INVESTIGATION OF FOAMED GLASS USING NATURAL WASTE MATERIALS AS FOAMING AGENT

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Abstract
The use of high-quality thermal insulation materials to improve the energy efficiency of buildings is strongly increasing. Foam glass, a durable and porous material that is resistant to almost all substance effects, is one of the best thermal insulation materials. Glass foaming is a complicated process that is affected by the types of foaming agents used in the initial composition of the mixture and the mode of foaming. The *influence of all components of the mixture - glass matrix and foaming agent - is discussed in this paper. Three types of glass powder (alkali frit, soda-lime silicate and borosilicate) were determined to be the matrix material. The foaming agents generate a gas phase via thermal decomposition of eggshell or a chemical reaction with the oxygen in the molten glass via SiC and coffee ground waste. The powder compacts fired at 900 °C for 10 minutes with a foaming agent content of 2 wt % presented excellent thermal insulation properties by using soda-lime silicate glass with SiC and eggshell foaming agents mixtures. The coffee ground waste-glass mixtures show inferior thermal insulation properties with each different glass powder.*

Keywords: *Glass, Waste, Foaming agent, Thermal conductivity.*

1. Introduction

Insulation materials have always piqued the interest of human civilization and society, beginning with clothing to keep the body warm and progressing to house construction and insulation (Østergaard, 2019). Building insulation standards are continuously improved to reduce energy consumption when heating homes. Increased insulating material thickness, as seen in many European countries for both walls and roofs (Papadopoulos, 2005), becomes a way to improve insulation. Unfortunately, increasing insulation thickness results in a lower living-to-house area ratio, which makes maintaining the same living area more expensive. As a result, developing new insulation materials or improving existing ones would be of great interest.

Traditional building insulation materials include mineral wool, extruded polystyrene (XPS), expanded polystyrene (EPS), and polyurethane (PUR), while recent state-of-the-art insulation materials include gas-filled panels (GFPs), vacuum insulation panels (VIPs), and aerogels (Jelle, 2011). The majority of primary insulation materials are organic, except for mineral wool, which is inorganic (Karamanos, 2008). Glass foam, another inorganic insulation material with good thermal insulation properties is not widely used yet. When comparing the thermal conductivity of common traditional insulation materials and glass foams, PUR has the lowest values down to 20 $mW.m^{-1}.K^{-1}$, while the remaining materials and glass foam have values in the 30-40 $mW.m^{-1}.K^{-1}$ range.

Glass foams can be used as a lightweight aggregate in concrete (Limbachiya, 2012) and road embankments as well as an insulation material. Glass foams have long lifespan, non-flammability, chemical and thermal stability, and closed porosity, making it waterproof (Colombo, 2003). Because of their properties and the fact that they can be made from various types of waste glass, glass foams are worth further investigation. The main foaming occurs during glass melting as a result of the decomposition of carbonates, hydroxyls, sulfates, and so on, or as a result of oxidation reactions, which are essentially the same processes that produce glass foams (Beerkens, 2006).

Material foaming is complicated because it is influenced by a variety of controllable parameters, including temperature, time, gas pressure, and gas atmosphere. The process parameters must be optimized when changing the material type (chemical composition) and particle size, especially because the composition affects viscosity and surface tension. Furthermore, the setup must differ depending on the material. Glass foams are created through high-temperature chemical reactions, dissolving gases in the molten glass during cooling, sol-gel processes, or freeze-drying sol-gel derived glasses.

The powder process is one of the most efficient and widely used foam glass manufacturing methods (Spiridonov, 2003). At the start of the process, the raw material, typically the glass cullet, is milled into powder and mixed with a powdered foaming agent (Abbasi, 2014). Before sintering, the powder mixture is heated and dried in a furnace. The purpose of the foaming agent is to create a gaseous phase in the glass matrix after sintering, resulting in a cellular glass structure.

Foaming agents, also known as gas-generating agents, are powdered substances added to glass powder to enable gas generation during foaming (Scheffler, 2005). Only a small amount of foaming agent is required for the gas-forming reaction, which can occur via decomposition or redox reaction (figure 1). Foaming agents are classified into two types based on their reaction behaviours. Because the type of foaming agent, its content, and solid residues all affect glass viscosity, foaming temperature, gas volume, pore structure, and crystallization, the foaming agent must be chosen based on the glass composition and the foaming process (König, 2016). The water absorption behaviour of foam glass is affected by the type of foaming agent and its concentration (Spiridonov, 2003).

This research work focuses on the utilization of natural waste foaming agents, especially eggshell and coffee ground waste. The United States Department of Agriculture (USDA) reported that approximately 8 billion dozen chicken eggs were produced in 2014. The eggshell contains about 94 wt% of calcium carbonates ($CaCO_3$). Although eggshell is not a hazardous waste, due to the large number of eggs produced, improper landfill disposal can result in significant environmental liabilities (Pokorny, 2011). Coffee consumption around the world generates a significant amount of solid organic waste known as coffee grounds, which harms the environment. This situation has accelerated the development of environmentally friendly applications for coffee grounds waste disposal, such as briquettes, soil fertilizer, biofuels, absorbent material, activated carbon, cosmetic products, polymeric films, porous materials, and light-weight aggregates (LWAs) (Busch, 2022).

