Appendix A

A.1 Carbonated Hydroxyapatite (CHA)

For carbonated hydroxyapatite (CHA), with the formula: $Ca_{10}(PO_4)_6(CO_3)_x(OH)_{2-2x}$, a fraction of x = 0.4 was chosen to accommodate the reduction in carbonate content experienced during heat treatment by bone, which usually has CO_3 = (4...6)%. The chosen value, x = 0.4, represents a $CO_3 \approx 2.4\%$ and a $CO_2 \approx 1.7\%$, with the latter value needed to calculate the K_{sp} value according to Ito et al. [1].

The CHA molar mass can be expressed as a function of pure hydroxyapatite molar mass, M_{HA}, and the carbonate content, x, as:

$$\begin{aligned} M_{CHA} &= 10M_{Ca} + 6(M_P + 4M_O) + x(M_C + 3M_O) + (2 - 2x)(M_H + M_O) \\ &= M_{HA} + x(M_O + M_C - 2M_H) \\ &= 1004.6162 + x(25.994) \\ &= 1004.6162 + 0.4(25.994) \\ &= 1015.010 \qquad \text{g mol}^{-1} \end{aligned} \tag{A.1}$$

A.2 Solubility Product (K_{sp}) and Equilibrium Calcium Concentration ($[Ca^{2+}]_{eq}$)

The general equilibrium equation for the dissolution of a sparingly soluble ionic compound MX_ν is given by the following expression from [2]:

$$MX_\nu(s) \rightleftharpoons M^{\nu+}(aq) + \nu X^{-}(aq) \tag{A.2}$$

The solubility product (K_{sp}) can be defined as:

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$$K_{sp} = [M^+][X^-]^\nu \tag{A.3}$$

with $[M^+]$, the concentration of M^+ ions in water and $[X^-]$, the concentration of X^- ions in water.

A generalised version can be expressed as:

$$K_{sp} = \prod_{i=1}^{n} C_i^{m_i}|_{eq} \tag{A.4}$$

with $C_i|_{eq}$ the concentration of constituents ions at equilibrium and m_i, their respective coefficients in the ionic compound.

A.2.1 Tricalcium Phosphate (TCP)

Tricalcium phosphate (TCP), whose chemical formula is $Ca_3(PO_4)_2$, has the following dissolution reaction:

$$Ca_3(PO_4)_2\ (s) \overset{37\ ^\circ C}{\rightleftharpoons} 3Ca^{2+}(aq) + 2(PO_4^{3-})(aq) \tag{A.5}$$

Assuming stoichiometric dissolution: $[PO_4^{3-}]_{eq} = \frac{2}{3}[Ca^{2+}]_{eq}$ and the solubility product can be expressed as:

$$\begin{aligned} K_{sp} &= ([Ca^{2+}]_{eq})^3([PO_4^{3-}]_{eq})^2 \\ &= ([Ca^{2+}]_{eq})^3\left(\frac{2}{3}\right)^2([Ca^{2+}]_{eq})^2 \\ &= \frac{4}{9}([Ca^{2+}]_{eq})^5 \qquad (\text{mol}^5\,\text{dm}^{-15}) \end{aligned} \tag{A.6}$$

Thus, the equilibrium calcium concentration is:

$$\begin{aligned} [Ca^{2+}]_{eq} &= \left(\frac{9}{4}K_{sp}\right)^{\frac{1}{5}} \\ &= \left(\frac{9}{4}10^{-(-\log_{10}K_{sp})}\right)^{\frac{1}{5}} \qquad (\text{mol}\,\text{dm}^{-3}) \end{aligned} \tag{A.7}$$

A.2.2 Pure Hydroxyapatite (HA_p)

Pure hydroxyapatite, whose chemical formula is $Ca_{10}(PO_4)_6(OH)_2$, has the following dissolution reaction:

$$Ca_{10}(PO_4)_6(OH)_2\ (s) \overset{37\ ^\circ C}{\rightleftharpoons} 10Ca^{2+}(aq) + 6(PO_4^{3-})(aq) + 2(OH^-)(aq) \quad (A.8)$$

Assuming stoichiometric dissolution: $[PO_4^{3-}]_{eq} = \frac{3}{5}[Ca^{2+}]_{eq}$ and $[OH^-]_{eq} = \frac{1}{5}[Ca^{2+}]_{eq}$, and K_{sp} can be expressed as:

$$\begin{aligned} K_{sp} &= ([Ca^{2+}]_{eq})^{10}([PO_4^{3-}]_{eq})^6([OH^-]_{eq})^2 \\ &= ([Ca^{2+}]_{eq})^{10}\left(\frac{3}{5}\right)^6([Ca^{2+}]_{eq})^6\left(\frac{1}{5}\right)^2([Ca^{2+}]_{eq})^2 \\ &= \frac{3^6}{5^8}([Ca^{2+}]_{eq})^{18} \qquad (mol^{18}\,dm^{-54}) \end{aligned} \quad (A.9)$$

Thus, the equilibrium calcium concentration is:

$$\begin{aligned} [Ca^{2+}]_{eq} &= \left(\frac{5^8}{3^6}K_{sp}\right)^{\frac{1}{18}} \\ &= \left(\frac{5^8}{3^6}10^{-(-\log_{10}K_{sp})}\right)^{\frac{1}{18}} \qquad (mol\,dm^{-3}) \end{aligned} \quad (A.10)$$

A.2.3 Carbonated Hydroxyapatite (CHA)

Carbonated hydroxyapatite (CHA), with the formula: $Ca_{10}(PO_4)_6(CO_3)_x(OH)_{2-2x}$ with x = 0.4, has the following dissolution reaction:

$$\begin{aligned} Ca_{10}(PO_4)_6(CO_3)_x(OH)_{2-2x}\ (s) \overset{37\,^\circ C}{\rightleftharpoons} 10Ca^{2+}(aq) + 6(PO_4^{3-})(aq) \\ + 0.4(CO_3^{2-})(aq) + 1.2(OH^-)(aq) \end{aligned} \quad (A.11)$$

Assuming stoichiometric dissolution: $[PO_4^{3-}]_{eq} = \frac{3}{5}[Ca^{2+}]_{eq}$, $[CO_3^{2-}]_{eq} = \frac{x}{10}[Ca^{2+}]_{eq}$ and $[OH^-]_{eq} = \frac{1-x}{5}[Ca^{2+}]_{eq}$, and K_{sp} can be expressed as:

$$\begin{aligned} K_{sp} &= ([Ca^{2+}]_{eq})^{10}([PO_4^{3-}]_{eq})^6([CO_3^{2-}]_{eq})^x([OH^-]_{eq})^{(2-2x)} \\ &= ([Ca^{2+}]_{eq})^{10}\left(\frac{3}{5}\right)^6([Ca^{2+}]_{eq})^6\left(\frac{x}{5}\right)^x([Ca^{2+}]_{eq})^x\left(\frac{1-x}{5}\right)^{(2-2x)}([Ca^{2+}]_{eq})^{(2-2x)} \\ &= \frac{3^6(2.5x)^x(1-x)^{(2-2x)}}{5^8}([Ca^{2+}]_{eq})^{(18-x)} \qquad (mol^{18-x}\,dm^{-(54-1.2x)}) \end{aligned} \quad (A.12)$$

Thus, the equilibrium calcium concentration is:

$$[Ca^{2+}]_{\text{eq}} = \left(\frac{5^8}{3^6(2.5\text{x})^{\text{x}}(1-\text{x})^{(2-2\text{x})}} K_{\text{sp}}\right)^{\frac{1}{18-\text{x}}}$$
$$= \left(\frac{5^8}{3^6(2.5\text{x})^{\text{x}}(1-\text{x})^{(2-2\text{x})}} 10^{-(-\log_{10} K_{\text{sp}})}\right)^{\frac{1}{18-\text{x}}}$$
$$= \left(\frac{5^8}{3^6 1^{0.4} 0.6^{1.2}} 10^{-(-\log_{10} K_{\text{sp}})}\right)^{\frac{1}{17.6}} \quad (\text{mol dm}^{-3}) \quad (A.13)$$

A.2.4 Calcium Carbonate (CC)

Calcium carbonate, whose chemical formula is $CaCO_3$, has the following dissolution reaction:

$$CaCO_3\ (s) \overset{37\ ^\circ\text{C}}{\rightleftharpoons} Ca^{2+}(aq) + (CO_3^{2-})(aq) \quad (A.14)$$

Assuming stoichiometric dissolution: $[Ca^{2+}]_{\text{eq}} = [CO_3^{2-}]_{\text{eq}}$, and K_{sp} can be expressed as:

$$K_{\text{sp}} = [Ca^{2+}]_{\text{eq}}[CO_3^{2-}]_{\text{eq}}$$
$$= ([Ca^{2+}]_{\text{eq}})^2 \quad (\text{mol}^2\ \text{dm}^{-6}) \quad (A.15)$$

Thus, the equilibrium calcium concentration is:

$$[Ca^{2+}]_{\text{eq}} = (K_{\text{sp}})^{\frac{1}{2}}$$
$$= \left(10^{-(-\log_{10} K_{\text{sp}})}\right)^{\frac{1}{2}} \quad (\text{mol dm}^{-3}) \quad (A.16)$$

A.3 Polymer Dissociation Constant (pK_{a}) for Copolymers and Blends

The dissociation constant K_{a} of a copolymer or polymer blend can be computed using the K_{a} values of their individual components, usually reported in literature, as shown for a two-components case:

$$K_{\text{a1}} = \frac{[H^+][R_1\text{-}COO^-]}{[R_1\text{-}COOH]} \quad (A.17)$$

$$K_{\text{a2}} = \frac{[H^+][R_2\text{-}COO^-]}{[R_2\text{-}COOH]} \quad (A.18)$$

The overall K_a value can be expressed as:

$$K_a = \frac{[H^+][R\text{-}COO^-]}{[R\text{-}COOH]} = \frac{[H^+]\left([R_1\text{-}COO^-] + [R_2\text{-}COO^-]\right)}{[R_1\text{-}COOH] + [R_2\text{-}COOH]} \tag{A.19}$$

Assuming random polymerisation, the possibility of finding a specific monomer at the end of a chain is equal to the molar fraction of said monomer:

$$[R_1\text{-}COOH] + [R_1\text{-}COO^-] = \frac{\alpha_1}{\alpha_2}([R_2\text{-}COOH] + [R_2\text{-}COO^-]) \tag{A.20}$$

As the ratio of undissociated to dissociated chains is large, the relationship can be approximated as:

$$[R_1\text{-}COOH] = \frac{\alpha_1}{\alpha_2}[R_2\text{-}COOH] \tag{A.21}$$

Given the following expression for the overall K_a value:

$$\begin{aligned} K_a &= \frac{[H^+][R\text{-}COO^-]}{[R\text{-}COOH]} = \frac{[H^+][R_1\text{-}COO^-] + [H^+][R_2\text{-}COO^-]}{[R_1\text{-}COOH] + [R_2\text{-}COOH]} \\ &= \frac{K_{a1}[R_1\text{-}COOH] + K_{a2}[R_2\text{-}COO^-]}{[R_1\text{-}COOH] + [R_2\text{-}COOH]} \\ &= \frac{K_{a1}[R_1\text{-}COOH] + K_{a2}\frac{\alpha_2}{\alpha_1}[R_1\text{-}COOH]}{[R_1\text{-}COOH] + \frac{\alpha_2}{\alpha_1}[R_1\text{-}COOH]} \\ &= \frac{K_{a1} + K_{a2}\frac{\alpha_2}{\alpha_1}}{1 + \frac{\alpha_2}{\alpha_1}} = \frac{K_{a1}\alpha_1 + K_{a2}\alpha_2}{\alpha_1 + \alpha_2} = \alpha_1 K_{a1} + \alpha_2 K_{a2} \end{aligned} \tag{A.22}$$

Resulting in a dissociation constant value for a copolymer or polymer blend of $pK_a = -\log_{10}(\alpha_1 K_{a1} + \alpha_2 K_{a2})$ with α_1 and α_2, the molar/ ratios of the two components of the copolymer or blend and K_{a1} and K_{a2}, their corresponding values of dissociation constant.

