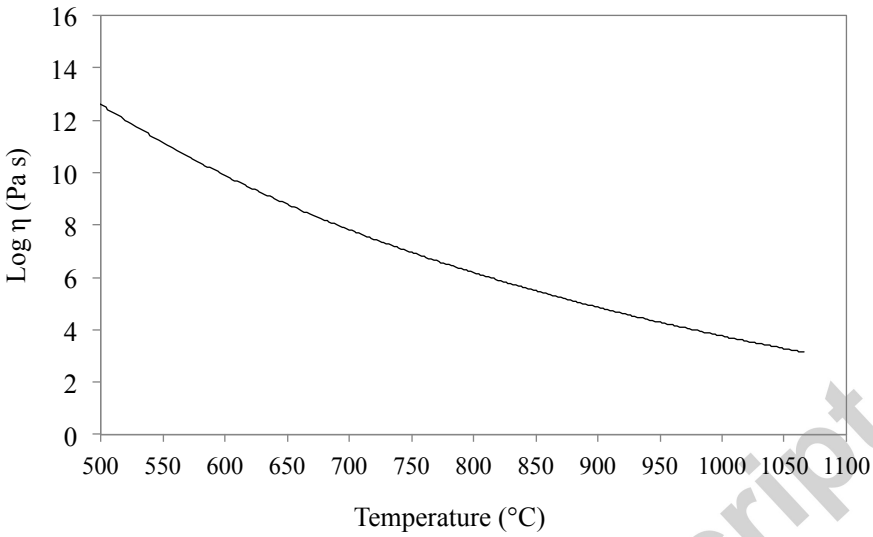


Figure 3



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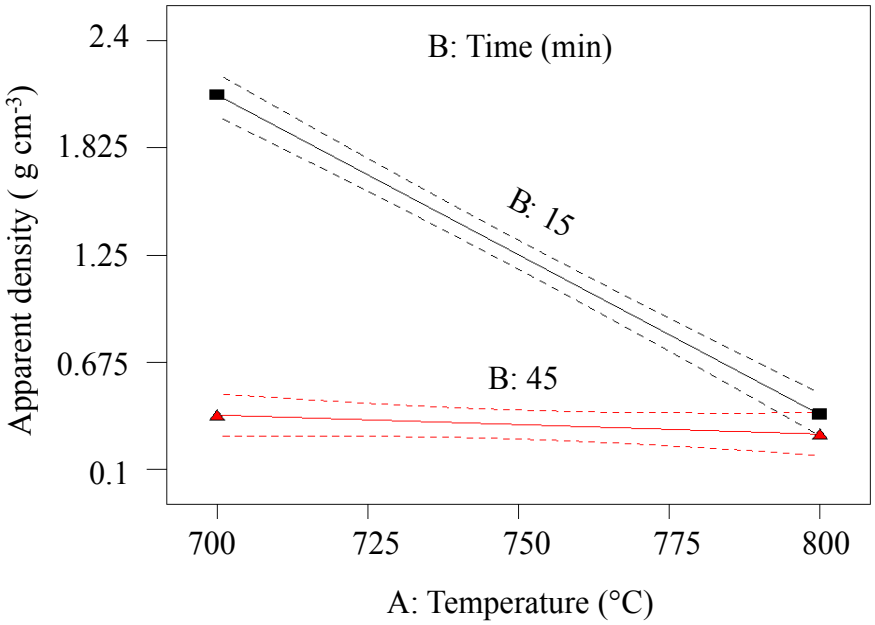

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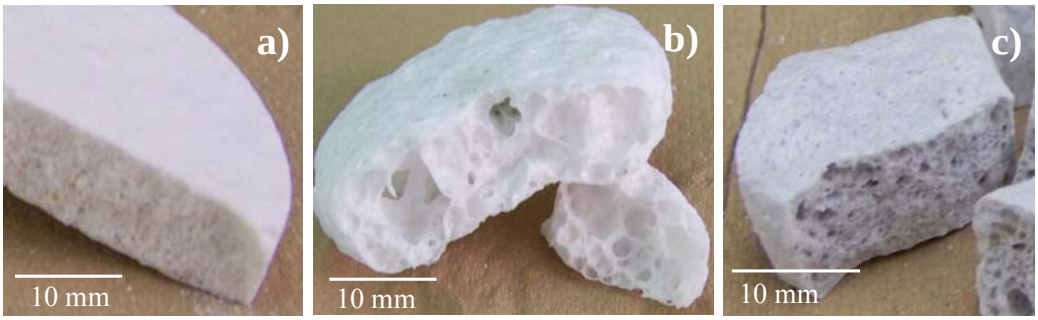

