



Chemical Recycling of Post-Consumer PLA Waste for Sustainable Production of Ethyl Lactate

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ABSTRACT

Though synthetic plastics are indispensable in our everyday life, the uncertainty surrounding the sustainability of fossil reserves has led to the development of a novel class of plastics, referred to as bio-based plastics. Poly(lactic) acid (PLA) is the most frequently used member of this family. However, due to the lack of a holistic recycling strategy, its large scale utilization can turn out to be an acute source of plastic pollution in the future. Unlike other attempts directed towards chemical recycling of PLA which violate the basic principles of green chemistry, the following research establishes an eco-friendly recycling concept aimed at the production of a valuable lactate ester through solvent assisted transesterification of PLA waste. The scope of this research is not only limited to the selection of an appropriate system (solvent, nucleophile and catalyst) but also extends to analysing the selectivity of the solvent towards the PLA fraction in a commingled stream and the effect of the concentration of nucleophile and different PLA substrates on the yield of the lactate ester. It was observed that, irrespective of the source of PLA, a high yield of ethyl lactate (approx. 80%) with complete retention of stereochemistry was obtained for a molar ratio of nucleophile per mole repeat unit of PLA ($n_{\text{NUC}}:n_{\text{PLA}}$) equivalent to 3. Thus, this work represents an attempt towards instituting circular bio-economy by overcoming the engineering and environmental challenges associated with PLA-waste management and production of ethyl lactate; while strictly adhering to the principles of green chemistry and sustainable chemical engineering.

1. Introduction

Although the mass production of synthetic plastics only dates back to 1950, they have become the most abundant anthropogenic materials and serve as a geological indicator of the Anthropocene era [1]. The global annual plastic production is expected to reach 1124 million tons by 2050; thereby, consuming 20% of the crude oil produced globally as opposed to 6% in 2014 [2,3]. Though these synthetic polymers are designed for their durable performance, their rapid growth as “materials of everyday use”, indiscriminate disposal and resistance to biological degradation presents an extensive threat to the environment [4]. In lieu of rising awareness about sustainability coupled with the pressure from global climate change over the past two decades, bio-based plastics have gained impetus as novel materials synchronous to the concept of sustainable production and utilization [4,5]. Though this class accounts for

less than 1% of the global annual plastic production, its global production capacity is estimated to increase from 2.11 million tons in 2020 to 2.87 million tons in 2025 at a compounded annual growth rate of 6.3% [6,7].

Amongst other bio-based polymers, PLA is the most promising polyester [3,5,8]. It is regarded as a sustainable alternative to synthetic, petrochemical plastics such as PET and PS on account of its similar mechanical properties [5]. Accounting for 62.5% of its total annual production, NatureWorks® (150,000 tons; USA) and Total Corbion PLA (75,000 tons; Thailand) are the major producers of PLA in the global market [9]. PLA has expanded itself in several markets, ranging from disposable cutlery and degradable sutures to rigid packaging and extrusion coatings [5,10–13]. This is evident from the fact that, the relative share of PLA in the total global production of bio-plastics has increased from 13.9% in 2019 to 18.7% in 2020 [7]. However, the food packaging sector continues to be the most dominant market for PLA

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Nomenclature*Abbreviations*

DSC	Differential Scanning Calorimetry
D-EL	Dextrorotatory Isomer of Ethyl Lactate
D-PLA	Dextrorotatory Isomer of PLA
EPA	Environment Protection Act
FDA	Food and Drug Administration
L-EL	Levorotatory Isomer of Ethyl Lactate
L-PLA	Levorotatory Isomer of PLA
LX175-EL	Ethyl Lactate obtained from Depolymerisation of Luminy® LX175
NAPCOR	National Association for PET Container Resources
PCS-PLA	Post-Consumer PLA
PCS-PLA-EL	Ethyl Lactate obtained from Depolymerisation of Post-Consumer PLA

SNAP	Significant New Alternatives Policy
WRAP	Waste and Resources Action Programme

Symbols

δ	Hansen Solubility Parameter
D	Dispersity
M_n	Number-average Molecular Weight
M_w	Weight-average Molecular Weight
$m_{TBD}:m_{PLA}$	Mass of the Catalyst (1,5,7-triazabicyclo[4.4.0]dec-5-en) per unit Mass of PLA
$m_{PLA}:m_{ace}$	Mass of the PLA per unit Mass of Acetone
$n_{nuc}:n_{rpu}$	Moles of Nucleophile per unit of Mole of Repeat Unit of PLA
T_c	Crystallization Temperature
T_g	Glass Transition Temperature
T_m	Melting Point

[11–13].

Though PLA is relatively biodegradable as compared to other synthetic polyesters, its biodegradability is subject to environmental conditions [3,5,14,15]. For instance, a PLA bottle will take 100 – 1000 years to decompose in a landfill as opposed to 3 months in an industrial compost maintained at 60°C and fed with a steady stream of digestive microbes [3,16]. In addition to this, due to similar applications and the lack of an appropriate collection infrastructure, post-consumer PLA waste often contaminates other plastic waste streams (especially PET); thereby, necessitating an additional supplementary effort using advanced sorting technologies in order to achieve a satisfactory reduction [17–19]. This disturbs the recycling strategies instituted for PET and destabilises the economic balance of this sector [18,19]. WRAP has proposed that, even trace contamination of PLA (about 1000 ppm) in conventional PET waste streams renders them unsuitable for mechanical recycling as it causes noticeable hazing and degradation of recycled PET [18–20]. In some cases, this problem has aggravated to an extent that some organisations (viz. NAPCOR) have refused to introduce PLA contaminated PET streams in their existing recycling infrastructure [20].

Conceivable routes for recycling PLA include landfilling/composting, incineration and mechanical/chemical recycling. Landfilling/composting of PLA results into a loss of the valuable polyhydroxy acid on account of its degradation into low value products [4,21]. It can also deteriorate the soil quality due to leaching of additives in the sump [22]. Though incineration is the most common waste management strategy for end-of-life PLA in countries emphasising on circular economy (viz. Germany), it leads to the production of toxic exhaust gases and suffers from inefficient energy recovery (calorific value of PLA is 19 MJ kg⁻¹ while the fossil energy required for its production from sugarcane is 28.8 MJ kg⁻¹) [4,23–25]. Mechanical recycling has the lowest environmental impact amongst other recycling strategies but it suffers from significant deterioration of properties during extrusion on account of the degradable behaviour of PLA and the presence of residual impurities, moisture and other contaminants [4,15,20,26]. This results in a loss of its market value as the recycle obtained has a lower quality than the feed. Therefore, mechanical recycling is not regarded as an infinite recycling strategy as retaining the value of the substrate in the supply chain is a major challenge [4,21].

Contrary to these strategies, chemical recycling offers a promising route to extend the life cycle of post-consumer PLA waste beyond its end-of-life scenario by valorising it for the production of constituent monomers and/or other valuable chemicals [15,21]. In the past decade, several attempts have been directed towards chemical recycling of PLA [27]. For instance, a conventional route to recycle PLA into lactic acid is through its hydrolysis [28]. However, harsh operating conditions

(120°C – 350°C; ~100 bar) and large quantities of concentrated acids or bases are required to hydrolyse small amounts of PLA (5% – 10% by weight) [29–33]. This raises several environmental and operational concerns; thereby, creating difficulties in its scale-up [26,33]. In addition to this, use of high temperature promotes undesirable side reactions that lead to optical degradation of the product (lactic acid) [21]. Alternatively, hydrolysis of PLA can also be catalysed by commercial lipases in the presence of organic solvents [34]. Though this process is highly selective and requires low reaction temperature (40°C), the relatively slower rate of conversion restricts its scalability [33,34]. Further, since the development of immobilized bio-catalysts is in its nascent stage, the reaction yields dilute lactic acid solutions containing a substantial amount of impurities; thereby, demanding considerable amount of energy for subsequent down streaming [33,35]. Another recycling route involves thermal depolymerisation of PLA at high temperatures (190°C – 250°C) under vacuum (5 mbar – 7 mbar) in the presence of alkoxides, chlorides or oxides of Sn, Zn, Zr, Ti, Al (as catalysts) to a cyclic dimer (lactide) [36]. While the use of high temperature leads to chemical and optical degradation of the product, the recovery of metal catalysts is highly energy intensive and imposes severe load on the environment [4,21].

