



## Bioinspired composites from freeze casting with clathrate hydrates



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### ABSTRACT

Freeze casting with isopropanol (IPA)–H<sub>2</sub>O as a freezing agent has shown the potential to create porous scaffolds with enlarged pores. Though not experimentally proven, this effect has been suggested to be the result of non-stoichiometric structures called clathrate hydrates forming during the freezing process. In this manuscript, we build upon these results to provide experimental evidence of the formation of clathrate hydrates during the freeze casting process when using IPA–H<sub>2</sub>O as a freezing agent and explain the observed maximum in pore area through observations of the enthalpy of the transitions. Additionally, these enlarged pores are harnessed in order to create two-phase bioinspired composites. These composites exhibit an increase in mechanical strength over both constituents, a phenomena that is common to complex biological composites. Previous reports have shown that the characteristic method of failure for many freeze cast scaffolds is buckling of the lamellar walls within the porous microstructure. It is proposed that this increase in mechanical strength is due to the support of the second phase, which resists this characteristic buckling failure mode.

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### 1. Introduction

Amongst the most common structural elements found within nature are layered two phase composites made up of interpenetrating ductile and brittle phases. These structures, for example, are found in mammalian bone [1], gastropod shells [2] and fish scales [3]. These composites are known for their excellent mechanical properties, which often exceed what would be expected from a simple mixture of their constituents [4]. As a result, there has been much research into bioinspired, two phase composite materials [5–7]. In most cases, to more closely mimic the nature of biological materials, these composites have consisted of ceramic and polymeric phases [5–7]. The freeze casting fabrication technique has been explored as a method to create such two phase composite materials [6,8,9].

The freeze casting process has been studied over the last decade due to its versatility, ease of use and inexpensive setup and operation [5,10,11]. Freeze casting is carried out by directional solidification, in a controlled manner, of a slurry made up of solid loading

(e.g. ceramic particulates) and a liquid freezing agent. The frozen scaffolds are then lyophilized (freeze dried) followed by sintering in order to form a final ceramic scaffold where the ice crystals have been converted into aligned pores and the solid loading has formed lamellar walls (when H<sub>2</sub>O is utilized as the freezing agent) [5,10,11]. Altering the slurry properties through the solid loading [12,13] and liquid freezing agent [14,15] characteristics have been reported to alter the final scaffold microstructure. Additionally, control of the final scaffolds have been reported through the application of external forces and processes such as changing the freezing rate [16] and applying electric [17] and magnetic fields [18].

After fabrication, porous freeze cast scaffolds can be infiltrated with polymers or metal melts in order to form interpenetrating ceramic–polymer composites [6,19–21]. There are a number of reported polymer infiltration methods including: particle centrifugation [22], *in situ* polymerization [4,23] and polymer solvent evaporation [24]. Amongst these, the most commonly applied method is *in situ* polymerization where a liquid monomer and catalyst are infiltrated into a scaffold under vacuum and then allowed to polymerize [4,5,23].

The recent work of Porter et al. [14] demonstrated the effect of isopropanol (IPA) as an additive to freeze casting with TiO<sub>2</sub> as the solid loading. The resultant scaffolds showed a large increase in

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pore area up to an observed maximum at 5 vol.% IPA. This increase in pore area was linked to a decrease in the scaffold mechanical properties. Mechanically, this was shown to be the result of buckling of the lamellar walls. The pore area increase was suggested to be the result of the formation of clathrate hydrates in the freezing process due to their known presence in frozen IPA–H<sub>2</sub>O binary mixtures [25]. While this proposed mechanism is supported by previous literature on IPA–H<sub>2</sub>O binary mixtures under steady state conditions, there is no current evidence of clathrate hydrates forming at the high cooling rates observed during the freeze casting process.

In this work we build upon our previous experience on IPA–H<sub>2</sub>O freeze casting [14]. We propose the use of IPA–H<sub>2</sub>O freeze casting as a simple method to create bioinspired structural composite materials. Additionally, evidence is presented to prove that clathrate hydrates are indeed forming in the freeze casting process and aiding in the creation of enlarged pores. In order to isolate the effect of the IPA–H<sub>2</sub>O freezing agent, freeze cast scaffolds were based in zirconia (ZrO<sub>2</sub>), which has applications as porous solid oxide fuel cells, thermal barrier layers and for biological implants [26].

### 1.1. IPA clathrate hydrates

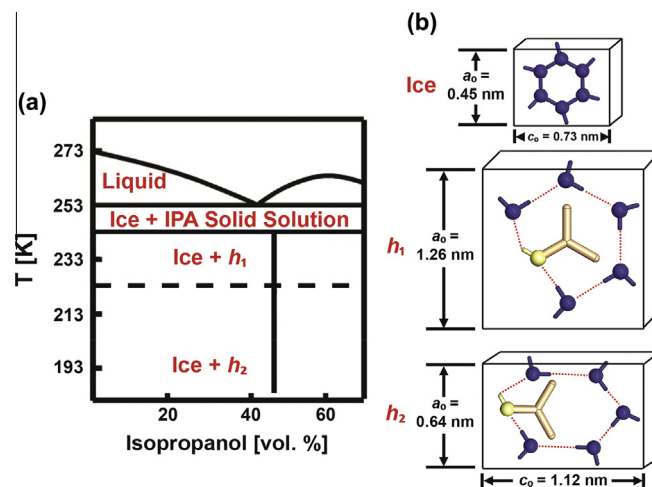
Clathrate hydrates are defined as non-stoichiometric structures where a hydrogen bonded molecule enclosure lattice (H<sub>2</sub>O) surrounds a guest molecule (e.g. IPA) with limited or no chemical bonding to the lattice [27]. While most clathrate hydrates are thermodynamically unstable at room temperature and ambient pressure, there are a number of H<sub>2</sub>O based solutions that produce clathrates at low temperatures or high pressures. Commonly reported clathrate hydrates include propane–H<sub>2</sub>O, which has been heavily studied for its effect on the oil and gas industry [28] and methane–H<sub>2</sub>O, which is commonly found at the bottom of the ocean [29]. In addition, binary systems of IPA–H<sub>2</sub>O have been reported to form clathrate hydrates at low temperatures and ambient pressures [25,30–33].

