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SiOC ceramic foams synthesized from electron beam irradiated methylsilicone resin

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Abstract A new method to prepare silicon oxycarbide (SiOC) foams has been developed and it consists of electron beam irradiation of a methylsilicone preceramic polymer followed by pyrolysis in an inert atmosphere. Methylsilicone resin foams were prepared by simultaneous curing and foaming, without the addition of calalysts or blowing agents. The polymer precursor was irradiated with 1.5 MeV EB up to a dose of 7.0 MGy and at a dose rate of 2.8 kG/s, in air. During irradiation the polymer melted, due to rapid increase in temperature, and simultaneously crosslinked by interaction with the ionizing radiation. Crosslinking occurred mainly by poly-condensation reactions and gaseous condensation products were released. The latter acted as an intrinsic foaming agent in the molten polymer. Foams obtained with radiation doses higher than 3.5 MGy showed a high degree of crosslinking with a ceramic yield of over 89% at 1,000 °C. Pyrolysis at 1,200–1,500 °C resulted in SiOC ceramic foams with dense struts and walls, with bulk density around 0.3 g/cm^3 and total porosity of 84%. Foams pyrolyzed at 1,200 °C revealed compression strength of 6.8 MPa.

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Introduction

Ceramic foams are highly porous brittle materials with large voids (cells). These voids have linear dimensions in the range of a few micrometers to a few millimeters. Cells can be surrounded by ceramic walls or the solid can be contained only in the cell edges (struts); cell windows, if present in the cells walls, create an interconnected structure (open cell walls) [1]. An increasing number of applications that require porous ceramics have appeared in the last decades, mainly for use in environments where high temperatures, extensive wear and corrosive media are involved. Such applications include filtration of molten metals, removal of particulates from diesel engine exhaust gases, high temperature thermal insulation, kiln furniture, catalyst supports, reinforcement in metal matrix composites, thermal protection systems and light weight sandwich structures [2–5]. These applications are possible due to a unique combination of properties like low density, low thermal conductivity, high temperature stability, low dielectric constant and high resistance to chemical attack [5, 6]. A wide range of technologies have been developed to manufacture ceramic foams, because the method of manufacture has a marked effect on the final microstructure and the variety of applications often requires materials with different properties [4, 7, 8]. The most common processing routes presently available can be classified as replica, sacrificial template, and direct foaming methods [7].

Direct foaming of preceramic polymer mixtures, followed by pyrolysis in an inert atmosphere, can be used to manufacture silicon oxycarbide (SiOC) ceramic foams with very good mechanical, chemical, and physical properties [8–11]. In the last few years, novel processing routes have emerged in which melts of silicon preceramic polymers were blown. One of these routes is the co-blowing of polyurethane and polysiloxane resin mixture. Polyurethane acts both as a blowing aid and as a structural template, and the cell geometry as well as the overall porosity is adjusted by adding surfactants to the silicone resin [9, 12]. A modified approach of this method is the blowing of a siloxane melt using a blowing agent without an additional polyurethane [13, 14]. Another method is blowing of a precursor polymer melt with gases generated in situ during crosslinking reactions [11, 15]. A poly(phenylmethylsilsesquioxane) containing small amounts of ethoxy and hydroxyl groups was foamed by this in situ blowing technique [16, 17]. All these methods posse advantages and characteristics in terms of achievable cell size, homogeneity of the cell size distribution, and the possibility to produce closed cell foams. The main drawbacks of these methods can be listed as: (i) production of SiOC foams with a non-optimal high temperature oxidation resistance, due mainly to the presence of some free carbon from the decomposition of the polyurethane; (ii) necessity to use flammable or noxious blowing agents; (iii) limitation in silicone resin composition, which requires polymers with enough reactive groups to allow crosslinking reactions with volatile compounds [8, 13].

This investigation proposes a new method of curing and foaming methylsilicone resin by using electron beam (EB) radiation. When a polymer is exposed to high-energy radiation, several radiochemical reactions take place resulting in chemical and physical modifications in the polymer structure. The main structural changes seen in irradiated polymers are variations in molecular weight distribution, due to main-chain scission, crosslinking, and endlinking [18].

For decades, polymers in general have been treated with high-energy radiation and industries such as wire and cable insulation rely on this technology [18, 19]. An advantage of using radiation as a method of curing is that once radiation has ceased, no further reaction takes place and the extent of curing is completely determined by the radiation dose. A further advantage is that the irradiated material itself is purer, without catalysts or foaming agents. However, studies about preceramic polymers treated with radiochemical reactions are very scarce. The few studies in which precursor polymers are cured by EB irradiation are related to the manufacture of non-oxide ceramic fibers. In order to reduce the oxygen content in the polycarbosilane (PCS) fiber, the conventional method of thermal oxidation curing was substituted by EB radiation curing in an oxygen-free atmosphere. The EB irradiated PCS fibers were converted to silicon carbide (SiC) fibers with very low oxygen content [20–23]. Also, radiation-cured PCS fibers were found to convert to silicon nitride (Si_3N_4) fibers by pyrolysis in NH_3 atmosphere [23, 24]. This technology has already been commercialized and SiC fibers synthesized with this curing method have excellent thermal resistance at temperatures up to 1,700 °C [25].

The aim of this work was to investigate the preparation of SiOC ceramic foams obtained via high-temperature pyrolysis of porous methylsilicone resin bodies produced by direct foaming using EB radiation curing.

Experimental

Radiation curing and foaming

The preceramic polymer used was a commercially available methylsilicone resin with a general formula of $(CH_3SiO_{1.5})_n$ with $n = 130–150$ (MK, Wacker AG, Burghausen, Germany). It is a solid resin in the form of powder at room temperature with density of 1.1 g/cm^3, average molecular weight of 9,500 g/mol and has a glass transition temperature of 41.9 °C [13, 26]. According to the manufacturer of this resin and published literature [13], the remaining active hydroxyl (–Si–OH) and ethoxy (–Si–OC_2H_5) functional groups are a few percent and these undergo crosslinking reactions at high temperature, generating water and ethanol.

