

Article

Design, Fabrication and Characterization of Biodegradable Composites Containing *Closo*-Borates as Potential Materials for Boron Neutron Capture Therapy

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Supplementary Material

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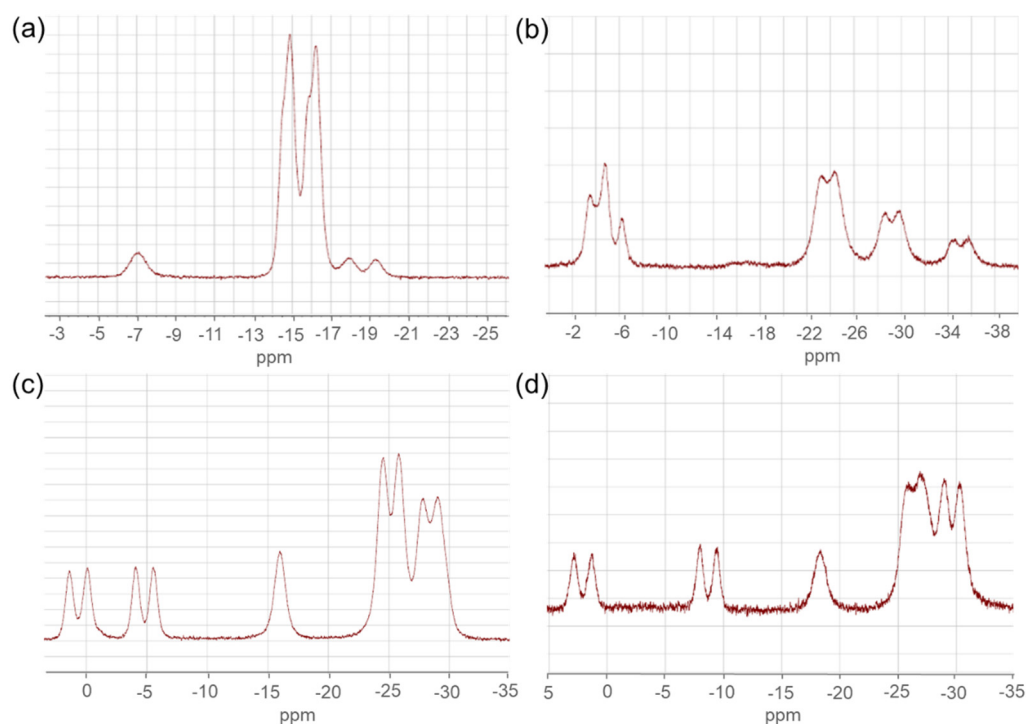


Figure S1. ¹¹B NMR spectra of used in adsorption *closo*-borates: Na[B₁₂H₁₁NH₃] \cdot 2H₂O (a), Na₂[B₁₀H₉OH] \cdot 2H₂O (b), Na[B₁₀H₉NH=C(NH₂)CH₃] \cdot 2H₂O (c), Na[B₁₀H₉NH=C(OH)CH₃] \cdot 2H₂O (d). The analysis was performed for a solution of compounds in CD₃CN at 96.32 MHz for ¹¹B.

