Title
A hybrid chemical-biological approach can upcycle mixed plastic waste with reduced cost and carbon footprint

Journal
One Earth, 6(11)

ISSN
2590-3330

Authors
Dou, Chang
Choudhary, Hemant
Wang, Zilong
et al.

Publication Date
2023-11-01

DOI
10.1016/j.oneear.2023.10.015

A hybrid chemical-biological approach can upcycle mixed plastic waste with reduced cost and carbon footprint

Chang Dou[1,2], Hemant Choudhary[3,4,*], Zilong Wang[3,5,6], Nawa R. Baral[2,3], Mood Mohan[3,4], Rolin A. Aguilar[1,7], Shenyue Huang[1,5], Alexander Holiday[8], D. Rey Banatao[8], Seema Singh[3,4], Corinne D. Scown[2,3,9,10], Jay D. Keasling[2,3,5,11,12,13], Blake A. Simmons[2,3], Ning Sun[1,2,14,*]

[1] Advanced Biofuels and Bioproducts Process Demonstration Unit, Lawrence Berkeley National Laboratory, Emeryville, CA, 94608, USA

[2] Biological Systems and Engineering Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA

[3] Joint BioEnergy Institute, Emeryville, CA, 94608, USA

[4] Department of Bioresource and Environmental Security, Sandia National Laboratories, Livermore, CA, 94551, USA

[5] Department of Chemical & Biomolecular Engineering, University of California, Berkeley, CA, 94720, USA

[6] QB3 Institute, University of California, Berkeley, CA 94720, USA

[7] Department of Chemistry, University of California, Berkeley, CA, 94720, USA

[8] X, The Moonshot Factory, Mountain View, CA, 94043, USA

[9] Energy Analysis & Environmental Impacts Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA

[10] Department of Bioengineering, University of California, Berkeley, CA 94720, USA

[11] Energy & Biosciences Institute, Berkeley, CA, 94720, USA

[12] Center for Synthetic Biochemistry, Institute for Synthetic Biology, Shenzhen Institutes of Advanced Technologies, Shenzhen 518055, China

[13] Novo Nordisk Foundation Center for Biosustainability, Technical University of Denmark, Kongens Lyngby, Denmark.

[14] Lead Contact:

[*] Correspondence: hchoudh@sandia.gov (H.C.), nsun@lbl.gov (N.S.)

Summary

Derived from renewable feedstocks, such as biomass, polylactic acid (PLA) is considered a more environmentally-friendly plastic than conventional petroleum-based polyethylene terephthalate (PET). However, PLA must still be recycled and its growing popularity and mixture with PET plastics at the disposal stage poses a cross-contamination threat in existing recycling facilities and results in low-value and low-quality recycled products. Hybrid upcycling has been proposed as a promising sustainable solution for mixed plastic waste; but its techno-economic and lifecycle environmental performance remain understudied. Here we propose a hybrid upcycling approach using a biocompatible ionic liquid (IL) to first chemically depolymerize plastics, then convert the depolymerized stream via biological upgrading with no extra separation. We show that over 95% of mixed PET/PLA was depolymerized into their respective monomers, which then served as the sole carbon source for the growth of *Pseudomonas putida*, enabling the conversion of the depolymerized plastics into biodegradable polyhydroxyalkanoates (PHA). In comparison to conventional commercial PHA, the estimated optimal production cost and carbon footprint are reduced by 62% and 29%, respectively.

Keywords: polylactic acid (PLA), polyethylene terephthalate (PET), ionic liquid (IL), cholinium lysinate, depolymerization, waste recycling, *Pseudomonas Putida*, Polyhydroxyalkanoates (PHA), techno-economic analysis, life-cycle assessment

Introduction

Plastics are ubiquitous in modern life. Due to their superior functional properties and low cost, the application of plastics has been expanding in almost all aspects of our life. Global plastic production has continually increased over the past half-century, totaling 391 million metric tons in 2021.[1] Due to the limited end-of-life solutions, most of these plastics end up in landfills or are leaked into the environment, contributing to the accumulation of microplastics and threatening oceans and wildlife.[2,3] Beyond environmental implications, the current “take-make-waste” linear plastic system consumes fossil fuels and contributes to greenhouse gas (GHG) emissions.[4] A 2016 study found that nearly 6% of the world’s oil production is used to produce plastics; that number is expected to expand to 20% by 2050, attributing to 15% of the global annual carbon budget - a significant level that should be taken seriously.[5] Cost-effective and energy-efficient processes for recycling or valorizing plastic waste streams are desperately needed to reduce the use of fossil fuel and divert plastic waste from landfills and the environment.[6]

