

COMPARATIVE ANALYSIS OF CELLULAR GLASS TYPES MADE BY THE NON-CONVENTIONAL TECHNIQUE OF MICROWAVE HEATING-A REVIEW

Lucian Paunescu¹, Sorin Mircea Axinte^{2,3} and Enikö Volceanov^{4,5}

¹ Daily Sourcing & Research SRL Bucharest, Romania, lucianpaunescu16@gmail.com

² National University of Science and Technology POLITEHNICA, Faculty of Applied Chemistry and Materials Science, Bucharest, Romania, sorinaxinte@yahoo.com

³ Daily Sourcing & Research SRL Bucharest, Romania, sorinaxinte@yahoo.com

⁴ National University of Science and Technology POLITEHNICA, Faculty of Engineering in Foreign Language, Bucharest, Romania, evolceanov@yahoo.com

⁵ Metallurgical Research Institute SA, Bucharest, Romania, evolceanov@yahoo.com

ABSTRACT: The comparative analysis of the cellular glass products manufactured by the non-conventional microwave heating method compared to those made on a large scale by conventional methods is presented in this paper. Applying the non-conventional method was carried out in recent years by authors of the current article. Four different testing versions were selected by the composition of the material mixture including the expanding agent as well as the operational parameters. SiC, CaCO₃, and Si₃N₄ separately constituted the expanding agents used in the analyzed experiments. Also, fly ash, red iron oxide, borax, and MnO₂ were other additional materials included into the mixture, also separately. The specific energy consumption of producing processes were very low under the conditions of using a microwave equipment at very small-scale (0.8 kW), there being the possibility of improving this parameter by up to 25 % by applying the method on an industrial-scale.

KEYWORDS: cellular glass, non-conventional heating, silicon carbide, calcium carbonate, energy efficiency.

1. INTRODUCTION

Numerous unique combinations of physical, thermal, chemical, mechanical properties are included in the new cellular bottles made from recycled residual glass with the contribution of expanding agents. The thermal input, usually conventional, is required for the development of chemical processes forming gas, that occur at elevated temperatures (750-1150 °C) and that generate numerous bubbles trapped in the bottle mass with lowered viscosity. The paternal residual glass transfers to the new cellular product durability, mechanical strength, resistance to fire, water, chemical or biological aggression, resistance to freeze-thaw cycle, etc. [1].

Producing the cellular bottle was started in the middle of the 20th century (in the USA and France) both by directly blowing some fluids (such as air, carbon dioxide, steam) into the molten glass mass, as well as by sintering the ground raw material, represented at the beginning by the new glass. In the mid-to-late of the 20th century, it was found that recycled residual bottle from consumed container bottle, window glass from the construction wrecking, etc. is suitable for the production of cellular glass. Also, thermal sintering methods have become a priority over the fluid injection into the molten glass mass [1].

Cellular glass allows light constructions, low transport costs, easy handling, and readily

combination with concrete. Its application areas are mainly in construction (for insulation of walls, roofs, floors, and ceilings) as well as in various other domains as alternative to mineral wool, expanded polystyrene, extruded polystyrene, polyurethane [2].

In general, the transformation of a residual glass powder into a cellular glass can be achieved by releasing a gaseous product through thermal decomposing or chemical reacting (mostly oxidation) at higher thermal level of the decreasing point of the glass viscosity in the range of 10⁵-10³ Pa·s [1].

The expanding agents that are suitable for their thermal decomposition in the case of cellular glass production are carbonates (CaCO₃ and Na₂CO₃). Both salts release CO₂, while calcium oxide and sodium oxide, respectively, enter the composition of molten glass. The two mentioned agents have different effects, CaCO₃ causing the maximum expansion of over 450 % using only 2 % agent, while Na₂CO₃ ensures the maximum expansion of 90 % for 5 % agent [3].

The expansion of the glass powder by reaction usually takes place through the oxidation of the carbon-based expanding agent such as carbon, silicon carbide, starch, sugar or organic waste. The O₂ required for oxidizing process in the form of atmospheric air exists into free interspaces betwixt fine solid grains. Foaming gases are CO₂/CO

mixture. The carbon types utilized as pore-forming agent are: coke, graphite, anthracite, and carbon black. Supplementary to oxidizing carbon in the oven environment, other reacting of this with glass components (H_2O , alkali, and sulfates) can contribute to the supply of gaseous products for the expansion process.

Several alternative processes and cellular products are known as innovations in cellular glass production. Froths from metal evaporating, high-silica froths from phase-separation bottles, bottle froth from silica gel, high-denseness bottle froth, partly crystallized bottle froth, and microwave heating for sintering/expanding are mentioned in the literature [1].

In this paper, we will review several experimental processes for making cellular bottle by the unconventional method of heating with electromagnetic waves. The main argument for making cellular glass using this innovative method is the excellent energy effectiveness than the traditional methods.

