# Ring-opening polymerization of ethylene brassylate in reactive extrusion and its end-of-life options

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# Ring-opening polymerization of ethylene brassylate in reactive extrusion and its end-of-life options

Giada Lo Re [a,b], Angelica Avella [a,b,*], Daniela Pappalardo [c], Rosica Mincheva [d]

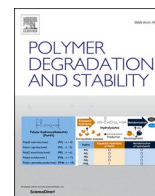[a] *Department of Industrial and Materials Science, Chalmers University of Technology, Rännvägen 2A, 41258, Gothenburg, Sweden*
[b] *Wallenberg Wood Science Center, Chalmers University of Technology, Kemigården 4, 41258, Gothenburg, Sweden*
[c] *Dipartimento di Scienze e Tecnologie, Università del Sannio, Via de Sanctis snc, 82100, Benevento, Italy*
[d] *Laboratory of Polymeric and Composite Materials, University of Mons, 20 Place du Parc, 7000, Mons, Belgium*

## ABSTRACT

Polyesters synthesised from renewable monomers via intensified and industrially relevant processes provide nowadays a science-to-technology breakthrough, especially if they offer a suitable end-of-life scenario for a circular economy. In this work bio-based macrolactone ethylene brassylate was polymerized by reactive extrusion and the properties of the polyester and its end-of-life options were studied. The ring-opening polymerization was tested with several catalytic systems, among which the organic base 1,5,7-triazabicyclo[4.4.0]dec-5-en (TBD) and the immobilized enzymes Lipase B from *Candida antarctica* and Lipase from *Pseudomonas cepacia* successfully synthesised poly(ethylene brassylate) (PEB). TBD served as both catalyst and initiator, yielding PEB with a molar mass of 8000 g/mol, melting temperature around 70 °C and main degradation temperature of 440 °C. Tensile tests showed that PEB had a brittle behaviour with Young's modulus of 290 MPa and elongation at break of 4 %. PEB lost 93 % of its initial weight after 90 days in compost, degrading through surface erosion. Lipase B from *Candida antarctica* was demonstrated successful for the enzymatic depolymerization. Therefore, enzymatic depolymerization and disintegration in compost were suggested as feasible pathways for PEB circular design.

## 1. Introduction

With the advancement of knowledge and understanding on plastics eco-effects, the requirements for sustainable alternatives to commodity polymers include not only the source of the materials (annually renewable resources, $CO_2$ or waists) but also the processing conditions (effective synthesis via intensified industrially relevant methods with the preferable use of renewable energy) and the circular end-of-life solutions [1]. After their service, recycling and biodegradation of polymers should be preferred to incineration and landfilling to limit their environmental impact [2]. Despite the growing production and utilization of biopolymers [3], few of the options available on the market meet all these aspects and alternatives are highly required.

With this respect, ethylene brassylate (EB), a renewable macrolactone derived from castor oil, generates a biodegradable aliphatic polyester poly(ethylene brassylate) (PEB) through ring-opening polymerization (ROP) [4]. With its renewability and biodegradability, as well as the commercial availability of the relatively low price monomer

in comparison to other lactones, PEB could be of interest for industrial production. Its synthesis has so far been reported only in scientific articles at small batch scale in solution or bulk, through enzymatic [5], organometallic [4,6–11], or organic [4,12–14] catalysis.

Indeed, EB belongs to the class of macrolactones, *i.e.* cyclic esters having more than 14 atoms in the ring. Such macrolactones lack of ring-strain, and their ROP is an entropy-driven process in contrast to the traditional smaller-sized lactones (*e.g.* lactide, glycolide or ε-caprolactone) for which the ROP is an enthalpy-driven process. As a result, the macrolactones have low polymerizability, giving rise usually to low molecular weight polymers. The number of catalytic systems that can efficiently promote such a ROP process is limited when compared to traditional smaller-sized lactones [15]. In the case of EB, moreover, the presence of two ester groups determines also frequent transesterification side reactions. The first report of ROP of EB carried out in the presence of commercially available lipases as catalysts documented the achievement of low molecular weight polymers [5]. A step forward was accomplished by using organocatalysts (*e.g.* 1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD)

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\* Corresponding author.
*E-mail address:* avella@chalmers.se (A. Avella).

or main-group metal-based systems. Pascual et al. described the use of TBD guanidine systems for the synthesis of PEB with higher activities and higher molecular weights [13,14]. In the presence of triphenylbismuth as the catalyst, high molecular weight PEB was obtained [4]. Recent reports described the use of sodium complexes bearing cavity-like conformations formed with the aid of sterically hindered phenoxide and 15-crown-5 ether ligands [10] and potassium phenoxide complexes bearing bulky yet flexible substituents [16], able to reduce deleterious transesterification reactions. The same concept was applied by using an iron-based bulky α-diimine catalytic system, where the transesterification side reactions were suppressed and higher activities than previously reported by organocatalysts or main-group metal-based catalysts were described [17]. However, there is not yet a continuous production probably due to some reactivity issues.

Industrially relevant polymer synthesis usually involves continuous processing in extruders, known also as reactive extrusion (REx). Some works have reported on REx use for the ROP of cyclic esters [18–20]. The process eliminates the need for organic solvents, it is flexible to materials chemistry and it is a highly scalable option for one-step polymerization. Thanks to the powerful mechanical stirring in the melt processing equipment, REx favours monomer diffusion during the polymerization, often hindered in bulk due to high polymer viscosity [13,14], thus leading to a complete monomer conversion [18]. ROP in REx presents challenges related to the reaction environment being exposed to air and humidity which could hinder or initiate the ROP, and the low viscosity of the monomer under the REx conditions could lead to monomer leakage. Taking into consideration the social and industrial importance of developing bio-sourced and biodegradable polymers, the ROP of EB by REx is of interest.

We have recently achieved the efficient ROP of EB via REx catalysed by TBD in the presence of cellulose nanofibrils [21], and catalysed by Lipase B from *Candida antarctica* supported on microcrystalline cellulose [22]. Herein we describe and compare the ROP of EB via REx by using diverse catalytic systems, among which the organic base TBD, the immobilized enzymes Lipase B from *Candida antarctica* (CALB) and Lipase from *Pseudomonas cepacian* (PC), and the anionic initiator sodium hydride (NaH). Compared to the traditional metal-based catalytic systems, either the lipases or the organic catalyst TBD may allow to avoid the leakage and contamination of the metal on the final polymers, therefore resulting in materials suitable for biomedical applications. Conversely, the NaH represents a cheap, non-toxic and safe initiator, already used for the ROP of other lactones [23,24]. To our knowledge, literature studies have examined the degradation of EB copolymers in terms of hydrolytic [11,25] or enzymatic degradation [26]. However, research on the degradation of EB homopolymer is still lacking. In the present work, the disintegration in compost and enzymatic depolymerization of the reactive extruded PEB were investigated and the results are presented and discussed.

## 2. Materials and methods

### 2.1. Materials

Ethylene brassylate (purity > 95 %), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), benzoyl alcohol, magnesium bromide, sodium hydride, Lipase B *Candida antarctica* immobilized on Immobead 150 (≥1800 U/g) and Lipase *Pseudomonas cepacia* immobilized on Immobead 150 (≥ 900 U/g) were purchased from Sigma Aldrich. TBD was purchased from VWR and used as received.

