ACCSCIENCE PUBLISHING

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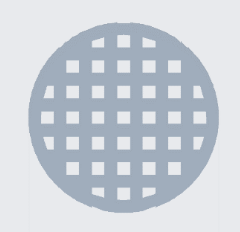
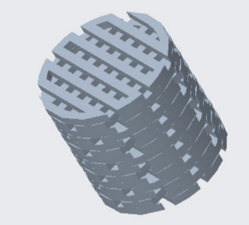
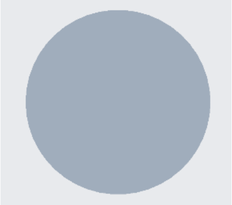
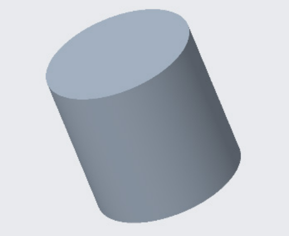
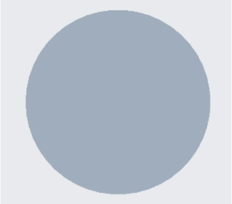
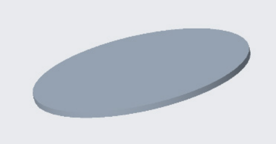
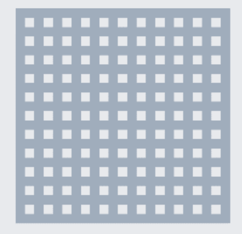
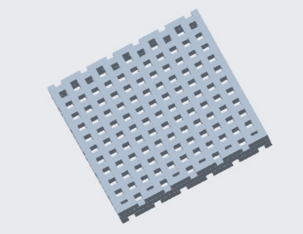
RESEARCH ARTICLE

3D printing of microstructured piezoelectric and bioactive PCL-composite scaffolds for bone regeneration

Supplementary file

Table S1. Overview of the printed geometries.

Size	Top view	Angled view	Use
Ø6.6 × 6 mm			Piezoelectric and mechanical properties
Ø6 × 6 mm			
Ø18 × 0.5 mm			Contact angle measurement
10 × 10 × 1.32 mm			Bioactivity

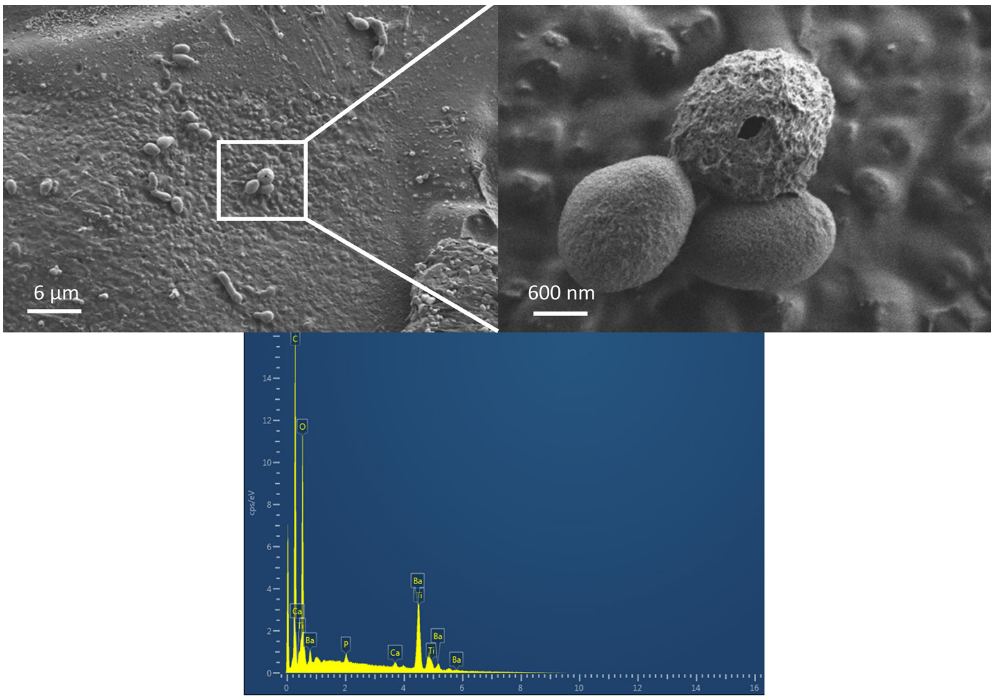


Figure S1. SEM and energy dispersive X-ray spectroscopy of the PCL/BTO/BG composite after 28 days in simulated body fluid. Abbreviations: BG: Bioglass 45S5; BTO: Barium titanate; PCL: Polycaprolactone; SEM: Scanning electron microscopy.

