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Vitrification of industrial and natural wastes with production of glass fibres

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Abstract

Solid wastes coming from the municipal incinerator of Reggio Emilia, Italy, and sludge excavated from the lagoon of Venice were successfully vitrified at 1350–1500°C. Glass cullet, coming from a community glass recycling program, was introduced in some of the batches as a melting aid. Several analyses performed on the glasses showed that the glass transition and devitrification temperatures shift to higher values with increasing amount of waste in the raw materials. The glasses obtained display a good durability. Two kinds of wastes tested in the experiments could be vitrified by themselves, with no addition of external raw materials. Glass fibres were drawn from the obtained glasses at various temperatures. Mechanical tests showed that the elastic modulus increases with the waste content, while it does not depend on the drawing temperature. The fibres possess a good tensile strength (a maximum value of 1.6 GPa was obtained).

Keywords: Fibres; Fly ash; Glass; Incinerator; Vitrification; Waste

1. Introduction

Waste management is a very important issue both from the public health perspective and the industrial point of view, because an ever increasing amount of hazardous materials need to be disposed of in a safe and economical way. The current Italian legislation encourages the valorization of disposable materials through their recycling as raw materials for the manufacture of useful products. The focus of the research, thus, has to shift from the mere inertization of toxic wastes to their use in a production cycle. Novel technologies and processes need to be developed and new markets and applications have to be found in order to progress significantly towards a global solution of the problem. In particular the development of new ceramic, glass and glass–ceramic materials, made by recycling wastes, is acquiring particular importance. Vitrification of hazardous wastes has been proposed for many years, [1–5] but so far it has been applied mainly to high level radioactive wastes. Its chief advantage is the fact that glass is the material which possesses the highest chemical stability, and it can homogeneously incorporate into its structure virtually any element of the periodic table (wastes usually have a very complex chemical composition). Furthermore, the vitrification process usually affords a large reduction in the volume of the wastes, with evident benefits in terms of long term storage or dumping. In Italy there are several typologies of waste which can be vitrified (see Table 1), and one could also consider the possibility of mixing them in order to try to obtain a raw material, and thus a product, with a constant composition. In this way, also, it would be possible to obtain a glass using only wastes as the starting material.

In Table 1 is also reported the approximate cost of dumping in 1994, an important datum to establish the

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Table 1
Typology of Italian wastes which can be vitrified (1994 data), with yearly amount produced and cost of dumping

Waste	Amount (ton/year)	Dumping cost (lit/kg) ($/kg)
Wastes containing asbestos	20,000 (in Italy)	1.400 (0.78)
Incinerator ash	57,000 (in Veneto region[a])	100–200 (0.06–0.11)
Slags	650,000 (in Veneto region)	150–300 (0.08–0.17)
Thermal power plant ash	72,000 (in Veneto region)	100–200 (0.06–0.11)
Tannery sludge	150,000 (in Veneto region)	150–200 (0.08–0.11)
Urban waters purification sludge	280,000 (in Italy)	70–80 (0.04–0.045)
Glass recycling wastes	160,000	–
Venice lagoon sludge	37,000	150–200 (0.06–0.11)

[a] Veneto is an Italian region.

overall economy of the process. To know the chemical composition of the waste is necessary for the designing of the vitrificable mixture and consequently of the characteristics of the glass or glass–ceramic products. In fact, each waste may contribute to supply an appropriate quantity of vitrifying (SiO_2, Al_2O_3...), melting (Na_2O, K_2O...) and stabilizing (CaO, MgO, ZnO, PbO...) agents in the final material, so that suitable physical–chemical properties can be obtained.[6,7] In particular, it has been shown that the matrices which are designed to develop basaltic compositions (CaO–MgO–Al_2O_3–SiO_2) possess the best properties (low leaching rate and high stability versus time and temperature changes).[8,9]

