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The selective recycling of mixed plastic waste of polylactic acid and polyethylene terephthalate by control of process conditions

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Abstract

The glycolysis of postconsumer polyethylene terephthalate (PET) waste was evaluated with catalysts of zinc acetate, zinc stearate and zinc sulfate, showing that zinc acetate was the most soluble and effective. The chemical recycling by solvolysis of polylactic acid (PLA) and PET waste in either methanol or ethanol was investigated. Zinc acetate as a catalyst was found to be necessary to yield an effective depolymerization of waste PLA giving lactate esters, while with the same reaction conditions PET remains as an unconverted solid. This provides a strategy to selectively recycle mixed plastic waste by converting one plastic to a liquid and recovering the unreacted solid plastic by filtration.

Keywords: polyethylene terephthalate; polylactic acid; recycling; catalyst, glycolysis; mixed plastic waste

1. Introduction

Plastics find application in almost all aspects of modern society but their waste and environmental management remains a challenge. In particular, the efficient recycling of mixed waste plastic has been identified as the next major challenge for the plastic recycling sector and needs the development of new processes [1]. Plastics have become an important environmental issue even though they do not generally possess a direct hazard to the environment [2]. Their environmental impacts arise as they consume non renewable resources and they are resistant to the biological degradation [3,4]. For example, in some areas marine debris reaches 90-95% plastic content e.g. polyamide netting and lines from fishing [5]. Plastics account for 20% of total waste by volume in landfills clearly this is not considered a sustainable option due to their long degradation time and their low weight/volume ratio [6]. Fortunately, a recycling infrastructure is developing for some plastics such as PET whose recycling has been widely studied [7, 8].

Bioplastics such as poly lactic acid (PLA) will help to address these problems since their degradation times are shorter than conventional petrochemical plastics [9] and they can be produced from renewable sources. Naturally, the extensive use of renewable feedstock in the chemical industry needs both the development of suitable processes and also a good market value for products made from renewable sources [10], for example such issues have been discussed for ethyl lactate [11]. Therefore, as bioplastics gain a market share a more sustainable chemical industry will be realised. Furthermore, PLA is also being widely studied as a biocompatible polymer for medical applications [12]. At present, PLA needs significant energy in its production that is currently derived from renewable sources [13] and PLA biodegradation is best carried out in industrial composting facilities to be efficient [14, 15]. Consequently, as PLA becomes more widely used and requires disposal on a large scale it would be best not to rely only on its biodegradation either in the environment or in composting facilities [16]. Therefore, to make PLA an even more sustainable material PLA recycling must be developed [17].

WRAP has raised some concerns that recycling bioplastics such as PLA, may disturb current recycling processes if it is mixed with conventional plastics [18]. This is especially the case of soft drinks bottles made of PLA. It is claimed that PLA bottles can contaminate the PET waste stream making its recycling process less efficient and increasing its cost by necessitating investment in new sorting equipment. It is noteworthy that these plastics cannot be easily or cheaply sorted by sight and the separation methods based on density are not efficient enough due to their similar densities. Only near infrared sensors can ensure good separation, but this technology requires an expensive initial investment and it is not common place in the current recycling facilities [19]. In July 2009, this possibility caused the National Association for PET Container Resources (NAPCOR) in the USA to refuse to introduce waste PLA in their current schemes for recycling PET [20]. It is therefore necessary to find a route for recycling PLA without compromising the recycling processes of other plastics especially PET.

Mechanical recycling of plastic waste is the most widespread technology in the UK [21]. Nonetheless, it may be difficult to convert PLA waste into useful products by these means as the degradable behaviour of PLA makes it especially vulnerable to mechanical degradation during extrusion. Therefore, after every cycle the product obtained has lower quality than the starting material and so its market value decreases

[22]. Naturally, maintaining the quality of the recyclate is vital in order to ensure the feasibility of the process and the market value [23].

Due to the difficulty of recycling PLA by mechanical means researchers have begun to explore the chemical recycling of PLA. Two processes have mainly been explored, firstly thermal degradation of PLA to obtain L,L-lactide, a cyclic dimer from which PLA can be repolymerized [24-26] and secondly hydrolysis of PLA at temperatures between 100⁰C and 250⁰C to obtain lactic acid [27, 28]. Although no literature was found reporting the effect of PET contamination in any of the routes mentioned above it seems likely that at the conditions used post consumer PET would (to some extent) undergo degradation leading to a less pure monomer produced from the waste PLA and therefore decrease the value of the final product.

