

Electronic Supporting Information (ESI) for

Lactide-derived ester oligomers for highly compatible poly(lactide) plasticizer produced through an eco-friendly process: renewable resources, biodegradation, enhanced flexibility, and elastomeric performance†

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Supporting Information consists of four figures over eleven pages.

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Annexure S1

Experimental

Materials

All air- or moisture-sensitive compounds were stored in a nitrogen charged glovebox after purification. Diethylene glycol (DEG, >99.0%, Sigma-Aldrich) was distilled three times afforded colorless liquid. Trimethylolpropane (TMP, $\geq 98.0\%$, Sigma-Aldrich) was dried at 70 °C in vacuum oven for 24 h. D,L-lactide (>99.5%, Corbion Purac, Netherland) were twice recrystallized in toluene. Tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$, 92.5–100%, Sigma-Aldrich) was distilled three times afforded colorless viscous liquid. All other reagent including ethanol (anhydrous, 99.5%, 200 proof, Sigma-Aldrich) and acetic anhydride (93.0 %, Ducksan) were used as received without further purification.

Characterizations

The ^1H NMR spectra of the oligomeric compounds, including the LO and ALO series, dissolved in CDCl_3 at a concentration of 5 mg mL^{-1} were obtained using a Bruker DPX-500 spectrometer (Bruker Bioscience, Billerica, USA) operating at 500 MHz. Proton chemical shifts were referenced to CDCl_3 (δ 7.26 ppm) using tetramethylsilane (TMS, δ 0.00 ppm) as an internal standard. The molar mass average values including the number (M_n) and the weight (M_w) were obtained by size-exclusion chromatography (SEC) using tetrahydrofuran as a mobile phase at 40 °C and the calibration curve, which was fitted with 7 polystyrene standards (Shodex, Showa Denko, Tokyo, Japan) on an Agilent 1260 Infinity LC system (Agilent Technologies, Santa Clara, USA) equipped with a refractive index detector. The synthesized LO and ALO oligomers samples were passed through Waters Styragel HT2, HT3, and HT4 columns ($10 \mu\text{m}$, $7.5 \times 300 \text{ mm}$) under a constant flow rate of 1 mL min^{-1} . Differential scanning calorimetry (DSC) measurements were performed using a Q20 (TA instrument, New Castle, USA). The samples (5–10mg) were loaded and heated up to 150 °C, held for 10 min to remove previous thermal history, and then allowed to cool to -80 °C . The samples were reheated up to 150 °C. The rates of heating and cooling were

10 °C min⁻¹. The values reported in this study were obtained from the second heating cycle. Thermal gravimetric analysis (TGA) was performed with a TA Q-500 TGA (TA instrument, New Castle, USA) under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ up to 600 °C. Scanning electron microscopy (SEM) was performed using a MIRA3 (Tescan, Brno, Czech Republic) to study the fracture surface, after sputter coating of the neat PLA and the PLA blends with platinum. Dynamic mechanical analysis (DMA) was conducted using an ARES-G2 rotational rheometer (TA instrument, New Castle, USA) under nitrogen atmosphere. The storage modulus were measured in the temperature range of -60 to 100 °C using torsion mode (a frequency of 1 Hz with a strain of 0.05%, and a ramp rate of 3 °C min⁻¹). Stress-relaxation was also tested using the above-mentioned DMA instrument at a constant strain of 5% for 80 min. Tensile testing of the neat PLA and the PLA films blended with ALO series were carried out using a universal testing machine (Instron 5567, Instron Corporation, USA) at room temperature and humidity of 40% to obtain normal strain–stress curves. The prepared specimens were evaluated by ASTM D1708 using 1 kN load cell and drawn until failure at a constant rate of 10 mm min⁻¹. All reported values are the average and standard deviation of at least five samples. Tensile recovery tests were also performed from 0 to 50 % at room temperature at a constant rate of 10 mm min⁻¹ for 20 cycles. Leaching tests were carried out to evaluate the migration ratio of the plasticizers added to the PLA blends. The 0.3 mm thick PLA blend films obtained by the above-mentioned compression molding method were cut into 1 cm × 3 cm sections and then placed in fresh solvent, including *n*-hexane as a common nonpolar solvent and water as a representative polar solvent, at room temperature for 24h. The specimens were removed from the solvent and put into a 70 °C vacuum oven until there was no more weight decrease. The weight loss was calculated based on the specimen weights of both the PLA blend films before the leaching test and after the drying process.

