

Novel Strategies for Recycling Poly(butylene adipate-co-terephthalate)-Starch-Based Plastics: Selective Solubilization and Depolymerization–Repolymerization Processes

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Cite This: *ACS Sustainable Chem. Eng.* 2023, 11, 14518–14527

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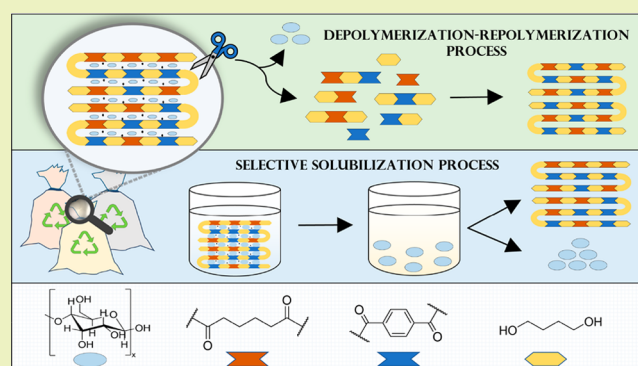
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ABSTRACT: Starch-based plastics (SBPs) containing poly(butylene adipate-co-terephthalate) (PBAT) are among the most produced bioplastics on the market and are currently managed at their end of life (EoL) through composting. In view of developing novel EoL approaches, SBPs were characterized here in terms of their main components (PBAT, starch, and plasticizer), and three strategies for their recycling were investigated: (I) the selective solubilization of PBAT with ethyl acetate; (II) a two-step depolymerization–repolymerization process that consists of the catalytic selective alcoholysis of PBAT into its oligomers, followed by their repolymerization to PBAT with no need of adding a new catalyst; and (III) the complete selective depolymerization of PBAT, followed by the recovery and purification of butanediol (1,4-BD), dimethyl terephthalate (DMT), and dimethyl adipate (DMA). Up to 99, 95, and 93% recovery of the SBP components was obtained, respectively, following these three methods. Extensive characterization of the recovered PBAT was performed through molecular weight and thermal and thermomechanical analyses, demonstrating the efficiency of the processes. The environmental sustainability of the proposed approaches was also preliminarily evaluated through the calculation of their environmental factor (E-factor).

KEYWORDS: PBAT, starch-based plastics, chemical recycling, physical recycling, recycling, selective depolymerization, methanolysis, alcoholysis, poly(butylene adipate-co-terephthalate), circularity, EoL, end of life, supermarket bags, disposable cutlery containers



INTRODUCTION

Since the 1950s, the first years of rapid growth in global plastic production, the annual production of plastic has increased nearly 200-fold, reaching 390 million metric tons (Mt) in 2021.¹ One of the most important issues of this exponential input of plastic in our world is its disposal at its end of life (EoL). Before 1980, plastic waste was almost totally discarded, but after that year, the recycling/valorization approach slowly emerged. Between 1950 and 2015, 6300 Mt of plastic waste had been generated in total, of which ~9% was recycled, 12% was energetically recovered through incineration, and 79% accumulated in landfills or was (accidentally or intentionally) leaked into the environment.² It is estimated that 5–13 Mt of plastic every year ends up in the sea, polluting waters and impacting wildlife health.³

In the last decades, biodegradable plastics have been produced and utilized, mostly in packaging, to overcome the environmental issues created by the plastic that ends up in our environment because of incorrect management. Biodegradable plastics can be composted together with organic waste, thus diminishing the need for plastics that require special disposal. However, the biodegradability of these plastics is strictly

dependent on the environment. The majority of biodegradable plastics require special conditions in terms of water, temperature, and microorganisms to be degraded in a reasonable time (like the ones in composting facilities); unfortunately, many become nondegradable in most open environments, thus contributing to plastic pollution in the exact same manner as nonbiodegradable plastics.^{4,5} It has been demonstrated that current international standards and regional test methods are insufficient in realistically predicting the biodegradability of bioplastic waste in wastewater, inland waters (rivers, streams, and lakes), and marine environments.⁶ A further complication arises from the fact that, although the material needs to rapidly degrade in natural environments, it must not degrade during its practical use.⁷ For these reasons, the use of biodegradable