An alternative process for converting PLA waste into useful chemicals is by transesterification with alcohols to lactate esters. These compounds have good solvent properties and show good environmental characteristics [29] and represent an alternative to traditional and more toxic solvents (i.e. chlorinated hydrocarbons) [30]. It is important to stress that identifying suitable green solvents is a priority in green chemistry [31].

Catalysts such as zinc acetate are widely reported to transesterify polyesters e.g. in glycolysis [32-38] and methanolysis under supercritical conditions of PET [39]. Similarly, zinc acetate can act as a catalyst in the thermal degradation of PLA [40]. Its effect as a Lewis Acid catalyst arises via binding to the carboxyl of the ester to facilitate the attack of the ethylene glycol [34].

In this study, firstly the glycolysis of postconsumer PET waste was evaluated with catalysts of zinc acetate, zinc stearate and zinc sulfate, to identify the most effective catalyst. Secondly, the transesterification of PLA waste in methanol and ethanol was investigated using zinc acetate as a catalyst. Finally, the effect of the process conditions on a mixture of PLA and PET was explored to identify conditions that selectively depolymerize PLA to a liquid monomer while leaving solid PET unconverted to enable its recovery by filtration.

2. Experimental

2.1 Materials

Post-consumer PET from cleaned Oasis soft drink bottles and PLA from cleaned BELU water bottles were cut into square chips measuring 3mm x 3mm [36], washed and dried. A stirrer bar and an electromagnetic stirrer were used to vigorously stir the reactions. Methanol, ethanol and ethylene glycol were analytical grade and used without any further purification. Zinc acetate dihydrate, zinc stearate and zinc sulfate were purchased from Sigma Aldrich and used without further purification.

2.2 Solvolysis reaction

Under a nitrogen atmosphere at atmospheric pressure, plastic waste (2 g) in a round bottom flask had added the appropriate solvent (6ml) (i.e. methanol, ethanol or ethylene glycol, noting that the glycolysis of PLA was not attempted). The zinc catalysts were used in the catalysed reaction at a fixed amount of 0.4 mmols. The solvolysis was allowed to proceed up to 15 hours at the boiling point of the solvent used.

The products of the solvolysis of PET were recovered by cooling the filtrate for 6 hours at 0°C to precipitate the dimethyl terephthalate (methanolysis), diethyl terephthalate (ethanolysis) or bis(hydroxyethyl) terephthalate (glycolysis). Precipitates were filtered, dried in the oven for 24 hours and weighed. The glycolysis products were purified by the method of Ghaemy and Mossaddegh [35], this involved extraction into water followed by filtration and concentration to crystallise the products and separate the catalyst and any remaining ethylene glycol. Unconverted plastics were dried in the oven for 24 hours and weighed.

To obtain the products from the alcoholysis of PLA the crude product of the reaction was filtered and the excess of solvent in the liquid fraction was removed under vacuum to obtain the lactate ester.

2.3 Analysis.

Surface analyses of unconverted plastics employed Field-Emission Scanning Electron Microscopy (FE-SEM) using a FEI XL30 after carbon coating.

Analysis of the glycolysis products was performed using a Shimadzu HPLC equipped with a c-18 column and a UV detector set at 254 nm. These experiments used methanol/water (70/30 v/v) as the mobile phase at a flow rate of 1ml/min. Purified bis(hydroxyethyl) terephthalate was used as a standard for the quantitative analysis.

IR spectra were recorded with KBr as dispersant using a PerkinElmer Spotlight 300.

^1H NMR and ^{13}C NMR spectra were recorded using a JEOL ECX-400 operating at 400 MHz (^1H NMR) and 100 MHz (^{13}C NMR), using dimethylsulfoxide (DMSO-d_6) as solvent.