### 2.2. Reactive extrusion

Before reactive extrusion, the reagents were dried overnight in a ventilated oven at 75 °C. The experiments were carried out in the molar ratios reported in Table 1 and S1 in Supporting information (SI). The reactions were performed in an Xplore microcompounder (total volume 15 cm$^3$) with a recirculating system under a constant nitrogen flow, with temperature, time and screw speed as reported in Table 1 and S1. An experiment was carried out at 130 °C starting from EB:TBD molar ratio of 42:1, and after 30 min of processing 3 ml of material were extruded and 3 ml of fresh monomer were fed. The same procedure was repeated at 60 min and the processing was stopped at 90 min when all the polymer was extruded. The extrusion force was recorded in line to monitor the reaction for all the processes. The extruded materials were further utilised without any purification. The extruded strands were injection moulded with an Xplore IM12 into dumbbell-shaped specimens, with a barrel temperature of 80 °C. The mould was kept at 25 °C and the injection followed a program of 2 s at 280 bar and holding for 10 s at 420 bar

### 2.3. End-of-life

#### 2.3.1. Disintegration under industrial composting conditions

Disintegration tests under aerobic composting conditions were performed on a laboratory scale for 90 days [27]. Materials from compression-moulded sheets were cut into squares (15 mm x 15 mm x 1 mm), which were weighed and placed in a textile mesh to ease their withdrawal during composting and to allow access to moisture and microorganisms. The specimens were buried at a depth of 4–6 cm in perforated plastic boxes containing a solid synthetic wet waste (10 wt.% of compost, 30 wt.% rabbit food, 10 wt.% starch, 5 wt.% sugar, 4 wt.% corn oil, 1 wt.% urea, 40 wt.% sawdust and extra 50 wt.% of water) and were incubated under aerobic conditions at 58 °C guaranteed by periodic mixing of the solid synthetic wet waste. Samples of each formulation were withdrawn from the disintegration container at different times, cleaned with distilled water, dried in an oven at 37 °C for 24 h, and weighed. The mass loss was calculated in comparison to the initial weight.

**Table 1**
Reagents and REx conditions for the polymerization of ethylene brassylate and the resulting monomer conversion and molar mass measured by $^1$H NMR in CDCl$_3$, molar mass and dispersity measured by SEC in CHCl$_3$.

| Entry | Catalyst | [M]:[Cat]:[I] | T [ °C] | Screw speed [rpm] | REx time [min] | Conv. [%] | $M_{nNMR}$ [g/mol] | $M_{nSEC}$ [g/mol] | Đ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | PC | 10 wt.% | 90 | 60 | 15 | 42 | 900 | 1200 | 1.6 |
| 2 | CALB | 10 wt.% | 90 | 60 | 15 | 100 | 3700 | 10700 | 2.1 |
| 3 | TBD | 42:1:1* | 80 | 100 | 45 | 100 | 4800 | 8900 | 2.1 |
| 4 | TBD | 42:1:0.33* | 80 | 100 | 45 | 97 | 6300 | 12300 | 2.3 |
| 5 | TBD | 42:1:0.17* | 80 | 100 | 45 | 98 | 5400 | 13600 | 2.3 |
| 6 | TBD | 42:1:0.17* | 100 | 100 | 45 | 98 | 5600 | 13200 | 2.5 |
| 7 | TBD | 42:1:0.17* | 130 | 100 | 30 | 98 | 4700 | 14200 | 2.3 |
| 8 | TBD | 42:1:0.08* | 100 | 100 | 45 | 98 | 6500 | 13800 | 2.4 |
| 9 | TBD | 42:1 | 130 | 100 | 30 | 93 | 7900 | 20600 | 1.9 |
| 10 | TBD | 60:1 | 130 | 100 | 30 | 60 | 7200 | 18000 | 2 |
| 11 | TBD | 84:1 | 130 | 100 | 30 | 19 | 3900 | 670 | 1.05 |

* BnOH was used as the initiator.

### 2.3.2. Enzymatic depolymerization

PEB (entry 9 in Table 1) was enzymatically depolymerized according to the procedure reported by Martinez-Cutillas et al. [28]. The sample was dissolved in toluene 0.5 % w/v in a round-bottomed flask with a magnetic stirrer, and 300 % w/w CALB was added. The reaction was carried out for 72 h at 55 °C and the products were analysed.

### 2.4. Characterization methods

#### 2.4.1. Size-exclusion chromatography (SEC)

The molar mass $M_{nSEC}$ and dispersity (Đ) of PEB were measured by SEC in chloroform. The tests were carried out at 30 °C using an Agilent (Diegem, Belgium) liquid chromatograph equipped with an Agilent degasser, an isocratic HPLC pump (flow rate = 1 ml/min), an Agilent autosampler (loop volume = 100 μl; solution concentration = 2 mg/ml), an Agilent-DRI refractive index detector, and three columns: a PL gel 5 μm guard column and two PL gel Mixed-B 5 μm columns (linear columns for the separation of molecular weight (PS) ranging from 200 to $4 \times 10^5$ g/mol). Polystyrene standards were used for calibration.

#### 2.4.2. Proton nuclear magnetic resonance ($^1$H NMR)

$^1$H NMR experiments were carried out in solution-state at 310 K on a Bruker AMX 500 MHz equipped with a 5 mm PABBO BB/19F-1H-D Z-GRD probe. CDCl$_3$ was used as a solvent and 0.3 wt.% tetramethylsilane (TMS, 0 ppm) was used as an internal chemical shifts reference. Spectra were recorded with a 12.0 ms pulse and 2 s relaxation delay. The EB monomer conversion was calculated as the ratio between the integrals of the $CH_2O_{EB}$ (4.31 ppm) and $CH_2O_{PEB}$ (4.27 ppm) signals. The molar mass ($M_{nNMR}$) was calculated according to Eq. (1):

$$M_{nNMR} = \frac{CH_2O_{PEB}}{2 * CH_2OH_{PEB}} * 270 + 139 \tag{1}$$

where $CH_2O_{PEB}$ and $CH_2OH_{PEB}$ are the integrals of the signals at 4.27 ppm, and 3.83 ppm, and 270 and 139 are the molar masses in g/mol of EB and TBD, respectively.

#### 2.4.3. Attenuated total reflectance Fourier-transformed infrared spectroscopy (ATR-FTIR)

ATR-FTIR was carried out using a Perkin Elmer Spectrum 3 spectrometer in transmission mode in the MIR range (4000–400 cm$^{-1}$) and resolution of 2 cm$^{-1}$. The films withdrawn from the disintegration in compost were washed with deionized water and dried before the acquisition of the spectra.

#### 2.4.4. Differential scanning calorimetry (DSC)

The thermal transitions of the materials were tested by DSC on a Mettler Toledo DSC 2 calorimeter equipped with an HSS7 sensor and a TC-125MT intercooler. The endotherms were recorded with a heating/cooling/heating profile from −80 °C to 130 °C at a heating rate of 10 °C/min under a nitrogen constant flow of 50 mL/min.

