

## H2020 Work Programme

# D4.3 - Eco-designed polymers based on PE hydrolysates

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This document is the UPLIFT project deliverable D4.3 titled: *Eco-designed polymers based on PE hydrolysates* (M43) lead by DTU and supported by the partners from WP2 ACIB, RWTH, AAU, AIMPLAS. This document provides a short and comprehensive description of the different tasks undertaken as part of fulfilling the deliverable. Additional advice and support can be sought from the coordinator.

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Deliverable Contributors				
	Name	Org.	Role / Title	E-mail
Deliverable leader	Anders E. Daugaard	DTU	WP leader	adt@kt.dtu.dk
Contributing Author(s)	Peter Jeppe Madsen	DTU	WP participant	pjma@kt.dtu.dk
Reviewer(s)	Belén M. Martínez	AIMPLAS	Primary outlet for materials	bmonje@aimplas.es
	Cristiano Varrone	AAU	Coordinator	Cva@bio.aau.dk
Final review and quality approval	Cristiano Varrone	AAU	Coordinator	Cva@bio.aau.dk

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# 1 Executive summary

The concept of UPLIFT is to introduce biological depolymerization technology as an addition and integration to established recycling practices, by converting persistent plastic waste into more easily recyclable and/or degradable polymers.

Deliverable 4.3 – “Eco-designed polymers based on PE hydrolysates” relates to the preparation of a range of polymers being readily recyclable through the UPLIFT technology. In terms of building blocks, the task has been aimed at exploiting specific cleavable linkers to achieve fast and easy depolymerization of polymers. This was investigated using prepolymers based on PE-hydrolysates as well as polyesters produced in Task 4.1.

PE-hydrolysates prepared in WP2 at AAU have been investigated in great detail and synthetic modifications of the mixed products have been attempted through a range of techniques. It was possible to achieve a partial modification and reaction on the raw product. However, this was deemed insufficient to exploit this technology as a full-scale recycling pathway. The PE-hydrolysates obtained from WP2 were assessed as being too inhomogeneous in their chemical structure to facilitate a direct upcycling to a valuable product. As an alternative, a similar approach to develop cleavable polyesters was investigated. A range of cleavable linkers was tested and evaluated as being effective for linking alcohol/acid functional polymers, and it was concluded that both anhydride and silyl ether linkers, as well as 4-hydroxyphenyl acetic acid (HPA) linkers, would be effective for improving the depolymerization through hydrolysis or enzymatic methods. Specifically, for the HPA linkers, this was ultimately applied across a range of polyesters spanning PLA, PC, PET(g), and PCL, which demonstrated fast and efficient hydrolytic cleavage (PLA>PCL>PC>PET(g)). Blends of PLA and the modified polyesters demonstrated accelerated hydrolysis and enzymatic depolymerization (reported in D2.7), confirming this as a generic concept for increasing accelerated conversion of commodity polymers to low MW building blocks.

The key exploitable result from this task has, therefore, been the establishment of a generic concept for increasing hydrolytic and enzymatic cleavage of common commodity plastics. That this can be achieved through simple blending of a polymer additive into the commodity plastics makes this a particularly attractive solution for industrial implementation. Regarding the PE, an alternative valorisation and upcycling strategy has been presented in D3.4.

## 2 Introduction

This document is the UPLIFT deliverable D4.3 “Eco-designed polymers based on PE hydrolysates” (M43) led by DTU in collaboration with the partners of WP2, where particularly AAU has been a close collaborator in the PE-hydrolysates and ACIB, RWTH, AAU, and AIMPLAS has been involved in the assessment of depolymerization in Task 2.7. The work has initially been aimed at exploiting the PE-hydrolysates produced by AAU to prepare new polymers containing specific cleavable linkers and to assess the best cleavable linkers to achieve fast and easy depolymerization of polymers. After the initial assessment of the different possible systems, the work has focused on the implementation of the best approach, which was found to be the incorporation of HPA as a functional linker molecule. The remaining time was dedicated to developing a scalable technology, and testing and validating this for direct implementation for the subsequent WPs.

In the following, we will report on the challenges of converting the PE-hydrolysates and on the incorporation of the sensitive linkers and demonstrate how this can be exploited as a generic concept. This report is intended for the public and will be substantiated by multiple publications that are currently being prepared and are expected to be submitted in autumn 2024 and to become public during spring 2025, which will further act to support D4.3 and extend the dissemination of the achieved results to the public.

## 3 PE-Hydrolysates

Through the work conducted in WP2, a range of PE-hydrolysates have been transferred from AAU to DTU, where the chemical reactivity was assessed for the different types of products. For an overview of the outcome of the hydrolytic treatment, we refer to the reporting in WP2. Briefly, the different PE-hydrolysates were analyzed as shown in Figure 1 in collaboration with AAU.

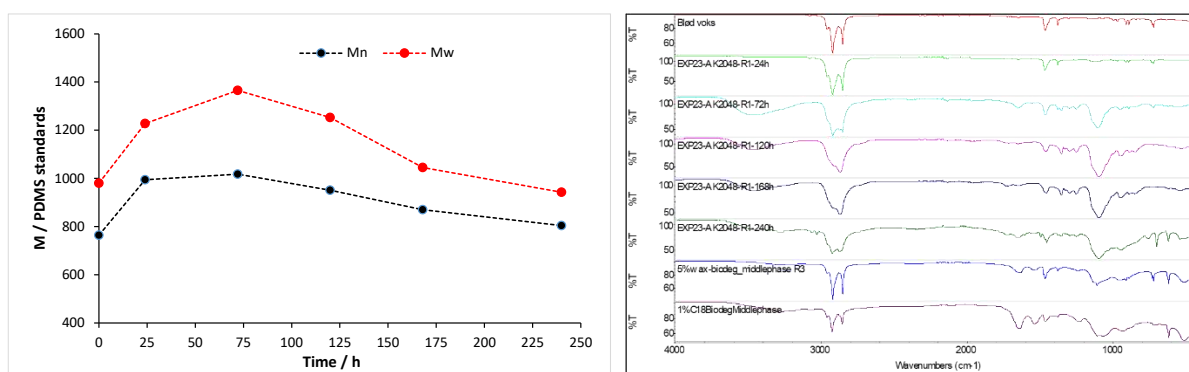


Figure 1 : Left : SEC data for the different PE-Hydrolysates. Right: chemical composition of the different polymers by FTIR.



It was concluded that the hydrolytic mixture contained oligomeric building blocks having a mixture of functional groups, including at least alcohol and carboxylic acid functional moieties.