Biodegradation tests were performed according to OECD (Organization for Economic Cooperation and Development) 301F. In brief, the inoculum derived from activated sludge and ALO plasticizers, including aniline as a reference, were inoculated and incubated in a bottle with a mineral medium that was prepared

as described in OECD (OECD guidelines for the testing of chemicals. Section 3: degradation and accumulation. Test 301: ready biodegradability) at 25 °C for 28 days. The percentages of biodegradation of the ALO series were calculated using both (1) biochemical oxygen demand (BOD, $\text{mg}_{\text{oxygen}} \cdot \text{mg}^{-1}_{\text{test substance}}$), where the oxygen uptakes in all the bottles were measured directly using a BOD measuring system (System OxiTop® Control, Wissenschaftlich-Technische Werkstätten GmbH (WTW), Weilheim, Germany) for 28 days to produce BOD curves for each test bottle; and (2) the theoretical oxygen demand (ThOD, $\text{mg}_{\text{oxygen}} \text{mg}^{-1}_{\text{test substance}}$), *i.e.* the maximum oxygen demand required for complete biodegradation of the test substance calculated from the molecular formula of the test substance. Tin concentration of the resulting plasticizers ALO1 was confirmed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) having the detection limit of 100 ppm. As ALO1 has the largest mass ratio of Tin(II) ethyl-hexanoate among the ALO plasticizer series, it was analyzed as a representative sample. According to data from ICP-AES, a negligible amount of Tin was found in new synthesized plasticizer (ALO1) after silica filtration (Sn content: Non-detectable), when compared to ALO1 crude product (Sn content: 245 mg kg^{-1}), which is much lower than 21-CFR-175.300 regulation of FDA and catalyst acceptable for food applications (1 weight percent).

PLA film preparation with plasticizer

PLA and plasticizers (10, 25, 50, and 65 phr) were premixed by solvent casting using CHCl_3 (10% w/v). After atmosphere drying and the subsequent complete vacuum-drying, the dried PLA blend films were cut into $5 \text{ mm} \times 5 \text{ mm}$ sections to facilitate the extrusion injection process. The prepared PLA blend pellets were dried in a 70 °C vacuum oven for 24 h to fully remove the residual CHCl_3 , then were put into a conical twin screw extruder (MC 15 HT, Xplore Instruments BV, Sittard, Netherland) at 150 rpm. The melt viscous liquids were transferred to an injection molder (IM 12 Xplore Instruments BV, Sittard, Netherland) at 50 °C, to produce microtensile bars (dog-bone shape) for tensile and recovery tests. The extruder temperatures for the PLA blends with the plasticizer contents of 10, 25, 50, and 65 phr were 150,

140, 130, and 120 °C, respectively, to maintain the torque values if possible. The pellets were also pressed at 150 °C for 1 min with a force of 50 kgf m⁻² to make thin films of 1.0 mm for transparency analysis, DMA, stress-relaxation, and leaching test.

