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Review

Use of Deep Eutectic Solvents in Plastic Depolymerization

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Abstract: Polymeric materials are widely used in every human endeavor (bottles, clothes, containers, toys, tools, etc.) due to their unique properties of chemical and mechanical resistance. They are, however, almost non-biodegradable, and their chemical recycling into monomers is difficult and costly, thereby allowing their accumulation into the environment. This review highlights recent advances in the use of deep eutectic solvents (DESs) as catalysts and/or green solvents in plastics degradation, with the aim of designing greener processes for polymers' chemical recycling, by reusing their monomers. These greener processes, in combination with other catalytic approaches, are aimed at introducing plastics as feedstock into the synthesis of other materials, according to the circular economy principles.

Keywords: deep eutectic solvents (DES); chemical recycling of PET, PU, PEF, PC, PLA; PolyEthylene Terephthalate (PET) plastic depolymerization; terephthalic acid (TPA); bis(2-hydroxyethyl)terephthalic acid (BHET); mono(2-hydroxyethyl)terephthalic acid (MHET); microwave irradiation (MW)

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1. Introduction

Due to their low costs and their unique properties of chemical and mechanical resistance, polymeric materials are widely used in all kinds of products in our daily life, such as bottles, clothes, containers, toys, tools, etc. Most of them, however, are almost completely non-biodegradable and have gradually accumulated into the environment with a consequent loss of energy/economic resources, combined with a cascade of environmental problems.

Polymers reuse is difficult and impractical often because of their contamination. When they are not correctly recycled and valued, most polymeric materials are destined to waste-to-energy plants for the production of energy/heat or end up in landfills, representing a global problem that does not seem to have adequate solutions to date. Their chemical recycling is a possible way to obtain fine chemicals or products with high added value (monomers, other polymers, etc.). There is, therefore, a strong need to develop new green technologies for the recovery, treatment, and chemical recycling of polymers derived from fossil hydrocarbons. According to the principles of the circular economy, these materials could be reused as new raw materials for the production of new products with high-added value [1].

In recent years, many studies have been carried out on the sustainable degradation of traditionally non-biodegradable plastics by using various catalysts [2–6] to reduce reaction time for polymer recycling, also via green approaches [7,8].

Ultrasounds (US), microwave irradiation (MW), and various catalysts have been used with volatile organic compounds (VOCs), which are able to dissolve polymers and oligomers. However, VOCs are flammable, toxic and often exhibit safety/environmental issues.

Among green media for organic processes, ionic liquids (ILs) have been introduced to replace conventional organic solvents, thanks to their ionic nature and their low volatility and flammability [9–12]. Their use in chemistry is characterized by several pros and cons. They are a combination of organic heterocyclic cations and organic or inorganic anions, often obtained through several synthetic steps and in the presence of volatile organic solvents, with a virtually unlimited number of possible combinations. The synthesis of ILs can also require long reaction times and the formation of by-products and waste. In addition, they are still too expensive for general use or large-scale operations since they need special procedures for preparation, purification, and recycling.

Moreover, they do not solve the main environmental problems of plastics' chemical recycling because of their low biodegradability and long-term accumulation [13,14].

In recent decades, a new generation of ionic solvents has emerged, the so-called deep eutectic solvents (DESs) [15,16], that combine most of the advantages of ILs (liquids at room temperature, low vapor pressure, good solvent capacity) with fewer disadvantages: they are easy to prepare, have a low cost, are less toxic, more biodegradable and biocompatible, thereby playing an important role in the field of sustainable chemistry [17].

The last advances in the use of DESs as catalysts and/or green solvents in plastics degradation are herein reported [18,19], with the perspective to design the future greener polymer treatment processes, also in combination with other catalytic approaches, toward refinery models that aimed at re-introducing plastics into the circular economy.

2. Deep Eutectic Solvents (DESs)

According to the original classification introduced by Abbott [20], deep eutectic solvents (DESs) are ternary or binary mixtures, liquid at room temperature, containing at least one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA) (e.g., Lewis or Brønsted acids and bases, anionic and/or cationic species) mixed in a well-defined molar ratio, with a melting point much lower than that of an ideal eutectic mixture, due to strong intermolecular interactions such as hydrogen-bond networks.

Depending on their chemical composition, DESs are classified into different types.

In most cases, HBA is a quaternary ammonium, phosphonium, or sulfonium salt with a halide counter ion, typically a Lewis base capable of interacting with a hydrogen bond donor (HBD). One of the widespread ammonium salts (HBA) is choline chloride (ChCl), also known as vitamin B_4, an essential non-toxic and biodegradable micronutrient for humans, produced on a million tons per year as a chicken feed additive and with many other applications [20].

A greater structural variability can be obtained for DESs composed of quaternary ammonium salts and HBDs such as alcohols, polyols, amino acids, or amides also of natural origin. A different class of eutectic mixtures can be obtained by mixing different Lewis acids, such as metal halides of aluminum, zinc, tin, etc., with different hydrogen bond donors (urea, glycerol, etc.).

Their properties and polarity are tunable through the combination of their components with hydrophilic or hydrophobic characteristics.

When DES components are from renewable natural sources (primary metabolites, sugars, amino alcohols and natural polyols, carboxylic acids, amino acids, vitamins, etc.), they are called natural deep eutectic solvents (NADES), and their formation in plants from primary metabolites has been suggested to be responsible for the transport and solubilization of macromolecules and other natural compounds [21–23].

