Supplementary data

Supplementary methods

1. X-ray diffraction pattern

 X-ray diffraction patterns were recorded with a Bruker D8 Advance system (Bruker, Karlsruhe, Germany) in a 2Theta range from 20-40° with Cu Ka radiation (40 KV/ 40 mA) with a step size of 0.02° and a total measurement time of 1 s/step. Quantification was performed by Rietveld refinement analysis using Topas software (Bruker, Germany). The amorphous content of the samples was calculated using the G-factor method with a crystalline corundum reference according to Hurle *et al* [S1].

Supplementary Tables

Supplementary Table 1. Proliferation of equine MSCs on C-PCaP scaffolds during cultivation for 14 days

Supplementary Table 2: Quantification of the XRD patterns by Rietveld refinement (TOPAS software, Bruker, USA), showing the conversion of α -TCP to an apatite phase.

Supplementary Figures

Supplementary Figure S1: A; Amplitude sweep representing LVR, B; Frequency sweep (relationship between angular frequency and complex viscosity), C; Frequency sweep (relationship between angular frequency and complex viscosity, obtained by using same material after performing time sweep test), D ; Frequency sweep (relationship between angular frequency and modulus), E; Frequency sweep (relationship between angular frequency and modulus, obtained by using same material after performing time sweep test).

Supplementary Figure S2: X-ray diffraction patterns of raw powder and scaffolds. Diffraction peaks in the raw powder can be assigned to crystalline α-tricalcium phosphate (PDF-No.: 09-0438) with a minor fraction of ß-tricalcium phosphate (PDF-No.: 09-0169, marked with "b"), possibly present as minor impurity in the α-TCP particle formulation. The fabricated scaffolds consisted of low crystalline hydroxyapatite (PDF-No.: 09-0432) from hydrolysis of α-TCP, as shown by the typical broad peaks peculiar of CDHA formation [S2], while the β-TCP fraction remained unreacted.($\alpha = \alpha$ -TCP, $\flat = \beta$ -TCP, $\ast =$ CDHA)

Supplementary Figure S3: Tangent Modulus of hardened cement structure produced from composition of α-TCP with and without nano-hydroxyapatite, B; Ultimate strength of hardened structure produced from composition of α-TCP with and without nano-hydroxyapatite. No significant differences were found between the two groups, suggesting that the added nano-HA does not have a relevant impact on the compressive properties of the produced cement. ($n = 6$ for each group).

Supplementary Figure S4: A; Representative stress-strain curves of NC-PCaP scaffolds at different porosities showing how to calculate tangent modulus and ultimate strength. B; Representative stress-strain curve showing how to calculate energy to failure. C; Energy to failure of NC-PCaP paste (grey) and C-PCaP paste (blue) scaffolds with different porosities. D; Merged image between fluorescence staining of nucleus (dapi: blue) and osteonectin protein (osteonectin: red) of equine MSCs that were cultured on a C-PCaP scaffold for 21 days in an expansion medium showed no sign of osteogenic upregulation. (Scale Bar = 100 µm.) E; Merged image between fluorescence staining of nucleus (dapi: blue) and osteonectin protein (osteonectin: red) of equine MSCs that were cultured on a C-PCaP scaffold for 21 days in an osteogenic supplement medium showed signs of osteogenic upregulation. (Scale Bar = $100 \mu m$.)

Supplementary Figure S5: A; Representative area under stress-displacement curve for calculation energy to failure. B; Interfacial toughness at the interface between chondral and bony compartment of an engineered osteochondral unit showing alterations due to differences in either interfacial architecture or compositions. The different construct types: GelMA on ceramic(unmodified surface; red), GelMA on ceramic (modified surface; bright green), microfibre reinforced GelMA on ceramic(non-anchor fibre; pink), microfibre reinforced GelMA on ceramic (anchor fibre; blue) and only GelMA hydrogel (mean (grey dotted line) \pm SD (grey filled area))

Supplementary Video SV1. Video showing the open and interconnected porosity within the inner structure of the porous 3D printed scaffolds, as shown through a series of μ CT sections of the constructs.

Supplementary references

[S1] Hurle, K.; Neubauer, J.; Bohner, M.; Doebelin, N.; Goetz-Neunhoeffer, F, Effect of amorphous phases during the hydraulic conversion of alpha-TCP into calcium-deficient hydroxyapatite, Acta Biomaterialia, 2014, 10, 3931-3941

[S2] Barba A, Diez-Escudero A, Maazouz Y, Rappe K, Espanol M, Montufar EB, Bonany M, Sadowska JM, Guillem-Marti J, Öhman-Mägi C, Persson C, Manzanares MC, Franch J, Ginebra MP. Osteoinduction by Foamed and 3D-Printed Calcium Phosphate Scaffolds: Effect of Nanostructure and Pore Architecture. ACS Appl Mater Interfaces. 9(48) (2017) 41722-36.