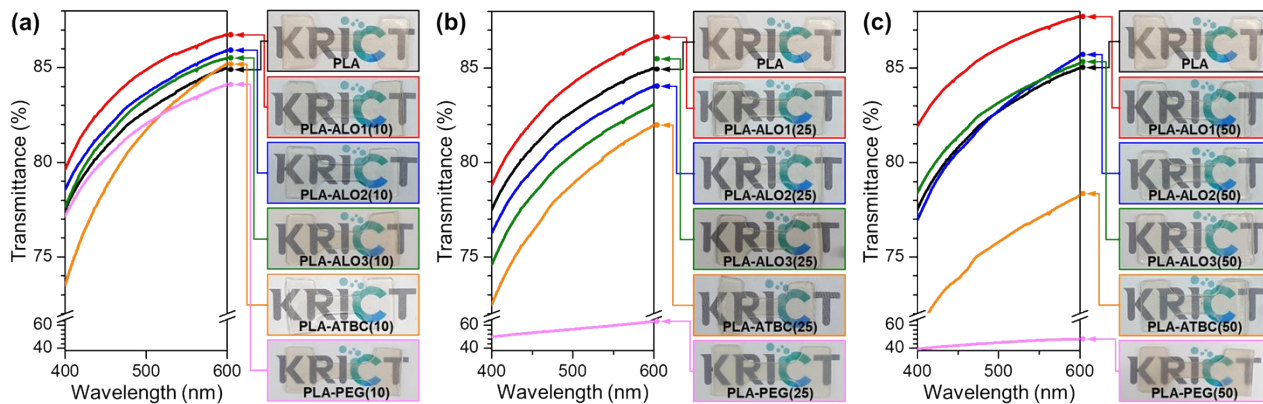


Fig. S1 UV-Vis transmittance spectra of all PLAs formulated by ALO1, ALO2, ALO3, ATBC, and PEG at (a) 10, (b) 25, and (c) 50 phr concentrations. Photographic images: all PLA dog-bones.

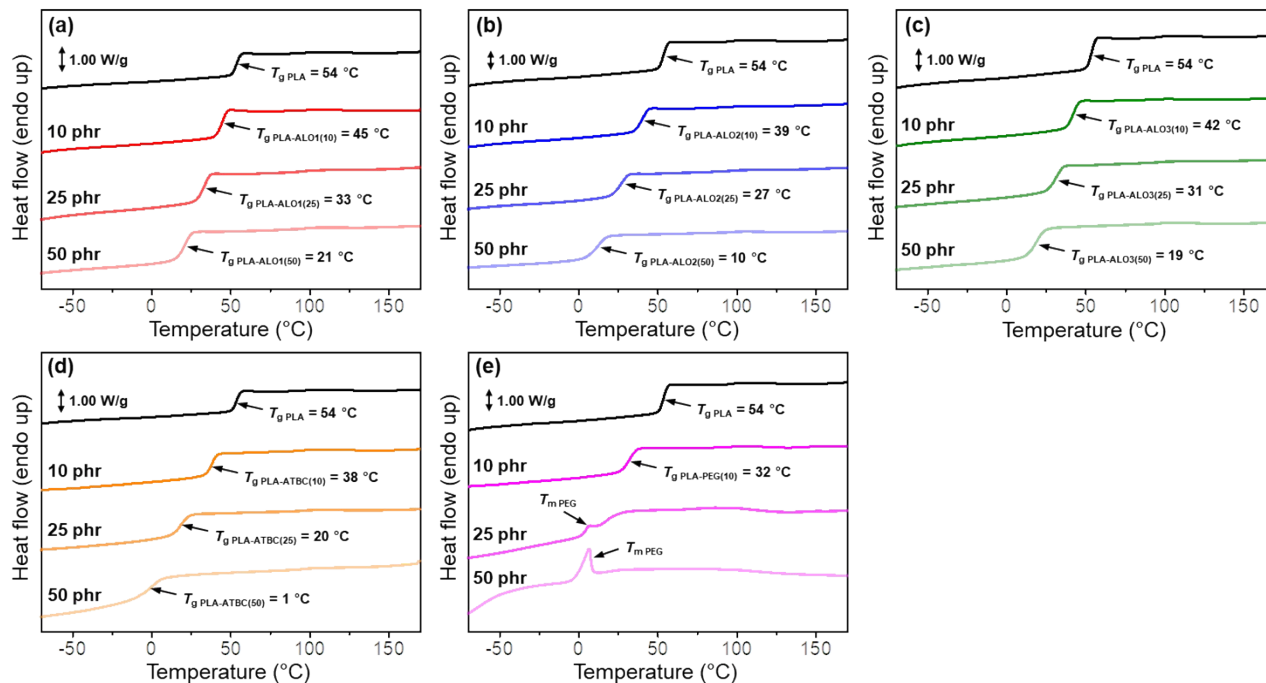


Fig. S2 DSC heat flow curves (arrows mean glass-transition temperatures (T_g) and melting temperatures (T_m)) for the PLA blended with (a) ALO1, (b) ALO2, (c) ALO3, (d) ATBC, and (e) PEG at 10, 20, and 50 phr concentrations.