Several reviews and book chapters have already been published in recent years on DESs chemistry [24,25] since they find wide applications not only in new metal-, bio-, and organocatalyzed synthetic methodologies but also in the separation [26–28] and materials science [29], and in the design of new green processes to reuse or reduce greenhouse gas emissions [30].

By fulfilling some Green Chemistry principles (2, 5, and 6), DESs represent an attractive green alternative to conventional solvolysis of plastic materials, as they (a) act as solvents and catalysts, and they provide nucleophilic sites for solvolysis and (b) allow to design biocompatible and/or environmentally friendly synthetic methods. The versatility of DESs, in combination with the use of milder reaction conditions, also allows a more efficient depolymerization process by decreasing the energy input required for the progress of the reaction.

3. Deep Eutectic Solvents (DESs) as Solvents and Catalyst in PET Depolymerization

Polyethylene terephthalate (PET) is a polyester widely used, e.g., for beverage bottles, and textile fabrics, thanks to its chemical and mechanical properties (remarkable impermeability to water and gas, chemical and mechanical resistance, and transparency).

Various solvents can be used for PET chemical recycling and depolymerization into different monomers, thanks to the cleavage of ester groups by solvolysis (hydrolysis, aminolysis, alcoholysis) [18,31–36].

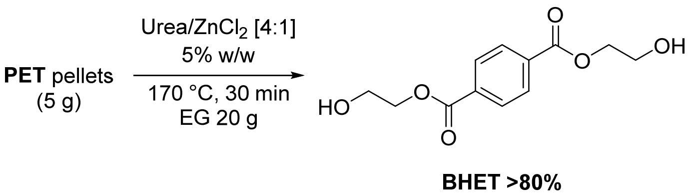
Water, glycols, methanol, and amines have already been used for PET transformation into high-value products such as terephthalic acid (TPA), bis(2-hydroxyethyl)terephthalic acid (BHET), mono(2-hydroxyethyl)terephthalic acid (MHET), phenylenediamines, etc.

However, these reactions produce PET monomers with slow reaction rates; the procedure requires high energy and huge volumes of solvents, jointly with complex and expensive purification processes that can hardly be transferred to an industrial scale. Depending on their nature, DESs act as effective solvents and catalysts in PET depolymerization, exhibiting a higher selectivity and faster reactions than ionic liquids or conventional solvolysis, due to the hydrogen bond network favoring the activation of the carbonyl function and thus the nucleophilic attack to the ester moiety [37].

3.1. PET Degradation with Lewis Acids Containing DESs

Lewis acids and bases are compounds that can accept and donate non-bonding electron pairs, respectively. Electron-deficient metals act as Lewis acids when they are capable of binding electron-rich substrates. The presence of metal as an electron pair acceptor in the composition of a DES gives it Lewis acid properties [38], allowing it to act as a catalyst in various organic reactions, including the chemical pre-treatment of recalcitrant polymers such as lignin [39].

DESs containing Lewis acids have been used in different reaction conditions to achieve solvolysis of PET [40]. Wang et al. reported one of the first PET glycolysis by ethylene glycol (EG) in the presence of eutectic mixtures based on urea/$ZnCl_2$ (4:1), urea/$Zn(OAc)_2 \cdot 2H_2O$ and urea/$Mn(OAc)_2 \cdot 4H_2O$ from 12:1 to 6:1 molar ratios (Scheme 1), affording BHET in high yields (up to 80%) after treatment of PET (pellets) at 170 °C for 30 min [37].



Scheme 1. PET depolymerization with $ZnCl_2$-containing DES.

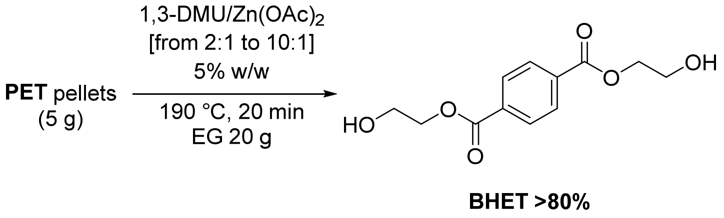
It was found that when the cation of the metal salt was Zn^{2+}, the change of the anions had no effect on the PET degradation.

On the basis of the proposed mechanism, the coordination between Zn^{2+} and the oxygen atom of the PET carbonyl increases the polarization of the C=O bond, while the urea interacts with the EG by lengthening the O-H bond and increasing O-nucleophilicity.

This favors the addition of the EG to the ester carbonyl, and the solvolysis of PET through the involvement of multiple catalytic active sites.

The treatment required 0.25 g of DES for 5 g of starting polymer. However, one of the drawbacks of this approach is the use of large amounts of water (900 mL) for the workup procedure, which needs to be evaporated at a reduced pressure for the recovery of the product by crystallization.

Very similar conditions and work-up procedures were used by Liu B. et al., [41] who reported a high conversion (>99%) of PET by 1,3-dimethylurea (1,3-DMU)/$Zn(OAc)_2$ DES, with a BHET yield >80%, calculated by HPLC on an aqueous solution (Scheme 2).



Scheme 2. PET glycolysis with 1,3-DMU/$Zn(OAc)_2$.

In this case, the possibility of recycling both DES and EG was also investigated: solvent and catalyst were reused for up to 6 cycles for further depolymerization reactions. ICP-MS analyses revealed a 22% decrease in Zn amount over 6 cycles (with respect to the starting zinc acetate) and a 24% of nitrogen decrease compared to the initial 1,3-DMU.

