



Evaluating the effect of increasing ceramic content on the mechanical properties, material microstructure and degradation of selective laser sintered polycaprolactone/ β -tricalcium phosphate materials

Heather Doyle*, Stefan Lohfeld, Peter McHugh

Biomechanics Research Centre (BMEC), Mechanical and Biomedical Engineering, College of Engineering and Informatics, National University of Ireland, Galway, Ireland

ARTICLE INFO

Article history:

Received 21 August 2014

Revised 26 March 2015

Accepted 9 May 2015

Keywords:

Selective laser sintering

Polycaprolactone

β -Tricalcium phosphate

Bone tissue engineering

Mechanical properties

Degradation

Accelerated ageing

ABSTRACT

Orthopaedic scaffold materials were fabricated from polycaprolactone (PCL) and composite PCL– β -tricalcium phosphate (PCL/ β -TCP) powders using selective laser sintering (SLS). Incorporating β -TCP particles is desirable to promote osteogenesis. The effects of increasing β -TCP content on the material's mechanical properties and microstructure were evaluated. The wt% of β -TCP and PCL particle sizes were found to influence material microstructure and mechanical properties, with increasing ceramic content causing a small but significant increase in stiffness but significant reductions in strength. Degradation of materials was achieved using accelerated ageing methods. The influence of β -TCP content on degradation at 7 weeks was evaluated through changes in mechanical properties and microstructure, and the ceramic particles were found to reduce elastic modulus and increase strength. The results of this study highlight the influence of ceramic content on mechanical properties and degradation behaviour of PCL/ β -TCP SLS materials, and indicate that these changes must be considered in the design of scaffolds for critical-sized defects.

© 2015 IPeM. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Biodegradable materials are of significant interest in the field of bone tissue engineering scaffolds. In the case of large bone defects in particular, such scaffolds can provide structural support during the initial stages of healing, and degrade over time allowing the body to replace the scaffold with new, native bone tissue. This is advantageous as in the long-term the defect is filled with bone produced naturally by the body. Synthetic calcium phosphates such as hydroxyapatite and β -tricalcium phosphate (β -TCP) are biodegradable ceramics that are similar in composition to natural bone [1] and are commonly used in orthopaedic applications [2–10]. Incorporating ceramic particles in polymer-based scaffold materials has been shown to have significant osteogenic benefits and to encourage new bone formation on scaffold surfaces [2,11,12]; however fully ceramic scaffolds can be quite brittle. Selective laser sintering (SLS) can be used to fabricate scaffolds from biodegradable polymer–ceramic composites, such as polycaprolactone (PCL) with β -TCP, in virtually any geometry, although scale is a limitation, making the fabrication of scaffolds to fit patient-specific defects a reality [13]. This type of composite

scaffold also has the advantage of being less brittle than a fully ceramic scaffold.

For orthopaedic scaffolds designed for critical-sized defects where a large portion of the body-weight is supported by the scaffold, the stiffness of the scaffold material is a critical design factor. Given the relatively high stiffness of ceramic materials in general, it is expected that increasing the ceramic content of a polymer–ceramic composite scaffold will result in an increase in stiffness. This is true for polymer–ceramic composite materials where a homogeneous cross-section can be achieved [14–18]. However, the stiffening effect of ceramic particles in polymer–ceramic SLS materials has been shown to be less than for solid materials with the same polymer–ceramic ratio [19], which is a significant concern for the design of load-bearing scaffolds. Increasing the ceramic volume impedes sintering of polymer–ceramic materials due to settling of ceramic particles on the surface of the polymer particles [10]. It is important to fully understand the effects of increasing ceramic content on the sintering of scaffold materials, and their mechanical properties, to ensure effective scaffold design and in-vivo performance.

The change in mechanical properties of biodegradable scaffold materials during degradation is another critical design factor. The influence of the in-vivo environment on the scaffold material mechanical properties needs to be fully understood, particularly for load-bearing scaffolds. Few studies report on the degradation behaviour of PCL/ β -TCP materials fabricated using SLS, however it is

* Corresponding author. Tel.: +353 91 493020.

E-mail address: heatherdoylenuig@gmail.com (H. Doyle).

known that the ceramic content of composite materials [20] and surface area [21] both influence the in-vivo material degradation rate.

Retrieval studies are the most accurate way to evaluate the in-vivo performance of biodegradable materials, however in reality this is not always practical. Laboratory testing (room temperature, dry conditions) is generally acceptable to evaluate mechanical properties, but does not necessarily accurately evaluate in-vivo material performance. In-vivo conditions can be replicated in-vitro by exposing materials to simulated physiological conditions by immersion in phosphate buffered saline (PBS) at 37 °C and pH 7.4. PCL has a long degradation time (2–4 years in-vivo [22–24]); long degradation times can be prohibitive for the timely development of new medical implants and devices. Accelerated ageing methods have been developed to increase degradation reaction rates so that polymer degradation can be assessed at reduced length scales through the use of temperature [25], pH [20,26] and the addition of enzymes to degradation media [26–28]. Temperature-based accelerated ageing methods can be characterised by assuming that the chemical reactions of the material degradation are described by the Arrhenius reaction rate function, which predicts that a 10°C increase in temperature doubles the reaction rate (ASTM F1980-02, Hukins et al. [25]). A major advantage of this approach is the clear relationship between the increase in temperature and degradation time, and data from accelerated ageing studies can relate back to real-time (degradation at 37 °C) data.