#### 2.4.5. Thermogravimetric analysis (TGA)

Thermal stability was studied with a TGA/DSC 3+ Star system (Mettler Toledo, Switzerland). Approximately 5 mg samples were pre-heated in 70 μl alumina crucibles from room temperature to 70 °C, with a 15 min isothermal segment for residual moisture evaporation. The samples were then heated to 550 °C at a rate of 5 °C/min, under a 50 mL/min flow of N$_2$.

#### 2.4.6. Tensile test

Tensile properties were evaluated with a Zwick/Z2.5 tensile tester (ZwickRoell, UK) equipped with a load cell of 2 kN at a crosshead speed of 2.5 mm/min (10 % strain rate). At least five dumbbell-shaped specimens with 25 mm gauge length, 5 mm width and 2 mm thickness were conditioned for 48 h at 23 °C and 53 % relative humidity before testing.

#### 2.4.7. Scanning electron microscopy (SEM)

The film surfaces of the PEB samples extracted after composting were investigated with an Ultra 55 FEG SEM (Zeiss Sigma). The surfaces were first sputtered with gold in vacuum for 1 min at 1.5 kV and 10 mA.

## 3. Results and discussion

### 3.1. Ring-opening polymerization in reactive extrusion

The bio-sourced monomer ethylene brassylate was polymerized by ROP in reactive extrusion, without the use of solvents. Several catalysts have been screened for polymerization and different extrusion conditions have been tested. The polymerization was carried out with TBD and DBU as organic catalysts, the enzymes PC and CALB, and sodium hydride. For some polymerizations, benzoyl alcohol was employed as an initiator. The catalysts were chosen because of their low toxicity and based on previous polymerizations of EB and other macrolactones. PEB with the largest molar mass, obtained with TBD, was further analysed. In addition to being bio-based, PEB has been claimed to be biodegradable [4,6]. Here, the enzymatic depolymerization and disintegration in compost have been tested to provide insight into the end-of-life of this polyester.

EB polymerization was performed in REx under a constant flow of nitrogen, and the conditions and reagent ratios are reported in Table 1.

The dual catalytic system with a combination of a nucleophilic organic base (DBU) and a Lewis acid (MgBr$_2$) was previously described by Naumann et al. [29] in the ROP of ω-pentadecalactone and other small lactones in toluene in a glove box with different combinations of organic bases and Lewis acids. The catalysts were mixed with ethylene brassylate during REx, however, the product was liquid at room temperature (Fig. 1a), similar to the neat monomer, and no conversion was observed under the conditions tested. The lack of reaction was possibly ascribed to the poor dual catalytic activity in REx or the choice of Lewis acid, which had been proven critical by Naumann et al. [29]. The poor catalytic activity of DBU had already been reported for the ROP of EB in bulk [30].

REx with NaH, either with or without BnOH as the initiator, also led to liquid products at room temperature (Fig. 1b). As shown by ATR-FTIR spectroscopy (Figure S1), the spectrum of the REx product fully overlapped with the neat monomer, indicating no polymerization of EB occurred in REx. Despite the catalyst was reported to be effective for the ROP of ε-caprolactone, both in bulk [23] and melt processing [31] setups, the lack of reaction with EB was attributed to the high reactivity of NaH in air, which deactivates the catalyst before the reaction can take place.

Enzymatic polymerization of lactones and macrolactones has been broadly studied [5,32,33], also via REx [18]. Two different lipases were tested for ROP, both immobilized on polymeric beads. The beads, however, clogged the recirculating channel of the microcompounder and partially hindered the mixing (Fig. 1f). As an attempt to counteract the clogging, the extrusion speed was changed from 60 to 30 and 100 rpm, although unsuccessfully. The recovered product polymerised at 60 rpm with PC and CALB (entries 1 and 2 in Table 1) were tested by SEC and $^1$H NMR. New signals related to the PEB chain (δ 4.27 OC$H_2$C$H_2$O) and its end-group (δ 3.83 C$H_2$OH) were present in the $^1$H NMR spectrum of the reaction products, compared to the spectrum of the monomer (Fig. 2). The evaluation of the spectra indicated a monomer conversion of 100 % and $M_{nNMR}$ of 3700 g/mol for PEB-CALB, while PEB-PC had a conversion of 42 % and $M_{nNMR}$ of 900 g/mol (Table 1).