Some experiments also disclosed the catalytic role of DES in the reaction: by comparing the depolymerization carried out in the presence of ketones or amines as catalysts, PET conversion occurred surprisingly only in the presence of amines, demonstrating that the nitrogen atom could be the "catalytic active site" of 1,3-DMU.

Additionally, a shrink-core model was employed to establish a correlation between the temperature and the reduction in the volume of spherical PET particles, as determined through kinetic studies.

The Arrhenius plot (Figure 1) reveals a strong linear correlation ($R^2 > 0.99$) between the volume loss over time at various temperatures. This correlation demonstrates that the optimal reaction conditions were observed at 190 °C, resulting in a complete conversion of PET within 20 min.

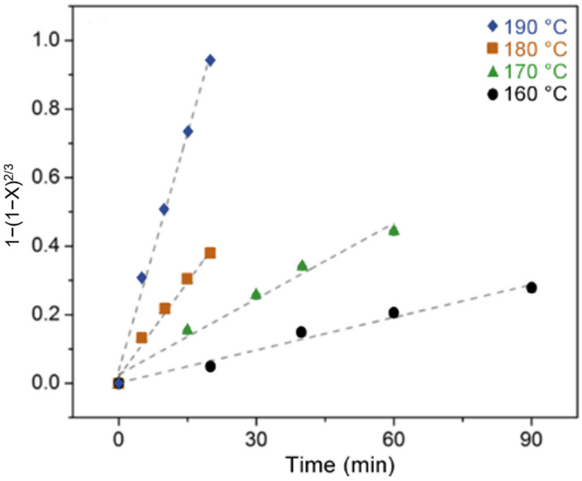
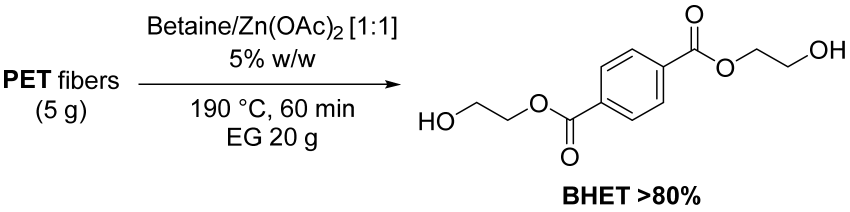


Figure 1. Effect of time and temperature on PET depolymerization by glycolysis. The term $[1 - (1 - X)^{2/3}]$ accounts for the volume loss of PET particles assumed to be spherical. Adapted with permission from Ref. [41]. 2019, American Chemical Society.

Liu L. et al. also investigated the glycolysis of PET with EG, using Betaine/Zn(OAc)$_2$ (1:1, Mp = 146 °C) as a catalyst (Scheme 3), under experimental conditions close to those of previous work (190 °C, 60 min) [42].



Scheme 3. PET glycolysis with betaine/Zn(OAc)$_2$.

The selective degradation was efficient for the separation of polyester from cotton fibers, which were recovered without damage after treatment with EG at 190 °C within 45 min.

The authors found that there was a correlation between the degree of nitrogen substitution of HBA and the catalytic activity of Zn-containing DES by using betaine, choline, and other ethanolamine derivatives (*N*-methylethanolamine, *N*,*N*-dimethylethanolamine) in the PET glycolysis with EG (Figure 2).

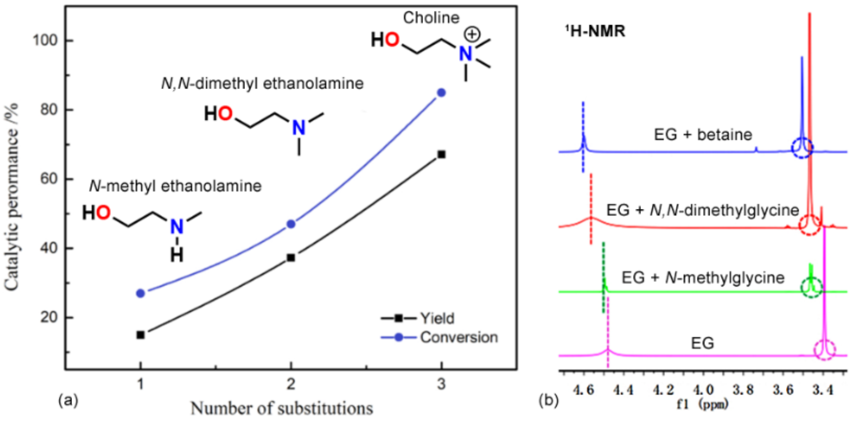
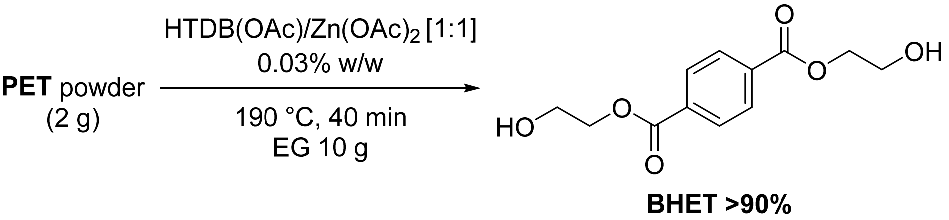


Figure 2. (**a**) Study of the influence of substituent number on catalytic activity of an ammonium salt in PET depolymerization with Zn-containing DES; (**b**) EG and HBDs interactions characterized by ^{1}H-NMR. Adapted with permission from Ref. [42]. 2022, Elsevier.

