A fully renewable, effective, and highly biodegradable plasticizer: di-n-heptyl succinate

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ABSTRACT

The ubiquitous environmental presence of industrial plasticizers such as di(2-ethylhexyl) phthalate (DEHP) and the known health and environmental impact has created a need to develop truly green plasticizers that are (i) non-toxic, (ii) rapidly biodegrade, and (iii) produced from renewable feedstocks across their whole life cycle including synthesis. For example, linear succinate diesters have been shown to provide similar or better plasticizing properties compared to DEHP, excellent biodegradation kinetics and no toxicity concerns. However, the feedstocks used to synthesize said succinates were petroleum-based. In this case study, diheptyl succinate (DHPS) was fully synthesized from the commercially available, renewable feedstocks succinic acid and n-heptanol. In addition, the synthetic route was improved upon by switching to a solventless process utilizing only nitrogen gas to remove water from the esterification reaction, thereby eliminating the need for a workup. The plasticizer effectiveness of DHPS in poly(vinyl chloride) (PVC) demonstrated similar or better plasticizing properties (glass transition temperature, tensile and rheological properties) than DEHP, and comparably to previously tested succinate diesters in terms of plasticizer effectiveness. Biodegradation experiments with the common soil bacterium *Rhodococcus rhodochrous* revealed rapid biodegradation kinetics in the timeframe of 2 weeks, without the buildup of stable metabolites. Taken together, the results indicate that DHPS is a fully renewably-sourced, biodegradable, low-risk, effective and thus green plasticizer for PVC.

KEYWORDS: Green plasticizer; renewable feedstocks; solventless synthesis; phthalate; succinate; biodegradation

INTRODUCTION

Plasticizers are usually small molecules used as additives to polymers to render these more flexible, malleable, and to facilitate polymer processing.[1] Approximately 90% of the worldwide plasticizer production is used to plasticize poly(vinyl chloride) (PVC) and plasticizers are added in concentrations up to 50% to PVC.[1, 2] Because external plasticizers are not chemically bound to the host matrix, they can leach out of the blend over time and thereby reach the environment.[3, 4] Historically, the most commonly used plasticizers were phthalate diesters such as di-(2-ethylhexyl) phthalate (DEHP) and diisononyl phthalate. Phthalates are now considered ubiquitous global contaminants due to their relatively slow biodegradation kinetics coupled with high use rates.[1, 5] This is of particular concern due to the growing evidence of the endocrine-disrupting effects of DEHP, which are attributed to its monoester MEHP, which is a stable metabolite produced during the (bio)degradation of DEHP.[6-13] Another DEHP metabolite of concern is 2-ethyl hexanol which is quickly oxidized to its corresponding acid, which resists rapid biodegradation and is more toxic than DEHP itself.[13, 14] Awareness of the adverse effects of DEHP and its metabolites on health and on the environment have made it subject to regulation around the globe, such as in children’s toys and food packaging in North America, Europe, and Japan.[15-18] As a result, there is a need to replace these compounds with safer, biodegradable alternatives, that exhibit similar or superior functionality in comparison to DEHP.

In response to this need, many plasticizer producers have introduced alternative plasticizers, including compounds such as diisononyl cyclohexane-1,2-

dicarboxylate (DINCH) or tri(2-ethylhexyl) trimellitate, which are close derivatives of the heavily regulated phthalates.[19] There is an increasing number of studies showing elevated levels of these compounds in various samples including fresh water, indoor air and sludge,[20-23] as well as medical devices that are seemingly plasticized with a plasticizer-mixture that also contains the problematic DEHP.[24, 25] While there is little information on the toxicity profile of the parent compounds, there are also indications that the monoester of DINCH may be problematic.[26, 27]

In order to create truly green plasticizers in the sense of green chemistry,[28, 29] a move away from derivatized versions of phthalates is in order, and such plasticizers would have to be designed to be non-toxic, rapidly (bio)degradable to avoid persistence and bioaccumulation, and be based on renewable materials.[30] There are efforts to produce plasticizers based on various plant oils such as tung oil, and waste cooking oil,[31, 32] yet their biodegradability and toxicity are still unknown, and their production involves several synthetic steps during which toxic reagents and/or catalysts are utilized. Another approach is the development of small, non-aromatic diesters based on, for example, succinic acid,[33-36] maleic acid,[37] or short, linear diols,[38, 39] carried out in this group and others. These compounds have been shown to be excellent plasticizers while also being very biodegradable and not producing stable metabolites during their breakdown. In addition, a series of toxicological assays and a multigenerational *in vivo* study raised no concerns about potential toxicity of these compounds.[27, 40, 41] However, one of the drawbacks of the studied compounds is that these still rely on the use of petroleum-derived feedstocks, and the synthetic route included the use of toluene.[33, 35]

Therefore, this study aimed to synthesize and evaluate di-n-heptyl succinate (DHPS) as a fully renewably sourced plasticizer based on microbially produced succinic acid and castor oil-based n-heptanol (Fig. 1A). The one-step sulphuric acid-catalyzed synthetic esterification method in equimolar amounts was optimized to eliminate the use of solvents and reduce the amount of waste generated during workup. Once synthesized, the fully renewably-sourced DHPS was tested for its plasticizer effectiveness in PVC as well as for its biodegradation kinetics using a common soil bacterium, and the results were compared to the commercially important DEHP and similar linear succinate diesters investigated previously.

EXPERIMENTAL SECTION

Materials: Unplasticized PVC (UPVC; K50) was obtained from Solvay Benvic (Chevigny, France). Renewably sourced n-heptanol (99.9%) and succinic acid (99%) were obtained from Arkema (King of Prussia, PA) and Reverdia (Cassano, Italy), respectively. Sulphuric acid (98%) and stearic acid (97%) were purchased from Fisher Scientific (Montreal, QC), and epoxidized soybean oil from Galata Chemicals (Southbury, CT).

The biodegradation experiment was carried out using the common soil bacterium *Rhodococcus rhodochrous,* American Type Culture Collection (ATCC) 13808 in Minimum Mineral Salt Medium (MMSM), containing 4.0 g/L NH_4NO_3, 6.0 g/L Na_2HPO_4, 4.0 g/L KH_2PO_4, 0.2 g/L $MgSO_4{\cdot}7H_2O$, 0.01 g/L $CaCl_2{\cdot}2H_2O$, 0.01 g/L $FeSO_4{\cdot}7H_2O$, and, 0.014 g/L Na_2EDTA (all Fisher Scientific).