Received: June 14, 2023

Revised: August 31, 2023

Published: September 20, 2023



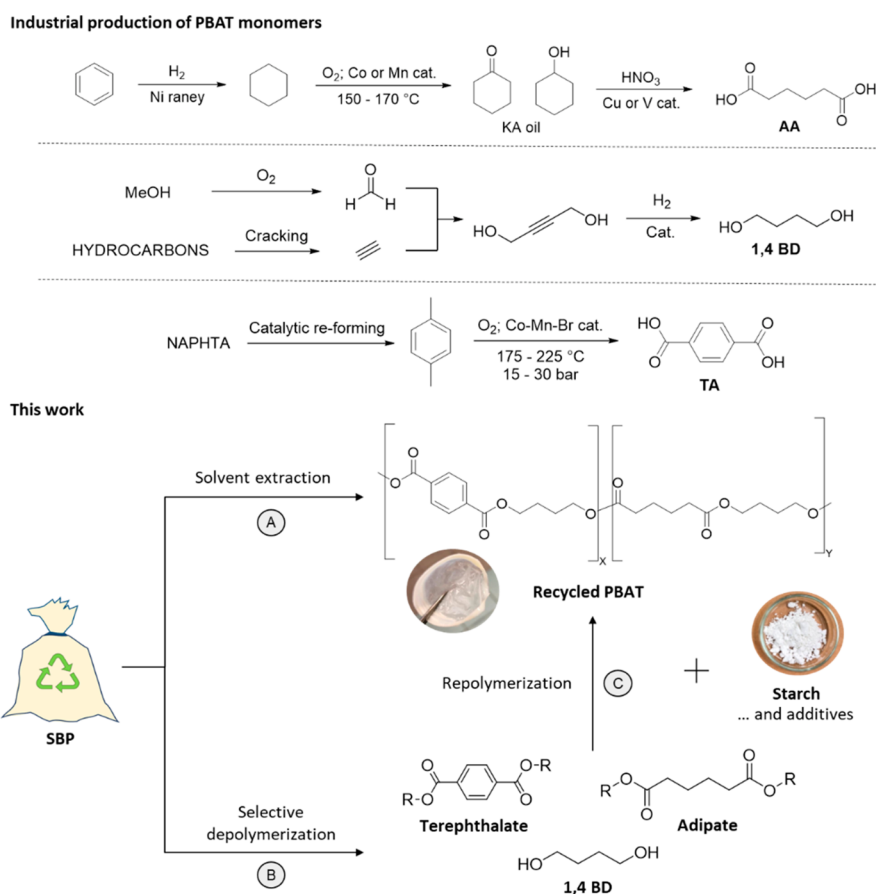


Figure 1. Most popular methods for the industrial production of AA, 1,4-BD, and TA (top).^{17–19} Investigated strategies for recycling SBPs (bottom): (A) selective solubilization; (B) depolymerization of PBAT to obtain DMT, DMA, and 1,4-BD; and (B) + (C) depolymerization–repolymerization process.

plastics should be limited to specific applications for which reduction, reuse, and recycling are not feasible (e.g., dolly rope, other fishing gear, or in agriculture to protect crops), where (partial) loss is considered unavoidable during normal use. Although recovery from the environment for reuse or recycling would be preferable, it is either impossible or disproportionately expensive for some of these applications.⁸ This means that reuse and recycling should be prioritized with respect to biodegradation, especially for all of the plastics (bio or not) whose loss to the environment can be avoided.⁹

Starch-based plastics (SBPs) with poly(butylene adipate-*co*-terephthalate) (PBAT; the main fossil-based co-polyester present in starch-based blends) are among the most produced bioplastics on the market today.¹⁰ They are mainly used in packaging, rigid materials, medical products, agriculture applications, and carrier bags. Even though SBPs are categorized as biodegradable plastics, their biodegradability is strictly dependent on the conditions adopted.^{11,12} This means that in some cases, it is too low,¹³ and they fail to achieve the regulatory standards for assessment of compostability.¹⁴ Moreover, composting these plastics means losing the building blocks from which they are made, which induces the need to produce new materials from virgin feedstock. This approach is in direct contrast with the concept of a circular economy, in which all products, materials, and raw materials are used for as long as possible; additionally, used products are cycled back for further production instead of becoming waste,¹⁵ thus reducing the environmental impacts related to their life cycle.¹⁶ The

industrial production pathways that are used today for manufacturing the PBAT monomers adipic acid (AA), terephthalic acid (TA), and 1,4-butanediol (1,4-BD) are based on fossil-based platform chemicals (e.g., benzene) and require highly energy demanding (e.g., cracking or reforming) catalytic multistep processes (Figure 1),^{17–19} which make PBAT-SBP composting an enormous waste of resources. While much attention has been focused on the recycling of bioplastics such as polylactic acid (PLA)^{20,21} and polyhydroxyalkanoates (PHAs),^{22,23} only a few studies have been conducted on PBAT and its starch-based blends: (i) the mechanical recycling of PBAT has been successfully proposed, demonstrating that it can be subjected to more cycles of reprocessing;²⁴ (ii) the slow pyrolysis of SBP bags has been used to obtain the main monomers of PBAT, TA, AA, levoglucosan, and char;²⁵ and (iii) the fungal fermentation of the starch component for the production of lactic acid has been reported.²⁶

Following our interest in the chemical recycling of wasted bioplastics in a circular perspective,²⁷ this work aims to propose alternative ways for the recycling of PBAT-SBP plastics. Three main approaches were investigated (Figure 1) and compared in terms of the physicochemical characteristics of the recycled PBAT and their environmental sustainability, which was determined by calculating their environmental factor (E-factor) values:

1. The selective solubilization of PBAT with ethyl acetate (EtOAc).

2. A depolymerization–repolymerization process: the catalytic selective depolymerization of PBAT with methanol (MeOH), giving 1,4-BD, and dimethyl ester monomers and monomethyl, mono-4-hydroxybutyl ester adducts of TA and AA; and the repolymerization of the obtained mixture into PBAT with no need of adding a new catalyst.
3. The complete depolymerization of PBAT, followed by the recovery and purification of 1,4-BD, dimethyl terephthalate (DMT), and dimethyl adipate (DMA).

The proposed strategies (1, 2, and 3) are intended to coexist with mechanical recycling approaches, which remain an important resource for plastic recycling. It is well-known that mechanical recycling can be adopted for a few cycles before the loss of a polymer's mechanical properties occurs (e.g., a molecular weight decrease);^{16,28} at this point, a chemical recycling approach can be applied, allowing to produce the polymer once more with its original characteristics.

MATERIALS AND METHODS

Materials. All chemicals were purchased from Sigma-Aldrich and used without further purification. Starch-based plastic (SBP) bags were obtained from local supermarkets (Ravenna, Italy) and can be found in most national supermarkets.

Plasticizer Recovery. SBP (6.5 g) and MeOH (17 mL) were placed in a 100 mL flask with a reflux condenser. The mixture was refluxed under magnetic stirring for 1 h. Then, the plastic residue (SBP_{res}) was recovered through filtration and washed with MeOH (15 mL). The resulting MeOH solution was rotary evaporated under vacuum, recovering the MeOH and yielding the plasticizer (i.e., sorbitol), which was weighed to give the yield based on the input material (wt %).

Selective Solubilization of PBAT. SBP_{res} and selected solvents were added to a closed-cap glass vial and magnetically stirred at 90 °C for 20 min. Then, the solution was centrifuged at 4000 rpm for 30 s. The supernatant was withdrawn, and the solvent was recovered by distillation, leaving the extracted PBAT, which was weighed to give the yield based on the input material (wt %). The starch (comprising the inorganic fraction) that was separated via centrifugation was recovered and weighed, and the yield was expressed based on the input material (wt %).

