Supplementary Materials: A systematic experimental and computational analysis of commercially available aliphatic polyesters

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S.1 Sample preparation

Softening temperatures for each polymer are listed in Table S.1.

Polymer	Softening temperature (°C)
PDLG 5002	85 ± 5
PDLG 5004	130 ± 5
PDLG 5010	180 ± 5
RG 505	130 ± 5
PDLG 7507	160 ± 5
RG 505 + HA	150 ± 5
PDLG 5004 + HA	100 ± 5

Table S.1. Softening temperatures for each investigated system.

S.2 Experimental data

Experimental data for all investigated polymers are summarized in Table S.2 – S.8 and are expressed as average of three independent measurements ± standard deviation. Only one measurement was made for raw material (*i.e.*, before thermal treatment). Raw data are available upon reasonable request.

S.2.1 PDLG 5002

Time (days)	MW_n (g mol^{-1})	MW_w (g mol^{-1})	PD (-)	T_g (°C)	LA (%)	GA (%)	Mass Loss (%)	Water uptake (%)	pH (-)
Raw material	8700	16400	1.8	36.92	53	47	nd	nd	nd
0	9000 ± 300	16500 ± 120	1.84 ± 0.06	36.60 ± 0.05	53	47	0.12 ± 0.06	0.74 ± 0.30	7.37 ± 0.01
7	7800 ± 200	14800 ± 350	1.89 ± 0.03	35.02 ± 0.34	53	47	-0.76 ± 0.06	1.34 ± 0.42	7.23 ± 0.04
14	3500 ± 300	7000 ± 500	2.00 ± 0.18	29.94 ± 0.49	53	47	-2.83 ± 0.42	4.37 ± 1.82	7.33 ± 0.04
21	2500 ± 40	4600 ± 100	1.88 ± 0.08	33.43 ± 0.18	57	43	79.54 ± 2.5	81.07 ± 0.93	6.79 ± 0.03

Table S.2. Summary of experimental data for PDLG 5002. (nd: not determined)

S.2.2 PDLG 5004

Time (days}	MW_n (g mol^{-1})	MW_w (g mol^{-1})	PD (-)	T_g (°C)	LA (%)	GA (%)	Mass Loss (%)	Water uptake (%)	pH (-)
Raw material	23600	42700	1.81	44.1	53	47	nd	nd	nd
0	24900 ± 380	40800 ± 780	1.64 ± 0.02	43.67 ± 0.47	53	47	1.06 ± 0.4	1.59 ± 0.77	7.48
7	20570 ± 340	35270 ± 620	1.71 ± 0.01	42.83 ± 0.14	53	47	-3.19 ± 1.21	3.67 ± 3.16	7.26 ± 0.08
14	9530 ± 290	17400 ± 450	1.83 ± 0.04	37.33 ± 0.83	53	47	-1.83 ± 1.87	2.25 ± 0.73	7.22 ± 0.07
21	2090 ± 90	5760 ± 170	2.76 ± 0.06	23.56 ± 0.87	54	46	-2.85 ± 1.46	9.03 ± 4.17	7.38 ± 0.02
35	4470 ± 590	9730 ± 1400	2.16 ± 0.18	36.41 ± 0.03	61 0.5	39	93.9 ± 0.99	1347.2 ± 433.3	6.4 ± 0.02

Table S.3. Summary of experimental data for PDLG 5004. (nd: not determined)

S.2.3 PDLG 5010

Time (days)	MW_n (g mol^{-1})	MW_w (g mol^{-1})	PD (-)	T_g (°C)	LA (%)	GA (%)	Mass Loss (%)	Water uptake (%)	pH (-)
Raw material	81500	157000	1.93	47.19	53	47	nd	nd	nd
0	69700 ± 5870	126070 ± 9600	1.81 ± 0.01	48.45 ± 0.40	53	47	0.02 ± 0.02	2.80 ± 1.11	7.49 ± 0.01
7	54150 ± 2850	98750 ± 4650	1.82 ± 0.01	45.97 ± 0.02	53	47	0.41 ± 1.2	6.14 ± 0.16	7.36 ± 0.1
14	32560 ± 210	61000 ± 340	1.89 ± 0.08	43.93 ± 2.6	53	47	-0.98 ± 0.62	1.93 ± 0.4	7.31 ± 0.07
21	5700 ± 780	13400 ± 2580	2.10 ± 0.08	35.64 ± 0.93	53	47	-3.10 ± 0.15	2.23 ± 0.46	7.18 ± 0.01
35	7050 ± 2750	19250 ± 8050	2.70 ± 0.1	41.72 ± 1.79	61	39	87.74 ± 0.34	1242.2 ± 101.5	6.55 ± 0.03
56[a]	2700	4800	1.78	42.16	72	28	-	-	-