Theoretically, the suitability of residual glass for microwave heating is minimal because the high weight proportion of silica (SiO_2), is not susceptible to electromagnetic waves. According to [4], this glass behaviour corresponds to room temperature. By increasing the temperature, the electrical conductivity of the glass also increases, so that at about 500 °C the silicate material becomes highly susceptible to microwaves. This theory issued in 1997 was obviously unfavourable to the industrial application of microwave heating of glass waste, because a conventional heating would be required in the temperature area below 500 °C of the oven and unconventional one above this temperature up to the final process. Knox and Copley's theory [4] has definitely changed the future position of manufacturers and researchers on the eventual utilizing microwaves in the bottle froth production [1, 5]. However, it has been practically proven that certain contaminants of bottle (such as Fe_2O_3 , Cr_2O_3), even in very low proportions, have the ability to significantly increase the wave susceptibility of bottle at ambient thermal conditions and the heating process has a continuous character [6].

Starting from this experimental discovery, the research team from the Daily Sourcing & Research society (Romania) has developed in the following period a testing program for producing porous bottle using microwave radiation.

According to [5], cellular bottle making technologies are currently industrially used in Europe, the USA, and China. These technologies operate using traditional warming methods. The microwaves as a source of rapid, ecological, and economic warming process are not used in the world on satisfactory level. The main industrial utilizations are limited to drying and increase in temperature methods for solid materials only at reduced thermal level. At the beginning of the 3rd millennium, it has been discovered that many material types (such as ceramics, organics, polymers, glass, sol-gel, metals, and composites) are suitable for the electromagnetic wave heating [7]. The condition for a material to absorb the radiation of these waves is for it to have microwave susceptibility, i.e. to be a so-called dielectric. Having few charge carriers, dielectrics absorb microwave power, which is converted into heat [8].

In contradiction to the traditional warming, the electromagnetic wave heating is a completely different process developed in the opposite direction. Thus, starting the heating takes place into the core of the dielectric mass through the contact of the wave flow with the surface of the target material. Through the conversion of microwave power, a high thermal energy center is formed in this area, which volumetrically propagates from inside to the exterior, that is the opposite of known heating type. Thus, the process is faster and more efficient, while massive materials that compose the oven no longer need to be heated to favour the heating of the target material. The process selectivity is a unique feature emphasizing its effectiveness [8, 9].

Considering the possibility of heating the glass powder with maximum efficiency starting from room temperature, discovered by the team of Romanian researchers [6], recently, several experimental manufacturing processes of cellular glass using the energy effect of microwave radiation have been tested.

2. THE-STATE-OF-THE-ART OF PREPARING CELLULAR GLASS BY CONVENTIONAL HEATING TECHNIQUE

In conformity with the literature, utilizing SiC as an expanding agent in traditional making techniques of cellular glass is a usual method. If recycled residual glass is the basic raw material, usually at least 90 % residue from consumed packaging bottle and the rest under 10 % flat glass waste from building demolition constitute the appropriate mixture. Practically, it was found that a weight proportion of over 10 % flat glass waste tends to generate the

structural inhomogeneity of cellular glass. According to [10], Geocell Schaumglas GmbH, one of the main world producers of cellular bottle gravel applies this recipe for the reason mentioned above.

Another use of SiC for manufacturing cellular glass-ceramic consists in substituting about 20 % of the dosage of post-consumer container glass with the by-product coal fly ash from the energy industry. By conventional heating the powder mixture at 1000-1050 °C, the optimal uniformity of the cellular glass microstructure was obtained as well as a compressive strength of 1.5 MPa, satisfactory for utilizing this product as a thermal insulation construction material [11].

A conventional method of producing cellular glass, very widespread both at the industrial level and in various small tests, is that of using calcium carbonate (CaCO_3) as an expanding agent. According to [1], a high mechanical processing by grinding of recycled residual glass (25-30 μm) allows obtaining the apparent density of 0.16 $\text{g}\cdot\text{cm}^{-3}$, heat conductance of 0.035 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (hence excellent heat-insulating properties), and compression resistance of 1.3 MPa. Also, it has been observed that this expanding agent has the ability to produce finer microstructures, although less homogeneous compared to those obtained with SiC.

The cellular glass production technique using 99 % glass waste recovered from the glass industry, 1 % CaCO_3 and 8 % water was tested by [12]. The mixture was pressed at 40 MPa and subjected to sintering by conventional heating at 850 °C, with medium warming rate of 10 °C/min. The porous material had porosity of 85.1 %, heat conductance within the limits of 0.031-0.050 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and compression resistance in the range of 0.7-1.3 MPa.