Depolymerization–Repolymerization of PBAT. Selective depolymerization (depoly) of PBAT was performed as follows: SBP_{res}, MeOH, and selected catalysts were charged in a closed-cap glass reactor. The methanolysis reaction was carried out under autogenous pressure and magnetic stirring. Afterward, the reaction mixture was cooled to room temperature (rt) and filtered to recover the starch, which was washed with MeOH (half of the amount that was used for conducting the reaction). The resulting solution (filtrate) was distilled to remove and recover MeOH, yielding a syrup composed of 1,4-BD, DMT, DMA, bis(4-hydroxybutyl) or methyl 4-hydroxybutyl esters of TA and AA, and the catalyst that was used.

Repolymerization (repoly) of PBAT was conducted as follows: the above-mentioned syrup was put in a 10 mL flask with a condenser to remove any MeOH that formed during the polymerization reaction. The air in the apparatus was evacuated and replaced with N₂. The esterification reaction was conducted under a N₂ flow at 150 °C for 1 h and then at 170 °C for 3 h. Afterward, the polycondensation reaction was performed under vacuum at 190 °C for 3 h. The obtained polymer was weighed after dissolution in CH₂Cl₂ and precipitation in MeOH, and it was characterized as described below. The catalyst ended up in the MeOH.

Complete Depolymerization of PBAT. SBP_{res} (6 g), MeOH (25 mL), and selected tin-based catalysts were charged in a closed-cap glass reactor. The methanolysis reaction was carried out under autogenous pressure and magnetic stirring at 140 °C for 7 h. Afterward, the reaction mixture was cooled to rt and filtered to

recover the starch, and the mixture was washed with MeOH (15 mL). The resulting solution (filtrate) was slowly evaporated, recovering the MeOH (for E-factor quantification) and allowing the DMT to crystallize; the DMT was subsequently filtered, recovered as crystals, and dried. MeOH was then removed from the resulting solution, leaving a mixture mainly composed of 1,4-BD and DMA, which were separated through a liquid–liquid extraction using water (10 mL) and cyclohexane (25 mL) as solvents. The water solution was then distilled to recover 1,4-BD, and the cyclohexane solution was distilled to recover DMA.

The Environmental Factor (E-Factor). The E-factor was calculated for monomers recovery and both the selective solubilization and depoly–repoly strategies using the following equation:²⁹

$$\text{E-factor} = \frac{\text{mass of waste (g)}}{\text{mass of products (g)}} \quad (1)$$

Analyses. Sample Derivatization. All obtained products (plasticizers, syrups, and monomer fractions) were derivatized as follows prior to gas chromatography–mass spectrometry (GC–MS) analysis: an aliquot (1–2 mg) was withdrawn, silylated for 30 min at 70 °C (with 0.1 mL of ethyl acetate, 0.04 mL of bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane, and 0.02 mL of pyridine), and analyzed by GC–MS as described below.

GC–MS Analysis. GC–MS analyses were performed using an Agilent 7820A gas chromatograph connected to an Agilent 5977E quadrupole mass spectrometer. The injection port temperature was 280 °C. Analytes were separated on an HP-5MS fused-silica capillary column (stationary phase 5%-phenyl-methylpolysiloxane, 30 m, 0.25 mm i.d., 0.25 μm film thickness), with a helium flow of 1 mL min⁻¹. Mass spectra were recorded under electron ionization (70 eV) at a frequency of 1 scan s⁻¹ within the 29–450 *m/z* range. The thermal program was set as follows: 50 °C for 5 min, followed by an increase to 250 °C at a rate of 10 °C min⁻¹, where the temperature was maintained for 5 min.

Nuclear Magnetic Resonance (NMR). ¹H NMR spectra were recorded on a Varian 400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm) from tetramethylsilane (TMS), with solvent resonance as the internal standard (CDCl₃, 7.24 ppm; D₂O, 4.79 ppm).

Elemental Analysis. The elemental analyses of the SBP, recycled PBAT, starch, and sorbitol were performed using an elemental analyzer (Thermo Scientific, Flash 2000, organic elemental analyzer) using the flash combustion technique. Ash content was determined by weight upon calcination for 5 h at 550 °C.

Gel Permeation Chromatography. The weight-average molecular weight (*M_w*) and polydispersity index (PDI) were determined in THF solution by size exclusion chromatography (SEC) using an HPLC Lab Flow 2000 apparatus working with a 1 mL min⁻¹ flow and equipped with a Rheodyne 7725i injector, a Phenomenex Phenogel 5 μm MXM column, and a Knauer RI K-2301 refractive index (RI) detector. Calibration curves were obtained using several monodisperse polystyrene standards.

Differential Scanning Calorimetry (DSC). DSC measurements were carried out on a TA Instruments Q2000 DSC modulated apparatus, equipped with an RCS cooling system. Each sample (3–5 mg) was heated from –70 to 200 °C twice at a rate of 20 °C min⁻¹ in a N₂ atmosphere with an intermediate quench cooling run. The crystallization temperature (*T_c*) and melting temperature (*T_m*) were taken at the peak maximum of the exotherm and endotherm, respectively. In the presence of multiple peaks, the temperature of the main peak was taken as *T_c* or *T_m* unless otherwise specified.

Dynamic Mechanical Thermal Analysis. Dynamic mechanical thermal analysis (DMTA) spectra were recorded on selected sample films obtained by solvent casting a 10% polymer solution in chloroform. The measurements were carried out using a 242E Artemis instrument (Netzsch, Germany). Three bar-shaped film (20 × 4 × 0.1 mm) specimens were tested for each product in tensile mode, heating from 0 to 70 °C (heating rate of 3 °C min⁻¹) with a 1 Hz oscillation frequency, a 5.0 N dynamic force, a 0.1 N constant

static force, a 1.1 proportional factor (PF; the ratio of static force to dynamic force), and a 50 μm strain. E' (25 $^{\circ}\text{C}$) is the conservative modulus at 25 $^{\circ}\text{C}$, as evaluated from the DMTA spectra.