A key challenge in recycling plastics is the commingling of different plastics in the recycling stream. Cross-contamination has significant ramifications including added burdens to the sorting process, decreased value of the recycled plastics, and compromised properties of recycled polymers. Polyethylene terephthalate (PET) is the most prevalent polyester and ranked as the most recycled plastic in the US.[7] Another polyester, polylactic acid (PLA) is a desirable plastic to consumers as it is bio-based and degradable, but still needs to be recycled. With the rapid expansion of the PLA market, there has been an increasing concern that more PLA will be present as contaminants that interfere to the existing PET recycling processes.[8,9] In particular, similar appearances, chemical functional groups, and applications of PET and PLA lead to new waste stream separation challenges in plastic recycling facilities including mechanical recycling of

PET.[8,10] While state-of-the-art sorting technologies (e.g. near infrared light) can distinguish between polymers such as PLA and PET, some cross-contamination remains unavoidable due to errors in mechanical sortation, especially given the vast volumes of waste processed in modern materials recovery facilities (MRFs).[9,11] Furthermore, the viability of incorporating a new plastic variant into MRFs is hindered by the expense linked to acquiring dedicated optical sorters and bunkers.[8,11] .

Chemical recycling has been highlighted as an alternative route to conventional mechanical recycling in dealing with cross-contaminated plastics.[6,12,13] The depolymerized products, usually monomeric precursors of plastics, can be separated and resynthesized into new polymers that maintain properties comparable to virgin plastics. Most chemical recycling of plastics involves catalysts such as metal-based catalysts and organocatalysts.[14–19] For instance, Pt, Sn, Ru, Ni, Ir, Al-based catalysts have been commonly employed in either plastic degradation or modification.[14–17] In a recent study, Sullivan et al. demonstrated a chemical process that employed Co(II) and Mn(II) co-catalysts in the autoxidation of mixed plastics.[19] After precipitation of Co/Mn catalysts as respective hydroxides, the oxidized stream was biologically valorized into bioproducts. However, metal-based catalysts can suffer from abundance scarcity or leaching of metallic sites into the solution increasing complexity in downstream processing including separation or microbial conversion.[19–21] Organocatalysts are considered as promising “green” substitutes to traditional metal-based catalysts.[18] Among the organocatalysts, ionic liquids (ILs, organic salts with melting point below 100 ºC) have proven to be catalytically efficient and are able to achieve high depolymerization and product yield for different types of plastics.[18] One of the most important characteristics of ILs is their tunable properties, a function of the specific combinations of cations and anions, making them task-specific.[22,23]

While many studies have utilized ILs to depolymerize PET and PLA, the majority of these depolymerization efforts were restricted to applying either pure ILs or ILs in organic solvents on individual polymers.[24–28] There has been relatively little emphasis on hydrolytic depolymerization of mixed plastics using ILs. Water is a good solvent for chemical reaction in terms of cost, process safety, and environmental impact. Applying water as the solvent also allows the potential biological use of depolymerized PET and PLA *via* microorganisms, as microbes have shown capabilities to consume terephthalate and lactic acid as the carbon sources.[29–34] A hybrid process that integrates bio-compatible chemical depolymerization and biological conversion without the need for initial chemical reagent separations would not only demonstrate an avenue to upcycle the mixed PET and PLA, but also validate the hybrid conversion approach as a solution for organic waste management on a broader scale. However, research on IL-based hybrid upcycling approach for mixed PLA and PET waste, as well as a comprehensive understanding of the techno-economic feasibility and lifecycle environmental performance, remains limited.