The methylsilicone resin was irradiated by EB and changed to a non-molten foam by forming a molecular network structure as a result of crosslinking. To carry out this process, the silicone resin powder was compacted in a uniaxial press into pellets of 25 mm in diameter and 2.5 mm in thick. For methylsilicone resin, the thickness must not exceed 4.5 mm owing to the limitation of EB penetration. This maximum sample thickness is a function of the beam energy and the material density [27, 28]. The samples were placed in a steel sample holder 500 × 35 × 25 mm^3 and covered with a thin metal film (0.1-mm thick aluminum foil). To irradiate, the sample holder was placed under an EB in an industrial EB accelerator (Dynamitron II model, Radiation Dynamics Inc., 1.5 MeV energy, 25 mA current and 37.5 kW power). The samples were continuously irradiated with doses of 1.0, 3.5, and 7.0 MGy. A dose rate of 2.8 kGy/s and current of 0.7 mA were used in air atmosphere without sample holder cooling. The temperature during irradiation was measured using an encapsulated Fe-Constantan thermocouple (type J). The thermocouple was placed on the top of a polymer pellet. The temperature of the empty sample holder was also measured during irradiation.

The degree of crosslinking can be estimated from the gel fraction (i.e., insoluble fraction). The gel fraction of the irradiated samples was determined gravimetrically by the Soxhlet extraction method and using a compatible solvent (based in ASTM 2765–01). Five samples were tested at each radiation dose. The samples were first weighed

($\sim$0.3 g) to obtain the initial dry weight and then wrapped in a permeable nylon fabric to prevent loss of any gel fragments during extraction. The samples were immersed in toluene (analytical grade) in a 150 mL Soxhlet extractor using a cycle of 24 h at room temperature. After extraction, the samples were dried to remove all traces of the solvent and a constant weight was registered. Then, the gel fraction was estimated using the equation:

$$\text{Gel fraction } (\%) = \frac{\text{mass after extraction} \times 100}{\text{mass before extraction}}$$

The changes in the chemical structure of the irradiated samples were assessed by infrared spectroscopy. The Fourier transform infrared (FTIR) spectra of the methylsilicone foams were obtained using a Nicolet Nexus spectrometer. A pellet sample was used in the spectrometer and this was prepared by grinding 1 mg of foam, mixed with 150 mg of dried KBr powder and pressed. The spectra were obtained in the wavenumber ranging of 4,000–400 cm^{-1}.

Pyrolysis process

The external surface of the crosslinked foams was removed by grinding and the foams were pyrolyzed in an electric furnace, in inert atmosphere and at final temperatures of 1,200 and 1,500 °C with a soaking time of 1 h. Samples were heated with at 5 °C/min up to 500 °C and then heated at 3 °C/min to the final temperature. The cooling rate to room temperature was 20 °C/min.

Differential thermogravimetric (TG) analysis of the foams was carried out in a (Perkin-Elmer, TGA-7) thermal balance in nitrogen and in air up to 1,000 °C with a constant heating rate of 10 °C/min. The bulk (apparent) density of the foams was calculated from the weight/volume ratio. The dimensions of the samples were determined by finding the average of five caliper measurements per side; and their mass was determined using a digital laboratory balance. Total porosity of the pyrolyzed foams was determined by Hg intrusion with a high-pressure porosimeter (Auto Pore III-Micromeritics). The microstructure and morphology of the foams, before and after pyrolysis, were examined in scanning electron microscopes (SEM-Philips XL 30; LEO-435 Pi). The composition of the phases was determined by X-ray diffraction (XRD) analysis using monochromated CuKα radiation and a Ni filter (Philips model PW 18/30). Specimens for XRD analysis were prepared by grinding the foams after radiation curing and after pyrolysis. The crushing strength of the foams irradiated with a dose of 7.0 MGy and foams pyrolyzed at 1,200 and 1,500 °C was measured by axial compression testing, in a universal testing machine (Instron 4301, Instron Corp., Canton, MA, USA). Stainless steel loading rams and a crosshead speed of 0.5 mm/min were used on samples with a nominal size of 6 × 6 × 12 mm^3. Each result represents the average value of five to ten separate tests.

Results and discussion

Curing and foaming with EB irradiation

Exposing methylsilicone resin to EB irradiation resulted in the formation of bubbles inside the polymer melt. Figure 1 shows SEMs of the fracture surface of methylsilicone resin before irradiation (Fig. 1a) and after EB irradiation with