### **3.1. Reactivity assessment of PE-hydrolysates**

This series of experiments aimed to explore the feasibility of functionalising the raw product mixture "PE-Hydrolysates" and to evaluate its potential as a feedstock for producing polymers that could be depolymerised using WP2 techniques. The investigation initially focused on assessing reactivity by reacting various mixtures with trichloroacetyl isocyanate (TAI), a generic reagent used for NMR quantification of alcohol and acid groups, as shown by Postma et al. Tests on standard reference compounds confirmed that the method was robust enough for quantification.<sup>1</sup> However, analysis of the different PE-hydrolysates showed an insufficient amount of alcohols/acids present in the system to justify continuing with the conversion into polymers. As an alternative pathway, the PE-hydrolysates were investigated as feed materials for bacterial polyesters in WP3 instead as this would enable use of the entire mixture of products for the highest valorization of the fraction.

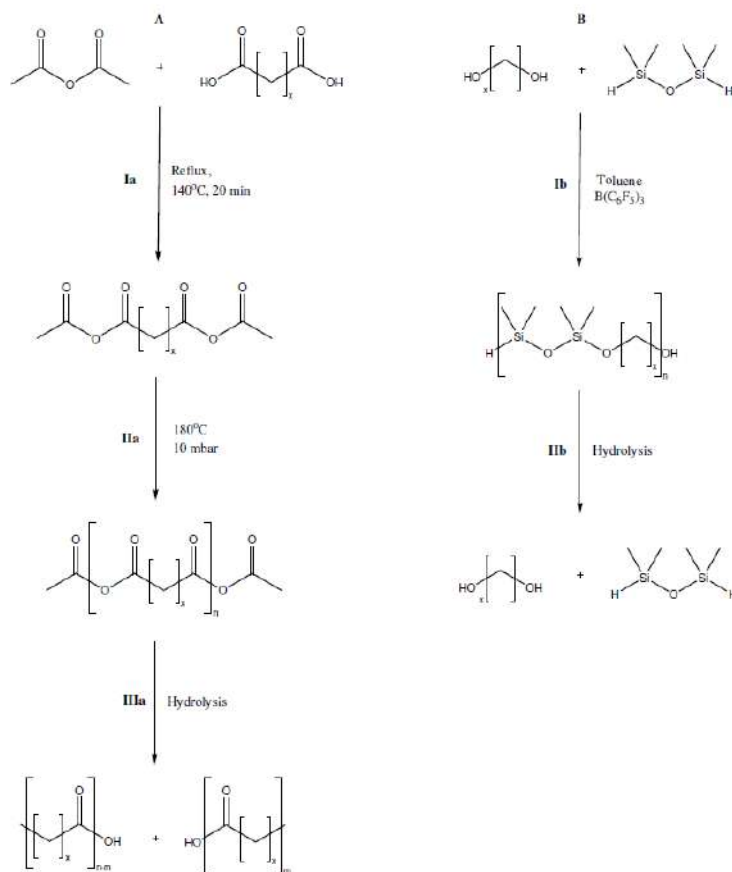
## **4 Preparation of polymers with cleavable linkers**

### **4.1. Linkers and evaluation**

Several different linkers were investigated to balance properties and rapid disassembly into building blocks.

Based on an initial literature survey and expected functional groups in the degraded polymer, the preparation of polymers with cleavable linkers based on anhydrides and silyl ethers was investigated (see Scheme 1).

Polyanhydrides can be prepared by self-condensation of acid groups and are, therefore, less sensitive to reagent purity than multi-component systems where the correct stoichiometry can be difficult to achieve. Polyanhydrides hydrolyze to the parent acid under mild conditions (see Scheme 1) and although the anhydride is highly prone to hydrolysis, polyanhydrides with long carbon chains are reported to hydrolyze strictly from the surface due to the hydrophobic environment in the bulk and would therefore be expected to be slower hydrolyzing under aqueous conditions. This type of degradation would, therefore, result in improved structural integrity for extended periods of time.



Scheme 1: A) Preparation and degradation of polyanhydrides according to reference (2). B) Preparation and degradation of silyl ethers according to reference (3). Note that the hydrolysis product of the silyl ether is drawn as a hydrosilane, although in practice it is more likely to be silanol groups.

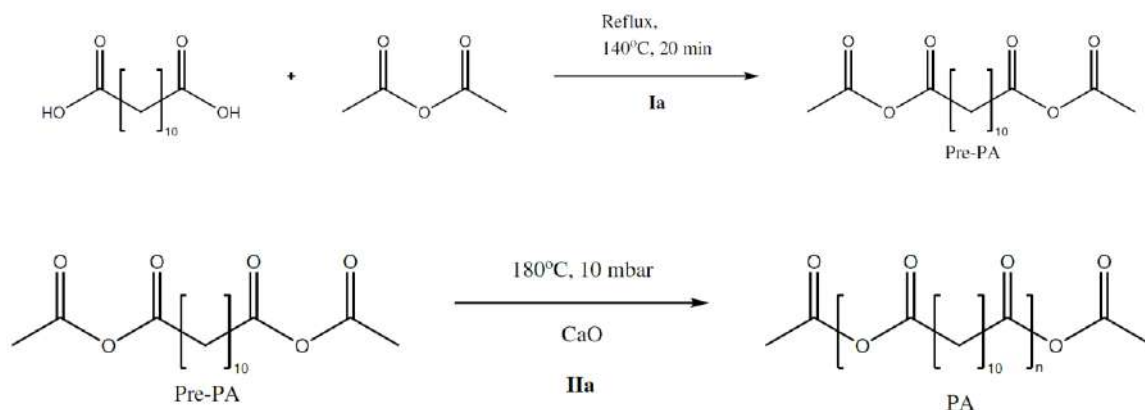
The silyl ether can be prepared efficiently from alcohol groups and will hydrolyze into the parent alcohol as well as an end-functional (poly)dimethylsiloxane (see **Fejl! Henvisningskilde ikke fundet.**).(4) Here, 1,1,3,3-tetramethyldisiloxane was used for the test synthesis. The cleavage of polymers containing this linker leads to the release of short disiloxanes, which are relatively soluble and quite volatile and, therefore, are expected to be easily removable.

## 4.2. Synthesis of specific systems

### Polyanhydrides

Initially, polyanhydrides based on dodecanedioic acid were prepared as model systems, using a published procedure by Domb and Langer (see Scheme 2).<sup>2</sup> The synthesis is done in the absence of solvent, but it is necessary to pre-functionalize the acid groups with an excess of acetic acid anhydride to form a crossed anhydride in order to get polymers of reasonable molecular weight.





