

# Porous Gelcast Ceramics for Bone Repair Implants

L.S. Gyger, Jr., P. Kulkarni, H.A. Bruck, and S.K. Gupta  
Department of Mechanical Engineering  
University of Maryland, College Park  
2181 Glenn L. Martin Hall  
College Park, MD 20742

O.C. Wilson  
Department of Biomedical Engineering  
The Catholic University of America  
131 Pangborn Hall  
620 Michigan Avenue NE  
Washington, DC 20064

## Abstract

Lightweight, porous ceramic structures are being developed for a variety of biologically-related applications. In bioengineering, there is interest in replacing metal-based implants with more functional implants consisting of porous bioceramics that are bio-resorbable. In the design of bioinspired ceramic structures, there is a desire to understand the coupling between geometric complexity and porosity in natural structures such as bone. However, it has been difficult to process ceramics with controlled porosity and geometric complexity. In this research program, the ceramic processing technology known as “gelcasting” has been employed to study the fabrication of model functional alumina implants that can possess physical characteristics similar to real bone. This technology, often used to make turbine blades and reactor parts, has been used here with added carbon impurity particles that are burned out during sintering to obtain porous microstructures. Gelcast alumina was used to fill a mold generated with a new mold design algorithm and machined using a new path planning algorithm that operated on a 3-D image of a real bone structure, permitting the creation of artificial bone structures. For this effort, the fabrication of porous microstructures was studied using two different types of carbon: activated and graphitic. The mechanical performance of the artificial bone was characterized to gain insight into the structure/property/performance relationship of these geometrically complex, lightweight structures. It was determined that the activated carbon can be used to create more closed porosity at porosity levels of up to 35%. Bone structures with 35% porosity formed from 10% activated carbon exhibited about 1/7 the strength, 1/4 the stiffness, and about 30% less ductility than structures with 10% porosity formed with no pore-forming agents.

## Introduction

In bioengineering, there is a desire to create lightweight, porous ceramic structures for a variety of applications. For bone repair, these structures can provide more functional implants than conventional metal-based implants. There is also interest in creating bioinspired ceramic structures that take advantage of the coupling between geometric complexity and porosity that is present in natural structures such as bone. The challenge has been to fabricate geometrically complex porous ceramic structures with conventional manufacturing technologies. Recently, a ceramic processing technology known as “gelcasting” has been used to create parts with complex geometries. In gelcasting, ceramic powders are mixed with a monomer solution and polymerized to create a mixture with gel-like characteristics. Upon heating, the ceramic particles are immobilized by the polymer, which allows for complex shapes to be produced without any secondary processes. The gel can then be poured or injected into a mold of any shape, dried, and sintered [1]. If a secondary process is necessary, the parts can also be machined in the green state, allowing for more tool versatility.

In addition to geometrically complex shapes, gelcasting can be used to tailor mechanical properties for specific applications. Since ceramics are usually strong but brittle, a metallic powder can be added to the slurry to create a composite with increased ductility. In some applications, specifically biomedical ones, porosity is desired to allow for tissue in-growth and fluid transport [2]. Porosity can be obtained using several different techniques, such as polymer sponge burnout, use of large

ceramic particles, and polymers and impurity particles used as pore-forming agents. The first of these methods includes cutting a polymer sponge to the desired shape and impregnating the sponge with the slurry [3], [4]. The use of powders comprised of large ceramic particles, can produce the desired porosity provided the particle diameters are around 20.0  $\mu\text{m}$  [5]. Another method involves the use of the polymer polyvinyl butyral (PVB) as the pore forming agent [6]. Maca *et al.* used cold isostatic pressing, another ceramic forming process, with carbon as the impurity particle to obtain highly controlled porous structures [7].

In this research effort, gelcast ceramics with pore-forming agents are used to fill molds to create model artificial bone structures. The molds are generated using a new mold design algorithm [8] and machined using a new path planning algorithm that operated on a 3-D image of a real bone structure. The gelcast ceramics incorporate two different types of carbon particles: activated and graphitic. The model artificial bones were then mechanically tested to gain insight into the structure/property/performance relationship of these geometrically complex, lightweight structures.