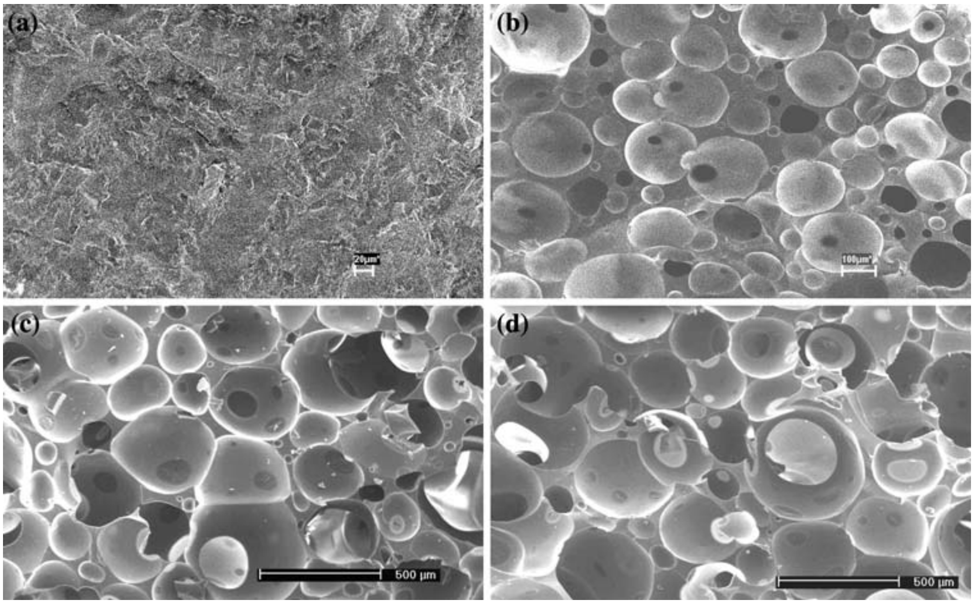


Fig. 1 SEM of the methylsilicone fracture surface: (**a**) un-irradiated sample; (**b**) irradiated with the dose of 1.0 MGy; (**c**) irradiated with 3.5 MGy; (**d**) irradiated with 7.0 MGy

radiation doses of 1.0, 3.5, and 7.0 MGy (Fig. 1b–d). The morphology of the foams is isotropic and the cells do not display any specific features related to either orientation or size gradients caused by EB penetration. The sample irradiated with 1.0 MGy dose showed less expansion than the samples of foams obtained with higher doses. Foams obtained with radiation doses of 3.5 and 7.0 MGy exhibited cell windows covered with a thin membrane, which disappeared almost completely upon pyrolysis.

Foam formation in methylsilicone during EB irradiation indicates that poly-condensation crosslinking mechanisms were activated by radiolysis reactions. The gaseous products acted as the blowing agent, resulting in a foam structure. Water and ethanol are the products released by the crosslinking reactions of the hydroxyl and ethoxy groups, according to the following reactions [16]:

$$\equiv \mathrm{Si{-}OH} \cdot + \cdot \mathrm{HO{-}Si} \rightarrow \; \equiv \mathrm{Si{-}O{-}Si} \equiv \; + \mathrm{H_2O}\uparrow \quad (1)$$

$$\equiv \mathrm{Si{-}OC_2H_5} \cdot + \cdot \mathrm{HO{-}Si} \equiv \rightarrow \; \equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{C_2H_5OH}\uparrow \quad (2)$$

The FTIR analysis of irradiated methylsilicone is shown in Fig. 2. There are no marked differences in the FTIR spectra between un-irradiated and irradiated methylsilicone samples. However, characteristic bands of the samples irradiated with curing doses of 3.5 and 7.0 showed a reduction in intensity compared to those of un-irradiated and 1.0 MGy irradiated samples. It was observed in the intensity bands of Si–C stretching (690 $\mathrm{cm^{-1}}$), Si–$\mathrm{CH_3}$ stretching (857 and 740 $\mathrm{cm^{-1}}$), and bending (1,269 $\mathrm{cm^{-1}}$) [29]. These changes can be attributed to partial transformation of the methyl groups during EB irradiation. Since no publications related to irradiation of methylsilicone resin were found to help explain structural modifications, we have used the studies related to irradiation of polydimethylsiloxane (PDMS). PDMS has a linear structure with methyl side groups, whereas methylsilicone resin is a non-linear polymer containing large amounts of oligomeric methyl silsesquioxane ($\mathrm{CH_3SiO_{3/2}}$). Miller [30] and Charlesby [31] have proposed a mechanism for crosslink formation in irradiated PDMS that is based on C–H and C–Si bond scission in the methyl ($\mathrm{CH_3}$) side chain. Crosslinks in PDMS can occur upon elimination of two hydrogen atoms only, upon elimination of one methyl and one hydrogen atom or upon elimination of two methyl groups. Due to these crosslinking reactions in PDMS, volatile products such as hydrogen, methane, and ethane are formed during irradiation [32, 33], according to the reactions:

$$\equiv \mathrm{Si{-}CH_2} \cdot + \cdot \mathrm{CH_2{-}Si} \equiv \; \rightarrow \; \equiv \mathrm{Si{-}CH_2{-}CH_2{-}Si} \equiv + \mathrm{H_2}\uparrow \quad (3)$$

$$\equiv \mathrm{Si{-}CH_2} \cdot + \cdot \mathrm{Si} \equiv \; \rightarrow \; \equiv \mathrm{Si{-}CH_2{-}Si} \equiv + \mathrm{CH_4}\uparrow \quad (4)$$

$$\equiv \mathrm{Si} \cdot + \cdot \mathrm{Si} \equiv \; \rightarrow \; \equiv \mathrm{Si{-}Si} \equiv + \mathrm{C_2H_6}\uparrow \quad (5)$$

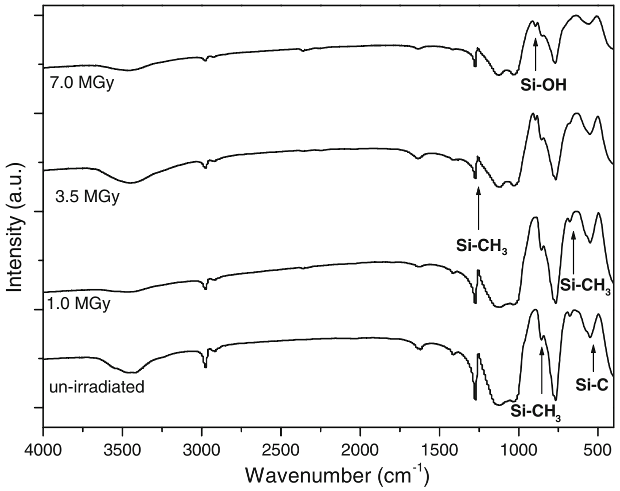


Fig. 2 FTIR spectra of the un-irradiated methylsilicone sample and after EB irradiation with doses of 1.0, 3.5, and 7.0 MGy

