Engineering porosity in polymer-derived ceramics

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Abstract

By employing carefully controlled processing methods, a large amount of porosity (>70 vol%) was introduced in ceramic materials derived from preceramic polymers (silicone resins) after pyrolysis at 1000–1200 °C in inert atmosphere. The resulting components have a bulk density ranging from ∼250 to 950 kg/m^3. Three main fabrication methods have here been employed: (1) direct foaming of a solution of a thermosetting silicone resin in a suitable solvent (with or without the addition of polyurethane precursors), acting also as a blowing agent; (2) the use of sacrificial fillers that decompose during pyrolysis, consisting in polymeric microbeads; (3) the mixing of preceramic polymers possessing different characteristics, in particular ceramic yield, depending on their molecular structure. In addition to that, several methods for developing micro- or meso-pores within the resulting SiOC macro-porous ceramics were explored, with the aim of fabricating components with hierarchical porosity. These include a controlled thermal treatment, the addition of fillers with a high specific surface area (SSA), the deposition of zeolites or meso-porous silica coatings, the infiltration with aerogels, selective etching of the SiOC material and the in situ formation of C-based nanostructures. Depending on the fabrication procedure adopted, cells with an average size ranging from the micrometer to the millimeter were obtained. All these processes are simple, economical and versatile, and large bodies with various shapes (tubes, plates, blocks) can be produced, possessing a wide range of morphologies and properties. Compression strength, flexural strength and Young's modulus vary with the morphology and density of the porous components. It is also possible to add to the preceramic polymers some filler powders, for instance possessing electrical conductivity or magnetic properties, leading to the production of functional cellular ceramics.
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1. Introduction

Highly porous ceramics (foams, honeycombs, fibers mats, etc.) find numerous applications in various engineering fields, including filtration (molten metals, particulate from diesel exhaust gases), radiant burners, catalyst supports, biomedical devices, kiln furniture, reinforcement for metal matrix composites, bioreactors, thermal protection systems, supports for space mirrors, components in solid oxide fuel cells, lightweight sandwich structures, heat exchangers (graphite foams), etc.[1] Different manufacturing processes for cellular ceramics have been proposed, including replica of a polyurethane foam, direct blowing of a ceramic suspension, the use of sacrificial fillers, extrusion or the bonding of fibers.[2]

In this paper, the main results concerning the fabrication of highly porous ceramics (mainly ceramic foams) from preceramic polymers will be discussed. Preceramic polymers, are organic–inorganic polymers whose backbone contains usually Si atoms, which give a ceramic residue through the elimination of organic moieties (by breaking of C–H bonds, and release of H$_2$ and CH$_4$ and other volatile compounds).[3] The polymer-to-ceramic conversion is achieved either thermally (pyrolysis, via conventional oven annealing, microwave or laser heating) or non-thermally (for instance by irradiation with ions), usually by processing in inert atmosphere. Nanostructured polymer-derived ceramics (PDC) in the systems Si–O–C, Si–N–C, Si–C, Si–E–N–C (with E = B, Al, Ti, etc.) can be thus produced[4]; the introduction of suitable fillers allows also to obtain engineering ceramics such as cordierite,[5] mullite[6] or SiAlON.[7] The production of ceramic materials from preceramic polymers offers unique opportunities, especially from a processing point of view. In fact, using preceramic polymers, it is possible to apply conventional plastic forming technologies (injection molding, extrusion, resin transfer molding, melt spinning, etc.), gener-

ally with low processing costs, to the fabrication of ceramic products.

The first suggestion that porous ceramics could be produced from preceramic polymers can be found in the patent literature – by direct blowing[8–10] or by solvent extraction from a phase-separated polysilane gel[11] – albeit very limited processing information or data are reported. Several papers have been since then published in the scientific literature by the present author and various collaborators, detailing a range of processing procedures, reporting extensive characterization of the products and describing their testing for diverse applications.[12–33] Alternative processing methods for the production of open or closed cell (macro-)porous ceramics have also been proposed by different researchers as well. These include the infiltration of a porous salt preform using a molten preceramic polymer,[34] coating of a polyurethane foam with a preceramic polymer,[35,36] evaporation of silane oligomers,[37] decomposition of a siloxane polymer during pyrolysis,[38] self-foaming by in situ evaporation of volatile condensation products generated during silicone crosslinking reactions,[39] foaming of a molten silicone by thermal decomposition of a solid blowing agent,[40] the dissolution of CO_2 gas into a preceramic polymer under pressure followed by introducing of a thermodynamical instability,[40–44] the use of expandable sacrificial polymeric microspheres,[5,45–47] the use of already expanded sacrificial polymeric microspheres,[48–50] the infiltration and pyrolysis of organic porous templates (wood structures),[51] the dissolution of colloidal silica sub-micron spheres,[52,53] or freeze-drying using camphene.[54]

