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SiOC glass modified by montmorillonite clay

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Abstract

The addition of inexpensive montmorillonite clay to a silicone resin employed as preceramic polymer was found to be advantageous for the production of SiOC glass matrix composites. Dense SiOC based monoliths were achieved with the addition of a substantial amount of calcined clay (30 wt.%) to the preceramic polymer; these composites exhibited remarkable hardness and fracture toughness, higher than those of SiOC glasses reported in the literature, due to the very small dimensions of silica and mullite crystal inclusions deriving from the decomposition of clay.

Microcellular SiOC glass based microcellular foams were also produced, from composites filled by both calcined and organically functionalized clay. The inclusions from the decomposition of clay provided for the retention of the microcellular structure even after oxidation at 1200 and 1450 °C. Functionalized clay showed a more pronounced effect in limiting the extent of the densification and collapse of microcellular shape than calcined clay. In both cases, the crushing strength after oxidation was found to be particularly remarkable.

Keywords: B: Nanocomposites; C: Mechanical properties; D: Glass; E: Thermal applications

1. Introduction

Silicon oxycarbide (SiOC) glasses are amorphous ceramics in which silicon atoms are bonded to both oxygen and carbon atoms. Owing to the fact that carbon may link more silicon atoms compared to oxygen (C may sustain four Si–C bonds, while O may sustain only two Si–O bonds) [1]. SiOC glasses are known to possess superior mechanical, thermal and chemical properties when compared to ordinary silica-based glasses. In particular, the characteristic temperatures of SiOC glasses are higher than those of the most refractory pure oxide glass, i.e. silica glass, so that a growing employment in high temperature applications is expected.

SiOC glasses may be produced from an important typology of preceramic polymers, that of polysilsesquioxanes with the general formula $[R_nSiO_{(2-0.5n)}]_m$. R represents the chemical groups that are directly linked to silicon atoms, such as methyl, vinyl or phenyl groups (in certain cases also hydrogen atoms). m represents the number of repetitive units in a macromolecule. If there are units with $n \leq 1$, exhibiting silicon atoms bonded to three or four oxygen atoms, the preceramic polymer possesses a three-dimensional structure, which is typical of ‘‘silicone’’ resins [1,2]. It must be noted also that hydroxyl-substituted variants (some of the R groups are –OH) are generally available, offering the possibility to introduce a certain degree of crosslinking between different macromolecules via condensation reactions at low temperatures (50–100 °C).

The polysiloxane is typically converted to SiOC glass via heat treatment in an inert atmosphere (pyrolysis), from a temperature of about 500 °C, although the completion of such reaction generally requires temperatures exceeding 1000 °C. This approach has however a significant technological limit: upon heat-treatment, the polymer/ceramic conversion occurs with the release of a great amount of gases (mainly hydrocarbons [1]), which results in a remarkable volume contraction (about 60%) typically accompanied by the formation of cracks and pores. Consequently, at present SiOC glasses are mostly employed for the definition of

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objects with limited dimensions, like fibers, thin films, microtubes [3] or thin-walled ceramic foams [4,5]. SiOC glass monolithic objects are mainly formed by high temperature (about 1600 °C) hot-pressing treatment of pre-pyrolyzed SiOC glass powders [1]. The need for exploiting the typical advantage of preceramic polymers, that of plastic-forming ability, consisting of the possibility of flowing above the glass transition temperature and cross-linking to retain the acquired profile after shaping, leads to the research of new processing routes for manufacturing SiOC objects directly after pyrolysis. A relatively large research activity has been conducted on monoliths whose structural integrity upon heat-treatment is due to the chemical reaction between the preceramic polymer and a reactive filler material [6]. The reaction between the polymer and metallic fillers, in fact, causes the formation of secondary phases, mainly consisting of carbides [6]. Reactive fillers may be regarded as "active" fillers, since they modify substantially the chemical composition of the preceramic polymer upon the same heat treatment. Less work has been conducted, however, on the introduction of inert, "passive" fillers, whose activity depends only on the "dilution" of the transforming mass upon pyrolysis. Inorganic materials, like various oxides, may represent passive fillers. It should be noted that, upon the oxidation of SiOC glasses, after pyrolysis, these oxides may react with the matrix, thus yielding a material with improved oxidation resistance.