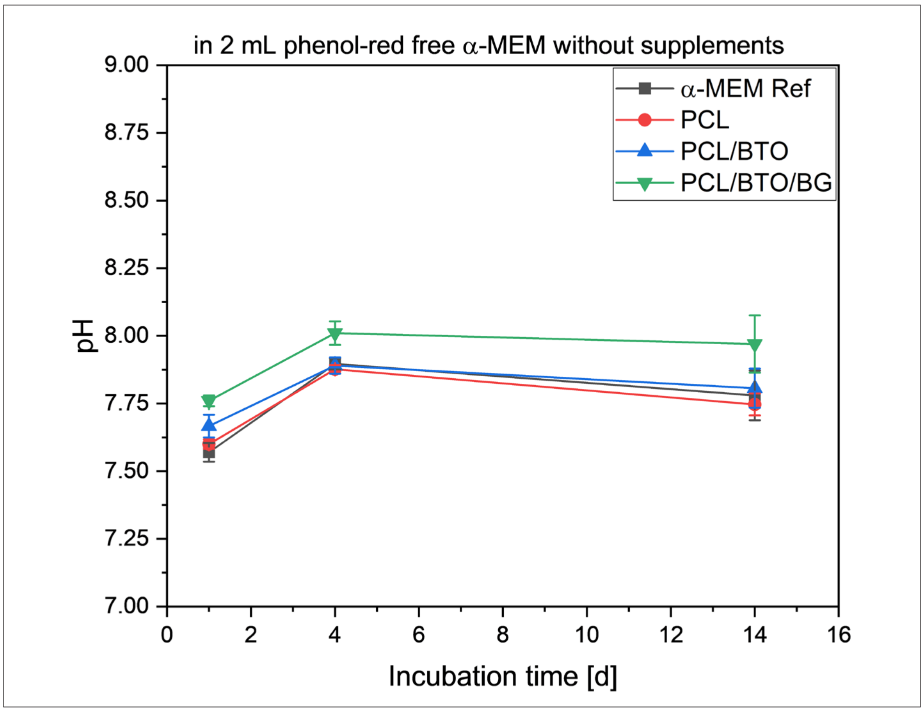


Figure S2. pH of the three groups incubated in αMEM for up to 14 days at 37°C, with no medium exchange in between; *n* = 3. Abbreviations: BG: Bioglass 45S5; BTO: Barium titanate; PCL: Polycaprolactone.