Moreover, several papers have been published dealing with the use of preceramic polymers to fabricate porous membranes (see for instance[55] and references therein), with pores sizes in the micro- and meso-range, and very recently the preparation of meso-porous ceramics via self-assembly of a preceramic polymer,[56] or via infiltration into meso-porous templates,[57,58]

or via synthesis of an inorganic–organic diblock copolymer[59] has been reported.

All these proposed processing methods allow to produce ceramics with engineered porosity affording varied and tailored characteristics, which are of interest for a wide range of applications.

2. Experimental details

A silicone resin (SR) preceramic polymer (polymethylsiloxane (MK, Wacker-Chemie GmbH, Munchen, Germany) was used to form a Si–O–C amorphous ceramic material upon heat treatment at temperatures >800 °C in an amorphous atmosphere. Three different typologies of porous ceramics were produced: (a) macro-cellular ceramic foams; (b) micro-cellular ceramic foams; (c) high porosity ceramic components. Different processing procedures were followed to obtain the samples with different morphology (see Fig. 1).

Samples (a) were obtained by dissolving the silicone SR into a suitable solvent with a low boiling point (pentane, freon, etc.) and adding a surfactant (and a catalyst – zirconium acetylacetonate – if necessary). If desired, fillers (ceramic or metal powders, ceramic fibers, etc.) can also be added at this stage to tailor the composition and properties of the resulting porous ceramic material. Additionally, polyurethane precursors (PU) can also be added (up to 50 wt%) in order to use their expansion capability to better control the morphology of the foam (production of open cells or of closed cells). Expansion was achieved by high speed mixing (introduction of bubbles in the solution) and heat treatment at 25–40 °C. Samples (b) were obtained by dry mixing the SR powder with a sacrificial template constituted by PMMA microbeads of different size. Fillers and if necessary a crosslinking catalyst for the SR can also be added at this stage. After uniaxial pressing (cold or warm—$T < 180$ °C), the PMMA beads were eliminated by heat treatment in air at
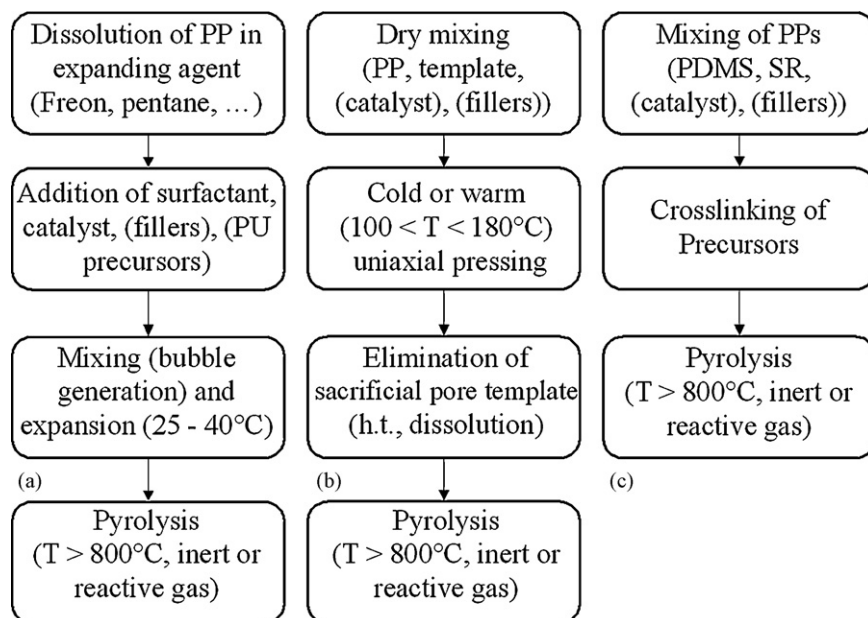