Table S.4. Summary of experimental data for PDLG 5010. [a]Only one sample could be analyzed due to the relevant mass loss. (nd: not determined)

S.2.4 RG 505

Time (days)	MW_n (g mol^{-1})	MW_w (g mol^{-1})	PD (-)	T_g (°C)	LA (%)	GA (%)	Mass Loss (%)	Water uptake (%)	pH (-)
Raw material	46400	81.5	1.8	49.39	51	49	nd	nd	nd
0	43300 ± 670	75060 ± 920	1.73 ± 0.01	48.73 ± 0.14	51	49	-0.66 ± 0.32	2.30 ± 0.80	7.45 ± 0.01
7	34670 ± 680	58870 ± 900	1.70 ± 0.01	47.60 ± 0.26	51	49	-1.09 ± 0.14	4.25 ± 0.47	7.46
14	23070 ± 210	39570 ± 340	1.71 ± 0.02	46.21 ± 0.04	51	49	-0.81 ± 0.19	6.07 ± 2.89	7.44
21	11130 ± 820	19670 ± 1670	1.76 ± 0.04	43.40 ± 0.92	51	49	-0.23 ± 0.50	6.64 ± 1.18	7.44 ± 0.01
35[a]	2760 ± 100	5760 ± 370	2.10 ± 0.08	35.33 ± 2.99	59	41	-	-	-
56	3150 ± 50	10400 ± 500	3.3 ± 0.1	-	67	33	-	-	-
70[b]	1700	2100	1.2		80	20			

Table S.5. Summary of experimental data for RG 505. [a]Some measurement could not be performed due to the relevant mass loss; [b]Only one sample could be analyzed due to the relevant mass loss. (nd: not determined)

S.2.5 PDLG 7507

Time (days)	MW_n (g mol^{-1})	MW_w (g mol^{-1})	PD (-)	T_g (°C)	LA (%)	GA (%)	Mass Loss (%)	Water uptake (%)	pH (-)
Raw material	56900	106500	1.87	50.07	76	24	nd	nd	nd
0	51000 ± 1620	91400 ± 3300	1.79 ± 0.02	49.67 ± 0.39	76	24	-0.49 ± 0.20	2.63 ± 1.54	7.49
7	46800 ± 2000	82530 ± 2150	1.76 ± 0.04	48.37 ± 0.24	76	24	-0.19 ± 0.05	4.08 ± 1.28	7.34 ± 0.09
14	32040 ± 1950	56000 ± 3580	1.76 ± 0.03	45.95 ± 0.21	76	24	-1.51 ± 0.16	7.00 ± 4.33	7.21 ± 0.02
21	16400 ± 1710	33060 ± 4260	2.02 ± 0.06	43.33 ± 0.9	76	24	-3.00 ± 0.23	8.65 ± 1.80	7.28 ± 0.07
35	3330 ± 290	13100 ± 640	3.90 ± 0.29	29.29 ± 0.46	77	23	-11.56 ± 1.85	10.17 ± 1.54	7.27 ± 0.06
56[a]	10400	20700	1.99	44.6	77	23	94.82 ± 1.79	1720.1 ± 228.1	6.54 ± 0.02
84[a]	2700	5100	1.86	-	87	13	-	-	6.1

Table S.6. Summary of experimental data for PDLG 7507. [a]Some measurement could not be performed due to the relevant mass loss. (nd: not determined)

