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Short Communication

A novel processing approach for free-standing porous non-oxide ceramic supports from polycarbosilane and polysilazane precursors

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Abstract

In this contribution, a low-pressure/low-temperature casting technique for the preparation of novel free-standing macrocellular polymer-derived ceramic support structures is presented. Preceramic polymers (polycarbosilane and poly(vinyl)silazane) are combined with sacrificial porogens (ultra-high molecular weight polyethylene microbeads) to yield porous ceramic materials in the Si—C or Si—C—N systems, exhibiting well-defined pore structures after thermal conversion.

The planar-disc-type specimens were found to exhibit biaxial flexural strengths of up to 60 MPa. In combination with their observed permeability characteristics, the prepared structures were found to be suitable for potential applications in filtration, catalysis, or membrane science.

Keywords: Polymer-derived ceramics; Polycarbosilane; Polysilazane; Support; Porosity

1. Introduction

Porous non-oxide ceramics such as SiC and Si_3N_4 are interesting materials due to their ability to bear high mechanical stresses, high temperatures, as well as corrosive environments, suggesting their suitability as support structures for catalysis [1] or membrane applications [2–4]. However, the generation of these macroporous structures typically requires partial sintering of particulates at high temperatures.

An alternative to conventional sintering-based consolidation approaches is the use of the polymer pyrolysis technique, in which non-oxide ceramics are produced through pyrolytic conversion of Si-based precursors such as polysilazanes or polycarbosilanes. This method allows for a high flexibility during processing, high purity of products, and decreased temperature requirements during consolidation [5].

Porous polymer-derived ceramics can be obtained through a combination of the polymer pyrolysis route with a variety of pore forming techniques, including replica forming, direct foaming, or by using sacrificial fillers [6,7]. The use of sacrificial fillers such as polymethyl methacrylate (PMMA) [8], polystyrene (PS) [9], or polyethylene (PE) [10], which are removed by thermal decomposition during the thermal conversion of the preceramic polymers, allows for a high tailorability and reproducibility of the pore structure, which is highly desired for potential applications with reproducible strength and permeability properties [11]. In the majority of reports, compaction processes (cold- or warm-pressing) were used for the consolidation of the precursor/porogen mixtures. While the use of liquid precursors in combination with sacrificial fillers has been described in the literature, the applied techniques (e.g., micromolding [9]) were strongly limited in terms of sample size and shape.

In this paper, we present a new, versatile technique to obtain porous, non-oxide, polymer-derived ceramics by

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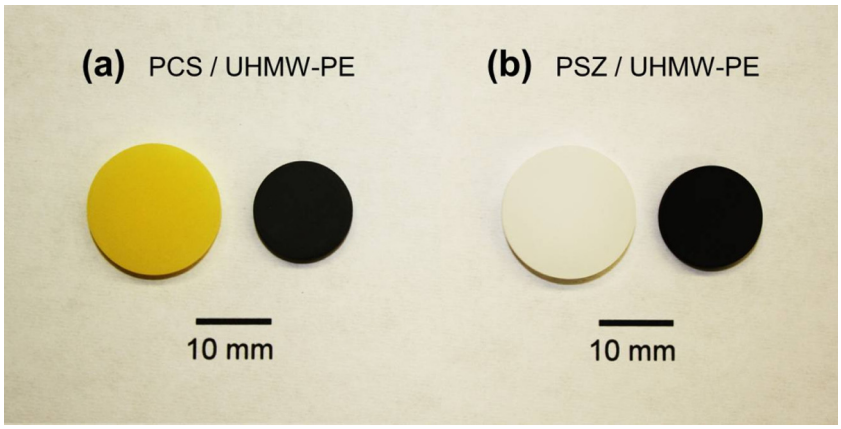

Fig. 1. Appearance of PCS (a) or PSZ (b) specimens containing UHMW-PE before (left) and after pyrolytic conversion (right).

following a sacrificial filler approach, employing a pressureless casting/cross-linking process with subsequent conversion of the precursors at low temperatures, thus facilitating the preparation of free-standing, macroscopic specimens with relative ease. This process is also expected to be easily scalable and capable of producing complex shapes. The objective of this work is the demonstration of the feasibility of this technique for different preceramic polymers, yielding porous non-oxide ceramics with homogeneous pore distributions, as well as strength and permeability characteristics facilitating potential applications as catalyst or membrane supports.

