Supplementary Information for

Mixed-Phase Titania foams via 3D-Printing for Pharmaceutical Degradation

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Supplementary information

Text S1. Quantum yield calculations

The quantum yield allows for an assessment of the photon efficiency, assessing the number of pollutant molecules undergoing degradation relative to the number of photons reaching the catalyst surface [1]. Based on the definitions contained in the IUPAC glossary, the following equations are proposed to calculate the quantum yield of photocatalytic foams:

$$k' = (k)(C_0)(V_{Illuminated})\ (mol\ s^{-1}) \tag{S1}$$

$$N_P = \frac{I_{\alpha\lambda} * S * t}{E_P}\ (-) \tag{S2}$$

$$q_{n,p} = \left(\frac{N_P}{t}\right)\frac{1}{N_A}\ (mol\ s^{-1}) \tag{S3}$$

$$\phi = \frac{k'}{q_{n,p}}\ (-) \tag{S4}$$

where, k' is the rate of pollutant degradation (mol s^{-1}), k is the kinetic constant (s^{-1}), C_o is the initial pollutant concentration (mol L^{-1}), $V_{Illuminated}$ is the volume of pollutant irradiated.

The number of photons can be calculated using Equation S1, where $I_{\alpha\lambda}$is the attenuated irradiance of the light source accounting for absorbance of the medium and the pollutant molecule(s) (W m^{-2}), S is the surface of the sample onto which the light impinges (m^2) and t is the time under irradiation.

$E_p = \frac{h * c}{\lambda}\ (J)$ is the photon energy at the wavelength emitted by the lamps, where h is Planck's constant, c is the speed of light and λ is the wavelength of light (m) from the lamps. The photon flux is the numbers of photons during irradiation of a mol of photons, where N_A is Avogadro's number (equation 3). Finally, the quantum yield (φ) is calculated using equation 4.

Text S2. Photocatalytic reactor energy consumption calculations.

To assess the viability of scaling up of the system, the energy consumption of the reactor was accounted for by using the electrical energy per order (E_{EO}), defined as the kilowatt hours of electrical energy needed to decrease the concentration of a pollutant by an order of magnitude (90%) in one cubic metre of solution. [2]

$$E_{EO} = \frac{P * t * I * 1{,}000}{V(log^{C_0}/_{C_t})} \quad \textbf{(S5)}$$

Where: P is the total power output of the 3 lamps onto the 12 cm long quartz tube (kW), t is the irradiation time (hrs) V is the volume of reservoir (L) and C_0 and C_t are the initial and final concentrations of pollutants respectively. As the foam occupied only a fraction of the quartz tube, the total power of the lamps, which act on the whole quartz tube, was multiplied by the volumetric fraction occupied by the foam (i.e. foam volume/quartz tube volume), to provide the effective power used for photocatalysis, considering that the contribution of photolysis is negligible. This is rendered necessary by the recirculating nature of the reactor, unlike a simple batch reactor, where the entire reservoir would be irradiated. In the present work, the external diameter of the foam corresponds to the internal diameter of the tube, so that the volumetric fraction is equivalent to the ratio of the foam's length to the total length of the quartz tube: 3 cm/12 cm = 0.25. For the recirculating foam reactors, three 5 W lamps were used, giving a P value of 15 X 10^{-3} kW, irradiation time was 120 minutes, volume of solution was 0.5 L, and the volumetric fraction 0.25.

Table S1: Final parameters for 3D printing of modified resin structures

From layer	To layer	Exposure time (s)	Lift hieght (mm)	Lift Speed up (mm/s)	Lift Speed down (mm/s)	Delay (s)
1	1	90	6	5	150	0.5
2	4	45	5.5	5	150	0.5
5	40	20	4	5	150	0.5
41	70	20	4	5	150	0.5
71	110	15	3.5	5	150	0.5
111	160	15	3.5	5	150	0.5
161	350	15	3.5	5	150	0.5
351	1203	15	3.5	5	150	0.5