It is probable that the evolution of these volatile species during EB irradiation also contribute toward bubble formation and expansion of the molten methylsilicone. Oxidation of methyl groups is another possible reason for the reduction in band intensities. This effect was observed in PDMS irradiated in the presence of oxygen, generating CO and $\mathrm{CO_2}$ during oxidation of the methyl groups, and the evolution of these gases increased with increasing irradiation temperature [34]. FTIR spectra of samples irradiated with 3.5 and 7.0 MGy also showed an additional band at 895 $\mathrm{cm^{-1}}$ (Fig. 2). This band was attributed to the Si–OH groups and it was also observed by Miller [35] in the infrared spectrum of irradiated PDMS. He proposed that the appearance of this band was due to main chain scission generating Si–O· radicals with the hydrogen absorbency. This last observation suggests that radiation doses above 3.5 MGy can cause some degradation in the polymer structure due to main chain scission.

Figure 3 shows the XRD analysis data of the methylsilicone resin before crosslinking and after EB irradiation with doses of 1.0 and 7.0 MGy. The XRD patterns reveal two peaks, at $2\theta \sim 10$ and 22°, regardless of the condition of the methylsilicone. This pattern was also observed in previous studies on the same methylsilicone (MK resin) at 30 °C, for molten methylsilicone (MK resin) at 90 °C [26] and another similar methylsilicone resin [36]. The most likely interpretation for the existence of two peaks is that the silicone resins contain an amorphous phase, corresponding to the broad peak around 22° and a relatively regular structure corresponding to the higher intensity peak at 10° [36]. The sample irradiated with 1.0 MGy dose shows an XRD pattern very similar to the un-irradiated

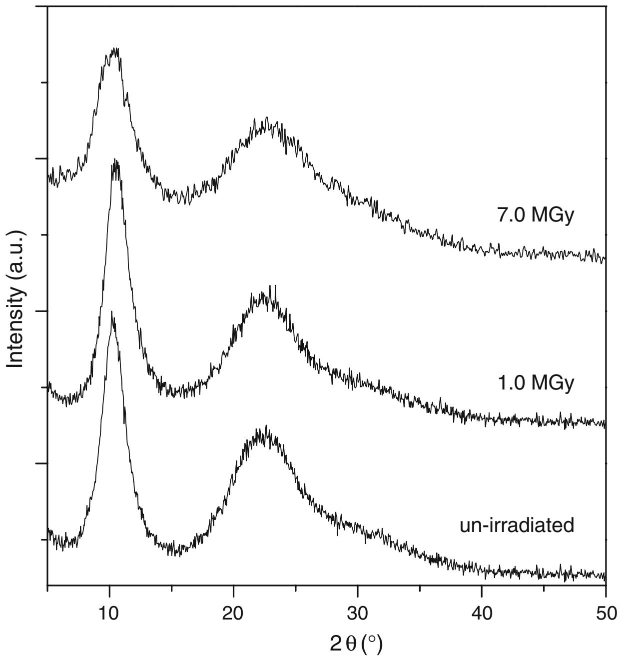


Fig. 3 XRD patterns of the un-irradiated methylsilicone and the foam obtained by EB irradiation with doses of 1.0 and 7.0 MGy

material. However, the XRD pattern of the sample irradiated with 7.0 MGy dose shows reduction in relative intensity and broadening of the peak corresponding to the regular structure at 10°. Takahashi et al. [26] calculate the *d*-spacing of structures of different silicone resins and concluded that the *d*-spacings of the regular structure is increased by the size of the substitutive organic group, which exists only on the outer side of the structure. Thus, the peak reduction and broadening of the sample irradiated with 7.0 MGy dose can be attributed to reduction in structure regularity caused by scission of Si–CH_3 bonds according to reactions (3)–(5).

When thermal crosslinking mechanisms govern in situ foaming of silicone resins, foam formation depends on time, and temperature of bubble nucleation, bubble growth, and concurring crosslinking reactions [13, 17]. The foam structure is stabilized by concurrent viscosity increase and curing of the polymer melt [13, 16]. In order to analyze foam formation in methylsilicone by radiation crosslinking, the temperature inside the sample holder during each irradiation was measured (Fig. 4). In the initial stages of irradiation, the temperature increased very fast and then it increased slowly, with increase in radiation dose, until a constant temperature was reached. There is a temperature gradient between irradiations carried out with and without a sample (empty sample holder), indicating exothermic radiolysis reactions which occur during EB irradiation. As soon as the EB accelerator is turned off, the temperature decreased very fast and reached about 50 °C in 6 min.

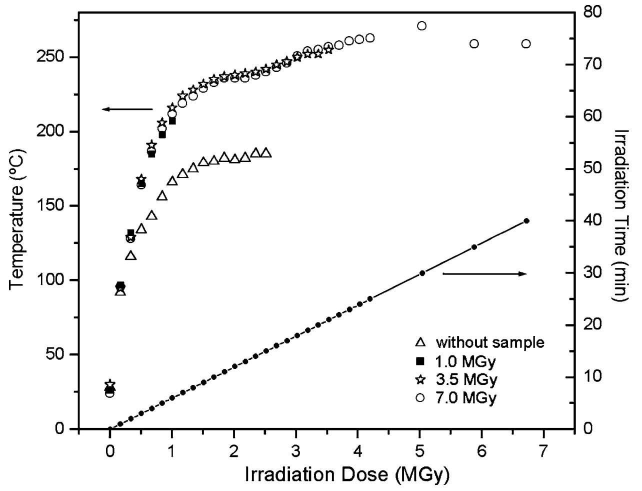


Fig. 4 Temperature during EB irradiation as a function of radiation dose. Temperature was measured without a sample and with sample at doses of 1.0, 3.5, and 7.0 MGy

Because of the higher temperature during irradiation, it is supposed that crosslinking reactions are activated not only by radiation crosslinking but also by thermal crosslinking, but to a lesser extent. When only thermal crosslinking is considered, longer heat treatments are necessary, about 2 h at 250 °C to obtain a totally crosslinked unmeltable thermoset foam [16, 17]. Therefore, ionizing radiation increases the rate of crosslinking in methylsilicone compared to thermal crosslinking.