The aim of the present work was the development of economical products, in which SiOC glass was modified with the introduction of inexpensive clay in the preceramic polymer. Clay aggregates are widely employed as filler in a very broad range of polymers [7]; further dispersion of the individual single clay layers leads to the formation of nanocomposites with dramatic improvements in the polymers' rheological and mechanical properties [8–12], and the same was found also when using silicone resins [13]. We employed organically modified montmorillonite clay with a specifically designed chemical functionalization for promoting dispersion in polymers. We also employed, for comparison, the same clay after a calcination treatment, in order to remove both the organic functionalization and the structural water content, which could be detrimental to the structural integrity of the SiOC glass based products, since they increase the amount of gases released upon pyrolysis.

2. Experimental

The preceramic polymer consisted of silicone resin SOC-A35 (Starfire Systems, Malta, NY, USA). Both pristine resin and fully cross-linked resin were employed. SOC-A35 is a methyl polysiloxane. The thermal cross-linking of the pristine resin usually starts from a temperature of 60 °C and occurs via the condensation of silanol groups. The polymer/ceramic conversion begins at about 500 °C [1].

The filler material consisted of hydrophobic montmorillonite clay I42E (Nanocor, IL, USA) modified with dimethyl,dioctadecyl-N^+ functionalization. Some clay was calcined overnight at 800 °C, in order to remove both the functionalization and the intrinsic structural water content. The weight loss upon calcination was evaluated, by using thermogravimetrical analysis (DSC g404, Netzsch Gerätebau GmbH, Selb, Germany), to be about 50%, as illustrated in Fig. 1.

Monoliths and microcellular foams were obtained by different processes. In the first case, functionalized clay or, as an alternative, calcined clay was added, in a concentration of 30 and 40 wt.%, to previously finely powdered SOC-A35 (grains with a few micrometers of average dimension); the mixtures were mechanically mixed for 30 min in a dry ball mill. The SOC-A35 powders consisted of a mixture of pristine and cross-linked resin (1/3 pristine – 2/3 cross-linked). The use of cross-linked resin followed what suggested in the literature for achieving bulk components [14].

The SOC-A35/clay mixtures were warm pressed at 15 MPa and 150 °C for 10 min. The produced discs, with a 40 mm diameter and about 3 mm high, were heat-treated in inert nitrogen atmosphere at 1200 °C for 2 h (2 °C/min heating rate), causing the polymer–ceramic conversion and the formation of SiOC glass matrix composites.

In the case of microcellular foams, functionalized clay or calcined clay was dispersed in a solution of pristine silicone resin (7 wt.%) in an alcoholic medium (95% ethyl alcohol, 5% acetone), magnetically stirred at room temperature for 2 h. The dispersions were firstly dried at 60 °C overnight, in order to remove the solvent and cause the partial cross-linking of the preceramic polymer, then dry ball milled for 30 min. The silicone resin embedding clay particles was dry mixed in a ball mill with commercial poly(methyl methacrylate) (PMMA) microbeads, with a nominal dimension of 10 μm (A210, Cray Valley Waterborne Polymers Department, Atofina Italia, Milan, Italy),

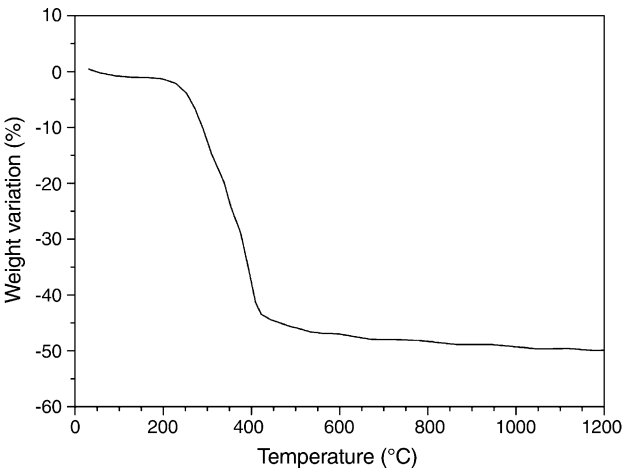

Fig. 1. Thermogravimetric plot of hydrophobic montmorillonite clay 142E.

previously dried at 60 °C. The weight ratio between the polymer/clay mixture and PMMA was fixed at 1:4. The polymer/clay/PMMA mixtures were subjected to the same warm-pressing treatment employed for monoliths. After warm-pressing, discs with a 40 mm diameter and about 8 mm high were heat-treated at 300 °C for 1 h (0.5 °C/min heating rate) in a furnace with an oxidative atmosphere, in order to burn-out the PMMA microbeads and obtain a microcellular structure in the preceramic polymer embedding the clay particles. The microcellular preceramic polymeric foams were converted to microcellular ceramic foams following the same heat-treatment in nitrogen atmosphere employed for the monoliths. After pyrolysis some samples were subjected to oxidation treatments, at 1200 or 1450 °C for 1 h, in air (5 °C/min heating rate).