A method that partly replaces residual bottle with coal fly ash (40 %), based on CaCO_3 (0.5 %) as pore-supplier product and adding borax (30 %) as a flux agent to the mixture was tested by [13]. The result of the involvement of fly ash as well as borax was obtaining a cellular glass-ceramic characterized by significantly higher compression strength (over 5 MPa), density of 0.46 $\text{g}\cdot\text{cm}^{-3}$, and thermal conductance of 0.36 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

Less used on an industrial scale, but considered an extremely effective pore-forming agent for making the cellular glass is silicon nitride (Si_3N_4). A powder mixture consisting of recycled residual glass, Si_3N_4 , and manganese dioxide (MnO_2) as an O_2 -supplier additional material was subjected to heating in an oxidizing environment at 800-850 °C into an oven with conventional heating, followed by a holding

time, which have generated the material expansion [14]. The obtained microstructure was inhomogeneous with coalescence cells. For this reason, the authors of this paper prepared the same mixture by pressing in the form of pellets and the heat treatment was similar, significantly reducing the coarse microstructure aspect of specimens and obtaining an increase in their mechanical strength.

According to the work [15], the association of expanding agents such as SiC, Si_3N_4 or AlN with metal oxides (such as MnO_2 , Fe_2O_3 or CeO_2) can contribute to the intensification of oxidation-reduction processes and can form much more homogeneous microstructures, with an adequate correlation between physical, mechanical, and morphological features of expanded materials.

Performing the porous bottle type characterized by the homogeneous distribution of pores and high mechanical strength was presented in [16]. The preparing method included Fe_2O_3 and Co_3O_4 with the role of oxygen suppliers in the mix of materials, except for glass waste. The expanding agent adopted by the authors was SiC representing 4 %. The expanding procedure that facilitated the formation of the porous structure was achieved by conventional heating of the mixture at 850 °C for 1 hour.

Under the conditions of using 0.4 % Fe_2O_3 , the porosity of the product reached 90 % and the flexural strength was 0.75 MPa. Through the addition of 1.2 % Co_3O_4 , the porosity slightly decreased to 80 %, while the flexural strength significantly increased up to 6.82 MPa. It was found that the addition of Co_3O_4 contributes to the creation of a tighter pore size repartition than the effect of the Fe_2O_3 addition.

3. CELLULAR GLASS MADE BY UNCONVENTIONAL HEATING TECHNIQUE

3.1 Methods

The method of heating the mixture prepared for making porous glass utilizes the ability of the wave flow distributed through the waveguide placed in the oven sidewall to convert its power into heat through contact with the surface of the material microwave susceptible. Since previous tests performed by the paper's authors indicated that the usual container material (silica-soda-lime type) is not appropriate for the non-conventional heating process with powers of about 1 kW and accepted frequency causing destruction of the internal macrostructure of the foamed product, it was reached the conclusion of the need to reduce the effect intensity by placing a thin protection shield realized from materials highly wave receptive (silicon carbide and nitride in 80/20

ratio). Thus, cylindrical tube with thin wall (2.5 mm) procured from China was adopted, allowing preponderantly direct and partly indirect warming as a result of the partial absorbing the wave field into the tube wall mass and, respectively, of the wall penetration by majority of the field which directly touches the surface of the target material. The heating is simultaneously achieved in two ways: one predominantly direct (unconventional) and one partially through thermal radiation (conventional) of the intensely heated tube surface [17]. All subsequent experiments used this equipment to temper the microwave effect and the consequence in terms of energy was the significant increase in the heating speed, reducing the procedure time, and reducing the energy requirement.

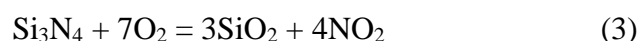
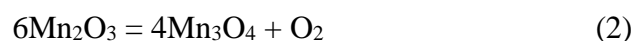
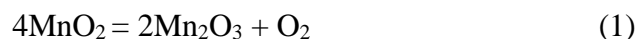
Four different versions of mixture composition were applied for preparing cellular glass through electromagnetic wave heating. In the first version [18], the fine ground glass waste (under 100 µm) was mixed with SiC as an expanding material and Fe₂O₃ as an O₂-supplying material. The required temperature of sintering/expanding process was 850 °C, at which SiC releases by oxidation carbon dioxide (CO₂) trapped as gas bubbles into the softened glass mass as well as SiO₂ that enters in the molten material composition.

The second preparing version of cellular bottle [19] is characterized by the addition to the ground glass-based raw material from post-consumer drinking bottles of at least 10 % flat glass waste from building demolition, 10 % coal ash, and 2.4 % silicon carbide as a foaming product. The process temperature (in the optimal version) increased to 975 °C compared to the first variant and the heating rate was 28.1 °C/min, considerably higher than conventional processes.

The third analyzed version [20] included colourless post-consumer drinking bottle, borax (2 %), CaCO₃ (between 1.0-1.6 %) as pore-forming product, and 8 % added water. The releasing method of CO₂ was based on the CaCO₃ decomposition in CO₂ and CaO. The sintering/expanding process temperature was lower (824-829 °C) compared to the process that use SiC, the heating speed being within the limits of 22.5-26.8 °C/min.