### Method and materials

The specific recipe that is being used in the current research for the gelcasting slurry is illustrated in *Table 1*. Alumina ( $\text{Al}_2\text{O}_3$ ) is the main powder constituent. Ultimately, a ceramic phase found in bone, hydroxyapatite (HAp) will be used, but alumina serves as a good alternative for model structures because it has similar characteristics with the advantage of being easier to acquire and more affordable. Two different carbon powders are added as pore-forming agents: activated carbon and graphite, in varying weight percentages up to 10% of the total mass of added powder, which are burned out when the sample is sintered.

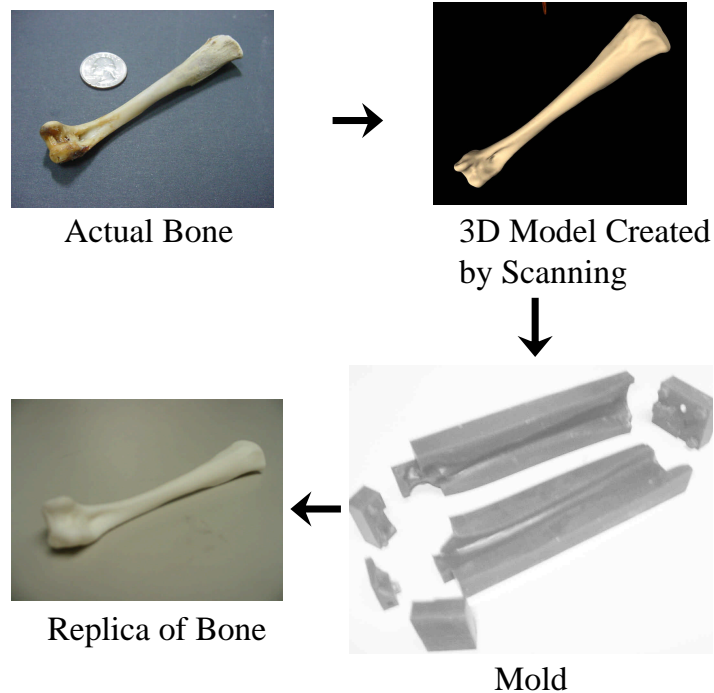
*Table 1 - Gelcasting Recipe*

Component Name	Weight Percent (%)	Volume Percent (%)
<i>Monomer</i> 15% HMAM solution	19.43	45.31
<i>Dispersant</i> Darvan C as received	2.34	5.93
<i>Polymerizing Agent</i> 10% AZIP solution	1.73	3.93
Powder	76.50	44.83

The alumina that has been used in the experiments is ERC-DBM, with  $d_{50} = 0.462 \mu\text{m}$  obtained from Baikowski Malakoff, Inc. A relatively small particle size has been chosen to try to increase the packing density of the alumina and thus reduce the size and frequency of pores caused solely by the processing of alumina. Eliminating these pores allows for a better interpretation of the results obtained by the addition of the impurity particles. The ground activated carbon, obtained from Aquaria, Inc., and the graphite powder, obtained from Asbury Carbons, both have mean particle diameters of 2-3  $\mu\text{m}$ . The monomer that has been used in the gelcast samples is N-(Hydroxymethyl)-acrylamide (HMAM) in a 15% solution, obtained from Sigma Aldrich, Inc. with Darvan C (Ammonium polymethacrylate), the dispersant, obtained from R.T. Vanderbilt Company, Inc. The cross-linking agent that has been used is a 10% solution of 2,2'-(Azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (AZIP).