Unlike the aforementioned methods, alcoholysis is an economically feasible and environmentally sustainable recycling strategy involving the disintegration of the ester backbone in the PLA macromolecule to corresponding lactate esters [37–39]. Several systems have been investigated for the alcoholysis of PLA [37–50]. However, while some attempts use chlorinated, carcinogenic and/or expensive solvents [38,39,41,47], others are directed towards using non-conventional and/or toxic, corrosive catalysts [39,43–50]. For instance, Román-Ramírez et al. investigated the upcycling of post-consumer PLA waste into low molecular weight lactate esters (namely, methyl- and ethyl lactate), catalysed by Zn(I)/Zn(II) complexes, in the presence of tetrahydrofuran (THF) [39,47]. It was observed that, at 50°C, Zn (II) complexes exhibit a higher catalytic activity towards transesterification of post-consumer PLA waste into ethyl lactate, than Zn (I) complexes [42]. However, critical concerns with regards to the reproducibility and stability of these complexes primarily limit their utilization on an industrial scale [42]. In another attempt aimed at alcoholysis of PLA, Whitelaw et al. demonstrated the use of Zr(IV)/Hf(IV) co-ordinated salalen complexes as catalysts in the presence of methylene chloride [50]. While the complexity involved in the synthesis of these catalysts limits their commercialization, the use of a halogenated solvent defies the third principle of green chemistry (less hazardous chemical synthesis). Petrus et al. reported the catalytic activity of magnesium and calcium alkoxides towards the transesterification of PLA into a corresponding lactate ester at 100°C [46]. However, the use of metal-based catalysts and a large

amount of alcohol ($n_{\text{nucl}}:n_{\text{PLA}} = 10$) to achieve a high yield of the lactate ester (88%) necessitates energy intensive down streaming; thus, violating the sixth principle of green chemistry (design for energy efficiency) [33,46]. Liu et al. and Song et al. investigated the use of ionic liquids for methanolysis of PLA between 90°C and 120°C [45,48,49]. Though ionic liquids serve the dual purpose of a catalyst as well as a solvent and are effective for the methanolysis of PLA, high production costs and insufficient information about their lifetime and toxicity impedes their immediate use on an industrial scale [43]. In addition to these novel catalysts, several conventional catalytic systems have also been investigated. Liu et al. has demonstrated the use of FeCl_3 as a Lewis-acid catalyst for the methanolysis of PLA between 100°C and 130°C [43]. However, though it is an inexpensive commercial catalyst, it is equally corrosive and results in severe environmental pollution [45]. Sánchez et al. investigated the alcoholysis of PLA in the presence of $\text{Zn}(\text{OAc})_2$ under mild process conditions [20]. However, the large batch cycle time (~15 h) required for obtaining an appreciable yield of the corresponding lactate ester (~70%) hinders its industrial realisation. Du Pont has patented an acid catalysed process for the degradation of PLA at temperatures ranging between 150°C and 190°C [44]. Though the process results in a substantial yield of alkyl lactates, the use of concentrated acid catalysts results in equipment corrosion and necessitates complex down streaming [33,43,45]. Zeus Industrial Products Inc. devised a chemical recycling strategy for the production of methyl lactate from PLA at 57°C involving $\text{Sn}(\text{Oct})_2$ as a catalyst and chloroform as a solvent [41]. However, the use of these process auxiliaries significantly reduces the green credentials of the process [39,47]. Alberti et al. demonstrated microwave-assisted depolymerisation of 16 different PLA commodities to methyl lactate at 180°C using 4-dimethylaminopyridine (DMAP) as a catalyst [40]. Nevertheless, severe operating conditions such as high temperature and microwave irradiation associated with this process limits its industrial implementation [48]. Leibfarth et al. reported the use of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) as an effective organo-catalyst for the alcoholysis of PLA at room temperature in the presence of methylene chloride [38]. Though TBD is an eco-friendly, organic catalyst, the use of a halogenated solvent defies the third principle of green chemistry (less hazardous chemical synthesis) and thus, negates the sustainability of this process. Therefore, despite numerous efforts, a holistic yet industrially feasible chemical recycling concept in adherence to the fundamental principles of green chemistry has not yet been developed.

2. Choice of the recycling strategy

While deciding on a recycling strategy, it is important to understand its technical and economic ability to retain value within current and future markets, in addition to its overall environmental and social impacts. The upcycling of PLA into valuable lactate esters through solvent-assisted alcoholytic depolymerisation has several advantages, such as a high yield of lactate ester, relatively simple down streaming and complete retention of stereochemistry [38,39]. This work aims at formulating a sustainable recycling concept, capable of resolving engineering and environmental challenges accompanying management of post-consumer PLA waste and production of lactate esters. The methodology adopted in this study can serve as rubrics; guiding future efforts directed towards adopting a circular economy for other bio-based and/or petrochemical plastics.

2.1. Choice of the nucleophile (alcohol)

Alcoholytic depolymerisation of the ester backbone in the PLA macromolecule represents a transesterification reaction which proceeds via the formation of an alkoxide (nucleophile) [38]. This nucleophile attacks the carbonyl group of the PLA macromolecule [20,38]. Thus, the extent of the reaction strongly depends on the strength of the nucleophile (alcohol). Further, the alcohol must also be synchronous to the

lactate ester that has to be synthesized [38]. The choice of the alcohol is, therefore, influenced by its availability, nucleophilicity and the subsequent market available for the synthesized ester. Though methanol is a better nucleophile than ethanol due to its smaller size (lesser steric hindrance) and high dielectric constant, it is deemed to be problematic owing to its toxic effects on human health [20,51,52]. On the contrary, ethanol is a safe and sustainable alternative [20,53]. It has also been reported that, the production of second generation ethanol from cellulosic (bio-ethanol) and lingo-cellulosic (2G ethanol) feedstock has reached a demonstration stage [54]. In addition to this, the use of ethanol as a nucleophile results in the production of ethyl lactate, a globally acclaimed bio-based solvent [54]. With its market value estimated to reach USD 92 million by 2024 and an installed annual, global production capacity of 1.2 million tonnes, ethyl lactate has the highest demand amongst other low molecular weight lactate esters [42,53,54]. On account of its biodegradability, compatibility with other aqueous as well as organic solvents, high boiling point and low surface tension, it is considered as a potential green substitute to several conventional, petrochemical solvents (NMP, toluene and xylene) [53–56]. Being an EPA approved SNAP solvent and a FDA approved food additive, it finds applications in the cosmetic, food and pharmaceutical sector [53,55,56]. Another application of ethyl lactate is its utilization as a solvent in the coating industry [56]. For instance, ethyl lactate can partly replace the hazardous air pollutants (MEK, MIBK) used in magnetic tape coatings [57]. In addition to this, repolymerisation of ethyl lactate offers the highest yield of lactide (precursor of PLA) as compared to other lactate esters; thereby, offering a potential opportunity for transition towards a circular economy [58]. Recent efforts towards synthesizing bio-based acrylates from ethyl lactate have succeeded on a laboratory scale [59–61]. However, the current cost of ethyl lactate ($\$3.30 \text{ kg}^{-1}$ and $\$4.40 \text{ kg}^{-1}$) severely limits its industrial utilisation for this purpose [54,61]. Further, ethyl lactate is also used as an eco-friendly solvent in the synthesis of cellulose-acetate based ultrafiltration membranes [56,62] and a green reaction medium for several organic reactions [56,63]. Therefore, ethanol was chosen as the nucleophile for the alcoholytic depolymerisation of PLA; thereby, adhering to the fourth (safer products by design), seventh (use of renewable raw material) and tenth (design for degradation) principle of green chemistry.