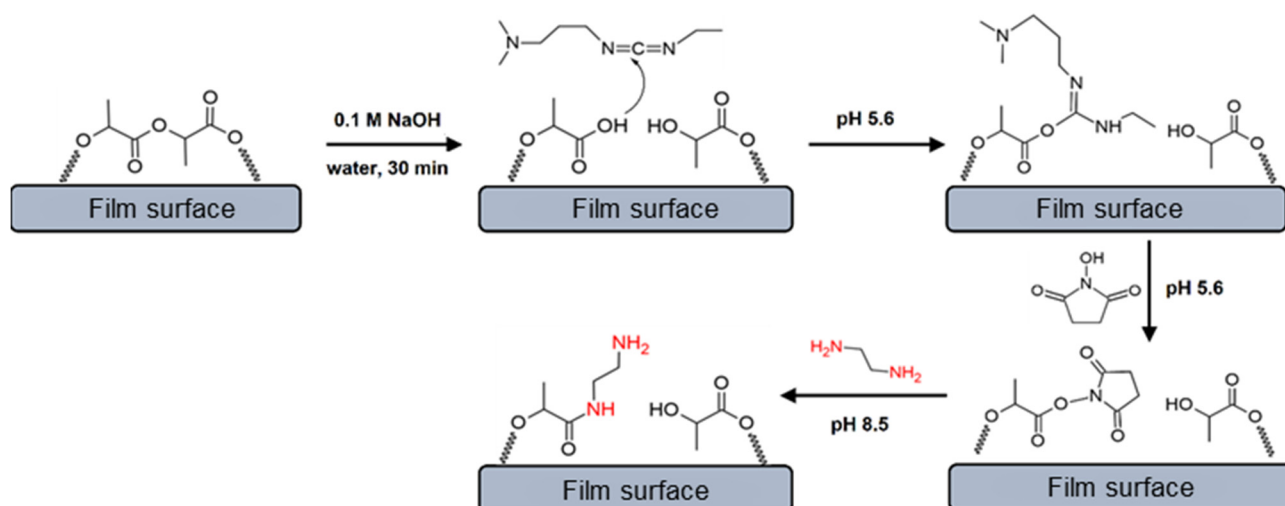


Figure S2. Scheme of the PDLLA surface hydrolysis and modification with ethylenediamine.

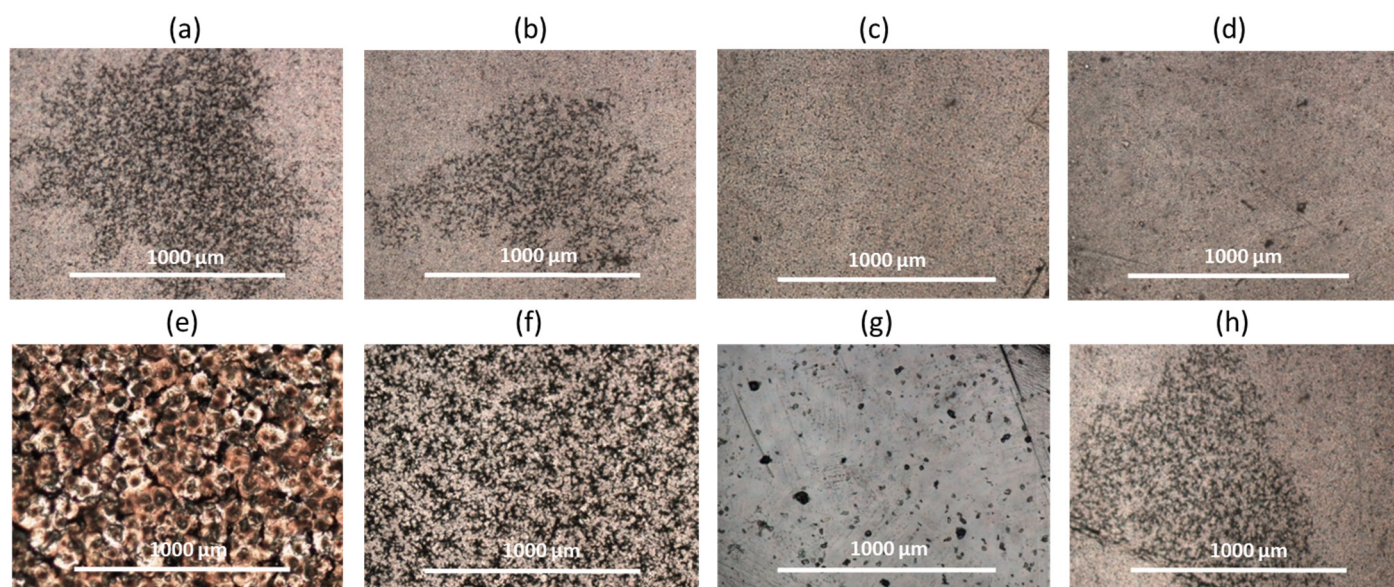


Figure S3. Images of some PDLLA and PCL films before and after $\text{Na}_2[\text{B}_{10}\text{H}_9\text{OH}]$ adsorption (optical microscopy, $\times 4$): PCL (image of a region with a higher degree of crystallinity) before adsorption (a), PCL with carboxyl and hydroxyl groups before (b) and after (h) adsorption, PCL-EDA after adsorption (c), PCL-PLys after adsorption (d), PCL/P(Lys-co-Leu) before adsorption (e), PCL/P(Lys-co-Phe) before adsorption (f) and PDLLA with carboxyl and hydroxyl groups after adsorption (g).

