Catalytic upcycling of PVC waste-derived phthalate esters into safe, hydrogenated plasticizers†

Simon Windels, [ID] [a] Thomas Diefenhardt, [ID] [b] Noopur Jain, [ID] [c] Carlos Marquez, [ID] [a] Sara Bals, [ID] [c] Martin Schlummer [ID] [b] and Dirk E. De Vos [ID] *[a]

Recycling of end-of-life polyvinyl chloride (PVC) calls for solutions to deal with the vast amounts of harmful phthalate plasticizers that have historically been incorporated in PVC. Here, we report on the upcycling of such waste-extracted phthalate esters into analogues of the much safer diisononyl 1,2-cyclohexanedicarboxylate plasticizer (DINCH), *via* a catalytic one-pot (trans)esterification–hydrogenation process. For most of the virgin phthalates, Ru/Al_2O_3 is a highly effective hydrogenation catalyst, yielding >99% ring-hydrogenated products under mild reaction conditions (0.1 mol% Ru, 80 °C, 50 bar H_2). However, applying this reaction to PVC-extracted phthalates proved problematic, (1) as benzyl phthalates are hydrogenolyzed to benzoic acids that inhibit the Ru-catalyst, and (2) because impurities in the plasticizer extract (PVC, sulfur) further retard the hydrogenation. These complications were solved by coupling the hydrogenation to an *in situ* (trans)esterification with a higher alcohol, and by pretreating the extract with an activated carbon adsorbent. In this way, a real phthalate extract obtained from post-consumer PVC waste was eventually completely (>99%) hydrogenated to phthalate-free, cycloaliphatic plasticizers.

Introduction

Throughout the previous century, plastics quickly evolved from inferior replicas of natural substances to highly sophisticated materials, leading to their role as the most defining materials in modern society.[1] As a result of their overwhelming success, the global plastics production was estimated at 370 million tons in 2019.[2] This success is, however, associated with a notorious environmental impact, such as land, water and air pollution, caused by their production, consumption and flawed waste management.[3] In order to simultaneously exploit the countless benefits and relieve the current environmental burden, the European Union is, amongst others, extensively investing in the development of a circular plastic economy.[4,5] One of the main challenges is the recycling of plastics containing legacy additives, such as brominated flame retardants and heavy metal stabilizers.[6] Legacy additives generally prove satisfactory for

their intended function, making them of significant value; however, based on the outcome of toxicological and environmental reports, international regulations now restrict the usage of many harmful compounds in new products.[7] Nonetheless, (European) waste-processing firms can expect to encounter plastics containing legacy additives for decades to come in long-lasting plastics (*e.g.* window profiles) or in imported plastics originating from geographic regions without such restrictions.[8] To date, these plastics have been discarded in landfills or incinerators, causing environmental issues, such as the leaching of noxious additives, the emission of greenhouse gases and the volatilization of heavy metal compounds.[6,9–11]

Among legacy additives, phthalate esters in flexible plastics are perhaps the best known. As a result of their excellent plasticizing properties, they were the industry's general purpose plasticizers for decades, which led to global production rates of approximately 3.5 to 4.5 M tons per year.[12,13] The vast majority are used in plasticized polyvinyl chloride (pPVC) applications, in which they add up to 40 wt% of the final product.[14,15] However, low molecular weight (LMW) phthalates, including dibutyl (DBP), diisobutyl (DIBP), benzyl butyl (BeBP) and bis(2-ethylhexyl) (DEHP) phthalate have recently been regulated by the European Chemicals Agency (ECHA) and by the United States Consumer Product Safety Commission (CPSC), due to strong concerns of endocrine disruption and reproductive toxicity.[16–22] While the production of LMW phthalates has consequently been phased out in Europe, it is still

[a]Centre for Membrane separations, Adsorption, Catalysis and Spectroscopy for sustainable solutions (cMACS), KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium. E-mail: dirk.devos@kuleuven.be

[b]Fraunhofer Institute for Process Engineering and Packaging IVV, Process Development for Polymer Recycling, Giggenhauser Straße 35, 85354 Freising, Germany

[c]Electron Microscopy for Materials Science (EMAT), University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium

ongoing in Asia, Latin America, Africa and the Middle East.[13] Furthermore, end-of-life PVC floor coverings (produced decades ago) still contain up to 20 wt% phthalate plasticizers and are currently appearing in waste management facilities.[23]

As an alternative plasticizer, diisononyl 1,2-cyclohexanedicarboxylate (DINCH) has been brought forward, with an obvious chemical similarity to phthalates, but with a much more positive toxicological evaluation.[24–29] The conversion of virgin phthalates (single, pure compounds) into dialkyl 1,2-cyclohexanedicarboxylate esters has been studied in open and patent literature, generally using supported noble metal catalysts operating at an elevated temperature (70–140 °C) and under high hydrogen pressures (60–200 bar).[14,30–39] In fact, this conversion has been industrially implemented, with a yearly production exceeding 200 000 ton (in 2014).[40–42] Additionally, Ni-based systems, demanding even more rigorous conditions, have also been investigated to a limited extent.[43–45] However, none of the aforementioned studies have tackled the complexity of an end-of-life feedstock, *i.e.* the conversion of a complex mixture of phthalate plasticizers recovered from plastic waste. In this paper, we present the successful revalorization of PVC waste-derived phthalate esters into safe plasticizer analogues *via* a catalytic hydrogenation process, using a metal supported catalyst, H_2 and a green solvent (Fig. 1).
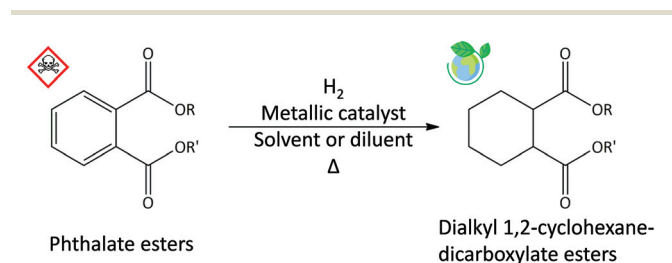

Fig. 1 Chemical detoxification of PVC-extracted phthalate plasticizers by catalytic ring hydrogenation.

Experimental section

Materials

All chemicals, including specifications and supplier, are enumerated in the ESI.† All products were used as received, unless otherwise specified.

Catalyst preparation

In addition to commercially available catalysts (Pd/C, Rh/C, Ru/C, Pd/C), several Ru-based systems were prepared by incipient wetness impregnation of a commercial support with an aqueous solution of $RuNO(NO_3)_3$. To that end, the required amount of the metal precursor salt was dissolved in distilled water (the water volume was equated to the pore volume of the support), after which the aqueous mixture was added to the support in a dropwise manner. Subsequently, the impregnated supports were dried at 60 °C, and the dry materials were granu-

lated to particle sizes between 250 and 500 μm. Finally, these granules were activated by reduction at 200 °C (240 min, 2 °C min^{-1}, 100 mL H_2 min^{-1}), preceded by a N_2 treatment at 120 °C (120 min, 4 °C min^{-1}, 100 mL N_2 min^{-1}) in a quartz U-tube. The catalyst preparation was based on a patent from Brunner *et al.*[41] and the activation step was further verified by a temperature programmed reduction experiment (ESI, Fig. S1†). The final metal loading of the samples is presented in Table 1.

Hydrogenation reactions

All reactions were performed in a 50 mL high-pressure Parr® reactor vessel (Series 5500, Stainless Steel 316, Model 4848 temperature controller). In a typical hydrogenation experiment, the reactor was loaded with 25 mL of an organic solution of a phthalate (0.5 mol L^{-1}) and a supported metal catalyst (0.1 mol% metal relative to the phthalate). Subsequently, the reactor was sealed, purged three times with N_2, three times with H_2 and, then pressurized with 50 bar H_2 at room temperature. Finally, the reactor was heated to 80 °C and stirred at 500 rpm using a magnetically driven impeller. The hydrogenation was stopped by fast cooling of the reactor in an ice-in-water bath and by evacuating the remaining H_2 gas. The catalyst was removed from the liquid plasticizer mixture by centrifugation.

Transesterification reactions

The reactor was loaded with 25 mL of a mixture of a phthalate (0.5 mol L^{-1}) and H_2SO_4 (5 mol% relative to the phthalate) in 2-ethyl-1-hexanol. Then, the reactor was sealed and purged with N_2. Finally, the reaction mixture was heated to 140 °C and stirred at 500 rpm.

Coupled (trans)esterification–hydrogenation reaction

For the coupled, one-pot reactions, the reactor was loaded with 25 mL of a mixture of a phthalate in 2-ethyl-1-hexanol (0.5 mol L^{-1}), H_2SO_4 (5 mol%) and a Ru-catalyst (0.05 or 0.1 mol%). Subsequently, the reactor was sealed, purged with N_2 and with H_2, and pressurized with 50 bar H_2 at room temperature. Finally, the reactor was heated to 80 or 140 °C and stirred at 500 rpm.