Dean-Stark synthesis of DHPS

Using n-heptanol (39.51 g, 340 mmol), succinic acid (20.0 g, 169.4 mmol) and catalytic amounts of H_2SO_4 in 200ml toluene, DHPS was synthesized by Dean–Stark esterification at 125°C, as described previously.[33] Briefly, the workup included, after cooling the mixture, neutralization with about 50 mL of $NaHCO_3$ and after the cessation of CO_2, extraction of the product with dichloromethane (DCM; 3 aliquots of 50 mL each) followed by drying with Na_2SO_4. Finally, solvent removal was done using a rotatory evaporator (95 ^{o}C and pressure = 1.2 kPa). The yield was 93% and purity was approximately 99% (^{1}H-NMR, Fig. 1B). δ (ppm) = 0.90 [t, 6H, $CH_2C\mathbf{H_3}$], δ (ppm) = 1.33 [m, 16H, $CH_2(C\mathbf{H_2})_{\mathbf{4}}CH_3$], δ (ppm) = 1.60 [m, 4H, $COOCH_2C\underline{\mathbf{H_2}}C\underline{H}_2$], δ (ppm) = 2.65[s, 4H, $CO(C\mathbf{H_2})_2CO$], δ (ppm) = 4.10 [t, 4H, $COOC\mathbf{H_2}CH_2$].

Solventless synthesis of DHPS

Using a similar setup as for the Dean-Stark synthesis, but lacking the solvent toluene, n-heptanol (297.0 g, 2.55 mol), succinic acid (150.0 g, 1.27 mol), and H_2SO_4 (1.10 g, 11.2 mmol) were stirred at 110°C for 120 min. During the last 90 min, nitrogen gas was bubbled through the reaction mixture at a rate of approximately 20 mL/min to strip water generated during the reaction, which was then collected in the Dean-Stark trap. The resulting liquid was not further purified. The yield was 98% and purity was approximately 98% (^{1}H-NMR, Fig. 1B). δ (ppm) = 0.90 [t, 6H, $CH_2C\mathbf{H_3}$], δ (ppm) = 1.33 [m, 16H, $CH_2(C\mathbf{H_2})_{\mathbf{4}}CH_3$], δ (ppm) = 1.60 [m, 4H, $COOCH_2C\underline{\mathbf{H_2}}C\underline{H}_2$], δ (ppm) = 2.65 [s, 4H, $CO(C\mathbf{H_2})_2CO$], δ (ppm) = 4.10 [t, 4H, $COOC\mathbf{H_2}CH_2$]. (^{13}C-NMR, Fig. 1C): δ (ppm) = 13.85 [S, CH_2CH_3], δ (ppm) = 22.54 [S, $\mathbf{C}H_2CH_3$], δ (ppm) = 25.90 [S, CH_2, $CH_2\mathbf{C}H_2CH_2$], δ (ppm)=28.54 [S, CH_2, $CH_2\mathbf{C}H_2CH_2$], δ (ppm)=28.90 [S, CH_2, $CH_2\mathbf{C}H_2CH_2$], δ (ppm)=29.10 [S, 1C, CH_2, $CO(\mathbf{C}H_2)_2CO$], δ (ppm)=31.69 [S, 1C, CH_2, $CO(\mathbf{C}H_2)_\mathbf{2}CO$], δ (ppm)=64.54 [S, CH_2, $CH_2\mathbf{C}H_2O$], δ (ppm)=172 [S, CO, $\mathbf{C}O(\mathbf{C}H_2)_\mathbf{2}\mathbf{C}O$]. Figure 1B) compares the ^{1}H NMR spectra for the DHPS made by the standard synthesis method against that made by the improved method while Figure 1C) shows the ^{13}C NMR spectra of the DHPS. The plasticizer was clear and colourless (200-1000 nm) and had a viscosity of 10.4 cP (22 °C).

Synthesis of monoheptyl succinate (MHPS)

MHPS was needed as a standard for the biodegradation experiments and was synthesized using the same solventless system as for the synthesis of DHPS. N-heptanol (29.51 g, 254 mmol), succinic acid (30 g, 254 mmol), and catalytic amounts of H_2SO_4 were heated to 110°C for 90 min, while nitrogen gas was continuously bubbled through the reaction mixture at a flow rate of approximately 20 ml/min. The resulting mixture was colorless, and the product was obtained by recrystallizing from hexanes. The yield was 80% and purity approximately 99% (^{1}H-NMR). δ (ppm) = 0.9 [t, 3H, $CH_2C\mathbf{H_3}$], δ (ppm) = 1.3 [m, 8H, $CH_2(C\mathbf{H_2})_\mathbf{4}CH_3$], δ (ppm)=1.6 [m, 2H, $COOCH_2C\underline{\mathbf{H_2}}C\underline{H}_2$], δ (ppm) = 2.63 [t, 2H, $CH_2OOCC\mathbf{H_2}CH_2COOH$], δ (ppm) = 2.69 [t, 2H, $CH_2OOCCH_2C\mathbf{H_2}COOH$] δ (ppm) = 4.10 [t, 2H, $COOC\mathbf{H_2}CH_2$].