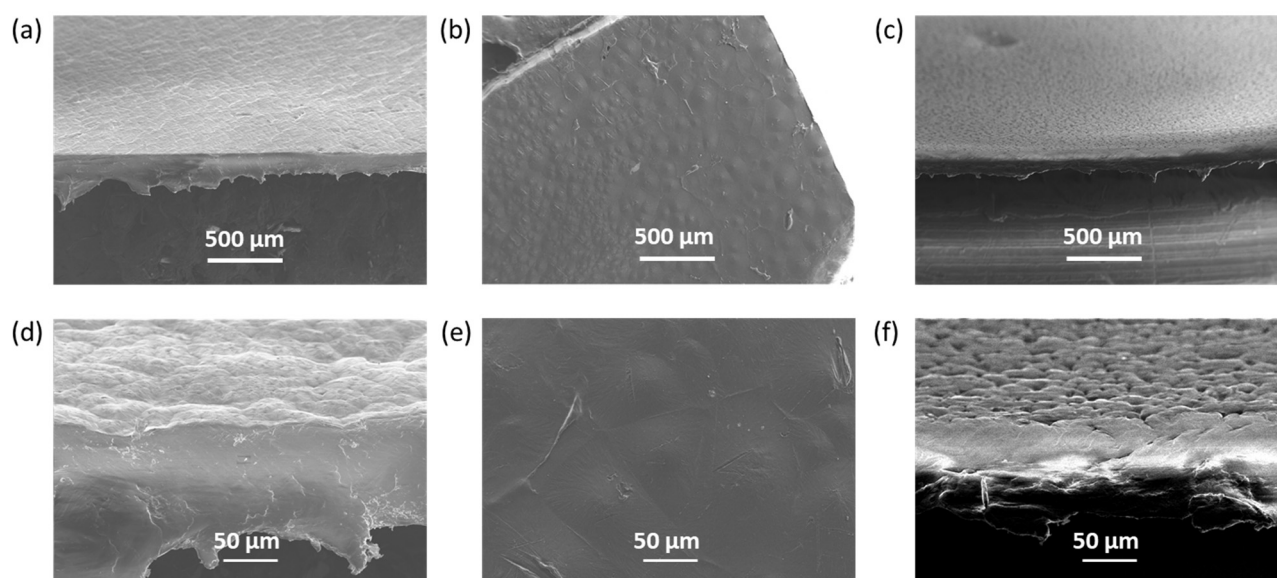


Figure S4. SEM images of pristine and composite PCL/polypeptide films with different magnification (x100, x500): PCL (a, d), PCL/P(Lys-co-Leu) (b, e) and PCL/P(Lys-co-Phe) (c, f).