After thermal treatments, both the monolithic and microcellular samples were subjected to mechanical testing. The monolithic SiOC glass matrix composites were cut into beam samples of about 3 mm × 2 mm × 25 mm. All samples were carefully polished to 1 μm finish, by using abrasive papers and diamond paste. The edges of the bars were beveled by using fine abrasive papers and diamond paste. Four point bending tests (20 mm outer span, 8 mm inner span) were performed by using an Instron 1121 UTS (Instron Danvers, MA), with a crosshead speed of 0.02 mm/min. Each data point represents the average of 5–10 individual tests. Polished samples were employed for Vickers' indentation tests, which yielded the hardness (H_V), at low load (500 g), and the indentation fracture (K_{IC}), at high load (2000 g), of the investigated materials. The indentation fracture toughness was calculated by using the well-known equation of Anstis et al. [15], starting from the measured length of cracks emanating from the corners of the Vickers' indents. The reference Young's modulus was measured by means of an acoustic resonance method (Grindosonic, J.W. Lemmens, Belgium). The apparent density of the SiOC glass compacts was measured by the Archimedes' principle. At least 10 fragments were analyzed for each sample. The skeleton density of the samples was measured from powdered samples by means of a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA).

The microcellular SiOC foam specimens were cut into ~6 mm × 6 mm × 6 mm specimens. The samples were gently polished with abrasive paper, and then subjected to compression tests by using the previously mentioned Instron 1121 UTS machine, with a crosshead speed of 2 mm/min. Each data point represents the average of 5–10 individual tests.

The fracture surfaces of both monolithic and microcellular samples were characterized by Scanning Electron Microscopy (Philips XL 30 ESEM). Selected composite samples, carbon-coated, were subjected to energy dispersive spectroscopy (EDS) analysis. Samples in powder form were investigated by X-ray diffraction (XRD, Philips PW3710), by using Cu Kα radiation (λ = 0.15418 nm).

Table 1
Geometric and bulk density of SiOC glass compacts modified with clay

Calcined clay addition (wt.%)	Bulk density (g/cm^3)	Skeleton density (g/cm^3)	Closed porosity (vol.%)
30	1.92 ± 0.29	2.30 ± 0.03	16.5
40	2.14 ± 0.04	2.34 ± 0.04	8.5

3. Results and discussion

3.1. SiOC monoliths

Preliminary tests on SOC-A35/clay mixtures demonstrated that only mixtures with relatively high weight fractions of clay were suitable for achieving composites with sufficient structural integrity. In fact, only with a remarkable dilution of the preceramic polymer "transforming mass", which undergoes substantial chemical and physical transformations upon heating, the polymer to ceramic conversion is not accompanied by excessive crack formation. This hypothesis was confirmed by the samples with preceramic polymer filled by functionalized clay; even though the functionalization promoted the dispersion of the clay particles into the polymer, there was a significant addition of by-products from the heat-treatment, consisting of the water present in the organically-modified clays. Only the addition of calcined clay, 30 and 40 wt.%, was found to lead to composites with no extensive cracking and limited porosity, as illustrated in Table 1. The porosity was calculated from the relative difference between bulk and skeleton density.

It must be noted that the most compact samples were those containing the highest fraction of clay. This result confirms our hypothesis on the reduction of the evolution of gases upon silicone/SiOC glass conversion with increasing calcined clay weight fraction.

The mechanical properties of the glass matrix composites are summarized in Table 2.

The mechanical data revealed a quite anomalous behavior. Although exhibiting the highest compaction degree, composites from a 40 wt.% clay addition showed a Young's modulus only slightly higher than that of composites from a 30 wt.% addition. Moreover, the bending strength, the Vickers' microhardness and the indentation fracture toughness were much lower. This "anomaly" can be elucidated by the analysis of the fracture surfaces, as illustrated in Fig. 2.

