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Technological properties of celsian reinforced glass matrix composites

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Abstract

Monoclinic celsian derived from an innovative route, i.e. cation exchanged zeolites heat-treated at low temperature, was added at different contents (10, 20, 30 wt%) to a glass matrix, in order to improve its mechanical and electrical performances. The effect of the celsian reinforcement was evaluated by testing several properties of the composite materials, such as the elastic modulus, abrasion resistance, flexural strength and electrical insulation. The results so far obtained suggest that the addition of the monoclinic celsian to the glass matrix may produce low-cost particulate composites with interesting technological properties.

Keywords: B. Composites; C. Electrical properties; C. Mechanical properties; D. Glass; Celsian reinforcement

1. Introduction

In the past, the monoclinic celsian (α-celsian) was extensively exploited in the manufacturing of composite materials [1–5]; in particular, it was mainly used as a matrix in fibre reinforced systems for high temperature applications. In a recent work, however, some authors also attempted an innovative approach which employed the monoclinic celsian as a reinforcement and not as a matrix [6]. As shown in previous researches [7,8], the celsian powder used in the composites fabrication could be produced by means of a non-conventional, low cost technological route, i.e. the thermal treatment of a 4A-type commercial zeolite. A tailored cation-exchange treatment of the zeolite [7] led to the insertion of a stoichiometric amount of barium ions in the structure, generating a precursor with a composition similar to that of celsian. A small concentration of residual sodium ions was left in the exchanged zeolite, since it could positively influence the formation of the monoclinic celsian during the subsequent thermal cycle that: (i) destroyed the zeolite structure; (ii) generated an amorphous solid from which, at temperatures lower than 1200 °C, monoclinic celsian crystals developed [8]. This particular synthesis proved to be economic, thanks to the cheap precursors employed and the low temperatures and short times required. Then, the feasibility of glass matrix–celsian reinforced composite materials was evaluated: a design of experiments (DOE) procedure was applied to optimize the fabrication route; the compaction pressure, as well as the temperature and soaking time, were assessed in order to obtain a fully dense material with a homogeneous particulate dispersion [6].

The present paper was focused on the evaluation of the overall technological performances of the celsian reinforced composite materials thus obtained. The properties which were taken into consideration span from the mechanical ones (flexural strength, elastic modulus, abrasion resistance) to the physical ones, and also included dc and ac electrical performance. Moreover, since the composite materials were produced with different celsian contents (10, 20, 30 wt%), the effect of various reinforcement volume fractions could be appreciated.

2. Materials and samples

The glass matrix was a commercial product (Trade name FFA 17, supplied by Colorobbia Italia, Italy): its composition was determined by means of a X-ray fluorescence (Philips, PW1480). In order to fabricate the composite materials, the glass, which was supplied in form of a frit, was ground in a ball mill and the resulting powder was sieved at 38 μm; the grain size distribution was determined by laser granulometry (Fritsch

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mod. Analysette 22). The powder was utilized to perform some characterization tests (as detailed in the following) and to produce some sintered specimens, later on designated as ''sintered glass''. These latter samples were fabricated by following the same route of the composite materials, as described in the following paragraph.

As already said, the monoclinic celsian was derived by ion exchanged 4A-type commercial zeolite, with a residual sodium ions content of 0.43 meq/g, which had been properly thermally treated; the complete production route was thoroughly described elsewhere [9]. The resulting celsian powders, which had been fully characterized in a prevoius work [6], were sieved at 38 μm and their grain size distribution was evaluated by laser granulometry as reported before.

The glass powder described above was then mixed at 10, 20 and 30 wt% of celsian, then humidified with 6 wt% distilled water and compacted under a pressure of 28 MPa, in order to obtain samples with different shapes: (i) disks with a diameter of about 34 mm and a thickness ranging from 3 to 4 mm, for the electrical characterization and mechanical tests; (ii) prisms of 4 mm × 3 mm × 45 mm, for the flexural tests; (iii) 50 mm × 50 mm square tiles of about 4 mm thickness, for the abrasion tests. Subsequently, all samples were dried for 5 h at 105 °C and subjected to the following thermal cycle: (i) from room temperature to 735 °C at a heating rate of 10 °C/min; (ii) isothermal treatment (at this temperature) for 30 min; (iii) cooling to 400 °C at 5 °C/min and subsequent quenching in air to room temperature. The conditions applied are those optimized in a previous paper through the DOE method [7].