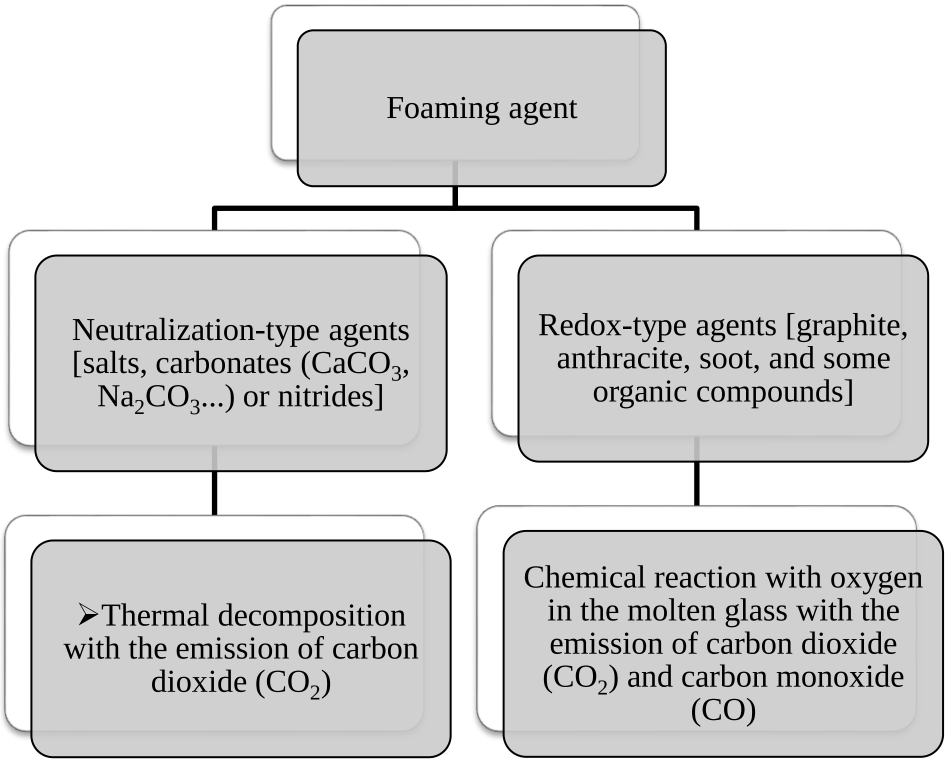


Figure 1. *Classification of the foaming agents*

2. Experimental procedures and methods

2.1. Materials and experimental procedures

In this research work, foam glass samples were created using various types of glass, including alkali frit, soda-lime silicate (SLS), and borosilicate glasses. In addition to eggshell and coffee ground waste as natural foaming agents, silicon carbide (SiC) was used as a reference foaming agent. To obtain glass powders suitable for foaming, the glass cullets were milled in planetary ball mill (Retsch PM 400) for 20 minutes at 200 rotations per minute (rpm) speed. After milling glass powders were sieved with 160 mesh. Before foaming the different glass powders and the different powder were weighed and mixed by hand together.

Figure 2. *Foaming agents used in this study (Coffee, eggshell and SiC)*

2 wt % of each foaming agent (silicon carbide, eggshell, and coffee ground waste) was mixed with the various glass powders, and 5 g of each mixture was poured into a stainless-steel mold and pressed for 10 seconds under 14 MPa into a cylindrical shape characterized by a diameter of 20 mm and a height of 16 mm. Five samples were prepared from each mixture, then the samples were sintered in an electric chamber furnace at 900°C with a heating rate of 5 °C/min and a holding time of 10 minutes.

