macromol

MDPI

Supplementary Materials

Comparative Study of Three Biomass-Derived Organosolv Lignins in Electrospun Systems for Tunable Release Applications

Simone Serrecchia[1,2], Daniele Bianconi[1], Fabrizio De Cesare[3,1], Silvia Mosca[1], Paolo Papa[1], Giuseppe Scioli[4], Anatoly Petrovich Sobolev[4], Anna Rita Taddei[5] and Antonella Macagnano[1]*

[1] Institute of Technologies and Environmental Intelligence (ITIAm), National Research Council (CNR), Montelibretti (RM), Italy; simoneserrecchia@cnr.it (S.S.); danielebianconi@cnr.it (D.B); silvia.mosca@cnr.it (S.M); paolo.papa@cnr.it (P.P.)
[2] Department of Chemical, Materials and Production Engineering (DICMaPI), University of Naples Federico II, 80125 Naples, Italy;
[3] University of Tuscia, Department For Innovation In Biological, Agro-food And Forest Systems, Viterbo, Italy; decesare@unitus.it (F.D.C.)
[4] Institute for Biological Systems, Italian National Research Council, Monterotondo, 00015 Rome, Italy; giuseppe.scioli@cnr.it (G.S.); anatoly.sobolev@cnr.it (A.S.)
[5] Electron Microscopy Section, High Equipment Centre, University of Tuscia, Building D, 01100 Viterbo, Italy; artaddei@unitus.it (A.R.T)
* Correspondence: antonella.macagnano@cnr.it (A.M.)

S1.1. Image-based CIELAB colour analysis

A descriptive colour analysis was performed on the stereomicroscopy image montage presented in Figure 1 using a custom Python script based on NumPy.

The image contained an sRGB colour-space tag. One rectangular region of interest (ROI), measuring 350 × 150 pixels, was selected at an equivalent central position within each panel, yielding 52,500 pixels per formulation. Panel borders, sample labels and scale bars were excluded geometrically. No colour-based thresholding, smoothing, contrast enhancement or additional white-balance correction was applied.

The sRGB pixel values were normalised to the range 0–1 and linearised using the standard sRGB transfer function. Linear RGB values were converted to CIE XYZ and subsequently to CIELAB using a D65 reference white and the CIE 1931 2° standard observer. These settings define the colour-space conversion and do not imply that the microscope illumination was measured as D65. Mean L*, a* and b* values were calculated after pixel-wise conversion. L* describes lightness, while a* and b* represent the green–red and blue–yellow axes, respectively.

Each ROI was subdivided into 15 non-overlapping tiles of 70 × 50 pixels. Standard deviations were calculated across the tile means to describe spatial variability within each image. These tiles were not treated as independent experimental replicates. Colour differences relative to PLA–Cur were calculated as the Euclidean distance between the mean CIELAB coordinates using the CIE76 equation:

$$\Delta E_{ab} = \left[\left(L_{sample} - L_{reference} \right)^2 + \left(a_{sample} - a_{reference} \right)^2 + \left(b_{sample} - b*_{reference} \right)^2 \right]^{1/2}$$

The analysis provides relative image-derived colour descriptors rather than calibrated measurements of scaffold reflectance. In the PLA–Cur–Lsh ROI, approximately 22.9% of pixels had

a blue-channel value of zero in the analysed RGB file, which may limit the fidelity of the derived colour coordinates.

Table S1. Image-derived CIELAB coordinates of the electrospun scaffolds and CIE76 colour differences relative to PLA–Cur. Values are reported as the mean of the ROI pixels ± standard deviation among the means of 15 spatial tiles within a single image per formulation.