Bis(hydroxyethyl) terephthalate. δ_{H} (400 MHz, $(\text{CD}_3)_2\text{SO}$) 3.7 (m, 4 H, HOCH_2CH_2), 4.3 (t, 4H, HOCH_2CH_2), 5.9 (t, 1H, OH), 8.1 (4H, s, ph); δ_{C} (100 MHz, $(\text{CD}_3)_2\text{SO}$), 59 (HOCH_2CH_2), 67(HOCH_2CH_2), 129 (ph), 134 (ph-C-CO), 165 ($\text{C}=\text{O}$). IR (KBr pellet): $\nu = 1712\text{cm}^{-1}$, s ($\text{C}=\text{O}$).

Methyl lactate: δ_{H} (400 MHz, $(\text{CD}_3)_2\text{SO}$) 1.20 (3H, dd, CH_3), 3.60 (3H, s, OCH_3), 4.11 (1H, m, CH), 5.37 (1H, br s, OH); δ_{C} (100 MHz, $(\text{CD}_3)_2\text{SO}$) 20.38 (CH_3), 51.45 (OCH_3), 65.95 (CH), 175 ($\text{C}=\text{O}$). IR (KBr pellet): $\nu = 1741\text{cm}^{-1}$, s ($\text{C}=\text{O}$).

Ethyl lactate: δ_{H} (400 MHz, $(\text{CD}_3)_2\text{SO}$) 1.15 (3H, t, HOCH_2CH_3), 1.21 (3H, dd, CHCH_3), 3.42 (3H, q, OCH_2CH_3) 4.07 (3H, m, CHCH_3), 4.50 (1H, br, $\text{CH}_3\text{CH}_2\text{OH}$) 5.40 (1H, br, CHOH); δ_{C} (100 MHz, $(\text{CD}_3)_2\text{SO}$) 14.30 (CH_3), 20.53 (CHCH_3), 60.43 (OCH_2), 66.37 (CH), 174.99 ($\text{C}=\text{O}$). IR (KBr pellet): $\nu = 1740\text{cm}^{-1}$, s ($\text{C}=\text{O}$).

Poly(lactic acid): δ_{H} (400 MHz, $(\text{CD}_3)_2\text{SO}$) 1.45 (3H, d, CH_3), 5.199 (1H, q, CH); δ_{C} (100 MHz, $(\text{CD}_3)_2\text{SO}$) 16.45 (CH_3), 68.66 (CH), 169.18 ($\text{C}=\text{O}$). IR (KBr pellet): $\nu = 1750\text{cm}^{-1}$, s ($\text{C}=\text{O}$).

3. Results and discussion

The results from all the reactions attempted are summarised in table 1.

Yields were calculated using the following formula [36]:

$$\text{Monomer yield (\%)} = (W_{\text{monomer}}/W_{\text{monomer},0}) \times 100$$

Where W_{monomer} is the weight of the monomer obtained after the reaction and $W_{\text{monomer},0}$ is the theoretical weight of the monomer if all the plastic was converted. The weight of the monomer of the glycolyzed product was calculated from the HPLC analysis while all the others products were weighted after their purification.

Recovered plastic was calculated as follows:

$$\text{Recovered plastic (\%)} = [(W_{\text{plastic},o} - W_{\text{plastic},f})/ W_{\text{plastic},o}] \times 100$$

Where $W_{\text{plastic},o}$ refers to the weight of the initial plastic and $W_{\text{plastic},f}$ refers to the weight of the plastic after the reaction.

Table 1. Results of alcoholysis of PET and PLA

3.1 Alcoholysis of PET

Figure 1. Glycolysis of PET

The catalysed depolymerisation of PET is a well studied transesterification reaction of plastic waste [32-38] (Figure 1). It is therefore a good reaction to evaluate the performance of other zinc catalysts where the anion was varied to include a surfactant anion (stearate) or a more weakly coordinating anion (sulfate). Table 1 shows the monomer yields achieved by the screened catalysts. Chromatograms and NMR spectra of the products can be found in the appendix 1.

It is noteworthy, that in all cases the PET chips were degraded and all the catalysts yielded PET monomer. As the solubility of the catalysts in ethylene glycol varied a relatively high catalyst concentration was used to try and ensure catalysis was observed. However, the zinc sulfate was insoluble under the reaction conditions and this led to its poor performance as a catalyst. Also it seemed to coat the surface of the PET flakes so that it hindered the uncatalysed reaction of PET with ethylene glycol. Zinc acetate proved to be the best transesterification catalyst tested showing the highest yield of monomer. Therefore it was decided to use zinc acetate as a catalyst in the following reactions with PLA.

