JOURNAL OF MATERIALS SCIENCE 16 (1981) 800–808

Formation of cellular-structure glass with carbonate compounds and natural mica powders

NORMAN M. P. LOW
Centre for Building Studies, Concordia University, Montreal, Quebec, Canada

Cellular-structure glass, or foamed glass, has been fabricated from mixtures of recycled colourless soda-lime waste glass powders and three separate different foaming agents by a simple sintering process. One of the mixtures consisted of glass powders and locally produced mica powders of the phlogopite-type, which act as a foaming agent as well as a component of the glass–mica composite material. The other mixtures consisted of glass powders and a carbonate compound, one being calcium carbonate and the other being sodium carbonate. The fabricated cellular-structure of the glass–mica composite material is found to have superior mechanical and thermal properties when compared with the cellular-structure glass formed with the carbonate compounds. The mechanisms of the formation of the cellular-structure by the two systems are discussed.

1. Introduction

Cellular-structure glass or foamed glass has recently found a wide range of applications as a premium thermal insulation material in industrial constructions and commercial structures. The advantages of employing cellular-structure glass for thermal insulation applications are its dimensional stability, superior structural strength and higher operating temperatures than conventional insulation materials, such as organic plastic foams, glass fibres or mineral wool fibres.

Cellular-structure glass is generally formed by mixing glass powders of suitable composition with a gas-forming foaming agent and then reacting the mixture at elevated temperatures. Under heating, the glass powders melt, forming a viscous liquid glass surface envelope. At the same time the gas-forming foaming agent undergoes a thermal decomposition thereby releasing its gaseous product. Because of the presence of the viscous liquid glass envelope, the released gas is trapped in the molten mass of the glass matrix and consequently a high gas pressure is developed by the continuous heating, forcing the molten glass mass to expand. Upon rapid cooling, the molten glass mass is solidified and a cellular-structure consisting of both closed and open cells is hence formed. A number of studies in the fabrication of cellular-structure glass have been carried out by various workers in the field in the past few years, and most of these studies have been based primarily on the use of one of the following three types of foaming agents: the carbonates of the alkali metals, such as $CaCO_3$ [1–8], carbon black [9–13] and reaction with a pressurized water steam [4, 8]. All these foaming agents have been known to be quite effective in the fabrication of the cellular-structure glass.

An experimental investigation conducted in the laboratory has found that locally produced fine mica powders of the phlogopite-type when mixed with recycled soda-lime waste glass powders can be fabricated into a composite material which exhibited a cellular-structure consisting of both closed and open cells. The fabricated glass–mica composite material was found to have superior physical, mechanical and thermal properties when compared with similar cellular-structure glass which is formed with the carbonate compounds as foaming agents. This paper describes the fabrication process of both the cellular-structure glass–mica composite material and the cellular-structure

0022–2461/81/030800–09$02.90/0

TABLE I Chemical composition of the recycled glass powders prepared.

Components	Weight %
SiO_2	71.30
Na_2O	11.30
CaO	8.39
Al_2O_3	2.24
MgO	0.09
Fe_2O_3	0.43
Other oxides	6.25

TABLE II Chemical composition of mica powders used

Components	Weight %
SiO_2	40.7
Al_2O_3	15.8
MgO	20.6
K_2O	10.0
FeO	7.8
F	2.2
Fe_2O_3	1.2
BaO	0.5
H_2O (combined)	1.0
H_2O (free)	0.01

glass formed with the carbonate compounds. The mechanisms of the fabrication process for the two systems and the variations of the properties of the fabricated products are compared and discussed.

2. Experimental procedure

The glass powders used for the present investigation were prepared from recycled colourless soda-lime glass cullets*. The glass cullets were first pulverized into fine grains (in the range 0.2 mm to 0.5 mm diameter) by a mechanical pulverizer. The pulverized glass grains were then ground into fine powders by a dry ball-milling process for a period of about 5 h. The corundum grinding media were used. The glass powders used for sample preparation were mostly in the 150–300 μm range. The compositions of the recycled glass powders were determined by chemical analysis and are shown in Table I.

For preparing samples of the carbonate–glass system, two forms of carbonate compounds have been used. These included calcium carbonate powders (Baker analysed Reagent Grade $CaCO_3$) with particles finer than 200 mesh and sodium carbonate powders (Anachemia Reagent Grade Na_2CO_3) with particles finer than 100 mesh.