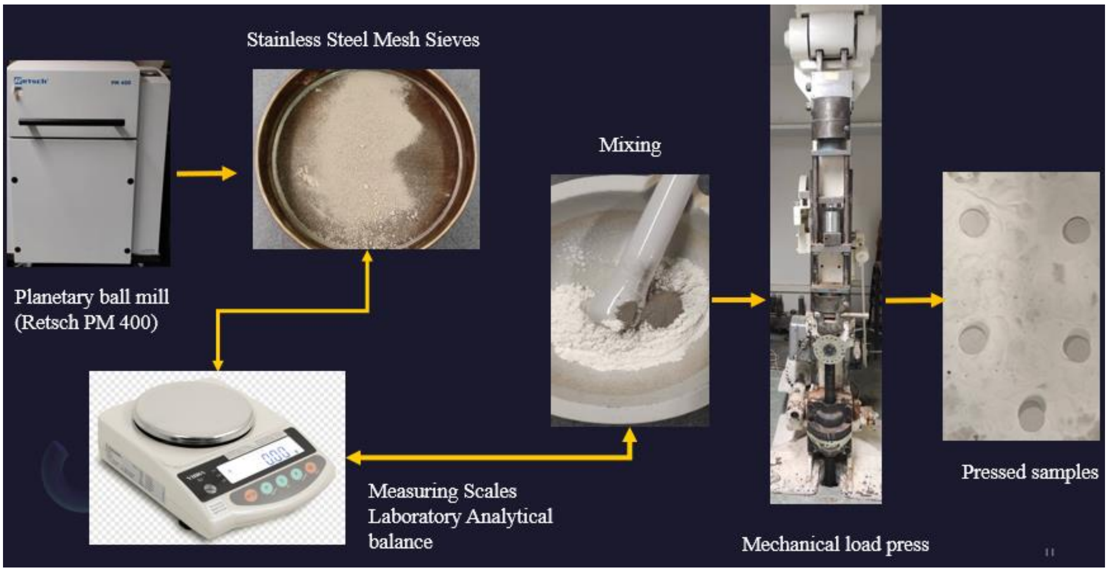


Figure 3. *Preparation process of glass foams samples*

2.2. Characterization methods

The experimental glass powder were analyzed by using a heating microscope (MicrOvis, Camar Elettronica), with specific heating parameters (start temperature: 30 °C, final temperature: 920 °C and photo sampling time: 5 °C). The different pressed glass powders (frit, soda-lime silicate and borosilicate), approximately 5 mm in height and 2 mm in diameter, were placed on an 8×10 mm alumina sheet and moved into a furnace where the silhouette change as a function of temperature is registered to identify the start of sintering, softening, sphere, half-sphere, and melting temperatures.

The thermogravimetric (TG) and differential thermal analysis (DTA) curves of the natural waste foaming agents (eggshell and coffee ground) were obtained from room temperature to 900 °C at a heating rate of 5 °C· min^{-1}. Thermal conductivity of the sintered samples was measured by a C-Therm TCi thermal conductivity analyzer applying the Modified Transient Plane Source method (conforms to ASTM D7984). The bulk density of the samples was calculated as mass per volume (g/cm^3).

The macrostructure of the obtained different glass foams mixture is determined by a digital camera photos taken on the top and cross section of the foamed samples to get an overview of the shape and size of cells and pores.

3. Results and discussion

3.1. Characterization of the raw materials

The glass powders were analyzed by a heating microscope to obtain their characteristic temperatures (sintering, softening, sphere, half-sphere, and melting temperatures). According to Table 1, the alkali frit had the lowest values, it started to melt at lower temperatures than the sphere state of SLS and borosilicate glasses.

Table 1. *Characteristic temperatures (°C) of the glass powders (by heating microscopy)*

Typical values	Glass powder types		
	Frit	Soda-Lime Silicate	Borosilicate
Sintering	623	682	740
Softening	709	_	_
Sphere	748	838	900
Half-sphere	789	_	_
Melting	812	_	_

The thermal properties of eggshell and coffee ground, as well as glass powders were first analyzed in order to investigate the foaming mechanism of foamed glass. Figure 4 depicts the TG-DTA curves of natural waste foaming agents from room temperature to 900 °C. As shown in Fig. 4a, a continuous weight loss of 48,49 wt% is observed around 770 °C, accompanied by heat release. This weight loss is caused by the thermal decomposition of eggshell and the release of carbon dioxide (CO_2). In Fig. 4b, a continuous mass loss of of 48,49 wt% is started at around 221 °C, accompanied by heat release. This mass loss is caused by the oxidation of coffee ground, which results in the release of CO and CO_2.