2.2. Choice of the solvent

The insolubility of PLA in ethanol and the presence of other polymeric impurities necessitates the use of an appropriate solvent selective towards the dissolution of PLA [20,38]. This choice was based on the relative affinity of the solvent towards PLA (evaluated on the basis of solubility parameters) and the eco-friendly nature of the solvent (dictated by its toxicity) [20,53]. Methylene chloride ($\delta = 20.3$), chloroform ($\delta = 19$), acetone ($\delta = 20.10$), ethyl lactate ($\delta = 21.7$) and THF ($\delta = 19.4$) were identified as some potential solvents for selective dissolution of PLA ($\delta = 20.3$) [20,64]. The toxic (carcinogenic) solvents like methylene chloride and chloroform are classified as undesirable as per the existing green solvent selection guidelines [51,52,55]. Though THF is recommended as per some solvent selection guidelines, there is ambiguity about its effect on human health as indicated by a threshold occupational exposure limit similar to methylene chloride (~50 ppm), in France [51–53]. Ethyl lactate has been used as a green alternative for selective dissolution of PLA [37]. However, it is quite expensive as compared to other conventional solvents [54]. Further, alcoholysis of PLA is a transesterification reaction; severely limited by equilibrium [38,39]. Thus, use of ethyl lactate as a solvent will defy the Le Chatelier principle and affect the yield of the reaction. Contrary to these solvents, acetone is cheap and is a preferred choice as per the Pfizer and GSK solvent selection guidelines [51,52,55]. In addition to this, Gironi et al. demonstrated that, the saturation solubility of PLA in acetone (25%) at 50°C is greater than its saturation solubility in ethyl lactate (16%) at 80°C; thereby, proving that acetone is more effective than ethyl lactate

with regards to the dissolution of PLA [65]. Further, the aprotic nature of acetone prevents the formation of solvation shells around the nucleophile (ethanol). Therefore, acetone was chosen as a solvent for aiding the selective dissolution of PLA; thereby, abiding by the third (less hazardous chemical synthesis), fifth (innocuous solvents), sixth (design for energy efficiency) and twelfth (safer processes) principle of green chemistry.

2.3. Choice of the catalyst

Previous studies revealed that, most of the catalysts employed for alcoholysis of PLA were either in their early stage of development [39,45,47–50] or entailed high economic and environmental costs [20,41,43,44,46]. Though transesterification reactions can occur in an acidic as well as a basic environment, industrial sectors usually prefer basic catalysts as they are less corrosive [66]. A case study on different guanidine bases for transesterification of rapeseed oil revealed that TBD exhibited the highest catalytic activity [66]. Leibfarth et al. also demonstrated the degradation of PLA to ethyl lactate at room temperature in a relatively short period of time using TBD as a catalyst [38]. However, the use of methylene chloride as a solvent expiated the green credits of this process [38]. While such catalysts can promote several organic reactions and are widely used in polymer synthesis, their application in the chemical recycling sector is rather limited [38,40,67–69]. Therefore, by virtue of its selectivity and sustainability, TBD was chosen as the catalyst, for this study [38,55,66–68]. This choice complies with the second (atom efficiency) and eighth (shorter synthesis) principle of green chemistry.

3. Materials and methods

3.1. Materials

Acetone (CAS No.: 67–64-1; purity: 100%) was purchased from VWR Chemicals™ while TBD (CAS No.: 5807–14-7; purity: 98%) was obtained from Sigma Aldrich. Ethyl lactate (CAS No.: 97–64-3; purity: >98%) was procured from TCI Deutschland GmbH. Ethanol (CAS No.: 64–17-5; absolute) was also purchased from VWR Chemicals™. All reagents were used as received without further purification. Two grades of virgin PLA, namely Luminy® LX 175 (Total Corbion PLA) and Ingeo™ 6302D (NatureWorks®) were used in order to determine the effect of the chain length of the polymer on the reaction. In addition to this, in order to demonstrate the robustness of the process, four different post-consumer PLA substrates were also subjected to depolymerisation in this study (Fig. 1). It should also be noted that, technical grade acetone and ethanol were used as the solvent and the nucleophile respectively, in order to affect the depolymerisation of these substrates.

3.2. Methods

3.2.1. Experimental procedure

Alcoholic depolymerisation of the ester backbone in the PLA macromolecule represents a transesterification reaction [38] (Fig. 2). In order to devise this strategy, an experimental setup consisting of a three-neck round bottom flask fitted with a vertical vapour condenser was constructed. A thermometer fitted to a thermostat was used to monitor and regulate the temperature. An oil bath was used for heating while a mechanical agitator provided uniform mixing. It should be noted that, alcoholic depolymerisation of post-consumer PLA substrates (Fig. 1) was carried out in a 2-L jacketed glass reactor. All experiments were performed at 50°C.

In order to confirm the selectivity of the solvent, a weighed quantity of polymeric impurities, namely PET and PP, was mixed with a known amount of PLA. The resulting mixture was subjected to dissolution at 50°C. At the end of the dissolution, the solution was filtered with an Erlenmeyer flask. The liquid phase and the residual solid fractions were

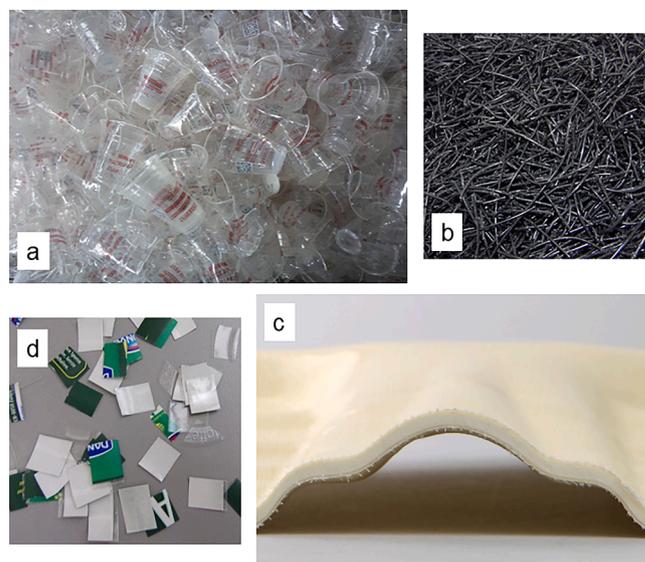


Fig. 1. Different grades of post-consumer PLA waste subjected to depolymerisation in this study (clockwise from top left; a. rinsed post-consumer PLA cups obtained from a music festival in Karlsruhe, b. 3-D printing filaments, c. PLA sandwich panel developed under the research cluster Fraunhofer CCPE for light-weight constructions, d. post-consumer yoghurt containers).

dried overnight in a vacuum oven at 64°C. These fractions were then weighed and subsequently, subjected to a FTIR-ATR analysis. The residual solid fractions were also analysed using DSC.

In order to determine the effect of the concentration of nucleophile and the chain length of the polymer on the yield of ethyl lactate, a weighed quantity of acetone and ethanol ($n_{\text{nuc}}:n_{\text{rpu}} = 1, 3, 6$) was heated to 50°C. To this mixture, a weighed amount of solid PLA ($m_{\text{PLA}}:m_{\text{ace}} = 0.11$) was added. This was decided so as to operate below the thermodynamic limit imposed by its saturation solubility. To the resulting mixture, a weighed amount of catalyst (2% of the polymer weight (m_{PLA})) was added and the reaction was allowed to progress for 2 h. Samples were periodically withdrawn from the reaction mixture and were immediately subjected to GC–MS measurements to analyse the concentration of ethyl lactate ($C_{\text{EL},t}$). It should be noted that, alcoholic depolymerisation involves transesterification of the ester linkage present in the repeat unit of the PLA macromolecule. Thus, analogues to other studies [31,43,48], the yield of ethyl lactate (Y_{EL}) is evaluated based on the molar mass of the repeat unit (Equation (1)).

$$\text{Yield of Ethyl Lactate} = Y_{\text{EL}} = \frac{C_{\text{EL},t}}{C_{\text{PLA},i}} \times \frac{M_{\text{rpu}}}{M_{\text{EL}}} \times 100 \quad (1)$$

where, $C_{\text{PLA},i}$ and $C_{\text{EL},t}$ represent the initial concentration of PLA ($t = 0$) and the concentration of ethyl lactate in the reaction mixture at specific intervals of time (t), respectively while M_{rpu} and M_{EL} is the molar mass of the repeat unit of PLA (72.06 g mol^{-1}) and ethyl lactate ($118.13 \text{ g mol}^{-1}$).

