Development of highly open polyhedral networks from vitreous carbon for orthopaedic applications

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Abstract. Highly open polyhedral networks were fabricated using an economical and environmentally friendly template route. Recycled cellulose foams were impregnated with a sucrose resin and then pyrolyzed in order to produce reticulated vitreous carbon foams with morphological features that closely resemble trabecular bone. Also, cell sizes ~1mm were achieved, a trait that will allow the mechanical reinforcement of such scaffolds using a biomaterial coating without compromising the pore size that favors osteoblast cell infiltration and growth (200–500µm). Moreover, initial studies showed that carbonization conditions have an effect on the mechanical properties of the synthesized foams and, therefore, such process parameters could be further evaluated towards the enhancement of the mechanical resistance of the scaffolds. The materials developed here are visualized as the porous component of a synthetic bone graft with features that could help overcome the current limitations associated with the medical treatments used for bone defect repair.

1. Introduction
Due to their remarkable surface and light-weight properties, carbon based porous materials have been studied for multiple industrial applications, especially for the fabrication of electrodes [1-4]. Conventionally, carbon foams are fabricated from phenolic resins because of their relatively high carbon yield [5-7]. Recently, sucrose-based resins have been used as an alternative that offers a low-cost and more environmentally friendly process for the preparation of the carbon precursor [8-10]. Lately, a few studies have explored the potential of reticulated vitreous carbon foams (RVC) for bone tissue regeneration applications [11-12]. For instance, Czarnecki and coworkers found that heat-treated RVC foams supported human osteoblast adhesion, mineralization and growth in vitro [12]. Moreover, the in vivo studies conducted by Pec et al. [11] indicated that, even though vitreous carbon is not biodegradable, it can positively integrate with the surrounding tissue upon implantation. This represents an advantage of the use of RVC foams as scaffolds, relative to traditional biodegradable ceramics, since RVC foams could provide a permanent material platform to guide bone remodeling at the defect site.

Nonetheless, one of the major limitations associated with the use of RVC foams for bone repair lies in their low mechanical properties. One way to circumvent this issue is through the reinforcement of the carbon foam with a phase that would allow it to withstand mechanical loading in vivo, while still preserving the morphology and porosity levels that favor osteogenic cell infiltration and proliferation. According to the literature, the optimal pore size for bone tissue growth ranges between 200 500µm [13]. Therefore, the main goal of the present work was to develop vitreous carbon polyhedral networks that: i) show morphological features that resemble trabecular bone, and ii) have cell sizes ~1mm, in order to eventually allow the mechanical reinforcement of such scaffolds using a biomaterial coating without compromising the pore size that favors osteoblast cell infiltration and growth. Toward this goal,
Vitreous carbon networks were fabricated via template route using a sucrose resin, and cellulose foams that were recycled from common fish tank filters were used as the sacrificial polymeric template. The results showed that it was possible to synthesize highly open polyhedral networks with similar structural properties to expensive, commercial RVC foams. Although the mechanical properties of the prepared foams still remain to be improved, our studies indicate that the effect of process parameters such as carbonization conditions could be further evaluated towards the enhancement of such properties.

2. Experimental

2.1. Fabrication of highly open polyhedral networks

Vitreous carbon polyhedral foams were fabricated from a sucrose resin, which was prepared from an aqueous solution (0.4 g/mL sucrose) in a Teflon® beaker. Concentrated HNO₃ was then added at a 1:1 molar ratio relative to sucrose, and the resulting solution was transferred to an oven at 120°C. After 7 h, the resin was removed from the oven and immediately used for the impregnation process. Recycled cellulose foams were thoroughly rinsed with water and then cut into 1×1×1 cm samples. After this, samples were immersed in the resin for a few seconds, followed by gentle extrusion to remove the excess resin. This procedure was repeated twice in order to ensure proper coating of the template. Samples were then dried at 250°C for 1 h prior to carbonization under nitrogen atmosphere at 900°C for 1 h. Two different heating ramps were used for the pyrolysis of the impregnated foams: 1 and 3.7°C/min.

