Improving the compressive strength of bioceramic robocast scaffolds by polymer infiltration

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ABSTRACT

The effect of polymer infiltration on the compressive strength of β-tricalcium phosphate (TCP) scaffolds fabricated by robocasting (direct write assembly) is analyzed in this work. Porous structures consisting of a tetragonal three-dimensional mesh of interpenetrating rods were fabricated from concentrated TCP inks with suitable viscoelastic properties. Biodegradable polymers (polylactic acid (PLA) and poly(ε-caprolactone) (PCL)) were infiltrated into selected scaffolds by immersion of the structure in a polymer melt. Infiltration increased the uniaxial compressive strength of these model scaffolds by a factor of three (PCL) or six (PLA). It also considerably improved the mechanical integrity of the structures after initial cracking, with the infiltrated structure retaining a significant load-bearing capacity after fracture of the ceramic rods. The strength improvement in the infiltrated scaffolds was attributed to two different contributions: the sealing of precursor flaws in the ceramic rod surfaces and the partial transfer of stress to the polymer, as confirmed by finite element analysis. The implications of these results for the mechanical optimization of scaffolds for bone tissue engineering applications are discussed.

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1. Introduction

Synthetic biodegradable scaffolds are today's most promising candidates for bone substitution and regeneration. The surgery involved in implanting synthetic bone substitutes is less invasive than for autografts (which require two surgical sites) and the former do not have the problem of available quantities of the latter. They are also free of rejection and disease transmission risks associated with xenografts. Biodegradable scaffolds provide structural support for cell growth during regeneration of the tissue, and they are eventually resorbed, leaving only the newly formed living tissue and the fully healed lesion.

Most of the limitations associated with conventional scaffold fabrication techniques (solvent casting, fiber meshing, gas foaming, etc.) are related to a limited control over the pore structure. Fortunately, solid free-form fabrication (SFF) techniques – stereolithography, three-dimensional (3-D) printing, fused deposition modeling, robocasting, etc. – can overcome these hurdles [1,2] since they are based on a layer by layer fabrication of structures with customized and complex 3-D shapes from a computer-aided design (CAD) model. They can therefore produce the optimal porous structures to attain the desired mechanical behavior, permeability and diffusion properties for a given application. Moreover, the CAD model can be obtained from medical scan data (computed tomography or nuclear magnetic resonance imaging), allowing the external shape of the scaffold to match the damaged tissue site.

Currently, biodegradable scaffolds are processed either from ceramics (calcium phosphates or bioglasses) or from polymers (polylactic and polyglycolic acids, ε-polycaprolactone, polydioxa-none, etc.). Ceramic scaffolds show a greater potential for bone tissue engineering applications because of their ability to bond directly to bone tissue and their higher elastic moduli [3,4]. Among the SFF methods capable of building ceramic scaffolds, robocasting (also known as direct write assembly or micro-robotic deposition) is unique in that it uses water-based inks with minimal organic content (<1 wt.%) and requires no sacrificial support material or mold [5–7]. This technique consists of the robotic deposition of highly concentrated colloidal suspensions (inks) capable of fully supporting their own weight during assembly. Thus, a 3-D structure is printed directly as a network of ink rods extruded through the deposition nozzle. With the recent development of robocasting inks made from β-tricalcium phosphate [8] (β-TCP) and hydroxyapatite [9–11] (HA) powders, this technique has allowed customized calcium phosphate scaffolds to be built for bone regeneration.

However, despite the improvement in pore architecture achieved with this SFF method, the main limitation of these ceramic scaffolds still lies in the poor mechanical resistance associated with their porosity [12]. A possible approach to achieving better mechanical performance would be to develop a composite material by infiltration of a biodegradable polymer into the ceramic
structures. The addition of a polymer phase to a ceramic scaffold has been shown to enhance toughness [13,14] and strength [15,16] in non-SFF scaffolds (i.e. with limited control of pore architecture). Although the toughness enhancement has been attributed to crack bridging by polymeric fibrils [13], which significantly increases the fracture energy, the actual role of the polymer material in the strengthening of the scaffolds remains unclear. Some workers have tentatively suggested that a reduction in scaffold porosity [15] would seem to be the most likely explanation of this effect, but probably because of the intractability of the geometries of their infiltrated scaffolds they did not elaborate any further.