The last preparing version considered in this paper [21] contained a mix of colourless, green and amber consumed container bottle, Si₃N₄ (1.9-2.0 %) as an expanding agent, MnO₂ (between 1.7 -2.9 %) as an oxygen-supplier, and 13.5-14 % water as a binder. The required temperature was between 818-837 °C, the heating speed reaching also high values (23.3-28.5 °C/min). In chemical terms, the process

contains more stages. At 485 °C, decomposing MnO₂ into Mn₂O₃ and O₂ is beginning, and at 590 °C its intensity reaches at the highest value. Decomposing Mn₂O₃ starts at 650 °C and the maximum intensity is reached at 800 °C, eliminating Mn₃O₄ and O₂. Oxidizing Si₃N₄ utilizing previously oxygen released oxygen occurs within the limits of 800-900 °C eliminating NO₂ into the melt glass.



The experimental microwave equipment was shown in several article published in the literature. Also, the constructive and operational principle of the equipment was presented in previous works. Figure 1 shows the main details of the plant.

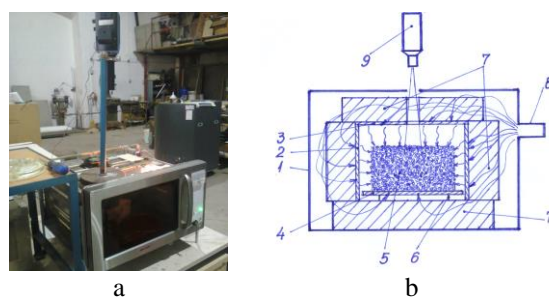


Figure 1 Testing microwave plant

a – wave oven; b – constructive and operational principle: 1 – furnace; 2 – cylindrical pipe; 3 – cover; 4 – metallic plate; 5 – warmed material; 6 – support; 7 – thermal protecting layer; 8 – waveguide; 9 – radiation pyrometer.

3.2 Materials

The utilized material during the test were: uncoloured, green, and brown consumed drinking bottle, clear window glass from building wrecking, fly ash, red iron oxide (Fe₂O₃), borax, manganese oxide (MnO₂), SiC, Si₃N₄, and CaCO₃.

The recycled residual bottle was the main raw material. The adopted processing methods included the following operations: cleaning, drying, shattering, crushing in a gristmill, and screening. These mechanical procedures were made at Bilmetal Industries Company from Popesti-Leordeni, Ilfov (Romania) and allowed reducing the maximum dimension limit of bottle particles to 63 µm. The chemical configuration of the four selected residual glass sorts is shown in Table 1.

Table 1. Chemical configuration of residual bottle (wt. %)

Chemical configuration	Uncoloured glass	Green glass	Brown glass	Window glass
SiO ₂	71.7	71.2	71.4	71.1
Al ₂ O ₃	1.9	1.8	1.9	1.3

CaO	12.0	10.2	10.3	9.3
Fe ₂ O ₃	0.03	0.4	0.3	0.2
MgO	1.0	2.2	2.3	3.9
Cr ₂ O ₃	0.02	0.2	0.1	-
Na ₂ O	13.3	13.0	13.2	14.2
K ₂ O	0.01	0.5	0.6	
SO ₃	0.04	0.3	0.3	-

Coal ash was offered by Paroseni-Thermal power plant (Romania) as a secondary product of energy producing industry having particle dimension under 250 µm and required its mechanical shredding in a mill to diminish the particle dimension under 100 µm. This by-product contained 51.4 % SiO₂, 26.5 % Al₂O₃, 1.5 % TiO₂, 4.8 % Fe₂O₃, 6.5 % CaO, 2.5 % MgO, 0.4 % Na₂O, 0.6 % K₂O, and 1.7 % SO₃. Fly ash has ability to favour the expanding process, ensuring good microstructural homogeneity of the foamed material, but significantly increases the process temperature.

Red iron oxide (Fe₂O₃) was commercially purchased in form of fine powder with particle size around 30 µm.

Borax as a flux agent was commercially purchased containing particle dimension below 400 µm being mechanical shredding for reducing this dimension below 80 µm.

MnO₂ as an oxygen-feeder was procured from the market being available at grain dimension smaller than 90 µm.

SiC was also commercially purchased, the product containing fine dimension of the grain less than 20 µm.

Silicon nitride (Si₃N₄) was the expanding agent chosen in the work [21]. The product is available as fine dust (under 10 µm), being adopted due to its remarkable effectiveness.

CaCO₃ used as an expanding agent in the work [20] is an available material in the market, having extremely fine particle size (below 6.3 µm).

3.3 Methods for determining the specimen features

The methods used in this work to determine the features of specimens are usual methods for this

objective. Apparent denseness was determined by the gravimetric procedure [22, 23] as well as by Archimedes' method (ASTM D792-20), while the porosity was identified by comparison procedure of apparent denseness and the "true" denseness [24]. The thermal conductance was determined applying the heat-flow technique (ASTM E1225-04) and the compression strength was measured with TA.XTplus Texture apparatus. The method of submerge specimens under water (ASTM D570) allowed the water-absorbing measurement and the use of Smartphone Digital Microscope ASONA 100X Zoom type was the method by which the microstructural aspect of specimens could be examined.

4. RESULTS AND DISCUSSION

4.1 Results

The feedstock used in the preparation of the four mixtures differed quite much both qualitatively and quantitatively.