2.2. Characterization of the vitreous carbon structures

Structural characterization of the synthesized foams and their commercial counterparts (ERG Aerospace Corp., CA, USA) was carried out using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Moreover, scanning electron microscopy (SEM) was employed to characterize the morphology of both types of RVC foams. Finally, a compression test was performed in order to measure the mechanical resistance of the fabricated networks (n=4-6 per sample).

3. Results

3.1. Characterization of the synthesized foams and their commercial counterparts

Figure 1. XRD (a) and FT-IR (b) spectra for the commercial and synthesized RVC foams.

Figure 1 represents the XRD and FT-IR spectra for the synthesized and commercial RVC foams. The XRD spectra show two broad peaks in the 22-25° and 42-46° ranges, which are associated with the semicrystalline reflections from the (0 0 2) and (1 0 1) planes of graphite [2,8,10]. The weak diffraction peaks confirm the presence of a disordered carbon structure [14], characteristic of vitreous carbon. Moreover, the FT-IR spectra show a broad band at ~3420 cm⁻¹, which can be attributed to O-H stretching vibrations from intercalated water [1,15]. The band at ~1625 cm⁻¹ can be attributed to C-C stretching
[16,17], whereas the band at ~1100 cm\(^{-1}\) can be ascribed to C-O-C stretching vibrations [16,17], a result that corresponds with the model proposed by Kakinoki, which defines vitreous carbon as a combination of tetrahedral and graphitic portions connected by oxygen bridges [18].

Furthermore, Figure 2 shows SEM characterization results for the synthesized and commercial RVC foams. As it can be observed, the morphology of the synthesized foams closely resembles that of trabecular bone. Also, it was possible to achieve cell sizes ~1 mm, which to the best of our knowledge, has not been previously reported in the literature. Such cell size will eventually allow significant mechanical reinforcement of the RVC foams using a biomaterial coating without compromising the pore size that favors osteoblast cell infiltration and growth.

![Figure 2. SEM images for the synthesized (a) and commercial (b) RVC foams. Scale bar=500 μm.](image)

3.2. Mechanical properties of the prepared foams: effect of the heat treatment

Figure 3(a) shows compressive strength measurements for the RVC networks synthesized by carbonization at 900°C using two different heating ramps (3.7°C/min and 1°C/min). As it can be noticed, a two-fold increase in the mechanical resistance of the foams was achieved by reducing the heating rate during pyrolysis. In order to gain insight into the possible causes of the observed differences, SEM imaging for both types of foams was performed. Figures 3(b)-(c) reveal that the RVC networks produced using a heating ramp of 1°C/min resulted in a more compact structure with significantly fewer defects.
relative to the 3.7°C/min sample. This could be due to the fact that a lower heating rate allowed a more gradual release of the gases produced during carbonization (mainly hydrogen, carbon monoxide and carbon dioxide), which in turn lead to a reduced generation of surface vacancies on the synthesized foams. These results are relevant as they provide insight into the mechanisms underlying the conversion of the sucrose resin into vitreous carbon and, thus, will aid the development of fabrication methods to produce RVC foams with improved structural stability using low-cost and more environmentally friendly approaches, relative to the traditional use of highly toxic phenolic resins.

4. Conclusions
In this work, highly open polyhedral networks were fabricated using an economical and environmentally friendly template route. Carbonization of recycled cellulose foams that were impregnated with a sucrose resin resulted in RVC foams with morphological features similar to trabecular bone. The pore size achieved will allow the mechanical reinforcement of such scaffolds with a biomaterial coating without compromising the pore size levels required for bone regeneration. Moreover, our results showed that carbonization conditions have an effect on the mechanical properties of the foams and, therefore, such variables warrant further investigation towards the enhancement of the mechanical resistance of RVC scaffolds that could be used as the porous component of a synthetic graft for bone defect repair.

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