A.4 Initial Degree of Pseudo-polymerisation

N_{dp0} ($\mathrm{Da\,Da^{-1}}$), the initial degree of pseudo-polymerisation, can be expressed as a function of M_{unit}, the molar mass associated to one ester bond (Da) and M_{n0}, the number-average molecular weight at the time origin (Da); or C_{e0}, the concentration of ester bonds in long chains at the time origin in the polymer phase ($\mathrm{mol\,m^{-3}}$) and C_{chain0}, the initial concentration of long polymer chains in the polymer phase ($\mathrm{mol\,m^{-3}}$) using $C_{e0} = \frac{\rho_{pol}}{M_{unit}}$ and $C_{chain0} = \frac{\rho_{pol}}{M_{n0}}$ with ρ_{pol}, the polymer density ($\mathrm{kg\,m^{-3}}$):

$$\frac{C_{\text{chain0}}}{C_{\text{e0}}} = \frac{\text{Initial number of chains}}{\text{Initial number of ester bonds}} = \frac{\frac{\rho_{\text{pol}}}{M_{\text{n0}}}}{\frac{\rho_{\text{pol}}}{M_{\text{unit}}}} = \frac{M_{\text{unit}}}{M_{\text{n0}}} = N_{\text{dp0}}^{-1} \tag{A.23}$$

A.5 Sauter Mean Diameter

Assuming spherical particles, the diameter which characterises the distribution in terms of volume and surface area, d_{eq}, would satisfy:

$$\begin{aligned}\frac{\text{Overall volume of particles}}{\text{Overall surface of particles}} &= \frac{\sum_{i=1}^{N} V_i}{\sum_{i=1}^{N} A_i} = \frac{\sum_{i=1}^{N} \frac{\pi}{6} d_i^3}{\sum_{i=1}^{N} \pi d_i^2} \\ &= \frac{N\frac{\pi}{6} d_{\text{eq}}^3}{N\pi d_{\text{eq}}^2} = \frac{d_{\text{eq}}}{6} \qquad \text{(m)}\end{aligned} \tag{A.24}$$

being V_i (m^3), A_i (m^2) and d_i (m), the volume, surface area and diameter of the ith particle respectively.

The Sauter Mean diameter, (*SMD* or $D[2, 3]$ or d_{32}), is defined as:

$$\begin{aligned}SMD = D[2,3] = d_{32} = \frac{d_{\text{v}}^3}{d_{\text{s}}^2} = \frac{N d_{\text{v}}^3}{N d_{\text{s}}^2} == \frac{\sum_{i=1}^{N} d_i^3}{\sum_{i=1}^{N} d_i^2} \\ = 6\frac{\sum_{i=1}^{N} \frac{\pi}{6} d_i^3}{\sum_{i=1}^{N} \pi d_i^2} = 6\frac{\sum_{i=1}^{N} V_i}{\sum_{i=1}^{N} A_i} \qquad \text{(m)}\end{aligned} \tag{A.25}$$

with d_{v} (m), the volume equivalent particle diameter and d_{s} (m), the surface equivalent particle diameter.

Thus, $d_{\text{eq}} = SMD = D[2, 3] = d_{32}$.

A.6 Geometric Mean and Geometric Standard Deviation

The geometric mean of a set of numbers $\{x_1, x_2, \ldots, x_N\}$ can be defined as:

$$\mu_{\text{g}} = \left(\prod_{i=1}^{N} x_i\right)^{\frac{1}{N}} = \sqrt[N]{x_1 x_2 \ldots x_N} \tag{A.26}$$

And the geometric standard deviation, more appropriately called geometric SD factor [3], can be calculated as:

$$\sigma_g = \exp\left(\sqrt{\frac{\sum_{i=1}^{N}\left(\ln\frac{x_i}{\mu_g}\right)^2}{N-1}}\right) \tag{A.27}$$

With $\{x_1, x_2, \ldots, x_N\}$ characterised by $(\mu_g \divideontimes \sigma_g)$

A.7 Characterisation of Poly(ethylene:hexamethylene/sebacate)

Figure A.1 includes the different repeating units of the poly(ethylene:hexamethylene/sebacate) block [4]. The copolymer had an estimated 50 mol% sebacic acid, a 25 mol% ethylene glycol and a 25 mol% hexamethylene glycol [5].

A random copolymerisation yields, on average, 1.75 ester bonds available per repeating unit, resulting in a M_{unit} value of:

$$\begin{aligned} M_{unit} &= \frac{\text{Molar mass of the average repeating unit}}{\text{Number of ester bonds per repeating unit}} \\ &= \frac{0.5M_{\text{sebacic acid}} + 0.25M_{\text{ethylene}} + 0.25M_{\text{hexamethylene}}}{1.75} \\ &= 146.481 \text{ Da} \end{aligned} \tag{A.28}$$

with $M_{\text{sebacic acid}}$, M_{ethylene} and $M_{\text{hexamethylene}}$, the molar masses of the different monomer repeating units.

Table A.1 includes the values of the polymer-specific parameters for poly(ethylene:hexamethylene/sebacate) block copolymer.

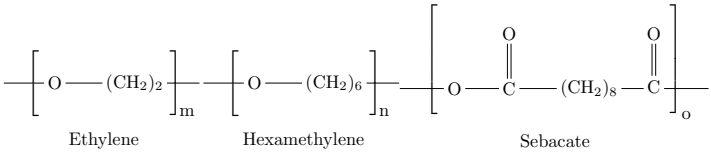

Fig. A.1 Structure of the repeating units of poly(ethylene:hexamethylene/sebacate) block copolymer, taken from [4]

Table A.1 Polymer-specific parameters for poly(ethylene:hexamethylene/sebacate) block copolymer. M_{unit} is the average molar mass associated to one ester bond, $\text{p}K_{\text{a}}$ is the negative base 10 logarithm of the sebacate segment acid dissociation constant at 25 °C and ρ_{pol} is the polymer density reported as midpoint of the typical density interval

Property	Value	Reference
M_{unit}	146.481 Da	See above
$\text{p}K_{\text{a}}$ at 25 °C	4.59	[6]
ρ_{pol}	1085 kg m^{-3}	[7]

Appendix B

This appendix contains information of all the analysed case studies in tabular format. Presented divided by ceramic filler and subdivided by polymeric matrix, each case study occupies a row containing the values of the four composite degradation constants (k_1, k_2', A_d and θ), in addition to several relevant characteristics. These characteristics are split into three different groups: polymer characteristics, such as polymer type and manufacturer; ceramic characteristics, such as ceramic type and manufacturer; and general sample characteristics, such as structure and morphology, fabrication method and degradation protocol. The TCP case studies can be found in Appendix B.1, followed by HA cases in Appendix B.2 and lastly, CC cases in Appendix B.3.

B.1 Tricalcium Phosphate Case Studies Modelling Results

TCP case studies with a poly(L-lactide) matrix are included in Appendix B.1.1, (Table B.1), followed by cases with a poly(D,L-lactide) homo- or copolymer matrix in Appendix B.1.2, (Table B.2), cases with poly(lactide-co-glycolide) matrix in Appendix B.1.3, (Table B.3), and lastly, cases with miscellaneous polymers matrixes in Appendix B.1.4, (Table B.4).

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B.1.1 Poly(L-lactide) Matrix

Table B.1 Results output by the TCP composites degradation model for cases with a poly(L-lactide) matrix. k_1 is the non-catalytic polymer degradation rate, k_2' is the autocatalytic polymer degradation rate, A_d is the ceramic dissolution rate and θ is the power ceramic dissolution law exponent. Abbreviations used to specify the tricalcium phosphate type can be found in Table 4.2. A dashed line between rows indicates that data displayed in those consecutive rows belong to the same researcher or research group. A solid line between rows indicates no known author relationship for the data

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)	Shimadzu Co., Ltd.; Kyoto, Japan (Lacty#5000)	1.4×10^{-11} (3.7×10^{-12})	2.1×10^{-11} (4.30×10^{-12})	β-TCP	Taihei Chemical Industrial Co., Ltd., Osaka, Japan	5.0×10^{-12}	2.0	Dense film: $10 \times 100\ mm^2 \times 4\ mm$	Polymer and ceramic dry-mixed + injection-moulded into final shape	In vitro: PBS (pH = 7.4) at 37°C, w/o shaking, w/o replacement	Kobayashi β-TCP [8]
Poly(L-lactide)	Purac Biomaterials B.V.; Gorinchem, The Netherlands	4.0×10^{-10} (1.1×10^{-11})	3.8×10^{-10} (1.0×10^{-11})	β-TCP	In-house production: granulated + sintered at 1000°C in air	1.0×10^{-12}	2.0	Dense cylinder: $\Phi = 6$ mm, L = 10 mm	Polymer and ceramic mixed in air at 60°C for 24 h + injection-moulded into final shape + γ-irradiation 25 kGy	In vivo: femoral implantation in rabbits following Kathagen protocol	Aunoble β-TCP [9]
Poly(L-lactide)	Purac Biomaterials B.V.; Gorinchem, The Netherlands	5.0×10^{-12}	1.3×10^{-11}	β-TCP	Degradable Solution AG, Switzerland	7.0×10^{-14}	2.0	Dense bar: $60 \times 9\ mm^2 \times 1.5\ mm$	Polymer and ceramic mixed in twin-screw extruder at 200°C+ milled to powder in liquid N_2 + compression-moulded into final shape + sterilised w ethylene oxide	In vitro: Simulated body fluid (SBF) (pH = 7.4) at 37°C, w/o shaking, w/o replacement	Adamus β-TCP [10]

(continued)

Table B.1 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)	Chengdu Organic Chemicals Co. Ltd, China	3.2×10^{-11}	3.8×10^{-11}	β-TCP	In-house production: wet chemistry route using $CaCO_3$ and H_3PO_4 + calcining at 950 °C for 2 h	3.0×10^{-14}	2.0	Porous (60%) cylinder: Φ = 5 mm, L = 10 mm	Polymer dissolved in chloroform + ceramic and porogen addition + composite precipitation in acetone and ethanol + compression moulding at 7 MPa and 25 °C + porogen leaching	In vitro: SBF (pH = 7.4) at 37 °C, w shaking, w replacement of 30 mL every 2 days, 100 mL/sample	Kang 07 S β-TCP [11]
Poly(L-lactide)	Chengdu Organic Chemicals Co. Ltd, China	2.2×10^{-11}	2.2×10^{-11}	β-TCP	In-house production: same as Kang 07 S	3.0×10^{-14}	2.0	Porous (60%) cylinder: Φ = 5 mm, L = 10 mm	Same as Kang 07 S	In vitro: SBF (pH = 7.4) at 37 °C, w constant buffer replacement at a flow rate of 0.02 mL/(mL min)	Kang 07 F β-TCP [11]
Poly(L-lactide)	Chengdu Organic Chemicals Co. Ltd, China	2.8×10^{-11}	3.4×10^{-11}	β-TCP	In-house production: same as Kang 07 S	3.0×10^{-14}	2.0	Porous (60%) cylinder: Φ = 5 mm, L = 10 mm	Same as Kang 07 S	In vitro: same as Kang 07 F	Kang 09 F β-TCP [12]
Poly(L-lactide)	Chengdu Organic Chemicals Co. Ltd, China	4.2×10^{-11}	5.8×10^{-11}	β-TCP	In-house production: same as Kang 09 F	3.0×10^{-14}	2.0	Porous (60%) cylinder: Φ = 5 mm, L = 10 mm	Same as Kang 07 S	In vitro: SBF (pH = 7.4) at 37 °C, w constant buffer replacement at a flow rate of 0.02 mL/(mL min) and dynamic loading at 0.6 Hz and 0.1 MPa	Kang 09 FL β-TCP [12]

B.1.2 Poly(D,L-lactide) Homo- and Copolymers Matrixes

Table B.2 Results output by the TCP composites degradation model for cases with a poly(D,L-lactide) or a poly(D,L-lactide) copolymer matrix. k_1 is the non-catalytic polymer degradation rate, k_2' is the autocatalytic polymer degradation rate, A_d is the ceramic dissolution rate and θ is the power ceramic dissolution law exponent. Abbreviations used to specify the tricalcium phosphate type can be found in Table 4.2. A dashed line between rows indicates that data displayed in those consecutive rows belong to the same researcher or research group. A solid line between rows indicates no known author relationship for the data