Product analysis and identification

The samples were analyzed by gas chromatography (GC), gas chromatography – mass spectrometry (GC-MS) and by proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) in order to determine the conversion and product distributions. GC-samples were prepared by combining 1–10 μL of anisole (external standard) with 25 μL of the reaction mixture and 975 μL of THF and injected on a Shimadzu GC-2010 instrument, equipped with a 30 m DB-1HT column and a flame ionization detector (FID). The analysis was optimized by applying a temperature program: the initial capillary column temperature (40 °C) was increased to 150 °C at 20 °C min^{-1}, kept constant for 5 min and then further increased to 300 °C at 5 °C min^{-1}. Complete product identification was achieved by GC-MS analyses on an Agilent 6890 GC instrument, equipped with a HP-1

MS column and a Agilent 5973 MSD mass spectrometer. A selection of the obtained MS data can be found in the ESI (Fig. S2–S18†).

In addition, especially for mixtures containing isomeric plasticizers, the mixtures were analyzed by ^{1}H-NMR by diluting 100 μL of the crude reaction sample with 500 μL of a solution of maleic acid in d_8-THF (0.1 M) and, subsequently, transferring the mixture to a NMR tube. Maleic acid (δ = 6.202 ppm, s, 2H) served as the external standard for the quantification of the compounds. The ^{1}H-NMR spectra were recorded on a Bruker Avance III HD 400 console with a Bruker Ascend™ 400 magnet, equipped with a 5 mm PABBO BB/^{19}F-^{1}H/D probe with z-gradients and ATM accessory for automatic tuning and matching. The interpretation of the ^{1}H-NMR spectra is provided in the ESI (Fig. S19–S21†).

Characterization techniques

The metal dispersion and the average size of the Ru particles of selected hydrogenation catalysts were determined by CO pulse titrations. Prior to the chemisorption measurement, the catalyst particles were dried in a vacuum oven at 60 °C for 16 h. The dry material was transferred to a U-shaped quartz tube and subsequently placed in a Quantachrome ChemBET pulsar equipped with a thermal conductivity detector (TCD). Prior to the pulse titration, the metal catalyst was *in situ* reduced at 200 °C (60 min, 10 °C min^{-1}, 120 mL H$_2$ min^{-1}) and subsequently treated with He while cooling to room temperature (120 min, 120 mL He min^{-1}). Eventually, the automated CO titration (75 μL CO pulses) was performed at 40 °C.

High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDX) were performed on a Thermo Fisher Scientific Osiris transmission electron microscope, equipped with a Super-X detector, operating at 300 kV. EDX maps were acquired using a beam current of 0.2 nA and an acquisition time of 20 minutes to generate the maximum counts per element and to visualize the spatial distribution of the elements. Quantitative results (atomic%) were derived from the maps. Thermogravimetric analyses (TGA) of (spent) Ru-catalysts were carried out under air atmosphere on a NETZSCH STA 449 F3 Jupiter® thermal analyzer with a heating rate of 10 °C min^{-1}. Prior to the characterization experiments, the samples were washed with methanol and then dried in a vacuum oven at 60 °C for 16 h. For STEM-EDX, the powder was diluted in ethanol (1 mg ml^{-1}) and drop casted on TEM grids.

Results and discussion

Catalyst and solvent screening

In a first set of experiments (Table 1, entries 1–4), several noble metals were tested for the deep hydrogenation of bis(2-ethylhexyl) phthalate (DEHP) into bis(2-ethylhexyl) 1,2-cyclohexanedicarboxylate (H6-DEHP). Under the studied conditions (0.5 mol L^{-1} DEHP in tetrahydrofuran; THF, 50 bar H$_2$ for 90 min at 80 °C), none of the carbon-supported noble metal catalysts reached a high phthalate conversion, although clear differences in activity were observed: while Pd/C and Pt/C proved unsuitable for these ring hydrogenations (<5% conversion), the Rh- and Ru-based catalysts showed promising activities (phthalate conversions of 24% and 40%, respectively). The hydrogenation over Rh- and Ru-catalysts proceeds *via* bis(2-ethylhexyl) 1,2-cyclohexene dicarboxylate (H4-DEHP), an intermediate which was hardly detected in Pd- or Pt-catalyzed reactions (Fig. 2; Fig. S22 & S23 in ESI†). In addition to the higher activity of the Ru-catalyst, no significant side-product formation was detected, resulting in >99% yield of H6-DEHP at increased reaction times (Table 1, entry 4.1). Because of the superior performance of Ru for these ring hydrogenations and its relatively low cost, this metal was selected for further studies.[46,47]

Table 1 Screening of noble metal catalysts for the hydrogenation of bis(2-ethylhexyl) phthalate[a]

Entry	Catalyst	M. loading [wt%]	Conversion [%]	$Y_{\text{H4-DEHP}}$ [%]	$Y_{\text{H6-DEHP}}$ [%]
1	Pd/C	5	1	<1	1
2	Rh/C	5	24	9	15
3	Pt/C	5	4	<1	4
4	Ru/C	5	40	10	30
4.1[b]	**Ru/C**	**5**	**>99**	**n.d**	**>99**
5	Ru/SiO$_2$	1	73	16	57
6	Ru/Al$_2$O$_3$ [basic]	1	71	14	57
7	Ru/Al$_2$O$_3$ [neutral]	1	54	10	44
8	**Ru/Al$_2$O$_3$ [acidic]**	**1**	**94**	**8**	**86**
9	Ru/SiO$_2$–Al$_2$O$_3$	1	74	14	61
10	Ru/ZrO$_2$	1	92	8	84
11	Ru/TiO$_2$	1	83	8	75
12[c]	Ru/Al$_2$O$_3$ [acidic]	0.1	76	6	70
13[c]	Ru/Al$_2$O$_3$ [acidic]	0.5	71	7	63
14[c]	Ru/Al$_2$O$_3$ [acidic]	1	60	12	48
15[c]	Ru/Al$_2$O$_3$ [acidic]	2.5	54	10	44
16[c]	Ru/Al$_2$O$_3$ [acidic]	5	45	8	37

n.d.: Not detected. [a] Reaction conditions: bis(2-ethylhexyl) phthalate in THF (0.5 mol L^{-1}, 25 mL), 0.1 mol% metal catalyst, 50 bar H$_2$, 80 °C for 90 min. [b,c] Reaction times: 6 hours and 30 min, respectively.
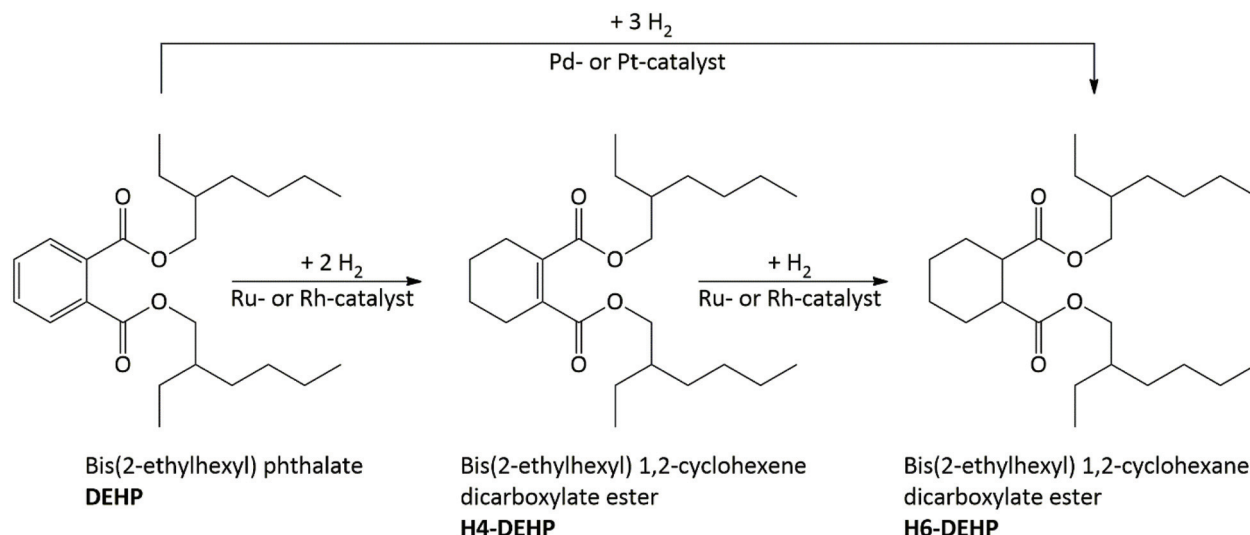
Fig. 2 Reaction scheme of the hydrogenation of dialkyl phthalate esters, with DEHP as model molecule.

In order to evaluate the effect of the chosen catalyst support (Table 1, entries 5–11) and the metal loading (Table 1, entries 12–16), several Ru-catalysts were prepared *via* incipient wetness impregnation using $RuNO(NO_3)_3$ as the Ru-precursor. Regardless of the support, all self-prepared catalysts proved highly active for the hydrogenation, generally reaching more than 70% phthalate conversion within 90 min of reaction time. Remarkably, two systems – Ru/Al_2O_3 [acidic], and Ru/ZrO_2 – exhibited an outstanding catalytic activity (>90% conversion), yielding 86% and 84% H6-DEHP, respectively. The former catalyst, Ru/Al_2O_3 [acidic], was then selected for further parameter evaluations, beginning with the effect of the Ru loading (Table 1, entries 12–16). The results clearly show a steady increase in catalytic activity as the metal loading is lowered, which could be related to a decrease of the average metal particle size. To verify this hypothesis, the metal catalysts were characterized by CO chemisorption (Table S1 in ESI†). The remarkably large amounts of adsorbed CO corres-

pond to high metal dispersions (>57%) and small metal particle sizes (≤2 nm). The data indicate that the hydrogenation activity is in fact inversely related with the size of the Ru particles, as the highest H6-yields were obtained with the catalysts containing the smallest metal clusters.