Scheme 2: Synthesis of polyanhydrides based on dodecanedioic acid. The procedure was based on<sup>(2)</sup>.

A <sup>1</sup>H NMR spectrum of a resulting polyanhydride is reproduced in Figure 2. It is possible to see a weak signal due to end-groups at 2.21 ppm, which allows an estimation of the molecular weight (although it should be emphasized that there is significant uncertainty due to overlap of the signals at the relatively low field used here).

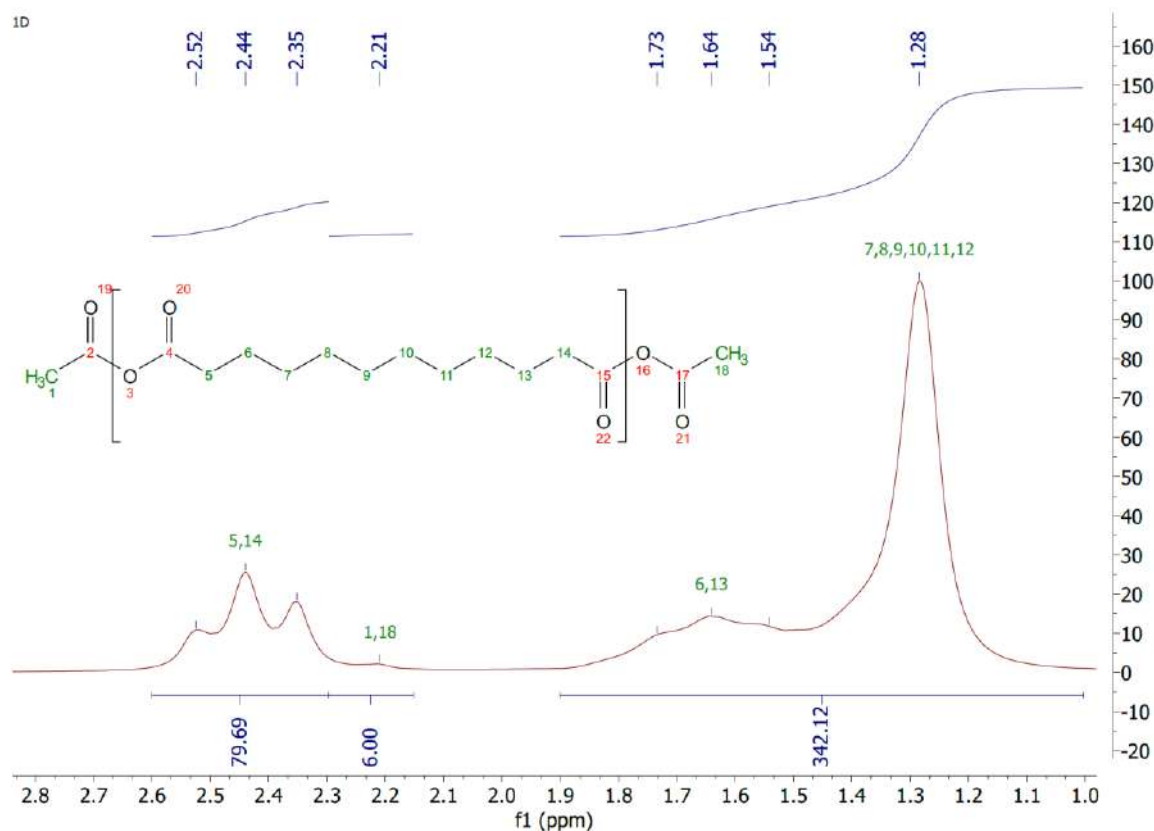


Figure 2 Assigned <sup>1</sup>H NMR spectrum of polyanhydride based on dodecanedioic acid. 80 MHz, CDC<sub>3</sub>

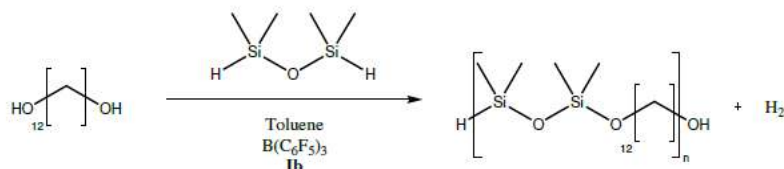
The reaction conditions were varied to explore the effect of polymerization temperature and time on the final copolymer (see **Fejl! Henvisningskilde ikke fundet.**). In general, higher temperatures and extended reaction times led to polymers with a significant amount of coloration. On the other hand, larger polymers with little coloration could be achieved in a matter of hours at lower temperatures. These polymers were in general hard and brittle.

Table 1 Reaction conditions for preparation of linear polyanhydride polymers

Entry	Acetic anhydride (mL)	Dodecanedioic acid (g)	Temperature (°C)	Time (h)	T <sub>g</sub> (°C)	Colour	NMR M <sub>n</sub> /g/mol
PA.2	2.00	1.003	180	16	-47	Brown	4700
PA.3	2.00	1.052	150	16	-	Brown	2000
PA.4 20min	2.00	1.046	180	0.33	-	White	5100
PA.4	2.00	1.046	180	4.5	-	Light yellow	3700
PA.5 20min	2.00	1.131	150	0.33	-	White	5800
PA.5	2.00	1.131	150	4.5	-45	Light yellow	6100
PA.6	2.00	1.093	180	48	-48	Dark brown	4700

### Poly(silyl ethers)

Model poly(silyl ethers) based on dodecane-1,12-diol were prepared using a Piers-Rubinsztajn reaction according to Scheme 3, adapted from a literature method.<sup>3</sup>

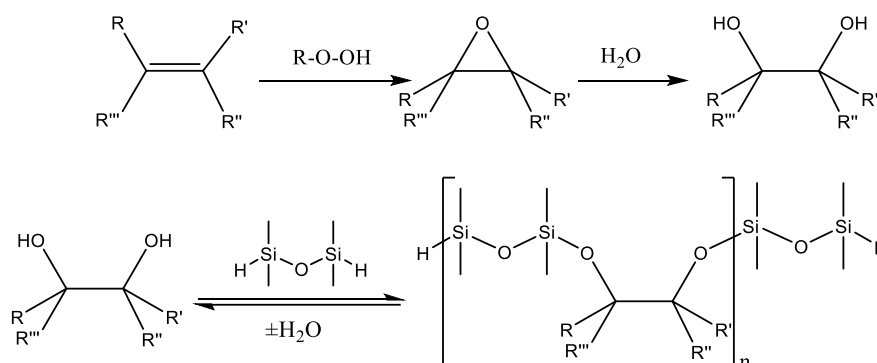


Scheme 3: Synthesis of poly(silyl ethers) based on dodecane-1,12-diol and 1,1,3,3-tetramethyldisiloxane

Size-exclusion chromatography indicated that polymer formation was possible, and this was also confirmed by the appearance of the material, which became significantly softer and gel-like than the starting crystalline alcohol. However, FTIR and NMR indicated a relatively low conversion of end-groups and despite several attempts of changing conditions, such as omitting solvent and adjusting stoichiometry, only relatively modest improvements were achieved.