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide)(4:96)	Purac Biochem B.V.; Gorinchem, The Netherlands	5.0×10^{-11}	5.0×10^{-11}	β-TCP	Biomatlante SA; Vigneux de Bretagne, France	5×10^{-12}	2.0	Dense cylinder: $\Phi = 6$ mm; L = 8 mm	Polymer + ceramic fed to twin-screw extruder + extruded into cylindrical billet at 50 rpm and (225...235) °C for 2.5 min + self-reinforcing + machined into final shape + γ-radiation (25 kGy)	In vitro: PBS (pH = 7.4) at 37 °C, w fortnightly replacement	Daculsi Vit β-TCP [13]
Poly(D,L-lactide)(4:96)	Purac Biochem B.V.; Gorinchem, The Netherlands	7.0×10^{-11}	7.0×10^{-11}	β-TCP	Biomatlante SA; Vigneux de Bretagne, France	1.0×10^{-11}	2.0	Dense cylinder: $\Phi = 6$ mm; L = 8 mm	Same as Daculsi Vit β-TCP	In vivo: condylar implantation in adult New Zealand white rabbits	Daculsi Viv β-TCP [13]
Poly(D,L-lactide)(4:96)	Purac Biochem B.V.; Gorinchem, The Netherlands (Purasorb PLD9655)	4.8×10^{-11}	4.8×10^{-11}	β-TCP	CAM Implants B.V., Leiden, The Netherlands	3.0×10^{-11}	2.0	Dense cylinder: Pure Polymer: Φ = (2.6...2.7) mm; Composite: Φ = (2.9...3.0) mm; L = 30 mm	Polymer granules mixed w ceramic particles + melt-extrusion into cylindrincal billet + solid state die-drawing at 120 °C to final diameter + γ-radiation (25 kGy)	In vitro: PBS (pH = 7.4) at 37 °C, w/o shaking, w fortnightly replacement	Niemela LD β-TCP [14]

(continued)

Table B.2 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\,mol^{-1}\,s^{-1}$)	Type	Manufacturer	A_d ($mol\,m^{-2}\,s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide)(50:50)	In-house production: ring-opening polymerisation of D,L-lactide	7.6×10^{-10}	7.2×10^{-10}	aβ-TCP	In-house production: wet chemistry route	7.0×10^{-12}	2.0	Dense film: 4 × $8\,mm^2$ × 1 mm	Polymer dissolved in chloroform + ceramic dispersed in ethanol + addition of ceramic dispersion + press moulding at 85 °C and (10...15) MPa for 10 min	In vitro: PBS (pH = 7.4) at 37 °C, w shaking at 100 rpm, 100 $mL\,g^{-1}$	Zheng aβ-TCP [15]
Poly(D,L-lactide)(50:50)	Merck; Darmstadt, Germany	2.6×10^{-10}	4.2×10^{-10}	β-TCP	In-house production: as-received TCP (Merck; Darmstadt, Germany) granulated and calcined at 1200 °C for 2 h + crushing, milling and sieving	7.0×10^{-10}	2.0	Dense cylinder: Φ = 5 mm, L = 40 mm	Polymer melted + mixed w ceramic + sintered at 90 °C and (50...80)mPa for 30 min	In vitro: saline at 37 °C	Lin β-TCP [16]
Poly(D,L-lactide)(50:50)	Boehringer Ingelheim, Germany (Resomer R270)	1.0×10^{-10}	9.0×10^{-11}	β-TCP (Assumed)	In-house production: as-received TCP (Fluka AG, Switzerland) milled in ethanol	7.0×10^{-13}	2.0	Dense rod: 20 × $3\,mm^2$ × 2 mm	Polymer and ceramic mixing + injection moulding + γ-irradiation 25 kGy	In vivo: dorsal muscles implantation in rats	Heidemann β-TCP [17]

(continued)

Table B.2 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-co-D,L-lactide)(70:30)	Boehringer Ingelheim; Ingelheim am Rhein, Germany (Resomer LR70x family)	9.8×10^{-11}	9.6×10^{-11}	β-TCP	CAM Implants B.V., Leiden, The Netherlands	3.0×10^{-11}	2.0	Dense cylinder: Pure Polymer: $\Phi =$ (2.6...2.7) mm; Composite: $\Phi =$ (2.9...3.0) mm; L = 30 mm	Polymer granules mixed w ceramic particles + melt-extrusion into cylindrincal billet + solid state die-drawing at 120 °C to final diameter + γ-radiation (25 kGy)	In vitro: PBS (pH = 7.4) at 37 °C, w/o shaking, w fortnightly replacement	Niemela LDL β-TCP [18]
Poly(L-co-D,L-lactide)(70:30)	Boehringer Ingelheim; Ingelheim am Rhein, Germany (Resomer LR70x family)	5.4×10^{-11}	5.4×10^{-11}	α-TCP	Not reported	3.0×10^{-12}	2.0	Porous (42 %) cylinder: $\Phi = 10$ mm, L = 15 mm	Ceramic and polymer granules mixed + sintered at 145 °C to final shape + γ-radiation (25 kGy)	In vitro: Sörensen buffer (pH = 7.4) at 37 °C, 50 mL/sample, pH kept constant at 7.4	Ignatius P α-TCP [19]
Poly(L-co-D,L-lactide)(70:30)	Biovision; Ilmenau, Germany (PolyPIN 2.0) and Boehringer Ingelheim; Ingelheim am Rhein, Germany (Resomer LR70x family)	4.5×10^{-11} (3.0×10^{-11})	3.2×10^{-11} (2.0×10^{-11})	β-TCP	Not reported	3.0×10^{-11}	2.0	Dense cylinder: $\Phi = 2$ mm, L = 35 mm	Ceramic granules added to heated polymer + injection-moulding at 210 °C + γ-radiation (28 kGy)	In vitro: Sörensen buffer (pH = 7.4) at 37 °C, 200 $mL\ g^{-1}$, pH kept constant at 7.4	Ignatius D β-TCP [19]

(continued)

Table B.2 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\,mol^{-1}\,s^{-1}$)	Type	Manufacturer	A_d ($mol\,m^{-2}\,s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-co-D,L-lactide)(70:30)	Purac Biochem B.V.; Gorinchem, The Netherlands (Purasorb PLDL7028)	1.9×10^{-11}	1.8×10^{-11}	β-TCP	Plasma Biotal Ltd.; Tideswell, United Kingdom	5.0×10^{-11}	2.0	Porous disk: Φ= 15 mm, t = 3 mm	Polymer dissolved in dioxane at 3 wt % + ceramic addition + stirring of the mixture + freeze drying	In vitro: PBS (pH = 7.4) at 37 °C, 10 mL/sample	Haaparanta 3w β-TCP [20]
Poly(L-co-D,L-lactide)(70:30)	Purac Biochem B.V.; Gorinchem, The Netherlands (Purasorb PLDL7028)	2.7×10^{-11}	2.5×10^{-11}	β-TCP	Plasma Biotal Ltd.; Tideswell, United Kingdom	5.0×10^{-11}	2.0	Porous disk: Φ= 15 mm, t = 3 mm	Polymer dissolved in dioxane at 2 wt % + ceramic addition + stirring of the mixture + freeze drying	In vitro: PBS (pH = 7.4) at 37 °C, 10 mL/sample	Haaparanta 2w β-TCP [20]

B.1.3 Poly-lactide-co-glycolide Matrix

Table B.3 Results output by the TCP composites degradation model for cases with a poly(lactide-co-glycolide) matrix. k_1 is the non-catalytic polymer degradation rate, k_2' is the autocatalytic polymer degradation rate, A_d is the ceramic dissolution rate and θ is the power ceramic dissolution law exponent. Abbreviations used to specify the tricalcium phosphate type can be found in Table 4.2. A dashed line between rows indicates that data displayed in those consecutive rows belong to the same researcher or research group. A solid line between rows indicates no known author relationship for the data

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide-co-glycolide) (70:30)	In-house production: ring-opening polymerisation of L-lactide and glycolide w stannous octoate	4.2×10^{-10}	2.8×10^{-10}	β-TCP (Assumed)	Forth Reagent Factory; Shanghai, China	3.0×10^{-11}	2.0	Porous (90 %) slab: 6 × 6 mm^2, L = 13 mm	Polymer dissolved in dioxane + ceramic addition + mixing + low-temperature deposition of the slurry using a computer-driven nozzle + freeze-drying	In vitro: distilled water w NaN_3 at 37 °C, w/o shaking, w/o replacement, 50 $mL\ g^{-1}$	Yang F. β-TCP [21]
Poly(L-lactide-co-glycolide) (70:30)	Changchun Institute of Applied Chemistry; Chinese Academy of Sciences, China	3.2×10^{-10}	3.2×10^{-10}	β-TCP	National Engineering Research Centre for Biomaterials; Sichuan University, China	3.0×10^{-13}	2.0	Porous cylinder: Φ = 6 mm, L = 12 mm	Polymer dissolved in chloroform + ceramic and porogen addition + freezing + solvent extraction w ethanol at −18 °C + porogen leached w water	In vitro: PBS (pH = 7.4) at 37 °C, w shaking at 50 rpm, weekly replacement, 4 mL/sample	Yang Y. S β-TCP [21]

(continued)

Table B.3 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\,mol^{-1}\,s^{-1}$)	Type	Manufacturer	A_d ($mol\,m^{-2}\,s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide-co-glycolide) (70:30)	Changchun Institute of Applied Chemistry; Chinese Academy of Sciences, China	3.5×10^{-10}	3.5×10^{-10}	β-TCP	National Engineering Research Centre for Biomaterials; Sichuan University, China	3.0×10^{-13}	2.0	Porous cylinder: $\Phi = 6$ mm, $L = 12$ mm	Polymer dissolved in chloroform + ceramic and porogen addition + freezing + solvent extraction w ethanol at −18 °C + porogen leached w water	In vitro: PBS (pH = 7.4) at 37 °C, w 8 $h\,d^{-1}$ of cyclic loading at 1 Hz and (0.5...0.6) mm displacement and w 16 $h\,d^{-1}$ of shaking at 50 rpm, weekly buffer replacement, 4 mL/sample	Yang Y. D β-TCP [22]
Poly(L-lactide-co-glycolide) (70.7:29.3)	In-house production: polymerisation using preset microwave power of L-lactide and glycolide w stannous octoate	2.0×10^{-9} (1.5×10^{-9})	2.2×10^{-9} (1.5×10^{-9})	β-TCP	In-house production: wet chemistry route using $Ca(NO_3)\cdot 4H_2O$ and $(NH_4)_2HPO_4$ + aging, filtering and drying + calcining at 800 °C for 2 h	7.0×10^{-12}	2.0	Semi-dense cylinder: $\Phi = 13$ mm, $L = 12$ mm	Ceramic added to initiator and monomers solution + polymerisation using microwave power	In vitro: SBF (pH = 7.4) at 37 °C, w/o shaking, w/o replacement, 15 mL/sample	Jin β-TCP [23]
Poly(D,L-lactide-co-glycolide) (44.6:55.4)	Mitsui Chemicals; Tokyo, Japan: polymerisation of D,L-lactide and glycolide using stannous octoate	3.0×10^{-9}	3.0×10^{-9}	β-TCP (Assumed)	Wako Pure Chemical Industries; Tokyo, Japan	5.0×10^{-11}	2.0	Dense film: 15 × 15 mm^2 × 0.5 mm	Polymer dissolved in dioxane + ceramic addition + freeze-drying of the solvent cast solution + compression moulding at 60 °C and 4.9 MPa	In vitro: PBS (pH = 7.4) at 37 °C, w/o shaking, weekly replacement, 40 mL/sample	Ara β-TCP [24]

(continued)