As a result of the overlapping of NMR spectra, there are different interactions between HBA derivatives and EG: an increasing deshielding of the EG-OH chemical shift was observed in the presence of an increasing number of substituents on the nitrogen atom, with a greater polarization of the O-H bond (higher δ^- on oxygen) in the interaction with an ammonium salt, and consequently, with a greater propensity of EG to give a nucleophilic substitution during the PET transesterification/glycolysis.

A very efficient DES-catalyzed PET glycolysis with EG was reported by Zhu et al. using a very small amount of 1,5,7-triazabicyclo[4.4.0]dec-5-enium acetate [HTBD(OAc)]/Zn(OAc)$_2$ DES as catalyst (0.03% *w*/*w*) for a full conversion in BHET (90% yield) after 40 min at 190 °C (Scheme 4) [43].

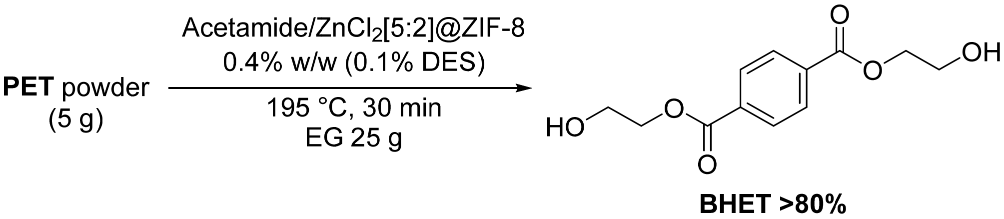


Scheme 4. PET glycolysis with HTBD(OAc)/Zn(OAc)$_2$.

This new eutectic mixture HTBD(OAc)/Zn(OAc)$_2$ was prepared and characterized, and its catalytic activity was studied by using NMR and computational models for Gibbs energy calculations for each reaction step.

This mechanistic study has revealed the importance of Zn-HTBD ligand cooperation in the synergistic activation of both the PET carbonyl and the hydroxyl of ethylene glycol for an efficient acyl substitution. Moreover, it is worth noting that HTBD(OAc)/Zn(OAc)$_2$ retained its activity after seven cycles of catalytic recycling of PET.

Among other ZnCl$_2$-based PET depolymerizations, glycolysis with acetamide/ZnCl$_2$ supported on Zeolitic Imidazole Framework type 8 (ZIF-8) was easily carried out at 195 °C for 30 min, with the solid catalyst being removed by filtration and reused in the subsequent reactions (Scheme 5) [44].



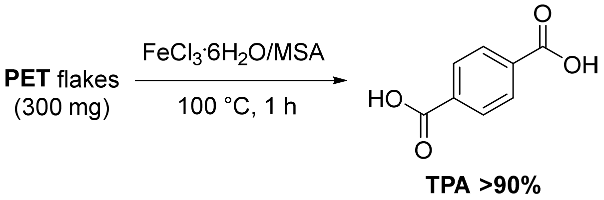
Scheme 5. PET glycolysis with acetamide/ZnCl$_2$@ZIF-8.

The authors described a simple procedure for the catalyst supporting, since the adsorption of DES on ZIF-8 occurred by stirring the single components in absolute ethanol for 8 h, followed by solvent evaporation to afford the active catalyst. The recycling of EG and acetamide/ZnCl$_2$@ZIF-8 was very efficient for up to 6 cycles with a very small erosion of BHET yield.

The advantages of this approach rely not only on the catalyst recycle, but also on the best PET conversion (DES@ZIF-8 conv. 83%, yield BHET 83%) when compared to the yields obtained in the presence of DES and ZIF-8 alone (DES conv. 85% yield BHET 76%; ZIF-8 conv. 72%, yield BHET 72%).

Among other Lewis acid-containing DES, an interesting work was reported by Ciancaleoni et al. for the hydrolysis of PET in Bronsted acids/Lewis acids-DES (BADES) [45]. In this case, the depolymerization reaction occurred at a much lower temperature (100 °C) than in other methodologies previously reported for PET (160–190 °C).

Moreover, differently from other papers, the used PET flakes deriving from waste plastics can be colored or not, without any differences in the quality of TPA, detected by NMR, IR, and elemental analysis after isolation by precipitation and filtration from an aqueous solution. The higher PET conversions percentages and TPA yields were observed when FeCl$_3$·6H$_2$O/methanesulfonic acid (MSA) and FeCl$_3$·6H$_2$O/*p*-toluensulfonic acid (*p*-TSA) were used as eutectic solvents (Scheme 6).



Scheme 6. PET hydrolysis in Bronsted acids/Lewis acids-DES (BADES).

Surprisingly, the ICP mass of the obtained product revealed a very low amount of iron from the eutectic mixture, as low as other heavy metal contaminants already present in the plastic wastes.

The effect of reaction time and temperature heating was also studied and correlated to PET conversion and TPA percentage.

As can be seen from Figure 3, the required energy to obtain a higher yield in TPA is supplied after 30 min between 80 and 100 °C.

