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Directionally aligned macroporous SiOC via freeze casting of preceramic polymers

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Abstract

A commercially available polysiloxane was used as a preceramic polymer for solution freeze casting to obtain directionally aligned porous silicon oxycarbide. We show how choice of solvent, polymer concentration, and freezing rate can affect the final pore network of the freeze-cast ceramic. Solvents of cyclohexane and camphene resulted in dendritic pores, while tert-butyl alcohol (TBA) produced intersecting cellular pores in the freeze-cast ceramic. Characterization of pore size distribution by mercury intrusion porosimetry of ceramics produced from cyclohexane–polysiloxane solutions with varying polymer concentrations and freezing rates demonstrated trends consistent with solidification theory. Fourier transform infrared spectroscopy and X-ray diffraction were employed to confirm that the freeze-casting process resulted in silicon oxycarbide of comparable chemistry and crystallinity to that produced via traditional preceramic polymer processing techniques.

Keywords: Porous ceramics; Preceramic polymers; Freeze casting; Silicon oxycarbide (SiOC); Polysiloxane

1. Introduction

Pores are often considered to be defects in materials, especially in ceramics, since they can act as stress concentrators and reduce the mechanical integrity of a component. The controlled inclusion of porosity, however, can provide structures with a lower relative density, leading to lightweight components, while also increasing surface area and transport capabilities [1]. Due to these benefits, porous ceramics have gained interest in applications such as filtration media, catalyst supports, scaffolds, thermal management materials, and electrodes for batteries and fuel cells [2,3]. Properties such as pore size, fraction, morphology, tortuosity, and interconnectivity define the pore network of a material, and consequently, its functionality [4,5]. Therefore, it is of great interest to be able to control and manipulate the pore network of any material during the fabrication process.

Methods for fabricating porous ceramics include techniques such as partial sintering, direct foaming, replication, additive manufacturing, robocasting, and sacrificial templating, each of which is capable of generating different pore morphologies and sizes [1,6,7]. Freeze casting is a form of sacrificial templating in which a frozen liquid phase acts as a template for the pores. In freeze casting, a material of interest is dispersed in a liquid medium (e.g., water), which is frozen to form a solid (i.e., ice) before it is sublimated to yield a porous network that is representative of the dispersing medium's frozen structure [8]. Through this process, structures with pore networks that are reminiscent of natural materials such as wood and bone can be readily fabricated, possessing directionally aligned pore channels with diameters on the order of a few to several tens of microns. These microstructures are inherently multifunctional, as the narrow, aligned cells optimize the mechanical properties in a particular direction while the pores facilitate functions such as pathways for flow and filtration.

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Freeze casting has been shown to be capable of producing unique pore networks in a simple and efficient manner. It is therefore not surprising that aside from porous ceramics, porous metallic [9] and polymeric [10,11] structures have also been fabricated by freeze casting. Metal and ceramic components are generally fabricated by freeze casting their respective powder dispersions and sintering the structure in the appropriate atmosphere. Polymers, on the other hand, are usually dissolved in a solvent to form a homogeneous solution before they are frozen. Although the majority of ceramic materials today are manufactured using traditional powder methods, ceramics can also be produced through the use of preceramic polymers [12].

Preceramic polymers are polymers that can be converted into a ceramic by pyrolysis in an inert atmosphere. Silicon-based precursors yielding SiC, SiCN, and SiOC are the most commonly used preceramic polymers [13]. However, additional compounds, such as boron-based materials, can be fabricated by simply altering the polymer used [14,15]. Thus, the use of preceramic polymers enables production of a wide variety of ceramic materials to be produced and expands upon the available manufacturing design space as compared to traditional powder processing [12,13]. Moreover, it has been shown that the addition of nano- and micro-sized powders to preceramic polymers allows one to fabricate a wide range of advanced silicate ceramics for different engineering applications [16]. It is also noteworthy to mention that preceramic polymers can develop micro- and meso-pores through controlled pyrolysis [17], and that the addition of suitable catalysts enables the in situ formation of nanowires [18], thereby leading to components with hierarchical porosity and high specific surface area.