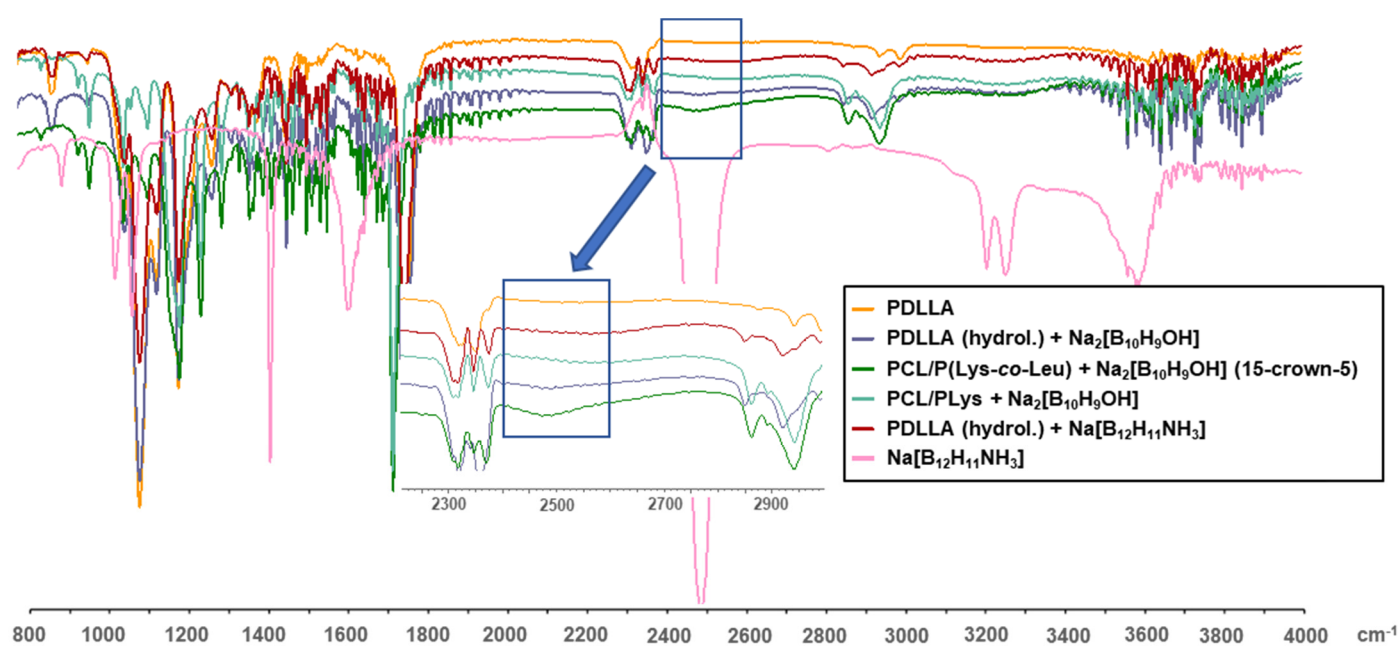


Figure S5. Examples of attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of obtained film materials before and after adsorption of *closo*-borates on their surface in comparison with the ATR-FTIR spectrum of Na[B₁₂H₁₁NH₃].

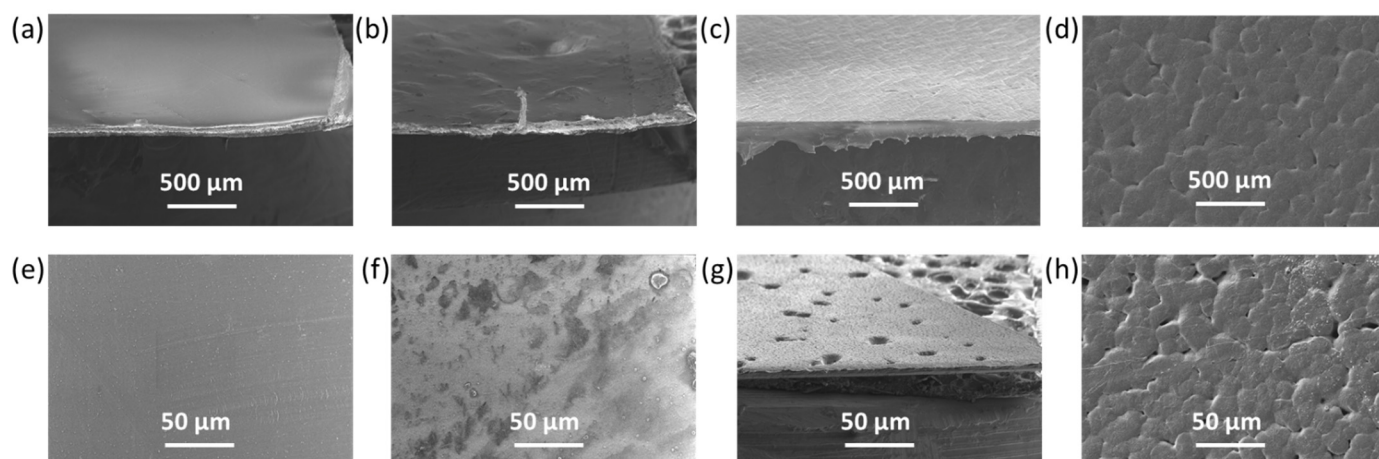


Figure S6. SEM images of pristine and composite PDLLA and PCL films containing dispersed *closo*-borate with different magnification (x100, x1000): PDLLA (a, e), PDLLA+5 wt% Na[B₁₂H₁₁NH₃] (b, f), PCL (c, g) and PCL+5 wt% Na[B₁₂H₁₁NH₃] (d, h).