The residual bottle types adopted in each experimental versions are shown in Table 2.

Table 2. Residual bottle types used in the experiment

Version	Consumed drinking bottle (%)			Window flat glass (%)
	Colourless	Green	Amber	
1	15	70	15	-
2	-	41.1	41.1	4.4
3	100	-	-	-
4	33.3	33.3	33.3	-

The weight proportion of all materials that constituted the starting mixtures (in the optimal version) are shown in Table 3. The operational framework recorded during the four testing sintering/expanding processes valid for each optimal version are presented in Table 4.

Table 3. Material configuration of the four versions (wt. %)

Version	Residual bottle	Fe ₂ O ₃	Fly ash	Borax	MnO ₂	SiC	CaCO ₃	Si ₃ N ₄	Added water
1	95.5	0.4	-	-	-	4.1	-	-	10.0
2	82.2	-	10.0	-	-	2.4	-	-	14.0
3	96.9	-	-	2.0	-	-	1.1	-	8.0
4	96.2	-	-	-	1.9	-	-	1.9	13.5

Table 4. Operational framework valid for each optimal version

Version	Sintering temperature (°C)	Warming time (min)	Warming rate (°C/min)	Specific energy requirement (kWh·kg ⁻¹)
1	850	30	27.7	0.69
2	975	34	28.1	0.74
3	825	31	26.0	0.67
4	823	29	27.7	0.63

By comparison with similar framework of conventional processes, the excellent energy effectiveness due to the use of electromagnetic waves in the warming process can be noted. Thus, the specific energy requirement values are within the limits of 0.63-0.74 kWh·kg⁻¹.

The literature provides too few data regarding the energy requirement of porous bottle making processes in the world. In accordance with the market study [5], the company Misapor (Switzerland) records a medium energy requirement of 100 kWh·m⁻³ (that is up to 0.83 kWh·kg⁻¹), to which 25 kWh·m⁻³ is added for shredding the feedstock. In the North American Pittsburgh Corning Co., the medium total energy requirement is 4.24 kWh·kg⁻¹, but it contains the residual glass

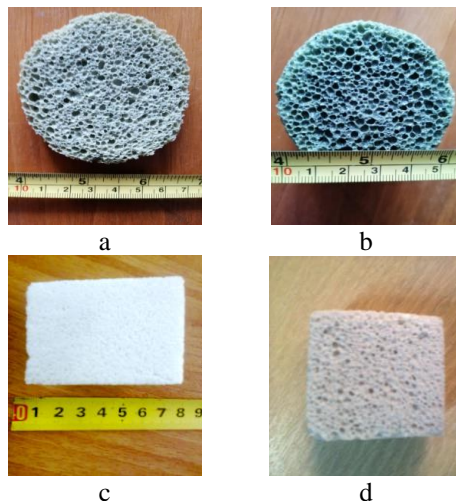
melting to correct its chemical configuration. According to [25], the medium consumption for making the cellular glass in the Geocell company is 140 kWh·m⁻³, that is about 0.7-0.8 kWh·kg⁻¹. According to [7], an industrial-scale microwave equipment can provide up to 25 % higher energy effectiveness than a small-scale equipment.

The optimal versions of the physio-mechanical, thermal, and morphological peculiarities of testing making processes of cellular glass by microwave radiation were compared. The values of these features are shown in Table 5.

Table 5. Physio-mechanical, thermal, and morphological peculiarities of porous bottle versions

Characteristic	Version 1	Version 2	Version 3	Version 4
Apparent denseness (g·cm ⁻³)	0.19	0.24	0.18	0.59
Porosity (%)	91.0	88.6	91.0	71.9
Thermal conductance (W·m ⁻¹ ·K ⁻¹)	0.049	0.060	0.042	0.097
Compression resistance (MPa)	1.48	1.27	2.6	6.6
Absorption of water (vol. %)	2.18	1.8	1.0	1.0
Pore dimension (mm)	0.3-1.2	0.4-1.3	0.10-0.25	0.1-0.4

The physical appearance of porous bottle samples, having the composition in Table 2 and operational frameworks in Table 4 is presented in Figure 2.

**Figure 2.** Physical appearance of porous bottle samples a – version 1; b – version 2; c – version 3; d – version 4.

According to the data in Table 5, all optimal versions obtained by fabrication the cellular glass under the effect of microwave radiation had excellent heat-insulating properties i.e. low values of apparent denseness and thermal conductance and high values of porosity. In the first two porous bottle variants, the compression resistance had relatively low values (1.48 respectively, 1.27 MPa), but satisfactory for thermal insulation material types intended for construction. By using borax in the mixture prepared in variant 3, the material strength increased to 2.6 MPa, without growing the apparent denseness and thermal conductance. On the contrary, values of the physio-thermal features

slightly decreased compared to those of variants 1 and 2, reaching $0.18 \text{ g}\cdot\text{cm}^{-3}$ and $0.042 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively. Variant 4, characterized by the use of Si_3N_4 as an expanding material and MnO_2 as an O_2 -supplying product, and also having the particularity of the lowest thermal requirement for the process of sintering, facilitated obtaining the optimal sample with the highest denseness ($0.59 \text{ g}\cdot\text{cm}^{-3}$), the highest thermal conductance ($0.097 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), the lowest porosity (71.9 %), and the highest compression strength (6.6 MPa), far above the other three optimal variants mentioned. Water-absorbing had low values (in the range of 1.0-2.18 vol. %), falling within normal limits.

