Full length article

Bioinspired intrinsic control of freeze cast composites: Harnessing hydrophobic hydration and clathrate hydrates

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ABSTRACT

Bioinspired ZrO_2-epoxy, two-phase composite materials were fabricated by the freeze casting fabrication technique followed by polymer infiltration. These materials were intrinsically controlled by adding varying concentrations of the monofunctional alcohols ethanol (EtOH), n-propanol (n-PrOH) and n-butanol (n-BuOH). The microstructures of freeze cast scaffolds created with these alcohol additives demonstrated maximum pore areas (peak A_p) at concentrations of 10, 5–7 and 3 vol% for EtOH, n-PrOH and n-BuOH respectively. Differential scanning calorimetry analyses of binary mixtures of these additives and water suggested only n-PrOH was capable of developing clathrate hydrates. Measurements of the adiabatic compressibility of complete freeze casting slurries showed that a similar room temperature phenomenon, hydrophobic hydration, was occurring in all cases with the maximum effect occurring at the same additive concentrations as the peak A_p values. This highlights that effects occurring within the slurry at room temperature and before freezing may have a significant effect on the freeze casting process. Analysis of the mechanical properties shows that infiltration of the scaffolds can provide resistance to Euler buckling, resulting in strengths of ~3 orders of magnitude greater than uninfiltrated (and therefore unsupported) scaffolds. This suggests that layered structural design elements, found throughout nature, may be harnessing this Euler buckling resistance to increase strength.

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1. Introduction

Freeze casting has been an attractive area of research in recent years as it offers the potential to fabricate controlled porous microstructures through a simple and inexpensive technique [1–5]. The process itself is carried out in four steps: (1) a slurry of solid loading (e.g. ceramic particles) and liquid freezing agent is prepared along with polymeric binders and dispersants, (2) the slurry is frozen in a directional and controlled manner with the solid loading forming lamellar walls (when H_2O is used as a freezing agent) [1–5], (3) the frozen scaffold is lyophilized (freeze dried) to remove the freezing agent, where aligned pores result from the sublimated ice crystals, (4) the scaffold is then sintered to enhance its strength.

Once fabricated, a fifth, post-processing step can be implemented. One method of post-processing is to infiltrate the bare scaffolds with polymers or metals to create two-phase interpenetrating composites [5–8].

These resultant, composite scaffolds have been fabricated into bioinspired designs similar in structure and properties to bone [9–13] and the nacre of abalone [1,14]. Biological layered structures such as these are found in successful organisms from deep sea sponges to beetles to humans where they are capable of providing significantly improved mechanical properties due to their hierarchical structuring [15]. Given this success, the study of these bioinspired composites is a field that provides great potential for structural and biomedical applications. While there are many methods to fabricate bioinspired designs, the ability within freeze casting to control the microstructure and mechanical properties of the resultant materials through relatively simple alterations to the processing conditions is key to the potential of the technique. More

importantly, freeze casting is capable of harnessing the same fundamental construction method as so many biological materials in templating. Where collagen provides a template for biogenic hydroxyapatite in bone [16] and fish scales [17], the ice itself provides the template for the ceramic of a freeze cast scaffold. By employing this similar technique, the hierarchical structures within biological materials can be easily mimicked and explored.

When considering control of the freeze casting process, an analogy can be drawn to the processes involved with the resistance to crack propagation in fracture mechanics where toughness is imparted through intrinsic (processes that occur ahead of a growing crack, occur on smaller length scales and are generally inherent to the material itself) and extrinsic (processes that occur in the wake of a growing crack, act on larger length scales and are often controlled by structural features) mechanisms [9,18]. Similarly, control of freeze casting can also be considered to be by intrinsic (those acting within the slurry that are inherent to its freezing and chemical interactions) or extrinsic (those acting on the freezing process through outside forces) mechanisms.

Recent work into intrinsic control of freeze casting with the monofunctional alcohol isopropanol (IPA) as an additive to the slurry reported the presence of clathrate hydrates in the freezing process leading to enlarged final porosity [19,20]. Clathrate hydrates are defined as non-stoichiometric structures where a hydrogen bonded molecule enclosure lattice (made of H_2O molecules) surrounds a guest molecule (e.g. monofunctional alcohols) with limited or no chemical bonding to the lattice [21]. These structures can be defined by the hydration number, n_h, which is defined as the number of H_2O molecules per guest molecule. Values of n_h vary depending on the guest molecule with most alcohols producing values of ~1−6. The enlarged unit cells of clathrate hydrates occurring during the freezing process have been shown to contribute to the observed increase in pore area in the final freeze cast scaffold [20]. However, there is still a significant unanswered question in this explanation as the pore area shows a parabolic relationship with the concentration of IPA additive. This is illustrated in Fig. 1, comparing results generated for this study (using the same parameters described below) along with previous studies for ZrO_2 [20] and TiO_2 [19] scaffolds. To account for the

discrepancies in processing parameters, the results in Fig. 1 are normalized to the pore area reported for a scaffold with no additive (0 vol% IPA = A_{p0}). In spite of this, all three trials demonstrated a maximum in pore area, described here as peak A_p, at the same concentration of 5−7 vol% IPA.