Sample	L*	a*	b*	ΔE*ab versus PLA–Cur
PLA–Cur	69.06 ± 1.13	4.46 ± 0.12	72.27 ± 0.96	—
PLA–Cur–Lhs	68.13 ± 1.18	5.16 ± 0.41	71.42 ± 1.00	1.45
PLA–Cur–Lsh	72.45 ± 1.66	−6.59 ± 0.47	74.43 ± 1.36	11.75
PLA–Cur–Lpp	70.54 ± 1.16	−2.68 ± 0.15	73.00 ± 0.99	7.33

S1.2. SEM imaging of electrospun membranes

This section presents representative SEM images of PLA–Cur, PLA–Cur–Lhs, PLA–Cur–Lsh, and PLA–Cur–Lpp membranes. Surface views at three magnifications provide an overview of the fibrous networks and details of individual fibre morphology, while cross-sectional views illustrate the arrangement of fibres through the membrane thickness.

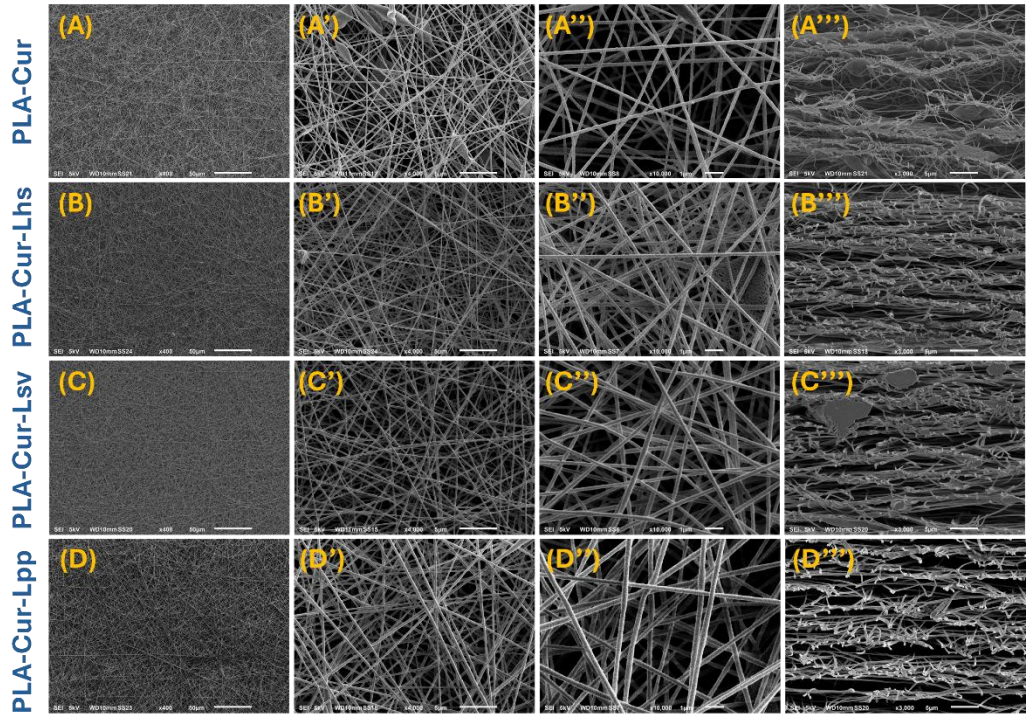


Figure S1. Scanning electron microscopy (SEM) images of electrospun PLA–Cur (A–A‴), PLA–Cur–Lhs (B–B‴), PLA–Cur–Lsh (C–C‴), and PLA–Cur–Lpp (D–D‴) membranes. Surface views are shown at increasing magnifications of ×400 (A–D), ×4,000 (A′–D′), and ×10,000 (A″–D″); cross-sectional views are shown at ×3,000 (A‴–D‴). Scale bars: 50 µm, 5 µm, 1 µm, and 5 µm for the first, second, third, and fourth columns, respectively.

S1.3. UV–Vis absorption spectrum of hazelnut-shell lignin in phosphate buffer

The UV–Vis spectrum of organosolv lignin extracted from hazelnut shells (Lhs) was recorded in phosphate buffer at pH 7.4 to examine possible spectral overlap with the curcumin-related absorption bands observed during release. The spectrum exhibits predominant absorption in the

UV region and a gradually decreasing tail towards the visible region, with no distinct maxima near 360 or 427 nm.