The wax samples that had been subjected to microbial degradation at AAU were examined for functional groups usable for coupling using either silyl ether chemistry, dehydration chemistry to form anhydrides or both into polyolefin-like materials with degradable linkers. Given that the microbial ensemble use did lead to some degradation of the chains, as indicated by a reduction in the molecular weight, the degradation products were expected to lead to olefinic compounds terminated with carboxylic groups. However, extensive testing using a trichloroacetyl isocyanate reagent, that allows sensitive detection of carboxylic acid, alcohol and primary amino groups by <sup>1</sup>H NMR,<sup>1</sup> did not reveal significant amounts of either functional group.

The  $^1\text{H}$  NMR spectra did however reveal a significant amount of double-bonds in the materials, why these were targeted for functionalisation (Scheme 4), following a procedure using hydrogen peroxide to form a peracid *in situ*.<sup>5</sup>



Scheme 4: Reaction of the double bond with peroxide and the reaction of resulting alcohols with 1,1,3,3-tetramethyldisiloxane

The initial results indicated some oxidation of the double-bonds as shown in the  $^1\text{H}$  NMR spectra in Figure 3, where the relative area of resonances assigned to double-bonds between 4.5 ppm and 6.2 ppm decreases as a function of the reaction.

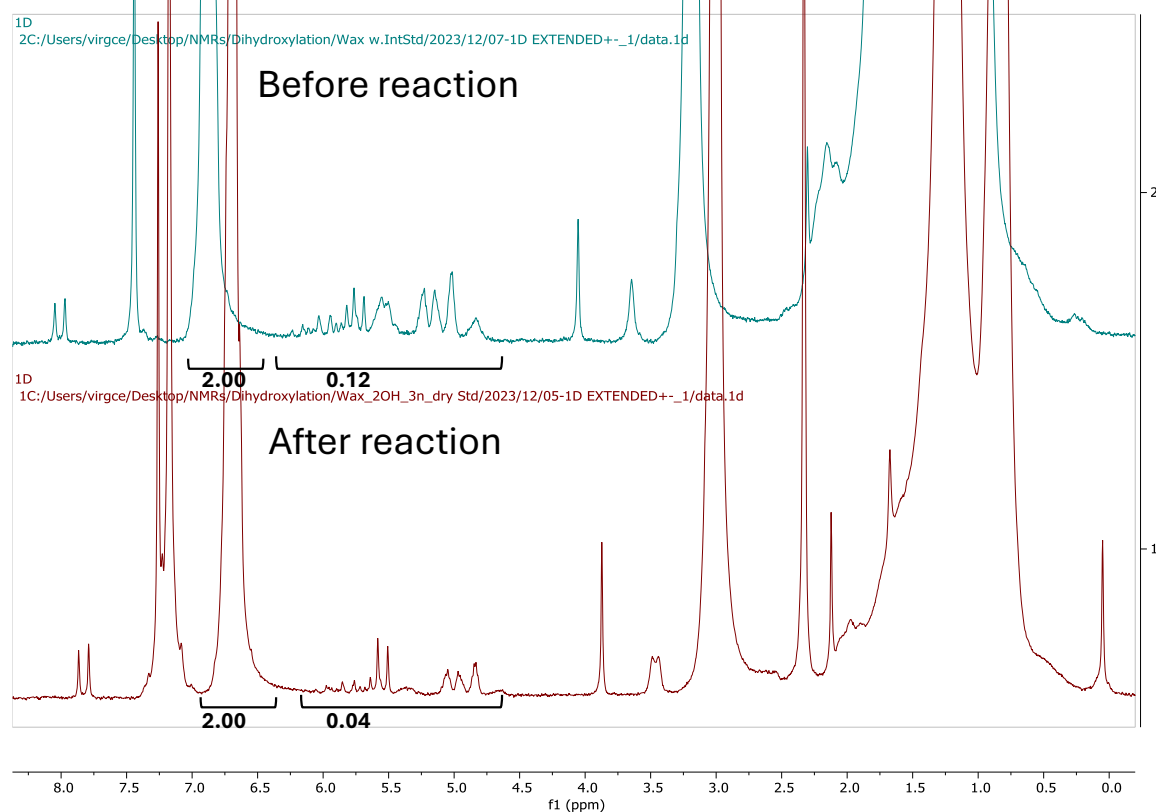


Figure 3 Oxidation of double bonds. Top: Before reaction. Bottom: After reaction

However, a series of experiments, where 1,1,3,3-tetramethyldisiloxane was added in amounts that corresponded to the calculated stoichiometry and allowed for some uncertainty in the determined amount of hydroxy groups, did not lead to any measurable increase in the molecular weight.

At this stage, it was found in WP3 that the resulting waxes were more useful substrates for the microbial formation of poly(hydroxybutyrate) PHB and mcl-PHAs (see D3.4), which is why this line of experimentation was not pursued further in task 4.3, as it was estimated to require significant additional resources to reach a useful purity of the starting material.

### 4.3. Hydrolytic degradation

The polyanhydride designated PA.3 (see **Fejl! Henvisningskilde ikke fundet.**) was subjected to hydrolytic degradation at 50 °C using either aqueous base, a mixture of water and tetrahydrofuran or both (see **Fejl! Henvisningskilde ikke fundet.**).

*Table 2 Hydrolytic degradation solvents and conditions*

Entry	Solvent	Temperature (°C)
H.1	0.1 M aq. NaOH	50
H.2	1:1 v/v 0.1 M aq. NaOH/tetrahydrofuran	50
H.3	1:1 v/v water/tetrahydrofuran	50

The mass loss as a function of time for the three sets of conditions is shown in Figure 4. Around 50 % mass loss is observed for the experiment containing base (NaOH) without organic solvent (THF) (H.1). This loss was accompanied by a decrease of pH, consistent with the formation of the parent acid, and this is believed to be a major cause of the reduction of weight loss rate.