Table B.3 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA (5050 DLG 5E)	2.4×10^{-9}	2.4×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + grinding + calcining at 1400 °C for 4 h + quenching + grinding and sieving through a 100 μm mesh + ball-milling for 1 h in acetone	1.0×10^{-12}	2.0	Dense disk: $\Phi = 3.5$ mm, t = 1 mm	Polymer dissolved in acetone + ceramic addition + solvent casting + injection-moulding at 135 °C and 0.5 MPa into cylinders + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Bennett nC α-TCP [25]
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA (5050 DLG 5E)	1.4×10^{-9}	1.4×10^{-9}	α-TCP	In-house production: wet chemistry route. Same as Bennett nC α-TCP	5.0×10^{-13}	2.0	Dense disk: $\Phi = 3.5$ mm, t = 1 mm	Same as Bennett nC α-TCP	In vitro: PBS (0.01 M, pH = 7.4) w 50 % v/v of D_2O at 37 °C, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Bennett nC D_2 50 α-TCP [25]
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA (5050 DLG 5E)	5.9×10^{-10}	5.9×10^{-10}	α-TCP	In-house production: wet chemistry route. Same as Bennett nC α-TCP	3.0×10^{-13}	2.0	Dense disk: $\Phi = 3.5$ mm, t = 1 mm	Same as Bennett nC α-TCP	In vitro: PBS (0.01 M, pH = 7.4) w 100 % v/v of D_2O at 37 °C, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Bennett nC D_2 100 α-TCP [25]

(continued)

Table B.3 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA (5050 DLG 5E)	2.4×10^{-9}	2.4×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + grinding into powder + calcining at 1400 °C for 4 h + grinding and sieving through a 38 μm mesh	3.0×10^{-12}	2.0	Dense disk: $\Phi = 3.5$ mm, t = 1 mm	Polymer dissolved in acetone + ceramic addition + solvent casting + injection-moulding at 135 °C and 0.5 MPa into cylinders + cut into final shape	In vitro: same as Bennett mC α-TCP	Bennett iC α-TCP [25]
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA (5050 DLG 5E)	2.4×10^{-9}	2.4×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + grinding into powder + calcining at 1400 °C for 4 h + quenching + grinding and sieving through a 100 μm mesh	1.0×10^{-10}	2.0	Dense disk: $\Phi = 3.5$ mm, t = 1 mm	Polymer dissolved in acetone + ceramic addition + solvent casting + injection-moulding at 135 °C and 0.5 MPa into cylinders + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Bennett mC α-TCP [25]
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA (5050 DLG 5E)	1.4×10^{-9}	1.4×10^{-9}	α-TCP	In-house production: same as Bennett mC	5.0×10^{-11}	2.0	Dense disk: $\Phi = 3.5$ mm, t = 1 mm	Same as Bennett mC α-TCP	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C w 50 % v/v of D_2O, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Bennett mC D_2 50 α-TCP [25]

(continued)

Table B.3 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA (5050 DLG 5E)	5.9×10^{-10}	5.9×10^{-10}	α-TCP	In-house production: same as Bennett mC	1.0×10^{-11}	2.0	Dense disk: $\Phi = 3.5$ mm, t = 1 mm	Same as Bennett mC α-TCP	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C w 100 % v/v of D_2O, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Bennett mC D_2 100 α-TCP [25]
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.0×10^{-9}	1.8×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + calcining at 1400 °C for 4 h + quenching + grinding and sieving to 75 µm	3.0×10^{-13}	2.0	Dense disk: $\Phi = 6$ mm, t = 2 mm	Ceramic dispersed in polymer using a co-rotating twin screw extruder + cut into pellets + injection-moulded to cylinders at 130 °C and 0.5 MPa + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement	Ege α-TCP [26, 27]
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA	2.8×10^{-9}	2.2×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + calcining at 1300 °C for 4 h + quenching + grinding and sieving to 75 µm + attritor-milled for 4 h in acetone	9.0×10^{-13}	2.0	Dense film: 8 × 8 mm^2 × 1 mm	Polymer addition to milled ceramic + solvent casting + hot-pressed at 150 °C into sheets + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Yang Z. 5050 nC α-TCP [28, 29]

(continued)

Table B.3 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA	2.8×10^{-9}	2.2×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + calcining at 1300 °C for 4 h + quenching + grinding and sieving to 75 µm	3.0×10^{-11}	2.0	Dense film: 8 × 8 mm^2 × 1 mm	Ceramic and polymer mixed + solvent casting + hot-pressed at 150 °C into sheets + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Yang Z. 5050 mC α-TCP [28, 29]
Poly(D,L-lactide-co-glycolide) (50:50)	Alkermes Medisorb; Cincinnati, USA	4.5×10^{-9}	2.9×10^{-9}	α-TCP	In-house production: wet chemistry route + drying for 2 d + grinding into powder + calcining at 1200 °C for 4 h + ball-milling for 11 h + sieving through a 75 µm mesh	3.0×10^{-11}	2.0	Dense disk: Φ = 15 mm, t = 2.3 mm	Polymer and ceramic kneading at 200 °C+ hot-pressed at 200 °C into final shape	In vitro: PBS (0.03 M, pH = 7.4) at 37 °C, w periodic agitation, w/o replacement, 30 mL/sample	Mellon α-TCP [30]
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Alabama, USA	2.1×10^{-9}	2.1×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + ball-milling for 4 h + sieving using a 75 µm mesh + calcining at 1400 °C for 4 h + attritor-milled in acetone for 4 h	5.0×10^{-12}	2.0	Dense disk: Φ = 8 mm, t = 900 µm	Polymer addition to milled ceramic + drying + hot-pressed at 90 °C into sheets + cut w a circular punch into final shape	In vitro: distilled-deionised water at 37 °C, w/o shaking, w/o replacement, 40 mL/sample	Barrett α-TCP [31, 32]

(continued)

Table B.3 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristicsSample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\,mol^{-1}\,s^{-1}$)	Type	Manufacturer	A_d ($mol\,m^{-2}\,s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	3.0×10^{-9}	2.4×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + grinding and sieving using a 75 µm mesh + calcining at 1200 °C for 4 h + grinding and sieving to 75 µm	5.0×10^{-10}	2.0	Dense disk: Φ = 10 mm, t = 1.5 mm	Polymer and ceramic kneading at 200 °C + hot-pressed at 200 °C into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w periodic agitation, w/o replacement, 166 $mL\,g^{-1}$	Ehrenfried α-TCP [33]
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.0×10^{-9}	1.8×10^{-9}	β-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + calcining at 1100 °C for 4 h + grinding and sieving to 75 µm	7.0×10^{-13}	2.0	Dense disk: Φ = 6 mm, t = 2 mm	Ceramic dispersed in polymer using a co-rotating twin screw extruder + cut into pellets + injection-moulded to cylinders at 130 °C and 0.5 MPa + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement	Ege β-TCP [26]
Poly(D,L-lactide-co-glycolide) (50:50)	Alkermes Medisorb; Cincinnati, USA	4.5×10^{-9}	2.9×10^{-9}	β-TCP	In-house production: wet chemistry route + drying for 2 d + grinding into powder + calcining at 1000 °C for 4 h + ball-milling for 11 h + sieving through a 75 µm mesh	9.0×10^{-12}	2.0	Dense disk: Φ = 15 mm, t = 2.3 mm	Polymer and ceramic kneading at 200 °C+ hot-pressed at 200 °C into final shape	In vitro: PBS (0.03 M, pH = 7.4) at 37 °C, w periodic agitation, w/o replacement, 30 mL/sample	Mellon β-TCP [30]

(continued)

Table B.3 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (75:25)	Lakeshore Biomaterials; Birmingham, Alabama, USA	1.6×10^{-9}	1.1×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + calcining at 1300 °C for 4 h + quenching + grinding and sieving to 75 µm + attritor-milled for 4 h in acetone	7.0×10^{-13}	2.0	Dense film: 8 × 8 mm^2 × 1 mm	Polymer addition to milled ceramic + solvent casting + hot-pressed at 150 °C into sheets + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Yang Z. 7525 nC α-TCP [29]
Poly(D,L-lactide-co-glycolide) (75:25)	Lakeshore Biomaterials; Birmingham, Alabama, USA	1.6×10^{-9}	1.1×10^{-9}	α-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging for 1 d and drying + calcining at 1300 °C for 4 h + quenching + grinding and sieving to 75 µm	3.0×10^{-11}	2.0	Dense film: 8 × 8 mm^2 × 1 mm	Ceramic and polymer mixed + solvent casting + hot-pressed at 150 °C into sheets + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement, 166 $mL\ g^{-1}$	Yang Z. 7525 mC α-TCP [29]

B.1.4 Miscellaneous Polymers Matrixes

Table B.4 Results output by the TCP composites degradation model for cases with a miscellaneous polymer matrix. k_1 is the non-catalytic polymer degradation rate, k_2' is the autocatalytic polymer degradation rate, A_d is the ceramic dissolution rate and θ is the power ceramic dissolution law exponent. Abbreviations used to specify the tricalcium phosphate type can be found in Table 4.2. A dashed line between rows indicates that data displayed in those consecutive rows belong to the same researcher or research group. A solid line between rows indicates no known author relationship for the data

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide- co-ε-caprolactone)(70:30)	Purac Biomaterials, The Netherlands (Purasorb PLC7015)	7.4×10^{-10}	3.4×10^{-10}	β-TCP	Plasma Biotal Ltd., United Kingdom	3.0×10^{-12}	2.0	Dense cylinder: $\Phi = 2.5$ mm, L = 2.5 mm	Polymer and ceramic fed to a co-rotating twin screw-extruder and processed at (25...130) °C into rod shape billets + cut to final shape + γ-irradiation (25 kGy)	In vitro: Sörensen buffer (pH = 7.4) at 37 °C, w shaking, w replacement every 2 days, 66 $mL\ g^{-1}$	Ahola 13 β-TCP [34]
Poly(L-lactide- co-ε-caprolactone)(70:30)	Purac Biomaterials, The Netherlands (Purasorb PLC7015)	5.8×10^{-10} (4.0×10^{-10})	3.8×10^{-10} (2.6×10^{-10})	β-TCP	Plasma Biotal Ltd., United Kingdom	3.0×10^{-12}	2.0	Dense cylinder: $\Phi = 2.5$ mm, L = 2.5 mm	Same as Ahola 13	In vitro: Sörensen buffer (pH = 7.4) at 37 °C, w shaking, w fortnightly replacement, 66 $mL\ g^{-1}$	Ahola 12 β-TCP [35]
Poly(L-lactide-co-ε-caprolactone)(92:8)	In-house production: bulk copolymerisation of L-lactide and ε-caprolac-tone using stannous 2-ethylhexanoate	1.8×10^{-10}	1.4×10^{-10}	β-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging, drying at 120 °C, pelletised in 125 μm + calcining at 800 °C	3.0×10^{-12}	2.0	Dense film: 5 × 20 mm^2 × 200 μm	Polymer and ceramic kneaded in a milled at 180 °C and 30 rpm for 10 min + cooled in air for 15 min + hot-pressed at 180 °C	In vitro: physiological saline (pH = 7.4) at 37 °C, w/o shaking, w/o replacement	Kikuchi PLCL β-TCP [36]

(continued)

Table B.4 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide) /poly(ethylene: hexamethy-lene/sebacate) block copoly-mer (75.3:24.7)	In-house production: ring-opening polymerisation of L-lactide in the presence of poly(ethylene: hexamethy-lene/sebacate) (60:40 in weight) using stannous octoate	2.3×10^{-10}	2.8×10^{-10}	β-TCP	Taihei Chemical; Tokyo, Japan	5.0×10^{-12}	2.0	Dense film: 20 × 30 mm^2 × 100 μm	Blending polymer and ceramic in a plastomill mixer at 180 °C and 50 rpm for 10 min + compression moulding at 180 °C and 19.6 MPa	In vitro: PBS (pH = 7.4) at 37 °C, w/o shaking, weekly replacement, 50 mL/sample	Imai L100 β-TCP [37]
Poly(L-lactide) /poly(ethylene: hexamethy-lene/sebacate) block copoly-mer (75.3:24.7)	In-house production: same as Imai L100	4.8×10^{-10}	4.9×10^{-10}	β-TCP	Taihei Chemical; Tokyo, Japan	1.0×10^{-11}	2.0	Dense film: 20 × 30 mm^2 × 250 μm	Same as Imai L100	In vitro: same as Imai L100	Imai L250 β-TCP [37]
Poly(L-lactide) /poly(ethylene: hexamethy-lene/sebacate) block copoly-mer (75.3:24.7)	In-house production: ring-opening polymerisation of L-lactide in the presence of poly(ethylene: hexamethy-lene/sebacate) (60:40 in weight) using stannous octoate	1.0×10^{-10}	1.2×10^{-10}	β-TCP	In-house production: wet chemistry route + calcining at 800 °C	5.0×10^{-14}	2.0	Dense film: 5 × 20 mm^2 × 3 mm	Blending polymer and ceramic in mill mixer at 180 °C and 20 rpm for 10 min + cooled in air to room temperature + compression moulding at 180 °C and 30 MPa + cutting to final shape	In vitro: physiological saline (pH = 7.4) at 37 °C, w/o shaking, 100 mL/sample	Kikuchi T800 β-TCP [38]
Poly(L-lactide) /poly(ethylene: hexamethy-lene/sebacate) block copoly-mer (75.3:24.7)	In-house production: same as Kikuchi T800	5.0×10^{-11}	1.4×10^{-10}	β-TCP	In-house production: wet chemistry route + calcining at 1100 °C	5.0×10^{-13}	2.0	Dense film: 5 × 20 mm^2 × 3 mm	Same as Kikuchi T800	In vitro: same as Kikuchi T800	Kikuchi T1100 β-TCP [38]