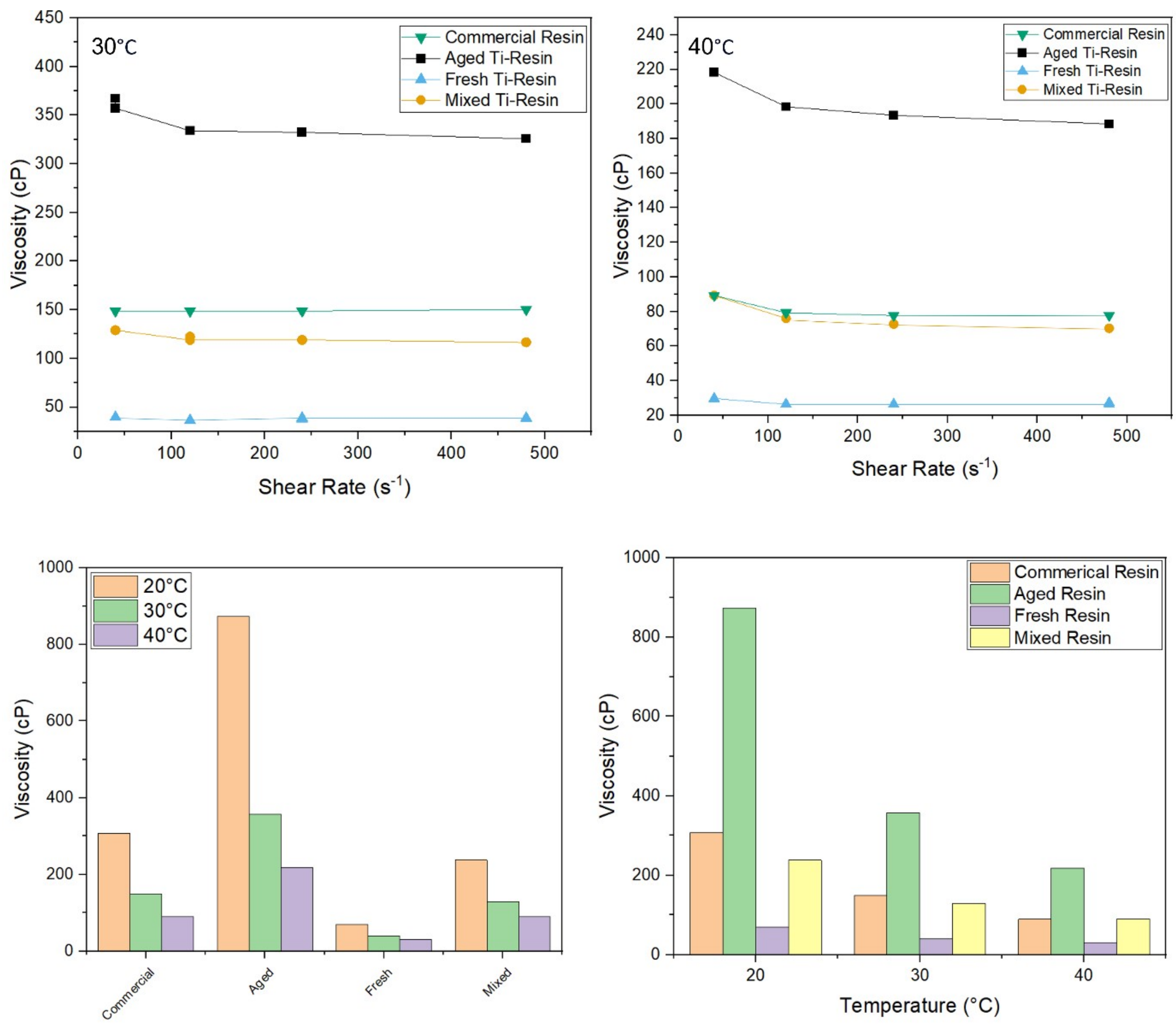

Figure S 1: Rheometric analysis of commercial and modified resins at a range of temperatures.