At 1.0 MGy radiation dose, the temperature increased from room temperature to 160 °C (without sample) and to 210 °C (with sample), in 6 min. The increase in temperature caused the polymer to melt and its viscosity was adequate for bubble formation and stabilization (Fig. 1b). At radiation dose of 3.5 MGy, the temperature increased to 180 °C (without sample) and to 250 °C (with sample) and the polymer viscosity was still appropriate to allow further expansion (Fig. 1c). The variations in polymer viscosity during irradiation processing are quite different from that reported during thermal processing. First, because it is not necessary to reach a certain temperature to activate crosslinking reactions as is required in thermal crosslinking. Consequently, the material can be foamed at lower temperatures, and this promotes higher polymer viscosity. Second, the high radiation crosslinking rate increases polymer viscosity, maintaining the foam structure. To illustrate this difference between thermal and radiation curing, in relation to polymer viscosity, we mention Takahashi and Colombo [13]. They have not succeeded in obtaining a foam morphology using a blowing agent in two samples of the same methylsilicone used in this work (MK resin) at 250 °C. One sample contained 0.04% of a catalyst and another previously heated at 200 °C for 60 min exhibited very low viscosity. In these the bubbles coalesced and escaped from the molten polymer.

The extent of crosslinking in the samples irradiated with the different radiation doses was evaluated from the gel fraction, which is the ratio of the dry weight of the foam soaked in toluene for 24 h and the initial weight of the foam. This method could not be used to measure the gel fraction of the samples irradiated with 1.0 MGy, because the crosslinked nucleation points were too small to be retained by the permeable fabric during extraction. Hence, the foam structure of the sample irradiated with 1.0 MGy (Fig. 1b) was not due to an increase in polymer viscosity caused by polymer crosslinking, but was probably due to rapid decrease in temperature when the EB accelerator was turned off. On the other hand, samples irradiated with doses of 3.5 and 7.0 MGy were almost insoluble with gel fractions of 95.2 ± 0.9 and 98.2 ± 0.6%, respectively. At higher radiation doses, overall crosslinking created a three-dimensional network structure that markedly reduced foam dissolution. Therefore, the maximum amount of crosslinking in methylsilicone, when EB radiation was used, occurred between 1.0 and 3.5 MGy at dose rate of 2.8 kG/s.

On the basis of these results, the changes that occur in the methylsilicone preceramic polymer morphology during the EB irradiation can be summarized (Fig. 5). Initially, the electrons are accelerated toward the methylsilicone pellets until a certain radiation dose at a dose rate of 2.8 kG/s (Fig. 5a). The heat induced by the high-energy radiation melts the polymer and simultaneously produce gases from radiolysis reactions, which acts as intrinsic foaming agents in the molten polymer (Fig. 5b). It is suggested that reactions occur mainly by the hydroxyl and ethoxy functional groups, generating water an ethanol. Gaseous species H_2, CH_4, and C_2H_6 could also be formed during irradiation, contributing to bubble growth. Upon increasing the radiation dose to 3.5 MGy and for a total time of 21 min, the methylsilicone resin becomes a thermoset foam with gel fraction of 95.2% (Fig. 5c).

Conversion to ceramic foams

The conversion of methylsilicone foam to SiOC ceramic was studied by thermogravimetry at temperatures of up to 1,000 °C (Fig. 6). The un-irradiated polymers and that irradiated with 1.0 MGy were studied only in air atmosphere (Fig. 6a), whereas the foams irradiated with 3.5 and 7.0 MGy were studied in air and N_2 atmospheres (Fig. 6a, b). The foam obtained with 1.0 MGy dose shows a TG curve typical of a methylsilicone with low degree of crosslinking