In this work, we report the results obtained for the vitrification of a mixture of cullet and ashes from a city incinerator and of sludge from the Venice lagoon. Fibres were drawn from the obtained glasses, with the intent to produce a marketable material from wastes, and thus reduce the overall cost of the process. Nowadays the most used disposal method for municipal trash is incineration (26.6 million tons produced in Italy in 1997).[10] This method is useful because it reduces by about 90% the volume of the municipal solid waste and exploits its calorific power to produce energy, but it leaves a considerable amount of solid residues. From 1000 kg of processed waste, the main residue fraction is the grate (bottom) ash (250–400 kg, waste to be disposed of in special dumps) and the boiler and filter ashes (25–35 kg, toxic waste that must be inertized before disposing in a dump). The Venice lagoon sludge comes from a project aimed at reclaiming lagoon soundings which would require the excavation from the lagoon of about 5 million m^3 of sludge in 10 years. A portion of this sludge is characterized by a content of hazardous substances (organic and metallic, mainly of industrial origin), whose natural disposal is forbidden by the Italian regulations. The glasses obtained from the incinerator bottom ash and the sludge were successfully drawn into fibres, which can find application as insulation or reinforcement materials. A complete characterization of the parent glasses and the fibres was performed.

2. Experimental

The incinerator ashes were obtained from the Reggio Emilia, Italy waste authority. Of all the solid residues coming from the municipal incinerator, bottom ash only was chosen since it is produced in greater quantity and is more suitable to develop vitreous products, as a result of its average chemical analysis (reported in Table 2, and compared to that of glasses for domestic uses). The other raw materials used and listed in the same table are sludge excavated from the Venice lagoon and glass cullet coming from a community glass recycling program. The sludge was dried (LOI = 52.6%) and treated at 1000°C in air to completely remove the organic compounds (hydrocarbons, phenols, amines, etc.) before performing the chemical analysis.

Both the bottom ash and the Venice sludge contain the characteristic constituents of glass, while glass cullet would ensure the presence of a significant amount of silica, glass former, and alkaline melting oxides which are able to decrease the viscosity of the melt. Fourteen different glasses were prepared by dry-mixing the Venice sludge (from 60 to 100 wt.%, hereafter labeled VE6–VE10 glass) or the bottom ash (from 0 wt.%, i.e. glass cullet only, labeled S0, to 100 wt.%, i.e. bottom ash only, labeled S10; the material S10 has been previously characterized)[11] with glass cullet and by melting the batches so prepared in refractory crucibles at 1350–1500°C. The melting conditions were chosen in order to keep the cost of the process as low as possible. In this work we will deal mainly with the four most representative glass compositions, i.e. S1, S5 and S10 (with 10, 50 and 100 wt.% of bottom ash waste) and VE10, i.e. 100 wt.% of lagoon sludge. These were selected to be drawn into fibres using a Pt/Rh monofilament drawing apparatus. All the fibres were obtained with a winding drum rate of 3200 rpm, but with a drawing temperature of 1275°C for the S1, S5 and S10 glasses, and of 1290, 1270, 1250, 1210 and 1190°C for the VE10 glass. The temperatures were varied in order to increase the tensile strength by decreasing the fibre diameter. Fibres S5 were also sized with γ-aminopropyl-trimethoxysilane with a double roller applicator. The

Table 2
Chemical composition of the wastes used in this study (in wt.% oxides) compared to that of glass for domestic use

Oxide	Municipal incinerator bottom ash[a]	Venice sludge	Glass cullet	Glass for domestic use
SiO_2	45.13	42.3	70.3	70–75
Al_2O_3	9.73	13.2	2.18	0.2–5
CaO	18.78	22.5	9.30	5–10
MgO	2.20	7.00	2.13	1–5
Na_2O	4.64	2.85	13.32	13–17 (Na_2O+K_2O)
K_2O	1.29	0.50	1.19	13–17 (Na_2O+K_2O)
BaO	0.17	410 ppm	0.15	–
B_2O_3	–		0.14	–
ZrO_2	0.29	285 ppm	0.06	–
PbO	0.01	500 ppm	0.074	–
TiO_2	0.93	0.72	0.068	–
Fe_2O_3	3.84	7.50	0.293	0.04–0.1
Cr_2O_3	0.04	115 ppm	0.071	–
ZnO	0.32	0.40	0.12	–
SO_3 tot	3.07	0.70	–	–
SrO	–	300 ppm	–	–
P_2O_5	1.25	0.90	–	–
MnO	–	0.11	–	–

[a] LOI (950°C) = 8%.

mechanical behavior of the fibres was evaluated at room temperature, as a function of both the composition and the drawing temperature.