Thermogravimetric Measurements. The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA), which was carried out on a TA Instruments SDT Q600 instrument. Each sample was heated in a Pt pan at a rate of 20 $^{\circ}\text{C min}^{-1}$ from rt to 500 $^{\circ}\text{C}$ under a nitrogen flow (100 mL min^{-1}) and then maintained at that temperature for 15 min.

RESULTS AND DISCUSSION

Preliminary Estimation of SBP Composition. The SBP used in the present work contained starch and PBAT as the main polymers;^{25,30,31} ash accounted for an average 2 w/w %, where rutile TiO_2 and CaCO_3 were the major inorganic components that were respectively used as a white pigment and a filler for enhancing the optical and mechanical properties, durability, smoothness, and ink adsorption. Sorbitol is known to be the main starch plasticizer used for SBP, and we confirmed this here through GC–MS analysis after derivatization (Figure S6).^{25,30,31} The elemental analysis of SBP was compared to that of its components (PBAT, starch, and sorbitol) to estimate an average composition. It was found that the SBP consisted of 64% PBAT and 34% starch and sorbitol, as well as 2% inorganic components (Table 1). Because sorbitol and starch have a similar elemental composition, it was not possible to discriminate between them through this analysis.

Table 1. Elemental Analysis of SBP and Its Components (PBAT, Starch, and Sorbitol) and an Estimation of SBP Composition

material	C (%)	H (%)	main components (%) ^a		
			PBAT	starch + sorbitol	ash
PBAT	62.8 \pm 0.5	6.7 \pm 0.1	100	-	-
starch	43.7 \pm 0.5	6.4 \pm 0.2	-	100	-
sorbitol	39.5 \pm 0.3	7.8 \pm 0.2	-	100	-
SBP	54.6 \pm 0.6	6.5 \pm 0.2	64	34	2

^aComposition was preliminarily estimated by analyzing the elemental composition of pure PBAT, starch, and sorbitol.

Plasticizer (Sorbitol) Recovery/Removal and Quantification. Before depolymerizing or extracting PBAT, the SBP plasticizer (sorbitol) was removed and recovered. This “pre-treatment” was completed because a preliminary extraction experiment of SBP with dichloromethane (CH_2Cl_2 , known to solubilize PBAT but not starch at rt)³² that was performed without removing sorbitol revealed that it was not possible to efficiently separate the starch from the PBAT, even when using harsh centrifuge conditions (18 000 rpm, 20 min; see Table 3, entry 1). A detrimental effect was also observed for the repolymerization and monomers recovery processes, which led us to hypothesize that the presence of sorbitol hampered each process and lowered the overall yield. Thus, sorbitol was removed using MeOH, the solvent with the lowest boiling point among the ones able to solubilize it; MeOH is also the same solvent used in the depolymerization experiments, so there was no need to eliminate it from the SBP_{res} in the next step. Several conditions were tested to determine the best time and temperature combination (Table 2): working under reflux conditions (entries 3, 4, and 5) gave a sorbitol recovery similar to that obtained by using a higher temperature (entries 1 and

Table 2. Screening Conditions Applied for Sorbitol Recovery with MeOH

entry	conditions ^a		sorbitol (%) ^c
	temp ($^{\circ}\text{C}$) ^b	time (h)	
1	120	1	5.9 \pm 0.5
2	110	2	4.9 \pm 0.5
3	70	3	5.1 \pm 0.3
4	70	1	5.6 \pm 0.1
5	70	0.5	5.5 \pm 0.1
6	rt	2	0.4 \pm 0.1

^aAll entries were subjected to double extraction. ^b110 and 120 $^{\circ}\text{C}$ = autogenous pressure present; 70 $^{\circ}\text{C}$ = reflux. ^cAverage of the three replicates.

2), while running the extraction at rt drastically decreased the sorbitol that was recovered (entry 6). It should be noted that the variations in sorbitol recovery that were observed could be due to the different source of the SBP. After MeOH evaporation and recovery, the average amount of sorbitol obtained was 5.5%. The sorbitol was analyzed through GC–MS after derivatization (Figure S6). This analysis allowed us to discriminate between the starch and sorbitol inside SBP, thus giving an overall average SBP composition of 64% PBAT, 28.5% starch, 5.5% sorbitol, and 2% inorganics.

PBAT Selective Solubilization and Quantification. The selective solubilization of PBAT was conducted on SBP_{res} in order to better quantify the SBP composition. Then, the PBAT and starch physical recycling through solvent dissolution was investigated by testing a variety of sustainable solvents in comparison to CH_2Cl_2 . Separation with CH_2Cl_2 (Table 3, entry 2) gave 63% PBAT and 30% starch (which included 2% inorganics that are not soluble in CH_2Cl_2), which confirms the estimated SBP composition if one considers the amount of sorbitol that was previously extracted (total recovery = 98.5%). The solvents γ -valerolactone (GVL), dimethyl carbonate (DMC), acetone, 2-methyltetrahydrofuran (2-MeTHF), ethyl lactate (EL), and ethyl acetate (EtOAc) were initially tested at rt; however, no dissolution or separation was observed (Table S1). While dissolution was observed when using these solvents when the temperature was increased to 90 $^{\circ}\text{C}$, only EtOAc gave a clear separation, efficiently recovering starch and PBAT at SBP_{res} concentrations up to 7.5 wt % (Table 3, entries 3–5); for all of the other solvents, only a partial dissolution and recovery was observed (Table S1). In this experiment, starch was recovered together with the inorganic fraction (2 wt %), which was not soluble in any of the solvents used.

The molecular weight characterization of the extracted polymers, as reported in Table 4, clearly shows that increasing the processing temperature for the extraction of the PBAT fraction does not negatively affect the quality of the obtained product. Indeed, when comparing sample E1 (extracted in CH_2Cl_2 at rt) and sample E2 (extracted in EtOAc at 90 $^{\circ}\text{C}$ for the shortest time), only a slight decrease in \overline{M}_w is observed. However, increasing the extraction time or the concentration leads to an even higher \overline{M}_w (samples E3 and E4) than in the case of CH_2Cl_2 extraction at rt. This observation suggests that sample E2 was affected by some fractionation during the extraction process, cutting off the highest molecular weight fractions that most likely required a longer time to be efficiently retrieved.