The microstructural aspect of samples was highlighted as a result of investigating the images in Figure 3.

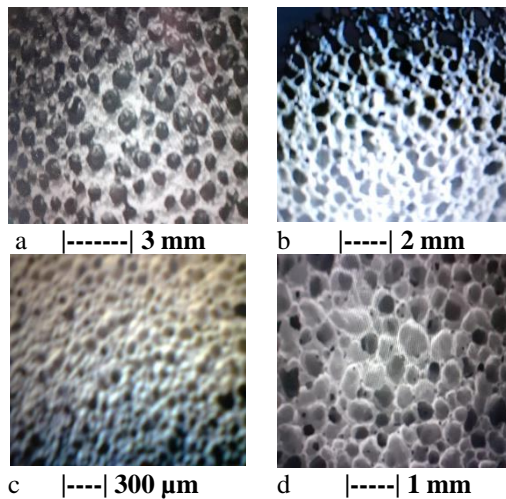


Figure 3. Microstructural appearance of specimens
a – variant 1; b – variant 2; c – variant 3; d – variant 4.

In general, pore size of optimal specimens fell within low limits. Among these, the largest dimensions were observed in the case of specimens corresponding to variants 2 (0.4-1.3 mm) and 1 (0.3-1.2 mm), while variants 3 (0.10-0.25 mm) and 4 (0.1-0.4 mm) had considerably lower value ranges.

The cellular glass specimen produced with SiC as an expanding agent with addition of fly ash (variant 2) according to a making recipe quite frequently found in the literature [11] had a homogeneous microstructure of cellular glass-ceramic type, a predominantly polycrystalline product made by the glass crystallization at a higher temperature of almost $1000 \text{ }^\circ\text{C}$ (due to the fly ash).

Apparent density and heat conductance had slightly higher values.

However, compression strength had the lowest value (1.27 MPa) of all the strength values obtained in this experiment.

It was known from the literature [1], that the pore size of a porous structure does not implicitly determine the value of the material compression strength.

An obvious example is the case of variant 3, which had the structure with the lowest pore sizes (below $250 \text{ }\mu\text{m}$), while the compression strength value was higher compared to the specimens of variants 1 and 2 characterized by pore size of four times bigger. But the main role in this strength increasing was played by borax, whose boron content usually favours obtaining products with relatively high strength.

The microstructure of the product made using version 4 was the result of utilizing the combination of Si_3N_4 as a very effective expanding agent and MnO_2 as an O_2 -supplier material.

The expanding process generated in this case pores with very small sizes (0.1-0.4 mm), which influenced increasing the denseness ($0.59 \text{ g}\cdot\text{cm}^{-3}$) and heat conductance ($0.097 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) values, but also the compression resistance that reached the highest value of these experiments (6.6 MPa).

4.2 Discussion

The comparative analysis of the most attractive cellular glass products manufactured by predominantly direct heating with microwaves generally showed their excellent physical, thermal, mechanical and microstructural properties, being adequate for using as thermal insulation products in construction.

Also, the specific energy requirement of making processes were very reduced (between $0.63\text{-}0.74 \text{ kWh}\cdot\text{kg}^{-1}$) under the conditions of using a microwave equipment at very small-scale (0.8 kW) and known from the literature that the energy efficiency of a microwave plant at industrial level can be improved by up to 25 % [7].

The analysis of the quality of products obtained through the four experimental variants mentioned above, taking into account the manufacturing recipes, operational parameters, physical, thermal, mechanical, and morphological characteristics, highlighted two variants that are almost as interesting through the prism of these criteria.

One of these is the cellular glass manufacturing method by using a mixture of consumed drinking bottle (70 % green glass, 15 % uncoloured glass, and 15 % brown glass) representing 95.5 % of the total solids, red iron oxide (Fe_2O_3) representing 0.4 %, and SiC (4.1 %) as an expanding agent. An addition

of water (10 %) completed the mixture prepared by pressing. The sintering temperature reached 850 °C achieved by the fast microwave heating with the rate of 27.7 °C/min.

Specific energy requirement was evaluated to 0.69 kWh·kg⁻¹. Denseness and heat conductance of the expanded material had very small values (0.19 g·cm⁻³ and respectively, 0.049 W·m⁻¹·K⁻¹), porosity reached very elevated values (91 %), the pore dimension having values between 0.3-1.2 mm.

The compression resistance had a normal value level of 1.48 MPa satisfactory for the purpose of manufacturing the product.

