Synthesis and evaluation of novel sustainable aliphatic plasticizers into different polymer systems.

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ABSTRACT

Plasticizers are essential to the polymer industry to (i) facilitate the processing and (ii) modify the mechanical and thermal performance of polymer materials. The need to reduce the environmental impact and toxicity of plasticizers means that viable alternatives to phthalates must be found. This has become a major current challenge. Bacterial polymers such as polyhydroxyalkanoates (PHA) like poly(hydroxy-octanoate) (PHO) appear to be promising precursors for meeting these expectations. Bacterially synthesized from sustainable resources such as plastic waste or biomass, PHOs possess ester functions and alkyl side chains that are relevant for plasticizing some rigid polymers such as PVC or thermoplastic polyurethanes (TPU). In this preliminary and conceptual study, oligomers of PHO with terminal hydroxyl functions (PHO-diol) were successfully synthesized by transesterification from PHO. The addition of alkyl chain ends was achieved by reaction with hexyl mono-isocyanate, to produce PHO-hexyl. These 2 compounds were tested for their plasticizing properties. Rigid PVC and TPU matrices were selected to evaluate the different additives (PHO-diol, PHO-hexyl and two conventional reference phthalates) at different concentrations. Polymer glass transition temperatures (T_g) were significantly reduced with all plasticizers. Plasticizing effects similar to those of phthalates were obtained with PHO-hexyl, both on the thermal and mechanical properties, compared to PHO-diol wich shows less plasticizing effects. The processability of a very rigid and brittle bio-based TPU was greatly improved with the addition of just 15 % of PHO-hexyl as plasticizer into the TPU matrix, as well as with the commercial phthalates. It is opening up a wide range of applications for this previously hardly exploitable sustainable betulin-based TPU. PHO-hexyl is thus emerging as a very promising example of a sustainable plasticizer and a potentially credible alternative to phthalates. This new plasticizer makes it possible to obtain high-performance materials that are more respectful of the environment.

KEYWORDS:

Plasticizer; TPU; PVC; Sustainable additive; PHA

INTRODUCTION

Additives are chemical compounds added to polymer matrices, in relatively low concentrations, except for some as fillers/reinforcements or plasticizers. Without additives, polymers would have virtually no properties for use, and often too little resistance over time. Additives play a crucial role in the behavior of materials in terms of appearance and properties (mechanical, thermal, electrical, optical …). They can also influence durability, stability, UV resistance, fire resistance... Additives can be classified into 4 distinct categories (Hahladakis et al., 2018): (i) functional additives (antioxidants, plasticizers, anti-UV…), (ii) colorants, (iii) fillers and (iv) reinforcements. Several literature reviews have already been published in this field (Allen and Edge, 2021; Ambrogi et al., 2017; Marturano et al., 2017), which shows that the choice of an additive is based on numerous criteria, such as the nature and structure of the macromolecules. The additive must be compatible and dispersible into the matrix.

Plasticizers are among the most widely used additives in the industry, with a market estimated at \$17 million, representing over 60 % of the additives market (MarketsandMarkets, 2023). They are defined by IUPAC as « *a material incorporated in a polymer to increase the polymer's workability, flexibility or extensibility* » (Wilkes et al., 2005). They are essential for enhancing polymer flexibility and mobility, improving processability (Vieira et al., 2011), with a great reduction of the glass transition temperature (T_g) of the matrix. Plasticizers also decrease the stiffness of the matrix as represented by Young's modulus (E) and increase the elongation at break (ε_{max}) (Vilics et al., 1997). They modify intermolecular forces and polymer crystallinity, by increasing the free volume and the chains mobility (Chandola and Marathe, 2008). They thus make it possible to adjust the thermomechanical properties of a material for a specific application or process. For example, some thermoplastics are too rigid and brittle to be easily shaped by conventional thermomechanical processes. Thanks to plasticizers, these polymers could be shaped more easily, acquiring new properties, opening up new fields of application.

Polyvinyl chloride (PVC) is the most plasticized of all polymers, giving it new properties and applications in e.g., packaging, construction materials, toys, healthcare... Over 80 % of plasticizers produced are used for PVC (Rahman and Brazel, 2004). Phthalates, which are esters of phthalic acids, represent the most common PVC external plasticizers, such as bis(2-propylheptyl) phthalate (DPHP) or diisodecyl phthalate (DIDP), whose structures are shown in Figure 1 (Wypych, 2004). These phthalates have many advantages, such as excellent compatibility, low volatility and low cost (Bocqué et al., 2016). The carbonyl groups are able to form weak bonds with PVC on the C-Cl dipole and thus increase their compatibility and miscibility, forming a network based on weak interactions. In addition, the fatty chains from these plasticizers increase the inter-macromolecular free space between the chains and thus bring mobility. Nevertheless, these external plasticizers can partially migrate outwards by

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exudation and/or volatilization, leading to problems of phthalate bioaccumulation in the human body and the environment (Eales et al., 2022). These fossil-based additives are suspected of causing health problems, such as endocrine disruption. Regulations have long been in place to limit the use of phthalates notably in toys for young children (Kamrin, 2009). Then, since 1999, the European Commission has banned the use of phthalates in children's toys. In 2005, an EU directive (2005/84/EC) made this ban permanent. This directive also extended the ban to childcare articles (Lioy et al., 2015). As a result, the interest in new plasticizers of renewable and sustainable origin has risen rapidly in recent years, as shown by an abundant recent literature. For instance, a multitude of biobased esters have been tested. Several literature reviews present plasticizers based on esters of vegetable oils, citric acid (called citrates) or sugar derivatives such as isosorbide (Bocqué et al., 2016; Jia et al., 2018).