This assumption is also supported by the thermal stability (T_d in Table 4) of the extracted PBAT samples, which, as

Table 3. Selective Solubilization of PBAT and Mass Recovery of the SBP Components (PBAT, Starch, and Sorbitol)

entry	conditions				yield (%) ^d			
	temp (°C)	n° extr. ^b	time (min)	solvent	C (wt %) ^c	starch	PBAT	total recovery ^e
1 ^a	rt	1	60	CH ₂ Cl ₂	3	8	87	bad separation
2	rt	1	30	CH ₂ Cl ₂	4	28	63	98.5
3	90	2	15	EtOAc	5	25.9	62.7	97.1
4	90	2	25	EtOAc	5	27.8	62.9	98.2
5	90	2	25	EtOAc	7.5	27.5	63.6	98.6
6	90	2	25	EtOAc	10	18	70	bad separation
7	90	1	30	EtOAc	7.5	27.8	63.1	98.4

^aAvoiding sorbitol removal. Centrifuge conditions: 18 000 rpm, 20 min. ^bThe number of consecutive extractions performed on the sample. ^cConcentration (wt %) of PBAT contained in SBP in the solvent. ^dOn total input material. ^eConsidering sorbitol ($\approx 5.5\%$) and inorganics ($\approx 2\%$).

Table 4. Molecular Weight Distribution, Thermal Properties, and Thermomechanical Properties of Selected Extracted and Repolymerized PBAT Samples

sample	molecular weight		DSC results		T_d (°C)	E' (25 °C) (MPa)
	\bar{M}_w (kDa)	PDI	T_g (°C)	T_m (°C) ^a		
E1, extracted (Table 3, entry 2)	44.3	2.2	-33	111, 129, 150, 156	375	121
E2, extracted (Table 3, entry 3)	41.3	2.2	-34	103, 128, 148, 155	372	104
E3, extracted (Table 3, entry 4)	46.9	2.1	-33	110, 130, 150, 156	385	170
E4, extracted (Table 3, entry 5)	46.1	1.9	-32	105, 127, 148, 155	380	141
R1, repoly (Table 5, entry 13)	20.7	2.2	-31	122–125	343	nd ^b
R2, repoly (Table 5, entry 14)	20.4	2.3	-33	121–126	340	nd ^b
R3, repoly (Table 5, entry 15)	22.1	2.6	-33	124–125	341	54

^aWhen multiple peaks are detected, a sequence of the temperature maxima is reported, from the lowest to the highest temperature. ^bSamples were too brittle to be analyzed. nd = not determinable.

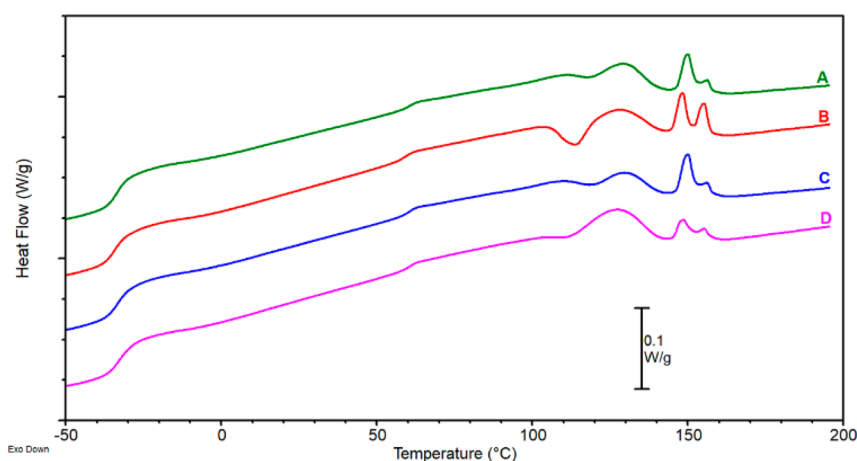


Figure 2. DSC thermograms (second heating scans) of the extracted PBAT samples: (A) E1, (B) E2, (C) E3, and (D) E4.

expected, increases with increasing molecular weight, as well as the conservative modulus E' , which was evaluated by DMTA at 25 °C. The latter values are found to be higher in the highest \bar{M}_w samples (E3 and E4), which also compare well with the literature data related to commercial, pure PBAT samples,³³ regardless of the influence of the monomer composition and molecular weight on the mechanical properties of PBAT.³⁴ DMTA spectra (Figure S5) were recorded in the 0–70 °C range with the aim of emphasizing the applicative behavior of the obtained polymers, and they all display an almost similar offset along the E' trend in the analyzed temperature window, reminiscent of the values reported in Table 4.

The thermal transitions of the extracted PBAT samples, evaluated using the second DSC heating scan in order to erase any previous thermal history of the specimens (Figure 2), are characterized by practically invariant subzero T_g values and the

presence of multiple-peak endotherms ascribed to the melting of the crystal phase. T_m , taken as the most intense peak value, is found to be around 150 °C for all of the products. PBAT samples are known to be able to crystallize, notwithstanding the intrinsic randomness of the distribution of the two dicarboxylate units (adipate and terephthalate) along the chain. It is indeed known that the two reference homopolymers PBA and PBT display widely different melting temperatures, namely $T_{m,PBA} = 60$ °C and $T_{m,PBT} = 170$ °C.^{35,36} Typically, upon the random distribution of the BA and BT units, an intermediate melting temperature in the range of 110–125 °C should be found.^{35,36} In the present case, however, the multiple endotherms, while displaying a low T signal in that range, also display narrower peaks at higher T values, suggesting the presence of PBT-rich segments with crystals undergoing subsequent melting and recrystallization