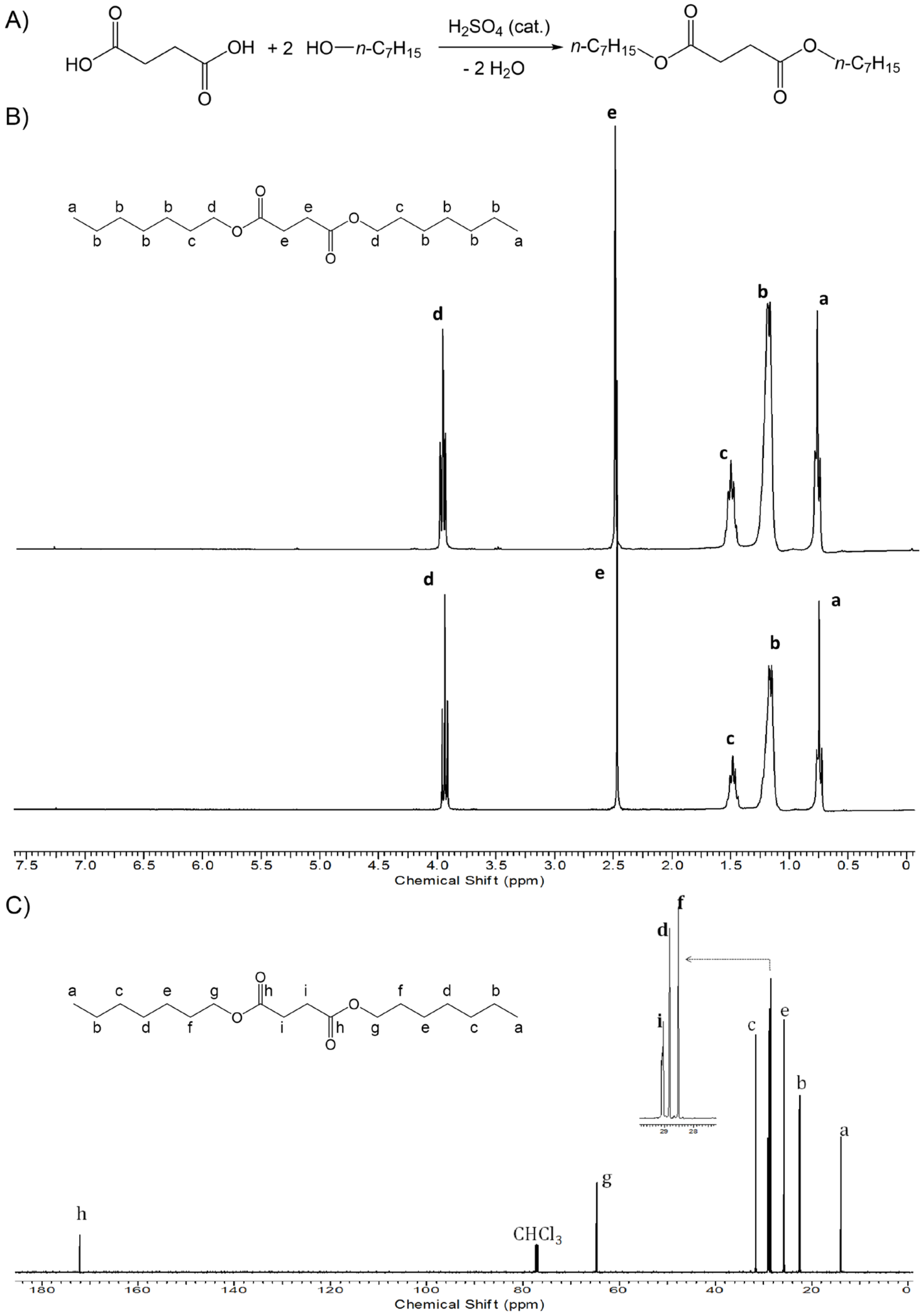

Figure 1. (**A**) Schematic of esterification reaction of succinic acid with n-heptanol to form DHPS and water. (**B**) ^{1}H-NMR of DHPS produced by (1) the classic Dean-Stark process with toluene and (2) the alternative, solventless process. (**C**) ^{13}C-NMR of DHPS produced by the alternative, solventless process.

Plastic formulation

Following a previously established protocol,[33] plasticized blends at a plasticizer concentration of 28.6 wt.-% (40 phr; parts per hundred rubber; typical loading for commercial blends) were prepared by extruding DHPS with unplasticized PVC using a Haake Minilab conical intermeshing twin-screw extruder (Thermo Electron Corporation, Beverly, MA) in a two-step process. In a first step, blends containing 20 phr of DHPS (plasticizer) were prepared, which also contained 5 phr of stearic acid (lubricant) and 4 phr of epoxidized soy bean oil (heat stabilizer). To this blend, another 20 phr of DHPS were added in a second step. The two-step method was required to ensure blend homogeneity and during each step, all material was passed the through the extruder at least twice, meaning all material had passed through the extruder at least 4 times. The extruder conditions were: rotation speed 60 min^{-1}; torque range up to 5 N·m; screw length 109.5 mm; screw diameter 5/14 mm (i.e., conical geometry); batch size 3 g; operating temperature 110°C (first step) and 130°C (second step). The final 40-phr blend was cut into small pieces for direct DSC analysis and the molding process described below.

Hot press molding

Following previously established protocols,[36, 42] tensile test bars and circular disks for rheology were produced using a heated manual hydraulic press (press: Carver, Wabash, IN; temperature controllers: Watlow, St. Louis, MO). The finely cut 40-phr blend was filled into the appropriate mold and pressed at 160°C for 50 min at increasing pressure from 0.1-0.3 kN/cm^2 (1-3 MPa). Test bar dimensions adhered to the standardized testing protocol ASTM-D638 for tensile properties[43] and were: thickness (T_o): 1.4 mm; width of narrow section (W_o): 3.3mm; length of narrow section: 17.8 mm; overall length: 64 mm; overall width: 10 mm. Disk dimensions were based on the radius of the rheological plates in accordance with ASTM-D4440:[44] radius: 12.5 mm; thickness: 1 mm.

Differential Scanning Calorimetry (DSC)

The glass transition temperature T_g of the DHPS/ PVC blend was measured in triplicate by temperature-modulated differential scanning calorimetry (mDSC) using a TA Instruments Q2000 (New Castle, DE). The temperature modulation allows for the separation of reversible transitions such as the T_g from non-reversible transitions such as the melting point.[38] In brief, following an established protocol,[33] several freshly cut thin slices of blend were placed into a standard DSC pan (TA Instruments, model #070221) and loaded into the instrument. Two heating cycles from -90°C - 100°C superimposed by a sinusoidal modulation of 1.27°C with a period of 60s were carried out and the T_g was determined from the recorded non-reversible heat flow of the second heating cycle using the half-height method according to ASTM-D3418.[45]

Tensile Testing

Tensile testing was carried out on a Shimadzu Easy Test instrument (Kyoto, Japan) equipped with a 500 N load cell following a previously established protocol[46] based on ASTM-D638.[43] Test specimens were desiccated for at least 48h prior to testing and the exact dimensions of each test bar recorded using a digital micrometer. Testing conditions were: initial grip separation (L_0): 32.6 mm; strain rate: 5 mm/min. The obtained stress-strain curves were used to obtain elongation at break, stress at break, and secant modulus at 25% elongation ($EL_{25\%}$) for 5 test bars.[33, 36]

Rheology

Oscillatory shear tests were performed using a strain-controlled Anton Paar MCR 302 rheometer (St-Laurent, QC) with parallel plate geometry (radius: 12.5 mm, distance between plates: 1mm), convection oven attachment (CTD 450), and under a nitrogen atmosphere to avoid sample oxidation. Following a previously established protocol,[42] test specimens were desiccated for at least 48h prior to testing, loaded into the cell and allowed to heat to 110°C, and trimmed to match the exact radius of the parallel plates. A strain amplitude within the linear viscoelastic range of 5% was applied over a frequency range from 0.3 – 300 rad/s (0.048-48 Hz) was applied at 10°C intervals from 110°C - 180°C. The software Rheoplus (V.3.61, Anton Paar) was used to calculate storage moduli (G') and loss moduli (G''). Master curves were generated using a customized time-temperature superposition algorithm that extended the frequency range of the individual measurements to a reference temperature of 140°C.[42]

Biodegradation Experiments

The common soil bacterium *Rhodococcus rhodochrous* was used as a model organism because of its capability to break down even relatively hydrophobic compounds such as plasticizers.[33, 47] Following a previously established protocol,[35] 500-ml Erlenmeyer flasks were filled with 100 ml of MMSM, 10 mM DHPS, 2 g/L hexadecane as carbon source, and 0.1 g L^{-1} yeast extract, fitted with a foam cap, and autoclaved at 121 °C and 100 kPa for 15 minutes (Steris Amsco Lab 250). Once cooled, flasks were inoculated with 1 ml of cell broth from a previously grown bacterial culture using sterile techniques. One flask was not inoculated and served as an abiotic control. The flasks were then put into an incubator-shaker (Multitron ll, Infors AG, Basel, Switzerland) at 30 °C and 140 rpm for the duration of the experiment. For each data point, whole shake flask extractions were carried out due to the inhomogeneity of the sample. The abiotic control was extracted at the same time as the last flask in the series (i.e., day 13). Before extraction, H_2SO_4 was added to adjust pH to 2-3 and the flask was extracted using 20 mL of $CHCl_3$ containing 2 g/L pentadecane as internal standard for gas chromatography (GC). Using a separatory funnel, the organic phase was collected and stored in vials at 4°C until GC analysis. Half-life was calculated for the first hydrolysis step from diester to monoester based on a first-order expression.