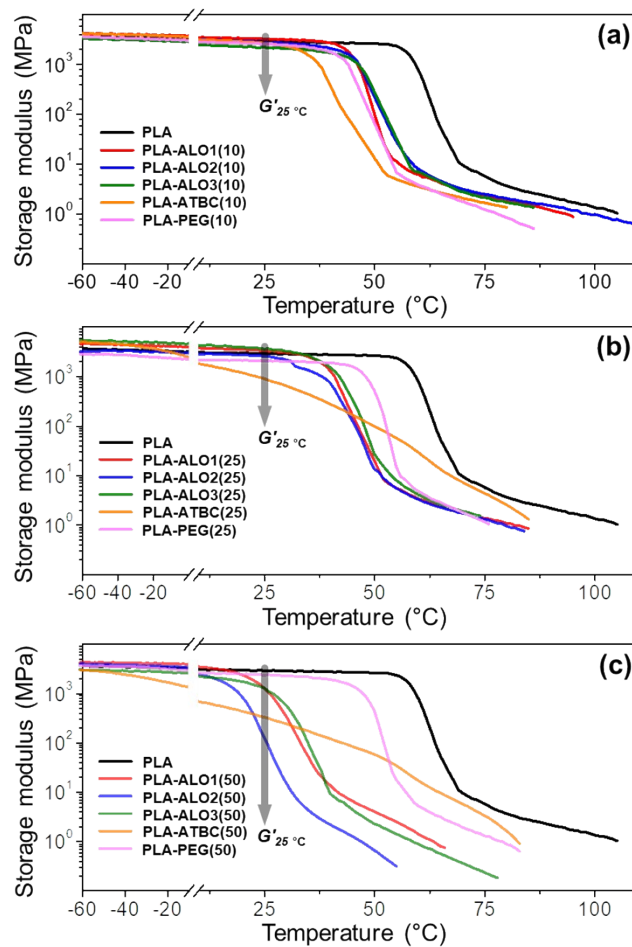


Fig. S3 Viscoelastic properties (storage moduli, G') as a function of temperature from -60 to 100 $^{\circ}\text{C}$ (torsion mode: a frequency of 1 Hz with a strain of 0.05% , and a ramp rate of 3 $^{\circ}\text{C min}^{-1}$) for PLA blends including ALO1, ALO2, ALO3, ATBC, and PEG at (a) 10, (b) 25, and (c) 50 phr concentrations.

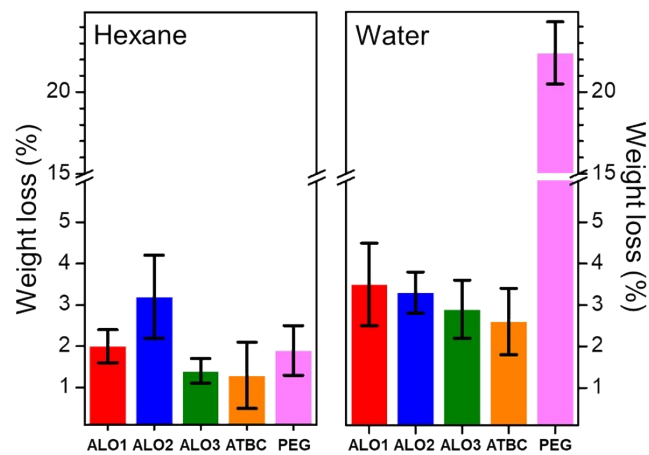


Fig. S4 Migration levels in leaching test PLA blends with ALO1, ALO2, ALO3, ATBC, and PEG at 50 phr concentration in hexane (left), a common nonpolar solvent, and water (right), a representative polar solvent, at room temperature for 24 h.