Table 2
Mechanical properties of the SiOC glass compacts modified with clay

Calcined clay addition (wt.%)	Young's modulus (GPa)	Bending strength (MPa)	H_V (GPa)	K_{IC} (MPa m$^{0.5}$)
30	78.8	62.3 ± 6.3	9.5 ± 1.2	2.2 ± 0.5
40	84.3	51.3 ± 16.8	8.3 ± 1.4	1.6 ± 0.3

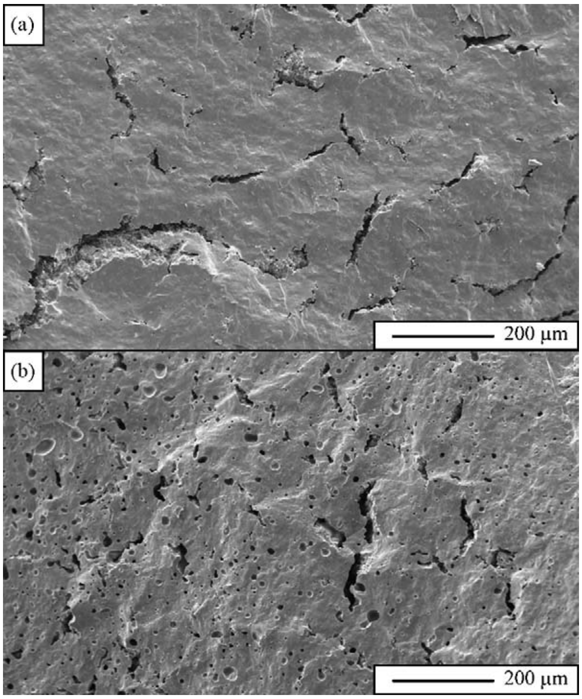

Fig. 2. SEM micrographs of the fracture surfaces of SiOC glass matrix composites: (a) 30 wt.% calcined clay and (b) 40 wt.% calcined clay.

Namely, the composites embedding 30 wt.% clay exhibited very compact and homogeneous areas divided by large cracks, originated by the pyrolysis process. On the contrary, composites embedding 40 wt.% clay had smaller cracks but also included a large number of small spherical pores. It has been already reported that, for silicate glass matrices of composites with a particulate reinforcement, the viscosity of the system greatly increases [16], especially in the case of sub-micron sized, plate- or fiber-like inclusions, causing a poor densification upon viscous flow sintering. This behavior is not consistent with the observed phenomenology, since the SiOC glass matrix originated from the polymer–ceramic conversion of a silicone resin, without sintering of previously formed glass particles; moreover, the processing temperature was far below the supposed transition temperature of silicon oxycarbide glass (T_g = 1350 °C [1,17]), so that no viscous flow was allowed. A further study on the effect of the inclusions on the formation and densification of SiOC glass upon pyrolysis of silicones will be the object of our future efforts.

Although the composites showed many residual cracks, bending strength was not very low. Since the origin of fracture in ceramics is the largest crack, and the residual cracks were many hundreds micron sized, this behavior could be attributed to the intrinsic fracture resistance of the composites, improved by the reinforcement (in an ordinary glass, the fracture toughness K_{IC} being about 0.7 MPa $m^{0.5}$, for a critical crack c of about 400 µm, the critical strength should be of about $K_{IC}(\pi c)^{-0.5} \approx 20$ MPa [18]). It is well known that in particulate composites the fracture behavior of the matrix is improved by subjecting it to a system of thermoelastic residual stresses, due to the embedding of particles with different elastic modulus and expansion coefficient, which cause crack deflection [19–23]. This hypothesis is confirmed by the indentation fracture toughness of the composites, which exceeds that of unreinforced SiOC glass. For example, Renlund et al. [17] reported an excellent value of 1.8 MPa $m^{0.5}$ for a SiOC glass fabricated by hot pressing at 1600 °C, while in more recent papers [24,25] the fracture toughness of SiOC glass did not exceed 0.7 ± 0.3 MPa $m^{0.5}$. Also the Vickers' hardness, especially in the case of 30 wt.% addition of clay (9.5 GPa), was found to be higher compared to the values reported in the literature [17,24]. It must be mentioned that both Vickers' microhardness and indentation fracture toughness analyses are referred to a very localized zone and express, when performed on the zones away from large cracks, the intrinsic behavior of the glass/reinforcement system.

