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Structural studies and electrical properties of recycled glasses from glass and incinerator wastes

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The electrical behaviour of different glass compositions obtained from mixing waste glass deriving from a community glass recycling program and silicate waste from the incineration of municipal solid residues (from Reggio Emilia city) have been investigated as a function of temperature and frequency. The electrical and dielectric properties were related to structural studies performed on the same glassy materials. As the amount of incinerator wastes increases, on account of lower alkali and higher alkaline-earth content in the final glass composition, conductivity and dielectric losses decrease approaching the behaviour of type E glass fibres, so envisaging a possible use of waste-containing glasses in the production of high voltage insulators.

1. Introduction

As the knowledge and attention to the environmental problems increase, the search of efficient disposal technologies for toxic, hazardous substances becomes more strenuous. For many industrial wastes such as fly ashes and incinerator wastes, vitrification has proved to be a successfull way to produce inert by-products [1–6]. These can not only be stored safely but also be re-used as new marketable building materials.

In the present paper the attention has been focussed on the grate ash coming from the incineration of municipal solid wastes and on waste glass coming from a community glass recycling program. The first represents the main residue fraction (approx. 25–40 wt%) of municipal waste combustion process that has several advantages. These are: the reduction in waste volume and mass in order to save scarce and valuable space on landfills, the complete destruction of all organic matter in order to guarantee a total disinfection of the waste stream, the detoxification of inorganic pollutants present in the waste, the utilisation of the energy contained in the waste stream and the possible production of high quality bottom ashes which could enable utilization [7]. The chemical composition of the grate ash exhibits the main constituents of glasses: glass forming oxides (SiO_2), melting and glass modifying oxides (Na_2O, K_2O) lowering melt viscosity and glass stabilizing oxides (CaO and MgO), which also lower melting temperature and viscosity. Therefore, this kind of by-product seems particularly suitable to undergo a vitrification process, through which the following useful benefits can be obtained: the immobilization of toxic elements, whenever present, the reduction of waste volume and the possibility to immobilize wastes of different origin with the same vitrification process.

Suitable amount of other raw materials have to or can be added to the waste to be vitrified in order to obtain a more homogeneous and stable vitreous melt and add further value to the final product. The introduction of conventional raw materials used for commercial glass-making, such as sand, would however be too expensive and the waste vitrification process would become unprofitable. This can be by-passed by the exploitation of other by-products. In this way, preliminary studies have shown the feasibility to obtain glasses from mixtures of cullets and incenerator waste at different percentages [4, 8] capable also to be drawn into fibres showing promising mechanical properties [9].

Following previos work carried out on different glasses and glass-ceramic formulations which have shown excellent electrical insulating characteristics [10], the aim of this paper is to investigate the insulating characteristics of these glassy materials belonging to the alkaline and alkaline-earth aluminum silicate system as a function of their composition and to envisage possible applications.

2. Experimental procedures

Six different glass batches were obtained by dry-mixing grate ash of municipal solid wastes incenerator with soda-lime cullets in different ratios and melting in the 1400–1500°C temperature range. Glass sheets were obtained by pouring the melt on a graphite mould. The

TABLE I Average chemical composition (wt%) ± 0.1 of the investigated samples analysed by ICP and their detailed composition

Composition	S0 0% i.g. + 100% w.g.	S2 20% i.w. + 80% w.g.	S5 50% i.w. + 50% w.g.	S8 80% i.w. + 20% w.g.	S9 90% i.w. + 10 w.g.	S10 100% i.w. + 0% w.g.
Oxide						
SiO_2	70	71	65	60	59	53
Al_2O_3	2.2	4.6	7.0	8.1	10	12
CaO	9.3	12	14	17	17	20
MgO	2.1	2.4	2.4	2.4	2.7	2.8
Na_2O	13	8.1	7.6	5.1	4.7	4.1
K_2O	1.2	0.96	1.3	0.81	1.2	0.95
Fe_2O_3	0.29	1.2	2.1	3.5	3.6	4.4
TiO_2	0.068	0.24	0.51	0.73	0.92	1.0

w.g. = waste glass.
i.w. = incinerator waste.

sheets were then annealed at 550°C for 2 hours. Their composition is reported in Table I. Heavy metals (Pb, Cr, Mn, Ba) are present as trace and are not reported. As the grate ash fraction increases, the colour of glasses turns from a ligth green to brown and black, due to the increase of Fe_2O_3 content.