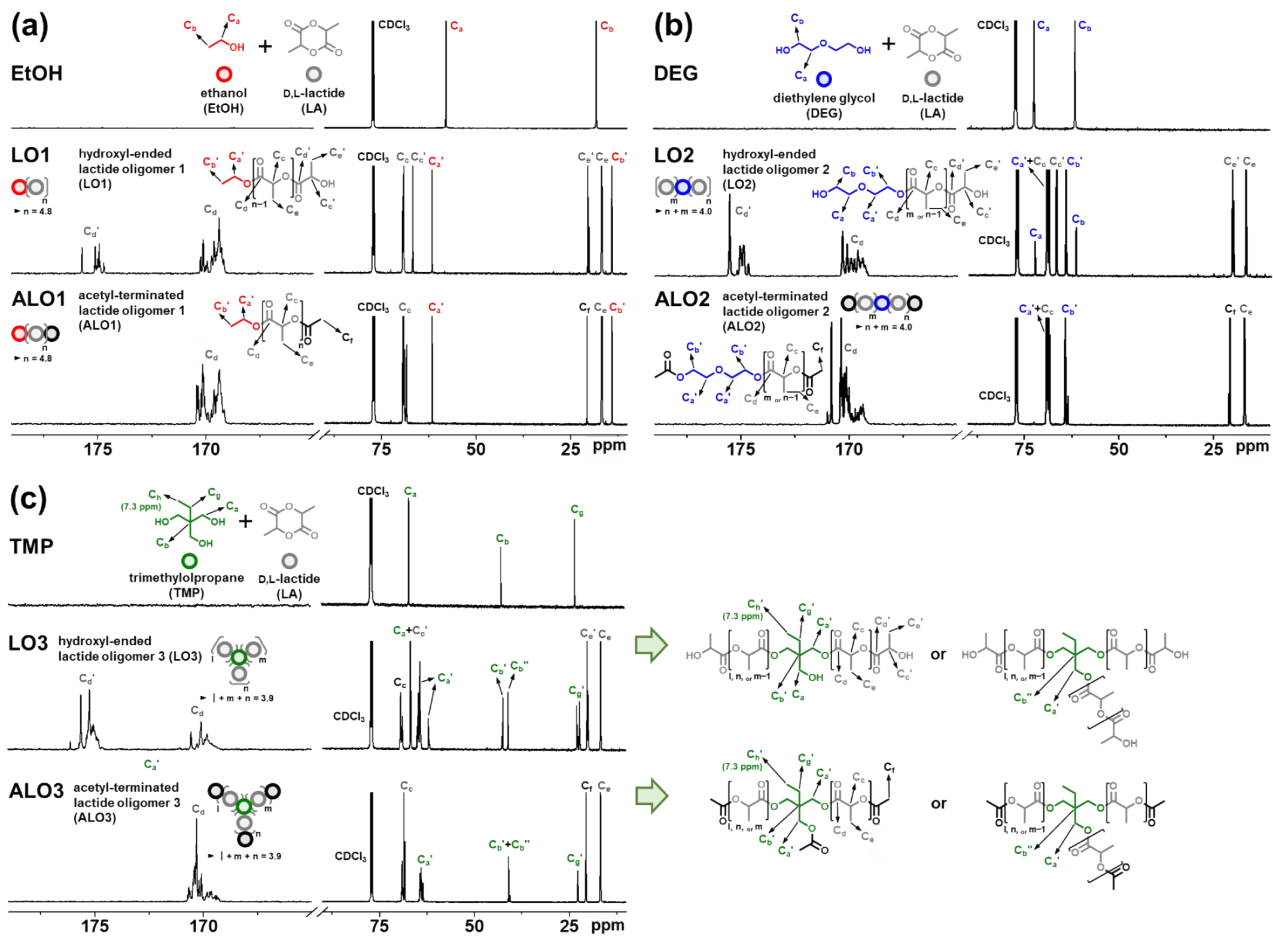


Fig. S5 ¹³C NMR spectra: (a) EtOH, LO1, and ALO1; (b) DEG, LO2, and ALO2; (c) TMP, LO3, and ALO3.