For preparing samples of the mica–glass system, the mica powders used were of the phlogopite-type†. Powders used for sample preparation were finer than 300 μm diameter and their chemical composition as reported by the producer is shown in Table II [14].

For most purposes of experimental evaluation, a 50 g specimen was prepared from the appropriate proportions of the recycled glass powders and the foaming agent. The weighed amounts of each powder were thoroughly mixed in an agate pestle and mortar. In order to facilitate the powder compaction process 3 ml of tap water was added to the powders during the mixing operation. The mixed powders were then compressed into a circular disc of about 50 mm diameter and 20 mm thickness employing a compaction pressure of about 1 $MN\,m^{-2}$. The compressed powder compact was then placed on a refractory brick and sintered in a Glo-Bar electric heating furnace, the temperature of which was raised to the selected level steadily with a heating rate of approximately 300° $C\,h^{-1}$. After soaking at the selected temperature level for the desired period, the furnace was rapidly cooled to about 600° C and equilibrated at that temperature for about 30 min before further cooling to about 300° C at a slow cooling rate. The total time required to complete the cooling cycle before the removal of the sintered specimen from the furnace was about 6 h.

Depending on the type of foaming agent used, a different combination of sintering temperature and time period was found necessary. A good quality cellular-structure glass product was prepared from the recycled colourless soda-lime glass by sintering at 780° C and 30 min for the glass–$CaCO_3$ system, at 825° C and 30 min for the glass–Na_2CO_3 system and at 850° C and 30 min for the glass–mica system.

The physical properties, such as bulk density, apparent porosity, water absorption and volume changes of the sintered specimens were determined according to the procedures described in the ASTM-C20 methods [15]. The compressive strength of the sintered compacts was measured with an Instron Universal Testing Instrument, and the thermal conductivity of the sintered sam-

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[*] Supplied by Consumer Glass Ltd, Montreal, Canada.

[†] The phlogopite-type mica powders are processed in Boucherville, Quebec (near Montreal) from a high purity ore by Marietta Resources International Ltd in joint venture with Societe Mineralugique Laviolette, Inc., Montreal, under a trade name known as SUZORITE mica.

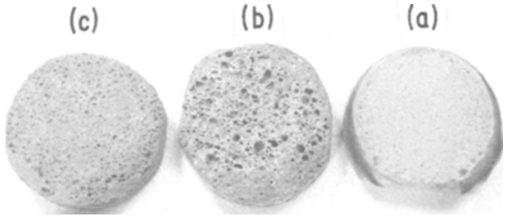

Figure 1 Cellular-structure glass formed with (a) $CaCO_3$, (b) Na_2CO_3 and (c) phlogopite-type mica powders.

ples was determined with a Dynatech Guarded Hot-Plate according to the testing procedure described in the ASTM-C177 method [16]. For the thermal conductivity measurement, a 300 g sample of 20 cm diameter was used in order to fit the Dynatech equipment.

3. Results

Rigid cellular-structure glass consisting of both closed and open cells was produced when calcium carbonate ($CaCO_3$) powders in the range of 0.5–3.0 wt% or sodium carbonate (Na_2CO_3) in the range of 1.0–7.0 wt% were added to the recycled soda-lime glass powders and sintered at the temperatures and time periods as indicated in this study. The physical appearance and cell size in particular of the cellular-structure glass varied slightly depending on the type of the foaming agent used. When $CaCO_3$ powders were used as a foaming agent, the cellular-structure consisted of cells mostly in the range 0.1–1.0 mm in diameter; when Na_2CO_3 powders were used, the cellular-structure consisted of cells mostly in the range 0.5–3.0 mm in diameter, with some cells as large as 6–7 mm in diameter. A composite material of glass and mica exhibiting a rigid cellular-structure was also produced when phlogopite-type mica powders in the range 7.5–15.0 wt% were mixed and reacted with the glass powders. The formation of this cellular structure was developed by the glass and mica powders alone, as no gas-forming foaming agent was added to the mixture. The cellular-structure of the glass–mica composite materials consisted of cells ranging from 0.2 to 2.0 mm in diameter. Fig. 1 shows the photographs of cellular-structure glass as formed in the three different systems. Fig. 1a, b and c show the cellular-structure formed with $CaCO_3$, Na_2CO_3 and phlogopite-type mica powders, respectively.