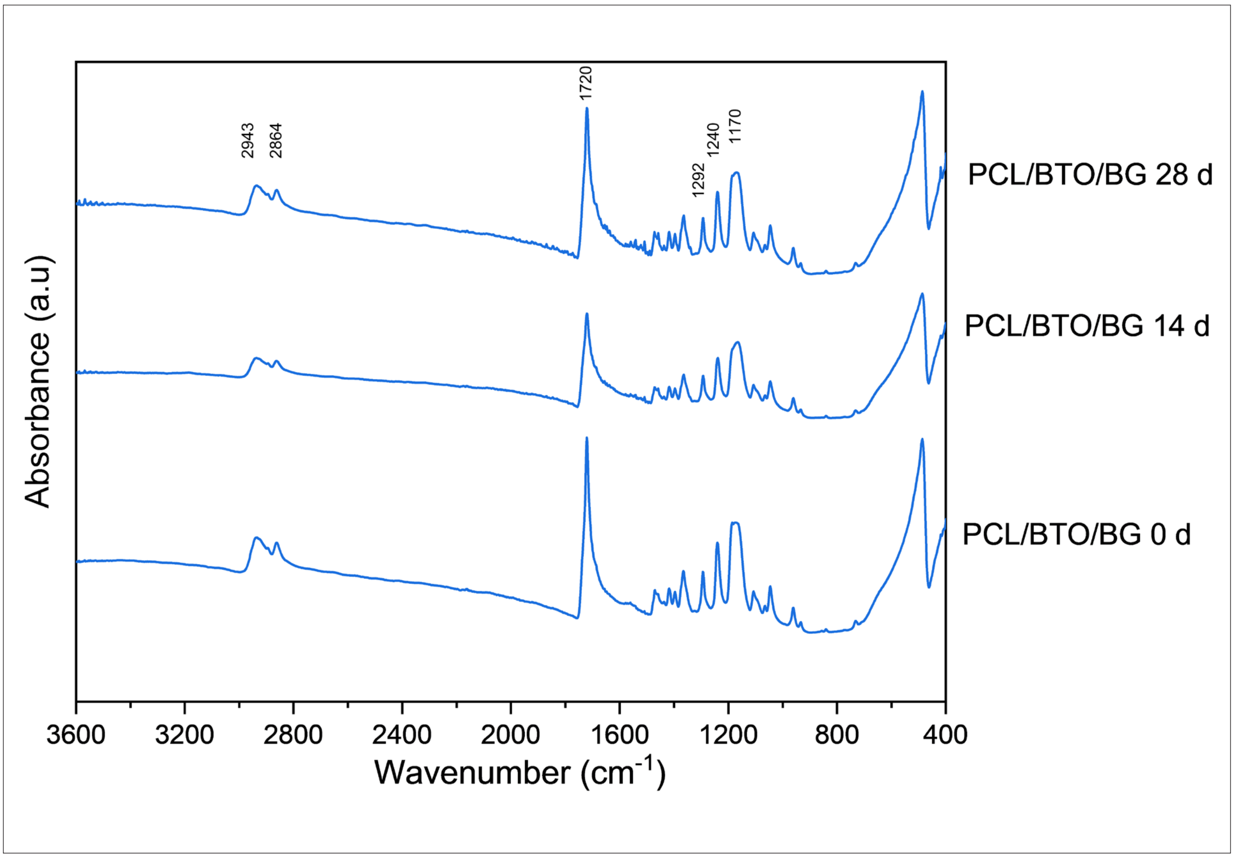


Figure S3. FTIR of PCL/BTO/BG at 0, 14, and 28 days. No significant difference was detected. Abbreviations: BG: Bioglass 45S5; BTO: Barium titanate; FTIR: Fourier transform infrared spectroscopy; PCL: Polycaprolactone.

Figure S3 shows the Fourier transform infrared spectroscopy (FTIR) spectra of the composite containing Bioglass 45S5 (BG) from 0 days to 28 days in SBF. The FTIR spectrum was recorded in the range from 3600 to 400 cm^{-1}. The peaks at 2943 and 2864 cm^{-1} can be attributed to asymmetric and symmetric vibrations of the $-CH_2$ groups. The strong absorption peaks at 1720 and 1170 cm^{-1} can be assigned to stretching vibrations in the carbonyl groups (C=O). The remaining peaks between 1200 and 1500 cm^{-1} are mainly due to C-O and C-C stretching vibrations.[1,2] We attribute the intense band with the pronounced shoulder around 500 cm^{-1} to characteristic vibrations of the Ti-O bonds. We could not identify characteristic peaks for the formation of a calcium phosphate (CaP) layer in the FTIR spectrum.[3] The loading with BG is relatively low and the degradation of the polycaprolactone (PCL) is slow, accounting for the significant delay in ion release, which inhibits the rapid and pronounced formation of an apatite layer.