Table 5. PBAT Selective Depolymerization and Repolymerization Screening Conditions and Yields

entry	depoly conditions					yield (%) ^a		
	temp (°C)	time (h)	catalyst	catalyst (mol %)	C (wt %) ^b	starch fraction ^c	repolymerized PBAT	total recovery ^d
1	140	5	-	-	20	91	-	-
2	140	5	Zn(OAc) ₂	3	20	33.7	NP	41.2
3	140	7	Zn(OAc) ₂	3	20	29.8	NP	35.3
4	140	7	Sn(Oct) ₂	3	20	91.2	-	-
5	120	5	Sn(Bu) ₂ (OAc) ₂	3	20	79.3	-	-
6	130	5	Sn(Bu) ₂ (OAc) ₂	3	20	55.2	-	-
7	140	5	Sn(Bu) ₂ (OAc) ₂	3	20	32.3	57	94.8
8	140	7	Sn(Bu) ₂ (OAc) ₂	3	20	29.7	59	94.2
9	140	7	Sn(Bu) ₂ (OAc) ₂	1	24	28.2	60	93.7
10	140	7	Sn(Bu) ₂ (OAc) ₂	1	49	32.2	57	94.7
11	140	7	Sn(Bu) ₂ (OAc) ₂	0.5	49	34.2	54.7	94.4
12	140	7	Sn(Bu) ₂ (OAc) ₂	0.25	33	30.4	59.1	95
13	140	7	Sn(Bu) ₂ (OAc) ₂	0.2	33	29.3	59.5	94.3
14	140	7	Sn(Bu) ₂ (OAc) ₂	0.15	33	29.8	60	95.3
15	140	7	Sn(Bu) ₂ (OAc) ₂	0.1	33	29.5	60.4	95.4
16	140	7	Sn(Bu) ₂ (OAc) ₂	0.05	33	28.7	44	78.2
17	140	7	Ti(OiPr) ₄	0.1	33	85.1	-	-
18	140	7	Ti(OiPr) ₄	0.3	33	67.2	-	-
19	140	7	Ti(OBu) ₄	0.1	33	80.7	-	-
20	140	7	Ti(OBu) ₄	0.3	33	44.6	-	-
21	140	7	Zn(OAc) ₂	0.3	33	32.3	NP	37.8
22	140	7	(Bu) ₂ SnO	0.1	33	29.7	58.9	94.1
23	140	7	(Bu) ₂ SnO	0.05	33	30.5	30.1	66.1

^aBased on the total input material. The starch fraction yield was obtained after the depoly step. The PBAT yield was obtained after the repoly step. For the repoly step, the same conditions were used for all entries (150 °C for 1 h; then, 170 °C for 3 h under N₂, and finally, 190 °C for 3 h under vacuum). NP = no polymerization occurred. ^bConcentration (wt %) of SBP in MeOH. ^cStarch fraction comprises inorganics (≈2%). ^dConsidering sorbitol (≈5.5%) and inorganics (≈2%).

processes during the scan. When comparing such results with the DMTA spectra, it can be seen for all of the extracted polymers that an *E'* loss appears in the region of 40–60 °C, which is also where a DSC feature clearly occurs. This temperature region may relate to PBA melting, possibly suggesting that there is also a minor alternating PBA-rich sequence in the polymers. Overall, these results confirm that all of the extracted PBAT samples are polymers with thermal and thermomechanical performances that compare well with their commercial counterparts, thus guaranteeing that this recycling process produces fully performing compounds.

Depoly–Repoly Process. The depoly–repoly process consists of two steps: (I) the selective catalyzed depolymerization of the PBAT contained inside SBP_{res} in MeOH, coupled with starch recovery, and (II) the repolymerization of the PBAT oligomers that were derived from (I) to obtain recycled PBAT.

The main purpose of the first step was to obtain oligomers that were soluble in MeOH so that they were separable from the starch and inorganics, not to depolymerize PBAT to its monomers (1,4-BD, DMT, and DMA). The success of the reaction was evaluated as follows: if the recovery of the solid precipitate (starch fraction, recovered together with inorganics that are not soluble in MeOH) after the workup was 28–31% of the total SBP input, the selective depolymerization of PBAT was considered completed and the second step was performed. If the starch fraction was >28–31%, PBAT was considered to not have successfully depolymerized, and if the solid precipitate was <28–31%, a portion or all of the starch was considered to have decomposed; in this case, a fraction of

methylated sugars and anhydrosugars was also detected in the GC–MS analysis.

Several catalysts were tested to selectively depolymerize PBAT rather than the starch. A preliminary catalyst screening found that both acids and bases could be used for this purpose. However, when Brønsted acids were used, such as H₂SO₄, the starch also depolymerized to its methylated anhydrosugars and sugars. When bases were used, the starch did not decompose, and a good separation was obtained. The bases DBU, NaOH, and K₂CO₃ were successfully tested (Table S2).

In the second step, the excess MeOH was distilled and recovered, and the residual oligomer syrup was directly polymerized without the addition of any other compound/catalyst. The first evidence of a catalyst also being active in the polymerization step is the amount of polymer recovered. It was determined that several of the catalysts that were efficiently active in the depolymerization step were inactive in the repolymerization step, with no polymer being formed. All of the tested bases were unable to polymerize the oligomer syrup back to PBAT (Table S2); this behavior was expected because the most active catalysts for polyester synthesis are metallic Lewis acid systems.³⁷ This class of catalysts was also tested. It was determined that Zn(OAc)₂ performed well in the depolymerization step, giving 29.8% starch fraction after 7 h at 140 °C, but it was not effective in the repolymerization step (Table 5, entries 2 and 3). Titanium-based catalysts (Ti(OiPr)₄ and Ti(OBu)₄), which are known to be good polymerization agents,³⁸ were poorly active in the depolymerization of PBAT; in fact, PBAT was still present at the end of the reaction, not allowing us to proceed with the repoly step (Table 5, entries 17–20). The tin(IV)-based catalysts