Fig. 1. Processing procedures for the fabrication of porous ceramic components from preceramic polymers.
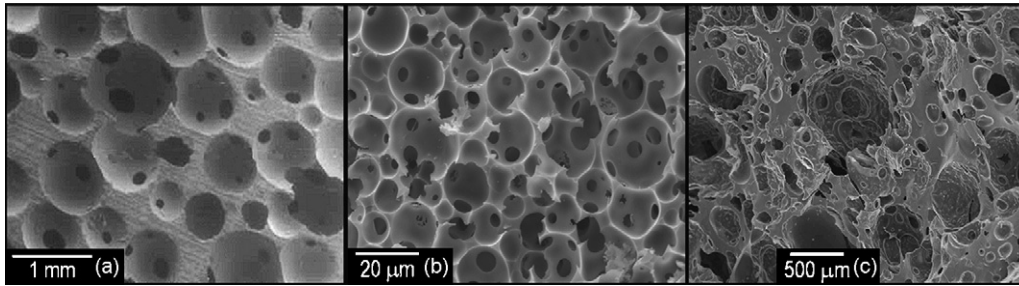
Fig. 2. SEM images of different porous morphologies obtained by pyrolysis of a silicone resin. (a) Macro-cellular open cell foam; (b) micro-cellular open cell foam and (c) high porosity sample.

300 °C, leaving a preceramic micro-cellular foam. Samples (c) were obtained by mixing two silicone polymers of different nature: a by-component liquid polydimethylsiloxane (PMDS, RTV 141 A and B; Rhodorsil, Rhône-Poulenc, France) and the MK silicone resin, followed by crosslinking of the PDMS. Pores were generated upon heating due to the decomposition and elimination of the polydimethylsiloxane from the component. All the preceramic samples were transformed into a ceramic material via pyrolysis in inert atmosphere (N_2 99.99%, 2 °C/min to maximum temperature—$800 < T < 1200$ °C, holding time 1 h).

The samples were characterized for different properties (relative density, compression strength, bending strength, elastic modulus, thermal shock, etc.) and their morphology (average cell and cell window size and size distribution) was investigated using several techniques (Optical and Electronic Microscopy, Image Analysis, Computer Tomography). The details are reported in the cited published literature.[12–33]

In order to produce porous ceramic components with hierarchic porosity (containing simultaneously micro-, meso- and macro-pores), different processing strategies were followed (see later).

3. Results and discussion

Depending on the processing procedure employed, it is possible to fabricate from preceramic polymers porous components possessing a varied morphology (see Fig. 2).

Macro-cellular foam samples (Fig. 2a) possessed a porosity >~70 vol% and a regular morphology comprised of spheroidal empty voids (cells) with a size ranging from ~150 μm to ~1 mm.[12–15] Micro-cellular foam samples (Fig. 2b) possessed a porosity >~70 vol% and a regular morphology comprised of spheroidal empty voids (cells) with a size ranging from ~1 μm to ~ 100 μm.[24,26] Porous samples (Fig. 2c) possessed a porosity ranging from ~40 to ~80 vol% with an irregular morphology in which the void size ranged from a few microns to several hundred microns.

Macro-cellular foams obtained from direct foaming can also possess closed cells, depending on the type of surfactant used and on the mixture employed. The cell size can be varied in a wide range of values according to the processing conditions, and this influences the properties (mechanical strength, permeability, thermal properties) of the components.[22] Because of the limited amount of defects in these macro-cellular foams (in particular dense struts with no cracks) – a characteristic deriving directly from the processing method employed (direct foaming) – they display a higher strength in comparison to conventional reticulated foams.[18] They possess good thermal shock properties, due to the low CTE of the SiOC ceramic,[21] and have a high temperature stability directly related to the pyrolysis temperature at which they were processed. The fabrication process is rather simple, economical and versatile, and large bodies with various shapes (tubes, plates, blocks) can be produced. The introduction of filler powders allowed for the synthesis of func-
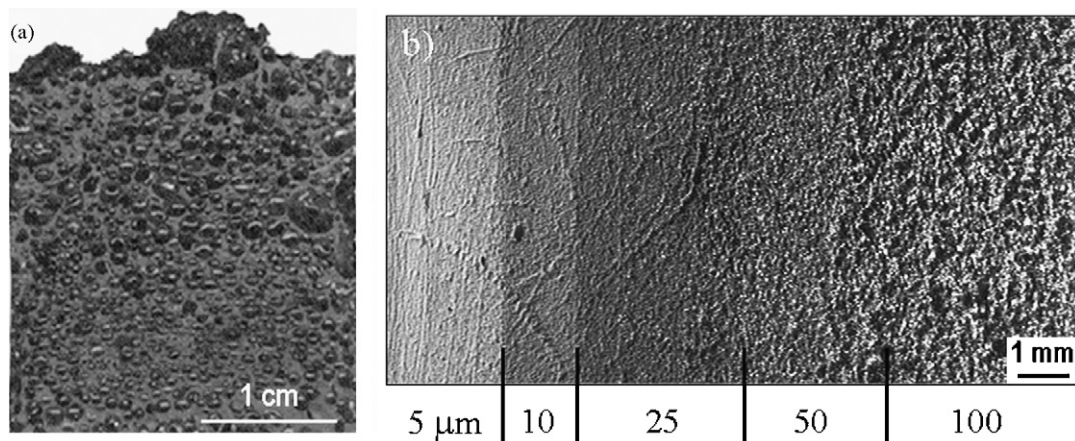