(continued)

Table B.4 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)/poly(ethylene: hexamethylene/sebacate) block copolymer (98.3:1.7)	In-house production: ring-opening polymerisation of L-lactide in the presence of poly(ethylene: hexamethylene/sebacate) (97:3 in weight) using stannous octoate	6.0×10^{-11}	2.2×10^{-11}	β-TCP	Taihei Chemical; Tokyo, Japan	3.0×10^{-12}	2.0	Dense film: 20 × 30 mm^2 × 100 μm	Blending polymer and ceramic in a plastomill mixer at 180 °C and 50 rpm for 10 min + compression moulding at 180 °C and 19.6 MPa	In vitro: PBS (pH = 7.4) at 37 °C, w/o shaking, weekly replacement, 50 mL/sample	Imai H100 β-TCP [4]
Poly(L-lactide)/poly(ethylene: hexamethylene/sebacate) block copolymer (98.3:1.7)	In-house production: same as Imai H100	6.8×10^{-11}	7.0×10^{-11}	β-TCP	Taihei Chemical; Tokyo, Japan	5.0×10^{-12}	2.0	Dense film: 20 × 30 mm^2 × 250 μm	Same as Imai H100	In vitro: same as Imai H100	Imai H250 β-TCP [4]
Poly(L-lactide-co-glycolide-co-ε-caprolactone)(75:11:14)	In-house production: bulk copolymerisation of L-lactide, glycolide and ε-caprolactone using stannous 2-ethylhexanoate	2.2×10^{-10}	2.8×10^{-10}	β-TCP	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aging, drying at 120 °C, pelletised in 125 μm + calcining at 800 °C	5.0×10^{-12}	2.0	Dense film: 5 × 20 mm^2 × 200 μm	Polymer and ceramic kneaded in a milled at 180 °C and 30 rpm for 10 min + cooled in air for 15 min + hot-pressed at 180 °C	In vitro: physiological saline (pH = 7.4) at 37 °C, w/o shaking, w/o replacement	Kikuchi PLGC β-TCP [36]

B.2 Hydroxyapatite Case Studies Modelling Results

HA case studies with a poly(L-lactide) matrix are included in Appendix B.2.1, (Table B.5), followed by cases with a poly(D,L-lactide) matrix in Appendix B.2.2, (Table B.6), cases with poly(lactide-co-glycolide) matrix in Appendix B.2.3, (Table B.7) and lastly, cases with miscellaneous polymers matrixes in Appendix B.2.4, (Table B.8).

B.2.1 Poly(L-lactide) Matrix

Table B.5 Results output by the HA composites degradation model for cases with a poly(L-lactide) matrix. k_1 is the non-catalytic polymer degradation rate, k_2' is the autocatalytic polymer degradation rate, A_d is the ceramic dissolution rate and θ is the power ceramic dissolution law exponent. Abbreviations used to specify the hydroxyapatite type can be found in Table 5.2. A dashed line between rows indicates that data displayed in those consecutive rows belong to the same researcher or research group. A solid line between rows indicates no known author relationship for the data

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)	In-house production: ring-opening polymerisation of L-lactide at 140 °C	4.6×10^{-10}	2.0×10^{-10}	hHA	In-house production: wet chemistry route using $Ca(NO_3)_2$ and NH_4PO_3 + sintered + milled	5.0×10^{-14}	2.0	Dense cylinder: $\Phi = 5$ mm, L = 10 mm	Polymer and ceramic mixed at 160 °C+ compression moulded	In vitro: PBS (pH = 7.4) at 37 °C, w shaking at 100 rpm	Huang hHA [39]
Poly(L-lactide)	In-house production: ring-opening polymerisation of L-lactide using stannous octoate	8.0×10^{-11} (1.2×10^{-11})	8.0×10^{-11} (1.2×10^{-11})	lHA	In-house production: wet chemistry route w $Ca(OH)_2$ and H_3PO_4	2.0×10^{-14}	2.0	Dense bar: 30 × 5 mm^2 × 2 mm	Polymer and ceramic blended at 190 °C for 5 min in the rheometer + hot press moulded at 190 °C and 15 MPa + annealed at 115 °C for 1 h	In vivo: intramuscular implantation in New Zealand white rabbits	Wang lHA [40]
Poly(L-lactide)	In-house production: same as Wang lHA	8.0×10^{-11} (1.2×10^{-11})	8.0×10^{-11} (1.2×10^{-11})	gP-lHA	In-house production: same as Wang nHA + PLLA polymerised on the nHA	5.0×10^{-15}	2.0	Dense bar: 30 × 5 mm^2 × 2 mm	Same as Wang nHA	In vivo: same as Wang nHA	Wang gP-lHA [40]
Poly(L-lactide)	Jamplast; Ellisville, Missouri, USA	3.5×10^{-10} (1.2×10^{-10})	2.3×10^{-10} (8.0×10^{-11})	lCCDHA	In-house production: wet chemistry route using Tris-base SBF	1.0×10^{-15}	2.0	Porous fibrous mat (t: NR)	Polymer dissolved in chloroform + ceramic added + ultrasonicated for 1 h + electrospinning	In vitro: standard conditions (PBS at 37 °C, 25 mL/sample)	Zhou lCCDHA [41]

(continued)

Table B.5 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)	Purac Biochem B.V.; Gorinchem, The Netherlands: polymerised after mixing HA w L-lactide	3.0×10^{-10}	2.4×10^{-10}	hHA	Merck; Darmstadt, Germany: as-received HA + sintered in N_2 + crushed and milled	1.0×10^{-12}	2.0	Dense film: 15 × $10\,mm^2$ × 3 mm	Polymerised in an ampule w ceramic + machined to desired dimensions	In vitro: PBS at 37 °C, weekly replacement, 40 mL/sample	Verheyen 92 Vit hHA [42]
Poly(L-lactide)	Purac Biochem B.V.; Gorinchem, The Netherlands: see Verheyen 92 Vit	1.3×10^{-10}	2.6×10^{-10}	hHA	Merck; Darmstadt, Germany: see Verheyen 92 Vit	5.0×10^{-12}	2.0	Dense film: 15 × $10\,mm^2$ × 3 mm	Same as Verheyen 92 Vit	In vitro: PBS at 37 °C, weekly replacement, w shaking, 10 mL/sample	Verheyen 93 hHA [43]
Poly(L-lactide)	Purac Biochem B.V.; Gorinchem, The Netherlands: see Verheyen 92 Vit	3.0×10^{-10}	2.0×10^{-10}	hHA	Merck; Darmstadt, Germany: see Verheyen 92 Vit	3.0×10^{-12}	2.0	Dense film: 15 × $10\,mm^2$ × 3 mm	Same as Verheyen 92 Vit	In vivo: subcutaneous implantation in mature female goats	Verheyen 92 Viv hHA [42]
Poly(L-lactide)	Biomer, Germany (L9000)	1.6×10^{-10}	1.0×10^{-10}	bnHA	Aldrich Chemistry, USA	1.0×10^{-14}	2.0	Porous (90 %) disk: $\Phi = 15$ mm, t: NR	Polymer dissolved in dioxane + blended w ceramic + freeze drying	In vitro: standard conditions (PBS at 37 °C, w/o shaking, 10 mL/sample)	Diaz PP/C bnHA [44]
Poly(L-lactide)	Biomer, Germany (L9000)	2.0×10^{-10} (1.6×10^{-10})	1.2×10^{-10} (1.0×10^{-10})	bnHA	Aldrich Chemistry, USA	1.0×10^{-14}	2.0	Porous (90 %) disk: $\Phi = 15$ mm, t: NR	Same as Diaz PP/C	In vitro: same as Diaz PP/C	Diaz C bnHA [44]

(continued)

Table B.5 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)	In-house production: ring-opening polymerisation of L-lactide using tin octoate and lauryl alcohol	1.2×10^{-10} (2.6×10^{-11})	6.0×10^{-11} (1.3×10^{-11})	pCHA	In-house production: wet chemistry route w $CaHPO_4$ and $CaCO_3$ in aqueous solution at 90 °C+ filtered and dried + milled and sieved	3.0×10^{-13}	2.0	Dense cylinder: $\Phi = 3.2$ mm, L = 30 mm	Ceramic and polymer mixed + extruded + compression moulded at 103 °C+ lathing	In vitro: standard conditions (PBS (pH = 7.4) at 37 °C, w/o shaking)	Shikinami 99 pCHA [45]
Poly(L-lactide)	In-house production: see Shikinami 99	1.2×10^{-10} (7.5×10^{-11})	3.0×10^{-11} (1.7×10^{-11})	pCHA	In-house production: see Shikinami 99	3.0×10^{-13}	2.0	Dense cylinder: $\Phi = 3.2$ mm, L = 30 mm	Same as Shikinami 99	In vivo: medullary cavity implantation in Japanese white rabbits	Furukawa Med pCHA [46]
Poly(L-lactide)	In-house production: same as Shikinami 99	1.2×10^{-10}	3.0×10^{-11}	pCHA	In-house production: same as Shikinami 99	3.0×10^{-13}	2.0	Dense cylinder: $\Phi = 3.2$ mm, L = 50 mm	Same as Shikinami 99	In vivo: subcutis implantation in Japanese white rabbits	Furukawa Sub pCHA [46]
Poly(L-lactide)	In-house production: same as Shikinami 99	1.2×10^{-10}	3.0×10^{-11}	pCHA	In-house production: same as Shikinami 99	3.0×10^{-13}	2.0	Dense cylinder: $\Phi = 3.2$ mm, L = 30 mm	Same as Shikinami 99	In vivo: intercondylar implantation in male Japanese white rabbits	Ishii pCHA [47]
Poly(L-lactide)	In-house production: same as Shikinami 99	8.0×10^{-11}	4.0×10^{-11}	pCHA	In-house production: same as Shikinami 99	5.0×10^{-13}	2.0	Dense screw: $\Phi = 1.6$ mm, L = 8 mm	Same as Shikinami 99	In vitro: standard conditions	Shikinami 01 pCHA [48]

(continued)