In general, clathrate hydrates are capable of forming into a number of different structures depending on the guest molecule size, chemistry and environmental conditions (e.g. pressure and temperature). However, most known clathrate hydrates form either into a structure I (*h*<sub>1</sub>) or structure II (*h*<sub>2</sub>). These structures are differentiated by their stacking and guest molecule cavity size with *h*<sub>1</sub> stacking on enclosure vertices and *h*<sub>2</sub> stacking on enclosure faces [28]. In the binary IPA–H<sub>2</sub>O system, stable clathrate hydrates form at an IPA concentration of 46 vol.% as an *h*<sub>1</sub> structure at 243 K, which converts to *h*<sub>2</sub> at 223 K. The phase diagram displaying this mixture is shown in Fig. 1a. Aladko et al. [25] reported on the *h*<sub>1</sub> and *h*<sub>2</sub> clathrate hydrates of the IPA–H<sub>2</sub>O system and determined that, in both cases the hydrophilic hydroxyl group of the guest IPA molecule replaces one of the H<sub>2</sub>O molecules in the enclosure lattice. This results in a cubic *h*<sub>1</sub> unit cell with *a*<sub>0</sub> = 1.26 nm and a tetragonal *h*<sub>2</sub> unit cell with *a*<sub>0</sub> = 0.64 nm and *c*<sub>0</sub> = 1.12 nm. Both clathrate unit cells are significantly larger than pure (hexagonal) ice where *a*<sub>0</sub> = ~0.45 nm and *c*<sub>0</sub> = ~0.73 nm. [34]. Diagrams representative of the unit cells found in the IPA–H<sub>2</sub>O binary phase diagram are shown in Fig. 1b.

## 2. Materials and methods

### 2.1. Sample preparation

Aqueous slurries were prepared with IPA to investigate the effects of monofunctional alcohols as additives to the freeze casting process. Slurries consisting of 10 vol.% ZrO<sub>2</sub> powders



**Fig. 1.** Phase diagram showing relevant features and unit cells for the IPA–H<sub>2</sub>O system at steady state. (a) Stable clathrate hydrates form at 46 vol.% IPA with an *h*<sub>1</sub> forming at 243 K then converting to an *h*<sub>2</sub> at 223 K; (b) Diagrams representative of the known unit cells for features of the IPA–H<sub>2</sub>O phase diagram: hexagonal ice (*a*<sub>0</sub> = ~0.45 nm, *c*<sub>0</sub> = ~0.73), *h*<sub>1</sub> clathrate hydrate (cubic, *a*<sub>0</sub> = 1.26 nm) and *h*<sub>2</sub> clathrate hydrate (tetragonal, *a*<sub>0</sub> = 0.64 nm, *c*<sub>0</sub> = 1.12 nm). H<sub>2</sub>O molecules are shown in dark blue, IPA molecules are shown in brown (the aliphatic group) and yellow (the hydroxyl group). Phase diagram and clathrate hydrate unit cell data adapted from Aladko et al. [25], hexagonal ice unit cell data adapted from Rottger et al. [34]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(200–500 nm diameter) (Sigma Aldrich, St. Louis, MO, USA) were mixed with 2 wt.% polyethylene glycol (PEG) with a molecular weight of 10,000 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). Eleven slurries were prepared by changing the volume fraction of IPA (J.T. Baker, Center Valley, PA, USA) with the concentrations of 0, 1, 3, 4, 5, 6, 7, 8, 10, 15 and 20 vol.% IPA. All slurries were ball milled in an alumina grinding media 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 [18]. After freezing, samples were lyophilized in a bench-top freeze dryer (Labconco, Kansas City, MO, USA) at 223 K and 350 Pa for 70 h. Immediately 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<sub>2</sub> scaffolds [18] and through experimentation provided stable but highly porous scaffolds. This process was repeated in order to prove reproducibility of the results.

After sintering, all scaffolds were infiltrated with a two part polymer epoxy, Epoxicure (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 vacuum (~0.02 Pa) for 20–30 min in order to force the liquid to infiltrate the scaffold pores. The infiltrated scaffolds were then allowed to polymerize for 24 h. At the same time, samples of pure epoxy were created to use as a baseline for mechanical properties.

### 2.2. Material characterization

All composite scaffolds were observed with scanning electron microscopy (SEM) at 10 kV and a spot size of 3.0 nm using a Philips XL30 field emission environmental scanning electron microscope (FEI Company, Hillsboro, OR, USA). For SEM preparation, all

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