The X-ray diffraction analysis of SiOC glass matrix composites, shown in Fig. 3, revealed the formation of cristobalite and traces of mullite crystals, as secondary phases in the SiOC glass matrix composites, for both clay fractions. Such phases are attributable to the decomposition of calcined clay (the pyrolysis of silicones results in fully amorphous materials), which leads to the formation of mullite ($3Al_2O_3 \cdot 2SiO_2$) and silica. It is well known that cristobalite is detrimental to the mechanical properties of ceramics, since it is subjected to a large volumetric change upon polymorphic transformation at 270 °C [26]; unlike the viscous liquid phase provided by feldspars in traditional porcelain stoneware production, SiOC glass was not able to dissolve silica from clay decomposition.

Further SEM observations, coupled with EDS analysis, confirmed the very limited dimension of the inclusions within SiOC glass, as illustrated in Fig. 4. In the micrograph,

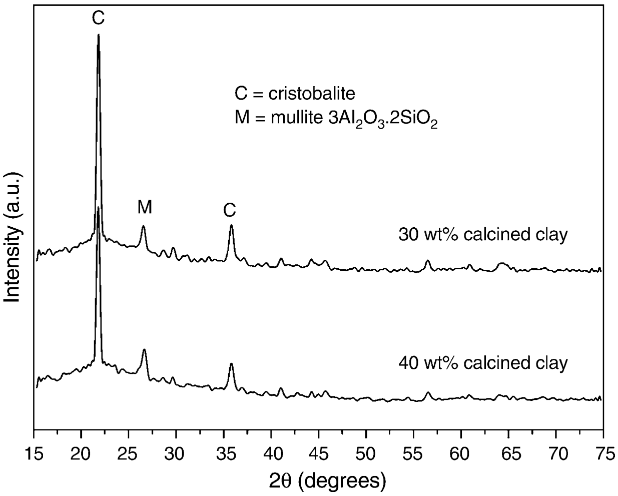

Fig. 3. XRD spectra of SiOC glass matrix composites.

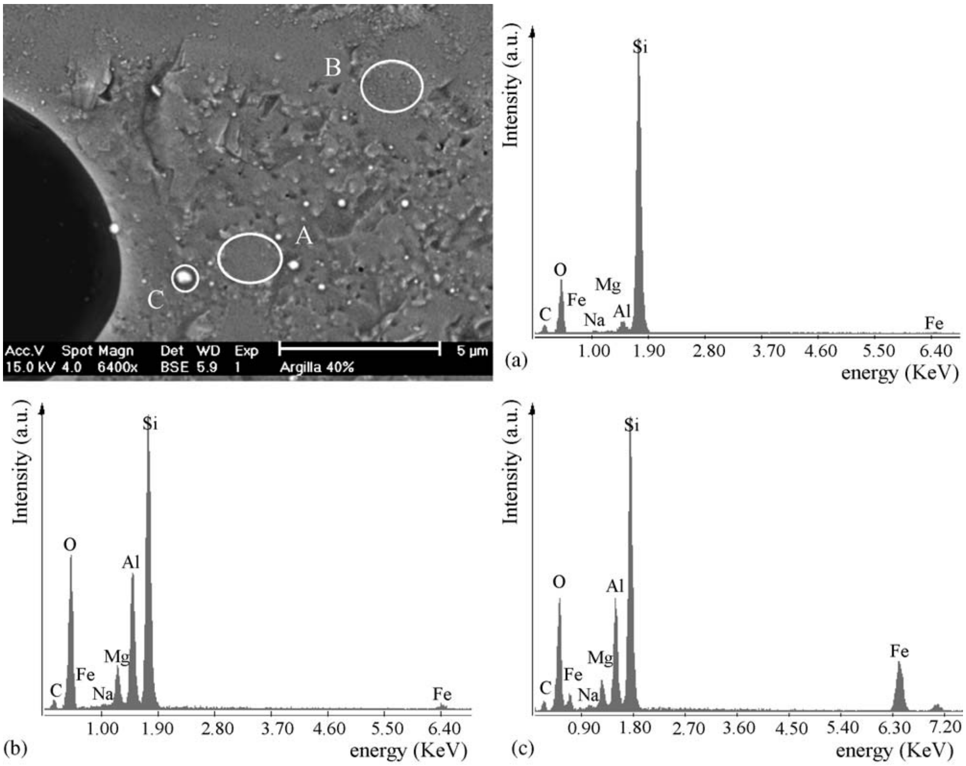

Fig. 4. High magnification SEM micrograph (back-scattered electrons) of a SiOC glass matrix composite (40 wt.% calcined clay), showing matrix zones (a) and sub-micron sized inclusions (b and c), together with the corresponding EDS analyses.