At the end of the reaction, the reaction mixture was filtered and fed to a rotary evaporator in order to recover the solvent (acetone) and the excess, unreacted nucleophile (ethanol). The liquid in the sump (primarily, ethyl lactate) was then examined using ICP-OES analysis and ^{31}P NMR spectroscopy.

3.2.2. Analytical methods

3.2.2.1. Differential scanning calorimetry (DSC). In order to measure the glass transition temperature (T_g), crystallisation temperature (T_c) and melting point (T_m), the residual PET and PP fractions obtained after selective dissolution of PLA were subjected to DSC analysis using a power compensated DSC1 (Mettler Toledo). The measurements were

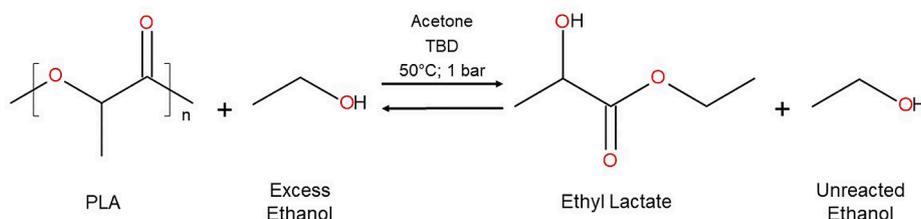


Fig. 2. Schematic representation of the alcoholic depolymerisation of PLA investigated in this study.

adjusted in order to record the characteristic transitions of PET and PP. The glass transition temperature of PP varies between -3°C and -7°C . Further, while PET melts around 250°C , PP undergoes degradation beyond 200°C . Thus, the PET fraction was heated from 20°C to 320°C while the PP fraction was heated from -50°C to 200°C , at a heating rate of $10^{\circ}\text{C min}^{-1}$, in a nitrogen environment.

3.2.2.2. Fourier transform infrared spectroscopy – Attenuated total reflection (FTIR-ATR). In addition to DSC analysis, the residual fractions obtained after dissolution were analysed for their FTIR-ATR spectra using a ThermoScientific Nicolet 6700® spectrometer coupled with a DuraScope® ATR unit. These analyses were carried out between 650 cm^{-1} and 4000 cm^{-1} with a resolution of 4 cm^{-1} .

3.2.2.3. Gas chromatography-Mass spectroscopy-Flame ionisation detection (GC-MS). In order to determine the concentration of ethyl lactate, samples of the reaction mixture were analysed with the help of a gas chromatograph GC-MS 6890 N (Agilent Technologies); equipped with a DB-FFAP column and a flame ionization detector. A sample volume ($1\text{ }\mu\text{L}$) was injected at 220°C with He as the carrier gas. The total flow rate was 130 mL min^{-1} . The temperature of the column was steadily ramped from 50°C to 220°C at a rate of $20^{\circ}\text{C min}^{-1}$ within a total run time of 20.5 mins. In most experimental runs, only one significant peak (excluding that of the solvent and the nucleophile) was observed; characterized by a retention time equivalent to pure ethyl lactate. In some trials, a second peak also appeared but was considerably less significant. This can be attributed to the formation of an ethyl lactate dimer as the reaction progressed [38]. The setup was calibrated with the help of an external standard calibration curve over the entire expected range of the concentration of ethyl lactate, measured as a linear response of the FID detector ($R^2 = 0.999$).

3.2.2.4. Gel permeation chromatography (GPC). SEC 1260 GPC (Agilent Technologies) equipped with a set of three columns, namely, Agilent-PLgel-MIXED-D, Agilent-OligoPore and PL-OligoPore preceded by a PL-gel column was used to measure the molecular weight of PLA. The GPC/SEC Multi-Detector Suite (G7800A) consisted of a UV detector (G1314F) operated at 254 nm , a RI-light scattering unit and a viscosity detector. A sample volume ($100\text{ }\mu\text{L}$) was injected at $30^{\circ}\text{C} - 35^{\circ}\text{C}$. Chloroform was used as the eluent. The total flow rate ranged between $0.75\text{ mL min}^{-1} - 1\text{ mL min}^{-1}$. PS standards (Agilent Technologies) with a molecular weight ranging between $162\text{ Da} - 3242\text{ kDa}$ were used for calibration.

3.2.2.5. Inductively coupled plasma – Optical emission spectrometry (ICP-OES). In order to examine the contamination of metal ions in the product obtained from the alcoholysis of post-consumer PLA substrates (Fig. 1), a qualitative ICP-OES analysis was performed. About 10 g of each sample was weighed into a Teflon tube and treated at 35°C in a vacuum oven for 4 days to evaporate the excess solvent. To this residue, 6 mL conc. HCl and 2 mL conc. HNO_3 was added. This sample was subjected to microwave irradiation for 30 mins at 60 bar (Multiwave 3000, Anton Paar) and was subsequently, diluted with 25 g to 30 g demineralised water. A full-spectrum qualitative analysis was conducted

with an inductively coupled plasma-optical emission spectrometer (ICP-OES, iCAP6300, Thermo Fisher Scientific Inc.).

3.2.2.6. Nuclear magnetic resonance spectroscopy (NMR). To determine the enantiomeric purity, two samples of ethyl lactate along with their corresponding PLA substrates were subjected to ^{31}P and ^1H NMR spectral analysis respectively, on a Varian Mercury-VX 400 (9.4 Tesla, Agilent, Palo Alto, US) NMR spectrometer using a 5 mm inverse probe. These spectra were evaluated in MestReNova 14.1.

The ^1H NMR spectra were measured using homo-nuclear decoupling pulse sequence. The irradiation of methyl protons (α 1 set to 1.57 ppm) results in simplification of the methine signal. About 5 mg of each PLA sample was dissolved in 0.7 mL deuterated chloroform (CDCl_3) which was then transferred into 5 mm NMR tubes. Eight scans were acquired by a 90° exciting pulse with an acquisition time of 5.1 s and a relaxation delay of 5 s . The spectral width was set to 6.4 kHz .

Further, about 0.75 mmol of each ethyl lactate sample was dissolved in 2 mL CDCl_3 . To these, a solution of 0.25 mmol PCl_3 in 2 mL CDCl_3 was added. These mixtures were stirred overnight at room temperature. ^{31}P NMR spectra with proton decoupling were acquired using a 90° exciting pulse with an acquisition time of 0.7 s and relaxation delay of 10 s . 160 accumulated scans were collected at a spectral width of 65 kHz .

4. Results and discussions

4.1. Selectivity of the solvent

The solubility parameter of PET ($\delta = 19.44$) and PP ($\delta = 18.8$) differs considerably from that of acetone ($\delta = 21.1$) [20,64]. This implies that, acetone can aid the selective dissolution of PLA ($\delta = 20.3$) [20] from a mixed waste-stream comprising of PET and PP. While polymer-solvent pairs with similar solubility parameters are mutually soluble [20], this is not always true [70]. Thus, the selectivity of acetone towards PLA was demonstrated quantitatively, by mass balance and qualitatively, by subjecting the dried residual fractions obtained post-dissolution to FTIR-ATR (Fig. 3) and DSC (Table 1) analysis.