The alumina and carbon powders are mixed prior to their addition to the monomer solution in order to achieve a more uniform impurity powder distribution and to reduce agglomerations. Two different powder mixing methods were tested, by hand and using a double-blade mixer, in an effort to characterize the effects of mixing on the resulting microstructures. After mixing, small quantities of powder are added to the monomer/dispersant solution at a time with approximately 10 minutes of stirring in between powder addition steps. After the addition of all of the powder, the polymerizing agent AZIP is added while the slurry is continuously stirred. The mixture is then heated in a gravity convection oven for 5 minutes to start the gelation process. When removed from the oven, the gel is immediately degassed in 30 mm Hg vacuum until bubbles no longer rise to the surface. After degassing, the gel is poured into the previously prepared mold. The gel is then heated in the gravity convection oven for 1 hour at 55  $^{\circ}\text{C}$  – 60  $^{\circ}\text{C}$  to remove a majority of the water from the sample and to continue the polymerizing process. Once cool and removed from the mold, the sample undergoes a controlled drying process in a humidity chamber for 36 hours. The sintering program in use consists of a constant heating rate of 150  $^{\circ}\text{C}/\text{hour}$  with a 4-hour dwell at 800  $^{\circ}\text{C}$  for polymer burnout and a 2-hour dwell at 1450  $^{\circ}\text{C}$  for diffusion of the alumina particles.

The samples were tested for porosity using the guidelines set forth by ASTM 20-00 [9]. With the focus on implants and bioinspired structures, several samples were fabricated using a mold in the shape of a bone, specifically a scaled-up duck femur as shown in *Figure 1*. These molds were fabricated using a new mold design algorithm [8] and machined using a new cutter selection algorithm that operated on a 3-D image of the real bone. The performance of these structures is dictated by their compressive load-bearing capacity; therefore the structures were tested in compression. Because the complex geometry is not ideal for testing, the ends of the specimens were set in epoxy to create flat ends that allowed for more precise axial loading conditions.



*Figure 1 - Bone generation process*

## Results

Comparing the two powder mixing methods, mixing the powders by hand results in a slurry of significantly higher viscosity for samples with higher graphite contents, whereas the activated carbon did not show a comparable viscosity increase. In order to reduce the viscosity of hand-mixed alumina-graphite slurries having a carbon content greater than 5%, more dispersant was added until the desired viscosity could be achieved. Overall, the total porosity obtained due to the addition of the activated carbon and the graphite powders is similar as depicted in *Figure 2*. However, the microstructures of the samples are affected by the addition of the carbon powders in different ways depending upon the relative weight percent of the powder added as shown in *Figure 3*, *Figure 4*, and *Figure 5*. The main difference in the porous networks formed by the two types of carbon is shown graphically in *Figure 6*. While the two types of carbon have similar results below 20% total porosity, which corresponds to 4% carbon content, the activated carbon causes a linear increase in the amount of closed porosity obtained in samples with higher carbon content. Alternatively, the graphite samples result in microstructures that show a nonlinear increase in the amount of open porosity above 30% total porosity, corresponding to samples above 7% carbon content. For both types of carbon, the open porosity remains dominant, even with the increase in closed porosity.