showing the microstructure of a composite (with a 40 wt.% calcined clay content) near a pore, micron-sized smooth zones (labelled ‘‘A’’), can be recognized near zones with a multitude of nano-sized particles (labelled ‘‘B’’). In addition, sub-micron sized (∼500 nm) light and almost spherical inclusions (labelled ‘‘C’’) are visible. The EDS analysis showed that the smooth zones, without any inclusion, corresponded to the SiOC glass matrix, while the zones including nano-sized particles could be attributed to the residues of clay (due to the remarkable content of Al). Also the inclusions indicated by letter ‘‘C’’ are attributable to clay residues, due to the presence of iron, which in turn is often included in montmorillonite.

The limited scale of both silica and mullite inclusions and the homogeneity of the dispersion, in the authors’ opinion, might cause the thermoelastic stresses due to polymorphic transformation to be sustainable, or even profitable, with crack deflection, as demonstrated by the improvement of fracture toughness.

On the basis of the above described phenomenology, the composite approach seems promising for the manufacturing of SiOC glass based monoliths; the future research will undoubtedly focus on the elimination of the large residual cracks, in order to extend the composites’ homogeneity and provide better bending strength. In addition, further investigation on the influence of cristobalite formation is expected, for example, by the use of clays with different alumina/silica ratio.

3.2. SiOC microcellular foams

The physical and mechanical properties of microcellular SiOC foams are reported in Table 3. The morphology of the obtained microcellular foams is illustrated in Fig. 5. The morphology of the composite foams after pyrolysis (Fig. 5a and d), consisting of nearly perfectly spherical micropores connected with each other by several openings, is analogous to that of unmodified SiOC (see [4,5]). In the case of calcined clay addition this morphology was preserved (Fig. 5b) after oxidation at 1200 °C, while for the oxidation at 1450 °C a certain densification phenomenon was observed (Fig. 5c, as depicted by the formation of large ‘‘struts’’). In the case of functionalized clay, a certain cellular morphology, although not similar to the one observed after pyrolysis, was maintained even after the oxidation at 1450 °C (Fig. 3f). One likely reason for this behavior is the increase in organic residues embedded in the preceramic polymer provided by these functionalizations; the burn out of these residues might increase the porosity (as illustrated by the decrease of relative density, see Table 3) and prevent densification. As for the monoliths, the densification phenomenon occurring in the microcellular foams needs further studies.

For open-celled foams, their crushing strength can be expressed by the Gibson–Ashby equation [27]: $\sigma_f = C\sigma_{bend}\rho_{rel}^{3/2}$, where C is a dimensionless constant, ρ_{rel} the relative density and σ_{bend} is the bending strength of the

Table 3
Physical and mechanical properties of microcellular SiOC foams

Thermal treatment	Bulk density (g/cm^3)	Skeleton density (g/cm^3)	Relative density, ρ_{rel}	Crushing strength, σ_f (MPa)	$K = (\sigma_f/\rho_{rel}^{3/2})$ (MPa)
Calcined clay					
Pyrolysis @ 1200 °C	0.49 ± 0.02	2.05 ± 0.03	0.24	2.1 ± 0.4	17.6
Pyrolysis @ 1200 °C, oxidation @ 1200 °C	0.67 ± 0.03	2.17 ± 0.04	0.31	19.5 ± 1.9	112.9
Pyrolysis @ 1200 °C, oxidation @ 1450 °C	0.69 ± 0.03	2.22 ± 0.03	0.31	8.2 ± 2.2	47.7
Functionalized clay					
Pyrolysis @ 1200 °C	0.33 ± 0.02	1.93 ± 0.04	0.17	2.2 ± 0.4	30.1
Pyrolysis @ 1200 °C, oxidation @ 1200 °C	0.34 ± 0.03	2.04 ± 0.05	0.17	2.8 ± 0.4	40.2
Pyrolysis @ 1200 °C, oxidation @ 1450 °C	0.31 ± 0.02	2.09 ± 0.05	0.15	2.5 ± 0.2	43.2

material which constitutes the solid fraction of the foam. The ratio $K = (\sigma_f/\rho_{rel}^{3/2})$ may be consequently considered as an expression of the bending resistance of the system SiOC glass/clay residues. It was found that this ratio is high compared to a large range of ceramic foams [4,5] and has a strong dependence on the typology of clay embedded in the SiOC glass and on the heat treatment.