Specimens, bubbles free, were in the form of disks up to 8 mm thick and 40 mm in diameter. Specimens surfaces were polished by SiC paper of decreasing grain size till a suitable planarity was obtained.

The chemical durability was assessed by leaching tests conducted in water (ISO 719), alkali (ISO 695) and acid (DIN 12116), which simply divide glasses into categories, with the lower category number designating better durability.

Structural studies were carried out by density measurements performed by the hydrostatic method with distilled water as immersion fluid, as reported elsewhere [11].

Electrical measurements were performed in air. The volt-amperometric method was used to determine the volume electrical conductivity by means of a three-terminal electrode configuration cell according to ASTM D 257 [12]. A suitable electrode configuration was created by gold deposition *under vacuum*. Preliminary measurements carried out on different samples of the same batch provided reproducible results, thus assuring the reliability of the glass making process. An electric field of 2 kV/cm was applied. The current flowing through the samples was recorded as a function of time till 3600 s at different temperatures between 25 and 200°C. Dielectric measurements were carried out as a function of temperature (from 25 to 100°C) in the frequency range from 10^2 to 10^5 Hz by an automated LCR bridge (Hewlett Packard 4284A).

3. Results and discussion

Table II summarises the results of the chemical durability test carried out as previously described.

All the investigated glasses have high water resistance (class 1) and show a very low alkali attack (class 1) but they are subjected to acid attack, however comparable to that of domestic glasses (class 3-4). These results are important to establish the final uses of the amorphous materials, particularly for fibres of reliable durability and stable mechanical properties.

TABLE II Chemical durability class of the glasses in three reaction environments

Composition	Water durability* ISO 719	Alkali durability** ISO 695	Acid durability*** DIN 12116
S0	3	1	3
S2	2	1	4
S5	1	1	4
S8	1	1	4
S9	1	1	4
S10	1	1	4

*1 = Very high resistance, 2 = High resistance, 3 = Medium resistance.
**1 = Low alkali attack, 2 = Slight alkali attack.
***3 = Slight acid attack, 4 = High acid attack.

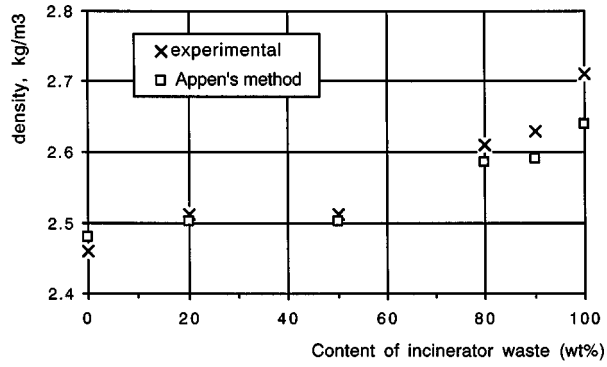

Figure 1 Density plot comparing the experimental data with those calculated by mathematical approach of Appen.

Fig. 1 reports density values of glasses: this parameter responds to variations in glass composition much more sensitively than any other physical property of glass. It is possible to compare experimental data with mathematical models (which consider each single oxide forming the glassy structure) and also to gain informations about the structure of the system by the V_M (the volume occupied by 1 mol glass) parameter [11]. The Appen mathematical model based on the addivity of "partial densities" of the oxides present in the glass,

$$d = \Sigma \delta_i m_i$$

where d is the glass density, δ_i is the density of the single i oxide bound in the glass and m_i is the mol% of oxide i, has been applied [13]. The partial quantities δ_i are constants evaluated for some specific glassy systems and are valid only over the range 0-m_i which is specified for each generic oxide i [13].

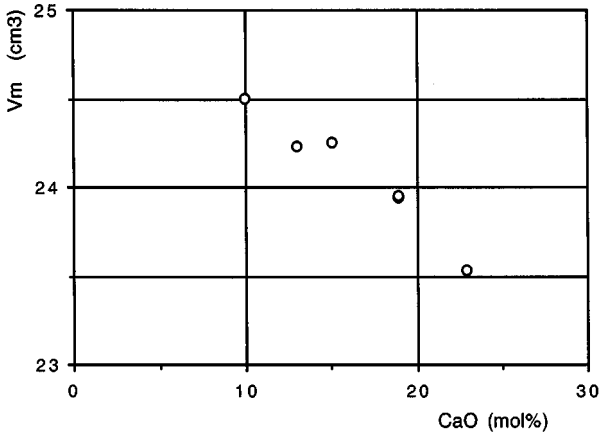

Figure 2 Plot of V_M versus the CaO mol% content.