Table B.5 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)	In-house production: see Shikinami 99	1.2×10^{-10} (7.5×10^{-11})	3.0×10^{-11} (1.7×10^{-11})	hHA	In-house production: pCHA production (see Shikinami 99) + calcined at 900 °C	5.0×10^{-13}	2.0	Dense cylinder: $\Phi = 3.2$ mm, L = 30 mm	Same as Shikinami 99	Same as Furukawa Med CHA	Furukawa Med hHA [46]
Poly(L-lactide)	In-house production: same as Shikinami 99	8.0×10^{-11}	5.0×10^{-11}	hHA	In-house production: same as Furukawa Med HA	5.0×10^{-13}	2.0	Dense cylinder: $\Phi = 3.2$ mm, L = 50 mm	Same as Shikinami 99	In vivo: same as Furukawa Sub CHA	Furukawa Sub hHA [46]
Poly(L-lactide)	In-house production: same as Shikinami 99	8.0×10^{-11}	5.0×10^{-11}	hHA	In-house production: same as Furukawa Med HA	1.1×10^{-12}	2.0	Dense cylinder: $\Phi = 3.2$ mm, L = 30 mm	Same as Shikinami 99	In vivo: same as Ishii CHA	Ishii hHA [47]
Poly(L-lactide)	In-house production: same as Shikinami 99	1.2×10^{-10}	2.0×10^{-11}	hHA	In-house production: same as Furukawa Med HA	1.0×10^{-13}	2.0	Dense miniplate: t = 1 mm	Same as Shikinami 99	In vitro: standard conditions	Shikinami 01 hHA [48]
Poly(L-lactide)	Shang Dong Institute (Dept. of Med. Pol.), China	6.0×10^{-12}	3.0×10^{-12}	lHA	In-house production: wet chemistry route using $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ w ultrasonic stirring	3.0×10^{-15}	2.0	Dense film: 20 × 20 mm^2 × 0.05 mm	Polymer-ceramic mixture solvent casting	In vitro: PBS (pH = 7.4) at 37 °C, w/o shaking, 15 mL/sample	Deng SC lHA [49]
Poly(L-lactide)	Shang Dong Institute (Dept. of Med. Pol.), China	1.0×10^{-11}	1.1×10^{-11}	lHA	In-house production: same as Deng SC	9.0×10^{-15}	2.0	Porous fibrous mat: 20 × 20 mm^2 × 0.05 mm	Polymer-ceramic mixture electrospinning	In vitro: same as Deng SC	Deng ES lHA [49]
Poly(L-lactide)	Shang Dong Institute (Dept. of Med. Pol.), China	8.0×10^{-12}	1.9×10^{-11}	lHA	In-house production: same as Deng SC	9.0×10^{-15}	2.0	Porous fibrous mat: 20 × 20 mm^2 × 0.05 mm	Polymer-ceramic mixture electrospinning	In vitro: same as Deng SC	Sui lHA [50]

(continued)

Table B.5 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)	In-house production: ring-opening polymerisation of L-lactide	5.2×10^{-10}	4.8×10^{-10}	gP-lHA	In-house production: wet chemistry route + grafting with PLLA	2.0×10^{-14}	2.0	Porous fibrous mat: 20 × 20 mm^2 × 0.2 mm	Polymer dissolved in chloroform + ceramic added + electrospinning	In vitro: PBS (pH = 7.4) at 37 °C, w shaking at 90 rpm, 40 mL/sample)	Xu PP/C gP-lHA [51]
Poly(L-lactide)	In-house production: same as Xu PP/C	1.1×10^{-9} (5.2×10^{-10})	8.0×10^{-10} (4.8×10^{-10})	gP-lHA	In-house production: same as Xu PP/C	4.0×10^{-15}	2.0	Porous fibrous mat: 20 × 20 mm^2 × 0.2 mm	Same as Xu PP/C	In vitro: same as Xu PP/C	Xu C gP-lHA [51]

B.2.2 Poly(D,L-lactide) Matrix

Table B.6 Results output by the HA composites degradation model for cases with a poly(D,L-lactide) matrix. k_1 is the non-catalytic polymer degradation rate, k_2' is the autocatalytic polymer degradation rate, A_d is the ceramic dissolution rate and θ is the power ceramic dissolution law exponent. Abbreviations used to specify the hydroxyapatite type can be found in Table 5.2. A dashed line between rows indicates that data displayed in those consecutive rows belong to the same researcher or research group. A solid line between rows indicates no known author relationship for the data

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\,mol^{-1}\,s^{-1}$)	Type	Manufacturer	A_d ($mol\,m^{-2}\,s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide)(4:96)	Nature Works LLC (#4042D)	1.7×10^{-10} (3.5×10^{-11})	1.7×10^{-10} (3.4×10^{-11})	lCHA	In-house production: wet chemistry route using bovine bone derived precursors	5.0×10^{-15}	2.0	Dense slab: 10 × 10 mm^2 × 4 mm	Ceramic and polymer mixed at 170 °C for 10 min + hot pressed at 180 °C and 14 MPa for 5 min	In vitro: SBF (pH = 7.4) at 37 °C, weekly replacement, 11.6 mL/sample	Rakmae 13 lCHA [52]
Poly(D,L-lactide)(4:96)	Nature Works LLC (#4042D)	1.7×10^{-10} (3.5×10^{-11})	1.7×10^{-10} (3.4×10^{-11})	pCHA	In-house production: above-mentioned lCHA heat treated at 800 °C for 3 h	1.1×10^{-13}	2.0	Dense slab: 10 × 10 mm^2 × 4 mm	Same as Rakmae 13 lCHA	In vitro: same as Rakmae 13 lCHA	Rakmae 13 pCHA [52]
Poly(D,L-lactide)(4:96)	Nature Works LLC (#4042D)	1.7×10^{-10} (3.5×10^{-11})	1.7×10^{-10} (3.4×10^{-11})	hHA	In-house production: above-mentioned lCHA heat treated at 1100 °C for 3 h	7.0×10^{-14}	2.0	Dense slab: 10 × 10 mm^2 × 4 mm	Same as Rakmae 13 lCHA	In vitro: same as Rakmae 13 lCHA	Rakmae 13 hHA [52]

(continued)

Table B.6 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\,mol^{-1}\,s^{-1}$)	Type	Manufacturer	A_d ($mol\,m^{-2}\,s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide)(4:96)	Nature Works LLC (#4042D)	7.0×10^{-11}	1.6×10^{-10}	hCHA	In-house production: ground and ball-milled bovine bone heat treated at 1100 °C for 3 h	7.0×10^{-14}	2.0	Dense slab: 60 × 10 mm^2 × 4 mm	Ceramic and polymer mixed at 170 °C for 10 min + heated to 180 °C for 15 min + hot pressed at 180 °C and 14 MPa for 5 min	In vitro: PBS (0.1 M, pH = 7.4) at 37 °C, weekly replacement, 11.6 mL/sample	Rakmae 12 hCHA [53]
Poly(D,L-lactide)(4:96)	Nature Works LLC (#4042D)	6.0×10^{-11}	1.7×10^{-10}	sA-hCHA	In-house production: above-mentioned hCHA modified with APES (3-Aminopropyl-triethoxysilane)	5.0×10^{-12}	2.0	Dense slab: 60 × 10 mm^2 × 4 mm	Same as Rakmae 12 C	In vitro: same as Rakmae 12 hCHA	Rakmae 12 sA-hCHA [53]
Poly(D,L-lactide)(4:96)	Nature Works LLC (#4042D)	6.0×10^{-11}	1.7×10^{-10}	sM-hCHA	In-house production: above-mentioned hCHA modified with MPTS (3-methacryloxy-propyltrimetho-xysilane)	5.0×10^{-12}	2.0	Dense slab: 60 × 10 mm^2 × 4 mm	Same as Rakmae 12 hCHA	In vitro: same as Rakmae 12 hCHA	Rakmae 12 sM-hCHA [53]
Poly(D,L-lactide)(15:85)	Purac Biochem BV, The Netherlands	2.0×10^{-10}	2.5×10^{-9}	hHA	Not reported: sintered, milled and sieved	3.0×10^{-11}	2.0	Dense film: t = (0.3...0.5) mm	Polymer dissolved in chloroform, ceramic added and mixture stirred + solvent evaporation	In vitro: PBS (pH = 7.2) at 37 °C, w/o replacement, w shaking, 11 mL/sample	Van der Meer hHA [54]

(continued)

Table B.6 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide)(50:50)	In-house production: ring-opening polymerisation of racemic D,L-lactide	2.1×10^{-10}	5.0×10^{-11}	pCHA	In-house production: wet chemistry route	1.0×10^{-13}	2.0	Porous cylinder $\Phi = 6$ mm, L = 15 mm	Composite fiber precipitation	In vivo: male Japanese white rabbits	Hasegawa pCHA [55]
Poly(D,L-lactide)(50:50)	In-house production: ring-opening polymerisation of D,L-lactide + modification with gellatin	4.3×10^{-10} (2.6×10^{-10})	8.0×10^{-11} (5.0×10^{-11})	Mixture of pHA and ns-lHA	In-house production: grown in-situ with SBF	5.0×10^{-14}	2.0	Porous fibrous disk: $\Phi = 11$ mm, t = (250...300) µm	Electrospun fibrous mats w in-situ grown ceramic	In vitro: PBS (pH = 7.4) w sodium azide at 37 °C, 20 mL/sample	Zou 12 Vit pns-lHA [56]
Poly(D,L-lactide)(50:50)	In-house production: same as Zou 12 Vit pns-lHA	1.4×10^{-10} (9.0×10^{-11})	1.5×10^{-10} (1.0×10^{-10})	Mixture of pHA and ns-lHA	In-house production: same as Zou 12 Vit pns-lHA	5.0×10^{-15}	2.0	Porous fibrous disk: $\Phi = 11$ mm, t = (250...300) µm	Re-electrospun after dissolving above-mentioned mat	In vitro: same as Zou 12 Vit pns-lHA	Zou 12 Vit R pns-lHA [56]
Poly(D,L-lactide)(50:50)	In-house production: same as Zou 12 Vit pns-lHA	4.4×10^{-10} (3.7×10^{-10})	4.7×10^{-10} (1.8×10^{-10})	Mixture of pHA and ns-lHA	In-house production: same Zou 12 Vit pns-lHA	5.0×10^{-15}	2.0	Porous fibrous cylinder: $\Phi = 5$ mm, L = 15 mm	Electrospun fibrous mats w in-situ grown ceramic	In vivo: subcutaneous implantation in male dogs	Zou 12 Viv pns-lHA [56]
Poly(D,L-lactide)(50:50)	In-house production: same as Zou 12 Vit pns-lHA	2.5×10^{-10} (2.0×10^{-10})	5.2×10^{-10} (2.0×10^{-10})	Mixture of pHA and ns-lHA	In-house production: same as Zou 12 Vit pns-lHA	1.1×10^{-14}	2.0	Porous fibrous cylinder: $\Phi = 5$ mm, L = 15 mm	Re-electrospun after dissolving above-mentioned mat	In vivo: same as Zou 2 Viv pns-lHA	Zou 12 Viv R pns-lHA [56]
Poly(D,L-lactide)(50:50) modified with carboxyl groups	In-house production: ring-opening polymerisation of D,L-lactide + modification with carboxyl groups	4.9×10^{-10}	2.3×10^{-10}	Mixture of pHA and ns-lHA	In-house production: grown in-situ using concentrated SBF	3.0×10^{-13}	2.0	Porous fibrous mat: t = 0.5 mm	Electrospun mats with in-situ grown ceramic	In vitro: PBS w sodium azide at 37 °C, w shaking at 100 rpm	Zou 11 C pns-lHA [57]

(continued)

Table B.6 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\,mol^{-1}\,s^{-1}$)	Type	Manufacturer	A_d ($mol\,m^{-2}\,s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide)(50:50) modified with carboxyl groups	In-house production: same as Zou 11 C pns-lHA	2.3×10^{-10}	2.9×10^{-10}	Mixture of pHA and ns-lHA	In-house production: same as Zou 11 C pns-lHA	3.0×10^{-13}	2.0	Porous fibrous mat: t = 0.5 mm	Re-electrospun after dissolving above-mentioned mat	In vitro: same as Zou 11 C	Zou 11 CR pns-lHA [57]
Poly(D,L-lactide)(50:50) modified with hydroxyl and carboxyl groups	In-house production: ring-opening polymerisation of D,L-lactide + modification with hydroxyl and carboxyl groups	2.8×10^{-10} (2.2×10^{-10})	2.5×10^{-10} (2.1×10^{-10})	Mixture of pHA and ns-lHA	In-house production: same as Zou 11 C pns-lHA	3.0×10^{-14}	2.0	Porous fibrous mat: t = 0.5 mm	Electrospun mats with in-situ grown ceramic	In vitro: same as Zou 11 C pns-lHA	Zou 11 HC [57]
Poly(D,L-lactide)(50:50) modified with amino, carboxyl and hydroxyl groups	In-house production: ring-opening polymerisation of D,L-lactide + modification with amino, hydroxyl and carboxyl groups	3.5×10^{-10} (2.0×10^{-10})	2.9×10^{-10} (1.8×10^{-10})	Mixture of pHA and ns-lHA	In-house production: same as Zou 11 C pns-lHA	1.1×10^{-14}	2.0	Porous fibrous mat: t = 0.5 mm	Electrospun mats with in-situ grown ceramic	In vitro: same as Zou 11 C pns-lHA	Zou 11 AHC pns-lHA [57]
Poly(D,L-lactide)(NR)	Jinan Daigang Bio-Technology Co. Ltd., China	6.0×10^{-11}	6.2×10^{-11}	bnHA	Berkeley Advanced Biomaterials Inc, USA	7.0×10^{-15}	2.0	Porous (80 %) cylinder: $\Phi = 10$ mm, L = 5 mm	Polymer dissolved in chloroform + ceramic and NaCl addition and dispersion + compression at 10 MPa and 25 °C	In vitro: SBF (pH = 7.4) at 37 °C, weekly replacement, w/o shaking	Chen PP/C bnHA [58]
Poly(D,L-lactide)(NR)	Jinan Daigang Bio-Technology Co. Ltd., China	8.0×10^{-11} (6.0×10^{-11})	9.0×10^{-11} (6.2×10^{-11})	bnHA	Berkeley Advanced Biomaterials Inc, USA	3.0×10^{-15}	2.0	Porous (80 %) cylinder: $\Phi = 10$ mm, L = 5 mm	Same as Chen PP/C	In vitro: same as Chen PP/C	Chen C bnHA [58]