The incomplete monomer conversion in PEB-PC was also suggested by the appearance of the product, partly liquid at room temperature (Fig. 1c), in contrast to the brittle solid PEB-CALB (Fig. 1d). SEC confirmed that PEB-CALB ($M_{nSEC}$ = 10700 g/mol and Đ = 2.1) had a higher molar mass than PEB-PC ($M_{nSEC}$ = 1200 g/mol and Đ = 1.6) (Table 1). In the second heating DSC curves of the polymerization products, multiple endothermic peaks were evident between 30 and 75
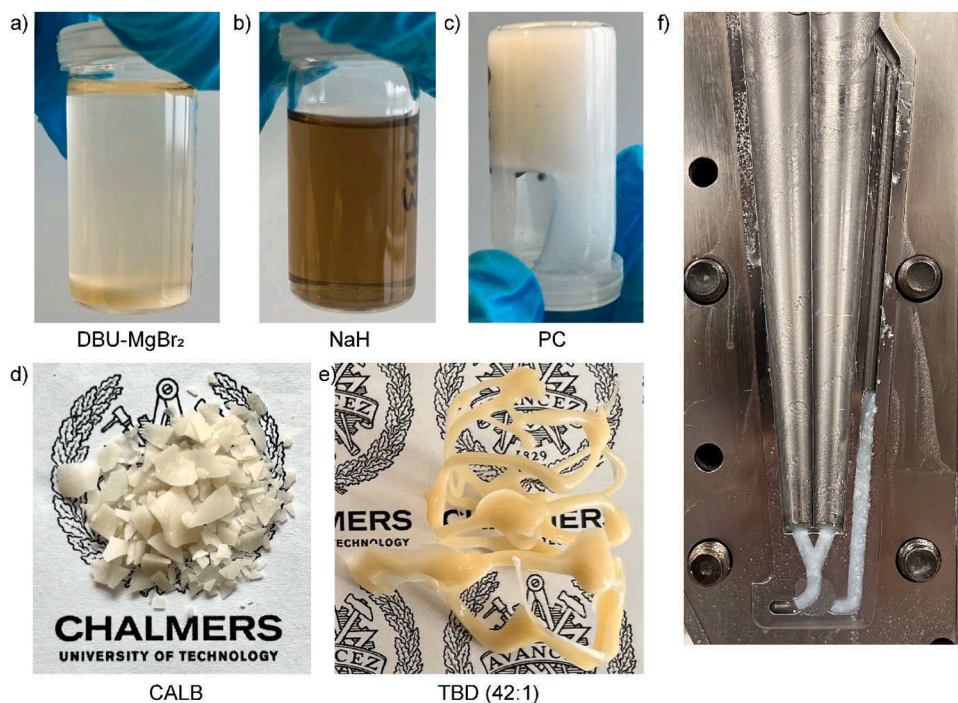
**Fig. 1.** Photographs of REx products with the catalysts a) DBU-MgBr₂ (entry 1 in Table S1), b) NaH (entry 2 in Table S1), c) PC (entry 1 in Table 1), d) CALB (entry 2 in Table 1), e) TBD (entry 9 in Table 1). f) Interior of the microcompounder showing the product mixed with supported enzyme stuck in the recirculation channel (entry 1 in Table 1).
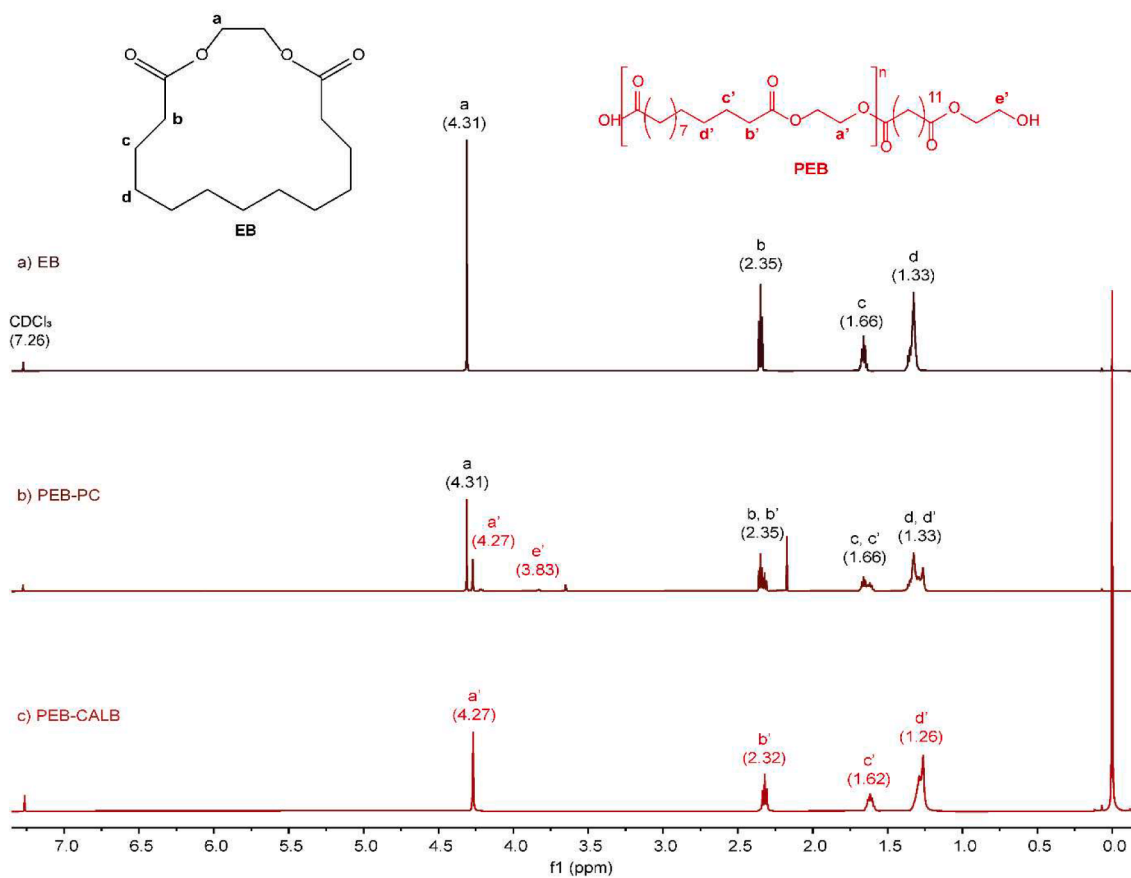


**Fig. 2.** ¹H NMR spectra in CDCl₃ of a) EB and the products of ROP with the enzymatic catalysts b) PC and c) CALB, with chemical structures of EB and PEB and corresponding signal assignment.

°C, indicating the melting of several crystalline forms of PEB, and possibly its oligomers (Fig. 3a). PEB catalysed with CALB did not show signs of monomer melting, in agreement with the full monomer conversion indicated by ^{1}HNMR . The TGA of PEB-CALB showed one degradation step with the onset of degradation (at 95 % weight) at 382 °C and the main degradation temperature at 440 °C (Fig. 3b). These results revealed that both enzymes were able to catalyse the ROP of ethylene brassylate, however CALB was more efficient under the same processing conditions. This difference can be attributed to the commercial enzymatic beads used, as the CALB has a catalytic activity of 1800 U/mg while PC 900 U/mg. For comparison, a reaction with 20 wt. % immobilized Lipase from *Pseudomonas cepacian* could be carried out, however decreasing the yielded quantity of polymer.

The nucleophilic organic base TBD has been reported in the literature to be successful for EB polymerization [4,13]. In the present work, the polymerization was carried out with or without BnOH as the initiator. First, the monomer:initiator molar ratio was varied between 42:1 and 42:0.08 while keeping a constant monomer:catalyst ratio (42:1), to increase the PEB molar mass.

The products of REx with TBD and BnOH were brittle solids at room temperature in all the compositions tested, and their molecular structure was analysed by SEC and ^{1}H NMR in CDCl$_3$ (Figure S2 and Table 1). In all the ^{1}H NMR spectra there is a clear signal related to PEB (δ 4.27 ppm, -OC$H_2$C$H_2$O-) and the corresponding signal in the monomer (δ 4.31 ppm, -OC$H_2$C$H_2$O-) had minimal intensity, indicating monomer conversions above 97 %. The spectra presented signals related to the polymer end groups, the hydroxyl group -C$H_2$OH (at δ = 3.83 ppm) [22] and the benzoxide C$_6$H$_5$C$H_2$O- (δ = 5.11 ppm) derived from BnOH [13], confirming its initiator role. From the integration of ^{1}H NMR signals, the molar mass varied between 4800 g/mol (EB:BnOH = 42:1) and 6500 g/mol (EB:BnOH = 42:0.08). These results showed that the variation of BnOH amount had a small effect on the conversion and the molar mass of PEB, explained by the suggested role of TBD as initiator in ROP [4,14, 21,34]. As the EB:TBD molar ratio was kept constant in the experiments (42:1), varying the amount of BnOH did not significantly alter the polymer chain length as also TBD contributed to the initiation. The role of TBD as initiator was also confirmed by the shift in the TBD signals in the polymer (δ 3.30, 3.24) compared to the neat TBD (δ 3.32, 3.28) [21].

For the reaction with EB:TBD:BnOH = 42:1:0.17 (mol), the REx temperature was varied (80, 100 and 130 °C) to gain an insight into the reaction kinetics. The extrusion force was monitored during REx, providing information on the viscosity which is proportional to the force (Fig. 4a). The reactions performed at the three temperatures all led to 98 % monomer conversion. When the temperature was increased from 80

to 130 °C, an increase in the force, and thus of the molar mass, was registered sooner, and a plateau was reached in a shorter time (between 20 and 30 min), confirming faster reaction kinetics that are of interest for potential scale-up of REx.