NMR spectroscopy

NMR spectroscopy was conducted using a Varian Unity-500 spectrometer (^1H = 500 MHz) with an average of 8 scans for ^1H-NMR and 512 scans for ^{13}C-NMR using deuterated chloroform ($CDCl_3$) as a solvent for DHPS, dimethyl sulfoxide-d6 (DMSO-d6) for MHPS, and tetramethylsilane (TMS) as internal standard. The chemical shifts δ are indicated in ppm.

Gas chromatography (GC)

A Thermo Scientific Trace GC Ultra with AI3000 autosampler (Waltham, MA) fitted with a Restek RTX-5 column (length 30 m, ID 0.32 mm, 0.25 µm film; Bellefonte, PA) and flame ionization detection (FID) was used for compound quantification. Calibration curves were prepared using the synthesized DHPS and MHPS, as well as commercial standards for heptanol, heptanoic acid and hexadecane.

Statistical Analysis

Statistical analysis was performed using GraphPad Prism software 5.0 (San Diego, California, USA). One-sample t-tests and one-way ANOVA tests with a Bonferroni post-test were carried out to determine significance. A p-value less than 0.05 was deemed significant.

RESULTS AND DISCUSSION

Synthesis of DHPS

This study explored the synthesis of completely renewably-sourced diheptyl succinate (DHPS) as both starting materials, succinic acid and n-heptanol, are commercially available and produced from renewable resources. Succinic acid, identified by the US Dept. of Energy as one of the top 12 value added chemicals from biomass,[48] is already being produced by industrial microbial fermentation processes on the scale of kilo-tonnes per year,[49] and processes utilizing non-edible "waste" biomass such as corn stover and crude glycerol as carbon sources are being developed.[50] Renewable n-heptanol is commercially produced from heptanal, a side product generated during the production of the nylon-11 precursor methyl-10-undecenoate from castor oil.[51]

DHPS was synthesized using two different approaches: First, it was synthesized using a 1:2 molar ratio of succinic acid to n-heptanol via the Dean-Stark esterification method employing catalytic amounts of concentrated H_2SO_4 and toluene as solvent. Using this process, DHPS was synthesized using bio-based succinic acid and n-heptanol in good yield (93%) and purity (99%). However, this approach relied on the solvent toluene, deemed "problematic" in a recent review of several solvent selection guides for various reasons. In addition, the removal of toluene (bp = 110.6°C) during the workup by using a rotatory evaporator is an energy-intensive step. The principal role of a solvent such as toluene in a classic Dean-Stark setup is to promote an efficient heat transfer within the reaction as well as stripping the produced water from the reaction mixture to drive the reaction to completion according to Le Chatelier's principle.

In the second approach, reaction conditions and time, catalyst load, and required workup steps were optimized, allowing for the reaction to be carried out without a solvent using the same Dean-Stark setup. In this modified reaction, the liquid reactant n-heptanol ensured an efficient heat transfer within the reaction mixture, and nitrogen gas was bubbled through the reaction vessel to strip water generated during the reaction, which was then collected in the Dean-Stark trap. The reaction was carried out at 110°C and thereby above the boiling point of water. Without requiring any workup, this solventless setup also produced DHPS in good yield (98%) and purity (98%). The slightly lower purity compared to the traditional Dean-Stark (99%) setup is likely explained by the lack of workup, meaning the catalyst (H_2SO_4) remained in the final product. In turn, the small presence of acid in DHPS produced by the solventless method may pose problems in certain applications and must always be considered.

Rough e-factor[52] calculations are 3 for the solventless method, and 11 for the classic Dean-Stark method employing toluene. This difference is explained by the lack of workup for the solventless method, where the only generated waste is nitrogen gas and liberated water, while in the classic Dean-Stark method, an aqueous neutralizing agent ($NaHCO_3$) and drying agent (Na_2SO_4) are generated as waste besides the solvent toluene. In addition, the distillation step on the rotatory evaporator with attached chiller has a power consumption in the order of several kW/h, which was completely eliminated in the solventless method. Further improvements of the solventless process could include performing the reaction in a closed nitrogen atmosphere that would allow for a relatively easy recycling step of nitrogen. It would simply have to be dried and re-pressurized, thereby further reducing the e-factor for the solventless method.

Plasticizer effectiveness and biodegradation kinetics of DHPS

While previous studies have shown the suitability of succinate diesters to serve as effective plasticizers for PVC,[34-36] DHPS was never previously evaluated as a plasticizer. In the following, DHPS' plasticizer effectiveness and biodegradation kinetics using a common soil model organism will be compared to previously published data on the commercial important plasticizer DEHP as well as a series of succinate homologues with even-numbered linear side chains (C_2-C_8), and the branched di-(2-ethylhexyl) succinate.[35, 36]

Plasticizer Effectiveness

DHPS was incorporated into non-plasticized poly(vinyl chloride, PVC) at a concentration of 40 parts per 100 parts rubber (40 phr), which corresponds to 28.6 wt-% plasticizer. This concentration is well within the range of commercially used plasticizer concentrations and 40 phr was chosen specifically to ensure that the results would be comparable to previous studies on succinate diesters in this group.

Glass Transition Temperature T_g

Plasticizer addition reduces the T_g of polymers by facilitating chain movement and therefore, one measure of plasticizer effectiveness is the ability of a plasticizer to reduce the T_g. DHPS was shown to effectively decrease the T_g of PVC from +82°C (non-plasticized PVC[53]) to -27 ± 0.7°C (40 phr DHPS in PVC). In comparison, DEHP only reduced the T_g to -5°C (Fig. 2A), suggesting that DHPS is superior to DEHP at reducing the T_g of PVC. When comparing T_g reduction potential to other linear succinate diesters, DHPS falls well into the trend of increased T_g reduction with increasing side chain length of the plasticizer (Fig. 2A).