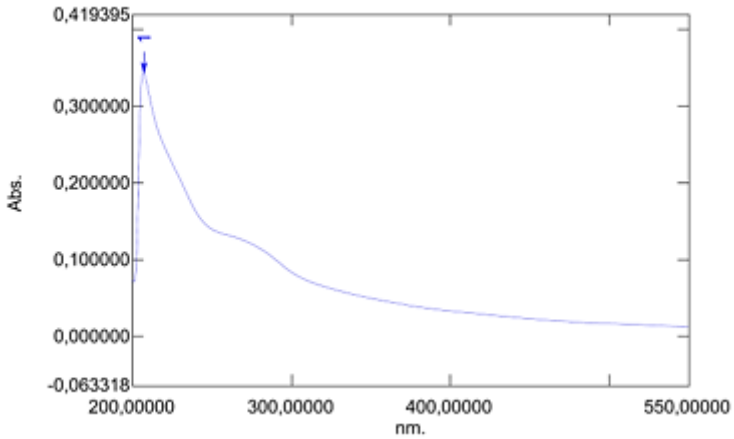


Figure S2. UV–Vis absorption spectrum of organosolv lignin extracted from hazelnut shells (Lhs) in phosphate buffer at pH 7.4, recorded as a reference to assess possible spectral overlap with the curcumin-related absorption bands in the release media.

S1.4. Proposed Role of Water and Matrix Interactions in Curcumin Mobilisation

The proposed roles of matrix organisation, non-covalent interactions, and water penetration in curcumin mobilisation are illustrated in Figure S4. The scheme shows how hydration of accessible regions may modify curcumin–matrix associations and facilitate transfer towards the surrounding medium.

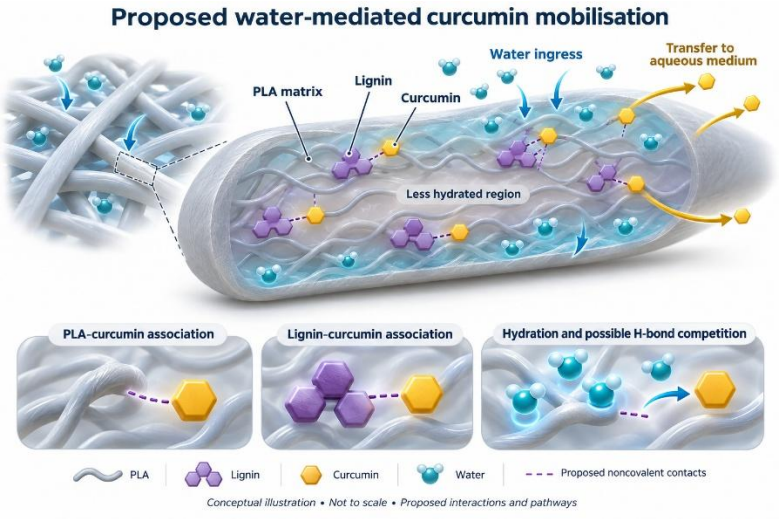


Figure S3. Conceptual illustration of water-mediated curcumin mobilisation from electrospun PLA–lignin fibres. The scaffold overview and enlarged fibre cutaway depict water ingress into accessible matrix regions and the proposed transfer of curcumin towards the aqueous medium. The three lower panels illustrate possible PLA–curcumin and lignin–curcumin associations and the potential competition of water for hydrogen-bonding sites. Grey chains, purple clusters, gold symbols, and

blue molecular symbols represent PLA, lignin, curcumin, and water, respectively. Dashed purple lines indicate proposed non-covalent contacts; blue and gold arrows indicate water ingress and curcumin mobilisation. The cutaway exposes the conceptual organisation of the matrix and does not imply a hollow or core–shell fibre architecture. Components and spatial arrangements are schematic and not to scale; the illustrated interactions and pathways are proposed rather than experimentally established.