Fig. 3. Example of graded porosity components. (a) Macro-cellular foam (by direct foaming) and (b) micro-cellular foam (the numbers refer to the average dimension of the sacrificial PMMA microbeads used in μm).

Table 1
Main characteristics of PDC porous components obtained following the three different processing methods (see Fig. 1)

Property	Macro-cellular foams	Micro-cellular foams	Porous components
Bulk density (kg/m^3)	250–700	260–600	450–950
Porosity (vol%)	68–90	72–88	55–80
Average cell size (μm)	100–2000	1–185	10–500
CTE$_{20-1100\,°C}$ ($\times 10^{-6}$ K^{-1})	3.75 ± 0.19	4.4 ± 0.20	4.6 ± 0.15
Thermal conductivity (W/mK)	0.104 ± 0.015 (at 400 °C, $\rho = 350 \pm 2$ kg/m^3)	0.106 ± 0.032 (at 20 °C, $\rho = 330 \pm 5$ kg/m^3)	n.m.
Electrical conductivity	$<10^{-16}$ (Ω cm)	$<10^{-16}$ (Ω cm)	$<10^{-16}$ (Ω cm)
Dielectric constant ($\rho = 350 \pm 2$ kg/m^3)	4.8 (at 0.2 GHz) 4.2 (at 20 GHz)	n.m.	n.m.
Magnetic constant ($\rho = 350 \pm 2$ kg/m^3)	0.8 (at 8–12.4 GHz)	n.m	n.m.
Compression strength (MPa)	1.2–12.5	2.1–18.3	n.m.
Flexural strength (MPa)	0.5–12.5	2.9 ± 0.01 ($\rho = 310$ kg/m^3)	n.m.
Elastic modulus (GPa)	0.4–7.6	1.4 ($\rho = 310$ kg/m^3)	n.m.
Fracture toughness (MPa m$^{1/2}$)	0.15–0.25	n.m.	n.m.

n.m. = not yet measured.

tional ceramic foams, possessing electrical conductivity[20] or magnetic properties,[22] or maintaining high specific surface area (SSA) values up to elevated temperature (1000 °C).[19] One of the characteristics of producing macro-cellular ceramic foams from direct foaming (if no PU precursors are present) is that graded structures are formed, with lower density and larger cells at the top of the sample (see Fig. 3a). If carefully controlled, this could provide a way of preparing ceramic matrices for interpenetrating, 3D graded composites (by infiltration with a metal[60,61] or a polymer or carbon precursors) with advanced properties.

In Table 1 are reported the main characteristics of SiOC macro-cellular porous ceramics, together with the data so far collected for porous components produced following the other two processing procedures.

SiOC micro-cellular foams have been demonstrated to possess superior mechanical properties, due to their small strut size which limits the dimension of the critical flaws present.[24] An influence of the cell size was also observed, with decreasing strength with increasing cell size.[26] As the interconnecting pores between cells (cell windows) are typically rather small (1–50 μm—see Fig. 2),[26,29] their permeability is lower than for conventional ceramic foams, but still suitable for applications such as aerosol filtration.[31] The cell size (and cell size window size) is related by a linear relationship to the size of the sacrificial microbeads template used, and the amount of porosity depends obviously on the quantity of microbeads employed. Closed cells can be obtained if the amount of sacrificial microbeads is kept below a certain value.[49] By stacking layers of microbeads with different size, it is possible to produce crack-free graded porosity structures, in which both the average cell size and the relative density can be varied along the main axis of the sample (see Fig. 3b).