The obtained glasses (quenched in air) were subjected to various characterizations: the chemical analysis was performed by induction coupled plasma (ICP, Varian Liberty 200); the thermal behavior was assessed by differential thermal analysis (DTA, Netzsch DSC 404), using glass powders less than 25 μm in size and a heating rate of 10°C/min in static air and by dilatometry (Dil, Netzsch 402 EP), using bar-shaped specimens of $4\times0.5\times0.5$ cm^3 and a heating rate of 10°C/min. The crystalline phase composition of the material was investigated using X-ray powder diffraction (XRD, Philips PW 3710); the chemical durability was assessed by leaching tests conducted in water (ISO 719), acid (DIN) and alkali (ISO 695) or in 0.5 M CH_3COOH water solution for 24 h at constant pH = 5 on crushed material with a grain size < 9.5mm. The mechanical properties of the fibres were investigated performing a tensile test using an Instron 1121 UTM with a crosshead speed of 1 mm/min. The fibre samples, approximately 7 cm long, were mounted on a paper frame, which was used to provide sufficient gripping and ensure that the fracture would occur far from the clamps. From the load vs displacement data, after measuring the fibre diameter using an optical microscope, the ultimate tensile strength, the elastic modulus and the elongation at rupture were determined. Obviously, considering the brittle behavior of the investigated material, at least 50 tests per fibre type were performed, and the relevant Weibull plots were obtained. The analysis of the fracture surface was carried out using scanning electron microscopy (SEM) (Cambridge Instruments). DTA and XRD analysis were also performed on the fibres, to investigate the possible changes induced by the drawing process.

3. Results and discussion

All the materials obtained by melting are aluminosilicate glasses, with the presence in some cases of alkaline and alkaline–earth oxides, as is shown in Fig. 1, from which it appears evident that the VE10 glass is particularly rich in Fe_2O_3. The iron oxide determines the yellow–brown color of both the bulk glass and the fibres of this composition and of the S10 one, being the remaining green or yellow.

The XRD analysis performed on the powders of the as-quenched samples confirmed their amorphous nature. In Table 3 are reported the main properties for the studied glasses. DTA and dilatometric experiments showed that the glass transition temperature, T_g, increases for the S series, with increasing bottom ash content, approximately from 570 to 640°C, while the crystallization onset temperature, T_c, shifts from 860 to 890°C. The devitrification effect becomes more evident with increasing the waste content, as expected. The linear thermal expansion coefficient, measured in the 25–500°C range, decreases with increasing the waste content, for both S and VE samples (see Table 3). Notwithstanding the complexity of the glass composition not allowing an easy interpretation, this effect is most probably attributable to the decrease of Na_2O in the resulting glasses.

Although is possible to produce fibres using any kind of glass having the suitable rheological characteristics (see Table 4), the choice of the glass composition depends mainly on the chemical durability as a function of the final uses. In this regard, the results of the tests conducted in water, ISO 719, acid, DIN, and alkali solution, ISO 695[12] are very relevant. These tests simply divide glasses into categories, where a low category number designates good durability. By adding bottom ash to glass cullet, the water durability improves (S0 = 3 = medium resistance; S1 = 2 = high resistance; S5 and S10 = 1 = very high resistance), the durability in alkali solution remains constant (S0, S1, S5 and S10 = 1 = low alkali attack) and in acid solution gets lightly worse (S0 and S1 = 3 = slight acid attack; S5 and S10 = 4 = high acid attack). Furthermore, leaching tests performed in 0.5M CH_3COOH water solution for the S-series and VE10 glasses show that all the heavy metals release values are lower than the limits imposed by the Italian environmental regulations.

Thus, considering these promising results, the glasses were drawn into fibres. This process does not cause

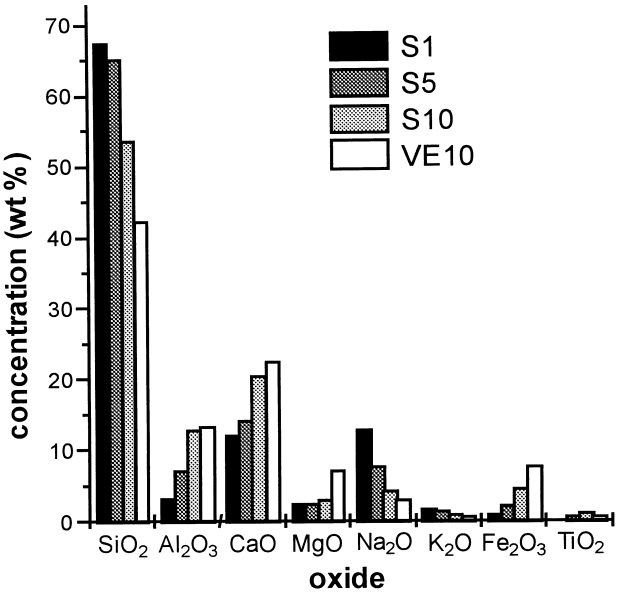

Fig. 1. Chemical composition (oxide wt.%) of the glasses studied.