In the literature, methanol and ethanol are used under supercritical conditions to depolymerize PET [39, 41, 42]. While here PET chips were recovered in approximately 100% yield after heating at reflux with ethanol and methanol irrespective of the use of a catalyst. These results suggest that PET failed to dissolve in the alcohol under reflux and so there was little reaction between the solvent and the plastic. Here, the small effect of the catalyst can be appreciated from the FE-SEM images of the recovered plastics (Figure 2). The surface of PET chips became rough when the catalyst was present in the reaction, this indicates a limited degradation. It was reported that zinc acetate disrupts the PET-solvent interface facilitating the interaction between the polar

solvent and the hydrophobic polymer [41] enhancing the degradation from the chip surface. This is likely here, although this effect is apparently not enough to catalyse extensive depolymerization at this temperature and pressure. A probable reason is that the zinc acetate coordinates to free carboxylic acid groups on the surface of the polymer, which switches the catalyst from a homogeneous to heterogeneous phase. This would also help explain why degradation seems so localized in figure 2c.

Figure 2. FE-SEM images of (a) post consumer waste PET, (b) recovered PET after uncatalysed methanolysis and (c) recovered PET after zinc acetate catalysed methanolysis.

3.2 Alcoholysis of PLA

Figure 3. Alcoholysis of PLA

Unlike PET, PLA can be converted to useful chemicals by methanolysis and ethanolysis under the conditions used (Figure 3). However, the transesterification needs zinc acetate as a catalyst (Table 1), to dramatically increase the yields of the monomers.

It is noteworthy that using the same conditions PLA was almost completely degraded while PET remained unconverted (with only slight surface degradation). There are several factors that may explain the difference in reactivity of the two polymers and it is likely that a combination of the factors discussed below is necessary.

One factor is their solubility in the alcohol since it has been reported to have a major influence on plastic methanolysis [43]. In order to predict the solubility of polymers in alcohols the solubility parameter can be used, where two materials with a similar solubility parameter are likely to have a better interaction [44]. These values have successfully predicted the partial solubility of PLA in tetrahydrofuran, toluene and chloroform [45]. From the solubility parameters of the reactants in table 2, it can be seen that both plastics have similar values and in both cases they are quite far from the

values of methanol and ethanol. Furthermore according to the solubility parameter, PET should exhibit better solubility in both alcohols due to the smaller difference between its value and the value of the alcohols. Indeed PLA has been reported as insoluble in both methanol and ethanol [46]. So it seems that the difference in reactivity exhibited by PLA and PET cannot be explained simply by their different solubility parameters.

Table 2. Selected solubility parameters of polymers and alcohols

It has been reported, that hydrolysis proceeds faster for aliphatic polyesters than for aromatic polyesters due to the higher steric hindrance of the latter [47]. Although the reaction solvent is different in this case, a related argument could explain the different reactivity exhibited by the two polymers, as it is probable that nucleophilic attack of the alcohol on the carbonyl group is important in this transesterification. Thus it is probable that the steric hindrance caused by the benzene ring in PET is reducing its reactivity towards the alcohols. Similar steric effects have been proved to have a major impact in the reactions between alcohols and esters in solution [48, 49].

It is likely that the higher depolymerisation seen with zinc acetate arises due to the stronger binding of zinc(II) ions to PLA compared to PET. It can be envisaged that the zinc(II) ions bind to the PLA by the formation of a 5-membered chelate ring (Figure 4), which they cannot with PET. In support of this, the reported crystal structures of zinc(II) lactate show such a structure [50-52]. Such a binding is expected to improve the catalysis of the transesterification [53, 54].

Figure 4. Formation of zinc lactate in the catalysed methanolysis of methyl lactate or PLA

Another factor for the different reactivity of PLA and PET is related to the amorphous content of their structures. It is reported that depolymerization processes of polymers

are initiated or easier in the amorphous region [55]. In addition, it has been discussed that PLA plastics tend to have higher content of mobile amorphous regions in their structure than PET [56]. Therefore, PLA depolymerization could be easier than PET due to the higher mobile amorphous content present in the PLA structure.