Poly(hydroxyalkanoate) (PHA) are non-toxic (co)polyesters, which are bioproduced by a wide range of bacteria as intracellular storage materials. These bacterial polymers can be synthesized by fermentation from a wide variety of carbon-based substrates. Different biomasses or waste plastics can be used as carbon sources. For example, poly(ethylene terephthalate) (PET) can be depolymerized at the end of its life by enzymatic or chemical hydrolysis into terephthalic acid and ethylene glycol. These monomers can then be converted by genetically modified bacteria to produce PHAs (Tiso et al., 2021). Depending on the substrate structure and the enzymes involved, a wide range of bacterial polymers can be obtained, differentiated by their number of carbons per repeat unit (Cerrone et al., 2023). Among them, medium side-chain length (mcl) PHAs have repeat units of 6 to 12 carbons, such as poly(3-hydroxy-octanoate) (PHO). The chemical structure of PHO is shown in Figure 1.

In this study, PHO is used as a plasticizer precursor thanks to the presence of (i) ester groups and (ii) relatively long pendant alkyl chains. Various plasticizers are synthesized from PHO and evaluated with PVC and rigid TPU matrices in a preliminary and conceptual approach. In a first step, the initial molar mass of PHO was reduced in a controlled manner to improve its plasticizing effect (Zhang et al., 2021). Hydroxyl-terminated oligomers (PHO-diol) were obtained by transesterification (Wendels et al., 2021) when BDO was selected as the diol. This latter can notably be obtained from biomass (Wendels et al., 2021) or from waste plastics, such as poly(butylene adipate terephthalate) (PBAT) or poly(butylene succinate) (PBS), which are depolymerized by chemical hydrolysis (Westhues et al., 2018). The chain ends of PHO-diol were then modified with hexyl (mono)isocyanate (HI), to obtain an end-capping with short alkyl chains (PHO-hexyl) with the aim to improve the additive's dispersion into the matrix, and its plasticizing effect. To test the different additives, formulations were made from rigid PVC and TPU, at different plasticizer concentrations. Commercial references based on phthalate groups, such as DPHP and DIDP were used. The chosen TPU was synthesized with a high content in cycloaliphatic sustainable betulin, which brings high rigidity and brittleness to the polymer, preventing its

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processability and thus making it hardly exploitable. These different formulations were then evaluated and characterized to determine the plasticizers efficiency, initially in terms of T_g evolution and mechanical properties.
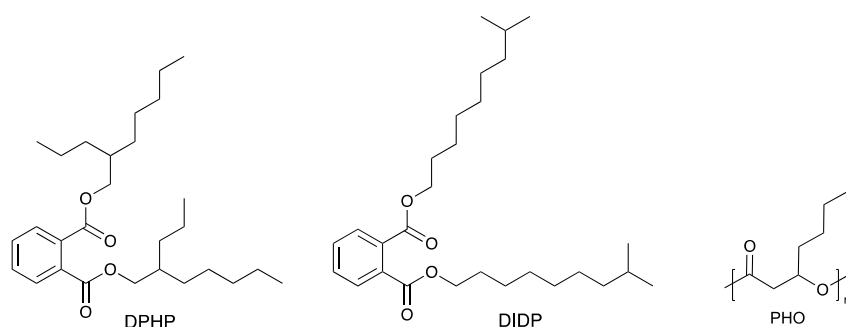

Figure 1. Chemical structures of phthalate-based plasticizers (DPHP et DIDP) and PHO.

MATERIALS AND METHODS

Chemicals and materials

BDO (99%), dibutyltin dilaurate (DBTL) (95%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%), chromium (III) acetyl acetonate (Cr(acac)$_3$, 97%), cholesterol (>99%), and HI were purchased from Sigma Aldrich. Bis(2 methoxyethyl) ether (diglyme) (99%) and deuterated chloroform (CDCl$_3$) were ordered from Acros Organics. Tetrahydrofuran (THF) (99.8%) was supplied by Fischer Scientific. Suprasec 1306 4,4'-diphenylmethylene diisocyanate (MDI) was obtained from Huntsman (USA). Poly(tetrahydrofuran) (PTHF) with a weight-average molar mass (M_w) of 650 g mol^{-1} (PTHF 650) was acquired from BASF (Germany), under the brand name PolyTHF®. Betulin (98%) was purchased from NST-Chemicals (USA). PHO was kindly bioproduced and supplied by the University of Dublin in the frame of MIX-UP Project (Horizon 2020 research and innovation program under grant agreement No 870294). PHO was bioproduced according to the protocol given by Cerrone et al. (Cerrone et al., 2023). Vinnolit S 4170 PVC ($Mn \simeq 65$ kg mol^{-1}) was supplied by Westlake Vinnolit (Germany). DPHP and DPIP were kindly supplied by SOPREMA (France).