The formation of a cellular-structure in the glassy matrix was generally found to be associated with a volume expansion in the bulk of the material. In the present study, the volume expansion was taken as the ratio (in per cent) of the difference between the final volume of the sintered sample and the initial volume of the unreacted sample to the initial volume of the sample; the volume expansion is plotted as a function of the concentration of the foaming agents in Fig. 2. From Fig. 2 it can be seen that the calcium carbonate exhibited the largest degree of volume expansion in the formation of the cellular-structure as compared with use of either Na_2CO_3 or mica powders. When $CaCO_3$ in the range 0.5–3.0 wt% was added to the glass powders, a volume expansion in excess of 100% was obtained and a maximum expansion of over 450% was attained when 2 wt% of $CaCO_3$ was added to the glass powders. On the other hand, when Na_2CO_3 was used as foaming agent, a much smaller degree of volume expansion was observed. A maximum volume expansion of only 90% was achieved when 5 wt% of the compound was added to the glass powders. It was found that when phlogopite-type mica powders in the range 7.5 to 15 wt% were added to the glass powders, a moderate degree of volume expansion was also produced, but a maximum volume expansion of only 60% was attained when 10 wt% of mica powders were added to the mixture. These experimental results indicate that the chemical compound Na_2CO_3 and the phlogopite-type mica powders could produce a similar degree of physical structural modification of the liquid glassy matrix.

Variations of the degree of volume expansion of the cellular-structure glass, as formed with different foaming agents, also produced a corresponding degree of variation of the bulk density of the cellular-structure glass. The bulk density of the cellular-structure glass formed with $CaCO_3$ as foaming agent is in the range $0.22–0.57 \times 10^3$ $kg\,m^{-3}$ with a minimum value of about 0.22×10^3 $kg\,m^{-3}$ when 2 wt% of the compound was added to the glass powders. On the other hand, the bulk density of the cellular-structure glass formed with Na_2CO_3 as foaming agent is in the range of $0.65–0.96 \times 10^3\,kg\,m^{-3}$ with a minimum value of about $0.65 \times 10^3\,kg\,m^{-3}$ when 5 wt% of the compound was added to the glass. The cellular-structure of the glass–mica composite material exhibited a

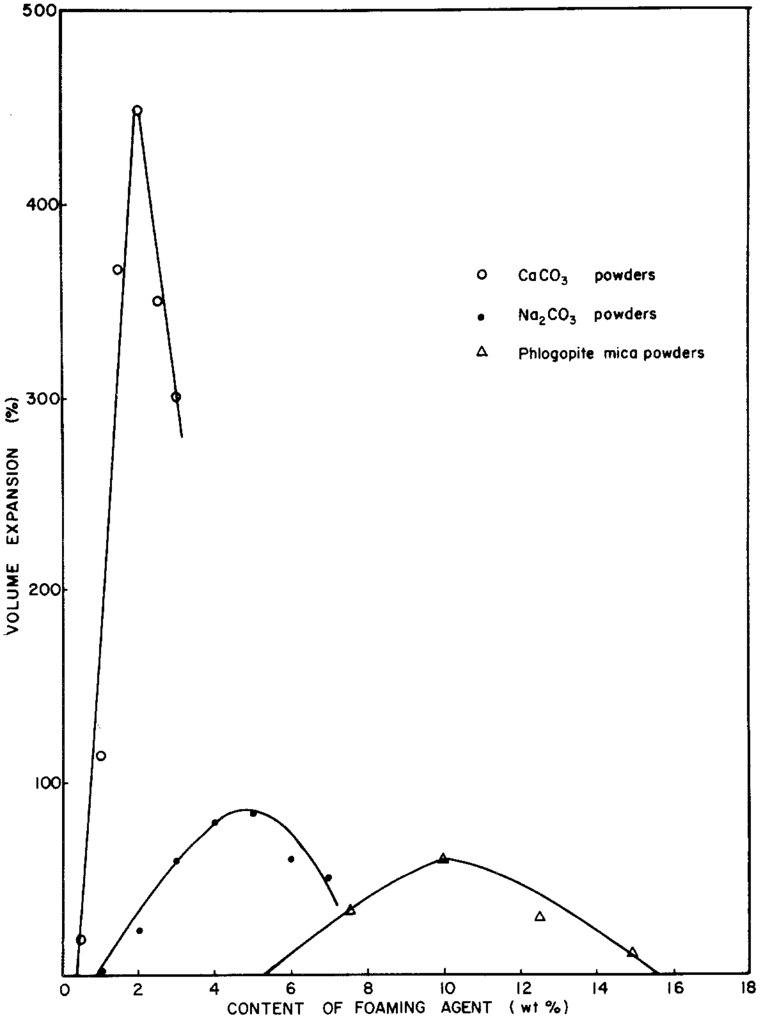

Figure 2 Variation of volume expansion with content of foaming agents in the formation of cellular-structure glass.