Next, the role of the solvent in the reaction was studied (Table 2), starting with some known PVC solvents,[48,49] as our vision is to ultimately integrate this plasticizer revalorization process in a pPVC recycling unit, operating *via* a dissolution–precipitation approach.[48,50,51] In such approach, the PVC and its plasticizers are dissolved in a solvent, allowing the removal of solid impurities (including additives and other plastics or fabrics). Then, a PVC anti-solvent is added to selectively precipitate the PVC resin, leaving the plasticizers in a mixture of the PVC solvent and anti-solvent. Since this anti-solvent usually is a low boiling alcohol (*e.g.* methanol), it could easily be removed by evaporation. Therefore, the use of the PVC solvent in the plasticizer hydrogenation process could signifi-

Table 2 Solvent screening for the hydrogenation of bis(2-ethylhexyl) phthalate[a]

Entry	Solvent	Conversion [%]	$Y_{H4\text{-}DEHP}$ [%]	$Y_{H6\text{-}DEHP}$ [%]
1	Tetrahydrofuran	94	8	86
2	Cyclohexanone	1	<1	<1
3	Methyl ethyl ketone	5	3	2
4	γ-Valerolactone	2	<1	1
5	No solvent	12	5	7
6	DINCH	54	7	47
7	2-Methyltetrahydrofuran	90	8	82
8	*tert*-Amyl methyl ether	98	4	94
9	**Cyclopentyl methyl ether**	**>99**	**n.d.**	**>99**
9.1[b]	Cyclopentyl methyl ether	91	8	83
10	2-Ethyl-1-hexanol	81	15	66
11	Isononanol	68	16	52

n.d.: Not detected. [a] Reaction conditions: bis(2-ethylhexyl) phthalate in the defined solvent (0.5 mol L⁻¹; 25 mL), 0.1 mol% Ru/Al_2O_3 [1 wt%], 50 bar H_2, 80 °C for 90 min. [b] Reaction time: 30 min.

cantly limit the total volume of employed solvents. However, cyclohexanone, methyl ethyl ketone (MEK) and γ-valerolactone (GVL) appeared to be incompatible with the hydrogenation reaction, as hardly any phthalate conversion was observed (<5%). Furthermore, the ketone solvents were unstable in the Ru-catalyzed reaction, forming the corresponding alcohol by hydrogenation (±10% solvent conversion after 90 min of reaction time). Consequently, PVC solvent recovery would have to occur prior to the hydrogenation process. Aiming to still limit the total process' solvent use, the hydrogenation of DEHP was subsequently studied in the absence of a solvent (Table 2, entry 5) and in DINCH (Table 2, entry 6), which can be considered as representative for the eventual products to be made. The removal of the PVC solvent seemed to slightly improve the conversion rate, but the conversion only amounted to 12%, implying the necessity of a process solvent or diluent. Actually, the hydrogenation of DEHP proceeds sufficiently fast in DINCH (54% conversion), which would greatly limit the solvents' use when a recycle reactor could be employed. Nonetheless, because of the remarkably high hydrogenation rates obtained in THF (Table 2, entry 1), some *green* THF alternatives were explored (Table 2, entries 7–9).[52] Both 2-methyltetrahydrofuran (MeTHF) and *tert*-amyl methyl ether (TAME) proved as effective solvents as THF for the hydrogenation, with phthalate conversions of 90% and 98%, respectively. The best results, however, are obtained when cyclopentyl methyl ether (CPME) is used as solvent. In fact, the CPME-system reached complete phthalate conversion after 90 minutes of reaction time (Table 2, entry 9); furthermore, it yielded 83% H6-DEHP after only 30 minutes (Table 2, entry 9.1). Additionally, some higher alcohol solvents (C8 and C9) were tested (Table 2, entries 10 and 11) and these protic solvents proved appropriate hydrogenation solvents, as significant conversions of 68% and 81% were obtained.

Coupled (trans)esterification–hydrogenation

In a subsequent set of experiments, some historically relevant phthalates (DIBP; DBP; DEHP; BeBP; diisononyl phthalate, DINP) were subjected to the hydrogenation process (Fig. 3, left). The hydrogenation of most dialkyl phthalates went smoothly, resulting in near complete conversions after only 90 min of reaction time. The relative hydrogenation rates ($v_{DIBP} \geq v_{DBP} > v_{DEHP} > v_{DINP}$) seem inversely related to the steric hindrance around the aromatic phthalate ring. A clear exception, however, is the benzyl containing plasticizer (BeBP): the conversion of this phthalate was surprisingly slow (20% conversion after 90 min of reaction time). Furthermore, the hydrogenation selectivity dropped considerably due to formation of toluene and a benzoic acid, namely monobutyl phthalate (MBP), as can be seen in Fig. 3 (right). This side product is obtained *via* the catalytic hydrogenolysis of the benzyl–oxygen bond, resulting in debenzylation, which is well known in deprotection chemistry.[53,54] In order to assess the reactivity of MBP, the hydrogenation was performed using MBP as the substrate. This carboxylic acid appeared to be virtually inert for the reaction, reaching only 6% conversion after 270 min of reaction time (Fig. 3, left). This led to the hypothesis that MBP strongly adsorbs on the catalyst, having a negative effect on the hydrogenation rate of other phthalates in the mixture. To further examine the influence of MBP on the catalytic system, the hydrogenation of DEHP (0.5 mol L^{-1}) was performed with the addition of 0.1 mol L^{-1} of benzoic acid. As observed in Fig. 3 (left), the hydrogenation of DEHP is indeed drastically hindered when the carboxylic acid is present in the reaction mixture. This phenomenon of strong adsorption of the formed carboxylic acid on the catalytic active sites is analogous to the decline in the hydrogenation rate when more strongly coordinating solvents, such as cyclohexanone or GVL, were employed.
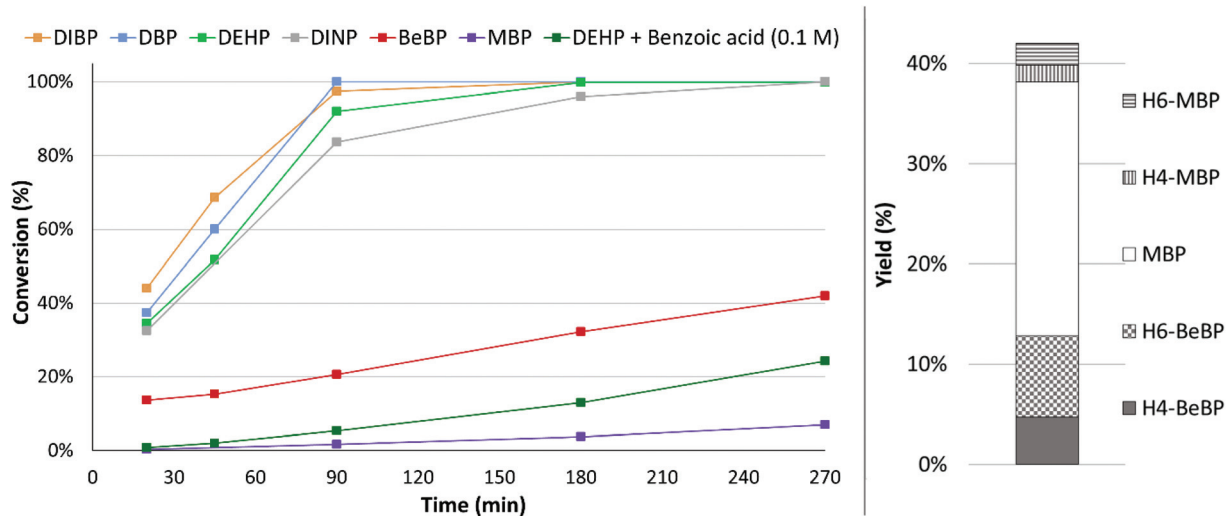

Fig. 3 (left) Time profiles of the hydrogenation of pure phthalate plasticizers and the effect of benzoic acid on the conversion rate of DEHP; (right) obtained product distribution in the hydrogenation of BeBP after 270 minutes of reaction time. Reaction conditions: the defined phthalate in MeTHF (0.5 mol L^{-1}; 25 mL), 0.1 mol% Ru/Al$_2$O$_3$, 50 bar H$_2$ at 80 °C for *x* minutes of reaction time.
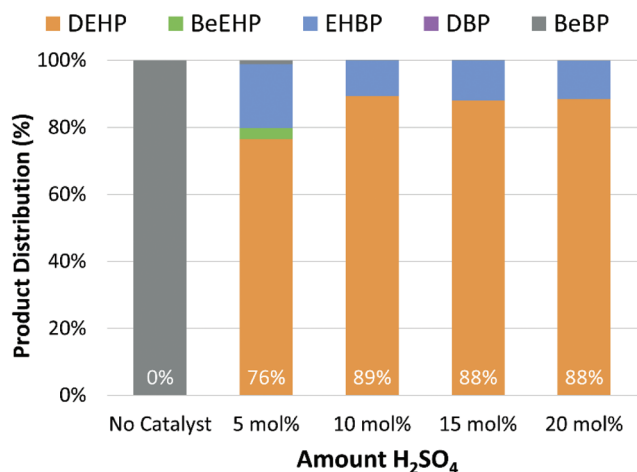
Fig. 4 Transesterification of BeBP to DEHP using H_2SO_4 as Brønsted acid catalyst. Reaction conditions: 0.5 mol L^{-1} BeBP in 2-EH (molar ratio: 1 to 11), defined amount of H_2SO_4 (0−20 mol%), at 140 °C for 16 h under N_2 atmosphere.