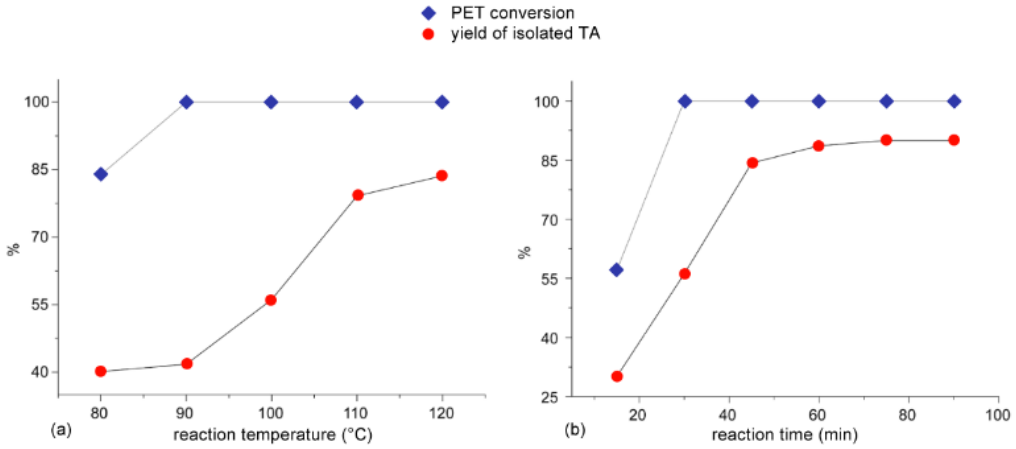


Figure 3. Study of (**a**) the reaction temperature and (**b**) the reaction time in PET hydrolysis in Bronsted Acids/Lewis acids-DES (BADES). Adapted with permission from Ref. [45]. 2023, Elsevier.

On the other hand, at 100 °C there is an exponential increase in the PET conversion and TPA yield between 20 and 40 min of reaction time because, beyond this time, a plateau of TPA yield is reached that does not increase further after a prolonged treatment up to 5 h.

Another critical point assessed by the authors is the amount of water present in the system and its influence on the success of the reaction. Indeed, the addition of 10 eq of water in $FeCl_3 \cdot 6H_2O$/*p*-TSA and $FeCl_3 \cdot 6H_2O$/MSA leads to a decreasing conversion from 100–96.4% to 23.8–15.5%, respectively.

Finally, the recycling of the system was also carried out by the addition of 300 mg of substrate after each reaction cycle of 1h to evaluate the catalytic capacity of substrate conversion into TPA.

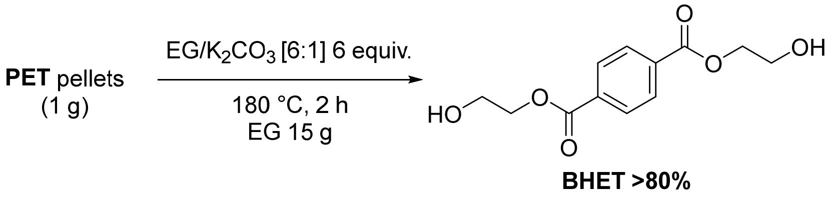
The catalytic system could be reused for four additional runs after the first cycle, revealing that this approach is not only more cost-effective but also environmentally friendly compared to other methods using DES both as catalyst and solvent. This was supported by calculating and comparing the E-factor and Energy Impact with other PET depolymerization methods present in the literature.

3.2. Lewis Acid-Free PET Solvolysis and Depolymerization by DESs

PET-glycolysis catalyzed by metal salts, metal oxides, and ionic solvents is one of the most used ways for high-performance PET depolymerization into high-quality oligomers and monomers.

In this section, less common metal-free base-catalyzed methodologies have been described as “greener” alternatives to address PET waste recycling.

Among other approaches of depolymerization without Lewis acids, Sert et al. reported a base-catalyzed PET-transesterification (glycolysis) in the presence of EG/K_2CO_3 (1:6) basic eutectic mixture as a catalyst at 180 °C (Scheme 7) [46].

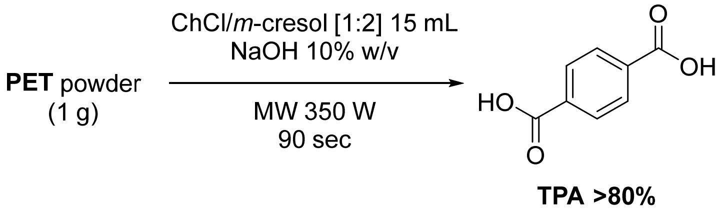


Scheme 7. PET glycolysis in EG/K_2CO_3 (1:6) basic eutectic mixture.

An EG/PET ratio of 15 to 1 was used for 2 h to reach a full PET conversion, calculated by the weight loss difference with respect to unreacted PET.

BHET was isolated in 70% yield, although the reaction mechanism was not fully investigated to demonstrate the effective role of EG/K_2CO_3 DES compared with K_2CO_3 alone.

A hydrophobic eutectic solvent [choline chloride (ChCl)/*m*-cresol 1:2] was alternatively used as a reaction medium for the hydrolysis of PET derived from waste plastics with a 15:1 DES/PET ratio in the presence of 10% *w*/*v* of NaOH as a catalyst by Attallah et al., by using a domestic microwave as the energy source (Scheme 8) [47].