comparatively higher bulk density with values in the range of 0.75–1.05 $\times 10^3 \text{kg m}^{-3}$ and a minimum value of about 0.75 $\times 10^3 \text{kg m}^{-3}$ when 10 wt % of mica was added to the mixture. Fig. 3 shows the variations of bulk density of the three cellular-structure glasses with concentration of foaming agents. The similarity of the behaviour of the bulk density with foaming agent concentrations between the Na_2CO_3 compound and the phlogopite-type mica powders is again evident.

Physical changes in the bulk of the compacted solid of ceramic materials that occur during the firing process are often related to changes in pore shapes or sizes. As discussed earlier, the cellular-structure glass consisted of both closed and open cells. When the relationship of the volume of the open pores of the specimen to its exterior volume was determined, as apparent porosity expressed in per cent, a significant variation was observed among the three cellular-structure products. Fig. 4 shows the variation of apparent porosity as a function of the concentration of the added foaming agents. It is evident that most of the cells present in the cellular-structure glass which was formed with $CaCO_3$ as foaming agent are of the open-cell type. At the optimum volume expansion when 2 wt % of the $CaCO_3$ compound was added, almost 85 % of the cell structures are of the open-cell type. As for the cellular structure which was formed with Na_2CO_3 compound, at the maximum volume expansion, only 50 % of the cell structures are of the open-cell type. The cellular-structure of the glass–mica composite material only contained between about 30 and 38% of the open-cell type cells.

Mechanical tests showed that the compressive strength of the cellular structure glass formed with all three foaming agents decreased as the degree of

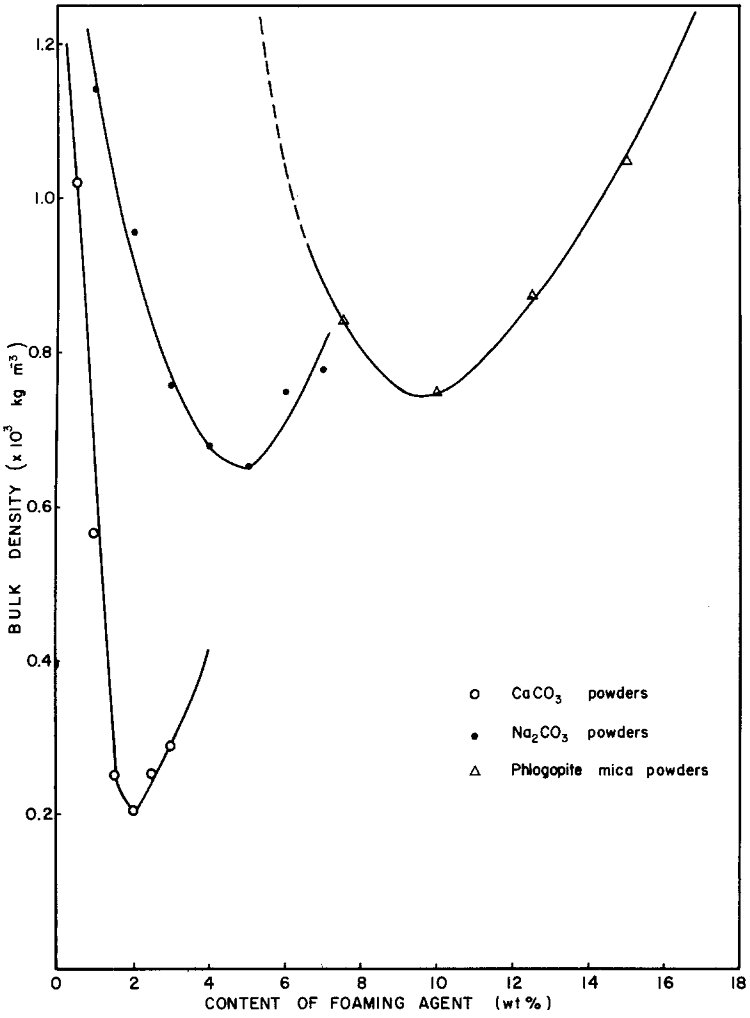

Figure 3 Variation of bulk density with content of foaming agents in the cellular-structure glass.