In order to circumvent the hydrogenolysis of the benzyl esters and the associated catalyst poisoning, the phthalate revalorization strategy was adapted to a combined (trans)esterification–hydrogenation. If the benzyl–oxygen linkage in BeBP is actually labile, the transesterification of this substrate with an aliphatic alcohol prior to the hydrogenation may resolve the poisoning issue, as the hydrogenation of dialkyl phthalate esters was previously shown to be successful in long-chain alcohol solvents (Table 2, entries 10 and 11). The transesterification of BeBP with 2-ethyl-1-hexanol (2-EH) at 140 °C did not occur in the absence of a catalyst. However, the addition of 5 mol% H_2SO_4 – a classical transesterification catalyst[55] – led to promising results, as the benzyl moiety was readily replaced (Fig. 4 and Fig. S24 in ESI†). Furthermore, the additional transesterification of the short butyl group also occurred under the applied reaction conditions (0.5 mol L^{-1} BeBP in 2-EH, at 140 °C under N_2 atmosphere for 16 h): the twice transesterified product (DEHP) was mainly obtained (76%), while the once transesterified products, *viz.* ethylhexyl butyl phthalate (EHBP) and benzyl ethylhexyl phthalate (BeEHP) accounted for the rest of the product distribution, with the compounds still bearing a benzyl ester accounting for less than 5% of the final plasticizer mixture. Increasing the H_2SO_4 concentration to 10 mol% or beyond, or increasing the reaction time brings the system to what seems to be its chemical

equilibrium, with 89% DEHP and 11% EHBP (Fig. 4 and Fig. S24 in ESI†). The obtained 1,2-dialkyl phthalate esters are then readily converted in the subsequent hydrogenation step (after the addition of the Ru-catalyst and H_2), which can be performed in the same alcohol solvent and reactor.

Assuming that the esterification of a carboxylic acid proceeds at least as fast as the corresponding transesterification, one could argue that MBP, formed *in situ* by hydrogenolysis of the benzyl–oxygen bond in BeBP, would be quickly converted to a dialkyl phthalate in the presence of H_2SO_4 and an aliphatic alcohol solvent. This could then again allow a smooth phthalate hydrogenation as the metal catalyst would no longer be inhibited by the strongly adsorbing carboxylic acid (Fig. 5). To that end, the one-pot (trans)esterification–hydrogenation of BeBP was subsequently investigated using H_2SO_4 in combination with the hydrogenation catalyst (Ru/Al_2O_3) and 2-EH as (trans)esterification agent and hydrogenation solvent at 140 °C under 50 bar H_2. The obtained product distribution, depicted in Fig. 6, demonstrates the effectiveness of this proposed strategy, as it enabled the complete hydrogenation (H6-yield >99%) of BeBP within a relatively short reaction time (240 minutes). Remarkably, 50% of the plasticizer was exclusively hydrogenated (H6-BeBP), while the other half has undergone additional (trans) esterifications. In contrast to the sequential transesterification–hydrogenation, this simultaneous strategy almost solely replaced the benzyl moiety, leaving the butyl chain mostly in place. Hence the twice (trans)esterified product only represents a small portion of the product distribution (6% yield of H6-DEHP).

Summarizing, the insertion of the (trans)esterification step now allows to upcycle even BeBP-rich plasticizer mixtures. Furthermore, the net exchange of the plasticizers' side chains is even desirable for additional reasons: (a) short chain plasticizers (*e.g.* DBP/H6-DBP) have proven less satisfactory for the use in PVC flooring, as these compounds are too volatile for safe PVC processing and/or too mobile for long lasting PVC applications;[50] (b) given that end-of-life PVC waste contains various phthalate esters in varying amounts, a more uniform product distribution could be obtained with the coupled strategy.

Kinetic experiments

The effect of the reactants and process additives (phthalate ester, hydrogen gas, H_2SO_4) on the hydrogenation rate was analyzed more deeply in a kinetic study. First, the order of reaction in the phthalate plasticizer and in hydrogen was determined by evaluating different time profiles of DEHP reactions, with hydro-
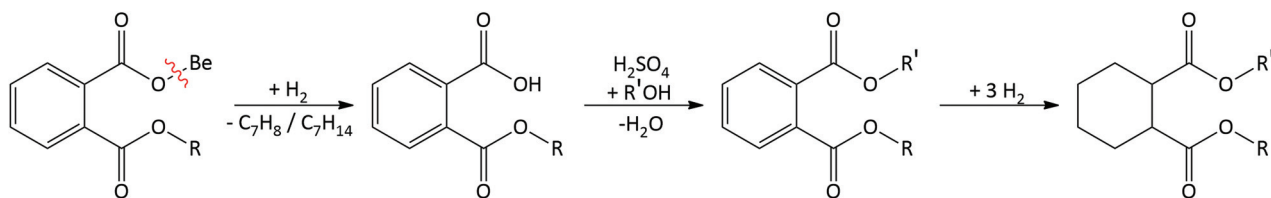

Fig. 5 Reaction scheme of the one-pot upcycling of benzyl phthalates: (i) selective hydrogenolysis of the benzyl–oxygen bond yields a catalyst-inhibiting carboxylic acid. (ii) The formed carboxylic acid is *in situ* esterified with an aliphatic alcohol solvent. (iii) Smooth hydrogenation of the obtained dialkyl phthalate.
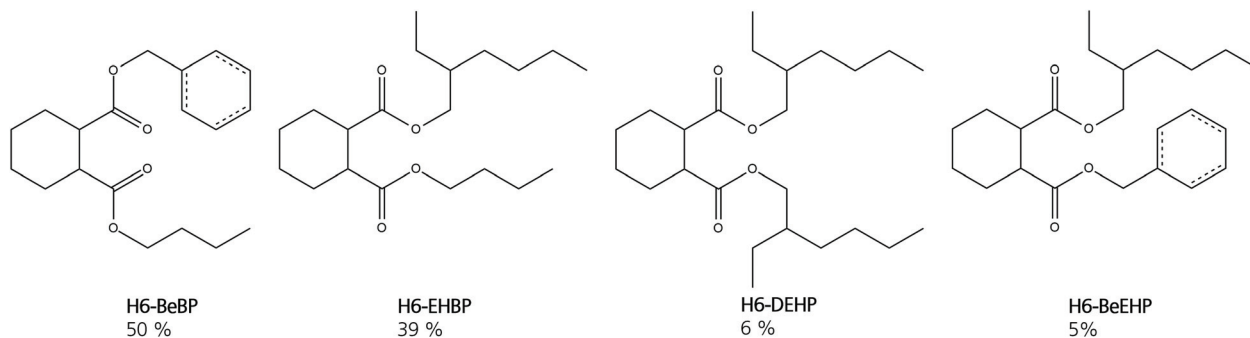
Fig. 6 Product distribution of the one-pot (trans)esterification–hydrogenation reaction of BeBP. Reaction conditions: BeBP in 2-EH (0.5 mol L^{-1}; 25 mL), 5 mol% H_2SO_4 and 0.1 mol% Ru/Al$_2$O$_3$ [0.5 wt%], 50 bar H_2 at 140 °C for 240 minutes.

gen pressures ranging from 10 to 50 bar (Fig. 7, left). Given that the conversion rate remained constant over time, the experimental data gave an excellent fit with a phthalate-independent rate law. This zero order with respect to the substrate could suggest a strong adsorption of the plasticizer on the catalyst's surface, which is commonly observed in liquid phase hydrogenations of aromatic molecules.[56–58] In addition, the positive correlation between the reaction rate and the hydrogen pressure (Fig. 7, left) was plotted in a log–log format (Fig. 7, right): the reaction order in hydrogen decreased from 1, at low H_2 pressure, to less than 0.5, at intermediate H_2 pressure (see ESI†). This trend suggests that at elevated H_2 pressures the catalyst's surface gets progressively more saturated with hydrogen, which clearly facilitates the hydrogenation of the aromatic ring.

Next, the effect of the transesterification catalyst (*i.e.* H_2SO_4) on the hydrogenation rate of DEHP was studied (Fig. 8). It appears that the conversion of the dialkyl phthalate is slightly slowed down when the concentration of the Brønsted acid is increased; this may suggest that the added

sulfuric acid competitively adsorbs to a limited extent on the active metal sites. Nonetheless, as was previously shown, the transesterification catalyst is necessary for the upcycling of benzyl containing phthalate esters.