THF was dried with 15 wt% of pre-activated molecular sieves 4 Å 24 h prior to use (molecular sieves activation: 150 °C in an oven under vacuum, 20 h). Betulin was dried in an oven vacuum at 40 °C overnight prior to use. The other products were used as received.

Plasticizers synthesis from PHO

PHO-diol was prepared from native PHO by transesterification reaction with BDO. The synthetic route for this oligomer is shown in Figure 2, according to a previous protocol (Wendels et al., 2021). In a two-

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neck round-bottom flask with a water cooler, 60 g of PHO are dissolved in diglyme (250 mL) and BDO (150 eq/OH), then magnetically stirred at 100 °C under argon until completely dissolved. The temperature is then adjusted to 160 °C. Then, DBTL (0.5 eq/OH) is added, followed by stirring under argon for 48 h. The progress of the reaction is monitored by ^{1}H NMR until a number-average molar mass (M_n) of around 800 g mol^{-1} is obtained. The reaction is then cooled down before purification. The product is dissolved in chloroform and washed three times with distilled water to remove the BDO in excess. The product is then distilled to remove traces of diglyme and water. An orange viscous oil is obtained.
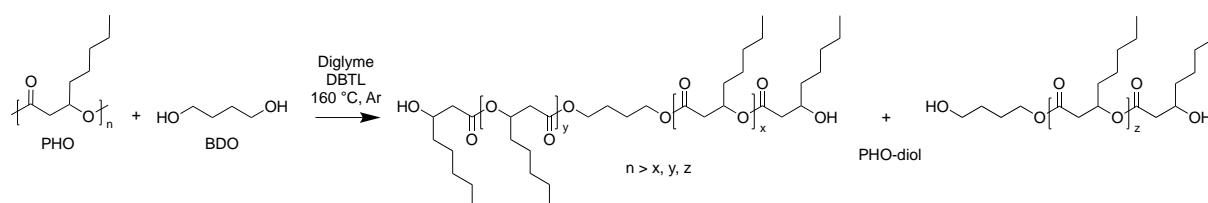

Figure 2. Synthesis of PHO-diol from PHO by transesterification with BDO.

To prepare PHO-hexyl, PHO-diol is placed in a two-neck round-bottom flask under an argon flow. HI (1.05 eq/OH) is then slowly introduced. The reaction is stirred for 1 h at 60 °C, under argon flow. The reaction pathway is shown in Figure 3.
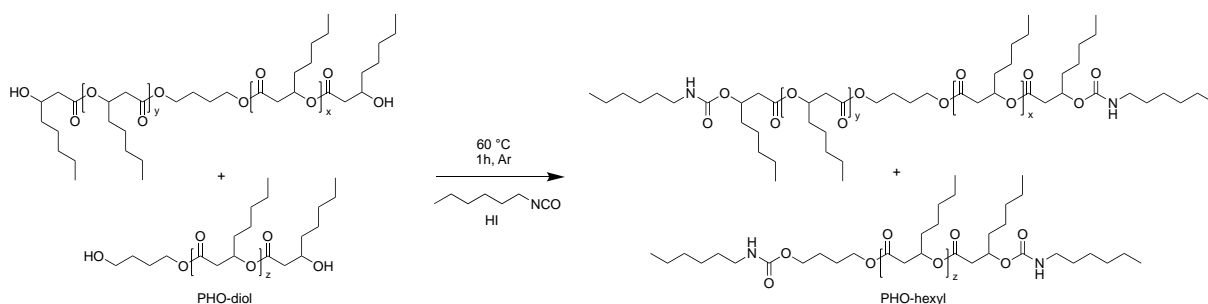

Figure 3. PHO-hexyl synthesis from PHO-diol with HI.

Characterization of synthesized plasticizers

The structure of the synthesized plasticizers was determined by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and quantitative ^{31}P NMR on a Bruker 400 MHz spectrometer. ^{1}H NMR spectra were obtained in CDCl$_3$, with calibration to the CDCl$_3$ chemical shift at δ = 7.26 ppm.

Quantitative ^{31}P NMR samples were prepared by dissolving 15-20 mg of product in 500 μL of CDCl$_3$, following a protocol from the literature (Duval and Avérous, 2016). Next, 100 μL of a standard cholesterol solution (0.1 mol L^{-1} in a 1/1.6 CDCl$_3$/pyridine mixture) containing Cr(acac)$_3$, an NMR relaxation agent, was added along with 50 μL of 2 chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

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Samples were stirred for one hour and then transferred into an NMR tube. ^{31}P NMR calibration is based on the reaction of water with the phosphylating agent, in pyridine/CDCl$_3$ at δ = 134.8 ppm. This technique quantifies the amount of OH groups in a (macro)molecule by reaction with a phosphorylated group, which is detected in ^{31}P NMR.