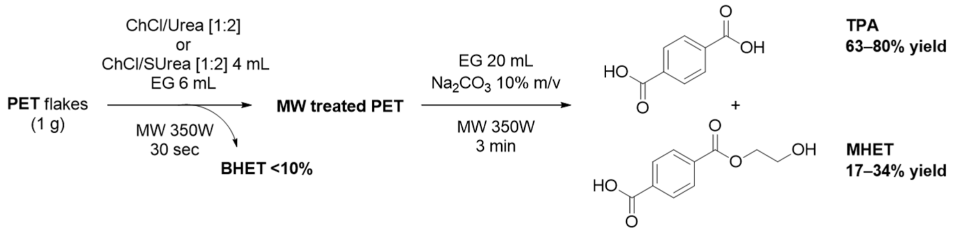
Scheme 8. PET base-catalyzed hydrolysis in ChCl/*m*-cresol (1:2) under MW irradiation.

The PET hydrolysis was optimized by a Box–Behnken design varying MW irradiation time, DES volume, and sodium hydroxide concentration as independent variables.

Under optimized conditions, the hydrolysis reaction was carried out for 90 s at 350 W, then water (35 mL) was added, and the unreacted PET and any insoluble oligomer were removed by filtration. An acidic work-up with conc. HCl allowed the TPA precipitation, while the hydrophobic DES was extracted with ethyl acetate.

However, the possibility of DES recycling was not investigated, although it could be useful for a mechanism elucidation, and also to confirm its stability under reaction conditions in light of the possible reaction between phenol groups and NaOH.

More recently, the same group has combined hydrophilic DES and MW for an efficient pre-treatment of PET flakes from environmental wastes, before their glycolysis and hydrolysis, with better conversion in comparison with the degradation of untreated polymers (Scheme 9) [48].



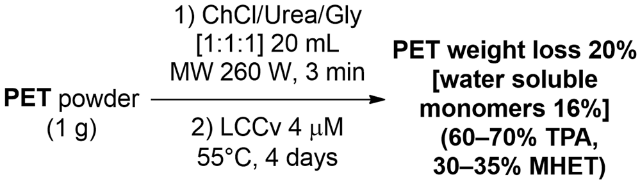
Scheme 9. PET glycolysis in ChCl/urea (1:2) under MW irradiation.

After a 30 s pre-treatment with MW at 350W in 4 mL of DES (ChCl/urea or ChCl/S-urea) and 6 mL of EG, only partial glycolysis (<10% conversion to BHET) was observed, although with an evident swelling of PET and a transformation of flakes morphology from crystalline to amorphous.

Pre-treatment was found to be of crucial importance for the following hydrolysis in MHET (17–34%) and TPA (63–80% yields) by reaction with 10% Na_2CO_3 under MW irradiation for 3 min at 350 W and a final acidic/aqueous workup.

The modification of PET particle morphology and crystallinity by DES/MW pre-treatment also allowed a better action of leaf-branched compost cutinase (LCCv) in chemo-enzymatic hydrolysis investigated by the same group [49].

After a short pre-treatment with MW in a ternary DES mixture ChCl/urea/glycerol (Gly), the enzyme-catalyzed hydrolysis of PET was carried out by incubation with a 4 µM solution of the LCCv enzyme in 10 mL of potassium phosphate at pH = 8 (PBS) for 4 days at 55 °C (Scheme 10).



Scheme 10. PET depolimerization in ChCl/urea/Gly (1:1:1) under MW irradiation followed by enzymatic hydrolysis.

The TPA was determined by HPLC analysis after acidification by HCl of the aqueous solution at the end of the reaction, while the remaining insoluble material was filtered and weighed to determine the weight loss of the PET. This study highlighted the efficacy of the combination of DES and microwaves in the pre-treatment of PET, which underwent greater depolymerization during the subsequent enzymatic hydrolysis if compared to untreated samples. However, regarding the chemoselectivity of the depolymerization process, the authors found that the distribution of the monomer was approximately 60–70% of TPA and 30–35% of MHET for both the treated and untreated samples.

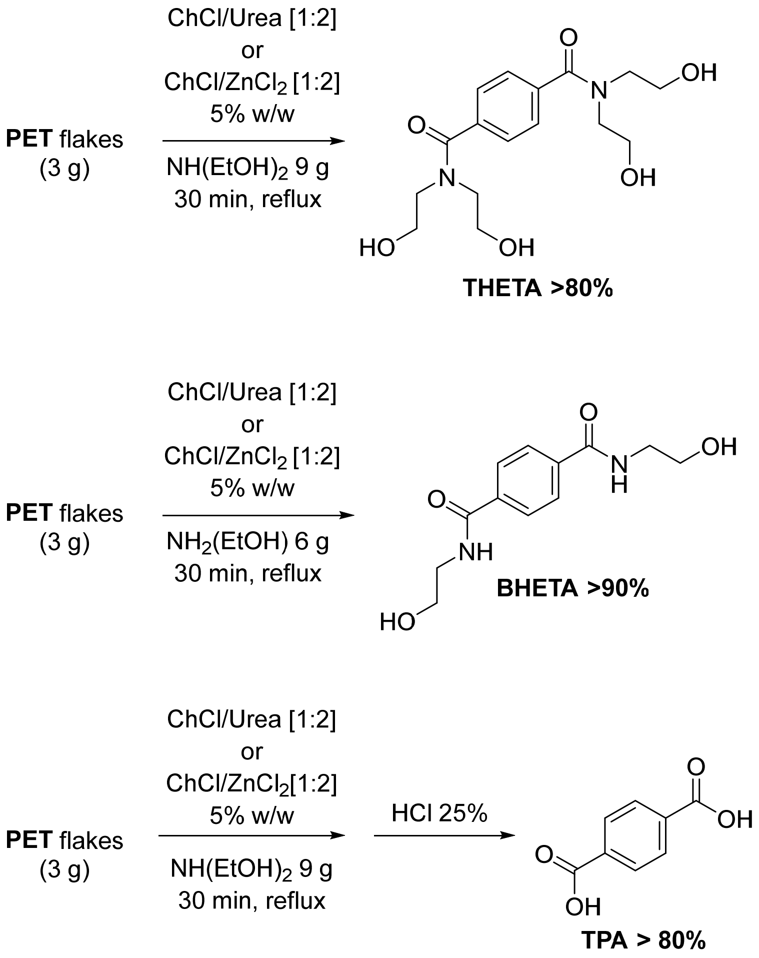
Finally, DES-catalyzed reactions have also been reported by using amines as nucleophiles for the acyl substitution in PET ester bond cleavage [18].