3. Characterization and tests

The glass thermal behaviour was investigated by means of a differential thermal analysis, DTA (NETZSCH—DSC 404) and a heating microscope analysis (Expert System Solutions, Misura ODHT HSM 1600-80); in both cases, the glass samples (powders) were heated from room temperature to 1400 °C at 10 °C/min. The coefficient of thermal expansion was measured (NETZSCH—DIL 404) by heating a bulk glass bar (45 mm × 5 mm × 5 mm) from room temperature to the glass softening point at 10 °C/min. Since the thermal treatment required by the composite materials production may induce a glass devitrification, a X-ray diffraction (Philips PW 3710) was performed on the sintered glass as well as on the composites (finely ground powder samples). Patterns were collected using a powder diffractometer (Philips PW3710) with a Ni-filtered Cu Kα radiation, working in the 10–60° 2θ range, step size 0.02° 2θ and 1 s data collection time step.

Scanning electron microscopy observations (Philips, mod. XL 40) were performed on the cross-section of the sintered glass and the composites.

The effect of the celsian addition on the mechanical performances was evaluated via flexural strength tests (three-point bending test; span length: 1.8 cm; number of tested specimens for each material: 20). Moreover the Young's (and shear) modulus of the sintered glass and the composite materials were measured by means of a resonance based technique (EMOD, Lemmens Grindosonic® MK5) on bar shaped specimens (about 52 mm × 20 mm × 5mm). The mechanical characterization also included abrasion tests, which were carried out according to the UNI EN standard.

Eventually, samples (cylindrical) were submitted to ac and dc electrical characterization in nitrogen atmosphere, by means of a three-terminal cell; the electrode configuration was obtained by surface gold coating under vacuum. The ac dielectric constant and loss factor were determined over the frequency range 10^{-2} to 10^{6} Hz (by means of the Novocontrol Instrument WinETA 3.9) and temperature range from 25 to 150 °C. The dc conductivity was measured over the same temperature range under an electrical field of 1 kV/cm, by the voltmeter–ammeter method (Keithley mod. 237 voltage supplier and mod. 6514 electrometer). Discharging currents were also recorded to investigate the ultra-low frequency ($<10^{-2}$ Hz) behavior of loss factor by means of Fourier transform.

4. Results and discussion

The glass matrix composition, as determined by XRF, is reported in Table 1, while the glass particle size distribution is represented in Fig. 1. The distribution shows a monomodal trend, with D50 at about 10 μm and D90 at about 12 μm. As a comparison, the granulometric analysis of the celsian powder, which is slightly finer, with D50 at about 4 μm and D90 at about 11 μm, is also plotted.

Table 1
Oxide wt% composition of the glass matrix

Oxide	wt%
Na_2O	0.16
K_2O	0.16
MgO	0.16
CaO	10.00
B_2O_3	30.50
Al_2O_3	13.50
SiO_2	37.15
Li_2O	1.37
BaO	7.00

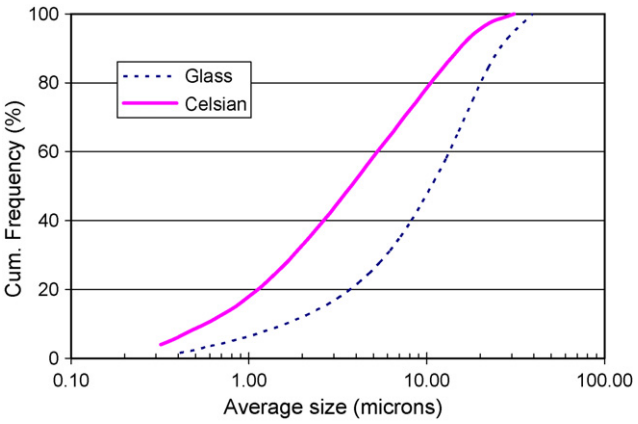

Fig. 1. Grain size distribution of the powders.