The number-average molar mass (M$_n$) of PHO-diol oligomers was obtained from ^{1}H NMR using Equation 1. $I_{3,6}$ represents the intensity of the peak at δ = 3.67 ppm, corresponding to the two protons in position α of the primary hydroxyl groups at the end of the chain. The end-of-chain unit with these chemical groups has a molar mass of 89.11 g mol^{-1}. $I_{2,4-2,2}$ represents the intensity of the peak between δ = 2,4 and 2,2 ppm which is based on the protons in α-position of the secondary OH groups at the end of the chain. The end-of-chain unit possessing these groups has a molar mass of 143.21 g mol^{-1}. $I_{2,6-2,4}$ represents the intensity of the peaks between δ = 2.6 and 2.4 ppm of the CH$_2$ in position α of the ester, corresponding to a hydroxy octanoate (HO) repeating unit with a molar mass of 142.20 g mol^{-1}.

$$(1) \qquad M_{n_{RMN}} = \frac{I_{3,6} \times 89.11 + I_{2,6-2,4} \times 142.20 + I_{2,4-2,2} \times 143.21}{0,5 \times (I_{3.6} + I_{2.4-2.2})}$$

Quantitative ^{31}P NMR is used to determine the hydroxyl value (i$_{OH}$ in mg KOH g^{-1}) of PHO-diol for the PHO-hexyl synthesis step, using Equation 2, where m is the sample mass in g. C and V are the concentration (in mol L^{-1}) and the volume introduced (mL) of the standard solution, respectively. I_1 is the intensity of peaks between δ = 133.5 and 134.6 ppm, corresponding to primary alcohols at the end of the chain. I_2 is the intensity of peaks between δ = 135.0 and 137.0 ppm, corresponding to terminal secondary alcohols. I_{BDO} is the intensity of the peak at δ = 134.2 ppm, corresponding to residual unreacted BDO. 56.1 is the molar mass of potassium hydroxide (KOH) in g mol^{-1}.

$$(2) \qquad iOH = 56.1 \times \frac{C \times V \times (I_1 + I_2 + I_{BDO})}{m}$$

M$_n$, weight-average molar mass (M$_w$) and dispersity (Đ) were also determined by size exclusion chromatography (SEC), on a Waters Acquity APC apparatus in THF (0.6 ml min^{-1}) at 40 °C. Three columns (Acquity APC XT 450 Å 2.5 µm 4.6 × 150 mm, 200 and 45) are used. The calibration was carried out using polystyrene (PS) standards.

Formulations based on plasticizers.

Different formulations with PVC and TPU matrices were prepared with the addition of plasticizers at different content (wt%), within plausible ranges for an application context (from 15 wt%). According to the literature, plasticizers contents between 15 and 50 wt% are recommended for PVC plasticization (Chaudhary et al., 2016). Moreover, the concentrations chosen are well beyond a potential anti-plasticization range commonly found at low concentrations for most plasticizers especially in PVC (Kinjo and Nakagawa, 1973). The formulations are presented in Table 1.

Table 1 : PVC and TPU-based formulations with different plasticizers, at various contents (in wt%).

Plasticizers:	DPHP:DIDP (50/50)	PHO-diol	PHO-hexyl
PVC Matrix	15	15	15
	30	30	30
	/	45	/
TPU Matrix	15	/	15
	30	/	30

To achieve this, 15 g of PVC are added to 150 ml THF at 50 °C and stirred until completely dissolved. The appropriate amount of plasticizer is then added. For the commercial plasticizers DPHP and DIDP, a 50/50 (wt%) mixture is made, denoted "DPHP:DIDP". The solution is stirred for a further 10 min, then poured into a glass Petri dish and left overnight in a fume hood for solvent evaporation. The final material was then placed in a vacuum oven at 50 °C for 6 h to remove the traces of solvent.