Fundamental literature about characteristic group frequencies in the infrared spectra by George Socrates [71] was used to identify pertinent signals corresponding to a particular group; thereby, locating fundamental alterations (if any) in the FTIR-ATR spectra of the residual fractions. For instance, as shown in Fig. 3, the FTIR-ATR spectra of all polyesters exhibit characteristic vibrations between $1800\text{ cm}^{-1} - 1700\text{ cm}^{-1}$ and $1300\text{ cm}^{-1} - 1000\text{ cm}^{-1}$. These vibrations are attributed to presence of the ester group in their structure ($\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$) [71]. Further, it has been reported that, the FTIR-ATR spectra of aromatic polyesters (viz. PET) (Fig. 3[B]) differs from aliphatic polyesters (viz. PLA) (Fig. 3[A]) at about 730 cm^{-1} [71]. This is due to the presence of an aromatic ring and is slightly shifted towards higher wave numbers on account of the interaction between the aromatic ring and the ester group [71]. Further, the infrared spectra of PET (Fig. 3[B]) exhibits two signals around 1260 cm^{-1} and 1130 cm^{-1} on account of the C-O-C asymmetric and symmetric stretching vibrations [71]. FTIR-ATR spectra of PP (Fig. 3[C]) shows strong bands near 2950 cm^{-1} and 1460 cm^{-1} on account of C-H stretching, deformation and rocking vibrations and near 1380 cm^{-1} due to considerable methyl branching [71]. Apart from these

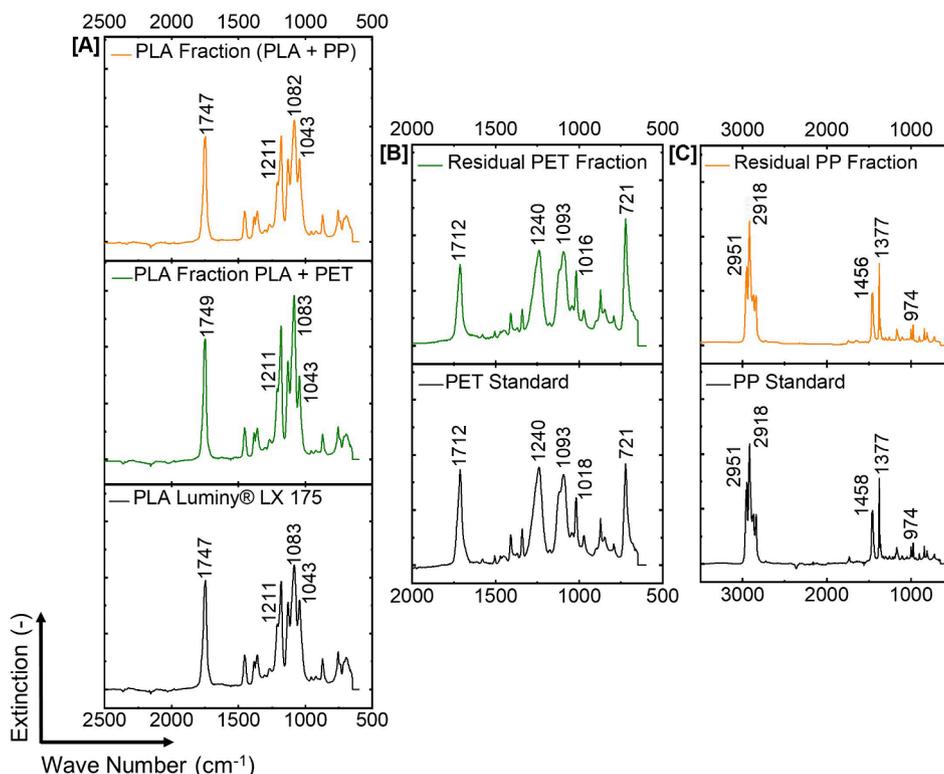


Fig. 3. Comparison of FTIR-ATR spectra of residual fractions of PLA [A], PET [B] and PP [C] obtained post-dissolution with their respective standards.

Table 1

Comparison of the glass transition temperature (T_g), crystallization temperature (T_c) and melting point (T_m) of residual solid fractions of PET and PP obtained post-dissolution (Section 3.2.1) with their respective standards.

Parameter (°C)	Sample under Consideration			
	PET Standard	Residual PET Fraction	PP Standard	Residual PP Fraction
T_g	82.96	80.65	×	×
T_c	193.91	191.97	131.66	132.15
T_m	249.38	249.61	167.75	167.79

characteristic signals, the FTIR-ATR spectra of PP (Fig. 3[C]) displays several sharp bands of medium intensity between 1250 cm^{-1} and 835 cm^{-1} which is a typical feature of an isotactic PP sample [56]. From Fig. 3, it can be observed that, the FTIR-ATR spectra of the residual fractions are superimposable with the standard spectra. Further, the results obtained from the DSC analysis of the residual solid fractions (PET and PP) (Table 1) show only a slight deviation from their respective standards which can be attributed to an intrinsic error ($\pm 5\%$) associated with DSC measurements.

Thus, the FTIR-ATR and DSC analysis of the residual fractions obtained post dissolution confirms that, acetone only aids the selective dissolution of PLA. In addition to this, it also justifies the methodology for the choice of a solvent used in this study by validating that, analysis of solubility parameters serves as a useful preliminary tool to shortlist suitable solvents for selective dissolution of a particular polymer.

4.2. Effect of concentration of the nucleophile

As mentioned previously, the alcoholic depolymerisation of the PLA macromolecule represents a reversible transesterification reaction [38]. In accordance to the Le Chatelier principle, an excess of one of the educts is essential to drive such reactions to completion. In several studies involving the methanolysis of PLA catalysed by FeCl_3 and ionic

liquids, it was observed that, the concentration of nucleophile (methanol) per mole repeat unit of PLA affects the yield of methyl lactate [43,45,48,49]. Similarly, the variation in the yield of ethyl lactate (Y_{EL}) for different concentrations of nucleophile (ethanol) per mole repeat unit of PLA ($n_{nuc}:n_{rpu}$) (Fig. 4) was investigated for the reaction under consideration (Fig. 2).

It was observed that, the concentration of ethyl lactate in the reaction mixture at the end of the reaction doubled with an increase in the concentration of nucleophile per mole repeat unit of PLA ($n_{nuc}:n_{rpu}$)

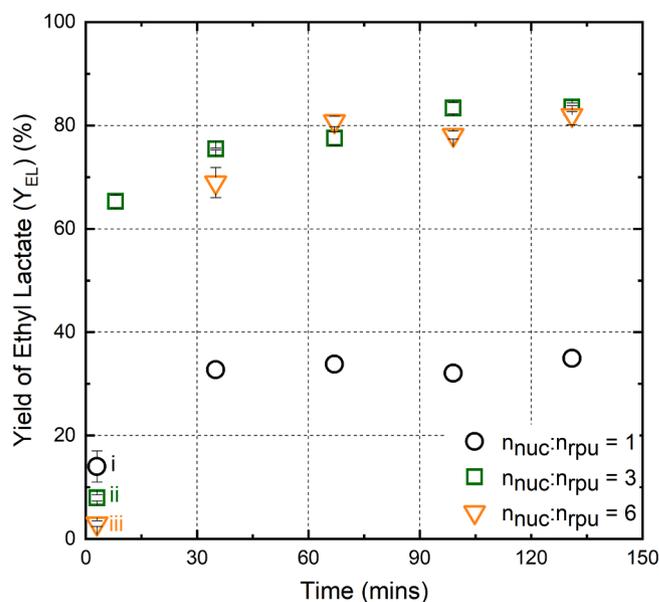


Fig. 4. Effect of concentration of nucleophile ($n_{nuc}:n_{rpu} = 1, 3, 6$) on the yield of ethyl lactate (Y_{EL}) (Luminy®LX 175; $m_{PLA}:m_{ace} = 0.11$; $m_{TBD}:m_{PLA} = 0.02$; $T = 50^\circ\text{C}$; $P = 1\text{ bar}$).