The decrease in T_g with increasing number of carbon atoms in succinate esters was also predicted in a recent computational study which compared the calculated performance of bio-based plasticizers including esters of succinic acid, levulinic, oleic and adipic acids with DEHP.[54] The study correctly predicted that succinate plasticizers, specifically the branched DEHS, would be more effective than DEHP in reducing the T_g of PVC. However it has been previously shown that dihexyl succinate (DHS), differing from DEHS only by the lack of the ethyl branch, is a similarly good plasticizer, suggesting that the ethyl branch is not required (Fig 2A).[36] This is important because the added ethyl branch results in the buildup of the recalcitrant and potentially problematic metabolite 2-ethyl hexanol during biodegradation,[33] which is not observed for DHS where the released linear n-hexanol is rapidly biodegraded.[35]

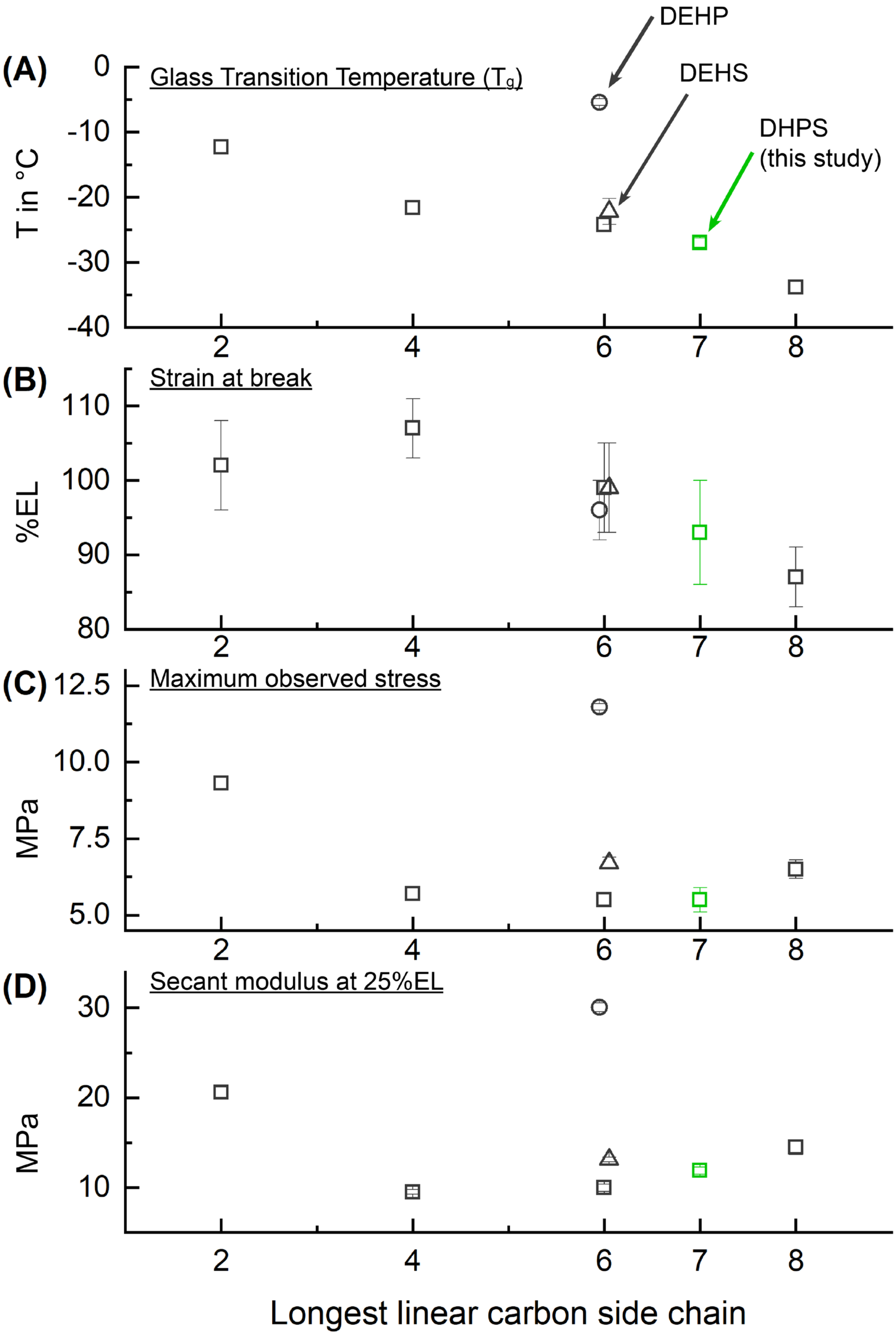(A)
Glass Transition Temperature (T_g)
T in °C
0
-10
-20
-30
-40
DEHP
DEHS
DHPS
(this study)
2
4
6
7
8
(B)
Strain at break
%EL
110
100
90
80
2
4
6
7
8
(C)
Maximum observed stress
MPa
12.5
10.0
7.5
5.0
2
4
6
7
8
(D)
Secant modulus at 25%EL
MPa
30
20
10
2
4
6
7
8
Longest linear carbon side chain

Figure 2: Measures of plasticizer effectiveness vs. longest side chain length for DHPS (green square, this study) in comparison to other linear succinates (gray squares; from literature: C_2: diethyl succinate, DES; C_4: dibutyl succinate, DBS; C_6: di-n-hexyl succinate, DHS; C_8: di-n-octyl succinate, DOS; branched di-(2-ethylhexyl) succinate (DEHS, gray triangle), and the commercially important di-(2-ethylhexyl) phthalate (DEHP; gray circles). (A) Glass transition temperature T_g, (B)-(D) Strain at break, tensile strength, and secant modulus at 25%EL from tensile testing experiments.[36] Error bars indicate standard deviation, n=5. Adapted from Erythropel et al.[35, 36] DEHP: di-(2-ethylhexyl) phthalate; DEHS: di-(2-ethylhexyl) succinate; DHPS: di-n-heptyl succinate; %EL: % elongation; MPa: mega-Pascals

Tensile testing

Generated stress-strain curves (see Fig. 3 for an example) were used to extract a variety of important parameters, such as elongation at break (highest value on x-axis), maximum observed stress (highest value on y-axis), and Young's modulus for materials with a linear stress-strain response (slope of linear curve). Because for the blends tested in this study, no linear section was present, the secant at 25%EL was calculated as per ASTM-638.[36] Generally, the better the plasticizer, the higher the strain at break, and the lower the tensile strength and modulus.

The tensile testing results indicate that blends with DHPS show a similar strain at break and a lower tensile strength and secant modulus at 25%EL than DEHP ($p < 0.001$, one-way ANOVA with Bonferroni post-test), suggesting a better plasticizer effectiveness of DHPS over DEHP (Fig. 2B-D). When comparing the results to previously tested linear succinate diesters of varying side chain length,[36] DHPS fits into the observed trends for strain at break (Fig. 2B; DHPS vs. DHS and DHPS vs. DOS: $p > 0.999$) and tensile strength (Fig. 2C; DHPS vs. DHS: $p > 0.999$; DHPS vs. DOS: $p < 0.001$). Similarly, the measured value for secant modulus at 25%EL of DHPS (Fig. 2D) lies between the reported values for DHS (C_6) and DOS (C_8; DHPS vs. DHS and DHPS vs. DOS: $p < 0.001$). Taken together, these results further support the previously hypothesized maximum plasticizer effectiveness of succinate diesters with a side chain length of C_4-C_6 for tensile testing experiments.[36] Nonetheless, DHPS was shown to be more effective than the commercial DEHP, and similarly effective as petroleum-based succinates of C_4-C_6 carbon side length.