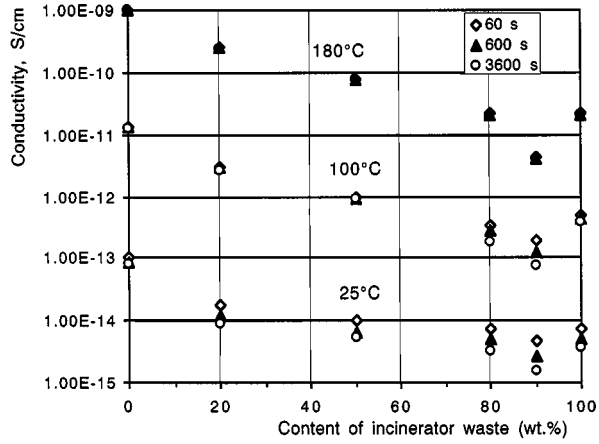

Figure 4 Conductivity after 60, 600 and 3600 s voltage application at 25, 100 and 180°C for all investigated glasses.

The satisfactory agreement between the experimental and the theoretical values calculated by the Appen method supports this mathematical approach as being the most reliable and up-to-date in the literature, since it considers both the atomic weight and the coordination number of the cations. The increase in density with the amount of incinerator wastes is in accordance with the variation in chemical composition. In Fig. 2, the volume of 1 mol glass ($V_m = \Sigma x_i M_i/\rho$, where x_i and M_i are, respectively, the molar fraction and the molecular weigth of each component i, and ρ is the experimental density of the glass [14]) is plotted as function of the CaO mol% in the glasses.

Indeed from S0 to S10 glass, the entrance of a growing amount of the alkaline-earth ions (especially Ca^{2+}, see Table I) in the interstitial holes of the network, produces a mass concentration related to a decrease in volume (Fig. 2) and a consequent densification (Fig. 1).

Fig. 3 shows the values of electrical conductivity after 60 s voltage application for all the investigated samples as a function of the reciprocal absolute temperature. Since the electrical conductivity of most common glasses results from ionic transport of monovalent cations, glasses that are free of this kind of ions exhibit very low electrical conductivities. The addition of alkaline oxides to any of the glass formers, leads to a significant increase (many orders of magnitude) in the cationic conductivity of the glass [15]. The electrical conductivity therefore decreases as the incinerator waste content increases because of the alkaline-earth oxides content (in particular CaO) increases, while alkaline oxides (in particular Na_2O) content lowers. Indeed, it is known that Ca^{2+} strengthens the silicate network, hindering the motion of alkali metal ions under the electrical field [16]. Therefore, S8, S9 and S10 compositions exhibit the lowest values of conductivity.

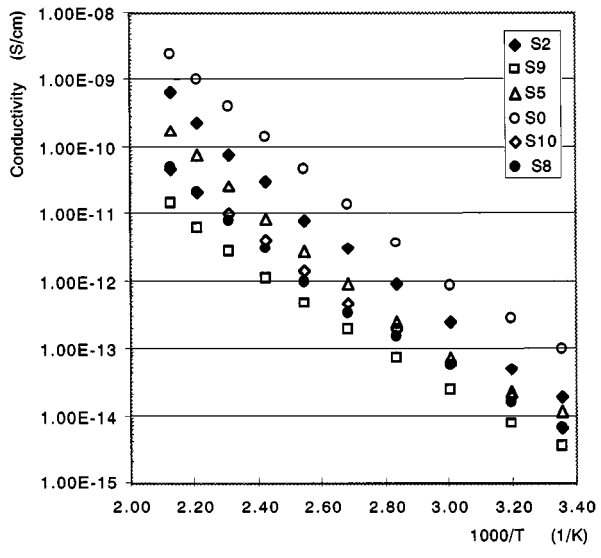

Figure 3 Electrical conductivity after 60 s voltage application as a function of temperature for all the investigated samples.