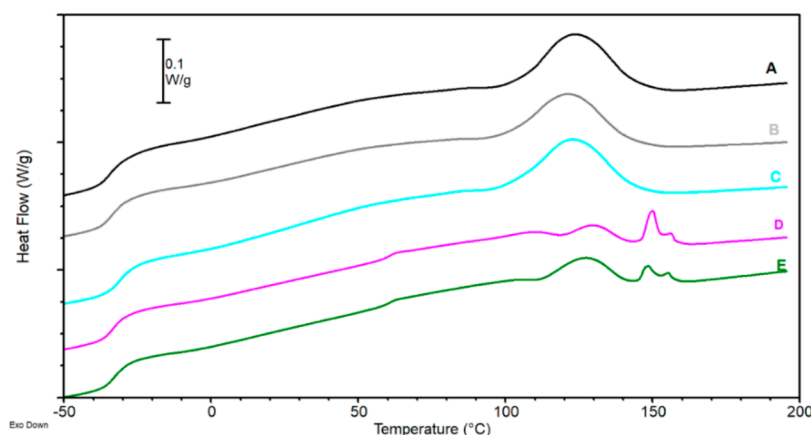
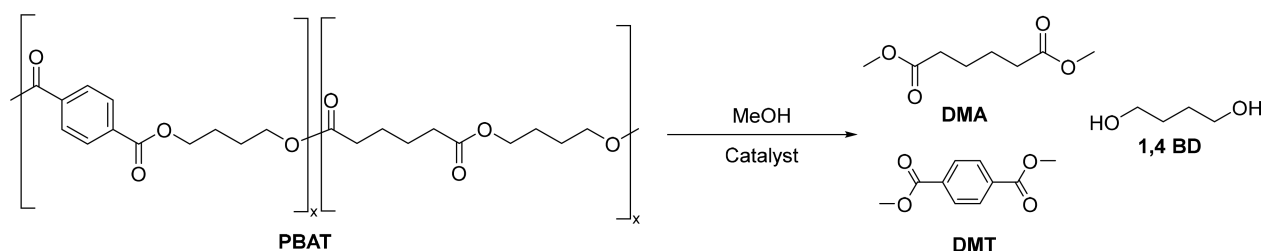


Figure 3. DSC thermograms (second heating scans) of the repolymerized PBAT samples: (A) R1, (B) R2, and (C) R3. For the sake of comparison, some of the extracted PBAT samples are also reported: (D) E3 and (E) E4.

Scheme 1. PBAT Depolymerization for Monomers Recovery



$\text{Sn}(\text{Bu})_2(\text{OAc})_2$ and $(\text{Bu})_2\text{SnO}$ were the best-performing catalysts for both the depolymerization and repolymerization steps, giving a max PBAT yield of 94.3% when using 0.1 mol % catalyst (Table 5, entries 15 and 22), while the $\text{Sn}(\text{II})$ -based catalyst $\text{Sn}(\text{Oct})_2$ did not work in the depolymerization step (Table 5, entry 4), as expected from the literature.³⁹

The $\text{Sn}(\text{IV})$ -based catalysts were then selected as the best ones for this kind of process, and further investigations of the polymers' characterizations were completed.

The molecular weights of the obtained samples with the highest recovered fractions (Table 5, entries 13–15) are all around 20 000 Da (Table 4, R1–R3). Even though this value is half that of the extracted PBAT samples (see the previous section and Table 4, E1–E4), it is still reasonably high.

An investigation of the thermal and thermomechanical behavior of the repolymerized PBAT samples, as well as a comparison with the extracted fractions of the polyester, provides some interesting insight into the behavior of the repolymerized products. Indeed, TGA measurements highlight the presence of a main weight loss characterized by a 2-fold degradation step that, with respect to the extracted PBAT samples, was slightly anticipated. Such a result may stem from some of the oligomers undergoing thermal degradation at lower temperatures. Moreover, the DSC thermograms that were recorded for the repolymerized samples (Figure 3) show T_g values that are in line with our previously discussed data and only one endotherm signal, which, unlike those of the extracted PBAT samples, compare well with the expected behavior of randomly distributed BA and BT units, lying in the same region reported in the literature at around 120–125 °C.^{35,36} Such an observation seems to rule out the presence of segments of BT units, which we have previously discussed, possibly due to a poorer BT unit content in the polymer. However, similar to the extracted samples, a slight thermal

phenomenon at around 40 °C can be detected and also observed in the DMTA spectrum for sample R3, which could suggest a possible BA-rich sequence. Both of these observations could also relate to the worse mechanical performance of these repolymerized products, which have E' moduli (based on the recorded DMTA data) that are much lower than the previously discussed data (Table 4, R1–R3). Altogether, the discussed thermal and thermomechanical behaviors of these repolymerized samples show the potential for recovering newly repolymerized PBAT, given that the polymerization process could be optimized through the use of higher-performing reactor systems that, for example, could achieve higher temperatures (here, the maximum working T that was achievable was 190 °C, while industrially, higher temperatures are used for PBAT synthesis)³⁴ or use a mechanical stirrer instead of a magnetic one, thus gaining the ability to efficiently stir at higher viscosities. Overall, the repolymerized PBAT samples were indeed able to match commercial PBAT in terms of composition and thermal behavior.

Monomers Recovery. The recovery of PBAT monomers (DMT, DMA, and 1,4-BD) was completed by the selective complete depolymerization of PBAT through transesterification with MeOH (Scheme 1). The reaction was monitored using GC–MS analysis; when all of the adducts of TA and AA (e.g., bis(4-hydroxybutyl) or methyl 4-hydroxybutyl terephthalate or adipate) disappeared in favor of DMT, DMA, and 1,4-BD, the reaction was considered complete, and workup for monomers recovery was done. Several catalysts gave good monomer formation with no starch loss, including the bases that were mentioned previously. However, for all of the catalysts, harsher conditions than the ones applied in the depoly–repol process were necessary in terms of the catalyst amount, MeOH loading, and time (Table S3). Here, the focus

was concentrated on the workup done to separate all of the components of the final mixture. Methanolysis completed with a tin-based catalyst was chosen for this purpose, even though almost the same conversions and starch recoveries were obtained with the Zn-based catalyst and some of the bases (Table S3).