In order to simulate a PVC waste-derived plasticizer feed, the effect of some expected contaminants (other PVC plasticizers, residual filler and residual PVC) on the hydrogenation of DEHP was analyzed (Fig. 9). In a first experiment, bis(2-ethylhexyl) adipate (DEHA) was added to the reaction mixture as a representative co-extracted plasticizer, given that aliphatic esters are reported to be the second most employed plasticizers. Furthermore, virtually all PVC plasticizers are di- or polyfunctional esters and thus expected to behave similarly as the adipate ester.[13,59] Before the catalytic experiment, DEHA was mixed with DEHP at room temperature to account for 5 wt% of the plasticizer mixture, which was subsequently employed in the hydrogenation reaction under kinetic conditions (0.05 mol% Ru/Al$_2$O$_3$, 5 mol% H_2SO_4, 50 bar H_2 at 80 °C). The conversion rate of the phthalate seemed slightly
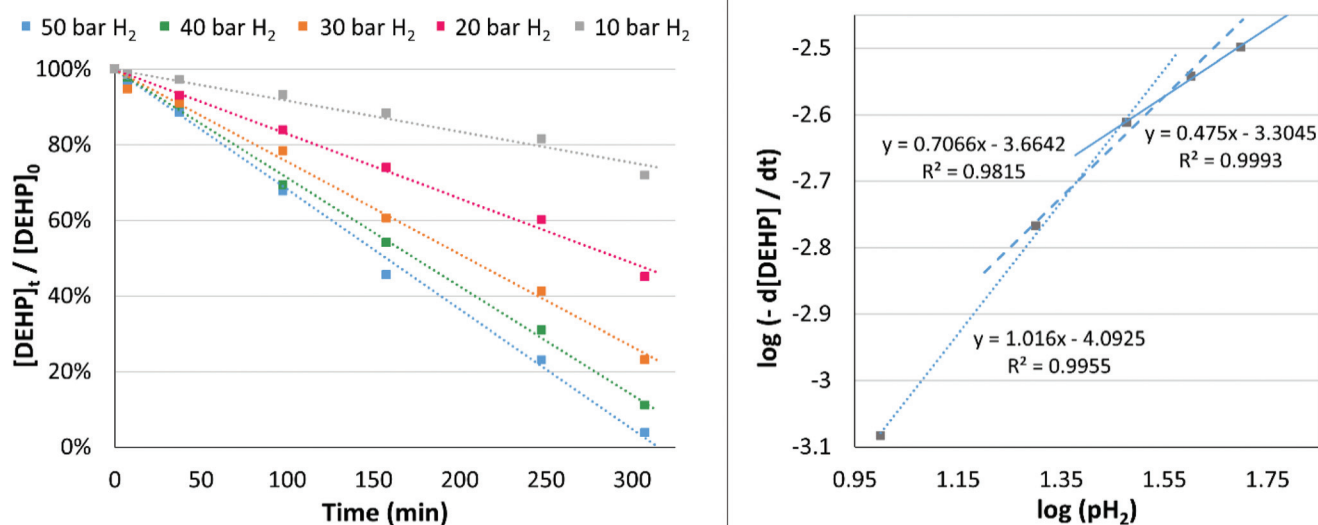

Fig. 7 Kinetic experiments for determining the order of reaction in phthalate esters and in hydrogen gas. Reaction conditions: DEHP in 2-EH (0.5 mol L^{-1}; 25 mL), 0.05 mol% Ru/Al$_2$O$_3$ [1 wt%], H_2SO_4 (5 mol%) under the defined H_2 pressure (10–50 bar), 80 °C for 300 min. Legend of right figure: dots for the obtained order between 10–30 bar H_2, dashes between 20–40 bar H_2 and a solid line between 30–50 bar H_2.
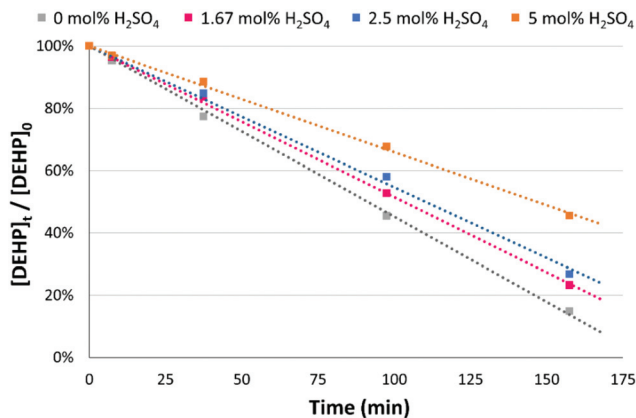
Fig. 8 Effect of H_2SO_4 on the hydrogenation rate of a dialkyl phthalate. Reaction conditions: DEHP in 2-EH (0.5 mol L^{-1}; 25 mL), 0.05 mol% Ru/Al$_2$O$_3$ [1 wt%], the defined amount of H_2SO_4 (0–5 mol%), 50 bar H_2 at 80 °C.

slower when DEHA was present in the reaction mixture (Fig. 9), which might indicate that the adipate esters also adsorb on the catalyst's surface, presumably *via* the similar ester groups. Nonetheless, the aromatic moiety of the phthalates appears to facilitate a stronger adsorption and thus its hydrogenation, leaving the conversion rate almost unaffected.

Given that the filler content of numerous PVC products lies between 30 and 60 wt%, the kinetic effect of CaCO$_3$ on the conversion of DEHP was subsequently investigated.[60] Note that the filler hardly dissolves in DEHP, as a turbid, supersaturated mixture was still obtained when only 1 wt% of CaCO$_3$ was added and stirred for 24 h at 100 °C. The kinetic effect of suspended CaCO$_3$ on the hydrogenation of DEHP appeared to be negligible (Fig. 9).

Finally, the effect of residual PVC on the conversion rate of DEHP was evaluated, as the complete removal of PVC from a solvent/anti-solvent/plasticizer mixture may be challenging. Therefore, virgin PVC was dissolved in DEHP (3 h at 100 °C) in an amount corresponding to 5 wt% of the plasticizer fraction; this mixture was, after cooling to room temperature, directly added to the reactor. Under mild hydrogenation conditions, the strongly inhibiting effect of PVC on the hydrogenation catalyst is clear: less than 6% of DEHP was converted after 300 minutes of reaction time (Fig. 9). Besides, a remarkable amount of solids were recovered from the reactor, which ^{1}H-NMR analysis revealed to be largely the PVC that had previously been dissolved in the plasticizer fraction. This PVC reprecipitation is presumably caused by the addition of the hydrogenation solvent (*i.e.* 2-EH) to the plasticizer mixture, as alcohols have been proven to be excellent anti-solvents for PVC.[48] In any case, the PVC precipitation can undoubtedly foul the heterogeneous hydrogenation catalyst, rendering it inactive. Next, we evaluated the possible removal of residual PVC before the Ru-catalyst is added to the mixture by mixing the plasticizer fraction (containing the PVC) with 2-EH for 16 h at room temperature, *prior* to the catalytic reaction. As expected, the PVC precipitated again and the formed solids

were removed by centrifugation (10 min, 3000 rpm). Consequently, PVC was no longer detected in the liquid phase by ^{1}H-NMR, even if it must be noted that ^{1}H-NMR may not have sufficient sensitivity to detect trace amounts of dissolved polymers. A fourfold increase of the catalyst's activity was observed in the subsequent hydrogenation experiment (Fig. 9). On the other hand, the conversion rate was only partially restored compared to its maximum observed in the pure DEHP hydrogenation and the catalyst's activity again declined over time, albeit in a less pronounced way than in the reaction with the non-centrifuged mixture. This might indicate that even small amounts of PVC could still physically attach to the catalyst over time and thus hinder the hydrogenation.
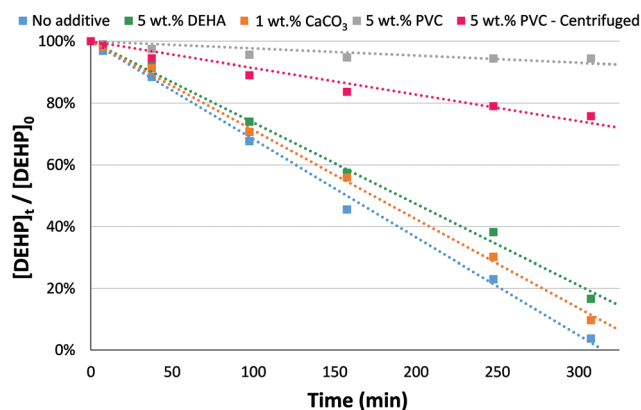

Fig. 9 Effect of co-extracted plasticizers (DEHA), residual PVC and residual filler (CaCO$_3$) on the hydrogenation rate of DEHP. Reaction conditions: DEHP-with-additive in 2-EH (0.5 mol L^{-1}; 25 mL), 0.05 mol% Ru/Al$_2$O$_3$ [1 wt%], 5 mol% H_2SO_4, 50 bar H_2 at 80 °C.