Table 2
Glass characteristic temperatures

Sintering point	711 °C
Softening point	782 °C
Sphere point	847 °C
Half-sphere point	873 °C
Melting point	902 °C

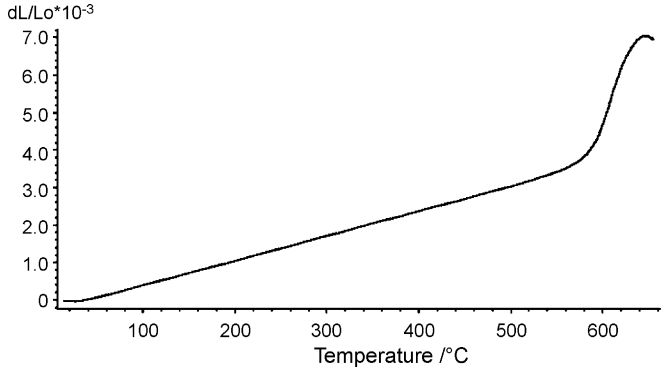

Fig. 2. Dilatometric curve of the bulk glass.

The DTA shows that the glass transition occurs at about 585 °C; if the temperature is further increased, the DTA curve does not exhibit significant peaks, thus suggesting that the glass remains substantially stable. The glass characteristic temperatures, as deduced by the heating microscope investigation, are listed in Table 2. The dilatometric curve (Fig. 2) confirms that the glass transition occurs at about 590 °C, while the softening point is reached at about 642 °C. The mean coefficient of thermal expansion, estimated from 100 to 500 °C, is $6.6 \times 10^{-6}\,K^{-1}$.

The diffraction analysis of the composite materials did not identify any significant crystal phase except the celsian which was used as reinforcement [6]. This proves that the glass did not experience any relevant crystallization during the composite materials production, coherently with the DTA results.

The microstructures of the sintered glass and the 30 wt% composite are reported in Fig. 3a and b, respectively: although some residual closed porosity is still present, as already found in [6], both materials appear to be rather compact. Moreover, as regards the composite, the white spots which represent the celsian crystals look to be efficiently embedded in the gray amorphous matrix.

The flexural strength of the glass matrix and the composites is reported in Fig. 4. Above 10% of celsian content, a steady increase is found till an almost double strength is achieved at 30%. The celsian content of 10 wt% is not sufficient to significantly improve the mechanical performances of the composite materials with respect to the glass matrix: it may be evinced that the addition of the celsian is effective only if the reinforcement weight fraction is not lower than 20 wt%. Therefore all the subsequent characterizations were performed on the composite materials containing 20 and 30 wt% of celsian.

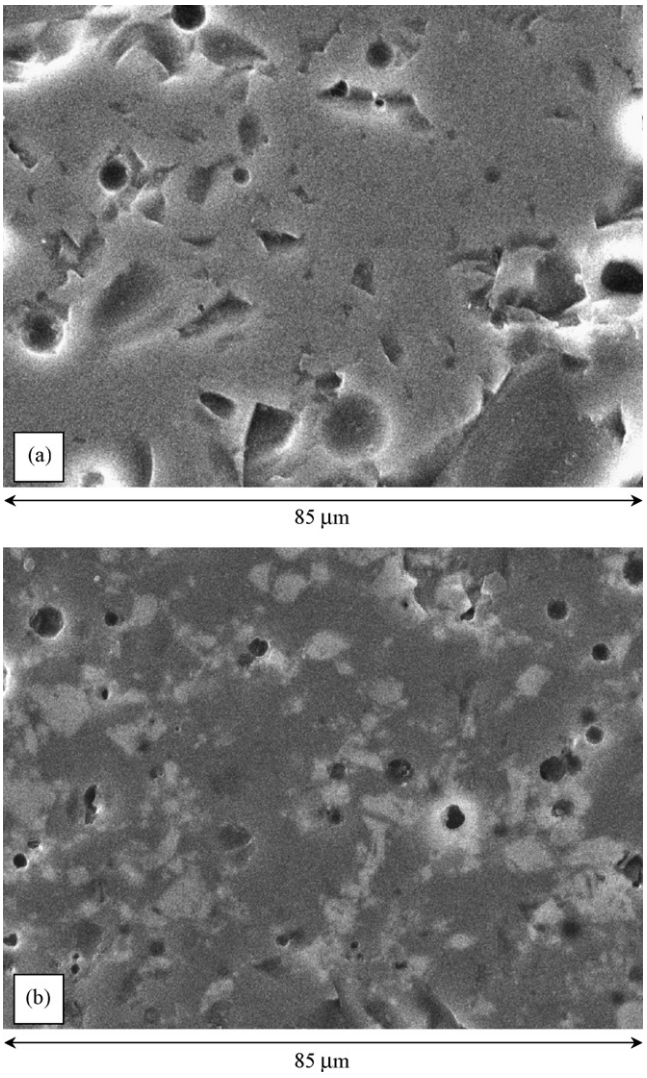

Fig. 3. SEM images of the sintered glass cross-section (a) and the 30 wt% composite material cross-section (b) (brighter areas: celsian reinforcement).