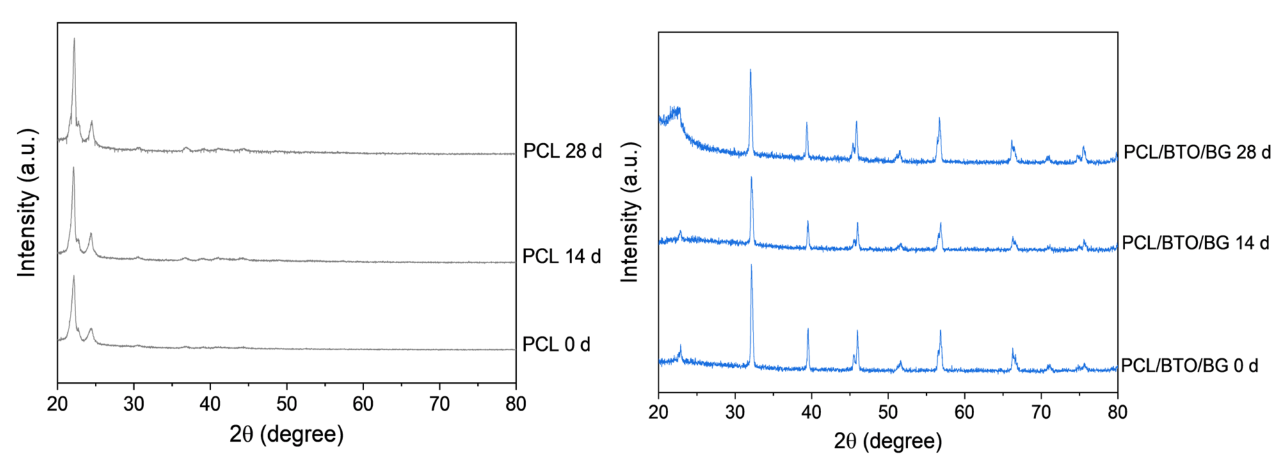


Figure S4. X-ray diffraction of PCL and the PCL/BTO/BG composite at 0, 14, and 28 days. Abbreviations: BG: Bioglass 45S5; BTO: Barium titanate; PCL: Polycaprolactone; XRD: X-ray diffraction.

The X-ray diffraction (XRD) spectrum shows the semicrystalline phases of PCL with corresponding peaks at 2θ = 21.3, 21.9, and 23.6°[4,5] depicted in Figure S4, left. In the overall spectrum of the PCL/BTO/BG composite (Figure S4, right), these peaks are no longer as distinct and appear to be superimposed by the prominent signal of barium titanate (BTO). The pattern of the PCL/BTO/BG composite confirms the presence of BTO and essentially corresponds to the ICDD profiles (cubic $BaTiO_3$ ICDD pdf 01-089-2475, tetragonal $BaTiO_3$ ICDD pdf 01-074-7965) of cubic and tetragonal BTO. In particular, the characteristic double peak at 45° 2θ indicates the tetragonal form, which is crucial for the piezoelectric properties. Since BG is amorphous, it is not detectable in the XRD pattern. Similar to FTIR, no characteristic peaks for calcium phosphates can be identified, as the bioactivity is limited by the small amount and slow degradation of the PCL matrix.