The other interesting variant was the one made from colourless consumed drinking bottle with an addition of 2 % sodium tetraborate as a fluxing product and 1.1 % CaCO₃ as a pore-forming powder.

Water addition with the role of binder represented 8 %. The process temperature was lower (825 °C), its duration being 31 min due to the medium warming speed of 26 °C/min.

The process energy efficiency was realized by obtaining a reduced energy requirement of 0.67 kWh·kg⁻¹.

The physical properties of the material (denseness and heat conductivity) were extremely low (0.18 g·cm⁻³ and respectively, 0.042 W·m⁻¹·K⁻¹), while the porosity reached the value of 91%.

The compression resistance reached relatively elevated level for this type of product (2.6 MPa) and the cell dimension had the lowest range of values (100-250 μm).

5. CONCLUSION

The work objective was the experimental demonstration of the superiority in energy terms of manufacturing the cellular glass by using the microwave radiation, without affecting the heat-insulating properties of products at the level of those obtained by conventional heating techniques. Worldwide, the adoption of electromagnetic waves as carriers of efficient energy in silicate material heating processes at high temperatures is still in various preliminary research phases, the distrust of manufacturers, but also of some researchers, coming from the high content of SiO₂ and Al₂O₃ of this material type, which indicates a weak microwave susceptibility, at least at room temperature. Experimental works recently carried out by Daily Sourcing & Research Company (Romania) have proven, however, that some glass components (chromium or iron oxides), even in very low

proportions, have the ability to ensure the electrical conductivity conditions required for the glass powder to become microwave susceptible starting from room temperature.

Four variants of cellular glass preparing by non-conventional heating at temperatures of over 800 °C were recently tested and are included in this paper. SiC, CaCO₃, and Si₃N₄ separately constituted the expanding agent, while fly ash, red iron oxide, borax, and MnO₂ have been additives included also separately into these mixtures.

Two of the four variants were considered optimal due to their excellent properties and very economical specific energy consumption.

In one of them (variant 1) composed of post-consumer drinking bottle, red iron oxide, SiC, and water addition, sintered at 850 °C by rapid microwave heating (27.7 °C/min), the energy requirement being 0.69 kWh·kg⁻¹, the final product had the density of 0.19 g·cm⁻³, thermal conductance of 0.049 W·m⁻¹·K⁻¹, compression resistance of 1.48 MPa, and pore size within the limits of 0.3-1.2 mm. The other optimal version (variant 3) prepared with CaCO₃, borax, and added water by sintering at 825 °C with the warming speed of 26 °C/min, and the energy requirement of 0.67 kWh·kg⁻¹ allowed to obtain an excellent cellular building material with density of 0.18 g·cm⁻³, thermal conductance of 0.042 W·m⁻¹·K⁻¹, compressive strength of 2.6 MPa, and pore size had the lowest range of values (100-250 μm).

6. REFERENCES

1. Scarinci, G., Brusatin, G., Bernardo, E., Foam Glass, in *Cellular Ceramics: Structure, Manufacturing, Properties and Applications*, Wiley-VCH GmbH & KGaA, Weinheim, Germany, Scheffler, M., Colombo, P. (eds.), pp. 158-176, (2005).
2. Jelle, B.P., Traditional, state-of-the-art and future thermal building insulation materials and solutions-Properties, requirement and possibilities, *Energy and Buildings*, Vol. 43, No. 10, pp. 2549-2563, (2011). <https://doi.org/10.1016/j.enbuild.2011.05.015>
3. Low, N.M.P., Formation of cellular-structure glass with carbonate compounds and natural mica powders, *Journal of Materials Science*, Springer Link, Vol. 16, pp. 800-808, (1981).
4. Knox, M.P., Copley, G.J., Use of microwave radiation for the processing of glass, *Glass Technology*, Vol. 38, No. 3, pp. 91-96, (1997). <https://www.britglass.org.uk/knowledge-base/digital-library-and-omformation->

[services/use-microwave-radiation-processing-glass](#)