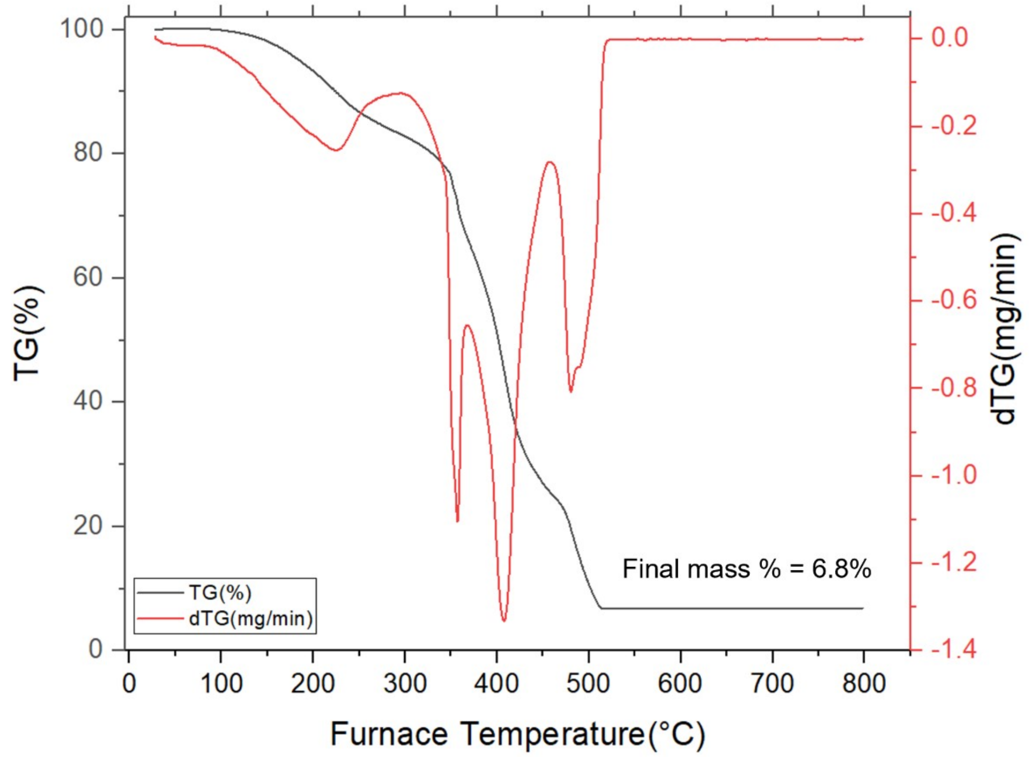

Figure S 2: Thermogravimetric analysis of the synthesised Ti (IV) acrylate photoresist.

Table S2: Normalised peak intensity of raman spectra for anatase and rutile TiO_2 peaks.

Sample	Anatase			Rutile		
	Normalised Raman intensity					
	E_g / 140 cm^{-1}	B_{1g} 395 cm^{-1}	A_{1g} 500 cm^{-1}	SOE 240 cm^{-1}	E_G 445 cm^{-1}	A_{1g} 610 cm^{-1}
650 °C, 1hr/ 600 °C, 30hr	1.000	0.078	0.049	0.048	0.176	0.242
750 °C, 1hr/ 700 °C, 30hr	0.659	0.000	0.021	0.186	0.898	1.000
850 °C, 1hr/ 800 °C, 30hr	0.130	0.000	0.009	0.203	0.917	1.000

Table S3: Normalised peak intensity ratio of raman spectra for anatase TiO_2 peaks.

Sample	Anatase					
	Normalised Raman intensity			Ratio		
	E_g / 140 cm^{-1}	B_{1g} 395 cm^{-1}	A_{1g} 500 cm^{-1}	A_{1g} / E_g	B_{1g} / E_g	A_{1g} / B_{1g}
650 °C, 1hr/ 600 °C, 30hr	1.000	0.078	0.049	0.049	0.078	0.628
750 °C, 1hr/ 700 °C, 30hr	0.659	0.000	0.021	0.032	0.000	/
850 °C, 1hr/ 800 °C, 30hr	0.13	0.000	0.009	0.000	0.000	/

Table S4: Normalised peak intensity ratio of raman spectra for rutile TiO_2 peaks.