10 g of a sustainable TPU was synthesized in a conventional two-step process with MDI as the diisocyanate, PTHF 650 as the polyether polyol and betulin as the chain extender. A prepolymer NCO/OH number (i_{NCO}) of 3 and a final $i_{NCO} = 1$ were chosen to obtain a specific rigid polymer with high T_g. The synthesis route is shown in Figure 4. After overnight to finalize the reaction in a vacuum oven at 50 °C, 100 mg of TPU were dissolved into 5 ml THF at 60 °C. Then, an appropriate amount of plasticizer is added, and the resulting solution is stirred for 5 min. The mixture is poured into a glass Petri dish and left overnight in a fume hood to evaporate the solvent. Traces of solvent are then removed in a vacuum oven at 50 °C for 6 h.
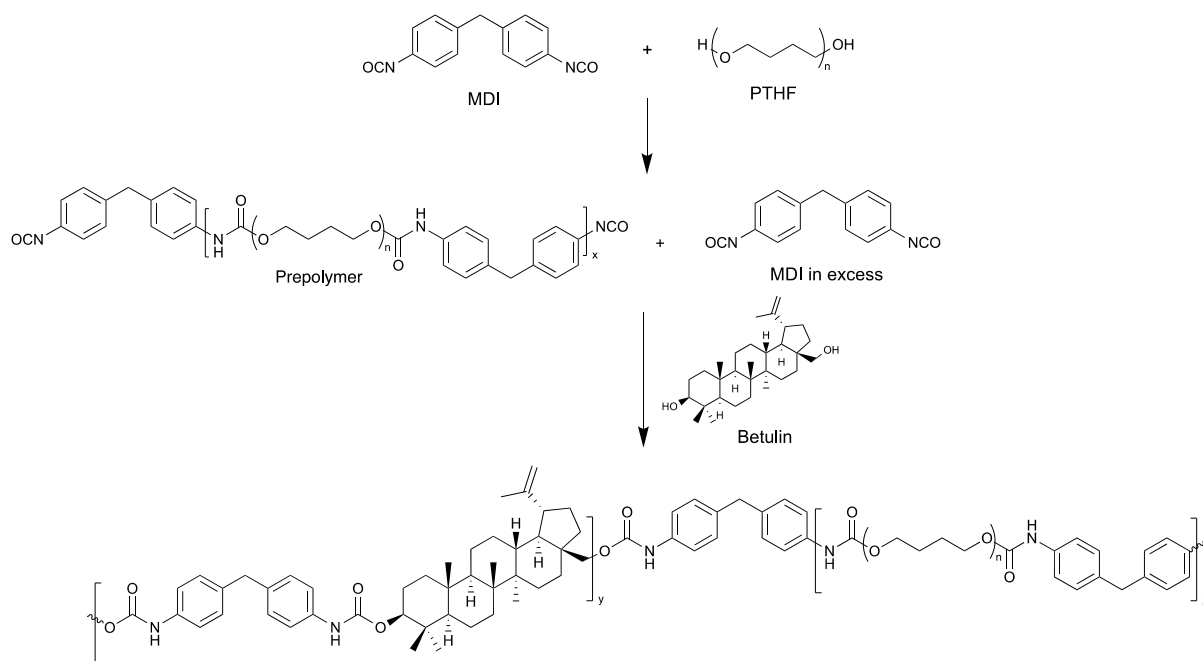
Figure 4. Two-step synthesis of rigid TPU matrix with MDI, PTHF 650 and betulin.

Formulation characterizations

Thermal analysis by differential scanning calorimetry (DSC) was carried out using a TA Instruments Discovery DSC 25. Approximately 10 mg of polymers were placed in sealed aluminum capsules, then analyzed under nitrogen flow (50 mL min^{-1}). A three-step procedure with ramps of 10 °C min^{-1} was applied as follows: (i) heating from 90 °C to 200 °C to erase the thermal history of the samples, (ii) cooling to 90 °C and (iii) heating from 90 °C to 200 °C. T_g values are determined during the second heating step.

Mechanical uniaxial tensile tests were carried out on an Instron 5567H (USA) with a 10 kN cell. Experiments were carried out at 20 °C with a constant crosshead speed of 20 mm min^{-1}. Series of at least five samples with dimensions of around $30 \times 10 \times 1$ mm^3 were taken. Young's modulus (E), strength at break (σ_{max}) and elongation at break (ε_{max}) were calculated. To produce the specimens, 1 mm-thick films were hot-pressed using a LabTech Engineering Company Ltd. press. For PVC, around 13 g of polymer were first preheated to 150 °C for 3 min in a 10 x 10 cm^2 mold, and then pressed between the plates at 160 bar and then cool down till room temperature for 5 min.

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RESULTS AND COMMENTS

Synthesis and characterization of plasticizers from PHO

The ester groups and the alkyl pendant chains of PHO could make it a good precursor for plasticizers. However, its M_n is 21.6 kg mol^{-1}, which is too high for a plasticizer (Zhang et al., 2021). A transesterification reaction strategy with a short diol was thus considered to obtain controlled low M_n oligomers. As PHO is not soluble in BDO, a sustainable reactive solvent, diglyme was therefore used as a co-solvent with high-boiling point, for a reaction at 160 °C. The reaction is shown in Figure 2. The progress of the reaction is monitored by ^{1}H NMR until to obtain a M_n close to 800 g mol^{-1}. After 48 h of reaction, a plateau is reached, and the M_n no longer varies. The M_n of the starting PHO and the final PHO-diol are measured by ^{1}H NMR and SEC and reported in Table 2. M_n value is thus reduced by 18 during the reaction. This M_n can be reached in 1.5 hours by increasing the amount of DBTL to 50 eq/OH. The ^{1}H NMR spectra of the starting PHO and the PHO-diol obtained are given in SI (Figures A9 and A10). The i_{OH} was calculated by ^{31}P NMR and reported in Table 2. The value is multiplied by two during this synthesis step.

Table 2. M_n obtained by RMN ^{1}H and SEC. i_{OH} obtained by RMN ^{31}P.

Samples	M_n by RMN ^{1}H (g mol^{-1})	M_n by SEC (g mol^{-1})	Đ	i_{OH} (mg KOH g^{-1})
PHO	/	21 600	1.47	77 ± 10
PHO-diol	729 ± 5	1 190	2.28	148 ± 9

To obtain an effective plasticizer, the ratio between polar and apolar groups must be appropriate. Indeed, the OH groups at the end of the PHO-diol can (i) improve plasticization by creating interactions between the plasticizer and the matrix, but also (ii) limit a good dispersion in the matrix by locally creating weak bonds with other plasticizer molecules to form micro-aggregates. To this end, studies have shown that grafting long alkyl chains onto polar chain ends is a good strategy for adapting the ratio between the number of polar and apolar groups (Pereira et al., 2020) and obtaining good chain mobility.