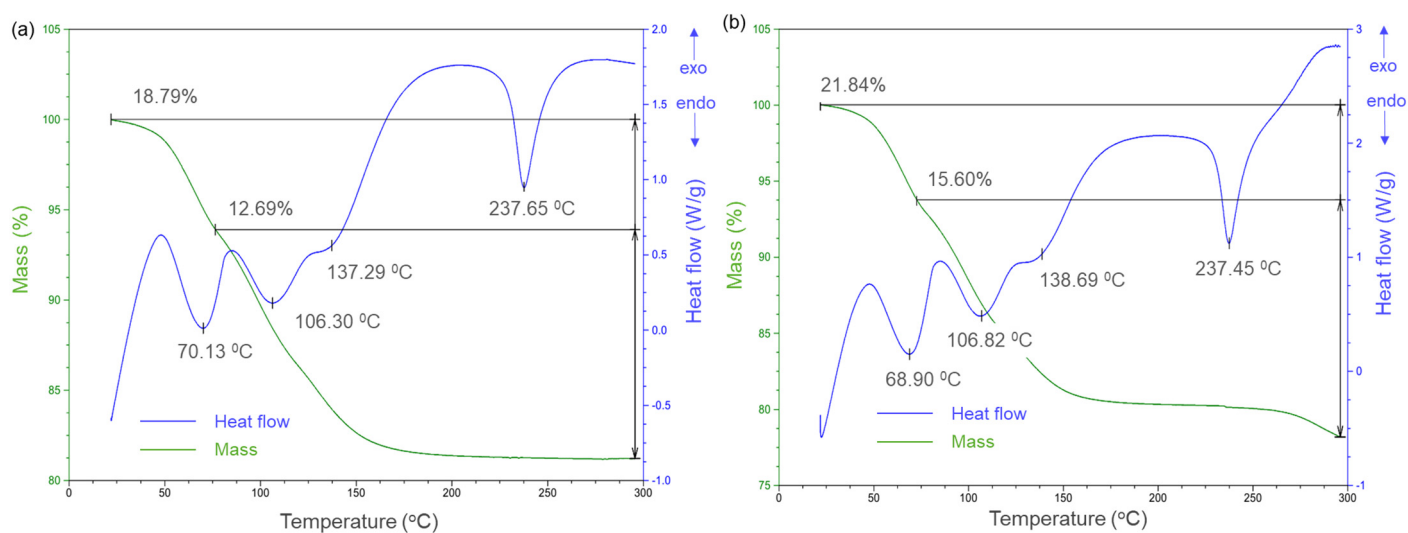


Figure S7. TGA-DSC curves for Na[B₁₂H₁₁NH₃]: (a) argon atmosphere, (b) air atmosphere.

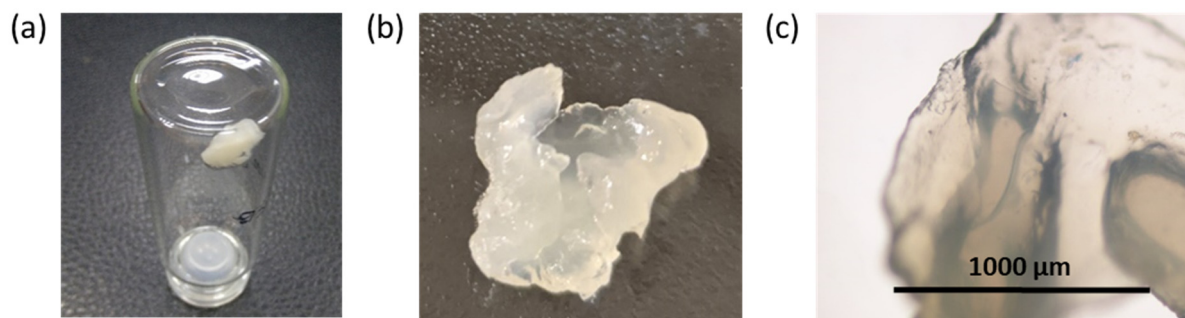


Figure S8. Images of alginate-gelatin hydrogel loaded with 5 wt% Na[B₁₂H₁₁NH₃]: photo (a, b) and optical microscopy (x4) (c).