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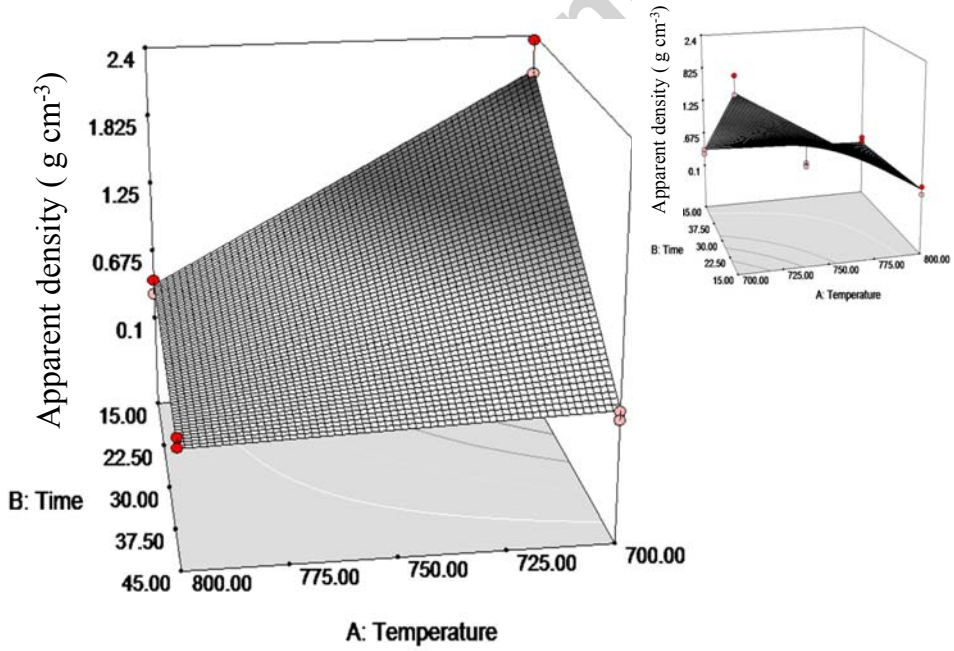

Figure 7

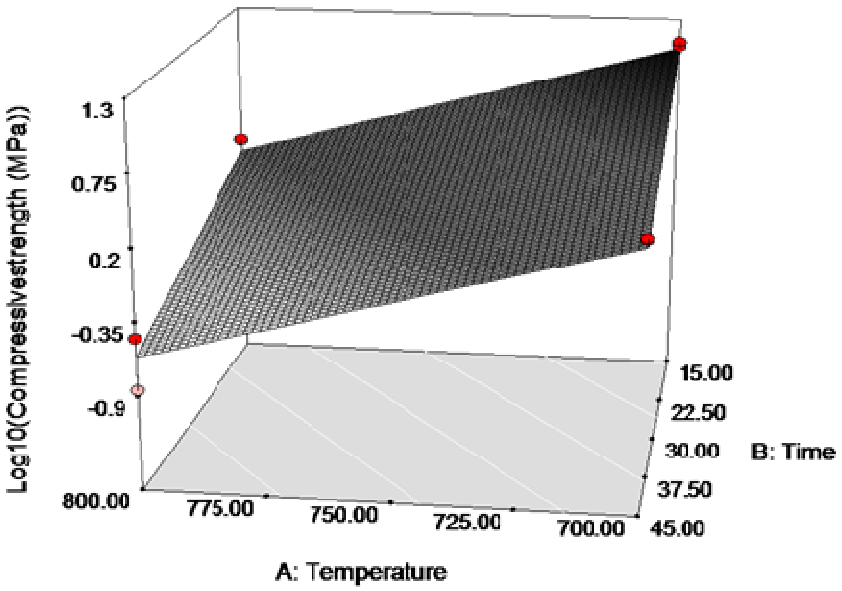

Figure 8