Electronic Supplementary Material

Preparation and Characterization of Polymer Composite Materials Based on PLA/TiO_2 for Antibacterial Packaging

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3. Results and discussion

3.1. Structural characterization.

X-Ray Diffraction

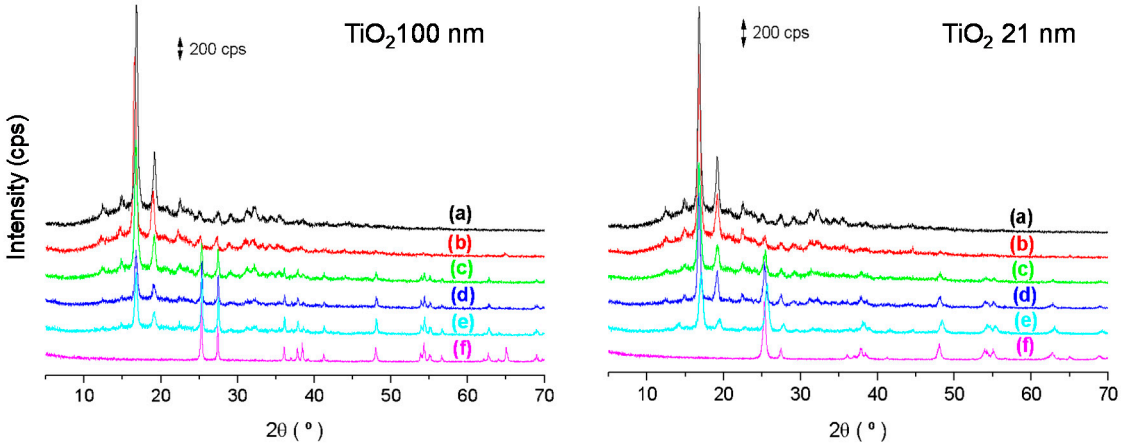

Figure S1.-X-Ray Diffraction patterns for the samples with TiO_2-100nm (left) and TiO_2-21nm (right) as a function of the content in TiO_2 nanoparticles: a) PLA-0; b) PLA/TiO_2-1; c) PLA/TiO_2-5; d) PLA/TiO_2-10; e) PLA/TiO_2-20 and f) pure TiO_2-100nm (left) or pure TiO_2-21 nm (right).

In both plots, the characteristic peaks of PLA-0 and TiO_2 were observed. Crystalline peaks in the nanocomposite materials associated with PLA appear in the interval of 2Θ = 15-25°. As the content of nanoparticles increases in the polymer matrix, the appearance of peaks from TiO_2 can

be observed. The peaks associated to TiO_2 showed lines that belonged to both anatase and rutile (see **Table S1**).

Table S1. XRD peaks of both polymorphs of TiO_2.

TiO_2 (Rutile)		TiO_2 (Anatase)	
2θ (°)	**(hkl)**	**2θ (°)**	**(hkl)**
27.4	110	25.3	101
36.1	101	36.9	112
41.2	111	37.8	004
54.3	211	38.4	112
56.6	220	48.0	200
64.0	310	53.9	105
65.0	221	55.0	211
		62.7	215/204
		69	116

Fourier Transformed Infrared Spectroscopy (FTIR)

Table S2. Band assignment for the PLA infrared spectrum in the MID-IR region [1,2]

Frequency (cm^{-1})	Band assignment	Frequency (cm^{-1})	Band assignment
2997	$\upsilon_{as}(CH_3)$	1209	$\upsilon_{as}(COC) + \rho_{as}(CH_3)$
2945	$\upsilon_{s}(CH_3)$	1180	$\circledcirc_{as}COC + \rho_{as}CH_3)$
2920	$\circledcirc_{as}(CH_2)$	1128	$\rho_{as}(CH_3)$
2881	$\circledcirc(CH_3)$	1082	$\circledcirc_{s}(COC)$
2850	$\circledcirc_{s}(CH_2)$	1043	$\circledcirc(C\text{-}CH_3)$
1747	$\circledcirc(C=O)$	957	$CH_3 + \circledcirc CC$
1452	$\delta_{as}(CH_3)$	918	$\rho(CH_3 + \circledcirc CC)$
1381	$\delta_{s}(CH_3)$	868	$\circledcirc(C\text{-}COO)$
1359	$\delta_{as}(CH_3)$	756	$\delta(C=O)$
1304	$\delta(CH)$	700	$\gamma(C=O)$
1267	$\circledcirc_{as}(COC) + \delta(CH)$		

[1]Auras R et al. Macromol Biosci 2004;4: 835–64. [2]Krikorian V, Pochan DJ. Macromolecules 2005; 38: 6520–7.