The observed "ideal" side chain length can be explained as follows: although several theories on exact plasticizer mechanism exist, it is clear that a good plasticizer needs to strike a balance between polar groups that ensure compatibility with the blended polymer (e.g., relatively polar ester groups that interact with the C=Cl bond in PVC) as well as non-polar groups that hinder chain-chain interactions within the polymer (e.g., non-polar alkyl chains). For succinate diesters, this balance seems to be around a side chain length of 5 carbons, with no added benefit of branching as evidenced by the higher stress and modulus values of the branched DEHS compared to the unbranched DHS or DOS (Fig. 2C-D). A more detailed discussion on the topic can be found elsewhere.[36]

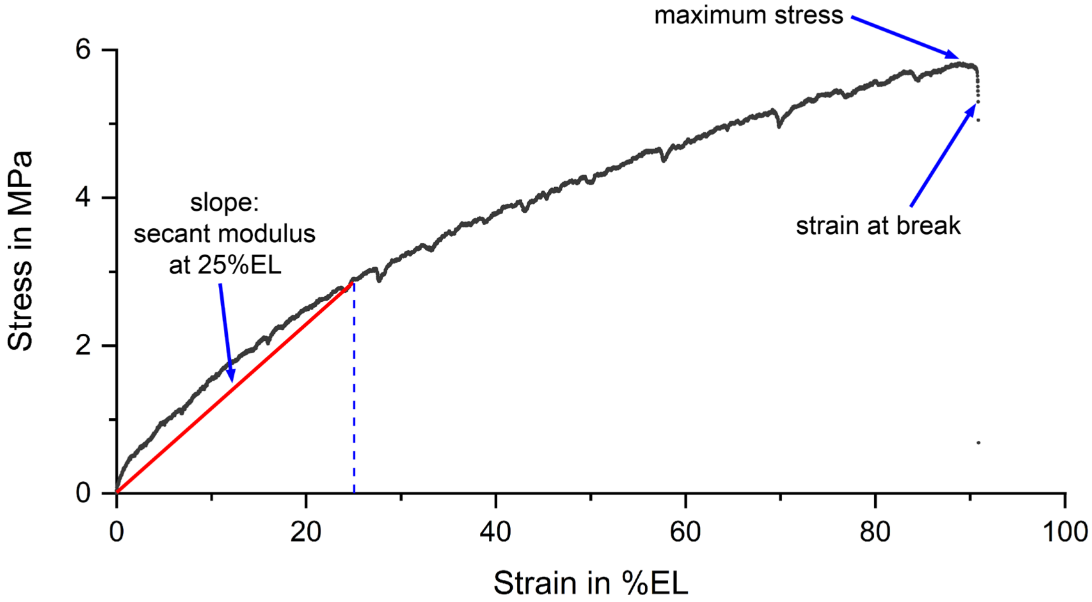

Figure 3. Example of a recorded tensile stress-strain curve for PVC/DHPS at 40 phr. Strain at break, tensile strength and secant modulus (slope in red) at 25%EL indicated.

Rheology

Rheological master curves were prepared to study processing parameters of PCV/plasticizer blends at elevated temperatures. Comparing the master curves (Fig. 4) generated with blends of PVC/DHPS to those of PVC/DEHP, it is apparent that for a given frequency (horizontal axis), the resulting moduli are lower for DHPS, suggesting superior plasticizer effectiveness at elevated temperatures. When comparing to master curves for the closely related DHS (C_6 side chains) and DOS (C_8 side chains) published previously,[42] DHPS (C_7 side chains) behaves similarly to DHS and better than DOS.

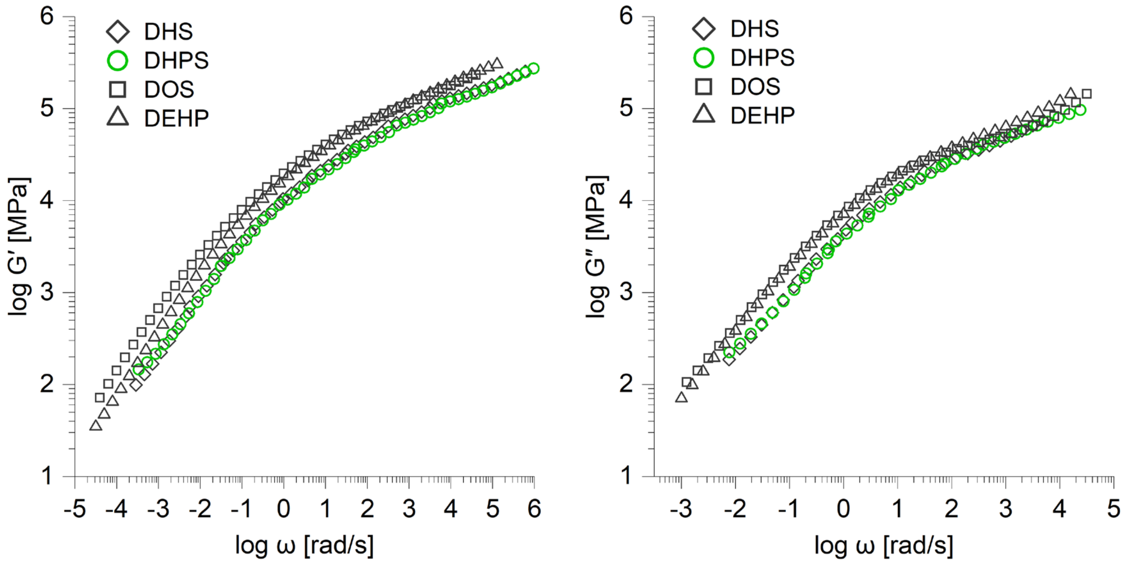

Figure 4. Rheological master curves of storage (G′) and loss (G″) moduli of a 40 phr DHPS/PVC blend (green circles) constructed by shifting 8 isotherms, $T_{ref.}$ = 140°C. Master curves for PVC blends plasticized with dihexyl succinate (DHS), dioctyl succinate (DOS) and di-(2-ethylhexyl) phthalate (DEHP)[42] included for reference. MPa: mega-Pascals; ω: frequency; rad: radians.