volume expansion increased. When the compressive strength was plotted as a function of the bulk density of the expanded glass, a linear decrease of compressive strength with bulk density is evident, as shown in Fig. 5. For samples which exhibit the largest degree of volume expansion or the lowest bulk density, the cellular-structure glass formed with $CaCO_3$ as foaming agent has a compressive strength of $0.166\,MN\,m^{-2}$ and that formed with Na_2CO_3 has a compressive strength of $0.220\,MN\,m^{-2}$. On the other hand, the cellular-structure of the glass–mica composite materials has a considerably higher compressive strength with an average value of about $0.874\,MN\,m^{-2}$. Because of the inferior compressive strength of the $CaCO_3$-formed cellular-structure glass this glass has a tendency to abrade under a moderate load or under a flame. The Na_2CO_3 formed cellular-structure glass has only slightly improved compressive strength compared with the $CaCO_3$-formed cellular-structure glass. However, the cellular-structure of the glass–mica composite material exhibited a higher compressive strength and also showed no abrasion under flame and no severed deformation under load.

Possible applications of cellular-structure glass or foamed glass, fabricated from recycled waste glass, as thermal insulating materials have been demonstrated in recent studies [5, 8]. Thermal conductivity measurements by the guarded hot-plate method, as conducted in the present study, have shown that the thermal conductivity values of the cellular structure glass which was formed with the use of carbonates as foaming agents and of the cellular structure glass–mica composite material are in the similar range of values varying from 0.120 to $0.282\,W\,m^{-1}\,{}^\circ C^{-1}$ when measured over the temperature range 25–120° C, as shown

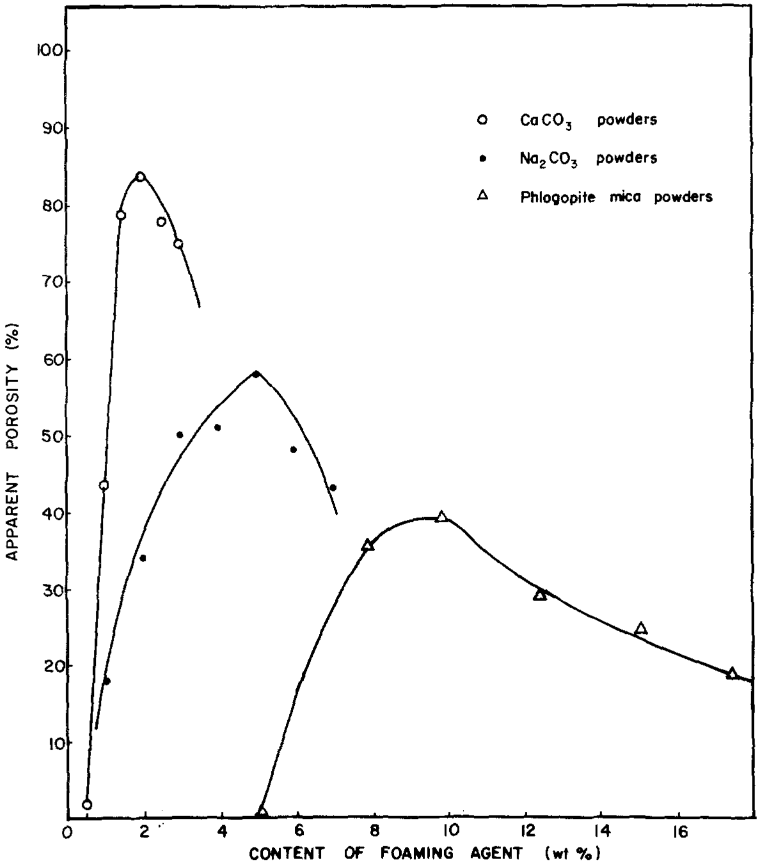

Figure 4 Variation of apparent porosity with content of foaming agents in the cellular-structure glass.