For the solutions containing tetrahydrofuran, the weight loss is significantly faster than for the solution only containing base. Although the mixture of water and tetrahydrofuran does not immediately dissolve the polyanhydride, the presence of organic solvent is suspected to have an influence on the transport of water into the bulk of the sample, and degradation products out, which may lead to a bulk erosion mechanism, rather than the surface erosion mechanism observed for aqueous samples. In particular, the presence of base in the mixed solvent system does not appear to have a large effect on the degradation rate (see Figure 4).

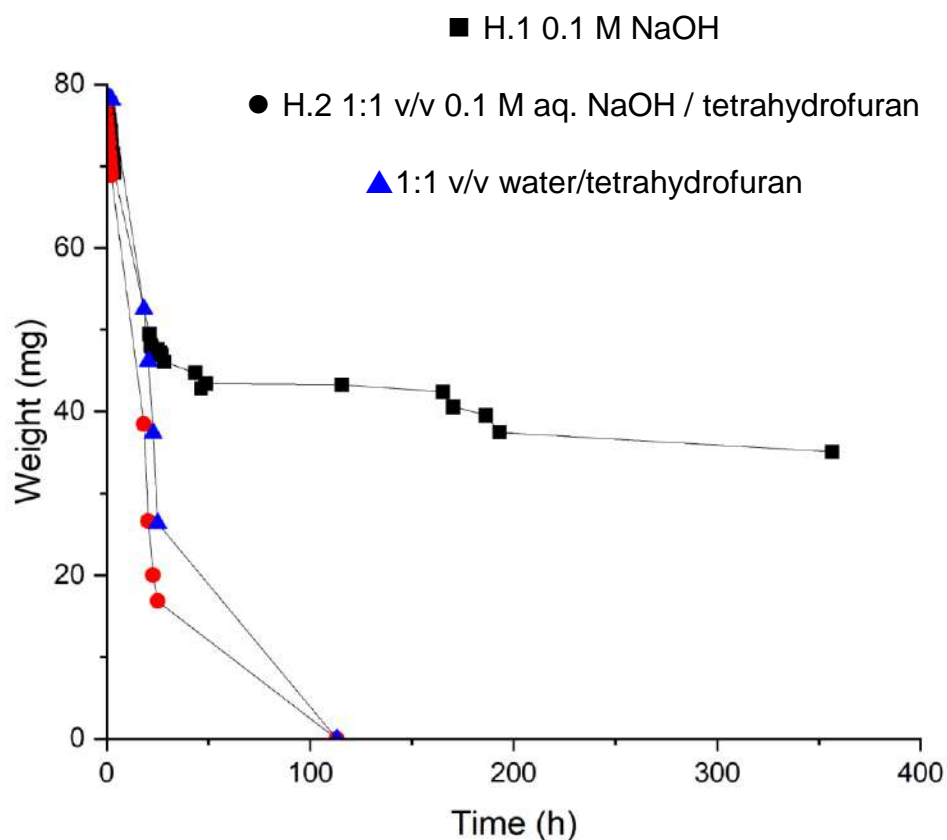
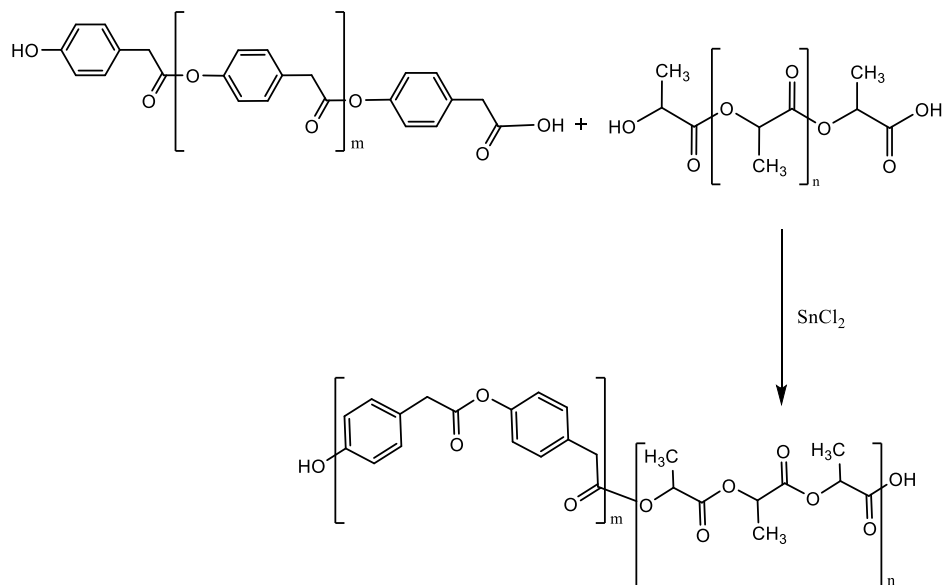


Figure 4 Hydrolytic degradation using aqueous sodium hydroxide, sodium hydroxide

The investigation of PHPA polymers in deliverable 4.1 revealed their potential as linkers for faster hydrolytic or enzymatic depolymerization. Simple homopolymers demonstrated quick and efficient hydrolytic degradation in water, prompting the study of aromatic PHPA integration into PLA via transesterification, as shown in Scheme 5.



*Scheme 5. Transesterification reaction of PPHA with purified PLA to yield PPHA-PLA multiblock copolymers (PPHA-b-PLA)*

The liquid crystalline behaviour of PPHA is crucial for its reaction with PLA. PLA melts at 175°C and needs this temperature to react or be processed. PPHA, however, becomes isotropic at 222°C - a temperature too high for PLA. Fortunately, PPHA has a liquid crystalline phase at 120°C, creating a processing window that allows it to be easily handled without needing to reach its higher melting point. This thermal property makes PPHA suitable for transesterification with polymers that have lower thermal profiles, enabling the formation of homogenous copolymers. This approach was similarly tried on other common polyesters, namely polycaprolactone (PCL) and glycol-modified polyethylene (PETG). For PPHA-b-PCL, the same reaction parameters as PPHA-b-PLA were used, while for PPHA-b-PETG, a homogenous copolymer was produced at 210°C, which was in all cases confirmed by FTIR where the copolymerization can clearly be seen (Figure 5).

The successful synthesis of the multiblock copolymers can also be confirmed by the SEC traces presented in Figure 6 (b). These traces show that the molecular weights of the synthesized copolymers fall between those of the parent PCL and PETG, as well as the PPHA. This is due to the transesterification reaction and ester bond reorganization, which result in the breakdown of polymer chains into shorter segments.