Proof of concept on PVC waste-extracted phthalates

With the insights obtained from experiments on virgin phthalates, upcycling tests were performed on plasticizers extracted from post-consumer PVC flooring waste. The used extract represents the crude output from a pPVC recycling unit that operates *via* a dissolution–precipitation approach and fully removes the employed solvents by evaporation; no additional purification steps were performed.[50,51] First, the volatile content of the plasticizer extract was analyzed by GC/GC-MS: only phthalate plasticizers (DIBP, DBP, BeBP, DEHP, isomeric mixtures of diisooctyl phthalate and DINP) and some co-extracted aliphatic esters like DEHA were clearly present; no other organic compounds were detected or identified. Based on the chromatogram, more than 75% of the detected plasticizers are phthalate esters and about 5% contains a benzyl–oxygen bond (BeBP; *vide supra*). Despite its apparent purity, the extract appears more viscous than virgin phthalates and it also has an orange-brown color (instead of being colorless). To further study the chemical content of this extract, the recovered plasticizer fraction was additionally analyzed by ^{1}H-NMR: while the extract again seems fairly pure, the broad proton signals between 4.3 and 4.7 ppm were indicative for the pres-
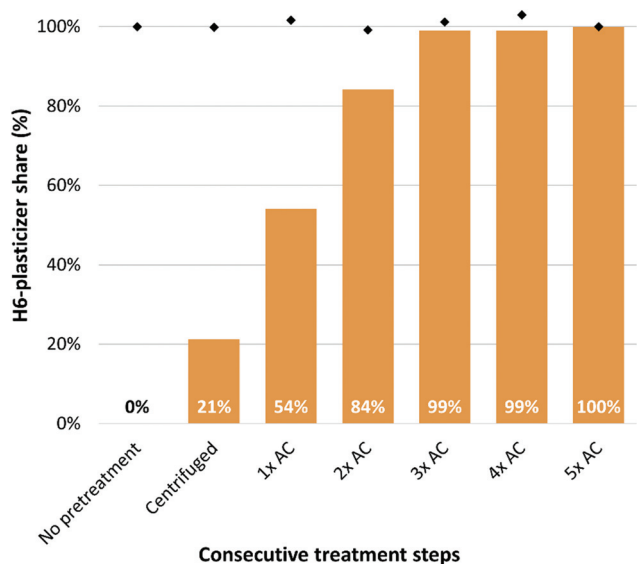
Fig. 10 Activated carbon as pre-treatment for the upcycling of waste-extracted phthalate plasticizers. Reaction conditions: addition of AC (see figure; 0.0125 g AC per mL liquid) to an extract-in-2-EH mixture (4.107 mL solvent per g extract), 1 mol% Ru/Al$_2$O$_3$ [1 wt%], 40 bar H$_2$ at 140 °C, for 240 min. Diamonds for the phthalate mass balance after each pre-treatment step, before the hydrogenation experiment.

ence of residual PVC (±2.5 wt% of the extract). This may explain the physical properties mentioned above; even slight, thermally induced dehydrochlorination of PVC can result in orange-colored conjugated polyenes.[49,61,62]

In view of the detected BeBP, the coupled (trans)esterification–hydrogenation was chosen for the subsequent upcycling of the extract. Additionally, the amount of Ru-catalyst was increased to 1 mol% to compensate for the rate-delaying effects caused by residual PVC and co-extracted aliphatic plasticizers. In a first hydrogenation test, the plasticizer extract was used as such, which did not yield any hydrogenation (Fig. 10). This is likely the result of the precipitation of residual PVC on the Ru-catalyst through contact with the alcohol solvent, just as observed in the kinetic experiment of Fig. 9. Henceforth, the extract was mixed overnight with 2-EH allowing the removal of the insoluble compounds by centrifugation prior to the catalytic process. Although the hydrogen-

ation still proceeded arduously (Fig. 10), the catalytic improvement corresponded to the data obtained in the PVC addition experiments. In order to further purify the extract, the plasticizer mixture was additionally pre-treated with activated carbon (AC; 0.0125 g AC per mL liquid, 16 h), as a cheap and widely applicable adsorbent material. After each purification step, a liquid sample was collected and tested in the catalytic upcycling process (Fig. 10): while the simple centrifugation of the reaction mixture as pre-treatment led to a conversion of 21%, one additional adsorption step with AC more than doubled the hydrogenation yield resulting in 54% H6. Moreover, complete hydrogenation of end-of-life PVC-extracted phthalate plasticizers was reached after only 240 min of reaction time when the extracted mixture underwent three or more consecutive pre-treatment steps with AC.

In short, proof of concept for the revalorization of PVC waste-extracted phthalate plasticizers has been established on lab-scale, *via* a two-step process (Fig. 11): (1) a pre-treatment of the extract with an alcohol solvent and activated carbon followed by (2) the coupled (trans)esterification–hydrogenation of phthalate plasticizers into DINCH-like structures. To the best of our knowledge this is the first successful upcycling strategy for end-of-life phthalates.

Characterization of catalyst and adsorbent after exposure to extract

A spent Ru-catalyst was characterized after a hydrogenation reaction of the extract, which was solely pretreated by centrifugation (*vide supra*; Fig. 10). In order to facilitate the possible detection of sulfur-containing contaminants in the extract, no H$_2$SO$_4$ was added in the described reaction. This spent sample was analyzed by scanning transmission electron microscopy – energy-dispersive X-ray spectroscopy (STEM-EDX) to obtain a clearer understanding of the compounds adsorbing on the catalysts' surface (Fig. 12 and Fig. S25 in ESI†). First, STEM images confirm the high dispersion of small Ru clusters on the alumina support (ESI, Fig. S26†). Moreover, the elemental mapping suggests a catalyst poisoning by S and Cl, as these atoms seem to be preferentially deposited near the Ru particles (Fig. 12). The inhibition by Cl can be readily ascribed to traces of PVC remaining in the extract mixture, even after precipitation of the major part of the polymer by an anti-solvent and by centrifugation. The inhibitory effect
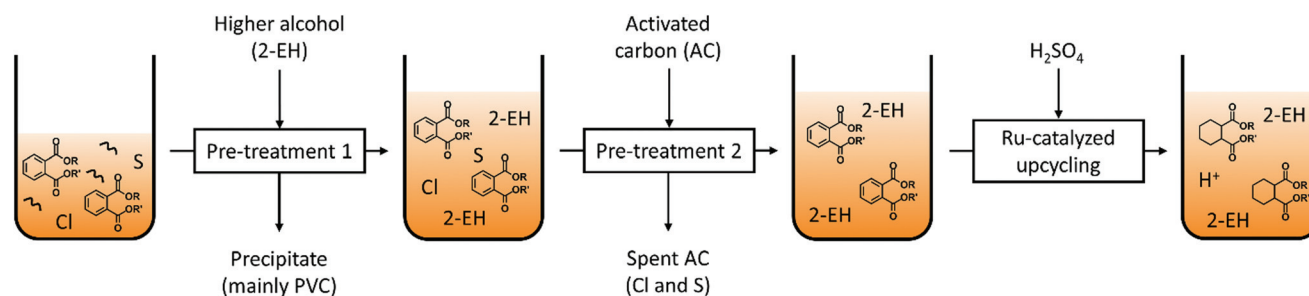

Fig. 11 Schematic overview of the upcycling of PVC waste-extracted phthalate plasticizers.
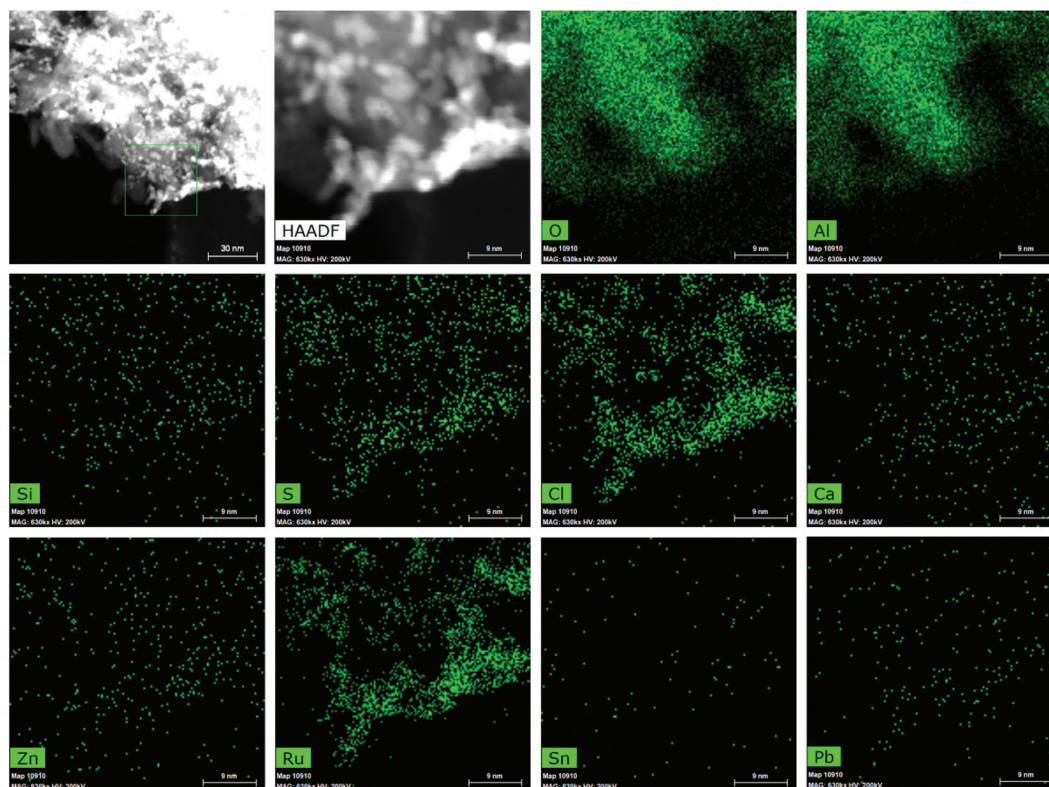
Fig. 12 HAADF–STEM images and corresponding STEM-EDX elemental maps of the spent Ru-catalyst. The catalyst was recovered after a reaction without H_2SO_4 and in which the insoluble PVC fraction was removed by centrifugation before the catalytic experiment.

of sulfur containing molecules is well-known in catalytic hydrogenation; in this particular case, the S-containing compounds likely originate from PVC additives, such as sulfonate plasticizers and/or isothiazolin biocides.