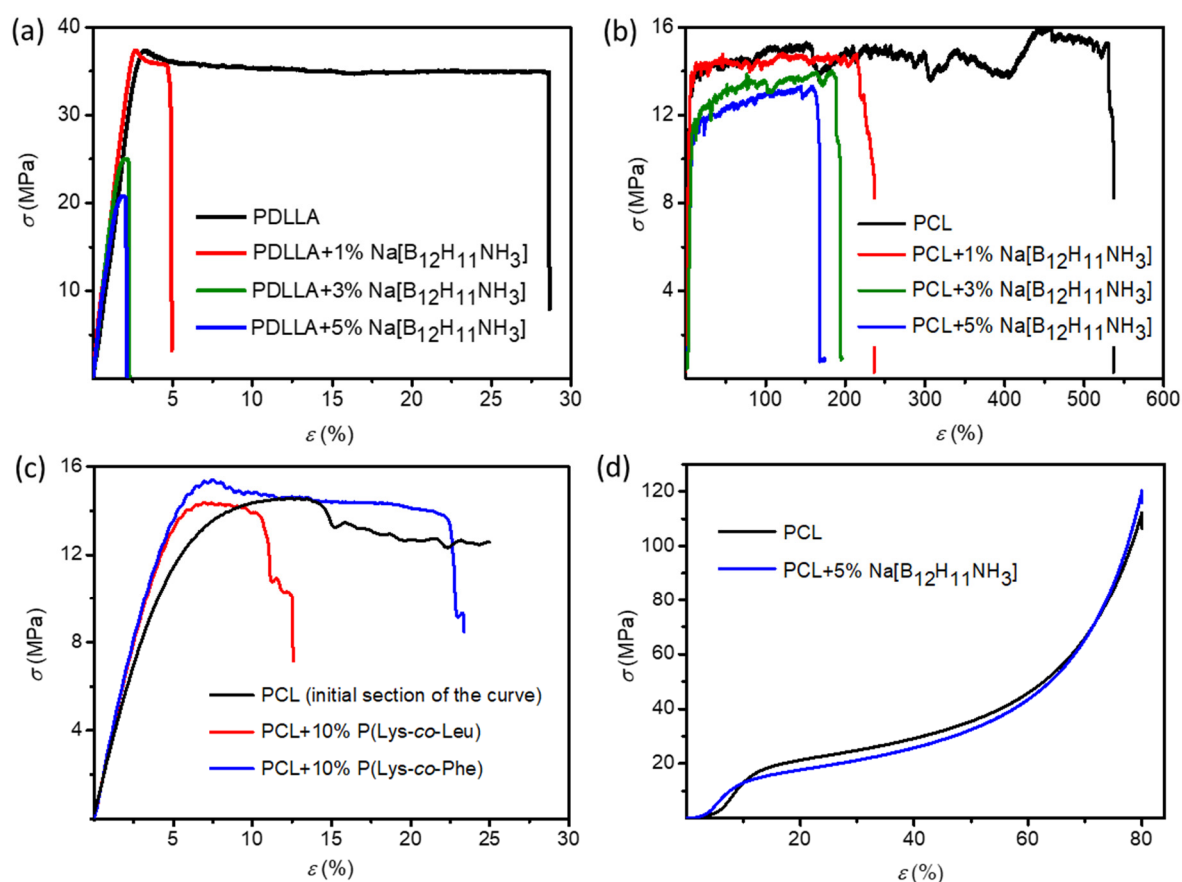


Figure S9. Tensile stress-strain curves for pristine and composite PDLLA and PCL films with Na[B₁₂H₁₁NH₃] or polypeptide (a–c) and compression stress-strain curves for monolithic PCL sample and its composite with Na[B₁₂H₁₁NH₃].