Catalytic amounts (5% *w*/*w*) of ChCl/$ZnCl_2$ and ChCl/urea eutectic mixtures, as well as $ZnCl_2$ and urea alone, have proven to be effective to catalyze after only 30 min the aminolysis of PET flakes from waste plastics, by refluxing ethanolamine and affording bis-hydroxyethylterephthalamide (BHETA) and tetra-hydroxyethylterephthalamide (THETA) (Scheme 11).

Although the reaction mechanism was not discussed, it can be deduced that ChCl/$ZnCl_2$, ChCl/urea eutectic mixtures, or $ZnCl_2$ and urea alone activate the carbonyl group of PET toward the nucleophilic substitution of ethanolamines, without competitive transesterification, due to the greater NH nucleophilicity.

The amide monomers were isolated by precipitation using methanol/ethyl acetate as solvent/non-solvent system and further re-crystallized in hot/cold water to obtain highly pure products. Terephthalic acid (TPA) was finally obtained by acidic hydrolysis with 25% HCl of the obtained amides.

In summary, many DESs act as catalysts favoring the depolymerization of PET, with very high efficiencies of up to 98% after a few hours of reaction. The experimental results confirm the efficacy of DESs to act both as solvents and catalysts in the depolymerization of PET, thanks to the synergistic activation of both the carbonyl function and the nucleophile in the solvolysis of the polyester.

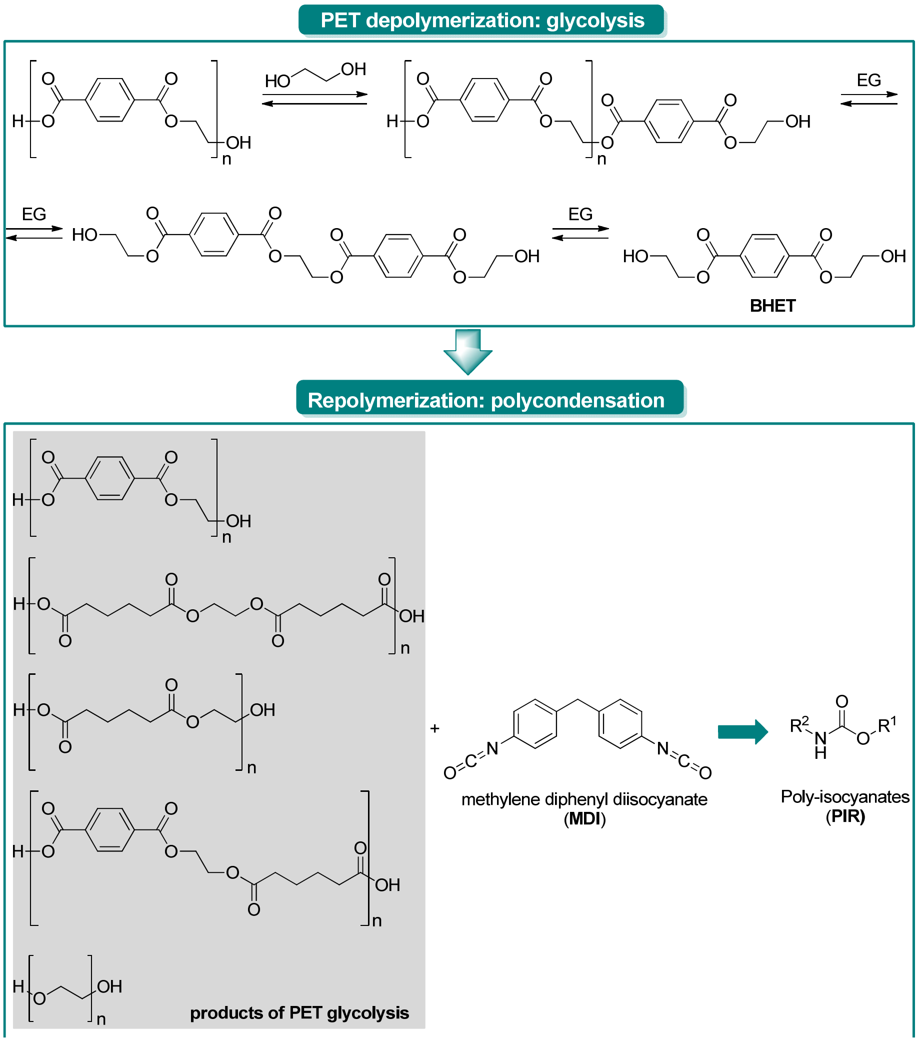


Scheme 11. PET aminolysis in ChCl/Urea or ChCl/$ZnCl_2$ deep eutectic mixtures.