Above 80 °C ($1000/T = 2.83$ K^{-1}), a linear trend of conductivity vs. the reciprocal absolute temperature can be assumed for all the samples (the correlation coefficient for the linear regression is higher than 0.99 in all glasses), and an apparent activation energy of 65 to 70 kJ/mol can be calculated: values characteristic of glasses containing alkali are in the range 29–84 kJ/mol [17].

Fig. 4 reports the values of conductivity after 60, 600 and 3600 s voltage application at 25, 100 and 180 °C, as a function of the incinerator waste amount. At room temperatures, values of conductivity decrease as the elapsed time from the setting of the electrical field increases on account of the electrical charge transient typical of insulating materials. A minimum for conductivity, at all investigated times, is found at 90 wt% of incinerator waste. This composition shows also the largest charge transient as a function of time. This effect may only be related to the composition difference detectable in samples S8 and S9, which differ only in the alumina content (8.1 to 10 wt%, Table I). Indeed the other oxides content is almost the same, particularly for those affecting electrical conductivity ($CaO + MgO$ 19.4–19.7 wt.%; $Na_2O + K_2O$ 5.9 wt.%; Fe_2O_3 3.5–3.6 wt.%). Indeed this effect cannot be noticed in Figs 1 and 2: hence it may be inferred that in almost the same glass structure, Al_2O_3 can play a significant role in decreasing the electrical conductivity. The conductivity increase, which instead takes place in the S10 sample, may be ascribed to the increase in iron content. As temperature increases, all charge transients are reduced and conductivity rapidly reaches almost steady-state values at the highest temperatures.

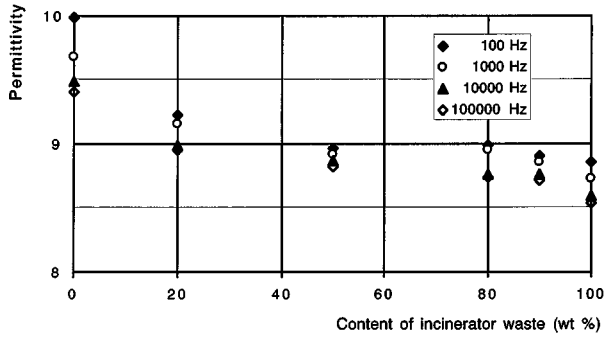

Figure 5 Permittivity as a function of glass composition and frequency at 25°C.

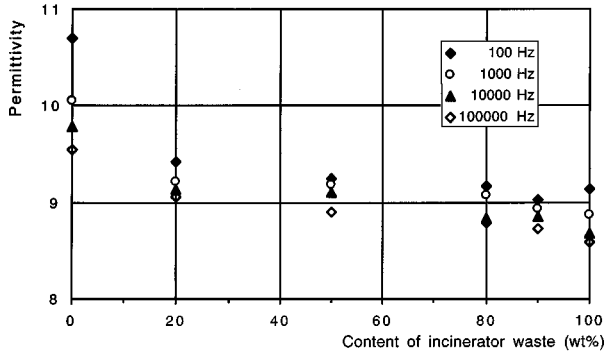

Figure 6 Permittivity as a function of glass composition and frequency at 50°C.

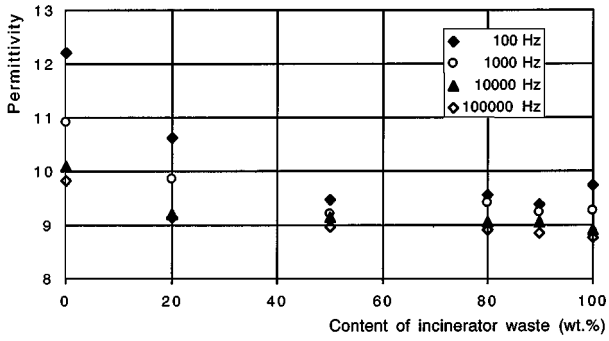

Figure 7 Permittivity as a function of glass composition and frequency at 100°C.

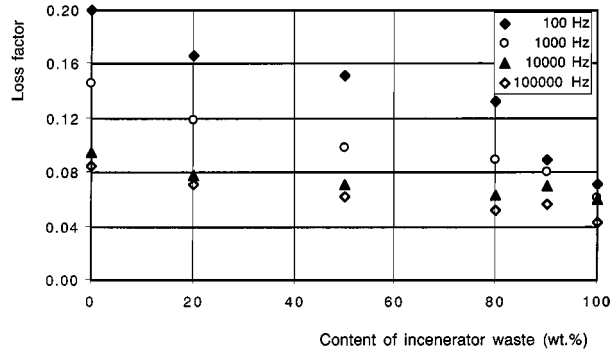

Figure 8 Loss factor as a function of glass composition and frequency at 25°C.