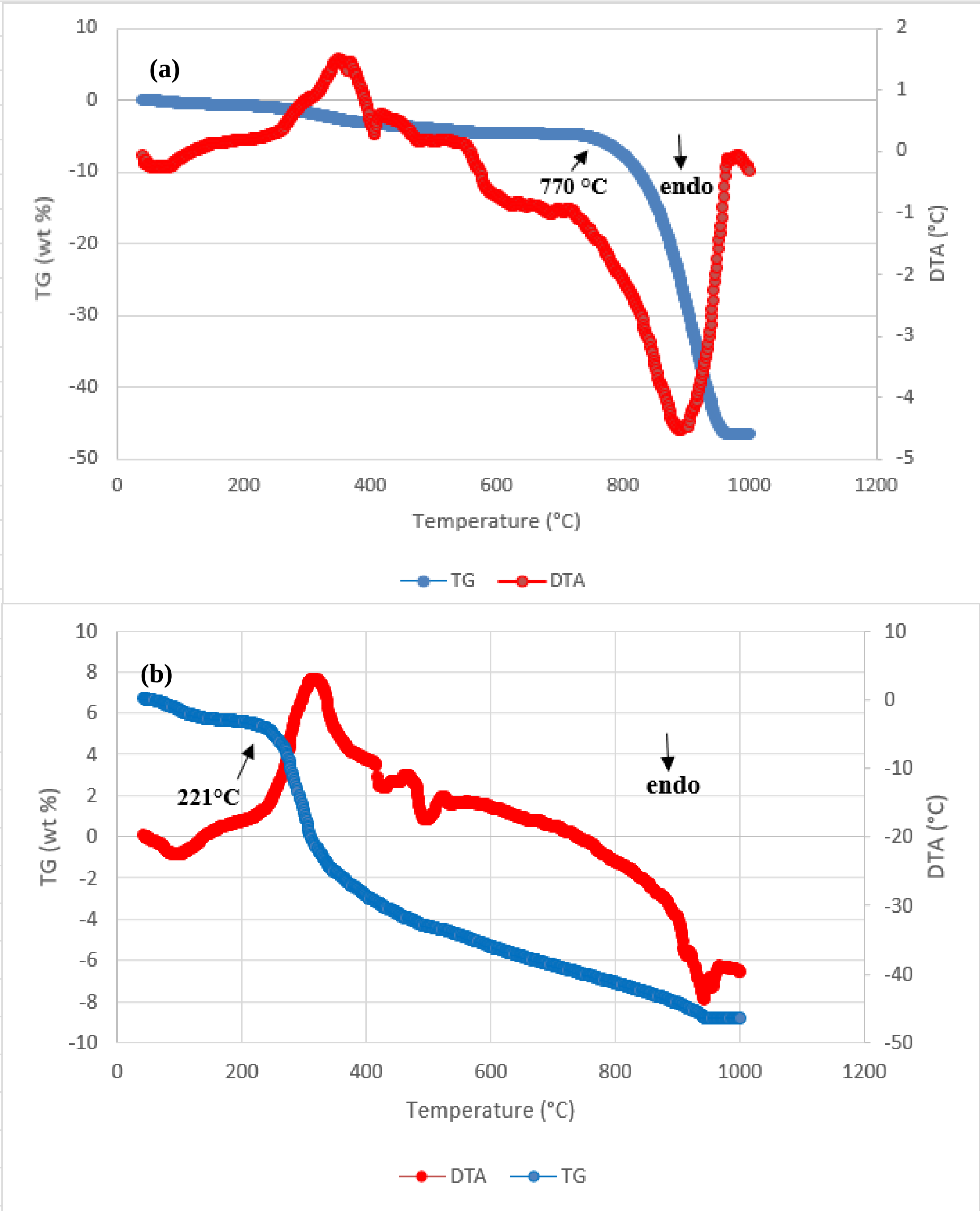


Figure 4. *TG–DTA curves of a) eggshell b) coffee ground*

3.2. Macrostructure

After firing, the macrostructure of the samples was recorded and represented in the following sections.

3.2.1. Foam glasses with SiC as foaming agent

SiC is a common foaming agent used in the foam manufacturing process (figure 5). Several cell structures can be seen in the images taken on the top and cross section of the foamed samples below. The foam glass made by borosilicate glass, had some larger cells embedded. The sample appears to be uniformly covered by a glassy shell. Frit glass had the most uniformly foamed structure, with large cells. Open cells can be found on the surface. Foams made from SiC (figure 6) and soda-lime silicate glass mixtures have a dense structure with small open pores on the surface.