ROP in REx was then performed at 130 °C without BnOH with EB: TBD molar ratio of 42:1 (Fig. 1e) and the reaction reached 93 % monomer conversion and the largest molar mass in this work ($M_{nNMR}$ = 7900 g/mol) (Fig. 5 and Table 1). This result confirmed the dual action of TBD as both catalyst and initiator. When the EB:TBD molar ratio was increased to 60:1 and 84:1, the conversion and the molar mass significantly decreased to 19 % and 3900 g/mol, possibly due to insufficient catalyst.

A REx process was designed to try to reach higher molar masses starting from EB:TBD molar ratio of 42:1, which was proven to reach high conversion. After 30 min of processing, 3 ml of material was extruded and 3 ml of fresh monomer was fed, under the hypothesis that the fresh monomer would increase the chain length. The same procedure was repeated at 60 min and the processing was stopped at 90 min. The extrusion torque recorded during the reaction (Fig. 4b) instantly zeroed at each withdrawal, as expected for the exponential drop of torque with the volume reduction at set processing conditions. After the re-feeding of the monomer, a torque steady growth was observed, indicating a viscosity increase assigned to the progress of the polymerization. The sample withdrawn at 60 min showed an increase in conversion and molar mass compared to the one after 30 min, confirming that the fresh monomer reacted, extending the already growing polyester chains (Figure S3 and Table 2). It is worth to note that not adding further TBD prevented new initiation. In contrast, having more monomer from the beginning of the reaction (entries 10 and 11 in Table 1) did not increase the molar mass because the majority of TBD initiated the chains, and few TBD molecules kept catalysing the polymerization. The only extension of the reaction time would not increase the molar mass and conversion [21], due to the absence of available monomer at so high reached conversion (96 %). The product recovered after 90 min showed a decrease in conversion and slightly lower molar mass, due to the large amount of monomer in relation to TBD and possibly because of thermal degradation (Figure S3 and Table 2). As shown in the TGA (Figure S4), the product recovered after 90 min has two degradation steps, one similar to the PEB recovered at 30 and 60 min (degradation temperature at 440 °C), the other step at 200 °C related to a PEB fraction with lower molar mass and residual monomer. The discrepancy between the 10 % weight loss in the TGA at 200 °C and the 45 % monomer from NMR analysis demonstrates the heterogeneity of the sample, therefore the analyses of few milligrams cannot represent quantitively the material composition.
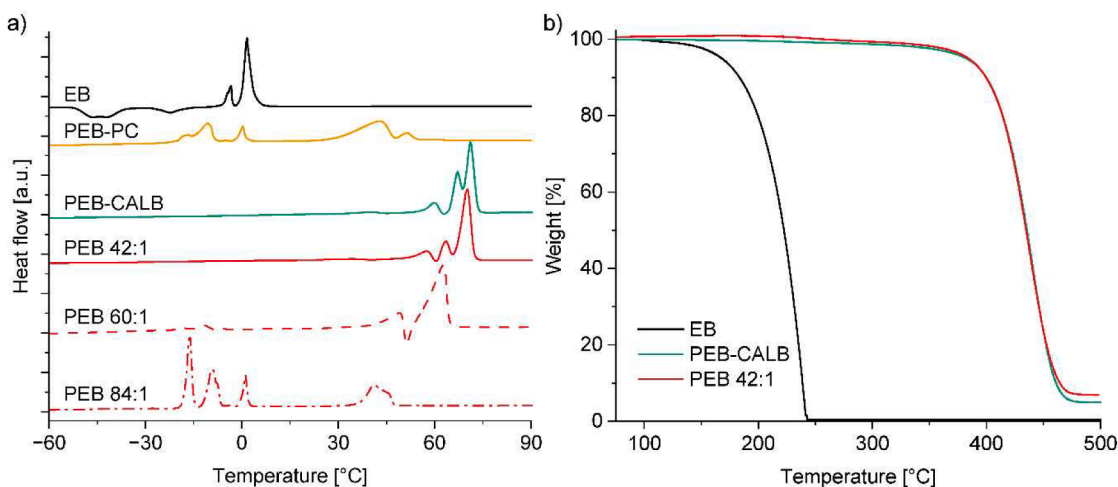


**Fig. 3.** a) Second heating scan of DSC (endothermic transitions upwards) of EB and the REx products with the catalysts PC, CALB and TBD in the molar ratio 42:1, 60:1 and 84:1. b) Thermogravimetric analysis in nitrogen of EB and the REx products with CALB and TBD in the molar ratio 42:1.
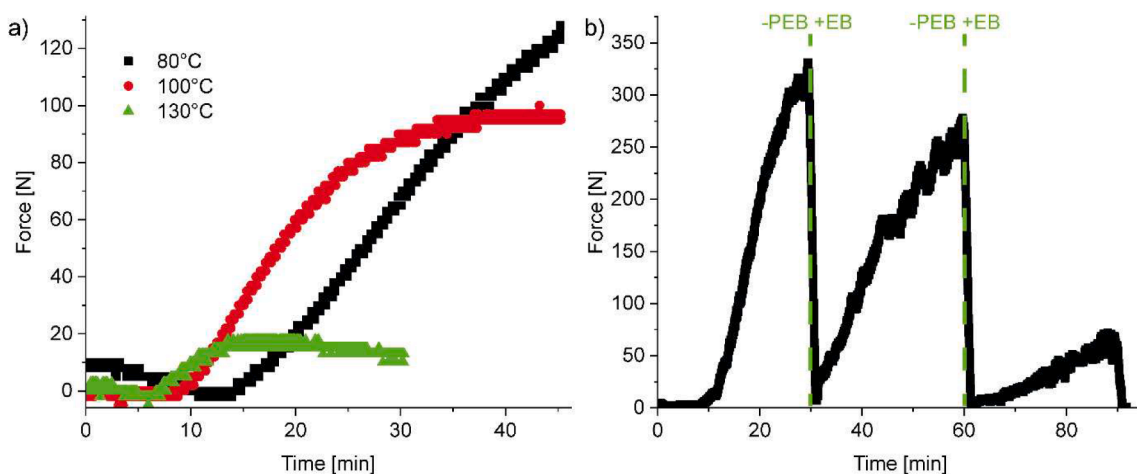
**Fig. 4.** Extrusion force recorded during a) REx of EB with TBD and BnOH in a molar ratio of 42:1:0.17 carried out at 80, 100 or 130 °C (entries 5, 6 and 7, respectively, in Table 1) and b) REx of EB with TBD in a molar ratio 42:1, with withdrawal of 3 ml PEB and addition of 3 ml EB at 30 and 60 min.
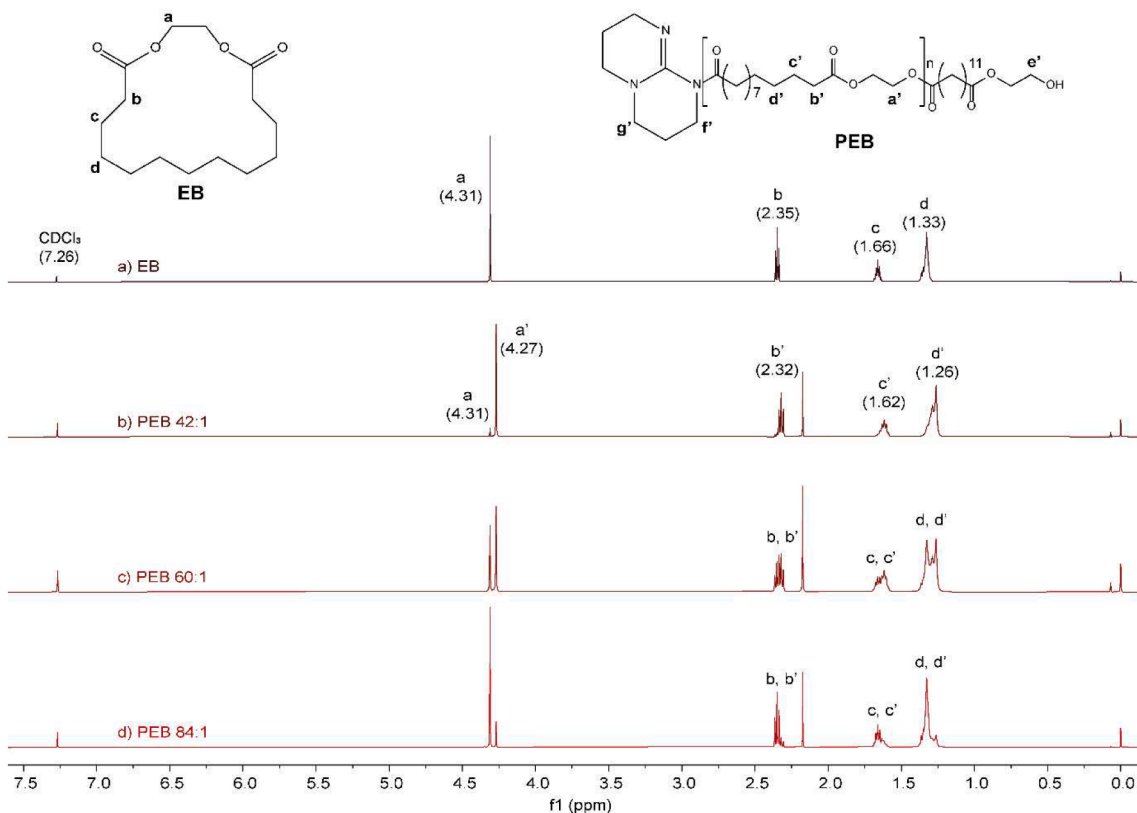