B.2.3 Poly-lactide-co-glycolide Matrix

Table B.7 Results output by the HA composites degradation model for cases with a poly(lactide-co-glycolide) matrix. k_1 is the non-catalytic polymer degradation rate, k_2' is the autocatalytic polymer degradation rate, A_d is the ceramic dissolution rate and θ is the power ceramic dissolution law exponent. Abbreviations used to specify the hydroxyapatite type can be found in Table 5.2. A dashed line between rows indicates that data displayed in those consecutive rows belong to the same researcher or research group. A solid line between rows indicates no known author relationship for the data

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (44.6:55.4)	Mitsui Chemicals Co.; Tokio, Japan	2.5×10^{-9}	3.8×10^{-9}	hHA	Maruo Calcium Co.; Akashi, Japan	2.0×10^{-12}	2.0	Dense disk: $\Phi = 5$ mm, t = 0.5 mm	Polymer dissolved in dioxane + ceramic addition + freeze-drying of the solvent cast solution + compression moulding at 60 °C and 4.9 MPa	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, weekly replacement, w/o shaking, 30 mL/sample	Tsunoda hHA [59]
Poly(D,L-lactide-co-glycolide) (44.6:55.4)	Shang Dong Institute (Dept. of Med. Dev.), China	3.2×10^{-10} (2.8×10^{-10})	5.2×10^{-10} (3.2×10^{-10})	hHA	In-house production: wet chemistry route + calcining at 1100 °C for 6 h	1.1×10^{-11}	2.0	Porous (≈ 90 %) disk: $\Phi = 6$ mm, t = 2 mm	Polymer-ceramic mixture solvent casting + particulate leaching using NaCl	In vitro: standard conditions (PBS (pH = 7.4) at 37 °C w/o shaking) 20 mL/sample	Li hHA [60]
Poly(D,L-lactide-co-glycolide) (47:53)	Purac Biomaterials BV, The Netherlands (Purasorb PDLG 5004)	1.7×10^{-9}	1.5×10^{-9}	bnHA	Aldrich Chemistry, USA	3.0×10^{-13}	2.0	Porous (≈ 90 %) film: 0.5 cm^2 × t (t: NR)	Polymer dissolved in dioxane + blended w ceramic + freeze drying	In vitro: standard conditions (PBS at 37 °C w/o shaking) 20 mL/sample	Diaz PLGA bnHA [61]
Poly(D,L-lactide-co-glycolide) (50:50)	Birmingham Polymers Inc.; Birmingham, Alabama, USA	4.0×10^{-10}	6.0×10^{-10}	hHA	Sigma Chemicals; St. Louis, Missouri, USA	7.0×10^{-12}	2.0	Dense cylinder: $\Phi = 5$ mm, L = 5 mm	Polymer dissolved in acetone + precipitated in ethanol + mixed w ceramic + compression moulding into final shape	In vitro: distilled water at 37 °C w/o shaking, w/o replacement, 10 mL/sample	Agrawal hHA [62]

(continued)

Table B.7 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.1×10^{-9}	2.0×10^{-9}	pCHA	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + ground, milled and sieved using a 180 μm mesh	1.0×10^{-12}	2.0	Dense disk: $\Phi = 2$ mm, t = 2 mm	Polymer and ceramic mixed in acetone + dried at 40 °C overnight + injection-moulded into cylinders at 140 °C and 0.5 MPa + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C,w/o shaking, w/o replacement, 166mL g^{-1}	Naik pCHA [63]
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.1×10^{-9}	2.0×10^{-9}	hCHA	In-house production: same as Naik pCHA + calcined at 800 °C for 4 h in an air atmosphere	5.0×10^{-12}	2.0	Dense disk: $\Phi = 2$ mm, t = 2 mm	Same as Naik pCHA	In vitro: same as Naik pCHA	Naik ca hCHA [63]
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.1×10^{-9}	2.0×10^{-9}	hCHA	In-house production: same as Naik pCHA + calcined at 800 °C for 4 h in a wet argon atmosphere	3.0×10^{-12}	2.0	Dense disk: $\Phi = 2$ mm, t = 2 mm	Same as Naik pCHA	In vitro: same as Naik pCHA	Naik cw hCHA [63]

(continued)

Table B.7 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.1×10^{-9}	2.0×10^{-9}	sMP-pCHA	In-house production: same as Naik pCHA + treatment w physisorbed 1 wt % mercaptopropyl trimethoxy silane (MPTMS) for 1 h	3.0×10^{-11}	2.0	Dense disk: $\Phi = 2$ mm, t = 2 mm	Same as Naik pCHA	In vitro: same as Naik pCHA	Naik f sMP-pCHA [64]
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.1×10^{-9}	2.0×10^{-9}	sMP-pCHA	In-house production: same as Naik pCHA + treatment w chemisorbed 1 wt % mercaptopropyl trimethoxy silane (MPTMS) for 1 h	3.0×10^{-11}	2.0	Dense disk: $\Phi = 2$ mm, t = 2 mm	Same as Naik pCHA	In vitro: same as Naik pCHA	Naik c sMP-pCHA [64]
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.1×10^{-9}	2.0×10^{-9}	sMP-hCHA	In-house production: same as Naik ca-hCHA + treatment w physisorbed 1 wt % mercaptopropyl trimethoxy silane (MPTMS) for 1 h	1.0×10^{-11}	2.0	Dense disk: $\Phi = 2$ mm, t = 2 mm	Same as Naik pCHA	In vitro: same as Naik pCHA	Naik fca sMP-hCHA [64]
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.1×10^{-9}	2.0×10^{-9}	sMP-hCHA	In-house production: same as Naik ca-hCHA + treatment w chemisorbed 1 wt % mercaptopropyl trimethoxy silane (MPTMS) for 1 h	1.0×10^{-11}	2.0	Dense disk: $\Phi = 2$ mm, t = 2 mm	Same as Naik pCHA	In vitro: same as Naik pCHA	Naik cca sMP-hCHA [64]

(continued)

Table B.7 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.0×10^{-9}	1.8×10^{-9}	hCHA	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aged for 1 d and dried + calcined at 800 °C for 2 h + ground and sieved using a 75 µm mesh	3.0×10^{-14}	2.0	Dense disk: $\Phi = 6$ mm, t = 2 mm	Ceramic dispersed in polymer using a co-rotating twin screw extruder + cut into pellets + injection-moulded into cylinders at 130 °C and 0.5 MPa + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement	Ege hCHA [27]
Poly(D,L-lactide-co-glycolide) (50:50)	SurModics Pharmaceuticals, USA	1.0×10^{-9}	1.8×10^{-9}	hHA	In-house production: wet chemistry route using $Ca(OH)_2$ and H_3PO_4 + aged for 1 d and dried + calcined at 1200 °C for 2 h + ground and sieved using a 75 µm mesh	1.0×10^{-13}	2.0	Dense disk: $\Phi = 6$ mm, t = 2 mm	Same as Ege hCHA	In vitro: same as Ege hCHA	Ege hHA [26] [27]
Poly(D,L-lactide-co-glycolide) (75:25)	Boehringer Ingelheim, Germany (Resomer RG750S)	3.4×10^{-10}	2.4×10^{-10}	hHA	Sigma Aldrich; St. Louis, Missouri, USA	1.0×10^{-13}	2.0	Porous fibrous mat: 20 × $5mm^2$ × t (t: NR)	Polymer dissolved in HFIP + blended w ceramic + electrospinning	In vitro: standard conditions (PBS (0.01 M) at 37 °C w/o shaking) 5 mL/sample	Lee hHA [65]
Poly(lactide-co-glycolide) (95:05)	In-house production	1.5×10^{-10} (2.8×10^{-11})	1.0×10^{-10} (1.9×10^{-11})	lHA	In-house production	1.0×10^{-14}	2.0	Dense bar: 60 × $6mm^2$ × 4 mm	Solution mixing + pressed + annealed at 110 °C for 30 min	In vitro: SBF at 37 °C (buffered to pH = 7.4), w shaking, 20 mL/sample	Liuyun lHA [66]
Poly(lactide-co-glycolide) (NR)	Not reported	6.6×10^{-10}	4.8×10^{-10}	hHA	In-house production: hydrothermal-electrochemical deposition using an electrolyte containing the precursors	3.0×10^{-13}	2.0	Dense film: 5 × $5mm^2$ × (0.05...0.08) mm	Polymer solvent casting on a Ti substrate w grown HA + delaminating	In vitro: SBF at 37 °C	Ban hHA [67]

B.2.4 Miscellaneous Polymers Matrixes

Table B.8 Results output by the HA composites degradation model for cases with a miscellaneous polymer matrix. k_1 is the non-catalytic polymer degradation rate, k_2' is the autocatalytic polymer degradation rate, A_d is the ceramic dissolution rate and θ is the power ceramic dissolution law exponent. Abbreviations used to specify the hydroxyapatite type can be found in Table 5.2. A dashed line between rows indicates that data displayed in those consecutive rows belong to the same researcher or research group. A solid line between rows indicates no known author relationship for the data

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\,mol^{-1}\,s^{-1}$)	Type	Manufacturer	A_d ($mol\,m^{-2}\,s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(ε-caprolactone)	Daicel Polymer Ltd.; Tokyo, Japan	6.0×10^{-12} (1.0×10^{-12})	2.3×10^{-11} (4.0×10^{-12})	bnHA	Nanjing Emperor Nano Material Co. Ltd., China	3.0×10^{-16}	2.0	Porous (≈ 70 %) film: 10 × 10 mm^2 × 3 mm	Polymer, ceramic and porogen mixed at 100 °C and 90 rpm for 15 min + compression moulding at 80 °C+ porogen leaching w distilled water	In vitro: PBS (pH = 7.4) at 37 °C, monthly replacement, w shaking	Wang PCL bnHA[68]
Poly(L-co-D,L-lactide)(70:30) and poly(L-lactide) for pure polymer sample	Boehringer Ingelheim, Germany (Resomer LR708)	4.4×10^{-11} (6.0×10^{-11})	4.4×10^{-11} (5.8×10^{-11})	hHA	CamCeram Coating Powder; Leiden, The Netherlands	3.0×10^{-13}	2.0	Dense screw: Φ = (2.62...4.5) mm, L = 30 mm	Polymer and ceramic mixed in a rotary blender + injection moulded into screw shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w shaking at 60 rpm, 50 mL g^{-1}	Hile hHA [69]
Poly(L-lactide-co-ε-caprolactone) (70:30)	Purac Biomaterials BV., The Netherlands (Purasorb PLC 7015)	1.5×10^{-10}	2.8×10^{-10}	bnHA	Aldrich Chemistry, USA	1.0×10^{-14}	2.0	Porous (≈ 90 %) film (dimensions: NR)	Polymer dissolved in dioxane + blended w ceramic + freeze drying	In vitro: standard conditions (PBS at 37 °C w/o shaking) 10 mL/sample	Diaz PLCL bnHA [70]

(continued)