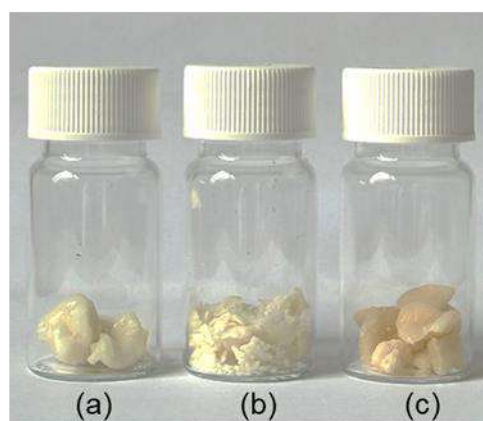
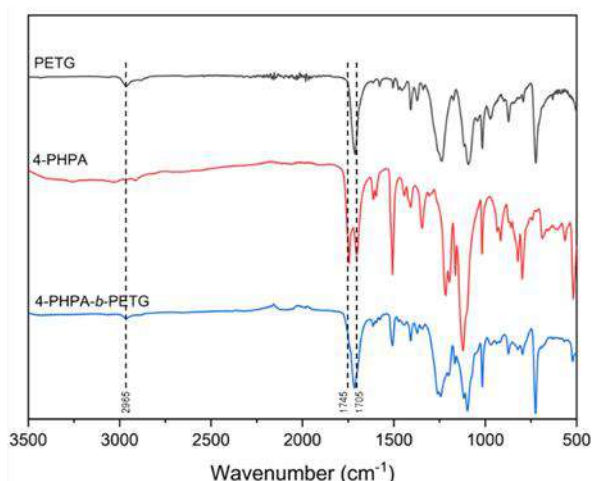
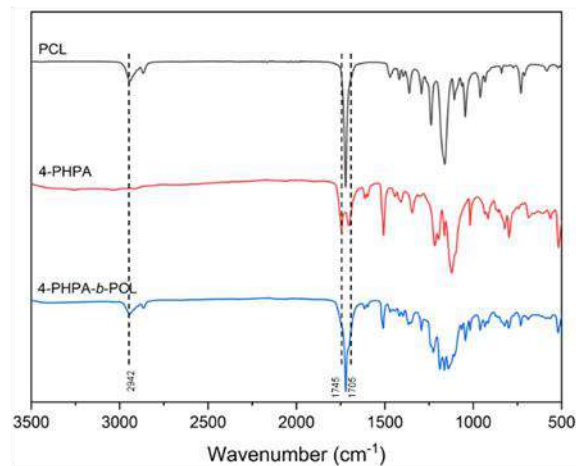
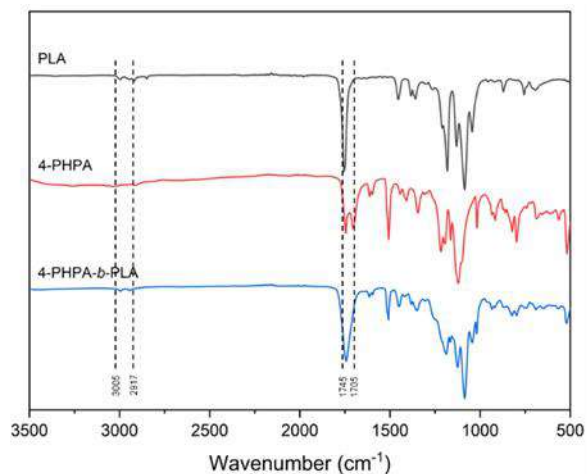


Figure 5 (a) PHPA-b-PLA: Yield: 86%. SEC: 4350 g mol<sup>-1</sup>,  $\bar{D}$  = 3.5 Esterification was confirmed from the peak shift at 1745cm<sup>-1</sup> (b) PHPA-b-PCL: Yield: 84%. SEC: 660 g mol<sup>-1</sup>,  $\bar{D}$  = 1.58, Esterification was confirmed from the peak shift at 1745cm<sup>-1</sup> (c) PHPA-b-PETG: Yield: 90%. SEC: 1570 g mol<sup>-1</sup>,  $\bar{D}$  = 1.63, Esterification was confirmed from the peak shift at 1745cm<sup>-1</sup> (d) (a) PHPA-b-PLA, (b) PHPA-b-PCL, (c) PHPA-b-PETG at room temperature.

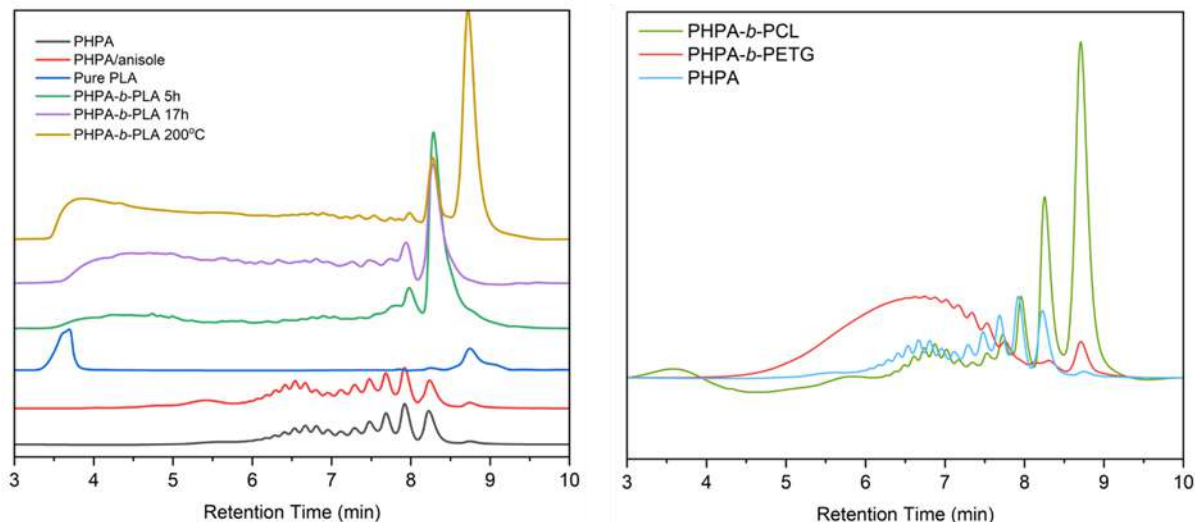


Figure 6 (a) Chromatograms of all PLA copolymers and their respective parent polymers, as recorded by DAD at the wavelength of 258nm. The only exception in terms of wavelength is PLA, of which the chromatogram illustrated above was recorded at 217nm. (b) Chromatograms of PCL and PETG copolymers and their respective parent polymers recorded by DAD at the wavelength of 258nm.