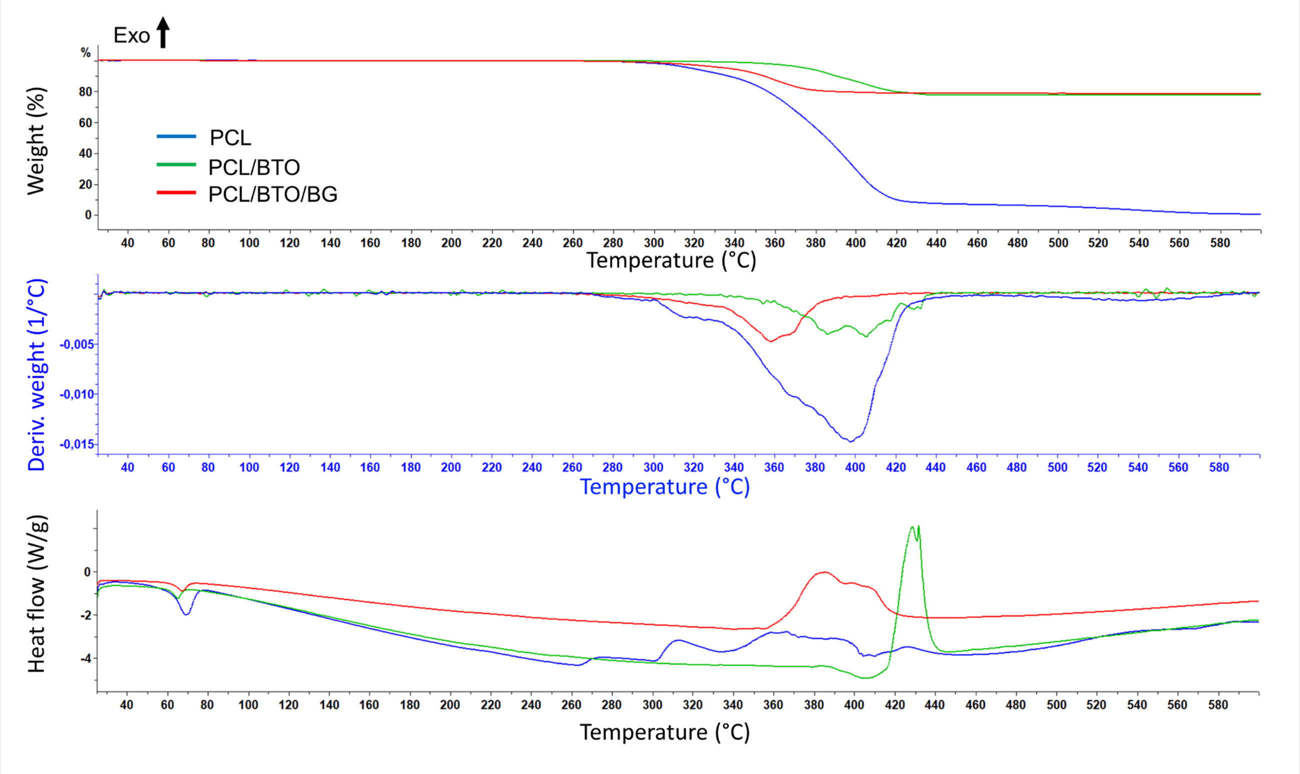


Figure S5. Thermal analysis (TGA and DSC) of 3D-printed PCL composites. Abbreviations: BG: Bioglass 45S5; BTO: Barium titanate; DSC: Differential scanning calorimetry; PCL: Polycaprolactone; TGA: Thermogravimetric analysis.

The thermal analysis showed that all three composites are stable over a wide temperature range, and the thermal degradation of the composites is not significantly influenced by the respective particle loading (Figure S5). The degradation of the PCL starts in all composites at about the same temperature, at 240°C, but then proceeds with slight differences. Pure PCL and PCL/BTO showed the highest mass loss between 380 and 400°C, while the PCL/BTO/BG composite already showed substantial thermal degradation between 340 and 360°C. The curves of the highly filled composites show a smaller decrease overall and indicate slightly better thermal stability. Other groups have already demonstrated this on PCL composites.[6]

The DSC signal's evaluation showed that the PCL's particle filling has a measurable influence on the melting behavior of the polymer. The melting point for the printed PCL was determined at 66.5°C and for the composite filled with BTO and BTO/BG at 62.9°C and 64.9°C, respectively. The differences here are presumably due to the changed heat capacity of the material caused by the high degree of filling. The melting process is endothermic, and the melting enthalpies are 73.8, 62.9, and 64.9 J/g for PCL, PCL/BTO, and PCL/BTO/BG, respectively. The measured differences result primarily from the different proportions of the polymer. While PCL fully reflects the behavior of the base polymer, the composites have a reduced polymeric content of 60 vol.% (PCL/BTO) and 57.5 vol.% (PCL/BTO/BG), affecting the overall energy necessary to melt the material. However, regarding the processing on a 3D printer, the subtle changes do not have a substantial impact. The comparison with the raw materials (before printing) supports the results of the thermal analysis of the composites (Figure S6). The filler materials (BTO, BG) show no thermal degradation within the range of up to 600°C, whereas $\mathrm{PCL_{raw}}$ shows a similar degradation behavior as in the already printed state.