The present work sought to shed light on this question by analyzing the effect of completely filling the macroscopic porosity of a β-TCP robocast scaffold with two different biodegradable polymers, polyactic acid (PLA) and poly(ε-caprolactone) (PCL), by means of infiltration. The controlled geometry of the robocast scaffolds allowed us to explore the effect of polymer infiltration on the stress field within the ceramic structure, using finite element modeling (FEM) simulations of uniaxial compression tests performed on real samples. Fully impregnating the structures fixes the variables porosity and amount of polymer deposited, thereby simplifying the analysis of the results. Furthermore, fully impregnated composite scaffolds might be of interest in themselves, since they could have superior mechanical properties and, given that the bioerosion rate of the polymer infiltrate is greater than that of the calcium phosphate skeleton, one would expect the generation of porosity in situ upon implantation, allowing bone in-growth.

Finally, the use of two different biodegradable polymers with very different mechanical properties provided information about how those properties affect the performance of the composite scaffold. The results provide valuable insight into the mechanical behavior of hybrid robocast scaffolds for bone tissue engineering applications and pave the way for future work aimed at optimizing the mechanical performance of such structures.

2. Experimental procedure

2.1. Materials and sample preparation

Commercially available Ca-deficient β-TCP powder (Fluka, Buchs, Switzerland), pre-calcined at 1300 °C to obtain a final 84 wt.% β-TCP/16 wt.% calcium pyrophosphate (CPP) composition [17] and attritor milled to around 1 μm particulate size, was used to prepare inks for robocasting with a final solid content of 40 vol.%, following a procedure similar to that of a previous work [8,12]. First, a stable suspension was prepared by dissolving 1.5 wt.% (relative to powder content) Darvan C dispersant (R.T. Vanderbilt, Norwalk, CT) in distilled water and gradually adding the β-TCP powder. An appropriate amount (7 mg ml liquid−1 in the final suspension) of previously dissolved hydroxypropyl methylcellulose (Methocel F4 M, Dow Chemical Co., Midland, MI) was then added to the mixture to increase the viscosity. Subsequently, the ink was gellified by adding 2 vol.% (relative to liquid content) polyethyleneimine (PEI) as flocculant. After each addition the mixture was placed in a planetary centrifugal mixer (ARE-250, Thinky Corp., Tokyo, Japan) for a few minutes to improve its homogeneity and stability.

3-D β-TCP scaffolds consisting of a mesh of ceramic rods were constructed layer by layer via direct write assembly of the ink using a robotic deposition device (3-D Inks, Stillwater, OK) (see Fig. 1). The printing syringe was partially filled with the ink and placed on a 3-axis motion stage, controlled independently by a computer-aided direct write program (Robocad 3.0, 3-D Inks). The ink was deposited through cylindrical metallic deposition nozzles (EFD Inc., East Providence, RI) with a diameter d = 250 μm, at a printing speed of 30 mm s−1. Each layer in the computer 3-D model of the structure consisted of parallel rods with a center-to-center spacing s = 500 μm. Rods in adjacent layers were orthogonal and the spacing between layers was set to h = 200 μm. The external dimensions of the scaffolds were set at about 14 × 14 × 10 mm so that a total of 50 layers were deposited. As shown in Fig. 1, the deposition was carried out in a paraffin oil bath to ensure uniform drying during assembly.

The samples were removed from the bath and dried in air at room temperature for at least 24 h, and then at 400 °C (1 °C min−1 heating rate) for 1 h to evaporate the organics. They were finally sintered at 1200 °C (3 °C min−1 heating rate) for 1 h to avoid micro-cracking [17]. At this sintering temperature full densification of the green samples cannot be completely achieved and important residual in-rod porosity (around 25% [17]) was observable in the sintered scaffolds, as shown in Fig. 2. This rod surface micrograph also shows that grain size in the scaffolds was around 3 μm.