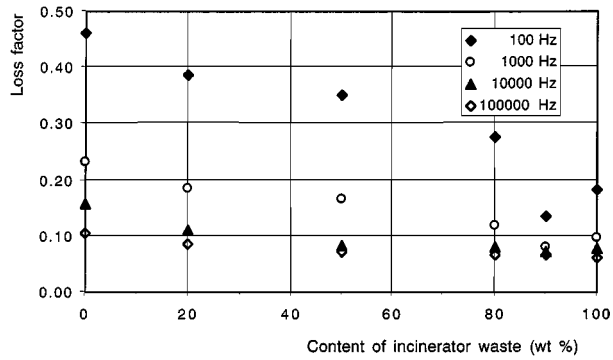

Figure 9 Loss factor as a function of glass composition and frequency at 50°C.

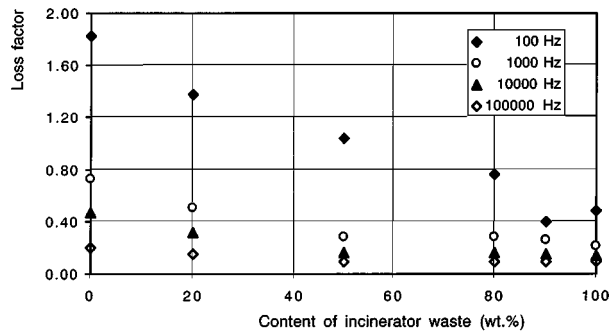

Figure 10 Loss factor as a function of glass composition and frequency at 100°C.

As far as the dielectrical behaviour of the glasses is concerned, Figs 5, 6 and 7 depict the values of permittivity as a function of glass composition at some frequencies at 25, 50 and 100 °C respectively. Values are somewhat higher than those recommended for E glass fibres (around 6 at 25°C [18]), however the increase in incinerator waste content lowers permittivity and the effect of temperature and frequency is levelled. Indeed, on introducing alkaline oxides into the glassy structure, this property, that is dependent on the atomic polarizability of the constituents, increases because of both the high polarizability of these ions and the increase of nonbridging oxygens, that are more polarizable than the bridging ones. Moreover, all glasses containing alkaline ions show an increase in permittivity with temperature due to their greater mobility: this is the reason why the effect of the temperature is reduced in the samples containing the highest incinerator waste content.

Figs 8, 9 and 10 depict the loss factor as a function of glass composition at different temperatures (25, 50 and 100°C) in the same investigated frequency range.

From the figures it can be noticed that the behaviour of the loss factor closely follows the trend previously outlined for conductivity (Fig. 4). Values steadily decrease as the incinerator waste fraction increases: a minimun is obtained for the S9 sample, except at room temperature, presumably due to the lower mobility of charge carriers. The contribution of charge carrier is further underlined considering that the minimum is particularly evident at 100 Hz. These results strenghten the conclusions drawn on the structure of the glassy network by elaboration of density measurements. It can be concluded that these glasses, which have been obtained from waste residues, exhibit interesting insulating characteristics both in a.c and particularly in d.c. conditions.

4. Conclusions

Incinerator wastes (Reggio Emilia, Italy) can be easily vitrified without modifying their composition. They exhibit good resistance to chemical attacks: if compared to glasses deriving from the traditional municipal waste recycling they present a reduced amount of alkaline oxides and an higher amount of alkaline-earth oxides. Their particular composition leads to a more compact amorphous structure of reduced molecular volume and higher density. Their electrical and dielectric properties are consequently affected: their conductivity is below 10^{-14} S/cm at room temperatures and remains at least one order of magnitude lower than that of traditional recycled glasses in a wide range of temperatures. Also their permittivity and loss factor show low values which only slightly increase as temperature rises or approaching the low industrial frequencies (100 Hz). The same considerations hold for mixtures containing up to about 20 wt% of recycled glass. A possible use of these materials to produce fibre reinforced insulators for medium-high voltage can be proposed: the increased value of the final by-product would thus lead to a more efficient recycling of incinerator wastes.

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