3.2. Thermal characterization.

Differential Scanning Calorimetry (DSC)

Table S3. Characteristic transition temperatures (T_g, T_c and T_m) obtained from the second heating scan in DSC experiments.

Sample	T_g (°C)	T_c (°C)	T_m (°C)
PLA-0	64.6	136.9	166.8
PLA/TiO_2-100-1	64.5	137.5	167.4
PLA/TiO_2-100-5	64.2	137.2	167.1
PLA/TiO_2-100-10	64.5	136.7	166.7
PLA/TiO_2-100-20	64.5	136.9	167.7
PLA/TiO_2-21-1	64.6	136.9	167.8
PLA/TiO_2-21-5	64.6	136.9	166.5
PLA/TiO_2-21-10	64.8	137.4	167.9
PLA/TiO_2-21-20	65.3	136.3	167.4

Thermogravimetry Analysis (TGA)

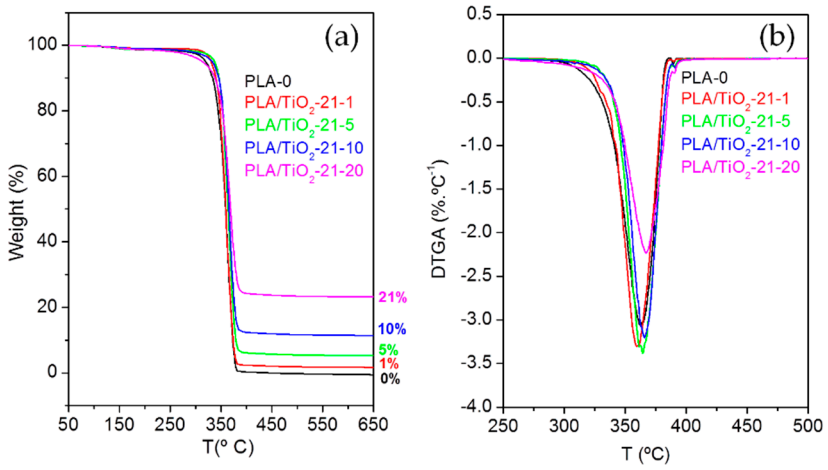

Figure S2. (a) Thermogravimetric analysis curve and (b) DTGA curve for the systems based on PLA/TiO_2-21.