Biodegradable polymers were infiltrated into selected scaffolds by immersion of the ceramic structures in a polymer melt. Commercial pellets of PLA (2002D, Natureworks, Minnetonka, MN) or PCL (Capa 6500, Purac, Barcelona, Spain), with average molecular weights according to the suppliers’ specifications of around 200 and 50 kDa, respectively, were used. Optimal soaking temperatures and times for infiltration of each polymer were selected by trial and error. Optimal melting temperatures were found to be 227 °C for PLA and 220 °C for PCL. After complete melting of the polymers the TCP scaffolds were immersed and soaked for 2 h and then cooled to room temperature.

Fig. 1. Schematic illustration of the robocasting fabrication process. The ceramic scaffold is built layer by layer from a computer design. A 3-axis robotic arm moves the injection syringe while pressing the ceramic ink through the cylindrical deposition nozzles, immersed in an oil bath, to create a self-supporting 3-D network of ceramic rods. Relevant dimensions of the scaffolds (rod diameter d, rod spacing s, and layer height h) are indicated.
Rectangular parallelepiped specimens with dimensions of around $3 \times 3 \times 6$ mm were cut from both the as-sintered scaffolds and the infiltrated structures for scanning electron microscopy (SEM) observation and subsequent mechanical characterization. Bulk specimens of the two polymers with similar dimensions were also prepared by the same melting and cutting procedure for comparison.

The density of the hybrid scaffolds and bulk polymers was evaluated by Archimedes’ method. Since two different polymers were infiltrated into the same scaffold geometry, and thus their volume fractions were the same, it was possible to determine this volume fraction (and thus the macroporosity of the bare TCP scaffolds) and the density of the ceramic rods from the corresponding rule of mixtures equations using the measured bulk polymer densities (Table 1). In-rod porosity was evaluated from the density of the ceramic rods by taking into account the theoretical density of β-TCP (Table 1).

### 2.2. Mechanical testing

Uniaxial compression tests were performed on the parallelepiped specimens using a universal testing machine (AG-IS10KN, Shimadzu Corp., Kyoto, Japan). Tests were performed in air, at a constant cross-head speed of 0.6 mm min$^{-1}$, in a direction perpendicular to the printing plane (i.e. orthogonal to the rod axis), which has been shown to be a weak direction in these ceramic structures [18]. Engineering stress–strain curves were calculated from the normalization of captured load vs. displacement data using the initial external dimensions of each sample. The compressive strength of the structure was estimated as the maximum stress applied in each test. A total of 17 samples were tested in each case in order to obtain statistically reliable values. Weibull statistics [19] were used for the analysis of the resulting strength data. Some tests were imaged from the side using a self-illuminating low power zoom optical system (Zoom 70, OPTEM International, Fairport, NY) to observe in situ the initiation and evolution of fracture modes.

The elastic moduli of the materials involved were evaluated using instrumented indentation (NanoTest, Micro Materials Ltd, Wrexham, UK) and used as input parameters in the numerical simulations. Berkovich indentation tests were performed on bulk samples of the PLA and PCL polymers and on sections polished to a 1 μm finish perpendicular to the rod axis of the TCP scaffolds. In the latter case a single indentation of about 40 μm wide was made in the center of each of the 10 β-TCP rods tested. This dimension was large enough compared with grain size to provide meaningful information about the mechanical properties of the rods (and not of individual grains), but small enough to avoid the influence of the free surface. The results of these measurements are summarized in Table 1, together with the Poisson ratios and densities obtained from the literature or the supplier’s specifications, as indicated.