S.2.6 RG505 + HA

Time (days)	MW_n (g mol^{-1})	MW_w (g mol^{-1})	PD (-)	T_g (°C)	LA (%)	GA (%)	Mass Loss (%)	Water uptake (%)	pH (-)
Raw material (RG 505)	46400	81.5	1.8	49.39	51	49	nd	nd	nd
0	48060 ± 1080	82730 ± 1790	1.72 ± 0.01	48.16 ± 0.19	51	49	-0.33 ± 0.25	1.68 ± 0.34	7.47
7	39930 ± 170	69160 ± 550	1.73 ± 0.01	47.29 ± 0.25	51	49	-3.06 ± 0.34	15.75 ± 2.38	7.46
14	27430 ± 1290	49460 ± 1030	1.81 ± 0.04	45.78 ± 1.01	51	49	-3.00 ± 0.60	27.14 ± 3.93	7.42 ± 0.01
21	18200 ± 280	32430 ± 490	1.78 ± 0.04	46.01 ± 0.88	51	49	-2.54 ± 0.22	40.38 ± 2.88	7.41 ± 0.01
35	3030 ± 590	9000 ± 3470	2.87 ± 0.68	29.45 ± 3.12	54	46	-9.63 ± 20.83	225.67 ± 57.92	7.25 ± 0.02
56[a]	3530 ± 400	10060 ± 4690	2.76 ± 0.94	48.14 ± 0.08	64	36	-	-	6.54 ± 0.02
70[a]	3700 ± 200	10150 ± 750	2.75 ± 0.05	-	73	27	-	-	6.1 ± 0.03

Table S.7. Summary of experimental data for RG 505 + HA. [a]Some measurement could not be performed due to the relevant mass loss. (nd: not determined)

S.2.7 PDLG 5004 + HA

Time (days)	MW_n (g mol^{-1})	MW_w (g mol^{-1})	PD (-)	T_g (°C)	LA (%)	GA (%)	Mass Loss (%)	Water uptake (%)	pH (-)
Raw material (PDLG 5004)	23600	42700	1.81	44.1	53	47	nd	nd	nd
0	21530 ± 400	40100 ± 490	1.86 ± 0.04	41.41 ± 0.71	53	47	-0.47 ± 0.49	3.39 ± 1.73	7.47 ± 0.01
7	21700 ± 220	37860 ± 310	1.75 ± 0.03	42.39 ± 0.15	53	47	-1.26 ± 0.36	17.60 ± 2.72	7.46 ± 0.01
14	16860 ± 120	29130 ± 1100	1.72 ± 0.05	42.44 ± 0.30	53	47	-2.73 ± 0.14	28.20 ± 5.68	7.45 ± 0.01
21	9130 ± 340	18960 ± 780	2.09 ± 0.03	41.15 ± 0.23	53	47	-4.59 ± 2.09	40.58 ± 3.47	7.45 ± 0.01
35	3160 ± 260	14460 ± 2350	4.57 ± 0.41	34.06 ± 1.61	56	44	8.58 ± 0.84	311.34 ± 69.94	7.28 ± 0.06
56[a]	2860 ± 240	8960 ± 3910	3.03 ± 1.03	29.99 ± 0.56	63	37	-	-	6.64 ± 0.01

Table S.8. Summary of experimental data for PDLG 5004 + HA. [a]Some measurement could not be performed due to the relevant mass loss. (nd: not determined)

S.3 Model input parameters

Input parameters are summarized in Table S.9.

Polymer density ϱ_{pol} (g cm^{-3})	1.2
Monomer diffusion coefficient D_M^0 (cm^2 s^{-1})	10^{-10}
Oligomer diffusion coefficient D_{olig}^0 (cm^2 s^{-1})	10^{-10}
Water diffusion coefficient D_w^0 (cm^2 s^{-1})	10^{-9}
Monomer molecular weight MW_{mon} (g mol^{-1})	83 (PLGA 50/50) 86.5 (PLGA 75/25)

Table S.9. Model input parameters.