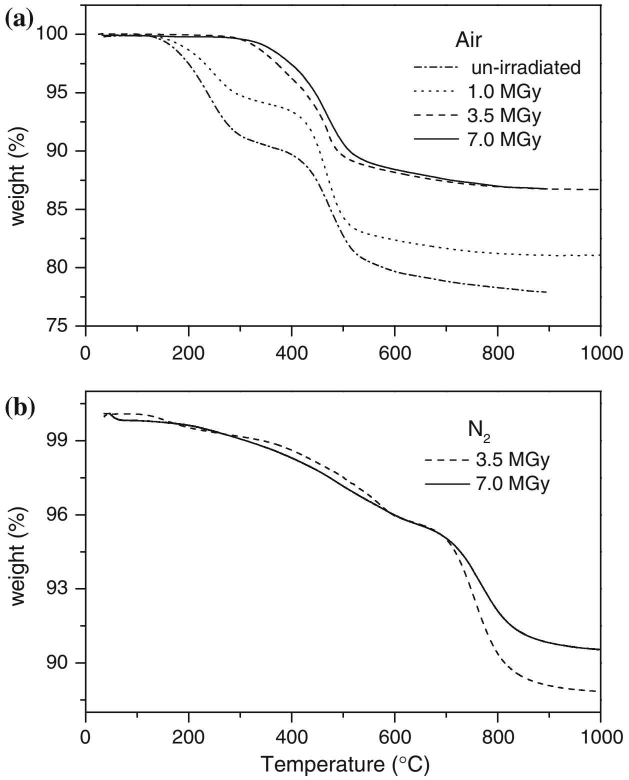
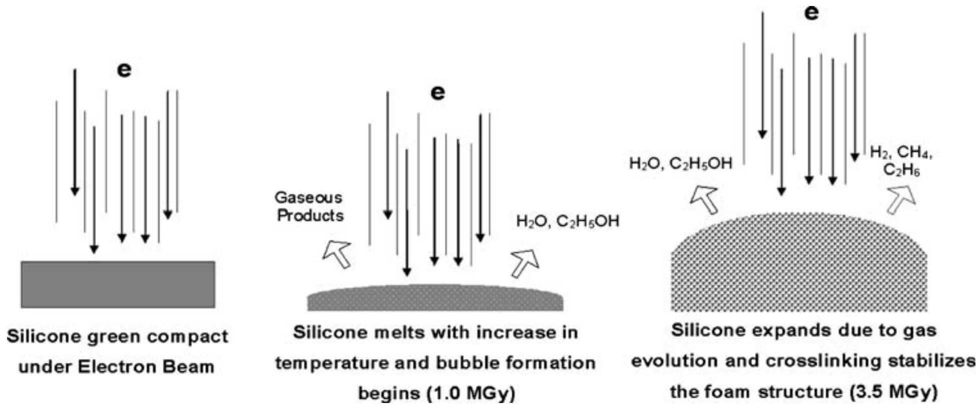


Fig. 6 TGA curves of the methylsilicone foams obtained by EB irradiation (heating rate of 10 °C/min): (**a**) in air atmosphere; (**b**) in N_2 atmosphere

Fig. 5 Sequence of changes in the methylsilicone during EB irradiation



[13]. This is in agreement with low bubble formation and the gel fraction results. The ceramic yield of this sample was about 81%, slightly higher than that of the un-irradiated polymer. Pyrolysis of the un-irradiated and the 1.0 MGy irradiated material shows that most of the weight change occurred in two steps, located around 200 and 400 °C. The first weight loss was lower for the foam than that for the un-irradiated polymer. Moreover, there was no weight change at 200 °C for the foams irradiated with doses of 3.5 and 7.0 MGy, in air atmosphere. These findings indicate that the first weight loss can be attributed to crosslinking reactions within the polymer, with release of gaseous by-products, or to the evaporation of low molecular weight components. The second weight loss can be attributed to the main degradation reactions of methylsilicone, which occur with cleavage of Si–(CH_3) and to oxidation reactions of the methyl groups [37].

TG curves of the foams obtained with 3.5 and 7.0 MGy dose showed similar behavior in each studied atmosphere (air and N_2), but small differences can be observed. In air atmosphere, the curve of the foam obtained with 7.0 MGy dose shifted to higher temperatures, but at about 900 °C the final ceramic yield was the same as that in the foam irradiated with 3.5 MGy dose (~87.5%). In N_2 atmosphere, there was a small difference in the final ceramic yield and these were 89 and 91%, for foams obtained with 3.5 and 7.0 MGy doses, respectively. These results indicate that the changes in polymer structure obtained by doubling the radiation dose do not have a significant effect in the thermal decomposition behavior.

Figure 7 shows the microstructural morphology of a sample irradiated with 3.5 MGy and pyrolyzed at 1,200 °C in N_2. The image was obtained by merging three separate SEM micrographs. The left side of the image corresponds to the top part of the sample and the right side to the bottom. Apparently, there is no density gradient between the top and the bottom parts. The cells do not display any features related to the direction of expansion, even though a broad distribution of cell sizes can be observed. There are no signs of melting of the preceramic polymer during the polymer-to-ceramic conversion, with concurrent loss of shape at any stage of the pyrolysis process. This indicates effective crosslinking of the methylsilicone by EB radiation curing.

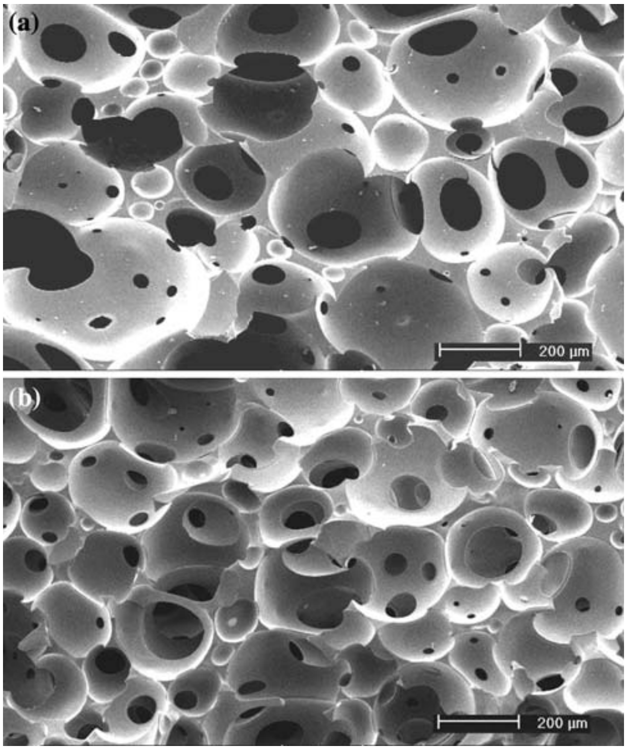
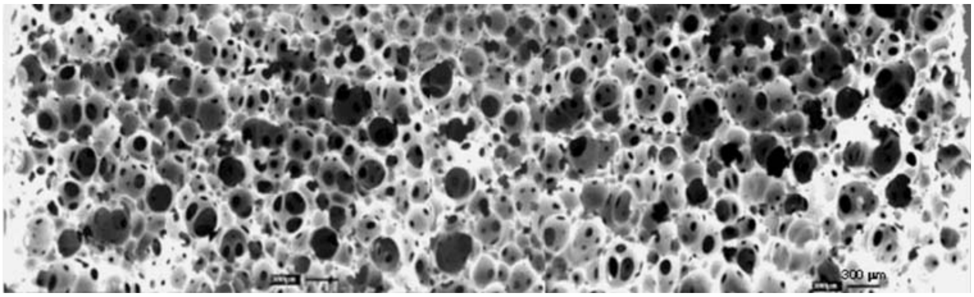