### 2.3. Numerical modeling

Finite element modeling (FEM) was carried out using ABAQUS/Standard® software (Hibbitt, Karlsson & Sorensen Inc., Pawtucket, RI) to compare the stress fields developed under uniaxial compression in infiltrated vs. bare scaffolds. The algorithm models the compression between two parallel rigid planes of a rectangular parallelepiped scaffold, either infiltrated or not infiltrated, as shown in Fig. 3. The rigid plane at the bottom is fixed, while the top one is free to move in the normal direction under the action of an applied force that is increased linearly up to 300 N. It is assumed that the contact between the scaffold and the rigid planes is frictionless and that the bonding strength at the ceramic–polymer interface is infinite.

The scaffold model consisted of 10 alternating orthogonal layers of parallel β-TCP rods with the dimensions $d = 220$ μm, $s = 400$ μm and $h = 160$ μm, which are the final dimensions after sintering, as will be shown in Section 3. The FEM grid for the scaffold system consisted of more than 350,000 linear tetrahedral elements for the unimpregnated scaffold (Fig. 3a) and 600,000 for the composite structure (Fig. 3b). The dimensions of the elements were not uniform throughout the model. Element size was around 80 μm for most of the model, but much smaller within the central unit cell depicted in Fig. 3a and 3b, in which elements in the vicinity of the external surfaces of the ceramic rods had a minimum dimension of ~5 μm. The stresses on the external surfaces of the rods were the most relevant, since it is there where failure will initiate during testing [10]. The selected refined element mesh thus allowed us to evaluate those surface stresses with greater precision. Unfortunately, due to constraints on computation time, refinement of the mesh had to be limited to a representative internal unit cell and could not be extended to the whole model. Consequently, the stress analysis will obviously be restricted to the data calculated within the selected unit cell, but without jeopardizing the general validity of the conclusions that will be drawn. Also, it is worth noting that while the actual rod shape in the scaffold may depart from a regular cylinder and this might modify the stresses in the system, since the FEM simulations performed here were only intended to compare the stress field between infiltrated and bare scaffolds, the actual quantitative values were of no importance provided that the geometries were identical for the two systems.

Isotropic elastic behavior was assumed for the entire system since, as we will show, fracture of the ceramic skeleton occurred before significant deviation from linearity was observed in the stress–strain curves of the composite scaffolds. The elastic...
constants given in Table 1 were used as input parameters for the simulation of each material.

3. Results and discussion

Fig. 4 shows SEM micrographs of representative as-cut specimens of the \(\beta\)-TCP robocast scaffolds before (Fig. 4a) and after impregnation with PCL (Fig. 4b) and PLA (Fig. 4c). These images confirm that the selected infiltration conditions were appropriate to completely fill the robocast structures, since the visible surfaces were all internal to the large infiltrated scaffold they were cut from. Moreover, in the SEM micrograph of Fig. 5, which shows a fracture surface on a PLA-infiltrated scaffold, it can be seen that the polymers infiltrated not only into the macropores but also into the open microporosity of the TCP rods. The mean dimensions of the ceramic structure as determined from the SEM observations of Fig. 4 were: \(d = 220 \pm 20 \, \mu m, \, s = 400 \pm 10 \, \mu m, \, h = 160 \pm 10 \, \mu m\) (see Fig. 1). Density measurements for PCL-infiltrated \(\beta\)-TCP (PCL–TCP) and PLA-infiltrated \(\beta\)-TCP (PLA–TCP) structures yielded \(\rho = 1.98\) and \(2.02 \, g \, cm^{-3}\), respectively. From these results it was determined that \(\sim 36\%\) of the volume in the composites was occupied by polymer, so that a similar percentage of macroscopic porosity was present in the bare scaffolds. In-rod porosity was estimated to be \(\sim 20\%\), yielding a total porosity of \(\sim 49\%\) in the bare \(\beta\)-TCP scaffolds.