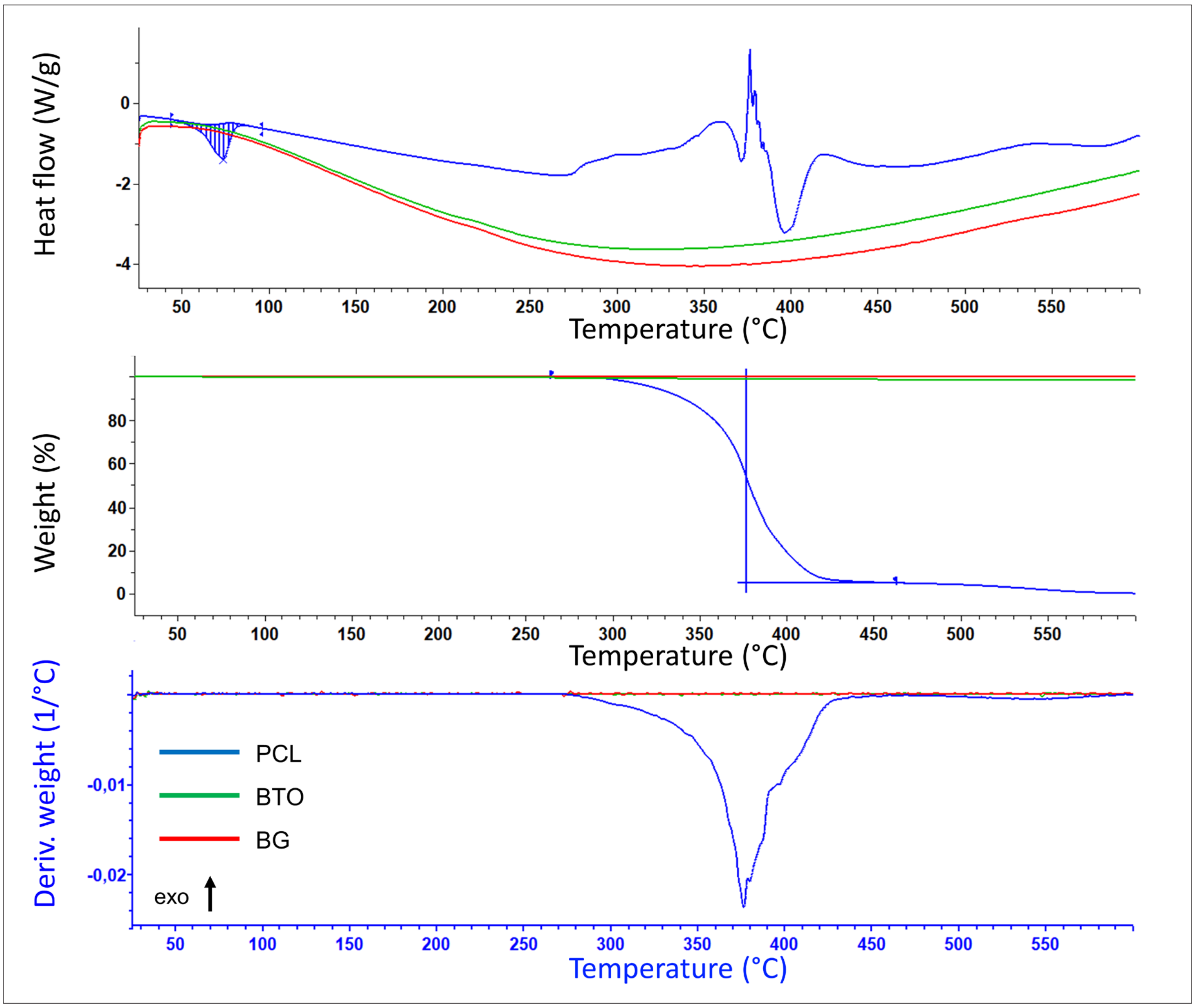


Figure S6. Thermal analysis (TGA and DSC) of raw materials (PCL, BTO, BG). Abbreviations: BG: Bioglass 45S5; BTO: Barium titanate; DSC: Differential scanning calorimetry; PCL: Polycaprolactone; TGA: Thermogravimetric analysis.

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