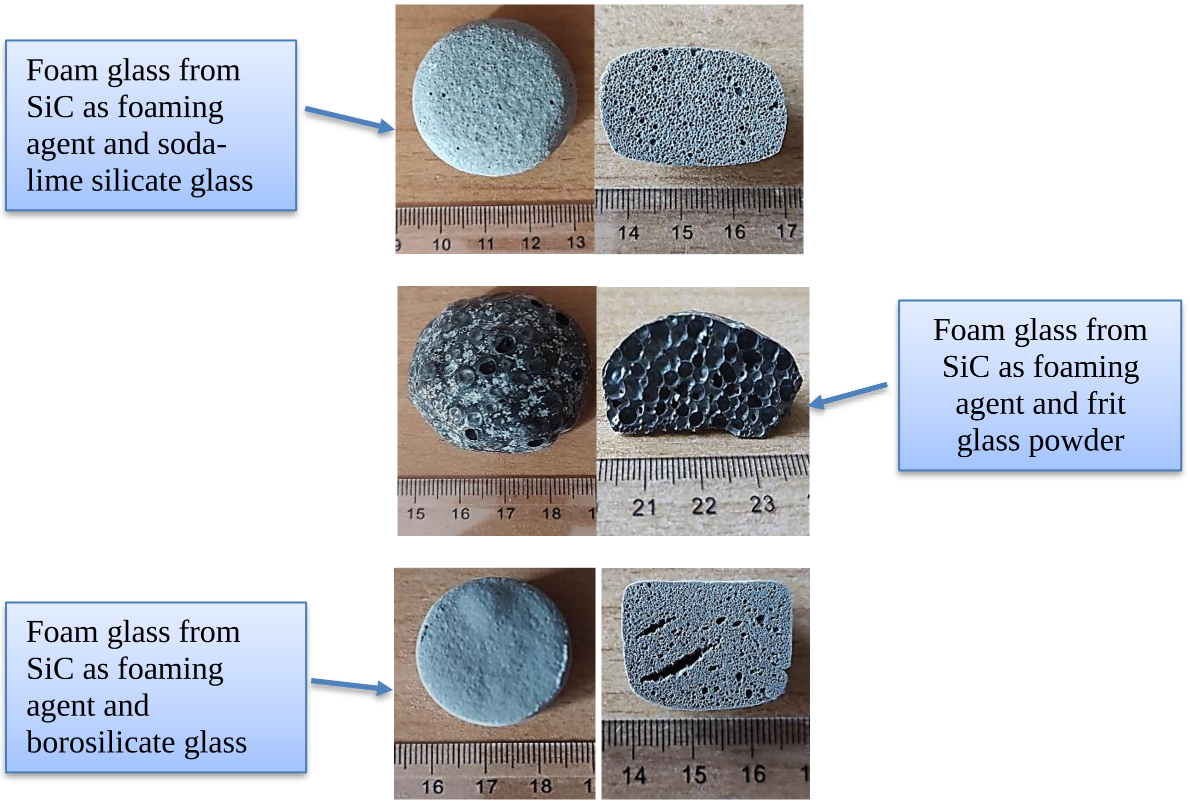


Figure 5. *Macrostructure of the foamed samples using SiC as foaming agent*

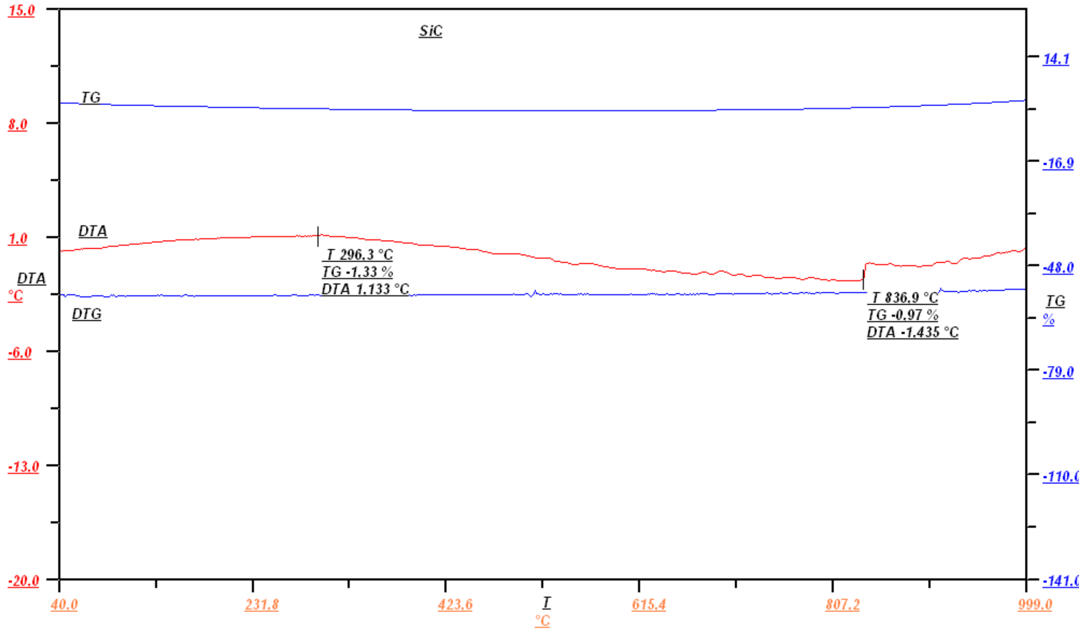
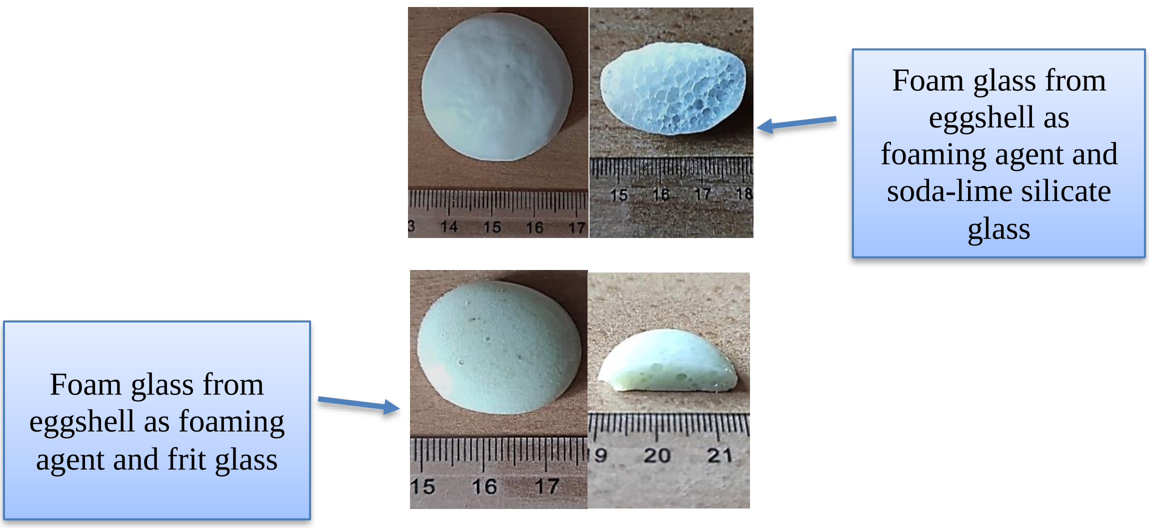