Then, a second synthesis step was carried out to add alkyl chain ends that could both promote additive dispersion in the matrix, but also increase the free volume between polymer chains and thus their mobility. To this end, a fast conversion reaction of PHO-diol to PHO-hexyl was carried out with HI under stoichiometric, solvent-free conditions. The structure of PHO-hexyl was confirmed by ^{1}H NMR (SI, Figure A11).

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Analysis of the PVC-based formulations

To determine the plasticizing efficiency of the synthesized additives and compare them with commercial references such as DPHP and DIDP, the plasticizers were incorporated into a PVC matrix at different contents (Table 1).

To determine the plasticizer effect, the T_g values of the different materials was determined by DSC. The greater the variation in T_g compared with the matrix alone, the greater the plasticizing effect with an addition of mobility. The T_g values are plotted in Figure 5. The addition of plasticizer leads to a very significant decrease in T_g, between 14 and 64 °C, for the different formulations. This result is the consequence of various associated phenomena which are linked to (i) the strong C-Cl dipole of PVC which interacts with the different dipoles carried by the plasticizers (ester and urethane functions) creating weak stabilizing interactions (limiting exudation) and forming a relatively structured network, and (ii) the pendant chains which themselves bring free volume and therefore mobility to the network formed.

The T_g decrease is more pronounced for formulations based on PHO-hexyl than on PHO-diol ones. It can also be noted that formulations containing PHO-hexyl have T_g comparable to those based on the conventional and commercial plasticizer mixture DPHP:DIDP. Indeed, the T_g decreases by only 20 °C for 45 wt% of PHO-diol (T_g = 63 °C), whereas it decreases by 50 °C for 30 wt% PHO-hexyl (T_g = 32 °C).

Same trends have been recently observed in the literature. A decreased of T_g of 77 °C was obtained with 30 wt% aliphatic polyesters with unprotected chain ends with PVC (Gao et al., 2018). A recent study showed that it is possible to adjust the plasticizing effect and therefore the T_g of materials, by playing on the length of the alkyl chain grafted onto polyester chain ends (Pereira et al., 2020). For example, T_g values below 30 °C have been achieved with alkyl chain ends with 8 or 12-carbons. Indeed, the OH groups at the end of the PHO-diol chain may tend to form aggregates due to the hydrogen bonds formed between plasticizer molecules. As a result, PHO-diol may be poorly distributed in PVC, reducing the efficiency of the plasticizing effect. Thus, the alkyl chain ends of PHO-hexyl would enable better dispersion in the matrix, beyond the increase in free volume.
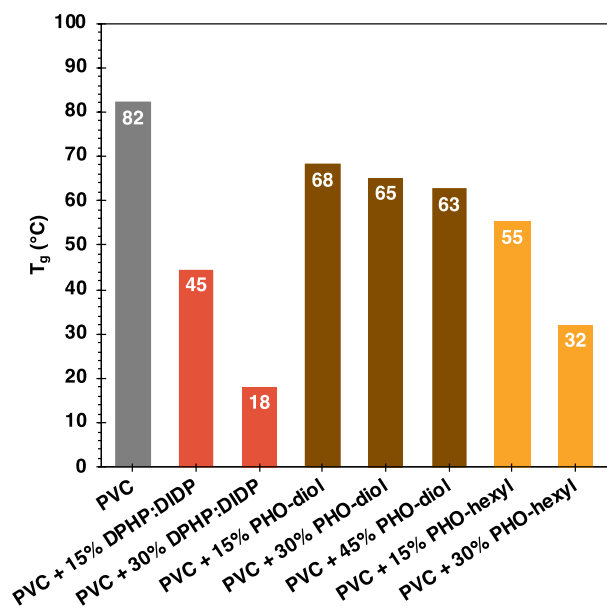
Figure 5*. Tg values of neat and plasticized PVC, from DSC.*

Uniaxial tensile tests were also carried out to determine the evolution of E and ε_{max} of formulations containing PHO-hexyl and DPHP:DIDP. The results are reported in Figure 6. All values for plasticized PVCs are similar, indicating a similar plasticizing effect between phthalates and the sustainable additive. Moreover, σ_{max} and E were at least divided by 6 and 13, respectively, compared to neat PVC values. The plasticization effect reduces the rigidity of materials and thus lowers E and thus σ_{max}. As a result, σ_{max} increased by a factor of at least 12, confirming the plasticizing effect of these molecules.