Although considerable work has been done on freeze casting of ceramic powders (suspension freeze casting) [19–22], little has been explored with regard to fabricating porous ceramics by freeze casting preceramic polymers (solution freeze casting). Namely, a study by Yoon et al. demonstrated the ability to produce polymer-derived SiC ceramics with a dendritic pore structure by freeze casting a polycarbosilane/camphene solution [23]. Since alumina/camphene suspensions have also been shown to yield a dendritic structure dictated by camphene's solidification behavior [24], one may infer from this study that freeze casting of ceramic suspensions and preceramic polymers are analogous. However, these two processes contain noteworthy differences. In particular, a polymer solution can also be used to fabricate microporous polymeric membranes with drastically different, bead-like, morphologies through a similar temperature-induced process [25–27]. These bead-like microstructures cannot be produced by freeze casting ceramic slurries, but only with polymer solutions. The difference is due to the formation of the microstructure through phase separation processes such as liquid–liquid demixing and spinodal decomposition, which do not occur when freeze casting ceramic suspensions. Despite numerous studies conducted on phase separation and its effects on polymeric membranes, freeze casting of preceramic polymers is a different process and requires increased attention. The ability to freeze cast preceramic polymers will generate opportunities for creating porous ceramics with a wider variety of material composition and pore networks.

In this work, polysiloxane was used as a model preceramic polymer for solution freeze casting due to its commercial availability and use, its high ceramic yield, as well as its ease in processing compared to most other preceramic polymers. Cyclohexane, camphene, and tert-butyl alcohol (TBA) were used as solvents for the polymer. These solvents were chosen primarily due to their relatively high melting temperatures (6 °C to 36 °C), which help make the freeze-casting process more feasible. Relationships between the polymer, solvent, and pore network achieved from freeze casting, as well as the ability to convert the freeze-cast polymeric body into stable SiOC are explored and discussed in this study.

2. Experimental details

2.1. Materials

A commercially available polysiloxane (Silres® MK Powder, Wacker Chemie, CH_3–$SiO_{1.5}$, Munich, Germany) was used as the preceramic polymer. Three solvents for the polysiloxane were compared: cyclohexane (m.p. = 6 °C, Sigma–Aldrich, St. Louis, MO, USA), camphene (m.p. = 36 °C, Alfa Aesar, Ward Hill, MA, USA), and tert-butyl alcohol (m.p. = 26 °C, Fisher Scientific, Waltham, MA, USA). Dibutyltin dilaurate (DBTDL, Dabco® T-12, Air Products, Allentown, PA, USA) was chosen as the cross-linking agent.

2.2. Processing

Typical procedures for freeze casting and processing polymer-derived ceramics (PDCs) were combined to create a protocol for producing porous ceramic structures, as shown in Fig. 1. First, the preceramic polymer was dissolved in a heated solvent to create a homogenous solution. A cross-linking agent was then added to partially cross-link the polymer chains while in solution. Next the solution was frozen, during which thermally-induced phase separation between the preceramic polymer solute and the solvent occurs. The solidified solvent was sublimated by freeze drying, resulting in a porous structure made of cross-linked polymer. Finally, the cross-linked polymer sample was pyrolyzed in an inert atmosphere to yield a ceramic.

In this work, each solvent was heated to 60 °C before adding the MK preceramic polymer. The polymer was allowed to dissolve for 10 min while the solution was mixed with a magnetic stir bar. Polymer concentrations of 5, 20, and 40 wt.% were used. After a homogeneous polymer solution was achieved, DBTDL was added (2–5 wt.% of solution), and the solution was mixed for 10 additional minutes. Excessive cross-linking of the polymer solution can cause gelation, which obstructs solvent crystallization and inhibits pore formation. Conversely, insufficient cross-linking can result in poor mechanical integrity in the polymeric state after solvent sublimation, or even melting and collapse of the porous structure when heated. For the present research, the amount of cross-linking agent used was established experimentally. Initially, a high DBTDL concentration of up to 12 wt.% of solution was used, but this resulted in gelation of the solution. The concentration was then incrementally reduced by