Figure 6. *TG-DTA curves of SiC*

3.2.2. Foam glasses with eggshell as foaming agent

All samples have uniformly covered surface free of visible open cells. Frit glass samples are glassy and mostly dense, with some larger cells inside. Again, borosilicate glass has the densest structure. Because it produced the most cellular structure, eggshell was the most efficient foaming agent in the case of soda-lime silicate glass (figure 7).



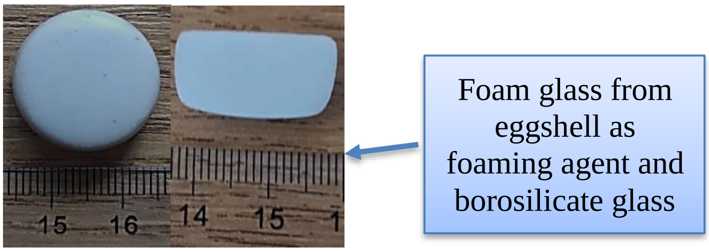


Figure 7. *Macrostructure of the foamed samples using eggshell as foaming agent*

3.2.3. Foam glasses with coffee ground as foaming agent

In terms of cell sizes and cellular structure of the foamed samples, coffee ground was the least effective foaming agent at that firing temperature. The structure of all fired samples is dense, with small cells (figure 8).

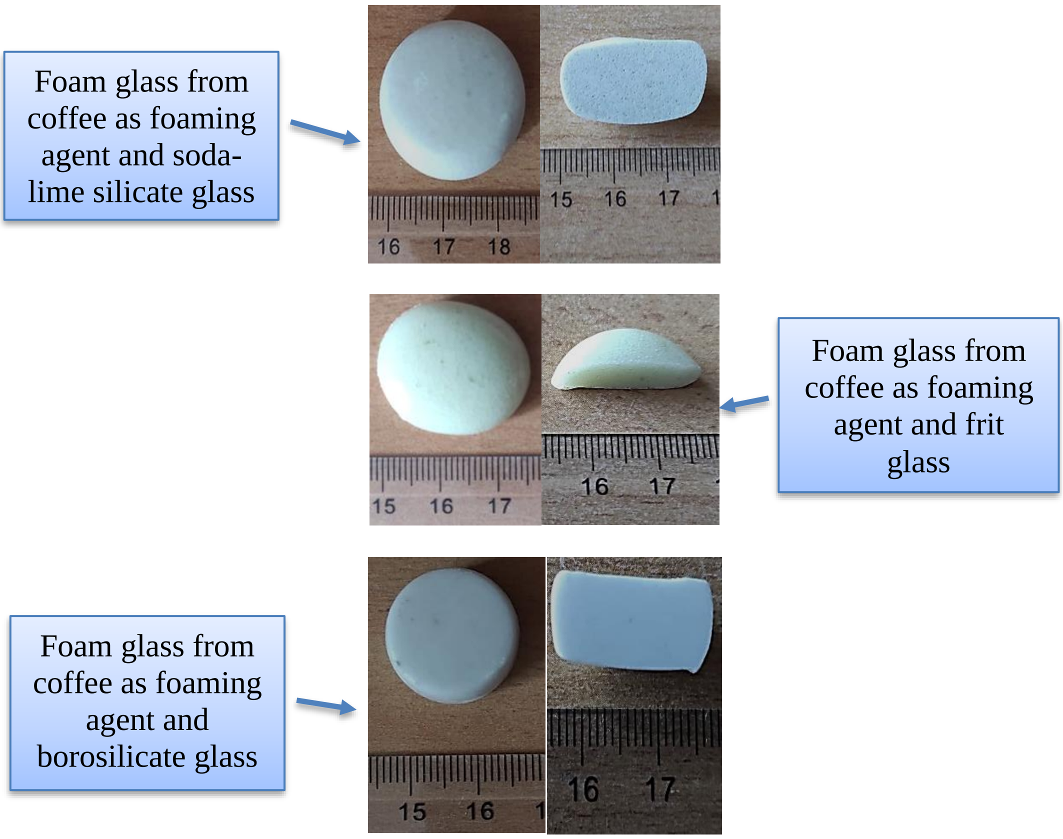


Figure 8. *Macrostructure of the foamed samples using coffee ground as foaming agent*

3.3. Physical and thermal Properties

The density of sintered foams ranges from 0.28 to 2.73 g·cm^{-3}, as shown in table 2. The lightest samples are the mixtures with silicon carbide foaming agent. The eggshell with frit glass and borosilicate glass types were the densest samples, while the soda-lime silicate and eggshell mixture present a light foam glass sample with a density of 0.39 g·cm^{-3} that meets the requirements of commercial foam glasses. Coffee ground with soda-lime silicate produces light foam glass with a density of 0.99 g·cm^{-3}, as opposed to borosilicate glass, which produces the densest samples with a density of 2.73 g·cm^{-3}.