Table 3
Main properties of the studied glasses

Property	T_g[a] (°C)	$T_{s(DIL)}$ (°C)	$T_{c(onset\ DTA)}$ (°C)	α_{25-500} ($°C^{-1}\times10^{-6}$)	H_V (GPa)
Composition					
S1	569	653	860	9.61	6.0
S5	608	696	868	8.75	5.8
S10	625	702	892	8.42	6.2
VE10	672	740	960	7.35	n.d.

[a] Average of DTA and dilatometric measurements.

Table 4
Calculated rheological characteristics of the glasses

Log viscosity (Pa s)	S5°C	S10°C	VE10°C
Logη 1	1510	1496	1353
Logη 2	1263	1292	1184
Logη 3	1101	1149	1070

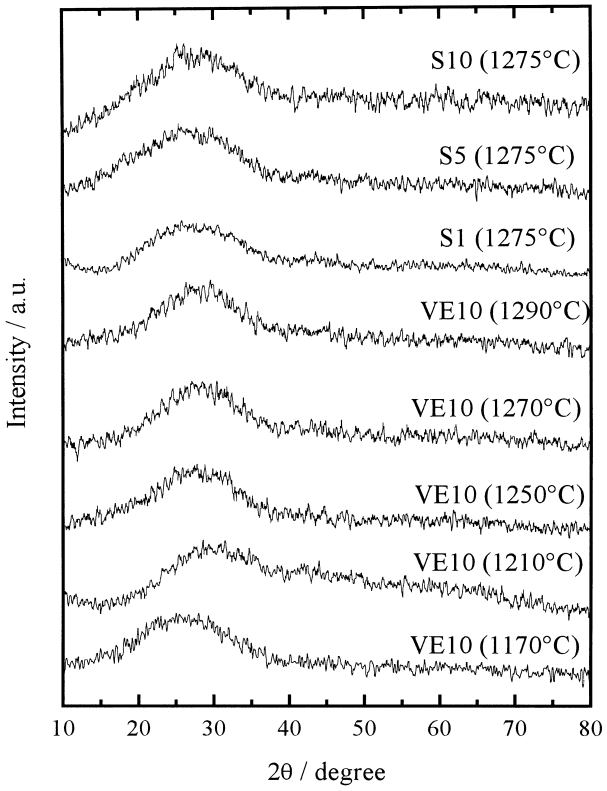

Fig. 2. XRD patterns for the eight fibres produced.

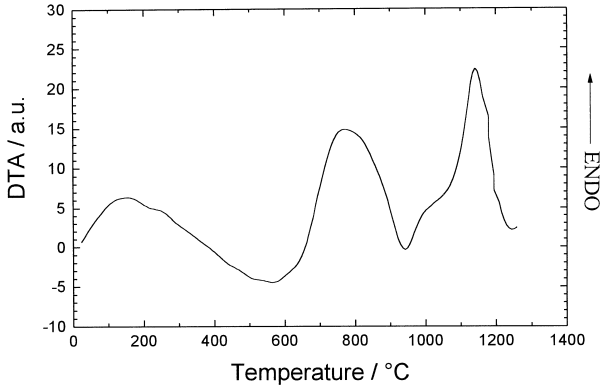

Fig. 3. DTA analysis for the S10 fibre glass.

significant modifications in the glasses. In fact, XRD and DTA analysis performed on the fibres confirm the results obtained for the bulk samples, i.e. the completely amorphous nature of the tested materials (XRD, see Fig. 2) independently of the chemical composition or of the thermal treatment, and the presence of the same thermal phenomena (glass transition, crystallization and melting temperatures) recorded in the starting as-quenched glasses (see Fig. 3). In Fig. 4 is reported a SEM micrograph of the fracture surface of a S5 fibre, whose morphology is that typical for a glass and the three regions of the mirror, mist and hackle are well visible.[13]