Here we bridge the knowledge gap by demonstrating the hybrid conversion process, where the biological conversion does not require separation of chemical reagents used in the chemical depolymerization step. Through investigating hydrolysis of PET and PLA using different ILs in water, we identified cholinium lysinate [Ch][Lys] with the highest depolymerization efficiency and monomeric product yields. This observation agreed with the results of molecular dynamic simulations, where [Ch][Lys] showed stronger polymer interaction over other studied ILs. Over 95% of theoretical monomer yields were achieved when applying [Ch][Lys] in hydrolytic depolymerization of PET and PLA mixture. *Pseudomonas putida* showed capability to utilize IL-depolymerized PET/PLA mixture as the carbon sources without additional feed of glucose. The use of aqueous biocompatible ILs eliminates the need for any separation steps before bioconversion. Based on that, we conceptualized a one-pot process to upcycle mixed PET and PLA into polyhydroxyalkanoates (PHA) for techno-economic analysis (TEA) and life-cycle analysis (LCA). The optimal production cost and carbon footprint of PHA are estimated to reach \$0.95/kg and 1.7 kgCO_2e/kg, respectively, representing a reduction of 62% and 29% compared to commercially produced PHA. Overall, our findings suggest that the hybrid upcycling approach holds promise as an economically and environmentally sustainable solution for closing the life-cycle loop of cross-contaminated plastic wastes.

Results and Discussion

Screening of ILs in depolymerization of PET and PLA

ILs have been employed to depolymerize individual polyesters such as PET and PLA.[18,25] Most of them are conventional imidazolium-based, including the ones that contain halometallates. With the progress in the IL research, economic and biocompatible cholinium-based ILs have attracted high interest.[35,36] Building upon this, the current study explored two cholinium-based ILs, cholinium lysinate ([Ch][Lys]) and cholinium phosphate ($[Ch]_3[Phos]$), along with two imidazolium-based ILs, 1-ethyl-3-methylimidazolium acetate ($[C_2C_1im][Ac]$) and 1-ethyl-3-methylimidazolium chloride ($[C_2C_1im]Cl$). The reaction temperatures (180 °C for PET and 130 °C for PLA) were set below the melting point of the employed PET (235 °C) and PLA (153 °C), as the main purpose is to compare the catalytic efficiency of different ILs in polyester depolymerization. Continuous stirring was employed throughout the depolymerization reaction process (details in the experimental procedures). Figure S1A demonstrates the appearance before and after reaction.

Figure 1 shows the depolymerization efficiency and product yield of PET and PLA using different aqueous ILs. The depolymerization efficiency of PET and PLA ranged widely across different ILs. Both polymers shared the same trend in response to IL depolymerization with the cholinium-based ILs demonstrating higher catalytic activity compared to the imidazolium-based ILs after 2 h reaction. In particular, [Ch][Lys] had the highest depolymerization efficiency – 54.7% and 40.2% for PET and PLA, respectively. Terephthalic acid (TPA) and lactic acid (LA) were obtained as the degradation products of PET and PLA, respectively. Consistent with the depolymerization efficiency, the product yield followed the same trend in descending order of [Ch][Lys] > $[Ch]_3$[Phos] > $[C_2C_1im]$[Cl] > $[C_2C_1im]$[Ac]. When using [Ch][Lys] as the catalyst, a maximum yield of 56.3% and 39.3% was achieved for TPA and LA, respectively. Conversely, depolymerization and product yield were negligible in the presence of $[C_2C_1im]$[Ac], indicating little IL catalytic activity under the given reaction condition. Note that both chloride and acetate salts of $[C_2C_1im]^+$-cation exhibited limited hydrolysis of both polyesters in contrast to previous report on hydrolysis of PLA using 1-butyl-3-methylimidazolium ($[C_4C_1im]^+$) ILs, where $[C_4C_1im]$[Ac] outperformed all other anion combination.[28] The difference in activity is supposedly due to the shorter side-chain of IL cation and higher amount of water in the present study. It should be noted that water, even in small amounts, has been known to influence IL physicochemical properties under certain operating conditions,[37] and this could explain the differences between the two studies.

Hydrolytic depolymerization of PET and PLA involves chain scission of ester linkages, where a carboxyl end group is released. PET and PLA depolymerization can occur under base catalysis, as the hydroxide ion deprotonates the oxygen atom of water and increases its nucleophilicity in attacking the ester groups. The pH of the reaction solution before and after depolymerization reaction (Table S1) aligns with the depolymerization efficiency across ILs, where cholinium-based ILs demonstrated higher pH over imidazolium-based ILs. To evaluate whether the pH influenced by IL was the major driving force of PET and PLA depolymerization, a set of control experiments were conducted using only water and alkaline water as the solvent (Figure 1). For the alkaline water, 0.006 M of NaOH was added to adjust the pH to mimic that of employed aqueous [Ch][Lys] (with pH 11.8). Surprisingly, the pH adjusted reaction system showed no difference versus the water control; both PET and PLA were barely depolymerized with negligible product yields. Our findings were different from some previous studies where alkaline conditions formed by 0.6-1.3 M NaOH (pH $\geq$ 13) were found to facilitate the depolymerization of PET and PLA.[38,39] This is likely due to the relatively lower NaOH molarity (and lower pH) in our control, as the PET hydrolysis has been shown to be positively correlated with NaOH concentration.[40] These control experiments, along with literature reports, strongly indicate that PET and PLA hydrolysis under the applied conditions require either higher concentrations of hydroxyl ions or possible intermolecular interactions with IL to enhance the hydrolytic cleavage. Understanding the intermolecular interactions between IL and polymer would be thus necessary.