Fig. 6 shows representative uniaxial compressive stress–strain curves (solid lines) for the three types of structure fabricated: bare \(\beta\)-TCP (TCP), PCL–TCP and PLA–TCP. Curves corresponding to PLA and PCL bulk polymers are included as dashed lines for...
comparison. Successive load drops were observed in the uninfiltrated scaffolds. These are associated with crack pop-in events responsible for fracture of the ceramic structure, as shown in the in situ micrograph of Fig. 7. The onset of the first of these cracks occurred during the elastic regime (i.e. within the linear regions of the curves), and usually corresponded to the maximum applied stress, thereby determining the compressive strength of the scaffold. These fracture events were also detectable in the infiltrated structures, but the curves were much smoother and the maximum stress values substantially higher, evidence for major strengthening upon infiltration. In all cases the stress decline after the maximum was progressive, indicating that the structure retained some significant mechanical resistance after multiple cracking events.
even in the case of the unimpregnated scaffolds. However, it should be noted that in this latter case the residual load-bearing capacity was provided by disjointed rods that would collapse if the load was removed [10], while in the infiltrated scaffolds it was a real effect, since the polymer provided the necessary link between the disconnected pillars. Qualitatively, the toughness (in terms of dissipated mechanical energy) of the structure was greatly increased after polymer infiltration, with the asymptotic nominal stress at high deformation increasing by more than one order of magnitude over the bare scaffolds. Nonetheless, it was evident that the mechanical improvement obtained upon infiltration was greater in the case of PLA, in terms of both strength and toughness. This was certainly due to the superior elastic modulus of this polymer relative to PCL (see Table 1).

The evidence for the strengthening effect of polymer infiltration is even clearer in Fig. 8, which shows a Weibull plot of the compressive strength data obtained in the uniaxial tests. The central value of the distribution increased from $\sigma_0 = 20 \pm 2$ MPa in the bare TCP scaffolds to $\sigma_0 = 60 \pm 10$ MPa and $\sigma_0 = 130 \pm 20$ MPa for PCL–TCP and PLA–TCP composites, respectively, i.e. a threefold (3.0) increase after PCL infiltration and a more than sixfold (6.5) increase after PLA infiltration. Furthermore, the Weibull modulus doubled in the impregnated structures, independently of the polymer – $m = 7.6 \pm 0.3$ and $7.7 \pm 0.5$ for PLA–TCP and PCL–TCP, respectively, as compared with $m = 3.0 \pm 0.1$ for bare TCP.

A first explanation for the observed strengthening would be that the presence of the polymer within the macropores of the TCP scaffold modified the stresses acting on the ceramic rods during the uniaxial compression tests. Fig. 9 shows the FEM calculated stress contours (at a load of 300 N) corresponding to the maximum tensile stress ($\sigma_{\text{max}}$) at each point on the TCP rod surface for each system: TCP (Fig. 9a), PCL–TCP (Fig. 9b) and PLA–TCP (Fig. 9c). For the sake of clarity and accuracy the results are shown only for the internal unit cell in which the FEM mesh was finer (see Fig. 3). It can be seen that, as expected, both of the polymer infiltrations modified the stress field. In particular, the surface stress gradients parallel to the rod axes decreased, so that stresses were larger far from the maxima but smaller at the maxima themselves, especially in the case of PLA infiltration. It is worth noting that of the local maxima apparent in the plots only those located close to the joints (indicated by dots in Fig. 9) were responsible for crack initiation. Indeed, as shown in the in situ optical micrograph of Fig. 7, cracks initiated close to the joints and propagated perpendicular to the rod axes, corresponding to the orientation (parallel to the rod axes) of the maximum stresses. The lateral maxima (indicated by x in Fig. 9), while having the same orientation, did not lead to any observable fracture, since they were slightly smaller in magnitude and the propagation of such cracks would soon be hampered by compressive stresses in the region located between layer-to-layer contacts.