Fig. 8 SEM of microcellular SiOC ceramic foam obtained from methylsilicone irradiated with the dose of 7.0 MGy and pyrolyzed in N_2-atmosphere: (**a**) 1,200 °C; (**b**) 1,500 °C

Samples irradiated with 7.0 MGy were pyrolyzed for 1 h at 1,200 and 1,500 °C in N_2. The methylsilicone foams maintained their microcellular structure at both pyrolysis temperatures. Figure 8 shows the SEM micrographs of the foams with large open cells and cell walls with pores induced by methylsilicone decomposition. The struts show a very dense aspect, without any porosity or cracks. The total porosity of these foams, as measured by mercury porosimetry, was of about 84%.

The corresponding crystalline phase of foams pyrolyzed at 1,200 and 1,500 °C were characterized using XRD (Fig. 9). The sample pyrolyzed at 1,200 °C shows an amorphous pattern attributable to amorphous SiOC ceramic,

Fig. 7 SEM of the SiOC ceramic foam obtained from methylsilicone irradiated with the dose of 3.5 MGy and pyrolyzed at 1,200 °C



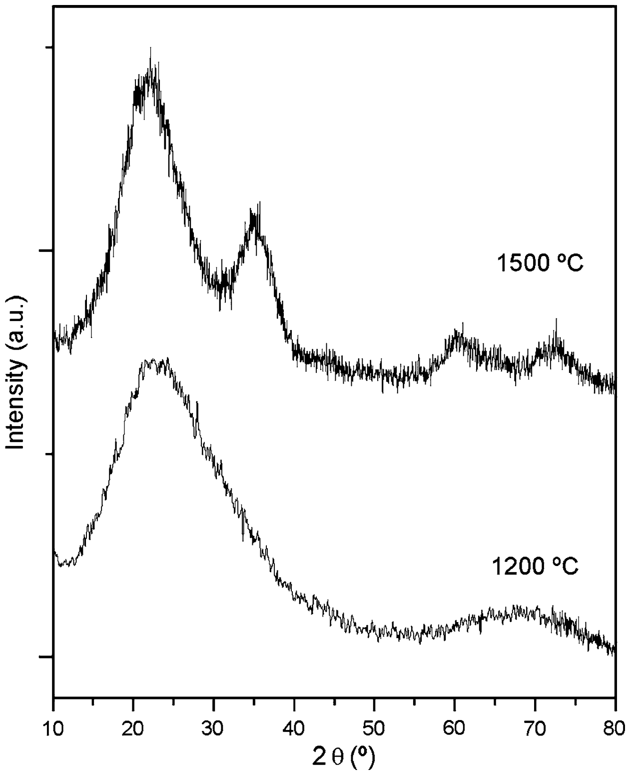


Fig. 9 XRD patterns of the pyrolyzed foams at 1,200 and 1,500 °C in N_2-atmosphere

Table 1 Bulk density and compression strength of methylsilicone foams and SiOC foams obtained after pyrolysis at 1,200 and 1,500 °C

Foam material	ρ (g/cm^3)	σ_c (MPa)
Methylsilicone (7.0 MGy)	0.19 ± 0.01	0.64 ± 0.09
SiOC (1,200 °C)	0.32 ± 0.02	6.8 ± 0.8
SiOC (1,500 °C)	0.31 ± 0.03	3.6 ± 0.4

which is typical when siloxane resins are used as preceramic precursors. The sample pyrolyzed at 1,500 °C shows two broad peaks at 2θ of ~22 and 35° with two main broad halos centered at 2θ at 60 and 72°, which permit precise assignment and to formation of β-SiC nanocrystals [37, 38].

The results of bulk density and compression strength of the methylsilicone foam obtained with 7.0 MGy dose and the SiOC foams pyrolyzed at 1,200 and 1,500 °C are shown in Table 1. The compression strength of the foams pyrolyzed at 1,200 °C was 6.8 MPa with a bulk density of 0.32 g/cm^3. Takahashi and Colombo [13] reported lower values of compression strength (2.0 MPa) for an SiOC foam with density of 0.3 g/cm^3 obtained from the same methylsilicone and with pyrolysis conditions similar to that used in this study. Using co-blowing of silicone and polyurethane mixtures, foams of SiOC showed similar compression strength as determined here, but for a foam with higher bulk density of around 0.5 g/cm^3 [9, 39]. With increase in pyrolysis temperature to 1,500 °C, the foams showed a marked decrease in compression strength (3.6 MPa), even though the bulk density remained unchanged (Table 1). At 1,500 °C it is supposed that some carbothermal reduction reactions take place [37, 38], causing strength modification with the evolution of devitrification of SiOC foams and formation of microcracks and intra-strut porosity.