**Fig. 5.** $^1$H NMR spectra in CDCl$_3$ of a) EB and the products of ROP with TBD in different molar ratios (b) 42:1, c) 60:1 and d) 84:1), with chemical structures of EB and PEB and corresponding signal assignment.

**Table 2**
Monomer conversion and molar mass measured by $^1$H NMR in CDCl$_3$, molar mass and dispersity measured by SEC in CHCl$_3$ of samples collected at 30, 60 and 90 min REx with TBD in a molar ratio 42:1, with withdrawal of 3 ml PEB and addition of 3 ml EB at 30 and 60 min.

| Material | Conv. [%] | $M_{nNMR}$ [g/mol] | $M_{nSEC}$ [g/mol] | Đ |
|---|---|---|---|---|
| PEB 42:1_t30 | 96 % | 7800 | 17600 | 2.3 |
| PEB 42:1_t60 | 98 % | 10300 | 20200 | 2.4 |
| PEB 42:1_t90 | 55 % | 8400 | 22000 | 2.4 |

This experiment provided insights for a potential scaling up of the ROP in REx, as side-feeding of EB in the extrusion line could improve the molar mass.

PEB was tested by DSC to analyse the influence of the molar mass and conversion on the thermal transitions. The second heating scans of the reaction products with TBD and BnOH (Figure S5) showed several PEB melting peaks between 50 and 75 °C and a broad low-intensity peak around 40 °C. The scans did not present peaks related to the monomer melting (around 0 °C), in agreement with the high conversion. The materials polymerized without BnOH showed melting in the same temperature range, and the peaks shifted to lower temperatures with the

decrease in molar mass (Fig. 3a). Peaks related to the melting of the monomer appeared in the thermogram of PEB with 84:1 EB:TBD molar ratio, in agreement with the low monomer conversion (19 %). In none of the curves there was evidence of glass transition. From our previous research on PEB [21], a glass transition around −20 °C has been detected by dynamic mechanical thermal analysis for samples with molar mass (from ^{1}H NMR) of around 8 kDa. However, in this study the glass transition was not visible from DSC in the conditions tested (heating rate of 10 °C/min) suggesting a small amorphous fraction and high crystallinity of PEB. The crystallinity cannot be quantified from DSC because of the lack in literature, in our knowledge, of the melting enthalpy ($\Delta H_0$) of fully crystalline PEB. However, we cannot exclude a glass transition below −60 °C for the lower molecular weight PEB. The TGA in nitrogen of PEB with the largest molar mass (entry 9 in Table 1) indicated an onset of thermal degradation (at 95 % weight) at 376 °C and a single degradation step with main degradation temperature at 440 °C (Fig. 3b).

The samples polymerised at 130 °C with and without BnOH (entries 7 and 9 in Table 1) were shaped into dumbbell-shaped specimens by injection moulding for tensile testing. In line with the target of single-step synthesis and manufacturing, the characterization was performed on the extruded and moulded materials without any purification. For the TBD-catalysed materials, this approach is even more relevant due to the challenge in the purification when the catalyst serves also as initiator. Both materials showed brittle behaviour, with elongation at break below 5 % and stiffness around 290 MPa (Table 3). The difference in molar mass of the two samples (4900 and 7900 g/mol for entries 7 and 9 in Table 1, respectively) did not significantly influence the tensile properties, as the differences between the values are within the scattering of the data. The similarity in the data could be a consequence of the low molar mass in both samples, which does not enable chain entanglement, thus imparting brittleness. Due to the brittleness of PEB, its potential application in common field of plastics, such as packaging, is restricted and requires the development of strategies to further improve its molar mass and consequently the mechanical properties.

### 3.2. End-of-life

Disintegration in compost and enzymatic depolymerization were investigated for the end-of-life of PEB. The PEB with the largest molar mass ($M_{\text{nSEC}}$ = 20600 g/mol; entry 9 in Table 1) was tested for both the options. It is worth noting that the disintegration in compost is only one of the requirements for classifying a material as compostable, therefore additional tests such as respirometry would be needed. Although PEB is referred to in the literature as a bio-based and biodegradable polymer, no studies addressing its biodegradation were found. Therefore, the present work contributes to fill this knowledge gap.