Biodegradation kinetics

Because plasticizers can be expected to leach into the environment over time due to the non-covalent nature of the polymer-plasticizer bonds,[4] it is imperative that plasticizers or their metabolites are not persistent which in turn could lead to potential other negative consequences.[19] In order to assess the biodegradation potential of DHPS, a previously established protocol using the common soil bacterium *Rhodococcus rhodochrous* as a model organism was utilized.[33] *Rhodococci* are known to be able to metabolize a wide variety of hydrophobic compounds[55] including plasticizers.[47]

As observed for a variety of diesters previously, the biodegradation of DHPS by *R. rhodochrous* occurred through the subsequent hydrolysis of the two esters bonds present, likely by esterase enzymes expressed on the cell envelope.[56] As shown in Fig. 5A, upon the first hydrolysis step, the monoester MHPS and one equivalent of n-heptanol are released, followed by a second hydrolysis step to yield succinic acid and another equivalent of n-heptanol. N-heptanol is then further oxidized to its corresponding organic acid, heptanoic acid. The liberated succinic acid was not quantified due to the extraction procedure geared towards lipophilic compounds.

The results of the DHPS biodegradation experiment are shown in Fig. 5B and indicate that DHPS is rapidly broken down within about one week, and the released heptanol, its oxidation product heptanoic acid, and MHPS are completely removed from the broth by day 13. Interestingly, the concentration of hexadecane remains stable throughout the course of the experiment, suggesting that the bacteria preferentially consumed the liberated heptanoic acid, and likely succinic acid, as a carbon source as has been observed previously.[35]

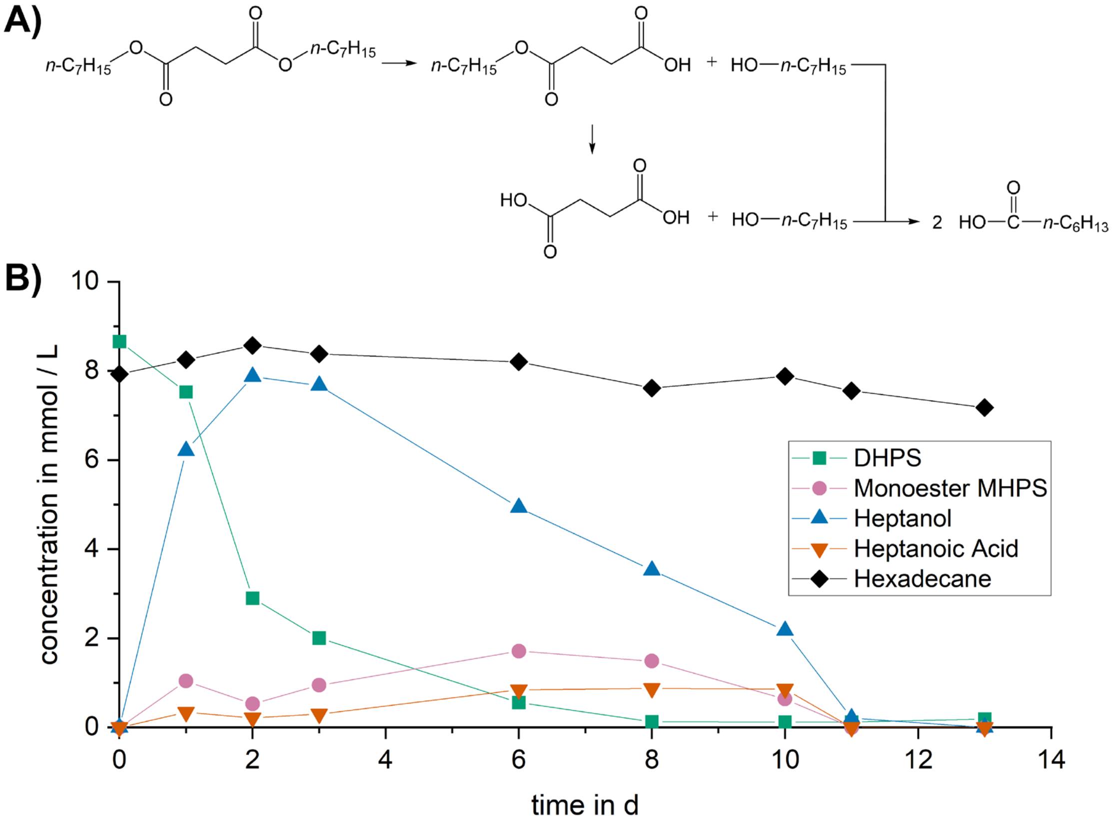

Figure 5. (**A**) Biodegradation pathway for succainte diesters by the common soil bacterium *Rhodococcus rhodochrous*.[33] (**B**) Biodegradation of DHPS by *R. rhodochrous* and appearance and subsequent degradation of metabolites over the course of 13 days in the presence of hexadecane as carbon source.

Assuming first order kinetics for the first hydrolysis step, a half-life of 1.3 d was calculated for DHPS. Fig.6A depicts the comparison of the calculated half-life to other linear alkyl succinate diesters analyzed previously[35] and shows that the calculated half-life fits the observed trend. The observed increase in half-life with increasing side chain length is likely a result of decreasing aqueous solubility of the compounds, thereby rendering the compounds less available to the microbes in their aqueous environment.[33]

It should be noted that this type of experiment is limited to ~30 d, during which little to no biodegradation of DEHP was observed.[33] Fig. 6B compares the time-frames until all produced metabolites were removed from the biodegradation broth, which is of similar importance as the breakdown of the parent compounds since the produced metabolites can sometimes be more problematic than the parent compound, such as in the case of DEHP.[13] The results for DHPS again fit into the observed trends of similar succinate diesters. As reported previously, plasticizers containing the branched 2-ethyl hexanol produce the stable metabolite 2-ethyl hexanoic acid, which is only very slowly broken down further, likely because the ethyl-branch in the β-position hinders β-oxidation.[57]

The performed biodegradation experiments were idealized as they do not reflect the various possible environmental consortia of microbes that leached plasticizers may be exposed to. As a result, the absolute values reported in Fig.6 do not represent "true" biodegradation rates of the tested compounds in the environment, but rather, the data serve to be able to compare the effects of side chain length on biodegradation potential.