The average tensile strength (σ), elastic modulus (E) and diameter (ϕ) of the eight tested fibres, along with their standard deviation, are reported in Table 5, in which values for typical commercial E and S glass fibres are included for comparison. The average fibre diameter was evaluated by SEM investigations. From the analysis of the data we can observe that fibres drawn at the highest temperature (1290°C) show a more constant diameter than those obtained at lower temperatures, at which the melt viscosity is higher. Low drawing temperatures, however, are usually preferred because smaller fibre diameters can be obtained, with a concurrent increase of the tensile strength. In fact, the tensile

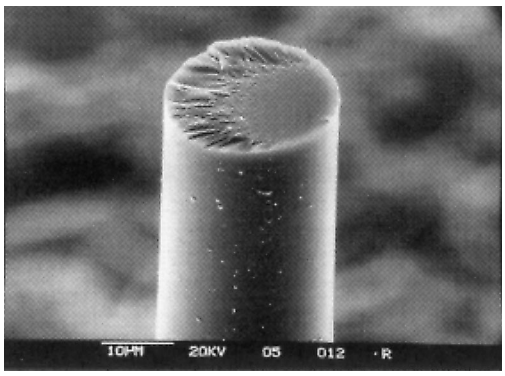

Fig. 4. SEM micrograph of the fracture surface of an S5 fibre.

Table 5
Average tensile strength (σ), elastic modulus (E), fibre diameter (ϕ) and Weibull modulus (M) for the produced samples

Sample (drawing T)	σ (GPa)	E (GPa)	ϕ (μm)	M
VE10 (1190°C)	0.78±0.26	72.9±16.2	18.2±1.8	n.d.
VE10 (1210°C)	1.58±0.58	75.2±11.8	16.4±1.5	5.18
VE10 (1250°C)	0.97±0.39	70.2±12.4	21.2±1.3	2.80
VE10 (1270°C)	1.07±0.61	70.4±14.4	24.1±1.0	1.41
VE10 (1290°C)	0.91±0.42	71.9±13.4	26.3±0.5	3.07
S1 (1275°C)	0.81±0.32	58.0±10.0	13.5±1.8	1.58
S5 (1275°C)	0.82±0.25	60.3±8.6	16.0±0.6	4.54
S10 (1275°C)	0.6±0.26	67.1±13.7	18.2±2.8	n.d.
S5[a] (1275°C)	1.21± 0.31	71.0±13.9	17.9 ±1.1	4.25
E glass	3.52	70.0	10	–
S glass	4.22	86.3	10	–

[a] With sizing.

strength of the fibres drawn at 1210°C (VE10) is the highest. Different is the situation for the bottom ash-containing series, whose drawing temperature was constant (1275°C), so that the glass composition only is responsible for the different mechanical properties. The processing conditions adopted in this study for the S-type fibres give the highest tensile strength for S1 and S5 fibres, while S10 fibres have the lowest strength value, the largest diameter, and the largest data dispersion. In Table 5 are reported the values of the Weibull modulus computed from the mechanical data by interpolating the survival probability P_S [defined in Eq. (1)] obtained by integrating the Weibull distribution[14]

$$P_S = \exp[-(\sigma/\sigma_0)^m] \quad (1)$$

m= Weibull parameter, σ_0=stress level at which the survival probability is 1/e, σ=applied stress.

The Weibull parameter m is a shape factor that determines the distribution width. The larger is m the narrower the distribution becomes, and typical values for glass are of a few units.

It can be observed that the strength values measured for all the samples are lower than those commonly reported for commercial fibres. This is due to the fact that the tested fibres were not coated with a protective polymeric layer after drawing, and this resulted in a surface damaged by handling and interaction with ambient moisture. In fact, a substantial improvement (about 40%) of the strength value is obtained for sized S5 fibres (Table 5). The elastic modulus values are consistent with the fibre composition and are comparable to that of E glass.

4. Conclusions

Municipal incinerator ash and Venice lagoon sludge were vitrified by themselves or after the addition of cullet. The obtained glasses possessed a good chemical durability, and were drawn into fibres without crystallizing. The glass transition and devitrification temperatures, as well as the devitrification tendency and the water durability, increased with increasing the waste content in the raw materials.

These findings demonstrate the possibility to convert wastes into a new marketable product with a high added value. The fibres produced had a strength lower than that of conventional fibres of glass, because their surface was not protected by a polymeric layer after drawing. The value of the elastic modulus, however, was comparable to that of E glass fibres, and increased with the solid waste content in the glass, while it did not depend on the drawing temperature.

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