Because of their very large geometric surface area (of the order of a few m^2/cm^3, because of the small cells and the presence of cell walls) they are ideally suited for the deposition of coatings of materials with different functionalities (for instance, zeolites[27,62] or meso-porous coatings[30]); furthermore, the complete interconnection of the porosity provides easy access to the precursors for depositing such layers, and their chemical inertness allows processing and use in harsh environments.

Again, filler with different properties can be added to the SR to modify the composition and properties of the porous ceramic produced. These fillers can be added up to a significant amount (up to more than 50 vol%, depending on the powder size) without disrupting significantly the morphology of the resulting porous ceramic. Besides functional porous components (heating elements, magnetic filters,[33] absorbers), ceramic materials with different compositions can be thus produced, including cordierite,[5] mullite,[63] SiC,[64] SiAlON[7] and wollastonite.[65]

Another strategy for producing highly porous ceramics from preceramic polymers is the mixing of precursors with different molecular architecture.[37] A silicone resin (poly-silsesquioxane) typically possesses a cage-like structure and has a high ceramic yield (>65 wt%) upon pyrolysis, while a conventional polysiloxane has a linear structure and, because of that, a low ceramic yield (<30 wt%). When mixing these two precursors to form a dense, green body, porosity is formed during pyrolysis, because of the different behavior that the two polymers display. Beside a very different weight loss, there are also differences in their relative shrinkage and in the amount of gas generated (all much higher for the siloxane with a linear structure than for the silicone resin).

Porous structures of various morphology can thus easily be produced depending on the composition of the starting mixture (see Fig. 2c as an example of a component obtained from 60 wt% PDMS and 40 wt% of SR). It can be seen that open porosity is present in the sample, and that the specimen had quite a complex morphology. Besides large pores of a few hundred microns in size, a large amount of smaller pores and cavities are present. The control of the pore size and shape in the porous component depends on the characteristics of the polymer mixture, the relative miscibility and amount of the precursors used, the degree of crosslinking before pyrolysis, and the (possible) use of a common solvent. Albeit the morphology of the porosity in these components is rather inhomogeneous, some properties of cellular materials depend solely on the relative density (the total amount of porosity) of a component, rather than on a specific cell/pore size value. This fabrication method is much simpler than the ones (a and b) reported above, and thus could be favored for the production of large size parts.

The porosity in polymer-derived ceramics can be further engineered by developing micro- and meso-pores (affording high SSA). Moreover, the combination of macro-pores (either in micro-cellular or macro-cellular samples) and micro- and meso-pores leads to components possessing hierarchical porosity, that can be employed in separation, gas storage, removal of pollutants and catalysis applications. One of the most effective methods for producing high SSA in polymer-derived ceramics is to perform a well controlled heat treatment cycle.[19,66–69] This approach takes advantage of the transient porosity generated upon heat treating a preceramic polymer in the temperature range at which the polymer-to-ceramic conversion occurs (generally 400–800 °C).[4,70] The build-up of internal pressure in the component, provoked mainly by the decomposition of the organic moieties in the preceramic polymer (with generation typically of CH_4 and H_2 gas) leads to porosity (with pore size typically below 50–100 nm). This (micro-)porosity is however transient, because it is eliminated (and thus the SSA value is drastically reduced) when the pyrolysis temperature leading to the completion of the ceramization process is increased, according to a densification mechanism based on surface reaction/pyrolysis accommodated by viscous flow.[70] The amount of produced specific surface area is stable up to the pyrolysis temperature reached, even after prolonged heating at the same temperature.

Other alternative routes that have been explored for developing hierarchical porosity components from preceramic polymers include the addition of high SSA fillers (such as carbon black[19]), the deposition of zeolites[27] or of meso-porous coatings,[30] the infiltration of an aerogel into open-celled foams,[71] etching in HF[32] and, recently, the in situ formation of nano-wires/-tubes.[72,73] In Table 2 are reported the typical SSA values obtained depending on the processing procedure followed.

Table 2
Typical SSA values obtained depending on the processing procedure followed for producing hierarchical porosity ceramic components

Processing route	SSA (m^2/g)	References
Controlled thermal treatment of preceramic polymers	400–700[a]	19,66–69
Addition of high SSA fillers	400–650[a]	19
Deposition of zeolites	150–300	27
Deposition of meso-porous coatings	60	30
Infiltration of aerogels into foams	150–220	71
Etching	150–600	32
In situ formation of nano-wires/-tubes	50–70	72

[a] at 600 °C.