^1H and ^{13}C NMR spectra of the products obtained from the ethanolysis and methanolysis confirmed the production of ethyl lactate and methyl lactate respectively (appendix 2 and 3). The spectrum of methyl lactate showed only water as a minor impurity (most likely from the hygroscopic d_6 -DMSO). However even after drying under vacuum, the product of the ethanolysis showed ethanol as an impurity (the ratio of ethanol to ethyl lactate was 3:1 and the yield of ethyl lactate was calculated considering this). Difficulties in producing pure ethyl lactate have been discussed by Zhou et al [11]. So it seems that forming methyl lactate from PLA is a simpler route practically.

Better yields are achieved in the catalysed methanolysis than in the ethanolysis even though the reaction temperature is higher in the latter reaction. A probable reason is that methanol is a better nucleophile than ethanol due to its smaller size and higher dielectric constant so its reaction with the carbonyl is easier. Additionally, the uncatalysed reaction in ethanol led to unreacted chips of PLA, while the uncatalysed reaction in methanol formed a homogeneous gel that rapidly hardened to a crystalline material upon cooling to room temperature. This indicates that the uncatalysed alcoholysis of PLA involves a better interaction with methanol than ethanol even though in both cases there was no major conversion to monomers. Again the smaller molecule of methanol (compared to ethanol) is more able to penetrate the amorphous parts of the PLA. However, efficient degradation would not be possible without the presence of the catalyst. A similar mechanism was reported for the methanolysis of PET under supercritical conditions [33]. The formation of a crystalline residue was reported in the hydrolysis of PLA at temperatures below its melting temperature (i.e. 160°C) [17], the explanation given was that the reaction degraded the amorphous part of the polymer.

The ^1H NMR and ^{13}C NMR spectra of the residue from the uncatalysed methanolysis were performed to study the nature of the crystalline material obtained (appendix 4). The ^1H and the ^{13}C NMR spectra are in good agreement with the expected values for PLA [57]. However, an extra signal is observed in both spectra (2.1 ppm in ^1H NMR

and 30.1 ppm in ^{13}C NMR), which corresponds to a methyl acting as a chain end (i.e. polymer- COOCH_3). For further clarification, IR spectra of pure PLA and the PLA obtained after the uncatalysed methanolysis were compared (Appendix 5). They appear as very similar compounds however an extra peak in the region of sp^3 C-H stretching is present in the residual PLA after uncatalysed methanolysis supporting the presence of a methyl ester at the end of the chain.

The surface of the unconverted PLA was analyzed and compared to the residual chips recovered after the uncatalysed ethanolysis and methanolysis (Figure 5). The pores observed in figure 5c compared to figure 5b indicate some surface degradation of PLA when methanol is the solvent. This agrees with the higher yield of lactate ester in the catalysed methanolysis compared to the catalysed ethanolysis (Table 1).

Figure 5. FE-SEM images of (a) waste PLA, (b) residual PLA after uncatalysed ethanolysis and (c) residual PLA after uncatalysed methanolysis.

The IR spectrum of the powder obtained after the catalysed methanolysis of PLA (Appendix 6a) shows two peaks in the carbonyl region. The peak at 1752 cm^{-1} is attributed to unconverted PLA while the peak at 1600 cm^{-1} indicates a carboxylate group. It is possible that in the powder there is a mix of unreacted PLA and zinc acetate that is bound on its surface. However, the carbonyl frequency of zinc acetate is lower at 1553 cm^{-1} (Appendix 6b) which suggests that another carboxylate is formed during the reaction, i.e. lactate. Figure 4 shows the formation of the chelate complex of zinc lactate from methyl lactate and zinc acetate and the peak at 1600 cm^{-1} agrees well with literature values for a metal lactate [58]. In addition, methyl acetate produced in the reaction in figure 4 has a boiling point of only 67°C and so would be evaporated during the purification which explains why it is not seen in the NMR spectrum of the methyl lactate obtained (Appendix 3).

As it seems that the solid obtained after the catalysed methanolysis is not pure unconverted PLA and the extent of degradation was higher than what was calculated from the simple weight of the recovered solid. Unfortunately precise quantification of

the remaining PLA is not possible from only the IR spectra analysis. This hypothesis suggests the reported yield of monomer (Table 1) can only be a guide to the extent of depolymerization as a fraction of it would have reacted with the catalyst and therefore less monomer was collected. Also as the zinc catalyst seems to react with the methyl lactate future work should involve recovery of the zinc catalyst after the reaction to avoid this happening.