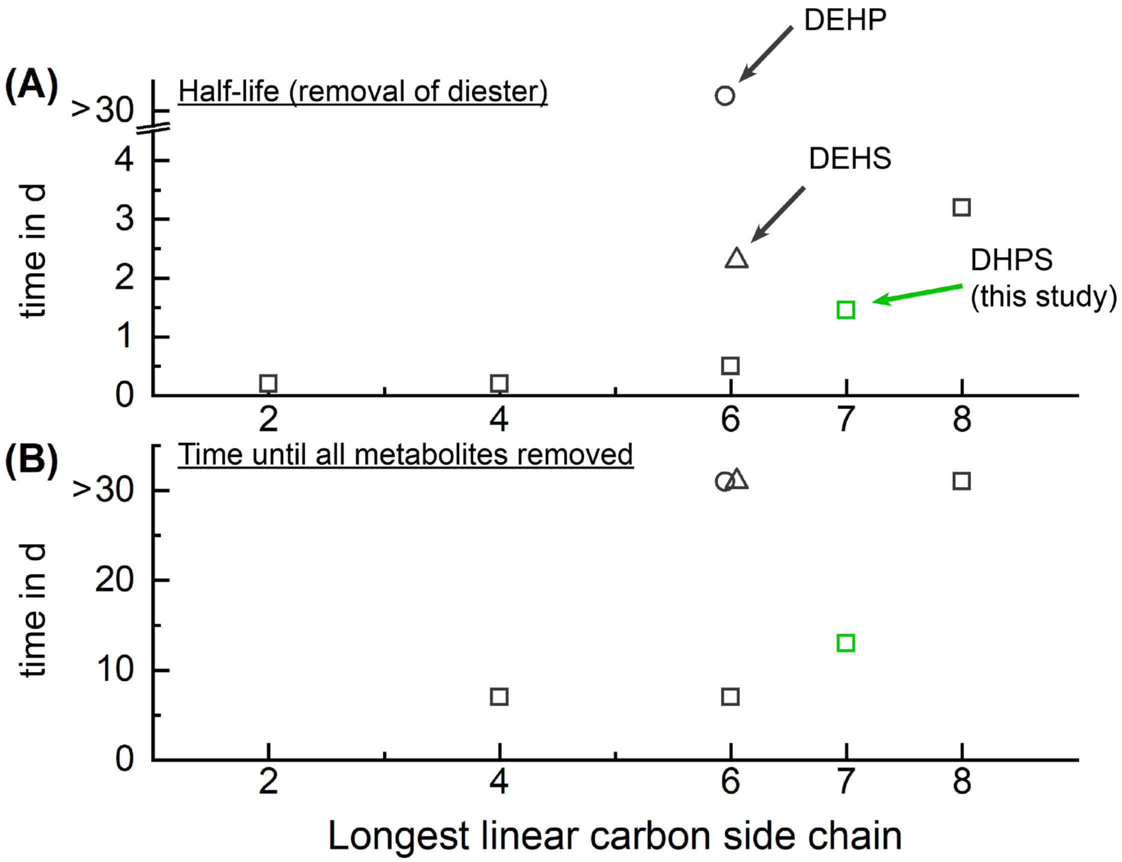

Figure 6: Biodegradation by *Rhodococcus rhodochrous* parameters vs. longest side chain length for DHPS (green square) in comparison to other linear succinates (gray squares; C_2: diethyl succinate, C_4: dibutyl succinate, C_6: di-n-hexyl succinate, C_8: di-n-octyl succinate), branched di-(2-ethylhexyl) succinate (DEHS, gray triangle), and the commercially important di-(2-ethylhexyl) phthalate (DEHP). (A) Calculated half-life (removal of diester) based on first order kinetics (B) Time until all metabolites were removed from biodegradation broth. Adapted from Erythropel et al.[35] DEHP: di-(2-ethylhexyl) phthalate; DEHS: di-(2-ethylhexyl) succinate; DHPS: di-n-heptyl succinate.

Toxicity considerations

While the toxicity of DHPS was not evaluated in this study, previous literature on several in-vitro and ex-vivo toxicological endpoints[40] as well as a multi-generational in-vivo study[27, 41] suggests the relative safety for DHS and DOS. Given that the only difference between the mentioned compounds and DHPS is the side chain length, differing only by carbon to DHS and DOS, DHPS can be expected to have a similar safety profile.

Cost considerations

Obviously, any green plasticizer considered as an eventual replacement for a phthalate must have competitive manufacturing costs. Here, we present a crude comparison using the prices we paid from small batches (about 1 x 55 gallon drum of for the Oleris n-heptanol (Arkema) and 100 kg bags of the Biosuccinum succinic acid from Reverdia) from the two key components. From the raw materials cost alone, we estimated a price between $4-5 US per pound. Comparing this to DEHP, which typically costs ~$1 US per pound in bulk (i.e. ton quantities), the raw materials for the di n-heptyl succinate are more expensive but the scales are different. We are assuming that raw materials costs are a major driver and do not consider other price factors to vary significantly (eg. we expect the reactor configuration to be similar to that used for DEHP). It is not unreasonable to expect that the raw materials price can be further decreased for the green plasticizer components with bulk quantities.

CONCLUSION

The environmental contamination and health hazards that arise from using phthalates as plasticizers justify the need to develop safer replacements to compounds such as di-(2-ethyl hexyl) phthalate (DEHP). In this study, di-n-heptyl succinate as a potential alternative plasticizer was fully synthesized from renewably-sourced platform molecules (succinic acid and n-heptanol), using an optimized, solventless, less hazardous synthesis strategy. This is well aligned with the principles of green chemistry[28, 29] as well as the "Grand Challenges" outlined by the U.S. National Research Council, such as challenge 4 (Renewable Chemical Feedstocks) and challenge 6 (Energy Intensity of Chemical Processing) that outlines the need for research into more energy- and cost-efficient chemical separations, especially effective alternatives to distillation.[58]

Furthermore, several measures of plasticizer effectiveness in poly(vinyl chloride) (PVC) showed that the fully renewable DHPS was as effective (elongation at break), or more effective (T_g reduction, modulus, melt rheology) than the commercially important plasticizer DEHP. Biodegradation experiments with the common soil bacterium *Rhodococcus rhodochrous* revealed that DHPS can be expected to be broken down rapidly when it enters the environment, without the buildup of stable metabolites as is the case for DEHP. In addition, DHPS' performance was compared to previously published data on succinate diesters of varying side chain length, suggesting that the side chain length plays an important role in determining the plasticizer effectiveness and biodegradation potential of alternative plasticizers. Collectively, these results suggest that DHPS would be an excellent green plasticizer for production and use in the plasticizer and PVC industries.

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Notes

The authors have no conflict of interest to declare.

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ABBREVIATIONS

DHPS, diheptyl succinate; DHS, dihexyl succinate; DOS, dicotyl succinate; DEHS, diethyl hexyl succinate

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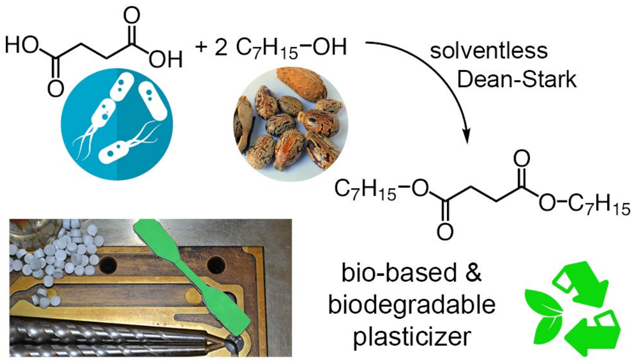

Synopsis:
Diheptyl succinate synthesized from the renewable feedstocks succinic acid and n-heptanol is a biodegradable, low-risk and effective plasticizer for poly(vinylchloride).