The objective of this study was to evaluate the impact of increasing ceramic content in polymer–ceramic SLS materials on the structure and mechanical properties of the resulting materials and their suitability for orthopaedic applications. SLS scaffold materials were fabricated from PCL and from PCL with two volume fractions of β -TCP. Firstly, the effect of increasing ceramic content on material microstructure and elastic properties was assessed. Secondly, degradation of these materials was achieved using accelerated ageing to replicate in-vivo degradation at 14 weeks, and changes in mechanical properties and material microstructure were evaluated. Discussion of the implications of the results for the performance and suitability of the material for the intended application is also included.

2. Materials and methods

2.1. Materials and fabrication

PCL powder (CAPA6506, Solvay, UK) (average molecular weight (Mn) 60,000, particle size 600 μ m) was cryogenically ground at Noll Aufbereitungstechnologie GmbH (Bobingen, Germany) to produce particle sizes in two ranges: <50 μ m and 50–110 μ m. Particles were separated into two particle size ranges using sieving. β -TCP (Fluka) (molecular weight = 310.18 g/mol, particle size = 3–5 μ m) was mixed with the PCL powder until well blended to produce PCL/ β -TCP powder blends for sintering with ratios of 90/10 wt% (3 vol% β -TCP) and 50:50 wt% (25 vol% β -TCP).

Individual scaffold struts were fabricated using SLS [29] in three ratios of powder blends: 100% PCL, 90/10 wt% PCL/ β -TCP and 50/50 wt% PCL/ β -TCP. The PCL and 90/10 wt% PCL/ β -TCP struts were fabricated using the larger PCL particle size to replicate the scaffolds used in Lohfeld et al. [10]. The 50/50 wt% PCL/ β -TCP struts were fabricated using the smaller PCL particle size as the inclusion of large quantities of β -TCP particles were found to inhibit sintering [10]. The outline scan method [30] was used to achieve a small strut cross section with a laser power of 7 W, laser spot diameter of 410 μ m, part bed temperature of 49 °C and powder layer thickness of 0.11 mm with the Sinterstation 2500^{plus} system (DTM, USA). The intended dimensions of each strut were: 13 mm length; cross section 0.55 mm \times 0.55 mm.

Strut tensile samples (Fig. 1) were prepared by gluing each strut end inside plastic tubes (inner diameter 1.6 mm) with a cyanoacrylate

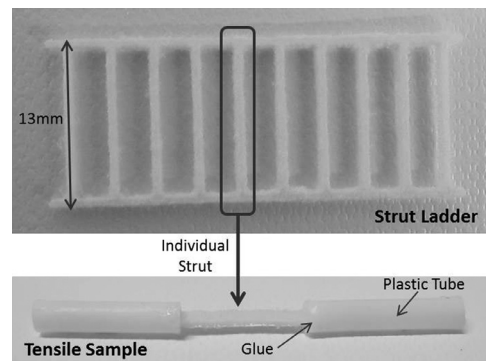


Fig. 1. Strut ladder and tensile sample assembly.

adhesive (Loctite® Power Easy™) for gripping during tensile testing [29]. Sample mass (m_0) was measured and recorded.

Strut tensile sample assembly fixation was significantly more challenging for the PCL struts compared to the composite struts, and frequent strut pull-out during tensile testing was observed due to incomplete glue bonding (corresponding data consequently not used). Further to extensive efforts to address fixation, improved results were found for smaller diameter plastic tubes (inner diameter 1.3 mm), reducing the bond gap between the strut and the inside of the tubes; bond gap is an important factor in the bond strength of cyanoacrylate glues [31]. These fixation issues resulted in a variation in successful tensile test sample numbers (n) at each time point: PCL $n = 4, 3, 5$, for tests at weeks 1, 4, 7, respectively; 90/10 wt% $n = 4, 8, 9$, for tests at weeks 1, 4, 7, respectively; 50/50 wt% $n = 7, 8, 10$, for tests at weeks 1, 4, 7, respectively.

2.2. Accelerated degradation

Accelerated degradation was achieved using a degradation temperature of 47 °C (i.e. +10 °C) to double the reaction rate relative to a baseline body temperature of 37 °C, assuming the Arrhenius reaction rate function (ASTM F1980-02, [25]). Although this assumption is employed here for practicality, note that this is a generalised correlation that might not necessarily relate exactly to the degradation rate of PCL. A real-time degradation time of 14 weeks was chosen to compare with the in-vivo performance of 90/10 wt% PCL/ β -TCP scaffolds in a study by Lohfeld et al. [10], corresponding to 7 weeks accelerated testing time. Note that the “10 °C rule” is intended for use below the polymer glass transition temperature (T_g), and is most commonly used with poly(L-lactide) (T_g of between 60 and 65 °C [32]). PCL, however, has a T_g of –60 °C and a melt temperature (T_m) of 60 °C [32], so although the degradation conditions presented here are above the T_g of PCL, so too are physiologically representative degradation conditions at 37 °C, and this method of accelerating degradation has been used successfully for PCL for temperatures of 45–50 °C [33,34].

To simulate in-vivo degradation conditions, tensile samples of each material were submerged in 1 l of PBS in sealed containers (pH 7.4), with one container per material. The containers were placed in an oven at 47 °C and both temperature and pH were monitored and remained constant throughout the course of the study, with no adjustments required.

2.3. Mechanical testing

The primary tensile testing reported here is for degraded PCL, 90/10 wt% and 50/50 wt% struts at 1, 4 and 7 weeks under accelerated degradation conditions, or 2, 8 and 14 weeks real-time degradation. Samples were removed from PBS and blotted with paper towels prior to testing at each time point. Tensile testing of undegraded PCL struts was also carried out. Additionally, previously reported tensile

Download English Version:

<https://daneshyari.com/en/article/875675>

Download Persian Version:

<https://daneshyari.com/article/875675>

[Daneshyari.com](https://daneshyari.com)