3.3 Catalysed methanolysis of mixed PLA and PET

Methanolysis catalysed by zinc acetate of a mixture of PLA and PET (1 gram each) was performed to show the selectivity for the reaction of PLA. A yield of 65% of methyl lactate was achieved and the solid fraction consisted of 1gram of plastic chips and 0.1g of powder. The IR spectrum of the plastic chips corresponds to unreacted PET. It is noteworthy that the presence of PET in the reaction does not seem to largely affect the yield of methyl lactate. In addition, the powder obtained had a similar weight to the powder collected when the reaction was conducted with only PLA. Considering that the amount of zinc acetate was the same in both cases while the PLA was halved in the mixed waste methanolysis this supports the hypothesis of the reaction between the catalyst and the monomer.

4. Conclusions

The glycolysis of postconsumer PET waste was evaluated with catalysts of zinc acetate, zinc stearate and zinc sulfate, confirming that zinc acetate was the most soluble and effective. Solvolysis of PLA in methanol or ethanol in a mild process and catalysed by zinc acetate successfully converts PLA into valuable feedstock chemicals namely lactate esters [11]. Additionally, the yield from the methanolysis was higher than ethanolysis. On the other hand, PET showed no reactivity in methanolysis or ethanolysis under the same conditions indicating its lower degradability.

By taking advantage of the different reactivity to alcoholysis of the two plastics a selective depolymerization process has been developed. It not only represents a promising process for the chemical recycling of PLA but also for the treatment of mixed PLA and PET as the separation is facilitated via the reaction sequence converting PLA to a liquid monomer from which the unreacted PET can be filtered. Such a process to selectively convert and then separate the plastics is presented in figure 6.

A referee quite reasonably asked whether the PLA and PET would be better separated first? Although this is an option sorting does have limitations so that it may not always be effective. For example a recent report by WRAP [59] noted that some PET packaging such as black crystalline PET, laminated trays and cups were rejected by Near Infra Red sorting and therefore the study reported here of alternative waste solutions is important to offer options for future developments in the packaging industry and hence the waste arising from it. Similarly, such a stepwise recycling process should also be studied with block-copolymers of PLA and PET [60].

Figure 6. Stepwise process to both recycle and separate PLA and PET mixed waste

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Appendix 1a The characterization of the glycolysis products, NMR spectra of the monomer of Bis(hydroxyethyl) terephthalate (BHET)

Appendix 1b The characterization of the glycolysis products, chromatograms.

- i. Glycolysed product without purification
- ii. BHET obtained after purification
- iii. Dimer obtained after purification

Appendix 2: (a) ^1H NMR and (b) ^{13}C NMR spectra of ethyl lactate

Appendix 3: (a) ^1H NMR and (b) ^{13}C NMR spectra of methyl lactate

Appendix 4: (a) ^1H NMR and (b) ^{13}C NMR spectra of the unconverted PLA after uncatalysed methanolysis.

Poly lactic acid: δ_{H} (400 MHz, $(\text{CD}_3)_2\text{SO}$) 1.45 (3H, d, CH_3), 5.199 (1H, q, CH); δ_{C} (400 MHz, $(\text{CD}_3)_2\text{SO}$) 16.45 (CH_3), 68.66 (CH), 169.18 (C=O)

Appendix 5: FTIR spectra of (a) waste PLA and (b) PLA after uncatalysed methanolysis.

Appendix 6: IR spectra of (a) the solid obtained after catalysed methanolysis of PLA and (b) zinc acetate.

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Figure 1. Glycolysis of PET

Figure 2. FE-SEM images of (a) post consumer waste PET, (b) recovered PET after uncatalysed methanolysis and (c) recovered PET after zinc acetate catalysed methanolysis.

Figure 3. Alcoholysis of PLA

Figure 4. Formation of zinc lactate in the catalysed methanolysis of methyl lactate or PLA

Figure 5. FE-SEM images of (a) waste PLA, (b) residual PLA after uncatalysed ethanolysis and (c) residual PLA after uncatalysed methanolysis.

Figure 6. Stepwise process to both recycle and separate PLA and PET mixed waste