Table 2. *Bulk density of the foamed samples*

Glass type	Foaming agent	Density (g·cm^{-3})
Frit	SiC	0.543
Frit	Eggshell	1.22
Frit	Coffee ground	1.470
Soda-lime silicate	SiC	0.282
Soda-lime silicate	Eggshell	0.396
Soda-lime silicate	Coffee ground	0.991
Borosilicate	SiC	0.936
Borosilicate	Eggshell	2.310
Borosilicate	Coffee ground	2.73

The thermal conductivity of the foamed glasses with 2 wt% of foaming agents (SiC, eggshell, and coffee) was measured. Figure.9. shows the variation of thermal conductivity with different glass foam mixtures. Insulating materials are those that have a thermal conductivity of less than 0.25 W.m^{-1}.K^{-1} (Francois Mear, 2007).

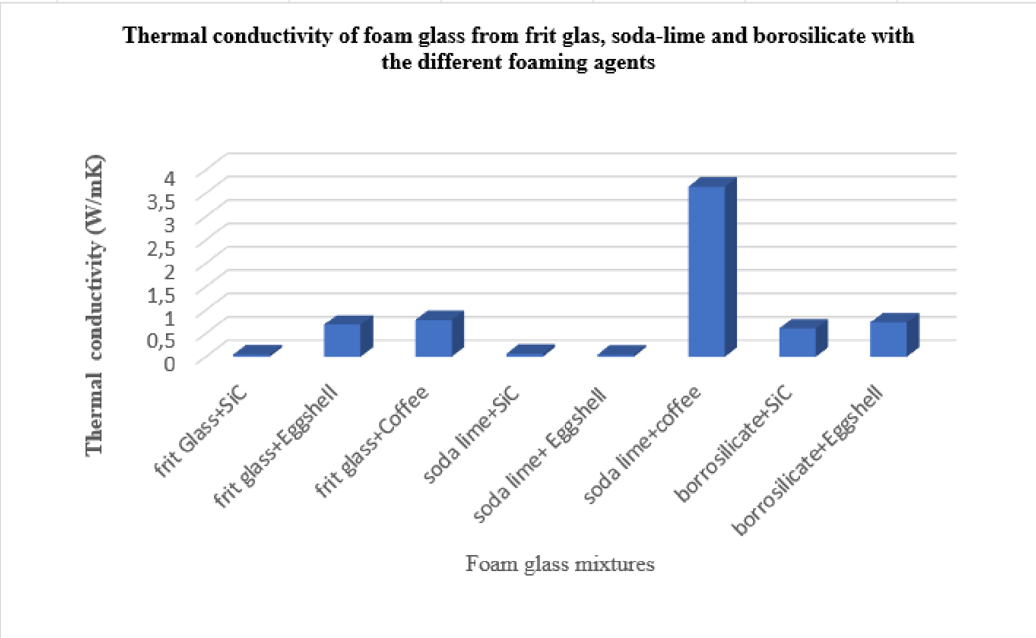


Figure 9. *Thermal conductivity of the foamed samples*

The silicon carbide foaming agent resulted the best thermal insulation properties with frit glass and soda-lime silicate glass types. Eggshell as foaming agent also presented an excellent thermal insulation value with the soda-lime silicate glass type. The other mixtures had a high thermal conductivity, especially in case of glass foams made from soda-lime silicate and coffee mixtures. The thermal conductivity of borosilicate and coffee ground mixture sample cannot be measured because the sample has not been sufficiently foamy.

4. Conclusion

Samples were prepared by combining several glass powders (frit, soda-lime-silicate, and borosilicate) and foaming agents, such as SiC, eggshell, and coffee ground. When the mixture is heated above the softening temperature of the glass, it becomes less viscous, and the foaming agent either decomposes or chemically reduces or oxidizes when it dissolves into the glass structure, forming gas. This results in a porous structure that is trapped by cooling. The foams were sintered at 900°C, presented excellent thermal insulation properties for the mixtures of frit glass and SiC (0.047 $W.m^{-1}. K^{-1}$), soda-lime silicate glass with SiC (0.063 $W.m^{-1}. K^{-1}$) and eggshell (0.044 $W.m^{-1}. K^{-1}$) foaming agents. The coffee showed inferior thermal insulation properties, with values varied between 0.78 $W.m^{-1}. K^{-1}$ (frit glass and coffee mixture) and 3.6 $W.m^{-1}. K^{-1}$ (soda-lime silicate and coffee mixture) which are higher than the thermal conductivity of the commercial foam glass produced by Pittsburgh Corning which equals (0.043-0.048 $W.m^{-1}. K^{-1}$) (Petersen, 2015).