from 1 to 3. This can be deduced by observing the trend in the yield of ethyl lactate with the progress of the reaction (Fig. 4). The yield of ethyl lactate increases from 34.93% at $n_{\text{nuc}}:n_{\text{rpu}} = 1$ to 83.51% at $n_{\text{nuc}}:n_{\text{rpu}} = 3$. With a further increase in the relative concentration of ethanol, no significant change was observed. This is contrary to the previous attempts aimed at methanolysis of PLA where the yield of methyl lactate decreased as the relative concentration of methanol per mole repeat unit of PLA ($n_{\text{nuc}}:n_{\text{rpu}}$) was increased from 5 to 6 [43,45,48,49]. Thus, it can be said that, the optimal molar ratio of ethanol per mole repeat unit of PLA ($n_{\text{nuc}}:n_{\text{rpu}}$) is 3 for the TBD-catalysed transesterification reaction addressed in this study. However, it should be noted that, the yield of ethyl lactate in the initial period was observed to decrease with an increase in the relative concentration of ethanol ($i < ii < iii$). Though the reaction appears to be heterogeneous, the dissolution of the PLA macromolecule in the reaction mixture is a necessary condition which influences the reaction dynamics [39,41,43,45,49,65]. Unlike hydrolysis of PLA where the reaction proceeds through a mechanism of surface erosion (diffusion of water in the polymer matrix), the solubility of PLA plays a crucial role in its alcoholysis [20,29,30,38,39,43,45,49,65]. It should be noted that, the scission reaction (transesterification of PLA to alkyl lactate) will occur only if it is not limited by mass transfer across the interphase boundary, i.e., the ester linkage is easily accessible in the solution [41]. Thus, alcoholic depolymerisation of PLA results from an interplay between the dissolution of PLA in the solvent (kinetics) followed by its subsequent transesterification by the alcohol (thermodynamics) [47]. On account of its insolubility, alcohols are commonly used as precipitating agents in solvent-assisted purification of PLA [20,41]. Thus, the presence of ethanol in the reaction mixture retards the rate of dissolution of PLA which predominantly influences the reaction rate during the initial period. An increase in the relative concentration of ethanol hinders the rate of dissolution of PLA in acetone; thereby, leading to a lower reaction rate. Therefore, the yield of ethyl lactate is relatively higher at a lower concentration of ethanol during the initial period. However, as the reaction progresses, a substantial amount of ethanol is consumed. This facilitates the dissolution of PLA in the solvent and the reaction experiences a dynamic transition from the kinetic to the thermodynamic regime in which, the relative concentration of ethanol in the reaction mixture has a proportional effect on the yield of ethyl lactate, i.e. higher the concentration of ethanol, higher is the yield of ethyl lactate. However, due to the lack of an *in-situ* measurement technique, it was not possible to identify the intricacies of this transition.

4.3. Effect of type of the substrate and its molecular weight

To analyse the effect of the molecular weight on the yield of ethyl lactate (Fig. 5), different PLA substrates with varying molecular weights (Table 2) were subjected to depolymerisation.

The rate of hydrolysis of PLA depends on its molecular weight [32]. However, it can be observed that, unlike hydrolysis, irrespective of the reaction regime (kinetic or thermodynamic), the yield of ethyl lactate does not depend on the molecular weight of the substrate. In hydrolysis, macromolecular PLA is broken down into its constituent monomer (lactic acid). Therefore, the rate of hydrolysis depends upon the molecular weight of the substrate which is an indirect measure of the amount of lactic acid condensed in the polymer. In addition to this, analogues to most solution-based depolymerisation reactions, hydrolysis also proceeds through random chain-end scissions along the polymer length [29,30,33,41]. However, alcoholic depolymerisation of PLA is a nucleophilic substitution reaction in which a nucleophile reacts with the easily hydrolysable ester backbone of the PLA macromolecule in order to produce a corresponding lactate ester [38,39]. In other words, it can be said that, alcoholysis of PLA does not result in the production of its constituent monomer (lactic acid). Therefore, the rate of reaction would primarily depend on the reactivity of the alcohol instead of depending on the chain length of the polymer [20,38]. In a study conducted by Leibfarth et al., it was postulated that, steric hindrances of the

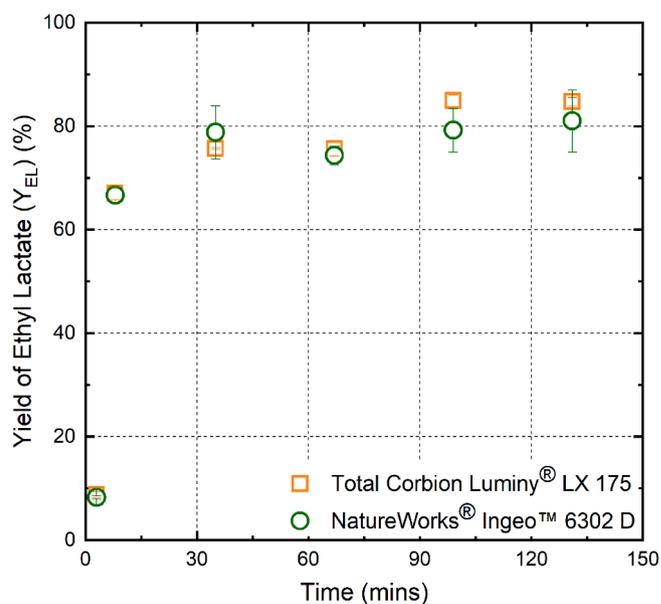


Fig. 5. Effect of molecular weight of different PLA substrates (Luminy® LX 175, Ingeo™ 6302 D) on the yield of ethyl lactate (Y_{EL}) ($n_{\text{nuc}}:n_{\text{rpu}} = 3$, $m_{\text{PLA}}:m_{\text{ace}} = 0.11$, $m_{\text{TBD}}:m_{\text{PLA}} = 0.02$; $T = 50^\circ\text{C}$; $P = 1$ bar).

Table 2

Characterisation of different PLA substrates by GPC-SEC measurements.

Sample Name	Property			
	Source	M_n (kDa)	M_w (kDa)	D
Luminy® LX 175	Total Corbion	84.41	128.49	1.52
Ingeo™ 6302 D	NatureWorks®	128.49	136.80	8.57
Post-Consumer PLA Cups	DAS FEST, Karlsruhe	72.55	127.35	1.75

alcohol retard the rate of the reaction [38]. To put this in perspective, 30 mins were required for complete depolymerisation of PLA in the presence of sterically hindered *iso*-propanol as opposed to 2 mins in the presence of ethanol, under similar operating conditions [38]. This can be attributed to the dual-activation mechanism of TBD-catalysed transesterification of PLA which prevents sterically bulky alcohols from accessing the crowded three component intermolecular intermediate [38]. Through several computational and experimental investigations, it has been reported that, the sp^2 -hybridized nitrogen atom in TBD is very selective towards protonating the alcohol while the sp^3 -hybridized nitrogen atom achieves a simultaneous activation of the carbonyl group; thereby, resulting in the formation of an intermediate which facilitates the cleavage of C-O bond [38,68]. Similar mechanism is observed in several other organic reactions involving guanidine based catalysts [72–74]. A preliminary schematic representation of the reaction mechanism is illustrated in Fig. 6. However, extensive analytical investigations are required in order to further confirm this.