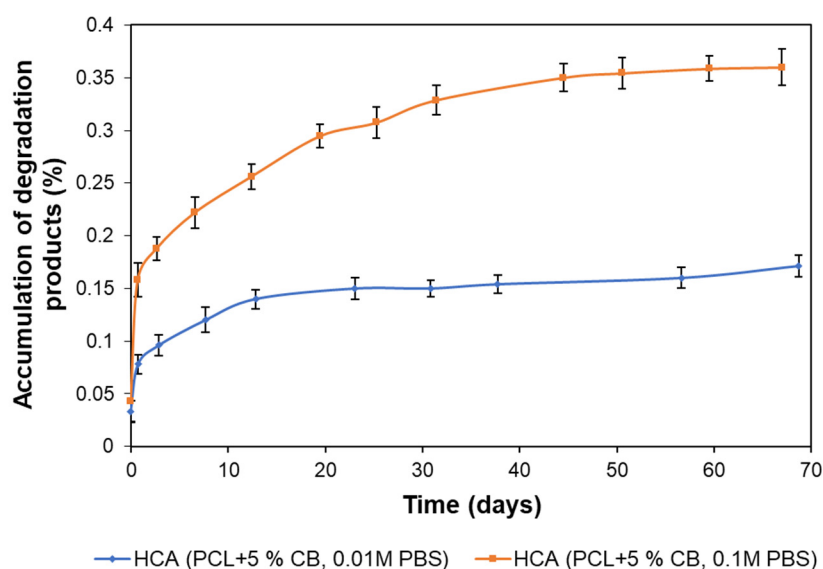


Figure S10. Profiles of accumulation of 6-hydroxycaproic acid (HCA) produced during degradation of PCL-based composite films obtained in sodium phosphate buffer with 0.15 mol/L NaCl (PBS, pH 7.4) with different buffer capacity. Conditions: 0.01 M or 0.1 M PBS in presence of lipase, 37 °C, monitoring by ¹H NMR spectroscopy.