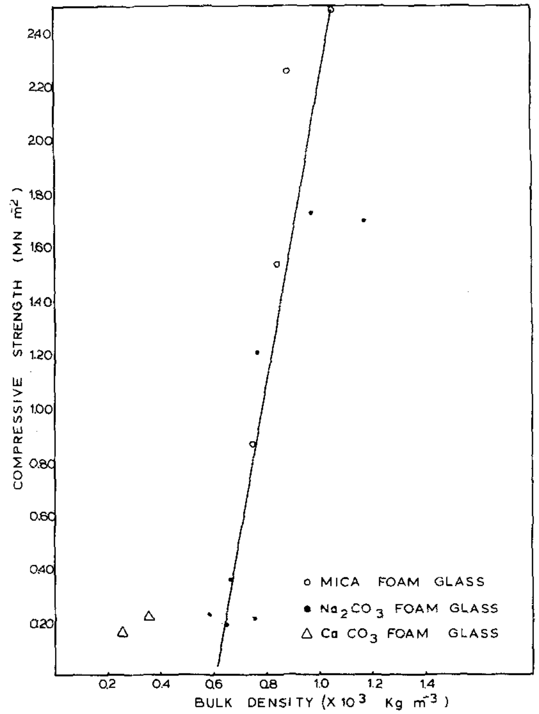

Figure 5 Dependence of compressive strength on bulk density of cellular-structure glass.

in Table III. The competitive thermal conductivity values of the cellular-structure glass–mica composite material suggest that this composite material could be employed as a rigid thermal insulating material.

4. Discussion

The formation of a cellular-structure composite from a mixture of glass powders and carbonate compounds of either calcium or sodium is the consequence of a series of solid state reactions. As the mixture of glass powders and carbonate powders is heated at elevated temperatures, the glass particles first begin to sinter and then gradually melt under continuous heating and increasing temperature. The melting of the glass particles probably begins from the surface and gradually propagates to the interior of the bulk of the sample. The melting of the glass particles therefore forms a viscous liquid glass envelope. At the same time, the carbonate particles of either calcium or sodium compound first undergo a thermal decomposition, forming an oxide and simultaneously releasing carbon dioxide as a gaseous product. The oxide is then incorpora-

TABLE III Thermal conductivity values of cellular-structure glass and glass–mica composite materials

Description of material	Temperature (° C)	Thermal conductivity (W m^{-1} ° C^{-1})
Cellular-structure glass foamed with $CaCO_3$	30–40	0.120
	80–90	0.133
	100–120	0.157
Cellular-structure glass foamed with Na_2CO_3	30–40	0.245
	60–75	0.272
	100–120	0.282
Cellular-structure glass–mica composite materials	25–30	0.245
	50–60	0.254
	80–90	0.270

ted into the molten glass mass and acts as a glass modifier thereby reducing the viscosity of the molten glass. The CO_2 gas which is released from the thermal decomposition of the carbonate compounds is trapped in the interior of the viscous glass envelope and its pressure is gradually increased, forcing the molten glass mass to expand. Upon sudden cooling the molten glass mass is solidified and a cellular structure is formed.

The development of a different magnitude of volume expansion in the formation of the cellular structure glass between the use of $CaCO_3$ and Na_2CO compounds as a foaming agent, as exhibited in the present study, is probably attributable to different characteristics of the liquid glass melt as a result of the incorporation of the oxide component from the decomposition of the carbonate compounds. It is generally recognized that both the viscosity and the surface tension of the liquid glass melt will be altered by the addition of either CaO or Na_2O to the silicate glass melt [17–20]. In the case of surface tension modification, the $Na_2O–SiO_2$ system has been reported to have a much lower surface tension value, compared with the $CaO–SiO_2$ system [17, 18]. The modification of the viscosity of the glass melt by the incorporation of the two oxides is probably dependent on the miscibility of the oxide system. A recent review has discussed details of the mechanism and kinetics of liquid-phase separation in glass-forming melts [20]. It has been reported that both $Na_2O–SiO_2$ and $CaO–SiO_2$ systems have a different immiscibility region. In the $Na_2O–SiO_2$ system, there is a region of sub-liquidus liquid–liquid immiscibility from about 0 to 20 wt % Na_2O with a maximum immiscibility temperature at 850° C and 10 wt % Na_2O; in the $CaO–SiO_2$ system, there is an extensive immiscibility region from about 0 to 40 wt % CaO including a stable immiscibility region from about 1700 to 2100° C. Phase separation in silicate and borosilicate glass melts has been found to have a pronounced effect on the viscosity; and the viscosity of a separated glass is known to depend on whether the high viscosity phase is continuous or discontinuous [21, 22]. It has also been reported that large increases of viscosity of up to five orders of magnitude during separation at constant temperatures have been experimentally observed. Based on these considerations, it is conceivable that the addition of between 1 and 3 wt % CaO to the silicate glass melt will give rise to a small degree of phase separation which consequently results in the formation of a glass melt with high surface tension but low viscosity, thus permitting a greater volume expansion of the molten mass. On the other hand, the addition of 2 to 7 wt % Na_2O to the glass melt will cause a larger degree of phase separation which leads to the formation of a glass melt with low surface tension but higher viscosity, thus limiting the volume expansion of the molten mass.