These results are similar to those obtained in the literature with polyesters based on 8- or 12-carbon alkyl chain ends. E values between 266 and 83 MPa and ε_{max} 83 and 303 % were obtained with 30 wt% of polyesters modified with dodecyl or octyl chain ends (Pereira et al., 2020).
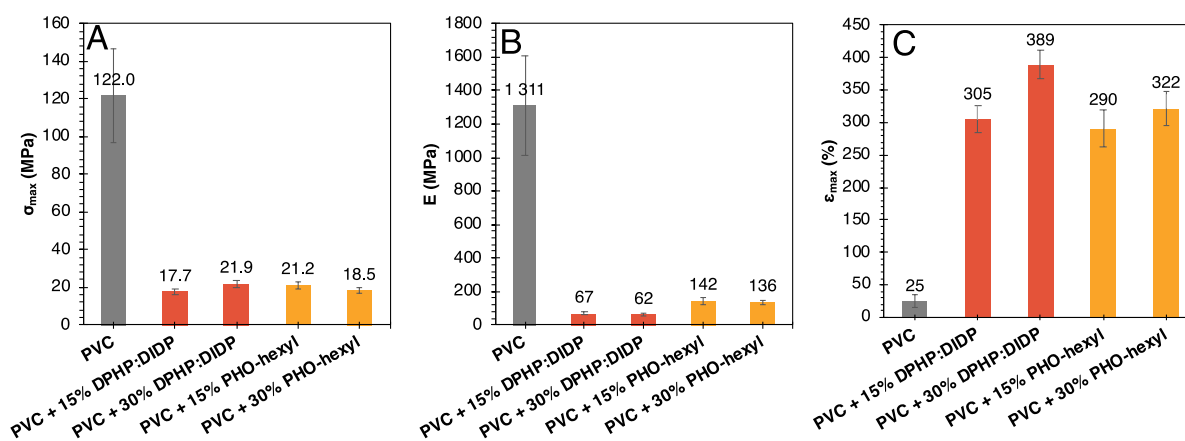

Figure 6. (A) σ_{max}, (B) E (C) ε_{max} values of plasticized PVC with DPHP:DIDP or PHO-hexyl, from uniaxial tensile tests.

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Analysis of the different TPU-based formulations

The field of TPU plasticization is marginal compared to that of PVC one. To analyze the potential of the plasticization of TPU, a particular renewable rigid TPU, hardly exploitable in its current state because of low processability, was synthesized and then plasticized. The objective is to show the interest and the contribution of the plasticization on a TPU that is hardly exploitable in its current state, as the worst possible case.

This highly rigid and sustainable TPU was synthesized using a conventional 2-step protocol from MDI, PTHF 650 (a medium-long polyether diol) and betulin (a rigid chain extender). The synthesis route is shown in Figure 4. Betulin is a cycloaliphatic terpene which can be obtained by chemical and/or biotechnological synthesis from sustainable resources such as plastic waste or biomass. The TPU rigidity is mainly provided by MDI and its aromatic rings and the betulin, which features 5 aliphatic rings. The obtained TPU is very brittle and has a high T_g (51 °C) as determined by DSC (Figure 7). PHO-hexyl and DPHP:DIDP were incorporated into TPU matrix as plasticizers at different content (Table 1) and their efficiency evaluated.

The addition of plasticizers to TPU reduces significantly the T_g by more than 50 °C, with only small differences between the plasticizer type and the concentration (Figure 7). This indicates that the plasticizing mechanisms of these additives also work on TPU architectures.

In rigid TPUs, the free volume is low due to numerous hydrogen bonds between the various rigid segments linked to the urethane groups. PHO-hexyl's action as a plasticizer is therefore multiple, due to its chemical structure. PHO-hexyl's ester and urethane groups can form interactions with TPU urethane groups, in particular. TPU-plasticizer interactions thus reduce TPU's own intra- and inter-chain interactions. They also minimize potential phase separation (demixing) with plasticizer volatilization or migration towards the sample surface. The alkyl-pendant chains of the HO units allow free volume to be gained by spreading the rigid TPU chains apart, which also reduces interactions between them. PHO-hexyl therefore has also a great potential as a plasticizer for rigid TPUs, even in small content.
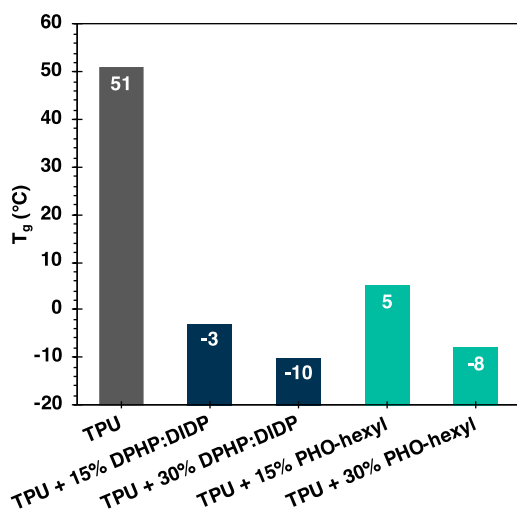
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Figure 7. T_g of neat and plasticized TPUs from DSC.

This neat rigid TPU could not be directly shaped by thermo-compression, as it was far too stiff and brittle to be demolded (Figure 8A). After plasticizing with 15% DPHP:DIDP or PHO-hexyl, the TPU-based materials could be processed and shaped into films. This clearly demonstrates the value of plasticizing rigid TPUs, opening up a whole new field of applications. The plasticized materials were then characterized in terms of mechanical properties using uniaxial tensile tests. The results are shown in Figure 8B. The ε_{max} of the two plasticized TPUs are similar, while the E and σ_{max} are about twice as high for the TPU plasticized with PHO-hexyl.

