Supplementary Information

Novel biodegradable and non-fouling systems for controlled-release based on Poly(ϵ -caprolactone)/Quercetin blends and biomimetic bacterial S-layer coatings

Eva Sanchez-Rexach, *a⁺ Jagoba Iturri, ^{b⁺} Jorge Fernandez, ^a Emilio Meaurio, ^a Jose-Luis Toca-Herrera^b and Jose-Ramon Sarasua ^a

^aDepartment of Mining-Metallurgy Engineering and Materials Science, University of the Basque Country UPV/EHU, Plaza Ingeniero Torres Quevedo 1, Bilbao 48013, Spain

^bInstitute for Biophysics, Department of Nanobiotechnology, University of Natural Resources and Life Sciences (BOKU), Muthgasse 11 (Simon Zeisel Haus), Vienna 1190, Austria

[†]These authors contributed equally to this work.

*Corresponding author email: evagloria.sanchez@ehu.eus



Fig. S1. (a) Step used to measure the thickness of the films obtained by spin coating. (b) Correlation between film thickness and spinning speed from 10 mg/mL PCL solutions, and AFM images of PCL thin films of different thicknesses.



Fig. S2. (a) First and (b) second scan DSC curves for PCL, Quercetin and PCL/Q blends. As can be seen in (a), due to the strong auto-association of the flavonoid, Quercetin is able to crystallize when there is more than 20 wt% of Quercetin in the blend, as reflected by the two melting endotherms corresponding to the pure components. Miscible polymer-drug systems show a single glass transition temperature (T_g) intermediate between those of the pure components. Traces taken after cooling from the melt (b) coupled with the results presented in the table, show how with the addition of more than 20 wt% of the flavonoid, crystals of Quercetin are formed, and there is no enough amorphous quercetin to increase the T_g . Consequently, the maximum Quercetin content in the blends for the formation of stable PCL/Q amorphous solid dispersions will be 20 wt%, as all the drug is in amorphous state.



1760 1750 1740 1730 1720 1710 1700 1690 1690 1690 1690 1650 1640 163600 3550 3500 3450 3400 3350 3300 3250 3200 3150 3100 3050 3000 Wavenumber (cm⁻¹) Wavenumber (cm⁻¹)

Fig. S3. (a) Carbonyl stretching region for pure Quercetin and PCL/Q blends of different compositions: pure PCL shows a peak at 1721cm⁻¹ representing the crystalline part and a slight shoulder at 1735 cm⁻¹ attributable to the amorphous part. Upon blending with Quercetin, a new band appears at 1700 cm⁻¹ in the intermediate compositions attributable to hydrogen bonded C=O groups in the PCL. (b) Hydroxyl stretching region: pure Quercetin shows a complex, broad band with at least two discernable components located at about 3280 and 3350 cm⁻¹. These locations can be attributed to the O-H stretching of hydroxyl groups participating in cooperative hydrogen bonds of different strength. The shift of the OH stretching band to higher wavenumbers is typical when O-H··O-H interactions are replaced by -C=O···H-O- ones.



Fig. S4. Water contact angle measurements of bare PCL and SbpA-coated PCL to confirm the stability of the coating.



Fig. S5. AFM Height micrographs showing the topographical features from (a) pure PCL, (b) PCL/Q 90/10, (c) PCL/Q 80/20 and (d) PCL/Q 60/40 films with a thickness of 200 nm. Micrographs clearly indicate a gradual variation of the usual multi-spherulitic structure of PCL as the amount of drug is increased. For low amounts of Quercetin, the contact area between spherulites seems to fragmentize (b), offering a tree leave-like morphology which continues evolving towards a patchy arrangement of decreasing individual patch sizes (c) and (d). This trend turns critical for the highest drug content, PCL/Q 60/40, which does not resemble anymore the PCL shape.