The disintegration of PEB was studied in a laboratory-scale simulated industrial composting according to the ISO 20200:2015 standard. The test was carried out for 90 days during which PEB films, enclosed in meshed pouches, were withdrawn at different times and their mass loss was recorded. The weight loss was fast between 7 and 60 days, when PEB lost around 89 % of its initial mass and after 90 days 93 % weight loss was recorded (Fig. 6b). The extracted films became brittle and broke down since day 28 and at the end of the test only fragments could be withdrawn (Fig. 6a). These remaining fragments should be further

**Table 3**
Average values with standard deviation of tensile properties at room temperature of PEB (entries 7 and 9 in Table 1).

| Material | Young's modulus [MPa] | Elongation at break [%] | Tensile strength [MPa] |
|---|---|---|---|
| PEB 42:1:0.17 | 289 ± 2 | 2.2 ± 0.4 | 6.0 ± 1.1 |
| PEB 42:1 | 293 ± 46 | 3.5 ± 1.0 | 8.9 ± 2.6 |

tested to investigate whether they could be assimilated by microorganisms for longer composting times. The surface of the samples extracted after 14 and 28 days in compost was analysed by SEM (Fig. 6d). As degradation led to brittleness, the morphology of samples after day 28 could not be analysed. With time, the surface became increasingly rougher with uneven holes, and there was no clear evidence of microorganisms forming a biofilm. Similar homogeneous erosion was observed on the surface of biologically aged PCL [35], with a similar chemical structure, or after hydrolytic degradation of ethylene brassylate and lactic acid copolymers [25]. A combination of abiotic hydrolysis and biotic degradation was therefore suggested. TGA of PEB indicated a decrease in the onset of degradation temperature from 376 °C, for neat PEB, to 366 °C after 14 days in compost (Figure S6). The lower thermal stability is ascribed to the decrease in molar mass as a consequence of the hydrolysis during compost. The films extracted from the disintegration in compost were also tested by ATR-FTIR in the mid-infrared range (4000–400 cm$^{-1}$) (Fig. 6c). The spectrum of PEB before compost was unchanged after 7 days, in agreement with the minimal weight loss registered. After 14 and 28 days, a broad peak appeared around 3300 cm$^{-1}$ related to hydroxyl groups. The presence of these groups can be attributed to the hydrolysis of the ester bonds during compost, resulting in the formation of carboxylic acids and alcohols. In these spectra, new peaks also appeared around 1580–1540 cm$^{-1}$ which could be attributed to carboxylate groups formed by hydrolysis in the basic compost environment promoted by urea [36].

As a potential green route for chemical recycling, PEB was enzymatically depolymerized in a toluene solution using 300 % w/w immobilized CALB [28]. After 72 h, ^{1}H NMR indicated a strong intensity reduction of the signal related to the PEB (δ 4.27 OC$H_2$C$H_2$O) and new peaks appeared between δ 3.75 and 3.59, which were assigned to the end-groups of EB linear oligomers and possibly to ethylene glycol as final degradation product [37] (Fig. 7a). After the depolymerization, the monomer signal (δ 4.31 OC$H_2$C$H_2$O) had similar intensity to the polymer one (δ 4.27 OC$H_2$C$H_2$O). The signals between δ 1.26 and 2.32 could be assigned to residual oligomers and possibly to the degradation product brassylic acid [38]. It is worth to note that the lack of detection of other signals related to cyclic oligomers [28] does not exclude their formation, which would require dedicated analyses. The depolymerization products were also tested by SEC, in which the intensity of the main elution peak of PEB was decreased and new peaks at higher retention times appeared, related to lower molar mass components (Fig. 7b). This work thus demonstrated the use of CALB as a green catalyst for both the polymerization and depolymerization of ethylene brassylate and its polyester.

In our previous work [21], the post-industrial mechanical recycling of PEB was simulated in an extruder for up to four cycles, without significant thermal degradation or loss in tensile properties, indicating mechanical recycling as a further option for the circularity of PEB.

### 4. Conclusion

This work aimed to investigate reactive extrusion methods for the ring-opening polymerization of the bio-based monomer ethylene brassylate, analyse the properties of the polyester, and study its degradation in relation to the end-of-life options. Several catalysts and different processing conditions were tested for identifying the systems enabling an effective polymerization in REx. Sodium hydride and the dual catalysts system DBU-Lewis acid could not polymerize EB under the conditions tested. Immobilized Lipase B from *Candida antarctica* and the organic base TBD led to the complete monomer conversion during REx within 30 min, and ≈ 3700 and 8000 g/mol molar mass was reached, respectively, while achieving same melting (≈ 70 °C) and degradation (≈ 440 °C) temperature. The tensile tests performed on injection moulded PEB indicated a brittle character, with 4 % elongation at break and Young's modulus of 290 MPa, due to the relatively low molar mass achieved. The proven initiator role of TBD resulted in unsuccessful
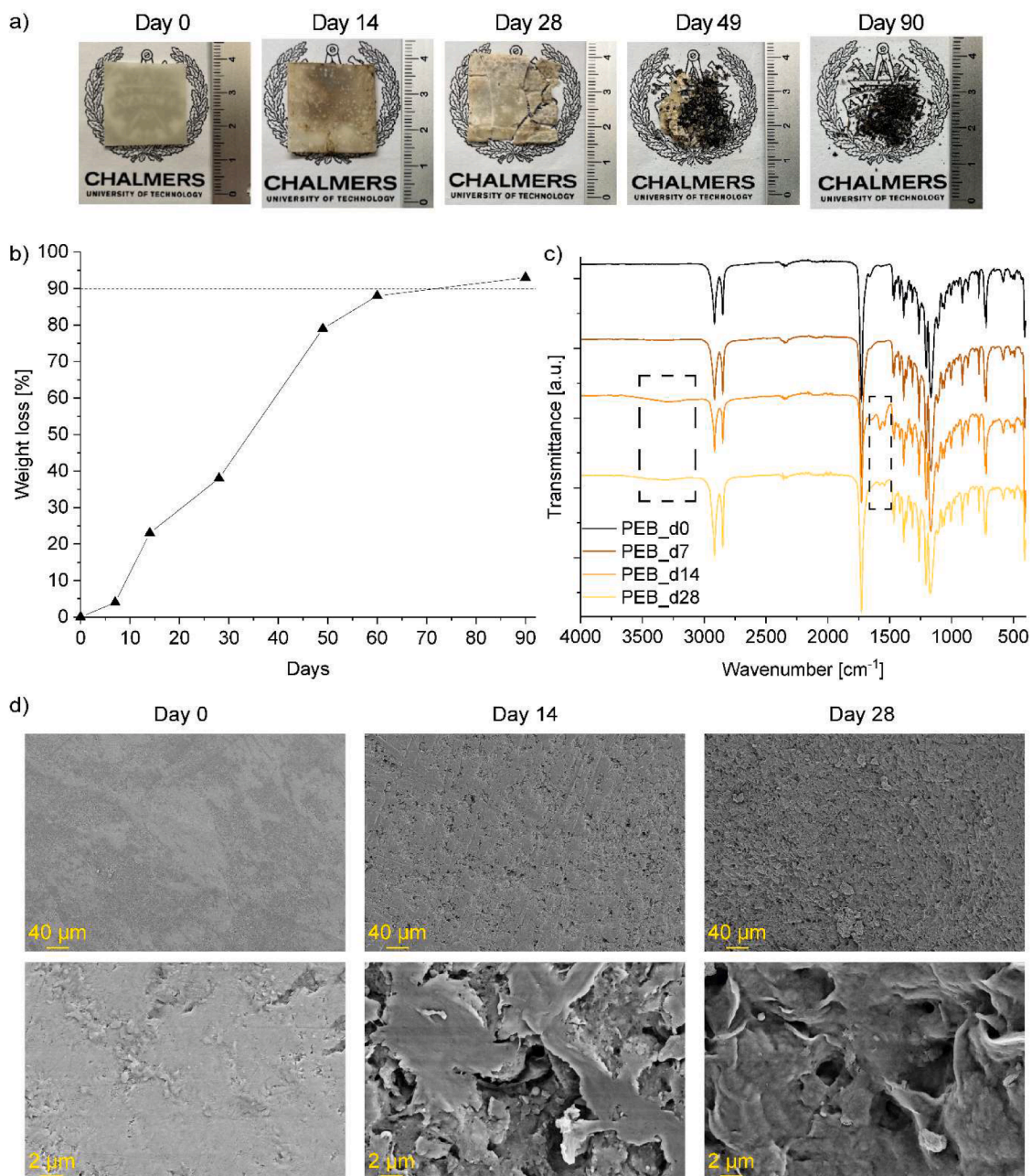
**Fig. 6.** a) Photographs of PEB samples b) average weight loss recorded during disintegration in compost. c) ATR-FTIR of the samples withdrawn during compost, with dashed lines indicating the areas where changes in the spectra are observed. d) Scanning electron microscopy of the surface of PEB films before and after 14 and 28 days in industrial composting, at two magnifications.