Conclusions

A novel process for producing SiOC ceramic foams has been proposed. Methylsilicone resin was foamed in a single step manufacturing process by EB irradiation. The polymer precursor was expanded by the gaseous products that evolved from the condensation crosslinking reactions during irradiation. The required irradiation dose for methylsilicone resin, at dose rate of 2.8 kGy/s, was found to be between 1.0 and 3.5 MGy. The foams obtained with radiation dose of 3.5 MGy exhibited a high degree of crosslinking (95.2%) and a high ceramic yield (89% in N_2 atmosphere). Pyrolysis of the methylsiloxane derived foam in an inert atmosphere led to the formation of amorphous SiOC ceramic foams at 1,200 °C, and partly crystalline SiOC at 1,500 °C, with large open cells and dense struts. Total porosity was about 84% with bulk density of 0.3 g/cm^3. The compression strength of foams pyrolyzed at 1,200 °C was about 6.8 MPa. The results of this investigation indicate that the proposed novel processing method is suitable for manufacturing porous SiOC ceramics from irradiated methylsilicone and suggests a new trend to study polymer derived ceramics by EB radiation curing.

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References

1. Saggio-Woyansky J, Scott CE, Minnear WP (1992) Am Ceram Soc Bull 71:1674
2. Nettleship I (1996) Key Eng Mater 122–124:305
3. Sheppard LM (1993) Ceram Trans 31:3
4. Scheffler M, Colombo P (2005) Cellular ceramics: structure, manufacturing, properties and applications. Wiley, Weinheim, p 645
5. Colombo P (2002) Key Eng Mater 206–213:1913
6. Lange FF, Miller KT (1987) Adv Ceram Mat 2:827. doi:10.1111/j.1151-2916.1987.tb05635.x
7. Studart AR, Gonzenbach UT, Tervoort E, Gauckler LJ (2006) J Am Ceram Soc 89:1771. doi:10.1111/j.1551-2916.2006.01044.x
8. Colombo P, Hellman JR (2002) Mater Res Innovations 6:260. doi:10.1007/s10019-002-0209-z

9. Colombo P, Hellmann JR, Shelleman DL (2001) J Am Ceram Soc 84:2245
10. Colombo P, Hellmann JR, Shelleman DL (2002) J Am Ceram Soc 85:2306. doi:10.1111/j.1151-2916.2002.tb00452.x
11. Colombo P, Gambaryan-Roisman T, Scheffler M, Buhler P, Greil P (2001) J Am Ceram Soc 84:2265
12. Colombo P, Modesti M (1999) J Am Ceram Soc 82:573
13. Takahashi T, Colombo P (2003) J Porous Mater 10:113. doi: 10.1023/A:1026031729278
14. Bao X, Nangrejo MR, Edirisinghe MJ (1999) J Mater Sci 34:2495. doi:10.1023/A:1004666326039
15. Gambaryan-Roisman T, Scheffler M, Buhler P, Greil P (2000) Ceram Trans 108:121
16. Zeschky J, Neunhoeffer FG, Neubauer J, Jason Lo SH, Kummer B, Scheffler M, Greil P (2003) Comp Sci Technol 63:2361. doi: 10.1016/S0266-3538(03)00269-0
17. Zeschky J, Höfner T, Arnold C, Weißmann R, Hourlier DB, Scheffler M, Greil P (2005) Acta Mater 53:927. doi:10.1016/j.actamat.2004.10.039
18. Clough R (2001) Nucl Instrum Methods Phys Res B 185:8
19. Berejka AJ, Eberle C (2002) Radiat Phys Chem 63:551. doi: 10.1016/S0969-806X(01)00553-9
20. Okamura K, Seguchi T (1992) J Inorg Organomet Polym 2:171. doi:10.1007/BF00696544
21. Idesaki A, Narisawa M, Okamura K, Sugimoto M, Morita Y, Seguchi T, Itoh M (2001) J Mater Sci 36:357. doi:10.1023/A:1004864126085
22. Idesaki A, Narisawa M, Okamura K, Sugimoto M, Morita Y, Seguchi T, Itoh M (2001) Radiat Phys Chem 60:483. doi:10.1016/S0969-806X(00)00394-7
23. Seguchi T (2000) Radiat Phys Chem 57:367. doi:10.1016/S0969-806X(99)00406-5
24. Kakimura S, Seguchi T, Okamura K (1999) Radiat Phys Chem 54:575. doi:10.1016/S0969-806X(97)00314-9
25. Shimoo T, Tsukada I, Seguchi T, Okamura K (1998) J Am Ceram Soc 81:2109
26. Takahashi T, Kaschta J, Münstedt H (2001) Rheol Acta 40:490. doi:10.1007/s003970100173
27. Fouassier JP, Rabek JF (1993) Radiation curing in polymer science and technology III. Mechanism of electron beam curing. Elsevier, London, p 301
28. Cleland MR, Farrell JP (1976) Proceedings of the 4th Conference on Application of Small Accelerators. Texas, USA
29. Bellany LJ (1975) The infrared spectra of complex molecules. Chapman and Hall, London
30. Miller AA (1960) J Am Chem Soc 82:3519. doi:10.1021/ja01499a011
31. Charlesby A (1991) Irradiation effects on polymer. Elsevier, London, p 39
32. Folland R, Charlesby A (1976) Int J Radiat Phys Chem 8:555. doi:10.1016/0020-7055(76)90022-X
33. Charlesby A, Folland R (1983) Radiat Phys Chem 15:392
34. Menhofer H, Zluticky J, Heusinger H (1989) Radiat Phys Chem 33:561
35. Miller AA (1961) J Am Chem Soc 83:31. doi:10.1021/ja01462a006
36. Takahashi T, Münstedt H, Colombo P, Modesti M (2001) J Mater Sci 36:1627. doi:10.1023/A:1017531415890
37. Renlund GM, Prochazka S (1991) J Mater Res 6:2723. doi: 10.1557/JMR.1991.2723
38. Pantano CG, Singh AK, Zhang HJ (1999) J Sol–Gel Sci Technol 14:7. doi:10.1023/A:1008765829012
39. Colombo P, Bernardo E (2003) Comp Sci Technol 63:2353. doi: 10.1016/S0266-3538(03)00268-9