Thus, unlike other catalysts which depolymerise PLA via a two-step mechanism, TBD-catalysed transesterification of PLA is a single step reaction [43,45,48,49,68]. This, in turn, explains the shorter reaction time required for nearly complete depolymerisation of PLA as opposed to conventional alcoholysis [20,41,43,45,48,49]. Further, organo-catalysts are used for structured chain scission of PLA in order to produce tailor-made, bio-resorbable polymers with controlled molecular weight and functionality [75]. It should be noted here that, GPC analysis of solid residues obtained from some preliminary experiments ($n_{\text{nuc}}:n_{\text{rpu}} = 3$, 50°C , 1 bar) revealed that the dispersity of these fractions ($D = 2.06$) increased with respect to the dispersity of the standard sample ($D = 1.52$). This is indicative that this reaction proceeds through a

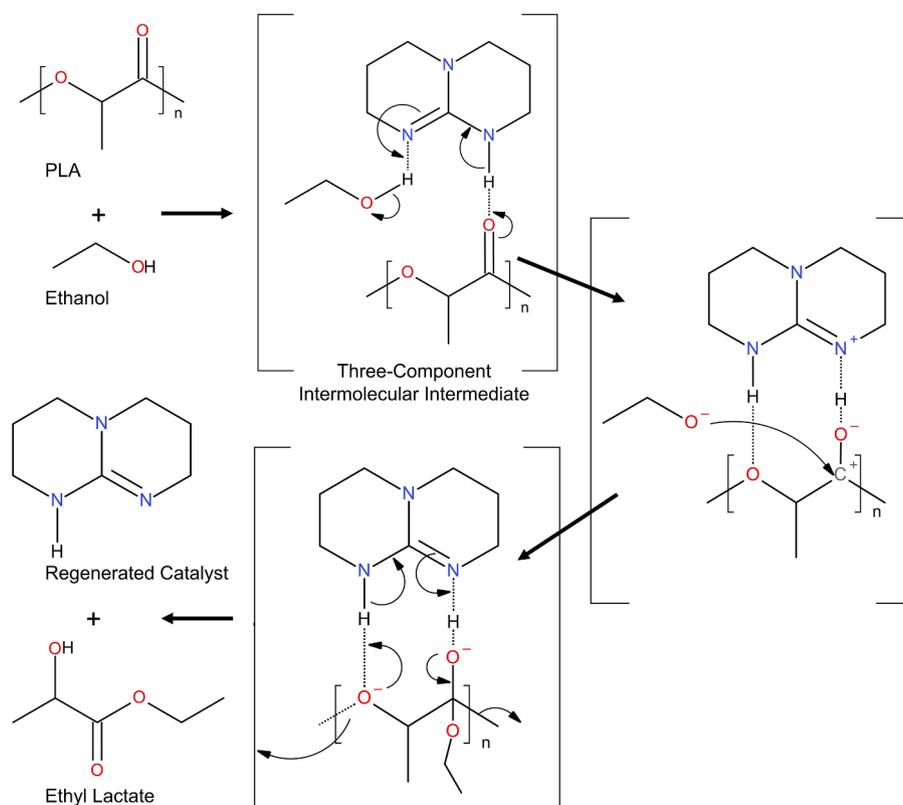


Fig. 6. Proposed reaction mechanism for TBD-catalysed alcoholic depolymerisation of PLA [38,72–74].

midpoint-chain scission mechanism as opposed to chain-end scission mechanism observed in conventional alcoholysis/hydrolysis [29,30,32,41,76]. However, comprehensive investigations are required in order to further confirm this hypothesis.

In order to demonstrate the robustness of this process, several post-consumer samples (Fig. 1) were subjected to depolymerisation in the

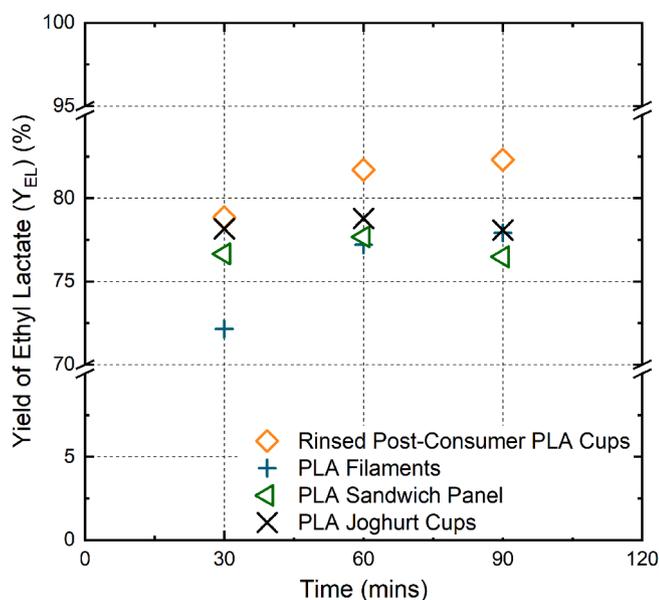


Fig. 7. Effect of different post-consumer PLA substrates on the yield of ethyl lactate (Y_{EL}) ($n_{nuc}:n_{rpu} = 3$, $m_{PLA}:m_{ace} = 0.11$, $m_{TBD}:m_{PLA} = 0.02$; $T = 50^{\circ}C$; $P = 1$ bar).

presence of technical grade reagents (Fig. 7). In addition to validating the flexibility of this process, this would also benefit its economics as these chemicals are considerably cheaper as compared to the analytical grade. Further, these substrates were not analysed for their molecular weight distribution due to the presence of miscellaneous additives which might significantly affect the analytical setup.

It can be observed that, the yield of ethyl lactate (Y_{EL}) does not vary with the type of the substrate. This can be attributed to the fact that, unlike hydrolysis of PLA which proceeds through surface erosion [65], its alcoholysis proceeds through solution-based scission reactions [41]. Thus, hydrolysis suffers from a low depolymerisation rate whilst handling crystalline and/or semi-crystalline PLA [33] as opposed to the investigated alcoholysis strategy which can handle a wide range of PLA grades from different value chains (Fig. 7). Surficial impurities present on these substrates have negligible impact on the efficacy of the process and can be easily separated from the resulting reaction mixture by filtration. In addition to this, a preliminary, qualitative full-spectrum ICP-OES analysis of the liquid obtained from the sump (primarily ethyl lactate) reveals no signals; thereby, ascertaining that it is not contaminated with metal ions. Further, absence of any other significant peak except that of the solvent (acetone), the nucleophile (ethanol) and the product (ethyl lactate) on the GC-MS chromatogram also confirms the absence of organic contaminants in the reaction mixture. Thus, it can be inferred that, the process is robust owing to the choice of an appropriate solvent, a highly selective catalyst and mild operating conditions which prevent undesirable side reactions.

4.4. Retention of stereochemistry

Conventional NMR spectroscopy cannot distinguish between dextro- and levorotatory isomers of PLA (D-/L-PLA) and ethyl lactate (D-/L-EL) respectively. However, Thakur et al. developed a method to quantify the

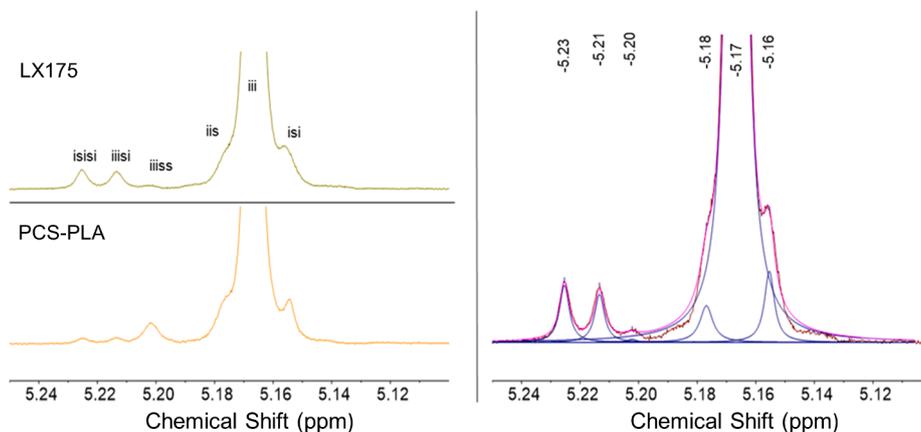


Fig. 8. Stackplot of the methine resonances in the homo-decoupled ^1H NMR spectra of the PLA samples (signal assignments are according to Thakur et al.) [77]

purity of L-PLA [77]. In a homo-nuclear-decoupled ^1H NMR spectra of L-PLA, characteristic methine signals representing minor impurities of D-lactide and *meso*-lactide in the RR stereochemistry have been observed. This was also evident from the experimental ^1H NMR spectra of two PLA samples considered in this study, namely, Luminy® LX175 and post-consumer PLA cups (PCS-PLA) (Fig. 8).