2. Experimental procedure

In this study, two commercially available liquid preceramic polymers were used. Allyl hydrido polycarbosilane (*PCS*; SMP-10, Starfire, USA) was used as a precursor for Si-C-based ceramics, and poly(vinyl)silazane (*PSZ*; HTT1800, AZ Electronic Materials, USA) was used as a precursor for Si-C-N-based ceramics. In both cases, 1 wt% of a radical initiator (Dicumyl peroxide, 99%, Acros Organics, USA) was added to promote cross-linking. An ultra-high molecular weight polyethylene powder (*UHMW-PE*, Mipelon PM-200, Mitsui Chemicals America, USA; molecular weight of 1.8×10^6 g mol^{-1}) with a mean particle size of 10 μm was used as sacrificial filler at a volume fraction of 30%. Before use, the polyethylene powder was dried in vacuum at 50 °C for 12 h.

Due to the reactivity of the polymer precursors with air and water, handling of the materials was conducted in inert atmosphere, using a glove-box. After fully dissolving the radical initiator in the polymers by magnetic stirring, and subsequent vacuum degassing, corresponding amounts of polymer and filler were mixed by magnetic stirring in vacuum for a minimum of 30 min. The obtained viscous mixture was cast in polydimethylsiloxane moulds (Mold Max XLS II, Smooth-On Inc., USA) with cylindrical cavities (diameter of 18 mm). Subsequently, the mixture was cross-linked at 105 °C for 16 h in flowing N_2. After demolding, a thermal post-curing step using the same conditions was carried out. The top and bottom surfaces of the cross-linked discs were ground to a 2000 grit finish. The specimens were fully crosslinked and pyrolyzed in high-purity flowing Ar (PCS-derived samples) or N_2 (PSZ-derived samples) atmosphere. The thermal treatment included an initial heating rate of 1 K min^{-1} (Lindberg Blue M HTF5534C, Thermo Scientific, USA) to the cross-linking temperature (PCS: 2 h hold at 130 °C and 1 h hold at 250 °C; PSZ: 2 h hold at 130 °C). Following this step, a heating rate of 0.5 K min^{-1} was used to heat the samples to the pyrolysis temperature (4 h hold at 800 °C).

The pore structure of the pyrolyzed ceramic discs with final diameters of around 14 mm and heights of around 2 mm was investigated by scanning electron microscopy (*SEM*; S4800, Hitachi, Japan). The bulk density was calculated from the sample weight and geometric dimensions. The total porosity and the pore opening size distribution were measured by mercury intrusion porosimetry (PoreMaster 33, Quantachrome, USA). The specific surface area was determined by N_2 adsorption employing the Brunauer–Emmett–Teller (BET) method (ASAP 2010, Micromeritics, USA). Before conducting the adsorption runs, the samples were degassed in vacuum at 200 °C for 24 h. To evaluate the mechanical strength of the samples, a biaxial flexural test employing a ball-on-three-balls (B3B) setup [12] was used with stainless steel balls of 9.525 mm diameter. A Poisson's ratio of 0.2 was assumed for both sets of samples. In order to estimate strength variability, 15 samples were tested for each composition.

Permeability of the pyrolyzed supports (8 samples per composition) was determined by a capillary flow porometer (CFP-1100-AEXS, Porous Materials, Inc., USA) at a pressure difference Δp up to 1 bar using Darcy's law, employing air as the fluid.

3. Results and discussion

The development and successful implementation of a low-pressure casting technique allowed for the reproducible production of large numbers of polymer-derived ceramic samples without the need to use pre-crosslinked precursor materials or time-consuming and shape limited consolidation techniques such as warm-pressing.

After cross-linking, bubble-free specimens were obtained, which were readily formable by cutting and grinding, thus yielding planar disc-shaped specimens. In addition to low heating