S.4 Initial and boundary conditions

Initial conditions are written assuming that the polymer is anhydrous and with a negligible monomer content before degradation onset. Statistical moments are related to polymer properties before degradation onset.

$$C_M(t=0) = 10^{-10}\,\frac{mol}{cm^3} \quad \text{(S.1)}$$

$$C_{olig}(t=0) = 10^{-10}\,\frac{mol}{cm^3} \quad \text{(S.2)}$$

$$C_w(t=0) = 10^{-10}\,\frac{mol}{cm^3} \quad \text{(S.3)}$$

$$\mu_0(t=0) = \frac{\rho_{pol}}{MW_n(t=0)} \quad \text{(S.4)}$$

$$\mu_1(t=0) = MW_n(t=0)\,\frac{\mu_0(t=0)}{MW_{mon}} \quad \text{(S.5)}$$

$$\mu_2(t=0) = DP(t=0)\,\frac{\mu_1^2(t=0)}{\mu_0(t=0)} \quad \text{(S.6)}$$

Focusing on boundary conditions, at polymer/disk interface (z = 0) no molar fluxes are present; this implies that the first derivative with respect to axial coordinate is equal to zero:

$z = 0$ polymer/disk interface

$$\left.\frac{\partial C_M}{\partial z}\right|_{z=0} = 0 \quad \text{(S.7)}$$

$$\left.\frac{\partial C_{olig}}{\partial z}\right|_{z=0} = 0 \quad \text{(S.8)}$$

$$\left.\frac{\partial C_w}{\partial z}\right|_{z=0} = 0 \quad \text{(S.9)}$$

At polymer/surrounding medium interface (z = L) the continuity of mass flux is imposed, assuming the presence of interphase mass transport resistances.

$z = L$ polymer/surrounding medium interface

$$-D_M(z=L)\left.\frac{\partial C_M}{\partial z}\right|_{z=L} = k_{c,M}(C_M(z=L) - C_{b,M}) \quad \text{(S.10)}$$

$$-D_{olig}(z=L)\left.\frac{\partial C_{olig}}{\partial z}\right|_{z=L} = k_{c,olig}(C_{olig}(z=L) - C_{b,olig}) \quad \text{(S.11)}$$

$$-D_w(z=L)\frac{\partial C_w}{\partial z}\Big|_{z=L} = k_{c,w}(C_w(z=L) - C_{b,w}) \quad \text{(S.12)}$$

where $k_{c,i}$ is the mass transport coefficient of the i-th compound (monomer, oligomer, water) and $C_{b,i}$ is the concentration of the i-th compound in the surrounding medium. Mass transport coefficient can be computed starting from the Sherwood number, equal to $2/\pi$:

$$Sh = \frac{2}{\pi} = \frac{k_{c,i}L}{D_{i,w}} \quad \text{(S.13)}$$

where $D_{i,w}$ is the diffusion coefficient of the i-th compound in the surrounding medium, equal to $2.3 \cdot 10^{-5}$ cm^2 s^{-1} for water and 10^{-5} for monomer and oligomers. $C_{b,i}$ is equal to 0 for monomer and oligomers, in order to take into account the change of the surrounding solution in the experiments, and to pure molar water density for water.

S.5 Numerical solution

The resulting system of partial differential equations (PDE) is solved by means of the method of lines. Axial coordinate is discretized using a suitable number of grid points and an ordinary differential equation (ODE), where the time is the only independent variable, is written for every variable in each grid point. Derivatives are expressed using a suitable finite difference scheme.

The resulting system of ODE is numerically integrated by means of *ode15s* algorithm implemented in MATLAB. Kinetic constant fitting was performed by means of *lsqnonlin* algorithm implemented in MATLAB.

S.6 Model consistency

Model consistency was evaluated through the closure of mass balance, exploiting the physical meaning of the first order moment, which accounts for the overall amount of monomer units present in the system (independently of how they are assembled in the polymer chains).

The closure of mass balance can be expressed as follows:

$$\mu_1(t=0)V - \int \mu_1(t,z)dV - \int_0^t \sum_{i=1}^{9} ik_{c,i}C_i(t,z=L)S_{ext} = 0 \quad \text{(S.14)}$$

where S_{ext} is the top surface of the cylinder that constitutes the interface between the device and the surrounding solution, across which fluxes occur.

It is more convenient to define a relative error ε, which provides a better estimation of the impact of the approximation due to the discretization and the numerical solution:

$$\varepsilon(t) = \frac{\mu_1(t=0)V - \int \mu_1(t,z)dV - \int_0^t \sum_{i=1}^{9} ik_{c,i}C_i(t,z=L)S_{ext}}{\mu_1(t=0)V} \cdot 100 \quad \text{(S.15)}$$

The number of grid points (200 – 300) has been chosen so that the error is kept below 0.5 %.