It should be noted that, isotactic (RR/SS) and syndiotactic LA-units are commonly represented as “i” and “s”, respectively [77]. For instance, a sequence of six LA-units labelled as “isisi” implies that these units are arranged in an alternate isotactic-syndiotactic configuration. Based on this practice, arrangements designated as “iisi”, “iiss” and “iisi” in Fig. 8 can be elucidated. The intensity ratio of the signal at 5.20 ppm differs considerably from that at 5.21 ppm and 5.22 ppm. These signals (isisi and iisi) at 5.21 ppm and 5.22 ppm correspond to the presence of D-lactide while the signal (iiss) at 5.20 ppm can be attributed to the presence of *meso*-lactide [77]. In case of post-consumer PLA cups, the signal (iiss) at 5.20 ppm was significantly higher than the signals (isisi and iisi) at 5.21 ppm and 5.22 ppm respectively. Thus, as opposed to Luminy® LX175 (0.2%), the content of *meso*-lactide is higher in the post-consumer PLA samples (4.8%). This could be attributed to their possible application in different sectors. Owing to its high L-lactide content, Luminy® LX175 is used for niche applications involving fiber spinning which demand higher crystallinity and better mechanical and thermal stability [5,10,12]. On the contrary, PLA with a comparatively higher *meso*-lactide content thoroughly meets the standards specified for affordable production of bulk packaging and disposable cutlery (post-consumer cups) [11–13]. On the evaluation of these spectra by deconvolution in order to determine the chemical composition of the PLA substrates, it was observed that, the content of L-PLA was 95.8% and 94.5% in Luminy® LX175 and post-consumer PLA samples, respectively (Table 3).

To quantify the enantiomeric purity of the ethyl lactate obtained from the transesterification of these substrates, two samples (PLA-LX175-EL and PCS-PLA-EL) were subjected to ^{31}P NMR spectral analysis in accordance to the procedure described by Feringa et al [78]. These samples were converted into their phosphonates by PCl_3 as a dimerization agent and quantitative ^{31}P NMR spectra were subsequently measured. Fig. 9 illustrates a ^{31}P NMR spectra of the ethyl lactate

Table 3

Chemical composition of the PLA samples (evaluated from the homo-nuclear decoupled ^1H NMR spectra).

Sample	Composition (%)		
	L-Lactide	D-Lactide	<i>meso</i> -Lactide
LX-175	95.8	4.0	0.2
PCS-PLA	94.5	0.7	4.8

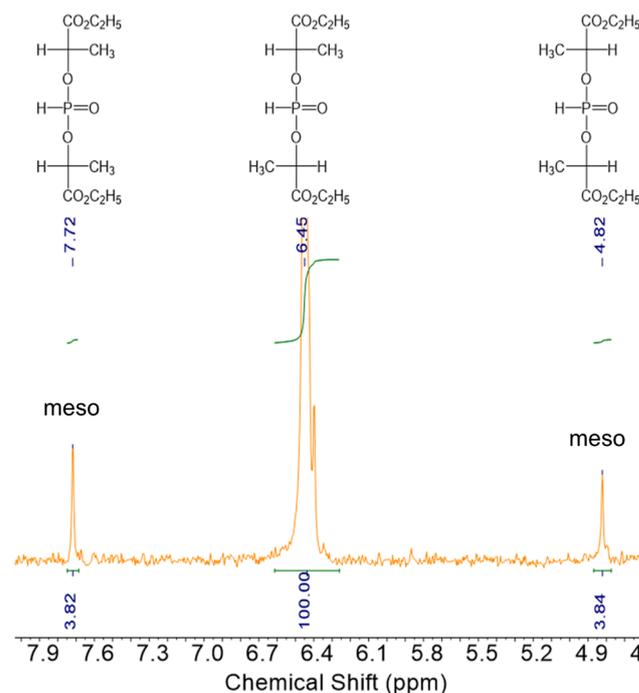


Fig. 9. Stackplot of the ^{31}P NMR spectra of the ethyl lactate samples (signal assignments according to Feringa et al.) [78]

obtained from post-consumer PLA (PCS-PLA-EL) including the structural assignments. A similar spectrum was obtained for the ethyl lactate obtained from Luminy® LX175.

The reaction of these samples with PCl_3 results in a mixture of stereoisomeric phosphonates, namely, RR (L-pair) and RS and SR (*meso*-pair). The RR resonance at 6.45 ppm corresponds to the L-form of the phosphonate whereas the two minor signals at 7.72 ppm and 4.82 ppm correlate with its *meso*-forms. Quantitative evaluation of the ^{31}P NMR spectra was followed by subsequent integration in order to determine the content of L-ethyl lactate in these samples (Table 4). It was observed that, the content of L-ethyl lactate was 92% and 93% in the ethyl lactate

Table 4

Enantiomeric purity of the ethyl lactate samples, (evaluated from ^{31}P NMR spectra).

Sample	Content of L-Lactide (%)
LX-175-EL	92
PCS-PLA-EL	93

obtained from Luminy® LX175 (PLA-LX175-EL) and post-consumer PLA samples (PCS-PLA-EL), respectively.

From the above analysis, it can be deduced that, the enantiomeric purity of the samples of ethyl lactate is almost identical to that of its respective substrate. Slight deviations can be attributed to the presence of residual solvent and unreacted nucleophile that was retained in the sump during product purification using a lab-scale rotary evaporator.

5. Conclusions

PLA is gradually manifesting into a high-volume commodity material owing to exhaustive research that promotes development of flexible and versatile applications and the implementation of several environmental policies that drives consumers towards sustainable materials. However, the process of production of PLA is highly raw material and energy intensive [20,28,33]. Therefore, adopting a sustainable strategy for recycling post-consumer PLA waste is the need of the hour.

This study investigates a holistic recycling strategy involving alcoholic depolymerisation of PLA into a valuable lactate ester. Mild operating conditions and the use of a conventional yet eco-friendly catalyst and a low-boiling solvent also presents this process as a sustainable alternative to the production of ethyl lactate. In addition to this, the methodology adopted for devising this strategy can serve as guidelines for prospective efforts towards adopting a circular economy for other petro-chemical and/or bio-based plastics.

This reaction scheme (illustrated in Fig. 2) resembles a reversible nucleophilic substitution reaction; thereby, necessitating the use of an excess of nucleophile (alcohol) in order to drive the reaction to completion. The optimal molar ratio of alcohol per mole repeat unit of PLA ($n_{\text{nuc}}:n_{\text{rpu}}$) was found to be 3 (Fig. 4). In addition to this, it was found that, the yield of ethyl lactate does not vary with the chain length (molecular weight) of the polymer (Fig. 5). Further, irrespective of their composition, the process can depolymerise a wide variety of post-consumer PLA substrates with no significant effect on the yield of ethyl lactate (Fig. 7). Therefore, the process is flexible and robust; i.e., it is capable of handling a range of PLA grades. In addition to this, it is also hypothesized that, the reaction proceeds through a mid-point chain scission mechanism and involves the formation of a three-component intermolecular intermediate (Fig. 6). However, further investigations are essential in order to confirm this hypothesis.

It was observed that, the FTIR-ATR spectra of the residual fractions (PLA, PET and PP) obtained post-dissolution were superimposable with that of the respective standard (Fig. 3). Further, DSC analysis of the solid residual fractions (PET and PP) reveals only a slight deviation (2.5%) from the standard (Table 2). This confirms that, acetone is capable of aiding the selective dissolution of the PLA fraction present in a commingled stream comprising of PET and PP at 50°C; thereby, resolving the problems arising due to the contamination of PLA in the conventional waste streams. In addition to this, despite slight deviations in the content of L-Lactide (1.5%–3.8%) (Table 3, Table 4) which can be attributed to the presence of impurities, ^1H and ^{31}P NMR measurements confirm that, the enantiomeric purity of ethyl lactate is almost identical to its corresponding PLA substrate. Thus, it can be said that, TBD-catalysed alcoholysis of PLA as investigated in this study proceeds with a complete retention of stereochemistry.

Thus, the strategy represents an ambitious yet industrially feasible alternative to bridge the gap between “bio-economy” and “circular economy” by upcycling post-consumer PLA waste into a value-added bio-based solvent (ethyl lactate); thereby, fostering the transition towards a “circular bio-economy”.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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