Table B.8 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-ε-caprolactone) (60:40)	In-house production: ring-opening polymerisation at 145 °C in N_2 atmosphere for 3 h	1.5×10^{-9}	1.2×10^{-9}	hHA	De Puy, Bioland, France (BRKO)	7.0×10^{-12}	2.0	Dense dogbone: DIN Standard 53448 F.2. Smallest dimension < 5 mm	Polymer dissolved in methylene chloride + mixed w ceramic + compression moulded at (70...90) °C and (2500...4500) kg	In vitro: Ringer solution (pH = (5.5...7.0)) at 37 °C, w shaking	Ural NS hHA[71]
Poly(D,L-lactide-co-ε-caprolactone) (60:40)	In-house production: ring-opening polymerisation at 145 °C under vacuum for 19 h	1.5×10^{-9}	1.2×10^{-9}	hHA	De Puy, Bioland, France (BRKO)	5.0×10^{-12}	2.0	Dense dogbone: DIN Standard 53448 F.2. Smallest dimension < 5 mm	Same as Ural NS hHA	In vitro: same as Ural NS hHA	Ural VL hHA [71]
Poly(L-lactide) and poly(ε-caprolactone) blend (28.4:71.6)	Cargill-Dow and Polysciences	8.0×10^{-12}	2.4×10^{-11}	bnHA	Sigma Aldrich	3.0×10^{-15}	2.0	Porous (≈ 90 %) disk: Φ = 6 mm, t = 3.5 mm	Polymer dissolved in dioxane + ceramic dispersed in solvent + mixed + freeze-drying + porogen leaching	In vitro: Phosphate buffer (pH = 7.4) at 37 °C, replacement every 2 weeks, w shaking, 200 $mL\,g^{-1}$	Rodenas CL bnHA [72]
Poly(L-lactide) and poly(ε-caprolactone) blend (86.4:13.6)	Cargill-Dow and Polysciences	2.6×10^{-11}	1.2×10^{-11}	bnHA	Sigma Aldrich	3.0×10^{-15}	2.0	Porous (≈ 90 %) disk: Φ = 6 mm, t = 3.5 mm	Same as Rodenas CL bnHA	In vitro: same as Rodenas CL bnHA	Rodenas LA bnHA [72]
Poly(D,L-lactide-co-glycolide)(50:50) and poly(ε-caprolactone) blend (84:16)	Purac Biomaterials BV; Gorinchem, The Netherlands (Purasorb PDLG 5010) and Sigma Aldrich; St. Louis, Missouri, USA	7.8×10^{-10}	9.4×10^{-10}	bnHA	Donated by Prof. Marc Bohner (Budenheim, Tri-Cafos P/C53-80)	1.0×10^{-14}	2.0	Porous mat (dimensions: NR)	Ceramic suspended in solvent + polymer added + electrospinning of the solution	In vitro: PBS (pH = 7.4) at 37 °C, w/o replacement, w shaking at 60 rpm 2 mL/sample	Ji bnHA [73]

(continued)

Table B.8 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide)(65:35) and poly(ε-caprolactone) blend (71.8:28.2)	Aldrich and Aldrich	2.2×10^{-10}	1.8×10^{-10}	hHA	Aldrich	9.0×10^{-12}	2.0	Porous (80 %) film: 5 × 5 mm^2 × 1 mm	Polymers dissolved in tetrahydrofuran + NaCl and ceramic addition + solvent evaporation + pressed at (41.4...68.9) MPa	In vitro: sterile water at 37 °C, no replacement	Dunn CLs hHA [74]
Poly(D,L-lactide-co-glycolide)(65:35) and poly(ε-caprolactone) blend (71.8:28.2)	Aldrich and Aldrich	2.2×10^{-10}	1.8×10^{-10}	hHA	Aldrich	3.0×10^{-11}	2.0	Porous (80 %) film: 5 × 5 mm^2 × 1 mm	Same as Dunn CLs hHA	In vitro: sterile water at 37 °C, replacement every 2/3 days	Dunn CLd hHA [74]
Poly(D,L-lactide-co-glycolide)(65:35) and poly(ε-caprolactone) blend (93.9:6.1)	Aldrich and Aldrich	3.0×10^{-10}	1.6×10^{-10}	hHA	Aldrich	3.0×10^{-12}	2.0	Porous (80 %) film: 5 × 5 mm^2 × 1 mm	Same as Dunn CLs hHA	In vitro: sterile water at 37 °C, no replacement	Dunn LGs hHA [74]
Poly(D,L-lactide-co-glycolide)(65:35) and poly(ε-caprolactone) blend (93.9:6.1)	Aldrich and Aldrich	3.0×10^{-10}	2.6×10^{-10}	hHA	Aldrich	5.0×10^{-12}	2.0	Porous (80 %) film: 5 × 5 mm^2 × 1 mm	Same as Dunn CLs hHA	In vitro: sterile water at 37 °C, replacement every 2/3 days	Dunn LGd hHA [74]

B.3 Calcium Carbonate Case Studies Modelling Results

Table B.9 Results output by the CC composites degradation model for all analysed case studies. k_1 is the non-catalytic polymer degradation rate, k_2' is the autocatalytic polymer degradation rate, A_d is the ceramic dissolution rate and θ is the power ceramic dissolution law exponent. Abbreviations used to specify the calcium carbonate type can be found in Table 7.2. A dashed line between rows indicates that data displayed in those consecutive rows belong to the same researcher or research group. A solid line between rows indicates no known author relationship for the data

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)	Purac Biochem B.V.; Gorinchem, The Netherlands (Purasorb)	1.1×10^{-10}	9.0×10^{-11}	μ-CC	In-house production: mixture of $Ca(OH)_2$ + aminopropyl-triethoxysilane (APTES) + methanol in a CO_2 atmosphere + dried at 110 °C	3.0×10^{-13}	2.0	Porous mat	Polymer and ceramic kneaded at 200 °C for 10 min + mixture dissolved in chloroform + electrospinning of the polymer and ceramic mix	In vitro: 5 mmol/L NaOH solution, w/o shaking, w/o replacement	Wakita K μ-CC [75]
Poly(L-lactide)	Purac Biochem B.V.; Gorinchem, The Netherlands (Purasorb)	1.4×10^{-11}	1.4×10^{-11}	μ-CC	In-house production: mixture of $Ca(OH)_2$ + aminopropyl-triethoxysilane (APTES) + methanol in a CO_2 atmosphere + dried at 110 °C	3.0×10^{-13}	2.0	Porous mat	Ceramic dispersed in chloroform + polymer dissolved in the mixture + electrospinning of the polymer and ceramic mix	In vitro: same as Wakita K μ-CC	Wakita M μ-CC [75]

(continued)

Table B.9 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(L-lactide)	Shandong Medical Device Company, China	5.0×10^{-11}	1.4×10^{-11}	λ-CC	In-house production: freshwater cultured lack luster pearls (*H. cumingii*) ground into powder using a grinder	5.0×10^{-12}	2.0	Porous cylinder: $\Phi = 9$ mm, L = 18 mm	Polymer dissolver in 1,4-dioxane + ceramic addition + stirring and sonication + freezing at −20 °C for 24 h + lyophilisation at −60 °C for 48 h + drying in a vacuum oven for 72 h	In vitro: PBS (pH = 7.4) at 37 °C, w shaking at 60 rpm, weekly replacement, 15 mL/sample	Liu λ-CC [76]
Poly(L-lactide)	Shandong Medical Device Company, China	5.0×10^{-11}	1.4×10^{-11}	μ-CC	In-house production: freshwater cultured lustrous pearls (*H. cumingii*) ground into powder using a grinder	3.0×10^{-12}	2.0	Porous cylinder: $\Phi = 9$ mm, L = 18 mm	Same as Liu λ-CC	In vitro: same as Liu λ-CC	Liu μ-CC [76]
Poly(D,L-lactide) (50:50)	In-house production: bulk ring-opening polymerisation of D,L-lactide at 145 °C using zinc powder	1.4×10^{-10}	8.2×10^{-10}	λ-CC	Inoteb; France (Biocoral)	3.0×10^{-10}	2.0	Dense film: 12 × $12\,mm^2$ (PDLLA) × 2.1 mm (PDLLA–λ-CC) × 1.4 mm	Polymer dissolved in acetone + blended w ceramic + vacuum drying at 40 °C for 2 d + compression at 10 MPa and 130 °C+ cut at 80 °C into final shape	In vitro: PBS (0.13 M, pH = 7.4) w 0.02 % NaN_3 at 37 °C, w/o shaking, w/o replacement, 30 mL/sample	Li λ-CC [77]

(continued)

Table B.9 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k'_2 ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (44.6:55.4)	Mitsui Chemicals; Tokyo, Japan: polymerisation of D,L-lactide and glycolide using stannous octoate	3.0×10^{-9}	3.0×10^{-9}	β-CC (Assumed)	Wako Pure Chemical Industries; Tokyo, Japan	3.0×10^{-10}	2.0	Dense film: 15 × $15\,mm^2$ × 0.5 mm	Polymer dissolved in dioxane + ceramic addition + freeze-drying of the solvent cast solution + compression moulding at 60 °C and 4.9 MPa	In vitro: PBS (pH = 7.4) at 37 °C, w/o shaking, weekly replacement, 40 mL/sample	Ara β-CC [24]
Poly(D,L-lactide-co-glycolide) (44.6:55.4)	Mitsui Chemicals Co.; Tokio, Japan	2.5×10^{-9}	3.8×10^{-9}	β-CC	Maruo Calcium Co.; Akashi, Japan	3.0×10^{-11}	2.0	Dense disk: Φ = 5 mm, t = 0.5 mm	Polymer dissolved in dioxane + ceramic addition + freeze-drying of the solvent cast solution + compression moulding at 60 °C and 4.9 MPa	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, weekly replacement, w/o shaking, 30 mL/sample	Tsunoda β-CC [59]
Poly(D,L-lactide-co-glycolide) (44.6:55.4)	Mitsui Chemicals Co.; Tokio, Japan	2.5×10^{-9}	3.8×10^{-9}	λ-CC	Maruo Calcium Co.; Akashi, Japan	3.0×10^{-11}	2.0	Dense disk: Φ = 5 mm, t = 0.5 mm	Same as Tsunoda β-CC	In vitro: same as Tsunoda β-CC	Tsunoda λ-CC [59]
Poly(D,L-lactide-co-glycolide) (50:50)	Birmingham Polymers Inc.; Birmingham, Alabama, USA	4.0×10^{-10}	6.0×10^{-10}	β-CC (Assumed)	Sigma Chemicals; St. Louis, Missouri, USA	3.0×10^{-11}	2.0	Dense cylinder: Φ = 5 mm, L = 5 mm	Polymer dissolved in acetone + precipitated in ethanol + mixed w ceramic + compression moulding into final shape	In vitro: distilled water at 37 °C w/o shaking, w/o replacement, 10 mL/sample	Agrawal β-CC [62]

(continued)

Table B.9 (continued)

Polymer characteristics				Ceramic characteristics				Sample characteristics			
Type	Manufacturer	k_1 (s^{-1})	k_2' ($m^3\ mol^{-1}\ s^{-1}$)	Type	Manufacturer	A_d ($mol\ m^{-2}\ s^{-1}$)	θ (1)	Structure and Morphology	Fabrication method	Degradation protocol	Case code and reference
Poly(D,L-lactide-co-glycolide) (50:50)	Lakeshore Biomaterials; Birmingham, Alabama, USA (5050 DLG 5E)	3.7×10^{-9}	3.2×10^{-9}	β-CC	Shiraishi Calcium Kaisha Ltd; Japan	3.0×10^{-12}	2.0	Dense disk: $\Phi = 3.5$ mm, t = 2 mm	Polymer dissolved in acetone + ceramic sonicated in acetone + mixing + solvent casting + cut into pellets + injection-moulding at 135 °C and 0.5 MPa into cylinders + cut into final shape	In vitro: PBS (0.01 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement, 166 mL g^{-1}	Ch6 β-CC [Chapter 6]
Poly(D,L-lactide-co-glycolide) (85:15)	Purac Biochem B.V.; Gorinchem, The Netherlands	1.5×10^{-10}	8.0×10^{-10}	β-CC (Assumed)	Sigma; St. Louis, Missouri, USA (SigmaUltra Grade)	3.0×10^{-10}	2.0	Dense screw: $\Phi = 9$ mm, L = 30 mm	Polymer dried under vacuum for 3 h at 40 °C+ blended w ceramic in a co-rotating twin extruder + injection moulded into screw shape	In vitro: PBS (0.05 M, pH = 7.4) at 37 °C, w/o shaking, w/o replacement, 250 mL/sample	Cotton β-CC [78]

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