Sample	Rutile			
	Normalised Raman intensity			Ratio
	SOE 240 cm^{-1}	E_G 445 cm^{-1}	A_{1g} 610 cm^{-1}	A_{1g} / E_g
650 °C, 1hr/ 600 °C, 30hr	0.048	0.176	0.242	1.375
750 °C, 1hr/ 700 °C, 30hr	0.186	0.898	1.000	1.114
850 °C, 1hr/ 800 °C, 30hr	0.203	0.917	1.000	1.091

Table S5: Comparison of normalised peak intensity ratios of raman spectra for anatase and rutile TiO_2 peaks.

Sample	Comparison		
	Ratio		
	An-E_g / Ru- A_{1g}	An-E_g / Ru- E_g	An-A_{1g} / Ru- A_{1g}
650 °C, 1hr/ 600 °C, 30hr	4.132	5.682	0.202
750 °C, 1hr/ 700 °C, 30hr	0.659	0.734	0.021
850 °C, 1hr/ 800 °C, 30hr	0.130	0.142	0.009

Comparison with literature.

Table S6: CBZ photocatalytic degradation kinetics for slurries and immobilised systems reported from literature.

Photocatalyst	Material	Degradation conditions	Eeo	QY	Ref
Immobilised Catalyst	TiO_2	Flow photocatalytic membrane reactor Volume 200 mL Xenon lamp(300 W, 76.7 mW cm^{-2})	2994.0	3.32 X 10^{-5}	3
	N-TiO_2		1000.0	7.06 X 10^{-5}	
	TiO_2	Batch reactor 500 mL volume Xe high intensity lamp (55 W, 1.26 mW cm^{-2}, 475 nm)	12902.7	3.84 X 10^{-7}	4
Nanoparticle suspension	TiO_2	Batch reactor 50 mL volume Hg Lamps (6 X 8 W, 1.6mW cm^{-2}, 365 nm)	191.0	4.66 X 10^{-5}	5
	ZnO	Batch reactor 100 mL volume Temperature: 25 ºC Xenon Lamp, (5 KW, 5.5 W cm^{-2}, 6000 K, 483 nm)	46.4	3.55 X 10^{-4}	6
	$ZnFe_2O_4$		4.6	3.52 X 10^{-3}	
	$ZnFe_2O_4$	Batch reactor 250 mL reactor Compact fluorescent lamp (9 W, 320 μW cm^{-2}, 365 nm)	4.6	3.52 X 10^{-3}	7
	C- TiO_2	Batch reactor 400 mL volume Tungsten lamp (150 W, 6.3mW cm^{-2}, 400 nm)	166.3	4.64 X 10^{-8}	8
	TiO_2	Batch reactor 350 mL reactor 9 W UV-A lamp, 3.16 Wm-2 (Radium Ralutec lamp, 9 W/78, λ=350-400 nm)	85.4	2.60 X 10^{-4}	9
Foam	ZnO	Recirculating reactor, flow rate 250 mL min^{-1}, 500 mL volume Lamps (3 X 5 W, 10.3 mW cm^{-2}, 254 nm) Recirculating reactor, flow rate 250 mL min^{-1}, 500 mL volume Lamps (3 X 5 W, 10.3 mW cm^{-2}, 254 nm)	19.5	2.63 X 10^{-3}	10
	ZnO		19.0	2.25 X 10^{-3}	11
	1% Co-ZnO		105.0	1.40 X 10^{-4}	12
	2% Co-ZnO		145.0	1.31 X 10^{-4}	
	1% Ni-ZnO		100.0	2.01 X 10^{-4}	
	2% Ni-ZnO		82.0	1.20 X 10^{-4}	
	1% Cu-ZnO		145.0	1.34 X 10^{-4}	
	2% Cu-ZnO		145.0	9.68 X 10^{-5}	
	TiO_2		67.6	7.58 X 10^{-4}	This work

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