The development of a cellular structure in the sintered glass–mica mixture within the narrow range of mica content between 7.5 wt % and 15.0 wt % can probably be explained by the following reasoning. As the sintering temperature is raised to the 850° C level, most of the glass grains near the surface of the powder compact would be melted, and the melting process gradually propagates to the interior of the compact. At this elevated temperature, the mica particles are known to undergo no thermal decomposition or cause any physical changes; however, the mica particles are known to undergo a dehydration process, thereby releasing both its free and combined water [14]. As the water is released from the mica particles in the matrix, it is expected that a small portion of the water will be dissolved in the liquid-phase glass. The dissolution of the water in the liquid phase glass will consequently cause a lowering of the viscosity of the glass–mica system, as has been observed in the reaction of water with glass by other workers [23, 24]. The undissolved portion of the water will be trapped in the interior of the matrix because of the presence of the viscous liquid glass envelope. As a result, the entrapped water vapour develops a strong vapour pressure which consequently forces the molten glass mass apart, causing the glass matrix to expand. As the liquid glass–mica is cooled suddenly, solidification of the composite matrix takes place and the formation of cellular structure occurs. It is quite likely that the vapour pressure developed by the entrapped water vapour from thermal dehydration of the mica particles is lower than that developed by the entrapped carbon dioxide gaseous product from thermal decomposition of the carbonate compounds; it therefore contributes to a different degree of volume expansion of the cellular structure of the glass–mica matrix.

5. Conclusion

The present experimental study has demonstrated that cellular-structure glass can be fabricated from recycled colourless soda-lime glass by mixing the glass powders with carbonate compounds of either calcium or sodium and sintering the mixtures at elevated temperatures in the range of 780–825° C. Results showed that the $CaCO_3$ compound produced a much larger volume expansion of the bulk of the material in the formation process compared with that produced by Na_2CO_3. This large volume expansion resulted in the development of a cellular structure glass with the lowest bulk density and an inferior compressive strength. The product also tends to abrade under a moderate load or under a flame. The Na_2CO_3-formed glass was found to exhibit a much lower degree of volume expansion but the product has a slightly higher compressive strength.

The significant finding in the present study is the discovery of the possibility of fabricating a good quality cellular-structure composite material from a mixture of recycled colourless soda-lime glass and phlogopite-type mica powders without the addition of a gas-forming foaming agent, such as the carbonates of the alkali metals. The mica particles themselves could perform a dual function as the composite component as well as the foaming agent. The cellular-structure of the glass–mica composite material was found to have a mechanical strength much superior to that of the carbonate foamed products. The thermal conductivities of the cellular-structure glass and cellular-structure glass–mica composite material were found to have similar values ranging from 0.120 to 0.282 $W m^{-1} {}^\circ C^{-1}$ when measured over the temperature range 25–120° C. The possession of superior mechanical strength and comparable insulation properties by the cellular-structure glass–mica composite material suggests that it is a potential building material for construction applications because of its effectiveness in energy conservation.

Acknowledgement

This research programme was supported by a research grant from the Natural Sciences and Engineering Research Council of Canada, under Grant No. A-1192. The author wishes to thank Mr. A. Clark for his assistance in material preparation and Mr. P. Guite for his assistance in the preparation of the line illustrations. The author also wishes to thank Consumer Glass Co. Ltd of Montreal for their supply of the recycled soda-lime glass cullets.

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Received 5 June and accepted 2 September 1980.