The analysis shows that combining an aromatic polymer like PHPA with various commercial aliphatic polyesters can produce copolymers that enhance compatibility in blends with their parent polymers and potentially introduce new properties.

#### 4.4. Blends

The optimized block copolymers discussed earlier were employed as additives in their respective polymers to examine the effect of incorporating aromatic 4-HPA into the polymer chains. Polymers with varying percentages of copolymer additive (3%, 5%, and 10% in each case) were physically blended in dichloromethane to create miscible and homogeneous mixtures. Initial blending tests revealed that PHPA and PLA were incompatible when mixed in solvent, leading to phase separation; consequently, PHPA was not used alone as an additive for polyester blends. Following preparation and drying, the polymer blends were injection moulded into bars with dimensions of 60x10x1 mm (Figure 7). This step is critical for any subsequent property analysis, as it ensures uniform shape and consistent properties throughout the samples. Additionally, during moulding, the polymer chains acquire a specific orientation, which can affect the properties of the polymer samples. These bars will then be precisely cut into smaller pieces measuring 1x5x10 mm using a laser cutter, ensuring all samples for hydrolytic degradation tests have uniform shape and comparable weight.

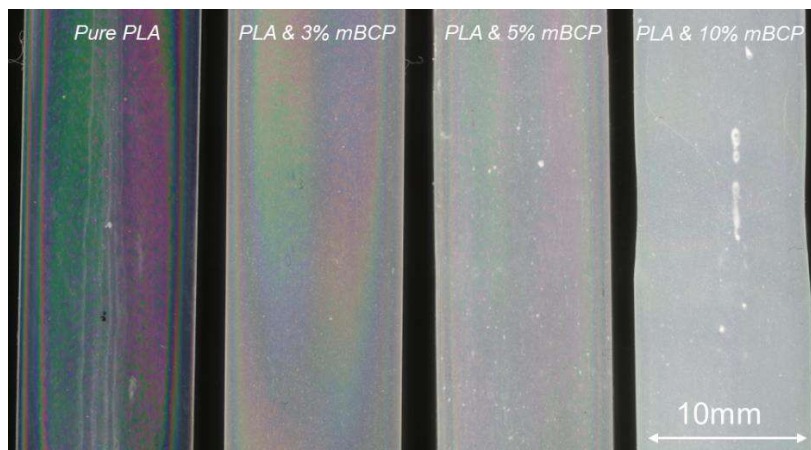


Figure 7 Injection-moulded bars of PLA polymer blends, containing 3,5,10% of multiblock poly(4-hydroxyphenylacetic acid)-b-poly(lactic acid), PHPA-b-PLA as additive. Picture taken by Polarized Optical Microscope at 2000  $\mu\text{m}$ .

#### 4.5. Hydrolytic degradation of polymers

The degradation of a polymer can be affected by its bulk characteristics, shape, and thickness. To guarantee consistency and achieve comparable and reliable data, the samples were prepared through injection moulding and laser cutting, as previously mentioned. This method ensured the uniformity of the test sample population, making the collection of comparable and reliable data feasible.

The different blends of PLA, PCL, and PETG with varying ratios of multiblock copolymers underwent hydrolytic degradation studies and were compared to the degradation profiles of their corresponding pure polymers prepared under identical conditions. Degradation refers to the chemical breakdown of polymer chains into lower molar mass products through ester bond hydrolysis. Testing the hydrolytic degradation rates of these blends is important because low molecular weight multiblock copolymers were used as additives. The ester bonds within the copolymer blocks act as 'weak linkages' when subjected to hydrolysis in solvent mixtures, potentially leading to easier and more rapid fragmentation of the polymer chains into shorter segments, thus accelerating and intensifying the degradation rate of the polymer blend.

The results of the hydrolysis study for all polymer blends are depicted in Figure 8. In Figure 8 (a), the hydrolysis rates of PLA and its blends are illustrated. The PLA reference blend demonstrates a very limited and slow hydrolysis rate, which is expected due to PLA's inherent slow degradation, attributed to the large methyl groups in its backbone that form a hydrophobic surface resistant to initial hydrolytic degradation. Upon adding 3% wt of PHPA-b-PLA into the blend, the mixture initially swells and subsequently accelerates in hydrolysis, achieving complete degradation after 50 hours. In contrast, the pristine PLA blend swells up to 33% above its initial weight and then reduces to 19% above its initial weight over the entire measurement period. When 5% and 10% of PHPA-b-PLA are incorporated, the hydrolysis remains rapid, leading to complete disintegration within approximately 90 hours, whereas the PLA shows almost no further

degradation. These findings suggest that even a minor addition of multiblock PHPA-b-PLA to the blends significantly enhances their degradation potential, achieving full decomposition between 50 and 90 hours of exposure to hydrolytic conditions.

In regard to the hydrolysis rates of PETG presented in Figure 8 (b), all blends, including the pure PETG blend, show swelling that amounts to nearly 50% more than their initial weight, followed by a steady decrease in weight over time. The blend containing 3% PHPA-b-PETG degrades slightly more efficiently compared to the other blends and the pristine one, suggesting that the addition of multiblock PHPA-b-PETG does not significantly impact the hydrolysis rate. Conversely, the hydrolytic degradation of PCL and its blends with the PHPA-b-PCL additive demonstrate rapid degradation under current testing conditions, where disintegration occurs within an hour, making weight measurements impossible, as depicted in Figure 8 (c).

