

Electronic Supporting Information

Sustainable coatings from bio-based, enzymatically synthesized polyesters with enhanced functionalities

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Potentiometric titration. For the AV determination, in a round flask approximately 0.5 g of the sample were precisely weighed and dissolved in ca. 30 mL tetrahydrofuran (THF) and ca. 7 mL methanol. The titration was performed with a 0.1 M KOH-solution in methanol with a Metrohm Titrino plus 848 fitted with a silver titrode.

The AV is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize 1 g of polymer resin.

$$AV = \frac{V_s * N * 56.1}{W_s}$$

In this equation AV = acid value (mg KOH/g), V_s = volume of methanolic KOH solution needed to titrate the sample (mL), N = normality of KOH solution (mol/L), 56.1 = molar mass of KOH (g/mol) and W_s = sample weight (g).

OHV determination was performed by dissolving approximately 0.5 g of the sample in ca. 30 mL tetrahydrofuran (THF). To this solution, 15 mL of 4-(dimethylamino)pyridine solution (10 g in 1 L THF) and exactly 5 mL of ca. 1.05 M acetic anhydride in THF were added and the mixture was stirred for 50 min. The reaction solution was then hydrolyzed with 10 mL of a solution containing 20 vol% water and 80 vol% THF.

For the titration, a Metrohm Titrino Plus 848 fitted with a silver titrode and a 0.5 M KOH-solution in methanol was used.

$$OHV = AV + \frac{(V_b - V_s) * N * 56.1}{W_s}$$

In this equation OHV = hydroxyl value (mg KOH/g), AV = acid value (mg KOH/g), V_b = volume of methanolic KOH solution needed to titrate the blank (mL), V_s = volume of methanolic KOH solution needed to titrate the sample (mL), N = normality of KOH solution (mol/L), 56.1 = molar mass of KOH (g/mol) and W_s = sample weight (g).

Enzymatic activity assay. The enzymatic activities of the immobilized Novozyme® 435 and SPRIN liposorb CALB were evaluated by the model esterification of lauric acid with 1-propanol in bulk (Figure S1)ⁱ. One unit of enzyme activity corresponds to the amount of enzyme preparation required to produce 1 micromole of propyl laurate per minute under standard conditions (60 °C).

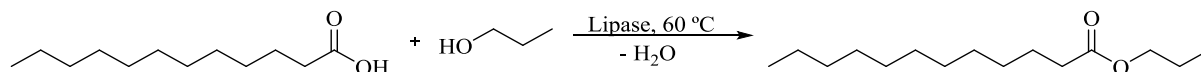


Figure S1 Esterification of lauric acid with 1-propanol in bulk.

In a 200 mL beaker, 24.0 g (0.12 mol) of lauric acid and 7.2 g (0.12 mol) of 1-propanol were mixed and melted at 60 °C. After taking the reference sample (blank), 200-300 mg of the enzyme was added to the mixture. The reaction solution was stirred at 60 °C for 20 min. A sample of the reaction mixture (100-180 mg) was taken every 5 min and dissolved in 7 mL of ethanol. To this solution, five drops of 0.1 w% phenolphthalein water/ethanol solution, used as indicator, were added. The decrease of the amount of lauric acid due to its enzymatic esterification was monitored via titration of the unreacted lauric acid with a 0.1 M ethanolic potassium hydroxide solution.

The activity U is calculated as the amount of micromoles propyl laurate formed in one minute by one gram of the enzyme, which was previously dried at 120 °C under reduced pressure for 24 h.

$$U = \frac{n_{lauric\ acid}}{m_{dry} \cdot t} \cdot \frac{AV_0 - AV_{sample}}{AV_0}$$

In this equation, $n_{\text{lauric acid}}$ is the amount in moles of lauric acid used, t the reaction time for a certain sample, AV_0 the acid value of the blank and AV_{sample} the acid value of the sample (mg KOH/g). The conversion of lauric acid was followed by AV measurements.

The activities showed to be 10700 and 16300 U ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{mol}^{-1}$) for Novozyme® 435 and SPRIN liposorb CALB, respectively. Thus, in order to achieve comparable activity for the polycondensation reactions, 10 wt% of Novozyme® 435 or 7 wt% of SPRIN liposorb CALB were employed.

Table S1. Molecular characterization of sorbitol-based polyesters with enhanced functionalities obtained by enzymatic polycondensation.

| Entry | Monomers | Sorbitol feed composition (mol%) | Sorbitol incorporated (mol%) | Potentiometric titration | | ³¹ P NMR |
|----------|------------------------|----------------------------------|------------------------------|----------------------------|-----------------------------|---|
| | | | | AV (mg KOH/g) ^a | OHV (mg KOH/g) ^a | Ratio Sec. vs. Prim. OH of sorbitol unit ^b |
| a | AA + sorbitol + 1,8-OD | 5.0 | 2.5 | 11.4 | 80.3 | 11.1 |
| b | DMA + | 5.3 | 1.4 | 0.0 | 51.5 | 6.7 |
| c | sorbitol | 10.5 | 3.2 | 0.0 | 72.5 | 9.7 |
| d | +1,10-DD | 15.8 | 3.1 | 0.0 | 83.8 | 9.7 |

AA = adipic acid; DMA = dimethyl adipate; 1,8-OD = 1,8-octanediol; 1,10-DD = 1,10-decanediol; ^a: Data obtained by potentiometric titration performed after precipitation in MeOH. ^b: Ratio of secondary vs. primary hydroxyl groups of the sorbitol unit obtained by ³¹P NMR after precipitation in MeOH.