In this work we present a homologous series of linear monofunctional alcohols as intrinsic templating additives: ethanol (EtOH, C_2H_5OH), n-propanol (n-PrOH, C_3H_7OH) and n-butanol (n-BuOH, C_4H_9OH). EtOH [22,23] and n-PrOH [24] have been reported to form clathrate hydrates in dilute binary mixtures at low temperatures. While there are no current reports on the presence of clathrate hydrates in n-BuOH, the branched butanol, tert-butyl alcohol has been reported to form clathrate hydrates in dilute concentrations [23]. In addition, we present data and analysis on the mechanics of bioinspired composites created with these scaffolds and are able to provide new insight into the structural support provided by the infiltration of freeze cast materials as well as layered structures in nature.

2. Materials and methods

2.1. Sample preparation

Aqueous slurries were prepared to investigate the effects of linear monofunctional alcohols as additives to the freeze casting process using EtOH (Koptec, King of Prussia, PA, USA), n-PrOH (Fisher Scientific, Fair Lawn, NJ, USA) and n-BuOH (J. T. Baker, Center Valley, PA, USA). Slurries consisting of 15 vol% ZrO_2 powders (200−500 nm diameter) (Sigma Aldrich, St. Louis, MO, USA) were mixed with 1 wt% polyethylene glycol (PEG) with a molecular weight of 10,000 g/mole (Alfa Aesar, Ward Hill, MA, USA), 1 wt% polyvinyl alcohol (PVA) with a molecular weight of 100,000 g/mole (Alfa Aesar, Ward Hill, MA, USA) and 1 wt% of an ammonium polymethacrylate anionic dispersant, Darvan 811 (R. T. Vanderbilt Company, Inc., Norwalk, CT, USA). Slurries were prepared by varying two parameters: the volume fraction (0, 1, 3, 5, 7, 10 and 15 vol%) and the additive (EtOH, n-PrOH and n-BuOH) for a total of 21 slurries. All slurries were ball milled in an alumina grinding medium for 24 h then degassed under low vacuum for 5−10 min. Samples of approximately 10 mL of the degassed slurry were poured into a freeze cast mold and frozen at a constant rate of 10 K/min using a custom built freeze casting device, as previously described [25]. After freezing, samples were lyophilized in a benchtop freeze dryer (Labconco, Kansas City, MO, USA) at 223 K and 350 Pa for 70 h. After freeze drying, the green scaffolds were sintered in an open air furnace for 3 h at 1623 K with heating and cooling rates of 2 K/min. This sintering procedure is similar to procedures reported as effective for ZrO_2 scaffolds [20,25]. This entire process was performed in triplicate to create three full sets of scaffolds (63 total scaffolds) and ensure reproducibility of the current results. In addition, one set of scaffolds were fabricated using the exact procedure described above with 0, 1, 3, 5, 7, 10 and 15 vol% isopropanol (IPA) to create a comparison between current and previously reported results (Fig. 1).

Each scaffold was infiltrated with a two-component polymer epoxy, Epoxicure 2 (Buehler, Lake Bluff, IL, USA) by in situ polymerization in order to form a ceramic-polymer composite for imaging and mechanical testing. Samples were immersed in a mixture of liquid monomer and catalyst under low vacuum for 20−30 min to force the liquid to infiltrate the scaffold pores. The infiltrated scaffolds were then allowed to polymerize for 24 h. Samples of pure epoxy were simultaneously created to use for comparative analysis of the mechanical properties.
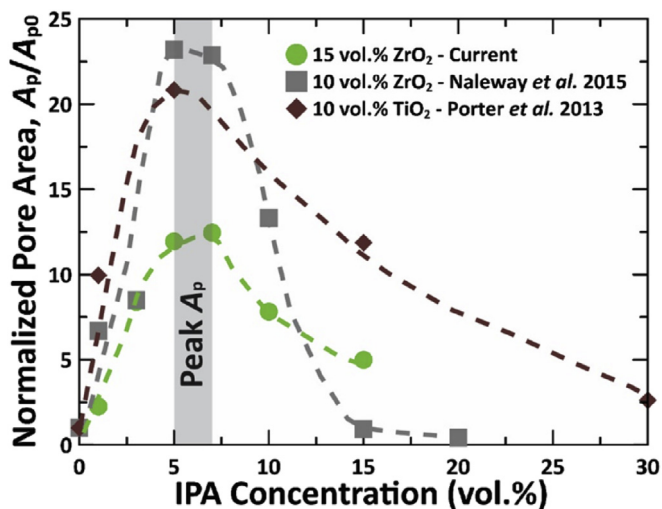

Fig. 1. Pore area, A_p, data for previously reported and current results using isopropanol as a freeze casting additive. Results are normalized to the pore area with no additive, A_{p0} (0 vol% IPA). Solid loading is different in each case: current results use 15 vol% ZrO_2, Naleway et al. [20] used 10 vol% ZrO_2 and Porter et al. [19] used 10 vol% TiO_2. In each case a parabolic relationship between pore area and IPA concentration is shown with a peak A_p at 5−7 vol% IPA. Data taken from Refs. [19,20].