A fresh AC sample and an AC sample that had been exposed to the extract were additionally analyzed by TEM-EDX.

Considering that the fresh AC exclusively contains C and O atoms (ESI, Fig. S27†), all other detected elements on the spent material (Fig. 13 and Fig. S28 in ESI†) should originate from the extract mixture. Therefore, the signals representing carbon or oxygen were excluded from the subsequent elemental analyses. In all investigated domains, Cl was the
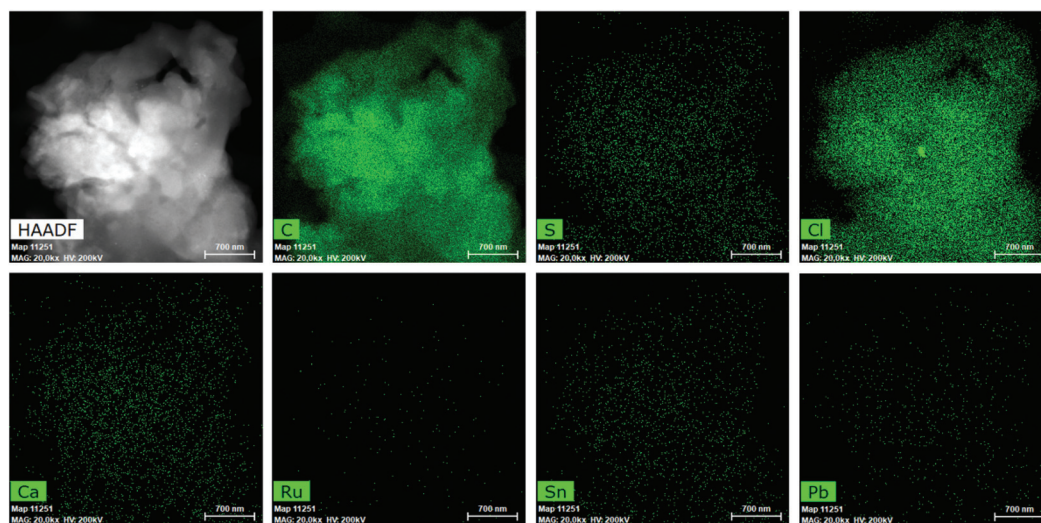

Fig. 13 HAADF–STEM images and corresponding STEM-EDX elemental maps of the spent activated carbon, recovered from the first pre-treatment (1× AC).
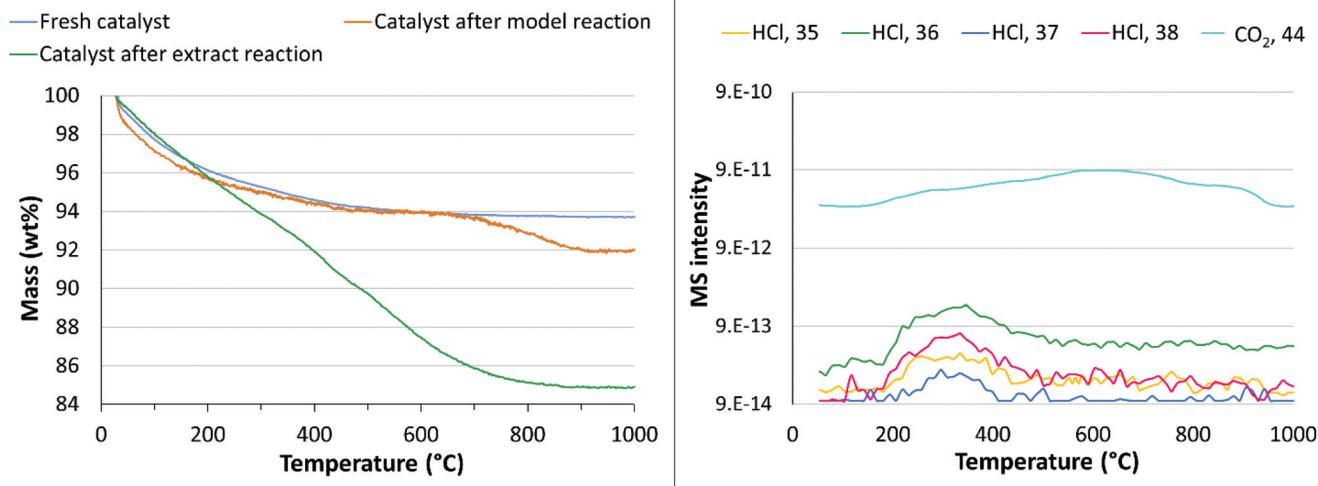
Fig. 14 (left) Thermogravimetric analyses of (spent) Ru-catalysts. (right) Mass spectra recorded during the thermogravimetric analysis of the spent Ru-catalyst after the extract reaction.

most abundantly element present (45–78%), followed by Ca (7–12%) and S (3–8%); Sn, Cd, Zn and Pb, which are encountered in some (historic) PVC stabilizers, were not detected in significant amounts (0–1%; Fig. S9 in ESI†). These results further imply that the observed increase in catalytic activity after extract purification (Fig. 10) largely originates from the adsorption of chlorinated compounds (presumably PVC and/or its oligomers) and additionally from the adsorption of sulfur-containing molecules on the AC. The adsorbed Ca clearly originates from the PVC filler, which has been shown to have little effect on the hydrogenation rate (Fig. 9).

In addition to the TEM-EDX analyses, the spent Ru-catalysts were further characterized by Thermogravimetric Analysis – Mass Spectrometry (TGA-MS). The recorded mass loss for the Ru-catalyst after a model reaction with virgin phthalate (0.5 mol L^{-1} DEHP in 2-EH, 5 mol% H_2SO_4, 140 °C, 50 bar H_2) is largely similar to that recorded for the fresh catalyst, with the small exception of an additional mass loss of 2 wt% observed around 700–900 °C (Fig. 14, left). On the other hand, a much larger mass loss (±9%) was recorded for a catalyst that had been in contact with a non-purified extract. The obtained MS intensities (Fig. 14, right) further confirm the adsorption of PVC on the catalyst, as HCl is clearly detected from 200 °C onwards, with a maximum around 350 °C. Furthermore, the steady increase in CO_2 could possibly be related to the oxidative removal of the polyacetylene structures formed *in situ* from heated PVC. These trends were not observed in the TGA-MS analysis of a catalyst recovered from the reaction with virgin phthalate (ESI, Fig. S29†).

Conclusions

The catalytic upcycling of phthalates, extracted from post-consumer PVC waste, has been demonstrated *via* a coupled (trans)esterification–hydrogenation process, preceded by a simple and cheap extract pre-treatment. For the ring-hydrogenation of pure, virgin phthalates, supported Ru-catalysts, especially Ru/Al$_2$O$_3$, proved to be highly suitable, in combination with *green* ether solvents, such as CPME. A screening of historically relevant phthalate plasticizers revealed that benzyl butyl phthalate (BeBP) is hydrogenolyzed to form monobutyl phthalate, which strongly inhibits the reaction with its carboxylic acid function. This issue was successfully circumvented by conducting the reaction in a higher alcohol, and adding a Brønsted acid catalyst which converts the carboxylic acid back to an ester functional group. In such a one-pot (trans)esterification–hydrogenation, even BeBP can be fully hydrogenated to cyclohexane derivatives.

When attempting to apply this process to phthalates derived from post-consumer PVC waste, the presence of residual PVC and S in the extract inhibited the hydrogenation catalyst. This complication was overcome by the use of activated carbon as an adsorbent for pre-treating the crude plasticizer extract. Eventually, this enables full conversion of the end-of-life phthalates to cyclohexanedicarboxylates, which are suitable to be re-used as safer plasticizers.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

References

1 H.-G. Elias and R. Mülhaupt, *Plastics, General Survey, 5. Plastics and Sustainability in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany, 2015, pp. 1–7.

2 PlasticsEurope, *Plastics – the Facts 2020: An analysis of European plastics production, demand and waste data*, 2020, https://www.plasticseurope.org/en/resources/publications/4312-plastics-facts-2020, (accessed June, 2021).

3 R. Geyer, J. R. Jambeck and K. L. Law, *Sci. Adv.*, 2017, **3**, e170082.

4 European Commission, *COM(2018)28 - A European Strategy for Plastics in a Circular Economy*, 2018, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=COM:2018 : 28:FIN, (accessed June, 2021).

5 European Commisision, *COM/2020/98 final – A new Circular Economy Action Plan: For a Cleaner and more competitive Europe*, 2020, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020DC0098#document1, (accessed June, 2021).