First, the starch fraction was recovered through filtration from the hot mixture after the reaction was completed (50–55 °C), with a 30% yield on the total material input. Then, the solution containing the PBAT monomers was cooled to 0 °C. In this condition, DMT crystallized due to its low solubility in MeOH at low temperatures, and it was recovered through filtration. This step was repeated after removing two-thirds of the volume of MeOH in order to recover the last fraction of DMT. The recovered DMT was then dried under reduced pressure and analyzed by GC–MS. After DMT recovery, the residual MeOH was removed from the resulting solution, leaving a mixture composed mainly of 1,4-BD and DMA. Water and cyclohexane (Cy) were added in order to separate 1,4-BD (soluble in water) from DMA (soluble in Cy), which remained in the upper layer due to having a lower density. The water phase was then extracted with Cy to recover the residual DMA. Lastly, the water was removed under reduced pressure to recover 1,4-BD. The total yield of the PBAT monomers was calculated based on both the PBAT content inside the SBP (64%) and the total SBP in the input material. With respect to the total PBAT present, a yield of 90.8% of the PBAT monomers was recovered, with 93.1% DMT, 88.7% DMA, and 90.6% 1,4-BD. With respect to the total SBP in the input material, 58% of the PBAT was recovered in the monomeric form, resulting in a total recovery of 93.5% (comprising 30% of starch fraction and 5.5% of sorbitol). The recovered monomers were analyzed through ¹H and ¹³C NMR (Figure S7). DMT, DMA, and 1,4-BD had good purity. A negligible contribution of DMT can be observed in the DMA ¹H NMR spectrum due to the fact that DMT could not be completely recovered because, even though it is poorly soluble at 0 °C, it was still present in the residual MeOH fraction containing DMA/1,4-BD.

The Environmental Factor (E-Factor) for the PBAT Recovery Strategies. The E-factor was calculated in order to very preliminarily evaluate the environmental sustainability of the proposed processes (Table 6). This was done by

Table 6. E-Factor Values for the Three Processes Here Proposed

process	E-factor
PBAT selective solubilization	0.14
depoly–repol process	0.16
monomer recovery	0.35

considering the SBP component yields and losses together with the solvent and catalyst recovery yields and losses that were calculated for every step (Table S4). The largest E-factor was obtained for the monomers recovery process (i.e., the complete depolymerization of PBAT), as its lower SBP recovery yield (93.5%), its larger number of steps, and the required quantity of solvent inevitably increase the losses and waste of the process. In contrast, both the depoly–repol process and the selective solubilization of PBAT have similar E-factors (0.16 and 0.14, respectively); the first method uses a lower amount of solvent and only requires MeOH for the

entire process, while the second method uses EtOAc as a solvent and does not require a catalyst.

CONCLUSIONS

In the present study, three novel protocols for the recycling of PBAT-composed SBP were proposed. First, a physical recycling process consisting of the selective dissolution of PBAT with ethyl acetate was demonstrated to efficiently recover high quality bioplastic. Second, PBAT was chemically recycled through the selective depolymerization of the polyester using tin-based catalysts, followed by the repolymerization of the obtained oligomers to afford new PBAT. This process produced PBAT in high yields and with good molecular weight and thermal and physicomechanical behaviors, and it can even be further optimized through the use of higher-performing reactor systems. Lastly, the selective alcoholysis process of PBAT was performed using bases or Lewis acids as catalysts in order to recover the polyester's monomers DMT, DMA, and 1,4-BD. E-factors were also calculated in order to preliminarily compare the environmental sustainability of the processes in terms of their generated waste; while the depoly–repol process had a similar E-factor as the selective solubilization process, the monomer recovery generated more waste (i.e., had a larger E-factor). The effectiveness of the two chemical recycling protocols suggests the possibility of adopting these strategies in combination with mechanical recycling processes. Specifically, when mechanical recycling is no longer able to produce PBAT with adequate physicomechanical properties, these chemical recycling techniques can be applied to produce new PBAT or to recover its monomers for the synthesis of other polyesters or chemicals. Overall, this work preliminarily illustrates the possibility of efficiently recycling PBAT-composed SBP, a bioplastic that is currently intended to be composted but whose recycling in a circular perspective would be preferable. Recycling SBP would avoid losing high-value components (mainly sorbitol and PBAT), whose decomposition in composting areas would inevitably require the use of new feedstocks, such as PBAT monomers (TA, AA, and 1,4-BD), that are industrially produced using fossil-based sources that require highly energy demanding catalytic multistep processes. Moreover, chemically/mechanically recycling PBAT and the ex novo synthesis of PBAT, starch, and sorbitol clearly seem to have significantly different environmental impacts due to the different number of processes that are required (1 versus >9) and the harsher conditions that must be adopted for the ex novo synthesis of PBAT monomers (e.g., up to 850 °C for steam cracking), not to mention the amount of energy required for the extraction and fractionation of the fossil sources needed for ex novo synthesis. A complete LCA analysis that considers every single aspect of these two scenarios would contribute to demonstrating these differences, establishing the real impact of the recycling approaches, and defining their boundaries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c03588>.

Tables: screening conditions for (S1) the selective solubilization experiment, (S2) the depoly–repol technique, and (S3) monomers recovery, and (S4) material recovery yields for E-factor quantification.

Figures: (S5) DMTA spectra recorded in the 0–70 °C range, showing E' ; (S6) GC–MS analysis of sorbitol; and (S7) ^1H and ^{13}C NMR data of the monomers recovered through the selective depolymerization of PBAT (DMT, DMA, and 1,4-BD) (PDF)

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Author Contributions

A.P.: conceptualization, investigation, methodology, validation of the work, writing of the original draft, and visualization. V.A.: investigation and validation. L.M.: investigation and writing (concerning the polymer characterization). C.S.: review, supervision, and funding acquisition. P.G.: review, supervision, and funding acquisition.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the University of Bologna (the RFO program), the Minister of Education, University and Research (MIUR), and Regione Emilia-Romagna (Bando “Alte competenze per la ricerca e il trasferimento tecnologico”—POR FSE 2014/2020, Obiettivo tematico 10) for Ph.D. funding.

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