Functionalized clay led to very lightweight foams after pyrolysis (the relative density being about 17%) with a remarkable crushing strength (2.2 MPa) when related to the K parameter (exceeding 30 MPa). Both the density and the crushing strength were almost constant after oxidation at 1200 and 1450 °C. The K ratio, however, slightly improved after oxidation at 1200 and 1450 °C.

Calcined clay led to foams, after pyrolysis, with higher density than the analogous foams from functionalized clay, but with almost the same crushing strength (2.1 MPa), thus giving a lower K ratio. The foams reached excellent crushing

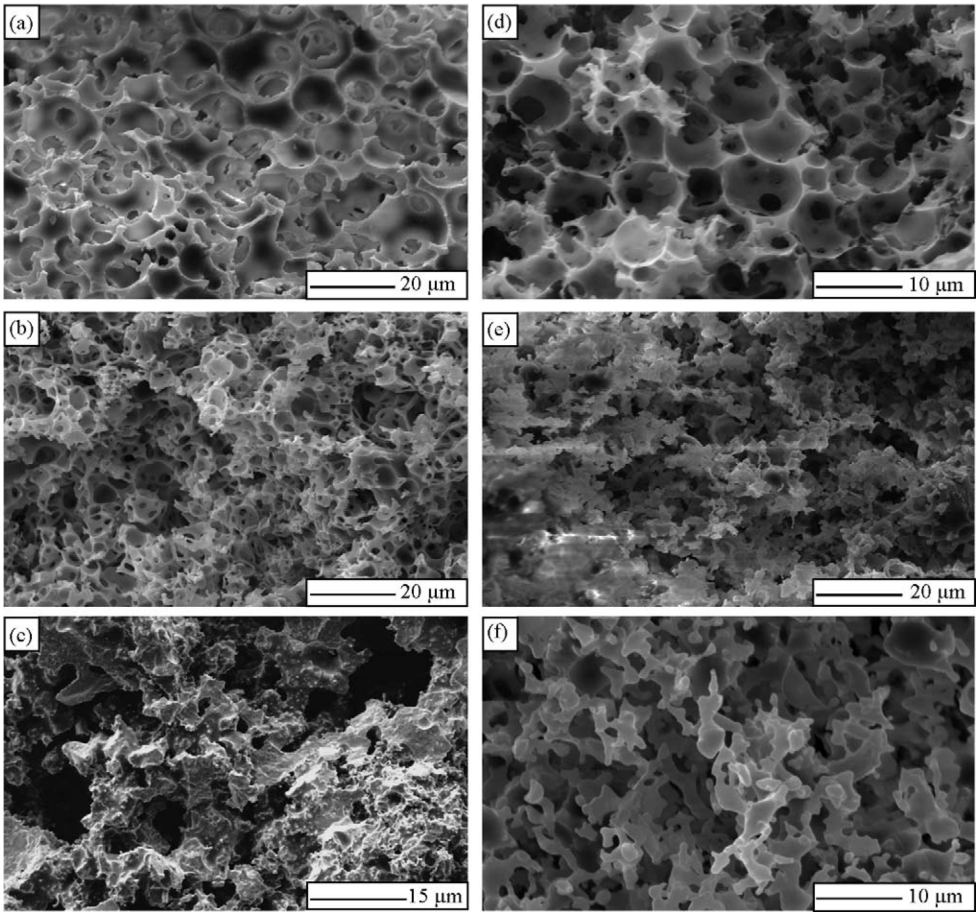

Fig. 5. SEM micrographs of fracture surfaces of microcellular SiOC/clay composite foams: (a) foam with calcined clay, after pyrolysis; (b) foam with calcined clay, after pyrolysis and oxidation at 1200 °C; (c) foam with calcined clay, after pyrolysis and oxidation at 1450 °C; (d) foam with functionalized clay, after pyrolysis; (e) foam with functionalized clay, after pyrolysis and oxidation at 1200 °C and (f) foam with functionalized clay, after pyrolysis and oxidation at 1450 °C.