Table 3 summarizes the data relative to the elastic properties of the investigated composites, as deduced by the resonance based measurements: it can be seen that the introduction of the celsian reinforcement is beneficial at both 20 and 30 wt% composites.

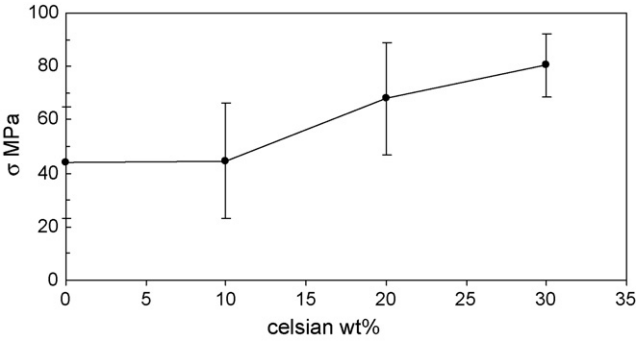

Fig. 4. Flexural strength of composites vs. the amount of α-celsian (confidence limits at 80% of probability).

Table 3
Young's and shear moduli

Sample	E (GPa)	G (GPa)
Glass	52.3	40.0
20 wt% composite	63.6	25.1
30 wt% composite	66.4	26.1

Table 4
Abrasion resistance

Sample	L_{av} (mm)	V_{av} (mm^3)
Glass	33.75	323
20 wt% composite	31.50	262
30 wt% composite	30.25	232

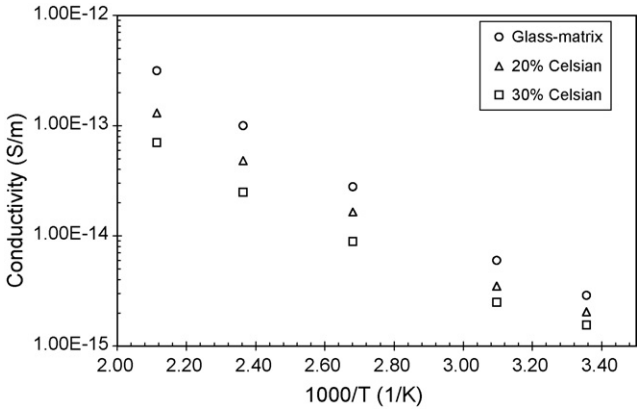

Fig. 5. Conductivity vs. reciprocal of absolute temperature for the glass matrix and the 20 and 30 wt% composites.

Abrasion test results are reported in Table 4, where L_{av} is the average radius of the abraded area and V_{av} is the average abraded volume of material (wear volume). The abrasion resistance of the composite materials, as well as the previously described mechanical performances, can be progressively increased with respect to the glass both at 20 and 30 wt% content.

As regards the electrical characterization of the composites, Fig. 5 reports the electrical conductivity at 3600 s after voltage application in the temperature range from 25 to 200 °C. At the highest celsian content, the electrical conductivity decreases up to 1 order of magnitude, thus enhancing the insulating properties of the materials. At higher temperatures, instead, all composites have almost the same conductivity (not reported); this result can be explained in terms of the increase in conductivity of the celsian phase, which is caused by the presence of the residual alkali ions in its structure as previously observed [10]. Figs. 6 and 7 show the dielectric constant and loss factor for the same samples of Fig. 5. Again, the addition of α-celsian decreases both the dielectric constant and dielectrical losses, providing a more efficient insulating material. It is important to notice, in the reported graphs, the absence of polarization processes of the Maxwell–Wagner–Sillars type (which would appear as maxima in the loss factor versus frequency plots), a feature which is further confirmed also in the ultra-low frequency range data (10^{-2} to 10^{-5} Hz) derived by Fourier transform of discharging currents and not reported for the sake of brevity. Since this process would arise from phase discontinuity in the materials, their absence can rule out the presence of porous interfaces, even of low dimension, between the glass matrix and celsian phase, thus confirming the previously described SEM microstructural features.