Phthalates and PHO-hexyl show a plasticizing effect improving the processability and increasing TPU flexibility, with better results for DPHP:DIDP. This also shows that a small gap (some °C) on the T_g of a plasticized polymer (Figure 7), can have a much greater impact on the mechanical properties and processability of the final materials, as also shown in the literature (Chen and Zhang, 2005).
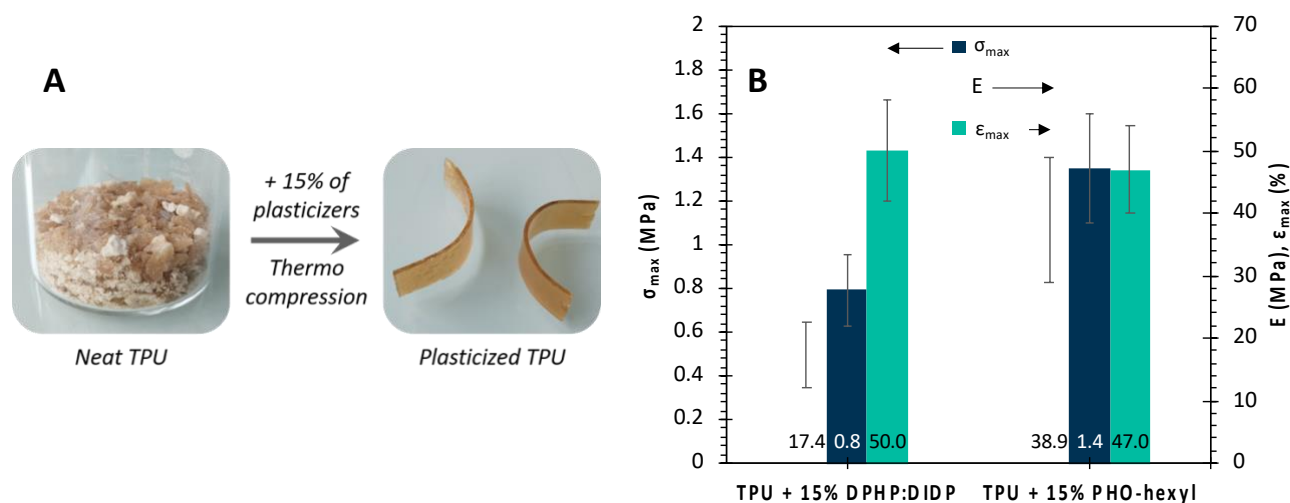

Figure 8. (A) Pictures of TPU samples before and after plasticization, followed by thermo-compression. (B) Results of uniaxial tensile tests on plasticized TPUs.

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CONCLUSION

Different sustainable plasticizers from bio-based and bacterially produced PHO were successfully synthesized and tested. From native PHO, oligomers with hydroxyl chain-ends (PHO-diol) were synthesized by controlled transesterification. Their end-capping with short alkyl chains was achieved by reaction with hexyl isocyanate, to produce PHO-hexyl, another potential plasticizer.

Both rigid PVC and TPU matrices were used to evaluate the different plasticizers at various contents: PHO-diol, PHO-hexyl and two conventional phthalates (DPHP and DIDP). The T_g of the polymers were significantly reduced, giving the material greater flexibility. Plasticizing effects similar to those of classically used phthalates were obtained with PHO-hexyl. The alkyl chain ends of PHO-hexyl enabled better dispersion of the additives in the matrices, as well as an increase in free volume, which was reflected in further improvement of the thermal and mechanical parameters compared to PHO-diol. Furthermore, in the case of a solid, brittle TPU (worst case), the incorporation of just 15 wt% PHO-hexyl plasticizer opened up a wide range of potential applications for this rigid TPU, which were previously more than limited by the fact that it was impossible to process.

PHO-hexyl thus appears to be a very promising example of a sustainable plasticizer, and as a potential credible alternative to phthalates in this preliminary and conceptual study. This new plasticizer appears to offer the potential to produce high-performance, environmentally friendly materials. It is possible to adjust the final properties of the materials, by adjusting the amount of plasticizer and the size of the grafted chain ends.

The prospects for this work and the potential additions to it are very broad. There are over 150 different chemical structures of PHAs, depending on the carbon substrate used and the biosynthesis conditions. It would therefore be possible to develop a very wide range of sustainable plasticizers, using a "chem-biotech" approach. This study needs to be extended in a number of ways, in particular to assess the mechanical properties and rheological behavior of the systems developed. It is crucial to consider plasticizer migration studies as an obvious perspective to this first conceptual approach for the valorization of PHO-based plasticizers. Moreover, the hexyl isocyanate used to add alkyl chain ends is highly toxic, thus another synthesis route could be developed to reduce its toxicity. In this frame, it would also be necessary to establish toxicity tests for the systems developed for a plausible approach to replacing phthalates for a future that is more respectful of the environment and health.

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CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Agathe Mouren: Data curation, Conceptualization, Writing – original draft, Visualization, Writing – review & editing.

Eric Pollet: Conceptualization, Writing – review & editing.

Luc Avérous: Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition, Validation.

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