5. Hurley, J., *Glass-Research and Development, Final Report*, A UK market survey for foam glass, The Waste and Resources Action Programme Publication, Banbury, Oxon, UK, March (2003).
6. Paunescu, L., Axinte, S.M., Grigoras, B.T., Dragoescu, M.F., Fiti, A., Testing the use of microwave energy to produce foam glass, *European Journal of Engineering Technology*, Vol. 5, No. 4, pp. 8-17, (2017).
7. Kharissova, O.V., Kharissov, B.I., Ruiz Valdés, J.J., Review: The use of microwave irradiation in the processing of glasses and their composites, *Industrial & Engineering Chemistry Research*, ACS Publications, Vol. 49, No. 4, pp. 1457-1466, (2010). <https://doi.org/10.1021/ie9014765>
8. Jones, D.A., Lelyveld, T.P., Mavrofidis, S.D., Kingman, S.W., Miles, N.J., Microwave heating applications in environmental engineering-A review, *Resources, Conservation and Recycling*, Vol. 34, No. 2, pp. 79-90, (2002). [https://doi.org/10.1016/S0921-3449\(01\)00088-X](https://doi.org/10.1016/S0921-3449(01)00088-X)
9. Kitchen, H.J., Vallance, S.R., Kennedy, J.L., Tapia-Ruiz, N., Carassiti, L., Modern microwave methods in solid state inorganic materials chemistry: From fundamentals to manufacturing, *Chemical Reviews*, ACS Publications, Vol. 114, No. 2, pp. 1170-1206, (2014). <https://doi.org/10.1021/cr4002353>
10. Cosmulescu, F., Paunescu, L., Dragoescu, M.F., Axinte, S.M., Comparative analysis of the foam glass types experimentally produced by microwave irradiation, *Journal of Engineering Studies and Research*, Vol. 26, No. 3, pp. 58-68, (2020).
11. Wu, J.P., Boccaccini, A.R., Lee, P.D., Kershaw, M.J., Rawlings, R.D., Glass-ceramic foams from coal ash and waste glass: production and characterization, *Advances in Applied Ceramics*, Vol. 105, No. 1, pp. 32-39, (2006).
12. Stiti, N., Ayadi, A., Lerabi, Y., Benhaoua, F., Benzerga, R., LeGenre, L., Preparation and characterization of foam glass based waste, *Asian Journal of Chemistry*, Vol. 23, No. 8, pp. 3384-3386, (2011).
13. Zhu, M., Ji, R., Li, Z., Wang, H., Liu, L., Zhang, Z., Preparation of glass ceramic foams for thermal insulation applications from coal fly ash and waste glass, *Construction and Building Materials*, Elsevier, Vol. 112, pp. 398-405, (2016). <https://doi.org/10.1016/j.conbuildmat.2016.02.183>
14. Llaudis, A., Orts, M.J., Garcia-Ten, J., Bernardo, E., Foaming of flat glass cullet using Si₃N₄ and MnO₂ powders, *Ceramics International*, Vol. 35, No. 5, pp. 1953-1959, (2009).
15. Garcia-Ten, J., Saburit, A., Orts, M.J., Bernardo, E., Colombo, P., Glass foams from oxidation/reduction reactions using SiC, Si₃N₄ and AlN powders, *Glass Technology-European Journal of Glass Science and Technology Part A*, Society of Glass Technology Publisher, Sheffield, UK, Vol. 52, No. 4, pp. 103-110, (2011).
16. Abbasi, S., Mirkazemi, S.M., Ziaee, A., Saedi Heydari, M., The effect of Fe₂O₃ and Co₃O₄ on microstructure and properties of foam glass from soda lime waste glasses, *Glass Physics and Chemistry*, Springer Link, Vol. 40, pp. 173-179, (2014).
17. Axinte, S.M., Paunescu, L., Dragoescu, M.F., Sebe, A.C., Manufacture of glass foam by predominantly direct microwave heating of recycled glass waste, *Transactions on Networks and Communications*, Vol. 7, No. 4, pp. 37-45, (2014).
18. Axinte, S.M., Paunescu, L., Dragoescu, M.F., Manufacturing the cellular glass from glass waste by an original unconventional technique, *Academic Journal of Manufacturing Engineering*, Vol. 19, No. 4, pp. 53-60, (2019).
19. Paunescu, L., Dragoescu, M.F., Axinte, S.M., Mixture of glass waste types for producing cellular glass through microwave radiation, *Academic Journal of Manufacturing Engineering*, Vol. 20, No. 2, pp. 87-93, (2022).
20. Paunescu, L., Axinte, S.M., Cosmulescu, F., Paunescu, B.V., The use of calcium carbonate as a foaming agent of glass waste for unconventional manufacture of a light glass foam with adequate mechanical strength, *The Bulletin of the Polytechnic Institute of Iasi, Chemistry and Chemical Engineering Section*, Vol. 68 (72), No. 4, pp. 93-106, (2022).
21. Paunescu, L., Axinte, S.M., Fiti, A., Cellular glass from post-consumer drinking glass non-conventionally prepared with silicon nitride and manganese dioxide as pore-forming agents, *Nonconventional Technologies Review*, Vol. 27, No. 3, pp. 22-28, (2023).
22. *Manual of weighing applications, Part 1, Density*, (1999). <http://www.docplayer.net/21731890-Manual-of-weighing-applications-part-1-density.html>
23. *Methodology in laboratory-Measurement of mass and derived values*, Radwag Wagi

- Elektroniczne, Radom, Poland, (2005).
<http://www.radwag.com>
24. Anovitz, L.M., Cole, D.R., Characterization and analysis of porosity and pore structures, *Reviews in Mineralogy and Geochemistry*, Vol. 80. No. 1, pp. 61-164, (2005).
<https://doi.org/10.2138/rmg.2015.80.04>
25. *Foam glass manufacturing*, Energocell Foam Glass, Debrecin, Hungary, (2014).
<https://www.energocell.hu/en/foamglass-manufacturing/>