Consequently, in order to analyze the influence of infiltration on scaffold strength, discussion needs to focus on the magnitude of the aforementioned relevant maxima in each system. Fig. 10 shows
the evolution of these maximum values as a function of nominal applied stress (i.e. applied load normalized by external section in the FEM model) for the three systems studied. It can be clearly seen that while PCL infiltration only very slightly (by \( \sim 1\% \)) reduced the intensity of the maximum stress in the ceramic rods, PLA halved it (\( \sim 53\% \) decrease). Indeed, such a remarkable reduction in the magnitude of the stresses in the system after PLA infiltration was evident in Fig. 9. The reason for this lies in the considerably larger elastic modulus of PLA, almost an order of magnitude greater than that of PCL (see Table 1), which leads to a greater portion of the load being transferred to the polymer phase. Since fracture of the ceramic skeleton occurred within the elastic region of the stress-strain curves of the composites (Fig. 6), it is only this mechanical property of the polymers that was relevant for this stress shielding mechanism. Obviously, increasing the amount (vol.%) of polymer would also augment the magnitude of this stress shielding, but this increment would not be able to counterbalance the stress increase associated with a reduced amount of ceramic phase.

In the light of these results, since PCL induces a negligible stress shielding of the TCP structure, the source of the threefold increase in PCL–TCP strength must be different. Analogously, while the stress relaxation induced by PLA would double (\( \times 2.1 \)) the compressive strength of the composite, it cannot explain the sixfold strengthening observed in PLA–TCP. It seems reasonable to assume that the same strengthening mechanism acting on PCL composites would be responsible for the remaining threefold (\( \times 3.1 \)) increase in strength in the PLA-infiltrated scaffolds.

This additional strengthening mechanism is defect healing by the infiltrated polymers. The polymers fill pre-existing surface defects in the \( \beta \)-TCP rods (see Fig. 5), bonding the defect walls together and thus increasing the stress needed for a crack to propagate from them. Such a healing effect has already been described in epoxy-coated glass with pre-existing Vickers flaws [20]. In principle, the stress improvement associated with defect healing would depend on the elastic modulus, the fracture strength and the work of fracture of the polymer, as well as on the adhesion strength of the polymer to the defect walls. However, the aforementioned study [20] established that sometimes the increase in the strength of the healed flaw was so large that cracks may start from altogether different, smaller and unfilled flaws. In that case, the strengthening associated with defect healing would not depend on the properties of the polymer. Such a full healing of the precursor flaws would explain the observed improvement in both the compressive strength and the reliability of impregnated sca-

![Fig. 10.](image)

**Fig. 10.** Plot of maximum tensile stress in the scaffold (maximum of \( \sigma_{\text{max}} \)) vs. the nominal applied stress (applied load normalized by initial cross-sectional area) for all the systems studied: bare TCP (dashed line), PCL–TCP (grey solid line) and PLA–TCP (black solid line) structures.

![Fig. 11.](image)

**Fig. 11.** Comparative plot of compressive strength for scaffolds fabricated in this work (circles), and literature reports [22–24] for conventional TCP scaffolds (squares); different literature sources are not distinguished. The results are plotted as a function of material density. The shaded band represents bone properties (including data dispersion) as a function of apparent bone dry density, estimated using an empirical power law model of T.S. Keller [25].

folds. Indeed, the observed increase in the Weibull modulus might be associated with the fact that, after infiltration, cracks initiate from a new flaw population whose size distribution would be narrower. This distribution would also have a lower mean value, which would explain the observed strengthening. The full healing hypothesis is supported by the fact that both polymers lead to similar Weibull moduli and flaw healing strengthening factors (\( \times 3 \)), despite the significantly superior stiffness and strength PLA—and its superior strength of bonding to other calcium phosphate materials such as HA [21]. Thus it would seem that both polymers succeed in completely healing the surface defects they infiltrated, so that fracture had to initiate from entirely different flaws. The nature of this residual population of unhealed flaws is open to speculation, but since they cannot be filled by polymers one would assume that they are either too narrow or closed defects/pores located just below the surface of the \( \beta \)-TCP rods (cf. Fig. 5).