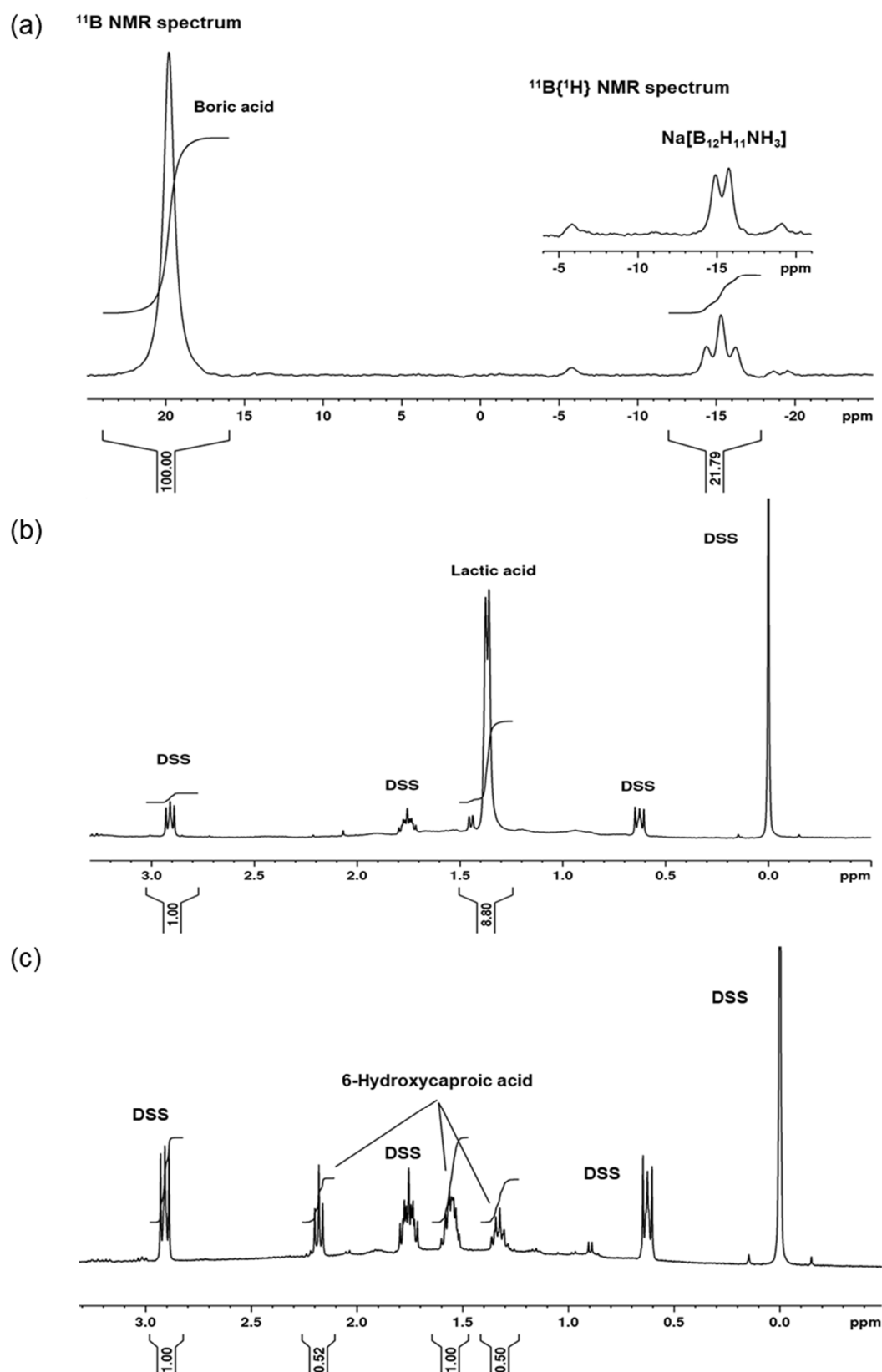


Figure S11. NMR spectra examples of degradation of PDLLA or PCL films filled with 5 wt% $\text{Na}[\text{B}_{12}\text{H}_{11}\text{NH}_3]$ in model physiological solution (pH 7.4, in presence of lipase, 37 °C): (a) release of *closo*-borate, (b) accumulation of lactic acid (from PDLLA) and (c) accumulation of 6-hydroxycaproic acid (from PCL). The analysis was performed with the use D_2O as a solvent at 400.13 and 128.378 MHz for ^1H and $^{11}\text{B}/^{11}\text{B}\{^1\text{H}\}$, respectively.

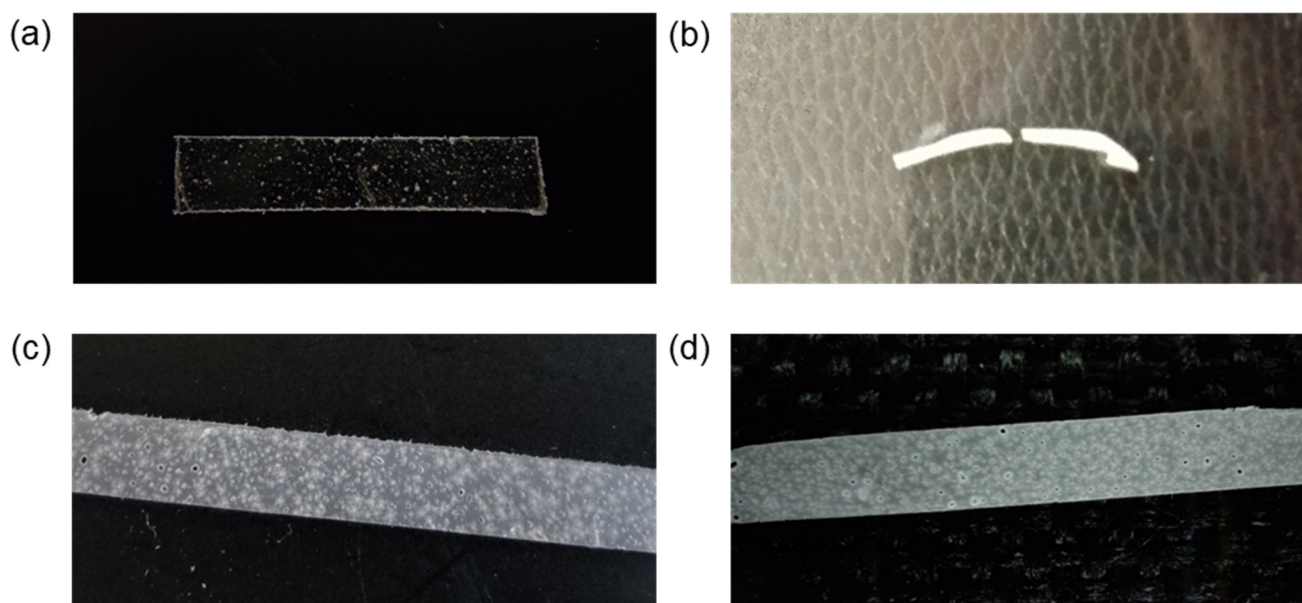


Figure S12. Photos of film samples based on PDLLA + 5 wt% Na[B₁₂H₁₁NH₃] before degradation (a), after 67 days of degradation (b) and based on PCL + 5 wt% Na[B₁₂H₁₁NH₃] before degradation (c) and after 67 days of degradation (d). Conditions: 0.1 M PBS, 37°C, in presence of lipase.