attempts to increase the molar mass by varying EB:TBD molar ratio. This limitation motivated deeper ongoing studies to further develop ROP strategies catalysed by Lipase B from *Candida antarctica* for higher PEB molar mass. To close the circularity of bio-based PEB, two end-of-life options were studied. The disintegration in industrial compost was tested to gain insights into the biodegradation, revealing that PEB lost 93 % of its initial weight after 90 days. The structural and morphological analyses of the samples extracted from the compost study at different times supported a hydrolytic mechanisms as main degradation path. Thanks to the dynamic nature of the enzymatic biocatalytic activity, an excess of Lipase B from *Candida antarctica* (300 wt.%) produced linear oligomers, indicating enzymatic depolymerization as viable second end-of-life strategy. Overall, this work demonstrates the circularity of bio-based PEB, starting from its polymerization in reactive extrusion to its end-of-life through enzymatic depolymerization and disintegration in

industrial compost, aiming to favour its industrial upscale.

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## CRediT authorship contribution statement

**Giada Lo Re:** Writing – review & editing, Validation, Supervision, Software, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Angelica Avella:** Writing – original
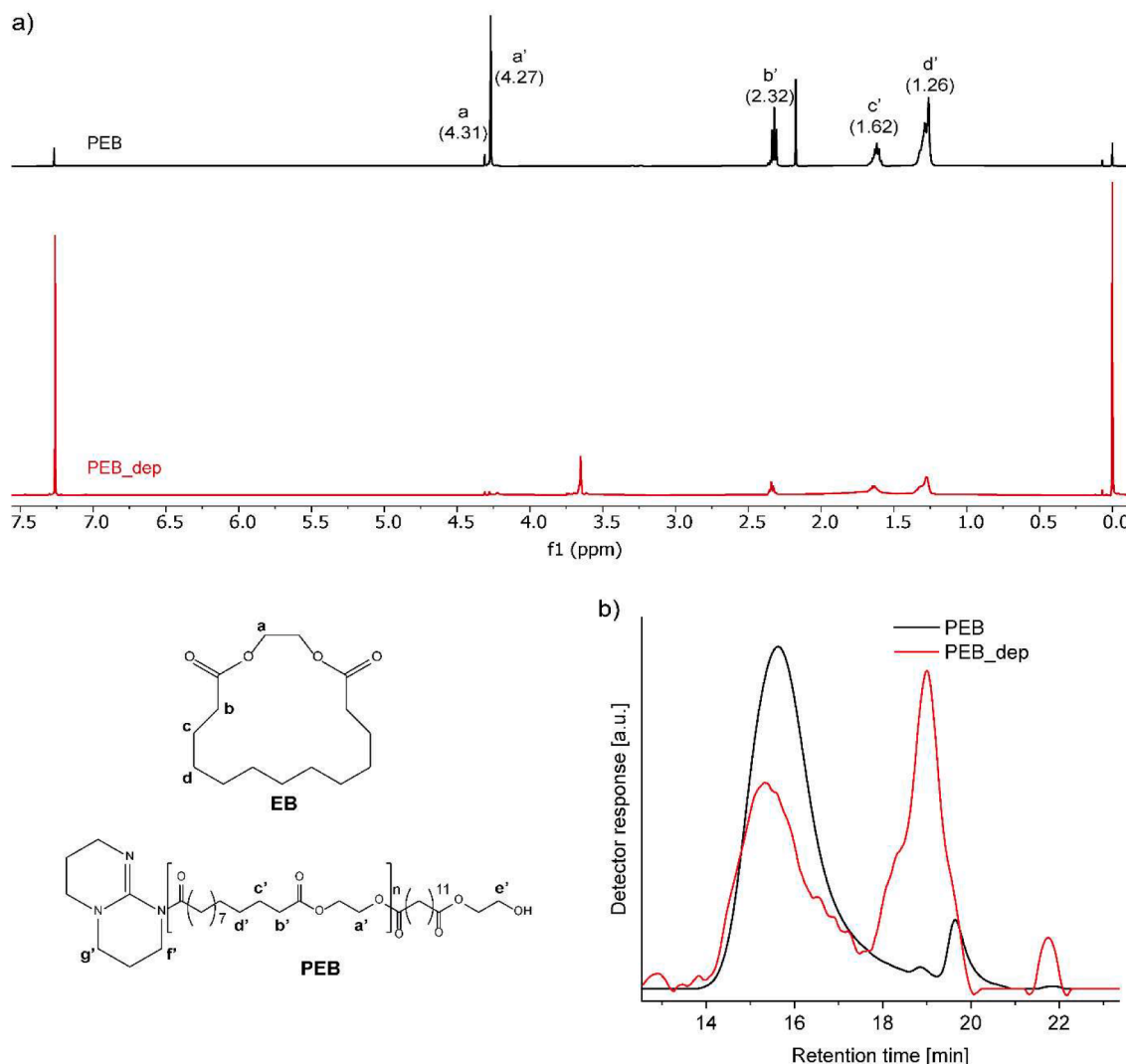
**Fig. 7.** a) ¹H NMR spectra in CDCl₃ of PEB (entry 9 in Table 1) and after 72 h of enzymatic depolymerization, with chemical structures of EB and PEB and corresponding signal assignment. b) SEC in CHCl₃ of PEB, before and after enzymatic depolymerization.

draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Daniela Pappalardo:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization. **Rosica Mincheva:** Writing – review & editing, Validation, Supervision, Methodology, Formal analysis, Conceptualization.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Giada Lo Re reports financial support was provided by Wallenberg Wood Science Center. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2025.111203.

## Data availability

Data will be made available on request.

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