To conclude, in Fig. 4 are reported some examples of possible applications for porous ceramic components produced from preceramic polymers.

Electrical conductivity (Fig. 4a) was obtained by the addition of α-SiC powders (40 wt%) to the SR (applied voltage differential = 200 V); the crater in the micro-cellular foam sample (Fig. 4b) was formed after the hit by a 1 mm Al ball projectile traveling at a speed of 4.5 km/s to simulate the conditions commonly encountered in a near-earth space environment by hypervelocity impact shields (on top of the foam there was a 0.4 mm thick sheet of Al 2017 alloy, to ensure a preliminary fragmentation of the incoming projectile); a ferromagnetic behavior was afforded to SiOC micro-cellular foams (Fig. 4c) by the introduction of iron silicide powders (40 wt%); a 3D interpenetrating composite (Fig. 4d) was produced by melt infiltration (130 MPa, 780 °C under inert gas, infiltration time 3 s) of Al (99.99%) into a micro-cellular foam with an average cell size of about 25 μm. Other applications for which SiOC-based porous ceramics have been so far tested for (not reported here for
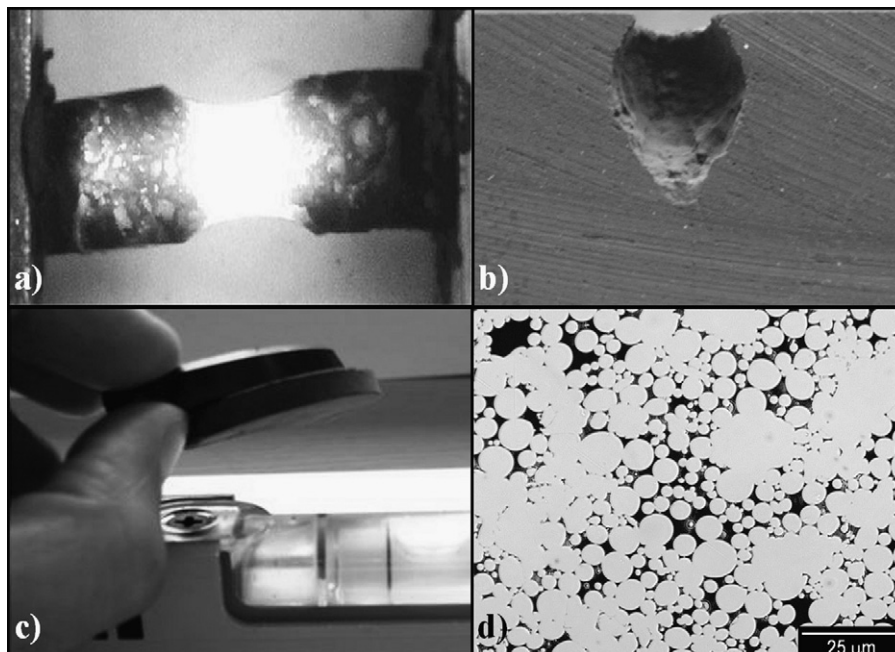

Fig. 4. Examples of different possible applications for preceramic polymer-derived porous ceramic components. (a) Macro-cellular heating element; (b) micro-cellular hypervelocity impact absorber; (c) micro-cellular magnetic component and (d) Al–SiOC interpenetrating composite (image courtesy of S. Vaucher, EMPA).

the sake of brevity) include thermal protection components for space vehicle re-entry, micro-reactors for chemical engineering applications, aerosol filter components and gas adsorbers. It is believed that these materials could find also use as high temperature acoustic insulation, as well as thermal shock-resistant components.

4. Conclusions

Porosity can be engineered in polymer-derived ceramics by employing several processing methods, which include replica of a polymeric template, direct foaming of a solution or slurry or the use of sacrificial pore formers. Macro-porous ceramics with a high total amount of porosity (55–90 vol%) and with pore (cell) size ranging in a very wide range of values ($\sim$1 µm to 2 mm) can be obtained, as well as micro- (<2 nm) or meso- ($2 < d_{pore} < 50$ nm) porous materials. Components with hierarchical porosity can also be produced either by controlled pyrolysis, deposition of various meso-porous layers, etching or the addition of suitable fillers. The produced ceramic components, possessing various compositions, morphologies and properties, have been tested with success in several diverse applications.

Acknowledgements

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