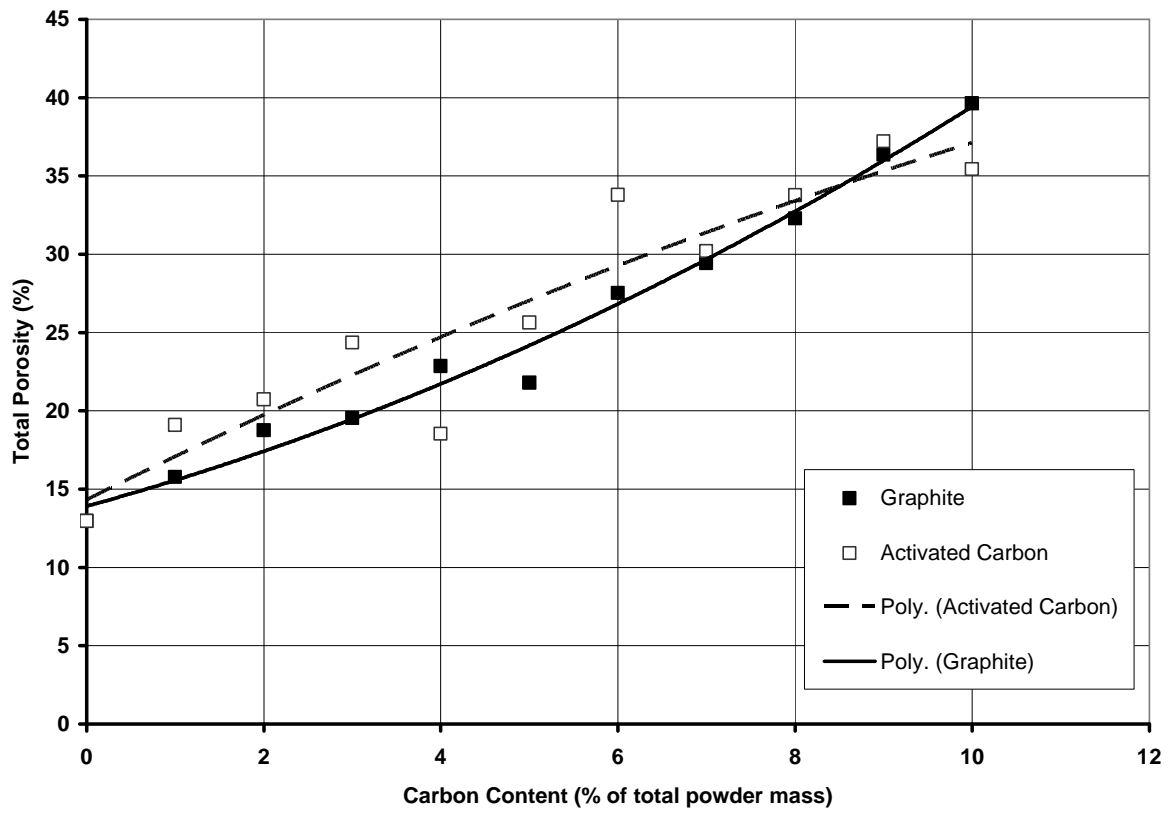


Figure 2 - Total porosity obtained vs. relative powder weight percent of carbon

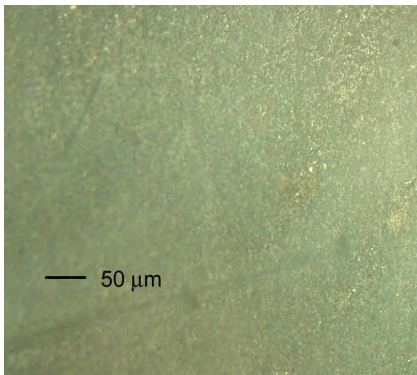


Figure 3 – Alumina with no fore-forming agent

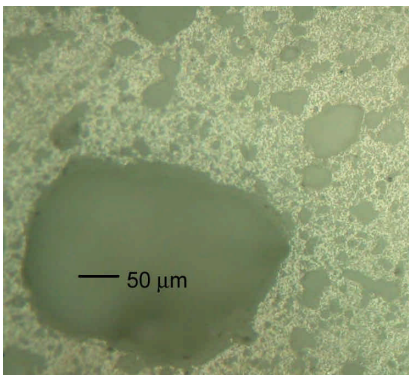


Figure 4 – Alumina with 10 % activated carbon

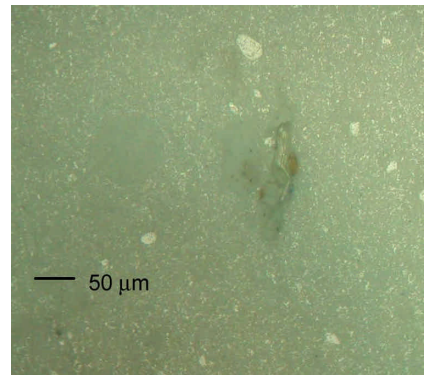


Figure 5 – Alumina with 10% graphite

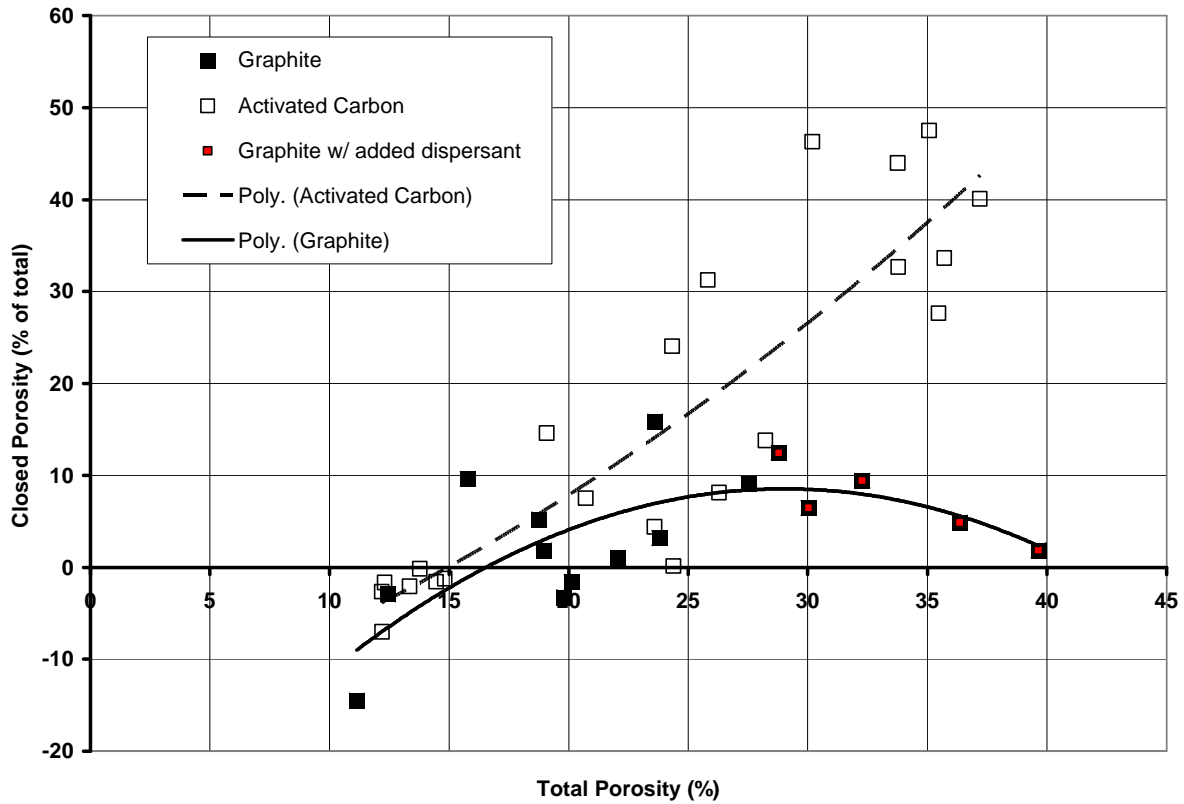


Figure 6 - Percentage of porosity which is closed vs. total porosity

Compression tests have currently been conducted on a 10% porous structure with no pore-forming agents and a 35% porous structure formed from 10% by weight of activated carbon. Both artificial bone samples are compared in *Figure 7*. The results show a large difference in resistance to deformation between the pure alumina samples and the samples with 35% total porosity that was obtained using activated carbon as the impurity particle. The 35% porous structure exhibits 1/7 the strength, 1/4 the stiffness, and about 30% less ductility than the 10% porous structure. The manner in which the samples failed was different as depicted in *Figure 8* and *Figure 9*. The 10% porous sample shattered into numerous pieces while the 35% porous sample demonstrated a less violent failure, only fracturing along one plane.