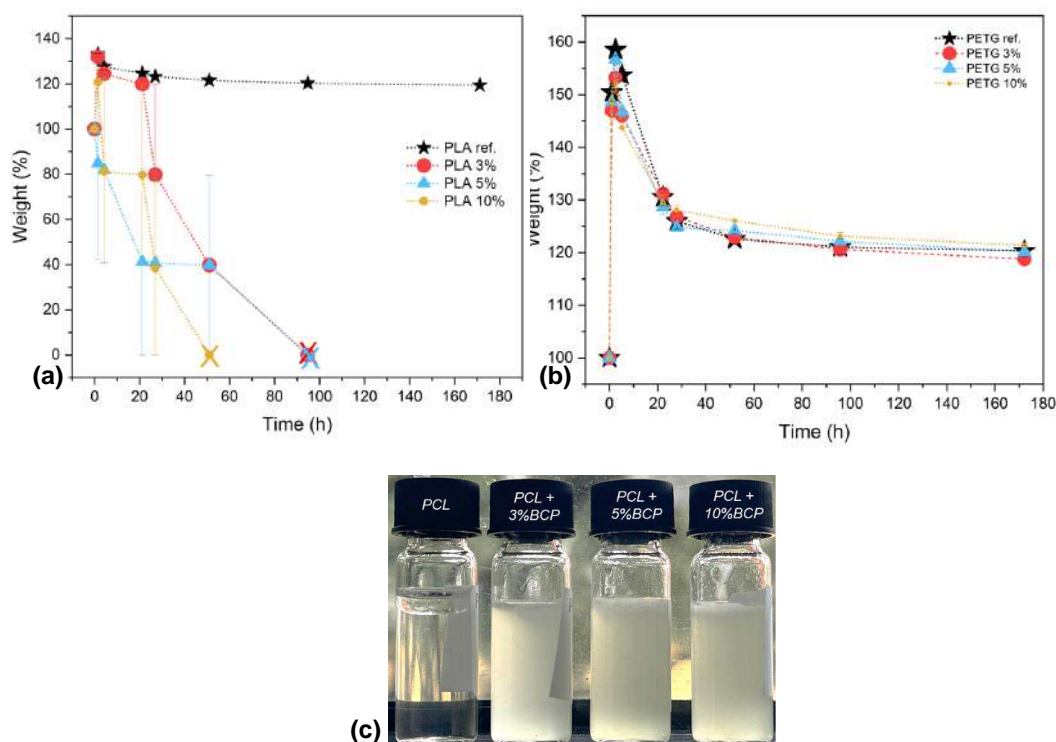


Figure 8 Hydrolytic Degradation of polymer blends in 0.1M NaOH in a 50/50 water/THF mixture at 50oc that demonstrates the remaining weight percentage (%) of samples over time during hydrolytic degradation of (a) PLA and its blends with PHPA-b-PLA, (b) PETG and its blends with PHPA-b-PETG (c) PCL and its blends with PHPA-b-PCL

#### 4.7. Mechanical tests

The incorporation of synthesized multiblock copolymers into PLA, PET, and PCL through blending required evaluation for their mechanical properties. These multiblock copolymers are composed of 50% aromatic PHPA and 50% aliphatic polyester. The



presence of an aromatic component in polymer chains is known to affect mechanical properties such as tensile strength and stiffness considerably. Nonetheless, this study concentrated on assessing the flexibility of the resulting blends, particularly addressing the issue of pristine PLA's inherent brittleness.

Bending tests with a DMA instrument were conducted on all versions of PLA, PCL, and PETG blends. Results in Figure 9 show that adding multiblock copolymers impacts the flexural modulus. Specifically, adding PHPA-b-PLA reduces the flexural modulus, with increases of 3%, 5%, and 10% leading to reductions of 7%, 17%, and 32%, respectively. Similarly, the flexibility of PETG decreased by app 18% for all compositions. In contrast, no change is observed in the flexural modulus of PCL, which remains lower than PLA and PETG regardless of the added multiblock PHPA-b-PCL.

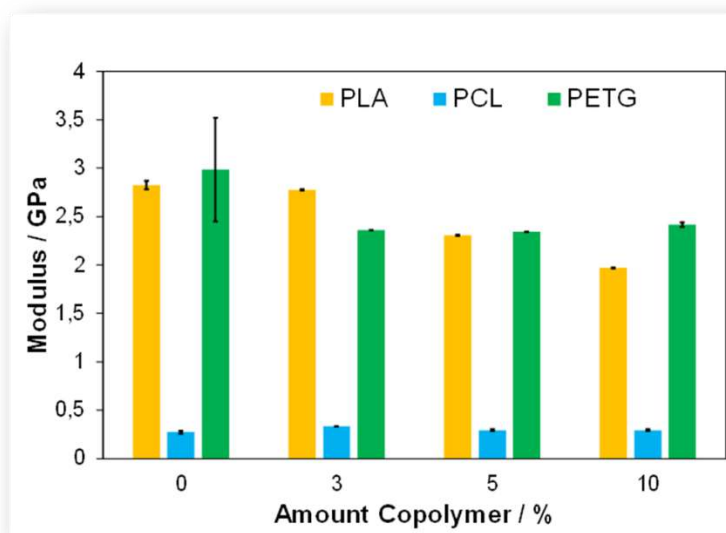


Figure 9 Addition of multiblock copolymers into blends leads to reduction of flexural modulus in PLA and PETG

#### 4.8. Testing with the different methodologies developed in WP2

Having established that different block copolymer structures could be prepared and that these were easily included in blends, provides a generic approach towards improving the depolymerization potential across a broad range of commodity polyesters. Therefore, these systems have been evaluated across the full range of systems, which has been reported separately in deliverable 2.7.

## 5 Summary and outlook

PE-hydrolysates prepared in WP2 at AAU have been investigated in great detail and synthetic modification of the mixed products have been attempted through a range of techniques. It was possible to achieve a partial modification and reaction on the raw product. However, this was deemed insufficient to exploit this as a full-scale recycling pathway. The PE-hydrolysates obtained from WP2 were assessed as being too inhomogeneous in their chemical structure to facilitate a direct upcycling to a valuable product. A range of cleavable linkers was tested and evaluated as being effective for linking alcohol/acid functional polymers, and it was concluded that both anhydride and silyl ether linkers, as well as 4-hydroxyphenyl acetic acid (HPA) linkers, would be effective for improving the depolymerization through hydrolysis or enzymatic methods. Specifically, for the HPA linkers, this was ultimately applied across a range of polyesters spanning PLA, PC, PET(g), and PCL, which demonstrated fast and efficient hydrolytic cleavage (PLA>PCL>PC>PET(g)). Blends of PLA and the modified polyesters demonstrated accelerated hydrolysis and enzymatic depolymerization (reported in D2.7), confirming this as a generic concept for increasing accelerated conversion of commodity polymers to low Mw building blocks.

The key exploitable result from this task has, therefore, been the establishment of a generic concept for increased hydrolytic and enzymatic cleavage of common commodity plastics. That this can be achieved through simple blending of a polymer additive into the commodity plastics makes this a particularly attractive solution for industrial implementation.

The material concept developed here has been forwarded to scaling through T4.4. and forwarded to industrial testing in WP6.



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