6 S. Wagner and M. Schlummer, *Resour., Conserv. Recycl.*, 2020, **158**, 104800.

7 A. Sevenster and J. Mater, *Cycles Waste Manage.*, 2014, **14**, 281–285.

8 H. A. Leslie, P. E. G. Leonards, S. H. Brandsma, J. de Boer and N. Jonkers, *Environ. Int.*, 2016, **94**, 230–234.

9 M. El-Fadel, A. N. Findikakis and J. O. Leckie, *J. Environ. Manage.*, 1997, **50**, 1–25.

10 J. Yu, L. Sun, C. Ma, Y. Qiao and H. Yao, *Waste Manage.*, 2016, **48**, 300–314.

11 J. N. Hahladakis, C. A. Velis, R. Weber, E. Iacovidou and P. Purnell, *J. Hazard. Mater.*, 2018, **344**, 179–199.

12 M. Bocqué, C. Voirin, V. Lapinte, S. Caillol and J.-J. Robin, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 11–33.

13 European Plasticisers, *Plasticisers*, 2020, https://www.plasticisers.org/plasticisers/, (accessed June, 2021).

14 D.-H. Phan-Vu and C.-S. Tan, *RSC Adv.*, 2017, 7, 18178–18188.

15 P. M. Lorz, F. K. Towae, W. Enke, R. Jäckh, N. Bhargava and W. Hillesheim, *Phthalic Acid and Derivatives in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany, 2007, pp. 131–180.

16 European Chemicals Agency, Annex XVII to REACH – Conditions of restriction: Entry 51, 2021, https://echa.europa.eu/substances-restricted-under-reach, (accessed June, 2021).

17 United States Consumer Product Safety Commission, *Phthalates Business Guidance & Small Entity Compliance Guide*, 2019, https://www.cpsc.gov/Business–Manufacturing/Business-Education/Business-Guidance/Phthalates-Information#, (accessed June, 2021).

18 C. Casals-Casas and B. Desvergne, *Annu. Rev. Physiol.*, 2011, **73**, 135–162.

19 K. A. Richardson, P. R. Hannon, Y. J. Johnson-Walker, M. S. Myint, J. A. Flaws and R. A. Nowak, *Reprod. Toxicol.*, 2018, **77**, 70–79.

20 K. J. Groh, T. Backhaus, B. Carney-Almroth, B. Geueke, P. A. Inostroza, A. Lennquist, H. A. Leslie, M. Maffini, D. Slunge, L. Trasande, A. M. Warhurst and J. Muncke, *Sci. Total Environ.*, 2019, **651**, 3253–3268.

21 M. Zarean, M. Keikha, P. Poursafa, P. Khalighinejad, M. Amin and R. Kelishadi, *Environ. Sci. Pollut. Res.*, 2016, **23**, 24642–24693.

22 European Commission, *IP/99/829 Ban of phthalates in childcare articles and toys*, 1999, https://ec.europa.eu/commission/presscorner/detail/en/IP_99_829, (accessed July, 2021).

23 K. Pivnenko, M. K. Eriksen, J. A. Martín-Fernández, E. Eriksson and T. F. Astrup, *Waste Manage.*, 2016, **54**, 44–52.

24 R. M. David, R. D. White, M. J. Larson, J. K. Herman and R. Otter, *Toxicol. Lett.*, 2015, **238**, 100–109.

25 Anses, *AVIS de l'Anses relatif à l'analyse de la meilleure option de gestion des risques (RMOA) pour le DINCH® (1,2-cyclohexanedicarboxylic acid, diisononyl ester, n° CAS 166412-78-8)*, 2015, https://www.anses.fr/fr/content/avis-de-l'anses-relatif-à-l'analyse-de-la-meilleure-option-de-gestion-des-risques-rmoa-pou-0, (accessed July, 2021).

26 European Chemicals Agency, *Substance Infocard: 1,2-Cyclohexanedicarboxylic acid, 1,2-diisononyl ester*, 2020, https://echa.europa.eu/nl/substance-information/-/substanceinfo/100.103.017, (accessed July, 2021).

27 BASF, *Hexamoll® DINCH - The trusted non-phthalate plasticizer*, 2019, https://www.hexamoll-dinch.com/portal/basf/de/dt.jsp?setCursor=1_1222841, (accessed on June, 2021).

28 J. E. Crespo, R. Balart, L. Sanchez and J. López, *J. Appl. Polym. Sci.*, 2007, **104**, 1215–1220.

29 HBM4EU, *Prioritiy Substance Group: Phthalates & Hexamoll® DINCH®*, https://www.hbm4eu.eu/the-substances/phthalates-and-hexamoll-dinch, (accessed July, 2021).

30 R. H. Schlosberg, J. G. Santiensteban, S. L. Soled, A. M. Malek, J. Baumgartner, S. Luo, S. Miseo and J. C. Vartuli, *US Pat*, 20060247461A1, 2006.

31 S. Soled, S. Miseo, J. Baumgartner, C. Kliewerand and H. Goris, *WO Pat*, 2016066410A1, 2016.

32 N. De Munck, H. Goris and E. Van Driessche, *WO Pat*, 2018046306A1, 2018.

33 M. Grass, B. Reeken, A. Tuchlenski, A. Kaizik and W. Buschken, *US Pat*, 20060167151A1, 2006.

34 M. Grass, A. Kaizik, W. Buschken, A. Tuchlenski, D. Maschmeyer, K.-A. Gaudschun and F. Brocksien, *US. Pat*, 20060183936A1, 2006.

35 Y. Xu, Y. Wang, C. Wu, H. Huang, Y. Zhang, J. Nan, H. Yu and Y. Zhao, *Catal. Commun.*, 2019, **132**, 105825.

36 Y.-C. Su, C.-C. Wang and C.-Y. Chen, *Chem. Eng. Res. Des.*, 2020, **161**, 178–186.

37 A. B. Lende, S. Bhattacharjee, W.-Y. Lu and C.-S. Tan, *New J. Chem.*, 2019, **43**, 5623–5631.

38 C. Mao, J. Zheng, B. M. Matsagar, R. K. Kankala, T. Ahamad, Y. Yang, K. C.-W. Wu and X. Zhang, *Catal. Sci. Technol.*, 2020, **10**, 2443–2451.

39 Y. Xu, C. Wu, Y. Wang, Y. Zhang, H. Sun, H. Chen and Y. Zhao, *Chin. Chem. Lett.*, 2021, **32**, 516–520.

40 M. Brunner, A. Böttcher, B. Breitscheidel, K. Halbritter, J. Henkelmann, L. Thil and R. Pinkos, *WO Pat*, 9932427, 1999.

41 M. Brunner, A. Böttcher, B. Breitscheidel, K. Halbritter, J. Henkelmann, L. Thil and R. Pinkos, *US Pat*, 6284917B1, 2001.

42 BASF increases plasticizer production, reorganizes businesses, *Addit. Polym.*, 2008, **2008**, 6, DOI: 10.1016/S0306-3747(08)70030-7.

43 J. Zhao, M. Xue, Y. Huang and J. Shen, *Catal. Commun.*, 2011, **16**, 30–34.

44 S. Nie, H. Li, J. Qin, Y. Wan, L. Niu, L. Chen and G. Bai, *Mol. Catal.*, 2020, **495**, 111156.

45 H. Bohnen, T. Klein and K. Bergrath, *US Pat*, 6740773B2, 2004.

46 Engelhard Industrial Bullion (EIB) Prices [USD per Troy Ounce], https://apps.catalysts.basf.com/apps/eibprices/mp, (accessed July, 2021).

47 Precious Metals Management: Metal prices, https://pmm.umicore.com/en/, (accessed July, 2021).

48 G. Grause, S. Hirahashi, H. Toyoda, T. Kameda and T. Yoshioka, *J. Mater. Cycles Waste Manage.*, 2017, **19**, 612–622.

49 D. Glas, J. Hulsbosch, P. Dubois, K. Binnemans and D. E. De Vos, *ChemSusChem*, 2014, **7**, 610–617.

50 Circular Flooring, https://www.circular-flooring.eu, (accessed July, 2021).

51 Recycling plastics - The CreaSolv® Process, https://www.ivv.fraunhofer.de/en/recycling-environment/recycling-plastics-creasolv.html, (accessed July, 2021).

52 D. Prat, A. Wells, J. Hayler, H. Sneddon, R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chem.*, 2016, **18**, 288–296.

53 A. J. Bissette and S. P. Fletcher, *Hydrogenolysis of Allyl and Benzyl Halides and Related Compounds in Comprehensive Organic Synthesis (Second Edition)*, Elsevier Ltd., 2014, pp. 1164–1184.

54 S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, John Wiley & Sons, Hoboken (United States), 2002.

55 W. Riemenschneider and H. M. Bolt, *Esters, organic in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany, 2005, pp. 245–266.

56 M. Besson, B. Blanc, M. Champelet, P. Gallezot, K. Nasar and C. Pinel, *J. Catal.*, 1997, **170**, 254–264.

57 H. Liu, R. Fang, Z. Li and Y. Li, *Chem. Eng. Sci.*, 2015, **122**, 350–359.

58 Y.-C. Su, C.-C. Wang and C.-Y. Chen, *Chem. Eng. Res. Des.*, 2020, **161**, 178–186.

59 D. F. Cadogan and C. J. Howick, *Plasticizers in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany, 2000, pp. 600–618.

60 B. Pelzl, R. Wolf and B. L. Kaul, *Plastics, Additives in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany, 2018, pp. 1–56.

61 E. D. Owen, M. Shah and M. V. Twigg, *Polym. Degrad. Stab.*, 1996, **51**, 151–158.

62 T. Kamenda, M. Ono, G. Grause, T. Mizoguchi and T. Yoshioka, *Polym. Degrad. Stab.*, 2009, **94**, 107–112.