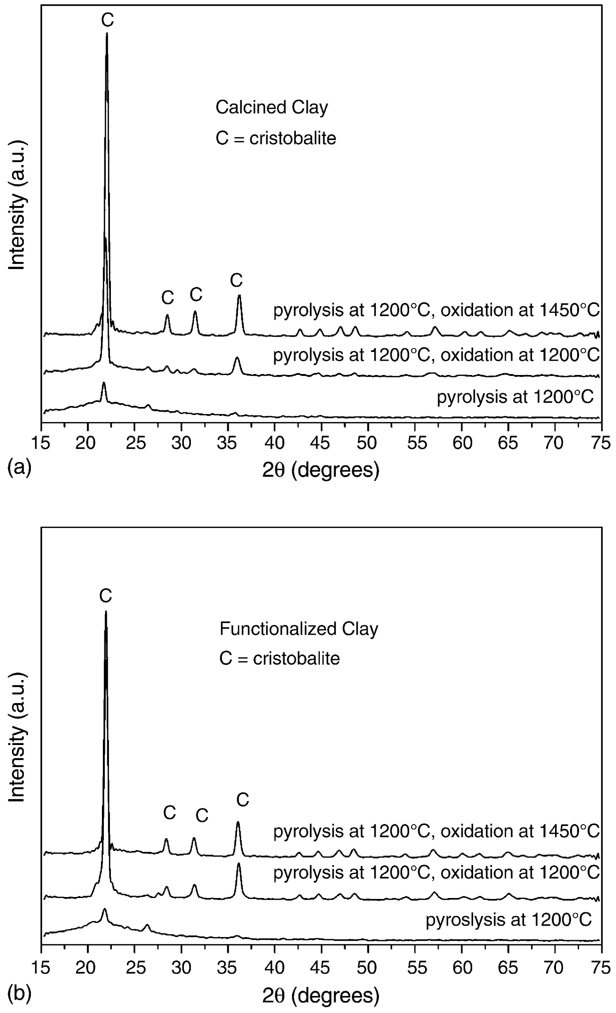

Fig. 6. XRD spectra of SiOC based composite microcellular foams: (a) foams with calcined clay and (b) foams with functionalized clay.

strength and *K* ratio values, approaching 20 MPa and exceeding 110 MPa, respectively, after an oxidation treatment at 1200 °C, with a substantial decrease after the treatment at 1450 °C.

In the authors' opinion, the mechanical behavior of the composite foams depends on the observed morphology; as pointed out for unmodified microcellular foams [4,5], the high crushing strength is related to the micron size dimension of the cell walls (namely, the strength of ceramics increases with the reduction of their size, due to the decrease in the probability of finding a flaw with critical dimension at the surface). When the dimensions of the cell walls increase, as found for foams with calcined clay upon oxidation from 1200 to 1450 °C, the strength shows a substantial decrease. On the other hand, for foams with functionalized clay, the burnout of residues from the functionalization probably limited the extent of densification and led to very lightweight structures, with micron-sized struts even after oxidation at 1450 °C.

As for the glass matrix composites, the X-ray diffraction spectra, shown in Fig. 6, revealed the presence of cristobalite crystals and slight traces of mullite crystals as secondary phases, from the decomposition of clay. Even in the case of foams, the precipitation of cristobalite, probably due to its distribution at a nanoscale level, did not prove detrimental to the mechanical properties.

On the basis of the reported evidence, the addition of clays to silicone resin may be considered as an advantageous way to produce composite ceramic microcellular foams with high mechanical and oxidation resistance.

4. Conclusions

The addition of inexpensive clay to a preceramic polymer, consisting of silicone resin, was found to be advantageous for the production both of SiOC glass based monoliths and microcellular foams.

In the first case, with the addition of a substantial amount of calcined clay (30 wt.%), the feasibility of dense SiOC glass matrix composites was demonstrated, resulting in materials with remarkable hardness and fracture toughness, much higher than those of pure SiOC glasses reported in the literature. This improvement was attributed to the presence of nano-sized silica and mullite crystal inclusions. With the reduction of the residual cracks caused by pyrolysis, there is the potential of achieving high strength glass matrix composites by simple and economic warm pressing of the preceramic polymer.

In the second case, promising SiOC glass based microcellular foams were produced from composites including both calcined and functionalized clay additions. The inclusions provided for the retention of the microcellular structure, even after oxidation treatment at 1200 and 1450 °C, resulting in remarkable mechanical properties for the foams. Functionalized clay showed a more pronounced effect in limiting the extent of the densification of SiOC foams, upon oxidation, than calcined clay. The complete understanding of the effects of the silicate-clay addition to the preceramic polymer would allow for the optimization of this approach, which seems to be promising for the production of ceramic microcellular foams with high mechanical and oxidation resistance.

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