Table S2. Solvent-cast coating formulations and related coating properties of poly(ester urethane)s based on sorbitol and 1,10-decanediol.

| Resin | OHV (mg KOH/g) | Film | Curing agent | Renewability (wt%) | Ratio NCO:OH | Acetone resistance ^a (d.r. 100) | Impact test ^a (1 kg,80 cm) | Av. Film thickness (μm) | Pencil hardness ^b |
|--------------------------------------|----------------|------|--------------|--------------------|--------------|--|---------------------------------------|-------------------------|------------------------------|
| c DMA + sorbitol + 1,10-DD | 72.5 | F21 | DES | 48 | 1:1 | + | + | 25 | 3B |
| | | F22 | DES | 56 | 0.8:1 | + | + | 22 | 3B |
| | | F23 | DES | 68 | 0.5:1 | +/- | + | 21 | 6B |
| | | F24 | IPDI | 68 | 1:1 | + | + | 16 | 4B |
| | | F25 | IPDI | 56 | 0.8:1 | +/- | + | 23 | 5B |
| | | F26 | DDI | 98 | 1:1 | +/- | + | 26 | 5B |
| | | F27 | EELDI | 97 | 1:1 | +/- | + | 19 | 5B |

DES: Desmodur N3600; IPDI: isophorone diisocyanate; DDI: dimer fatty acid diisocyanate; EELDI: ethyl ester L-lysine diisocyanate. ^a: + = good, +/- = moderate and - = poor. ^b: 6H to 2H = very hard to hard; H, F and B = moderate hard; 2B to 6B = soft to very soft.

Table S3. Molecular and thermal properties of the homopolyesters, *viz.* poly(octane adipate) and poly(decane adipate), synthesized *via* enzymatic polycondensation.

| Resin | M_n^a (kg/mol) | PDI ^a | OHV ^b (mg KOH/g) | T_m^c (°C) | ΔH_m^c (J/g) | T_c^d (°C) |
|----------------------|---------------------|------------------|--------------------------------|-----------------|-------------------------|-----------------|
| Poly(octane adipate) | 8.7 | 2.1 | 19.0 | 68 | 98 | 50 |
| Poly(decane adipate) | 6.3 | 1.7 | 30.7 | 74 | 115 | 55 |

^a: Based on SEC measurements of the precipitated polyesters, performed in HFIP and using poly(methyl methacrylate) as standard; ^b Data obtained by potentiometric titration performed after precipitation in MeOH.

^c: Data obtained *via* DSC from the second heating run; ^d: Data obtained *via* DSC from the cooling run.

Table S4. Thermal properties and crystallinity of the starting sorbitol-based polyester polyols and the related poly(ester urethane)s after curing.

| Resin | OHV (mg KOH/g) | Before curing | | | | | After curing | | | | | | | |
|--|-------------------|-----------------|-----------------|-------------------------|-----------------|--------------|--------------|--------------|-----------------|-----------------|-------------------------|-----------------|--------------|------------------|
| | | T_g^a (°C) | T_m^a (°C) | ΔH_m^a (J/g) | T_c^b (°C) | X^c (%) | Film | Curing agent | Ratio OH:NCO | T_m^a (°C) | ΔH_m^a (J/g) | T_c^b (°C) | X^c (%) | Max X^d (%) |
| c DMA + sorbitol + 1,10-DD | 72.5 | -20 | 67 | 100 | 52 | 58 | FS12 | DES | 1:1 | 59 | 70 | 25 | 36 | 47 |
| | | | | | | | FS13 | DES | 1:0.8 | 59 | 71 | 25 | 42 | 49 |
| | | | | | | | FS14 | DES | 1:0.5 | 46/65 | 15 | 16/43 | 51 | 52 |
| | | | | | | | FS15 | IPDI | 1:0.8 | 63 | 58 | 26 | 55 | 52 |
| | | | | | | | FS16 | DDI | 1:1 | 51 | 31 | 15 | 31 | 39 |
| | | | | | | | FS17 | EELDI | 1:1 | 54 | 46 | 15 | 39 | 51 |

DES: Desmodur N3600; IPDI: isophorone diisocyanate; DDI: dimer fatty acid diisocyanate; EELDI: ethyl ester L-lysine diisocyanate.

^a: Data obtained *via* DSC obtained from the second heating run. ^b: Data obtained *via* DSC from the cooling run. ^c: Crystallinity index from X-ray diffraction data is calculated using PeakFit. ^d: Maximum crystallinity calculated as: $(\text{Mass polyester} * X_{\text{polyester before curing}}) / (\text{Mass polyester} + \text{Mass cross-linker})$.

Cross-link density calculation based on DMTA measurements. The value of T_g extrapolated *via* DMA measurements is based on the response of a material to an applied oscillatory strain (or stress), and how that response varies with temperature, frequency, or both. The cross-link density was calculated according to the theory of rubber elasticity where the equilibrium elastic modulus is given by

$$\nu_e = \frac{G'}{RT} = \frac{E'}{3RT}$$

In this equation ν_e is the cross-link density expressed in mole of elastically effective network chains per cubic meter of sample, G' is the shear storage modulus, E' is the elastic storage modulus, R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the absolute temperature at which the experimental modulus is performed. Assuming that the samples do not undergo volume change with tensile strain, G' can be considered equal to $E' / (2(1 + \nu))$ where ν is the Poisson coefficient with a value of 0.5.

ⁱ Ferrario, V.; Veny, H.; De Angelis, E.; Navarini, L.; Ebert, C.; Gardossi, L. Lipases Immobilization for Effective Synthesis of Biodiesel Starting from Coffee Waste Oils *Biomolecules* **2013**, *3* (3), 514-534.