Water-soluble fractions were analyzed to understand the depolymerization of plastics under the tested conditions. Molecular weight distribution profiles of the depolymerized stream from each polymer corroborate the observed product yield (Figure S2). Based on the calibration standards, [Ch][Lys]-based reaction solutions had signals on the far right (indicating the smallest MW fraction) while all other IL-based reaction mixtures showed presence of intermediate MW (less than 1500 Da) (Figures S2A-S2B). Interestingly, large MW fractions were obtained with alkaline water (that is in presence of NaOH) only but did not afford any notable signals corresponding to mono-, di-, or oligomers (Figures S2B-S2C). It should be stressed that PET glycolysis dominates the literature compared to hydrolysis - where the GPC of the reaction mixture was not discussed in literature.

Molecular dynamics simulated polyester-IL interactions

To understand the effect of IL/water mixtures and water on the depolymerization of polyesters, molecular dynamics (MD) simulations were performed using PLA as a model substrate (Figure S3). MD simulations are a widely used computational method for examining the interactions between molecules in binary solutions and were employed in this study to explore the depolymerization mechanism of polyesters (Table S2).

To obtain the structural arrangements and microscopic interactions, radial distribution functions (*g(r)* or RDFs) between PLA and the investigated solvent systems were calculated. The RDF (*g(r)*) is defined as the probability of identifying a molecule at a distance of 'r' from the reference molecule.[41] The RDF plots are a powerful tool for analyzing the structural and explicit interactions between solute and solvent(s). In general, *g(r)* intensity is related to the strength of contact probability between the solute and solvent. In this study, the RDF was plotted between the oxygen (O) atom of the PLA molecule and the anion/cation of IL and water, and the results are depicted in Figure 2A-B. The first and largest solvation shell in Figure 2A exhibited at a distance of 2.65 Å between the PLA and cation of $[Ch]_3[Phos]$ and [Ch][Lys] with a *g(r)* intensity of 5 and 10, respectively, indicating that cholinium cation forms regular and definite coordination spheres around PLA at a distance of 2.65 Å, and the RDF plot was primarily dominated by the first coordination shell. While, for $[C_2C_1im][Ac]$/water, $[C_2C_1im]Cl$/water, and water systems, the RDF peak was attained at a distance of 2.2-2.35 Å with low *g(r)* value~1. These results agree with the experimental results, that is, [Ch][Lys] has about two and ten times stronger contact probability with PLA compared to $[Ch]_3[Phos]$ and imidazolium-based IL systems, respectively. On the other hand, the RDF peak between PLA and anions of ILs obtained at a relatively higher distance with a lower *g(r)* value (Figure 2B), implying that cation may have a stronger contact probability with PLA than the anions in ILs. Further, the MD simulated non-bonded interaction energies (i.e., electrostatic and van der Waal (vdW) interactions) for PLA-IL systems were also computed and supported depolymerization efficiency using [Ch][Lys] (Figure S4). It is important to highlight that the stronger interactions between PLA-cation and PLA-anion were established in [Ch][Lys], thus the enhanced solvation of PLA with both $[Ch]^+$ and $[Lys]^-$ ions compared to other cation and anions in this study (Figure S4).

Furthermore, the RDF and number of hydrogen bonds (HBs) between water and anion of ILs have been calculated, and the results are shown in Figure 2C-D. The RDF peaks between the anions of IL and water were obtained at a distance of 2.65-2.85 Å with a *g(r)* intensity of ~2 to 5. Lysinate anion had shown lowest *g(r)* peak intensity, implying that the hydration (thereby the interaction with water) of lysinate anion was weaker compared to phosphate, acetate, and chloride anions (Figure 2C). This is further evidenced by computing the number of HBs between water and anions of IL (Figure 2D). From Figure 2D, the number of HBs between lysinate and water was relatively lower than other anions, validating the weaker hydration of $[Lys]^-$ anion. In other words, anions other than lysinate (i.e. phosphate, acetate, and chloride) are heavily surrounded by water molecules, leading to weaker contact probability with PLA and hence lower depolymerization efficiency.