5. Acknowledgements

The research reported here was carried out as part of the PhD research studies with the support of Ildikó Tasnádi for thermal conductivity measurements and Károly Gál for thermogravimetry and heating microscopy measurements.

References

[1] Papadopoulos, A. M. (2005). State of the art in thermal insulation materials and aims for future developments. *Energy Build*, 37, 77–86. **https://doi.org/10.1016/j.enbuild.2004.05.006**

[2] Abbasi, S., Mirkazemi, S. M., Ziaee, A., Saeedi Heydari, M. (2014). The effects of Fe_2O_3 and Co_3O_4 on microstructure and properties of foam glass from soda lime waste glasses. *Glas. Phys. Chem*., 40, 173–179. **https://doi.org/10.1134/S1087659614020023**

[3] Beerkens, R. G. C., van der Schaaf, J. (2006). Gas release and foam formation during melting and fining of glass. *J. Am. Ceram. Soc*., 89, 24–35. **https://doi.org/10.1111/j.1551-2916.2005.00691.x**

[4] Andreola, F., Borghi, A., Pedrazzi, S., Allesina, G., Tartarini, P., Lancellotti, I., Barbieri, L. (2019). Spent coffee grounds in the production of lightweight clay ceramic aggregates in view of urban and agricultural sustainable development. *Materials*, 12, 3581. **https://doi.org/10.3390/ma12213581**

[5] Colombo, P., Brusatin, G., Bernardo, E., Scarinci, G. (2003). Inertization and reuse of waste materials by vitrification and fabrication of inertization and reuse of waste materials by vitrification and fabrication of glass-based products. *Curr. Opin. Solid State Mater. Sci.*, 7, 336–239. **https://doi.org/10.1016/j.cossms.2003.08.002**

[6] Méar, F., Yot, P., Viennois, R., Ribes, M. (2007). Mechanical behaviour and thermal and electrical properties of foam glass. *Ceram. Int.*, 33, 543–550. **https://doi.org/10.1016/j.ceramint.2005.11.002**

[7] Jelle, B. P. (2011). Traditional, state-of-the-art and future thermal building insulation materials and solutions - Properties, requirements and possibilities. *Energy Build.*, 43, 2549–2563. **https://doi.org/10.1016/j.enbuild.2011.05.015**

[8] Karamanos, A., Hadiarakou, S., Papadopoulos, A. M. (2008). The impact of temperature and moisture on the thermal performance of stone wool. *Energy Build.*, 40, 1402–1411. **https://doi.org/10.1016/j.enbuild.2008.01.004**

[9] König, J., Petersen, R. R., Yue, Y. (2016). Influence of the glass particle size on the foaming process and physical characteristics of foam glasses. *J. Non. Cryst. Solids.*, 447, 190–197. **https://doi.org/10.1016/j.jnoncrysol.2016.05.021**

[10] Limbachiya, M., Meddah, M. S., Fotiadou, S. (2012). Performance of granulated foam glass concrete. *Constr. Build. Mater.*, 28, 759–768. **https://doi.org/10.1016/j.conbuildmat.2011.10.052**

[11] Long, B. (1934). *Glass product and method of manufacturing sponge-like glass*. US Patent 1,945,052.

[12] Arulrajah, A., Disfani, M. M., Maghoolpilehrood, F., Horpibulsuk, S., Udonchai, A., Imteaz, M., Du, Y. J. (2015). Engineering and environmental properties of foamed recycled glass as a lightweight engineering material. *J. Clean. Prod.*, 94, 369–375. **https://doi.org/10.1016/j.jclepro.2015.01.080**

[13] Petersen, R. R., König, J., Iversen, N., Østergaard, M. B., Yue, Y. (2019). The foaming mechanism of glass foams prepared from Mn3O4, carbon and CRT panel glass.

[14] Petersen, R. R. (2015). *Foam glass for construction materials: Foaming mechanism and thermal conductivity*. Aalborg University (PhD Thesis).

[15] Pokorny, A., Vicenzi, J., Pérez Bergmann, C. (2011). Influence of heating rate on the microstructure of glass foams. *Waste Manag. Res.*, 29, 172–179. **https://doi.org/10.1177/0734242X10364209**

[16] Binner, J. (2005). Mousses céramiques. In Colombo, P. (Ed.) *Cellular Ceramics: Structure, Manufacturing, Properties and Applications* (chapitre 2.1., pp. 33-56). 1ère éd.; Scheffler, député, Wiley-VCH : Weinheim, Allemagne.

[17] Spiridonov, Y. A., Orlova, L. A. (2003). Problems of foam glass production. *Glass Ceramics*, 60, 313–314. **https://doi.org/10.1023/B:GLAC.0000008234.79970.2c**