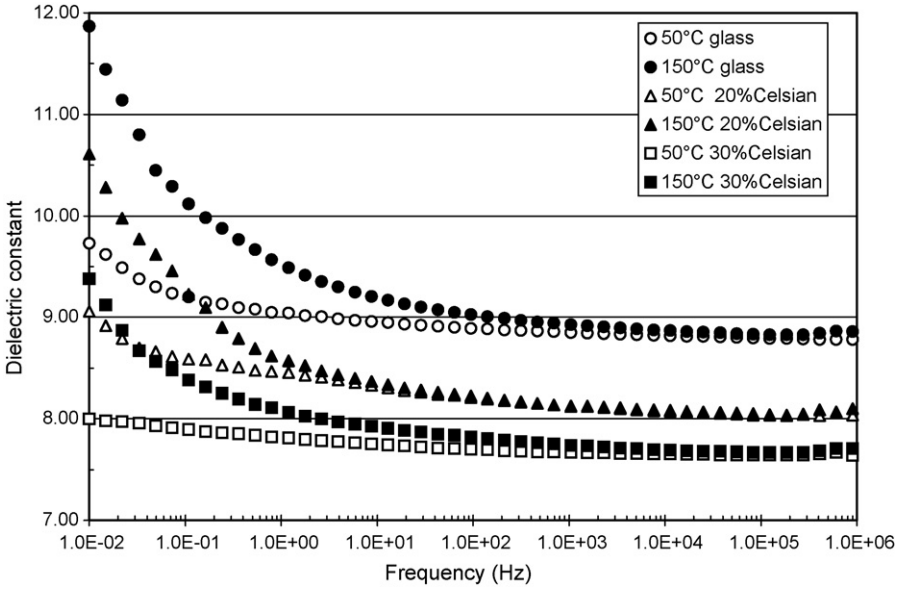

Fig. 6. Dielectric constant vs. frequency for the glass matrix and the 20 and 30 wt% composites at different temperatures.

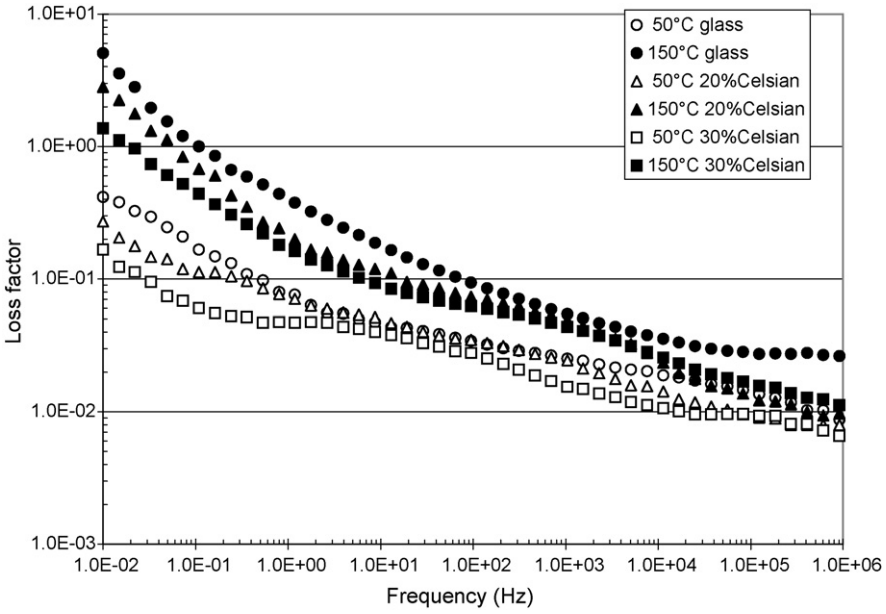

Fig. 7. Loss factor vs. frequency for the glass matrix and the 20 and 30 wt% composites at different temperatures.

5. Conclusions

The present research proved that it is possible to obtain composite materials starting from a commercial glass matrix and a low-cost α-celsian derived by an innovative production route: such composites have compact microstructures and good thermal stability. The mechanical and electrical characterization of these composite systems, which were produced with different reinforcement weight fractions (up to 30 wt%), prove that interesting performances can be achieved. In fact, though low celsian contents (10 wt%) are not sufficient to relevantly improve the composites properties with respect to the glass, higher celsian concentrations (20 and 30 wt%) result in increased mechanical and electrical insulating properties, since the Young's modulus, flexural resistance and abrasion resistance are enhanced, while bulk conductivity, dielectric constant and dielectric losses are decreased.

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