In addition to MD simulations, Hansen solubility parameter (HSP) was also taken into consideration to understand why [Ch][Lys] outperformed other ILs studied here. HSP is a critical property of a molecular species that analyzes polarity and quantifies the "like seeks like" principle. For instance, a given solute (e.g., PET or PLA) is considered to be highly miscible/soluble in a given solvent (ILs in the present case), if the HSP values of the solute and the solvent are similar. The HSP values of PET, PLA, ILs, and water are presented in Table S3. The total HSPs (δ_t) of PET and PLA are 21.66 $MPa^{1/2}$ and 20.87 $MPa^{1/2}$, respectively. On the other hand, the solubility parameter of [Ch][Lys] and $[Ch]_3$[Phos] are 26.30 $MPa^{1/2}$, and 28.25 $MPa^{1/2}$ which are close to the PET and PLA's HSP values, suggesting higher miscibility of these polyesters in [Ch][Lys] and $[Ch]_3$[Phos]. In contrast, the solubility parameters of $[C_2C_1im]$[Ac], $[C_2C_1im]$Cl, and water are much higher than PET and PLA, implying that $[C_2C_1im]$[Ac], $[C_2C_1im]$Cl, and water have weaker affinity for these polyesters resulting in a lower depolymerization and conversion rates. Accordingly, it can be established that polyester depolymerization is largely influenced and governed by the choice of ion combination in any given IL. The order of solvent HSP values that is close to polyesters is as follows: [Ch][Lys] > $[Ch]_3$[Phos] > $[C_2C_1im]$Cl > $[C_2C_1im]$[Ac] > water, which is in line with the experimental observations.

Depolymerization of PET/PLA mixtures using [Ch][Lys]

As discussed previously, the current waste management facilities will not completely eliminate the PLA contamination when sorting PET for recycling. With the increasing prevalence of PLA, it is likely that more PLA will end up in the PET recycling stream. Herein, we prepared a PET/PLA mixture by combining PET and PLA at 1:1 mass ratio and investigated the IL-catalyzed hydrolysis of these polyester mixtures. Given its high catalytic activity, [Ch][Lys] was selected as the IL in the reaction. It should be emphasized that [Ch][Lys] is a favorable choice not only because of its high depolymerization efficiency but also because it is economic, biocompatible, less toxic, and environmentally friendly.[35,42,43]

A range of IL loading (10-90 wt% [Ch][Lys]) was applied to maximize depolymerization efficiency and product yields of the PET/PLA mixture. The initial set of experiments was carried out at 160 °C for two hours. As Figure 3A shows, the depolymerization efficiency varied across different IL loadings. The depolymerization efficiency started low (50.8%) at 10 wt% IL loading and increased with the increasing IL loading, reaching up to 99.5% at 60 wt% IL loading. The product yields of TPA and LA followed a similar trend to depolymerization and peaked at 45 wt% IL loading, where the TPA and LA yields reached 79.6% and 93.8%, respectively. Interestingly, increasing the IL loading beyond 45 wt% did not show a benefit. While the depolymerization remained high at 60 wt% IL loading, the product yields were lower than that of 45 wt% IL loading (77.2% for TPA and 53.1% for LA). More surprisingly, at 90 wt% IL loading, that is pure IL (and no water), the depolymerization efficiency decreased to 91.5%. Meanwhile, the TPA yield turned to be negligible (1.5%) and the LA yield was merely 40.9%. The reasons are manifold. On one hand, the major hydrolytic reaction was found to occur on the external surface of polyester where the solubility is the reaction rate determining step.[27,40] ILs could dissolve PET and PLA to facilitate depolymerization at higher IL loading.[36,44,45] On the other hand, the lack of water likely impeded hydrolytic reaction and resulted in incomplete depolymerization. Both the product yields and the gel permeation chromatography (GPC) results provide clues to this explanation. At higher IL loadings of 60 and 90 wt%, GPC revealed partial depolymerization into monomers and oligomers along with partial (low molecular weight) polymer dissolution (Figure S2D). In this scenario, [Ch][Lys] was efficient in dissolving these polyesters at 160 °C (Figure S1B); whereas, in the absence of water, only a partial polyester depolymerization (i.e. hydrolysis) could be afforded.