3.3. Antimicrobial behaviour.

3.3.1. Study of biofilm development on the surface of the materials

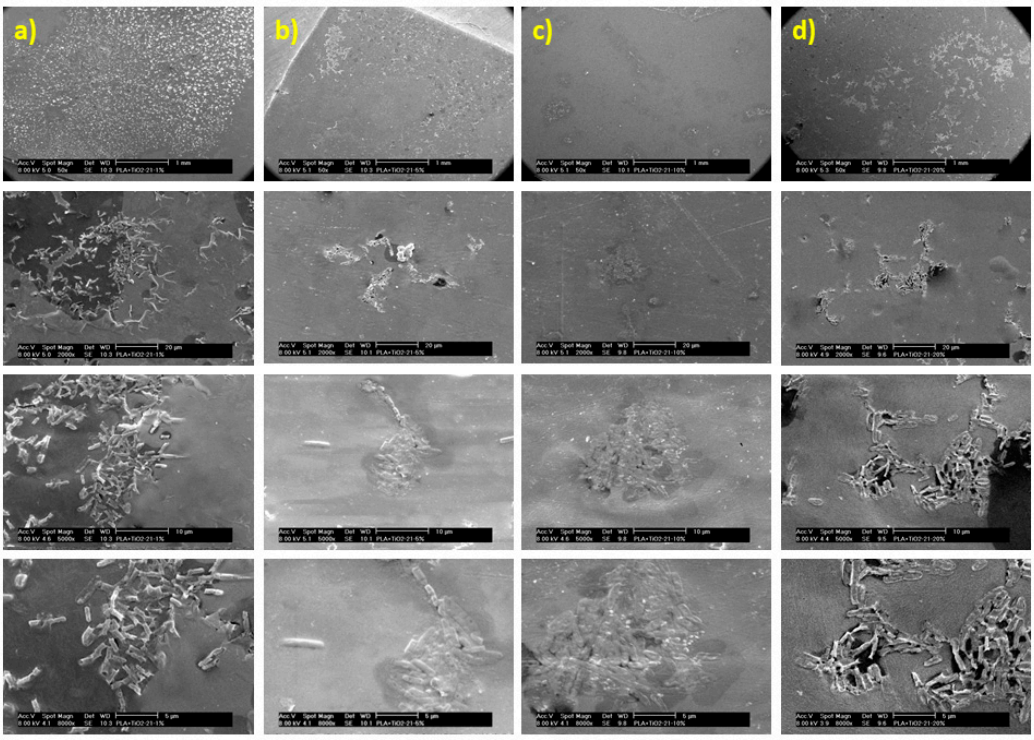

Figure S3. From top to bottom: Each row corresponds to SEM micrographs obtained at different magnifications: 50 ×; 2000 ×; 5000 × and 8000 × PLA/TiO_2 nanocomposite materials ($\phi \sim 21$ nm) as a function of the content in TiO_2 nanoparticles in each column: a) 1%; b) 5%; c) 10% and d) 20% (wt%).

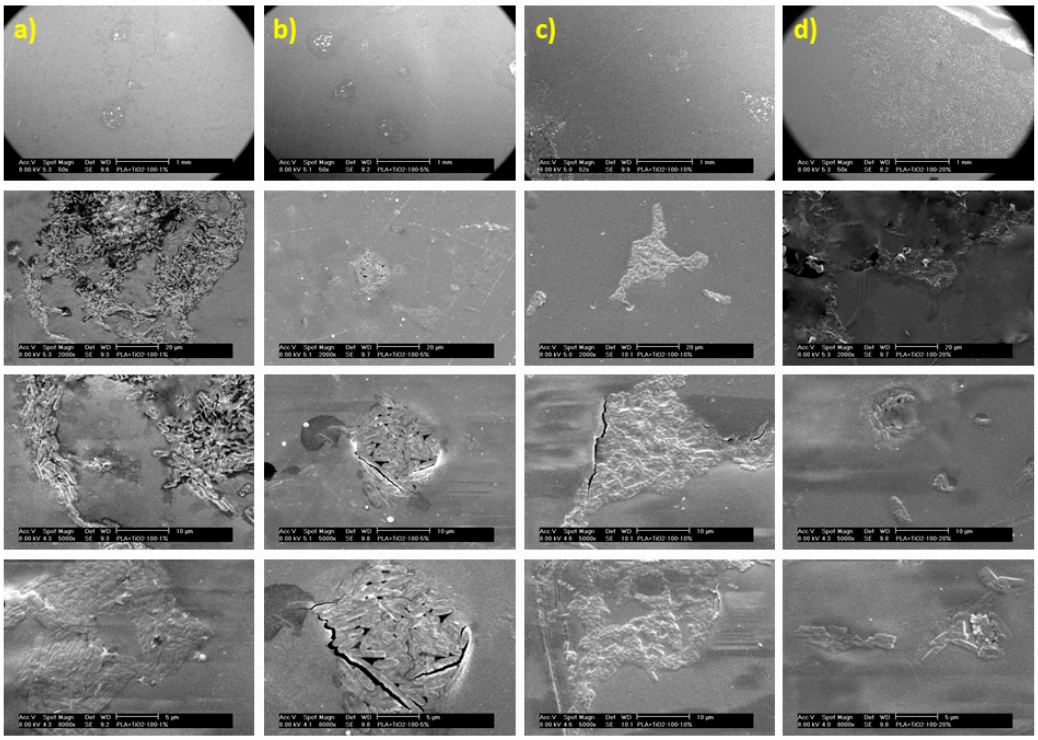

Figure S4. From top to bottom: Each row corresponds to SEM micrographs obtained at different magnifications: 50 ×; 2000 ×; 5000 × and 8000 × PLA/TiO_2 nanocomposite materials ($\phi < 100$ nm) as a function of the content in TiO_2 nanoparticles in each column: a) 1%; b) 5%; c) 10% and d) 20% (wt%).