Finally, Fig. 11 compares the compressive strength of the materials fabricated in the present study with data reported by other workers for conventional scaffolds [22–24] and with the properties of natural bone. The latter are represented by a shaded band (indicating the data dispersion) as a function of apparent bone dry density, estimated using the empirical power law model of T.S. Keller [25]. The first thing to notice in this plot is that the strength of bare robocast scaffolds beats that of conventional scaffolds with only a slightly (\( \sim 10\% \)) lower density by a significant factor (a fourfold increase). This strength enhancement is not attributable exclusively to the higher density but also to the larger, more homogeneous strut dimensions produced by robocasting, relative to structures with similar porosities created by conventional scaffold fabrication techniques. However, despite the significant improvement provided by the use of this SFF technique, the compressive strength of the bare \( \beta \)-TCP scaffolds was still far from that of bone at the same density. The gap was bridged, however, by polymer infiltration, and the PLA–TCP hybrid scaffolds that were fabricated exhibited a compressive strength similar to cortical bone, as a result of the two strengthening mechanisms discussed above. While the lower stiffness of PCL does not allow the corresponding hybrid structure to reach bone-like strengths, it illustrates the still significant improvement that can be achieved solely by flaw healing.

Certainly, if the scaffold macropores were not completely filled, although the subsequent stress shielding strengthening would be
reduced, the defect healing effect would not be affected, as long as the rod surfaces were completely coated and, hence the defects were completely filled. Therefore, our results suggest that for the rod surfaces were completely coated and, hence the defects reduced, the defect healing effect would not be affected, as long as either a PCL or PLA film, without affecting its ability to induce bone in-growth.

Nevertheless, as already mentioned in the introduction, the use of fully filled composite scaffolds such as have been studied here could also be of interest in itself. These dense materials could have mechanical properties superior to those of simply coated structures due to stress shielding, provided the infiltrating polymer was stiff enough, as in the case of PLA. Besides, since the bioerosion rate of the polymer infiltrates was greater than that of the calcium phosphate skeleton, one would expect the generation of porosity in situ upon implantation, allowing bone in-growth. Preliminary in vivo studies are currently under way to test this assertion. Such progressive in situ creation of porosity might allow materials to be developed that will remain strong enough to support loads until the regenerated bone can take over. Moreover, stress shielding of the surrounding tissue would not be an issue in this in situ pore generation scheme since, as the material is resorbed, more and more of the load will be transferred onto the surrounding bone, providing the proper loading environment required for bone regeneration. Obviously, determining the appropriate composition, microstructure, pore architecture and surface properties to ensure the maintenance of strength and stability throughout the regeneration process remains a scientific challenge.

4. Conclusions

Optimization of the mechanical properties of calcium phosphate scaffolds is a critical issue, since these biomaterials would likely be subjected to some degree of loading during their use in vivo. The present results have provided new proof of the advantages in terms of mechanical performance of fabricating hybrid ceramic/polymer structures rather than pure calcium phosphate scaffolds. As also has been reported by other workers, infiltrating polymers into the porous ceramic structure was shown to considerably boost the strength and toughness of the material – threefold and more than sixfold increases in scaffold compressive strength were found with PCL and PLA infiltration, respectively. Indeed, as shown in Fig. 11, the PLA–TCP composite not only greatly exceeded the mechanical performance of other TCP scaffolds reported to date, but had strength values similar to those of cortical bone with the same density.

The capacity of robocasting to fabricate porous calcium phosphate scaffolds with a controlled architecture and the selection of fully impregnated structures as the focus of this work, enabled us to analyze in detail the mechanical response of the scaffold under uniaxial compression, based on FEM calculations of the stress fields in the fabricated systems. This analysis clarified the dual effect of the polymer on the mechanical strength of the structure: on the one hand it acts as a healing agent of pre-existing flaws in the ceramic scaffold surfaces, and on the other it can help sustain the applied load provided that it has a sufficiently high elastic modulus (as in the case of PLA). For the polymers analyzed here, defect healing alone produces a threefold increase in the strength in both cases, while stress shielding is only significant for PLA, amounting to an additional twofold strengthening.

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Appendix A. Figures with essential colour discrimination

Certain figures in this article, particularly Figures 1 and 3, are difficult to interpret in black and white. The full colour images can be found in the online version, at doi:10.1016/j.actbio.2010.05.024.

References