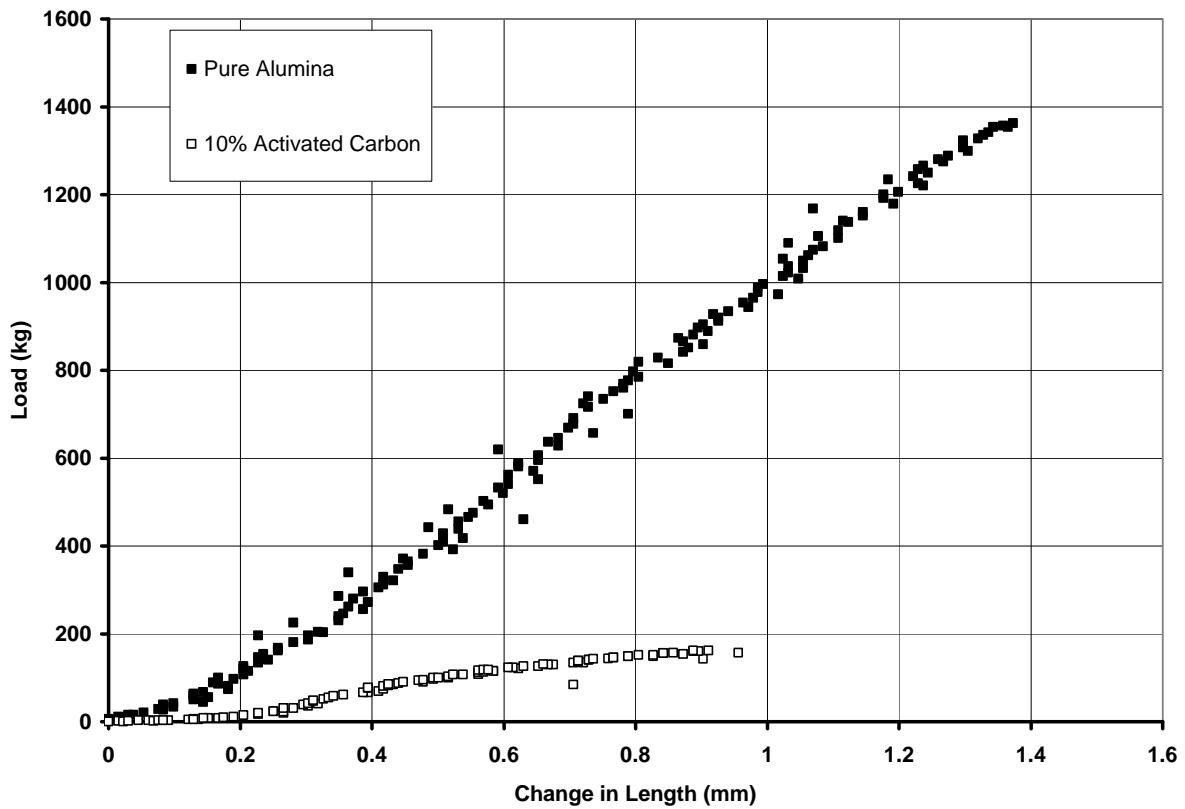


Figure 7 - Compression test data for bone-shaped samples

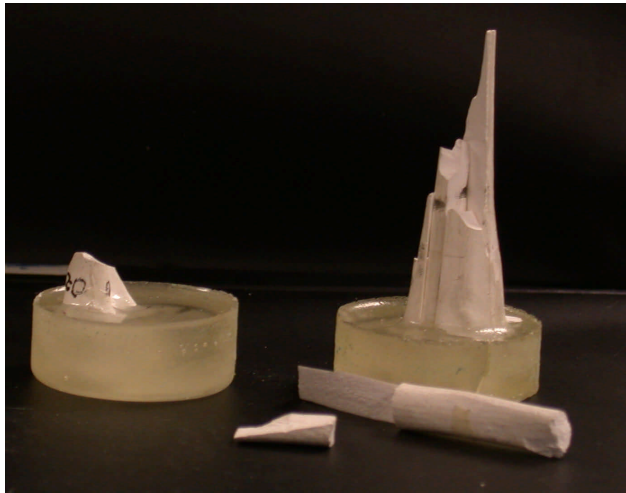


Figure 8 – 10% porous sample after compression test

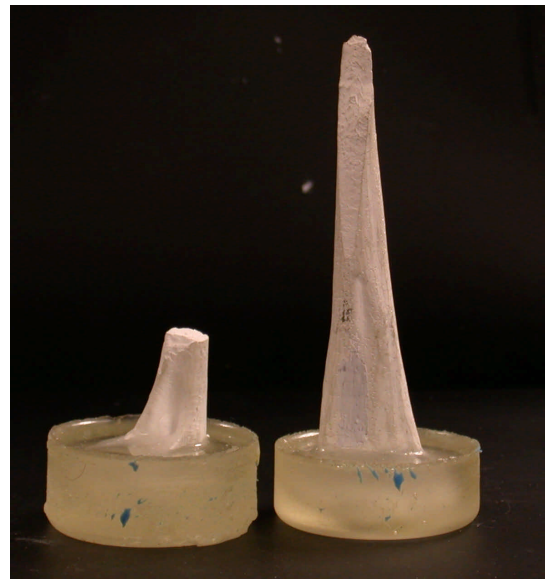


Figure 9 - 35% porous sample after compression test

### Discussion

The increased viscosity of the samples with higher graphite content is believed to be caused by the inherent lubricity of graphite. The graphite particles repel the dispersant, resulting in poor mixing and agglomerations. Alternatively, the activated carbon is adsorbent and amorphous allowing interaction with the dispersant, resulting in better mixing and dissemination. The

linear relationship of the closed porosity to the total porosity for the activated carbon samples can be attributed to two facts. First, the activated carbon is more uniformly dispersed in the slurry prior to drying and second, because it starts to burn out prior to the diffusion of the alumina particles. Since there are not many large agglomerations of the activated carbon, when the carbon particles are burned out, the surrounding alumina particles are able to diffuse around some of the remaining pores, resulting in more closed porosity with increasing activated carbon content.

The nonlinear relationship of the closed porosity to the total porosity for the hand-mixed graphite samples can mainly be attributed to the agglomerations of the graphite particles and the higher burnout temperature of the graphite. When the agglomerations burn out, open pores are left behind which are too large to be completely closed up by the partially diffused alumina particles, resulting in a porous network consisting of a majority of open pores. The results of the compression tests indicate linear resistance to deformation for both porous alumina samples. The porosity greatly influences the strength of the samples, permitting axial cracks to propagate more easily through the 35% porous structures than the 10% porous structures. More tests are needed to elucidate on the effects of porosity on the structure/property/performance relationship of the gelcast samples.

## Conclusions

A new technology has been developed for creating bio-resorbable porous ceramic implants and model bioinspired structures to understand the coupling between geometric complexity and porosity. This technology combines gelcasting with molds created using a new mold design algorithm operating on 3-D images of natural structures. Artificial bone structures were fabricated from porous alumina using gelcasting technology with carbon additives that produced porous networks with greater than 35% total porosity. Two different types of carbon have been utilized to analyze the effects on the formation of the porous networks. Activated carbon particles cause an increase in closed porosity with increased impurity powder content. Graphite as the pore-forming agent results in a more open network of pores, but both types of carbon result in total porosities that exhibit a linear relationship with carbon content. The effects of porosity and geometric complexity on structural performance were studied using compression tests to provide insight into the structure/property/performance relationship of porous gelcast ceramics. These indicate that the 35% porous structure formed from activated carbon had 1/7 the strength, 1/4 the stiffness, and 30% less ductility than the 10% porous structure with no pore-forming agents.

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