However, among new unexplored frontiers, there are processes that not only decompose PET but also effectively valorize the monomers produced by the degradation process through their transformation into high-added-value products.

Among these processes, the recent work by Lee and Jung emerged as a robust upcycling process for the transformation of waste PET into polyisocyanurate foam (PIRF), as reported in Scheme 12 [50].

Polyols such as BHET and its derivatives derived from PET depolymerization have been effectively recycled to form a polyisocyanurate foam (PIRF), used as an insulating and flame-retardant material, by reaction with dangerous diphenylmethane diisocyanate (MDI) [51]. In this study, potassium acetate or octanoate-based DESs were used for the depolymerization of waste PET and for the one-pot repolymerization into recycled PIRF, which was also more thermally stable with a limiting oxygen index (LOI) of approximately 26.9% and heat release rate (HRR) of approximately 68.8 W/g).



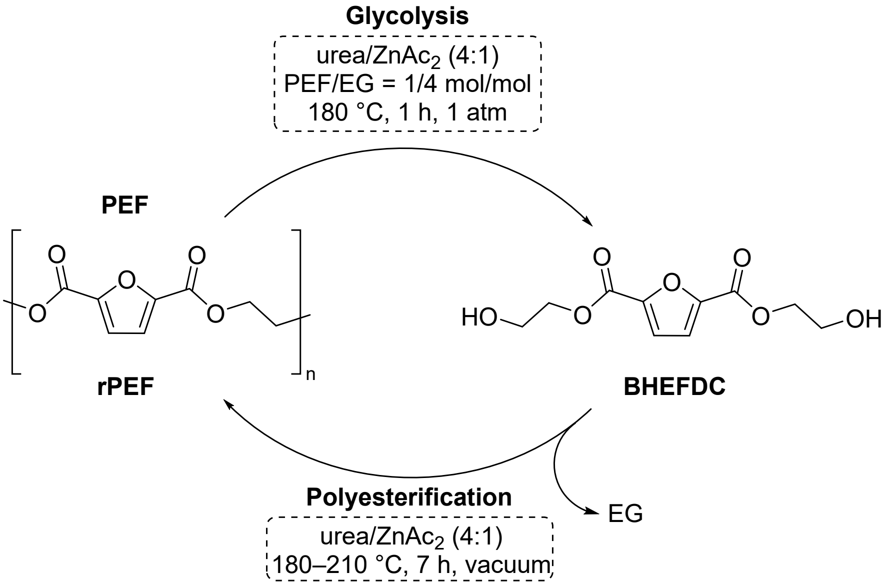
Scheme 12. PET solvolysis and simultaneous PIR synthesis. Adapted with permission from Ref. [50].

4. Bio-Based Polymers Degradation with Deep Eutectic Solvents

4.1. Depolymerization of Poly(ethylene 2,5-furandicarboxylic acid) (PEF)

Among bio-based polymers, poly(ethylene 2,5-furandicarboxylic acid) (PEF) represents a promising polyester obtained from D-fructose or D-glucose feedstocks [52]. Due to its valuable thermal and mechanical features, PEF represents a feasible substitute for PET in packaging and in many other uses.

In the context of changing from a linear to a circular economy model of development, in 2022, Agostinho et al. first developed an innovative closed-loop procedure, based on the employment of a biodegradable and safe-to-handle DES, for the chemical recycling of PEF into rPEF under mild conditions [53]. In particular, the eutectic mixture urea/$Zn(OAc)_2$, 4:1 mol/mol, revealed to be an efficient and green catalyst with a dual ability to catalyze both depolymerization and poly-esterification recycling of this polyester (Scheme 13).



Scheme 13. Circular recycling of PEF using the DES urea/Zn(OAc)$_2$ to catalyze glycolysis and polyesterification reactions.

PEF glycolysis was performed for 1 h at 180 °C, at atmospheric pressure, to produce bis(hydroxyethyl 2,5-furandicarboxylate) (BHEFDC) as the main product.

Moreover, the same DES was also able to catalyze the polymerization reaction of the unpurified BHEFDC into rPEF, reaching a product yield of 69%, Scheme 13 [52].

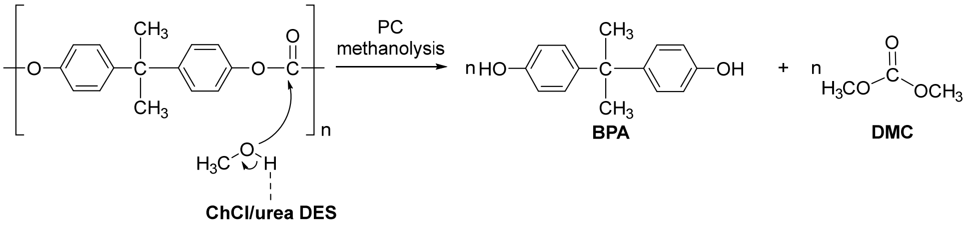
4.2. Depolymerization of Polycarbonate (PC)

In 2020, the eutectic mixture composed of ChCl/urea (1:2) was proven to be a highly active and reusable catalyst to perform methanolysis of polycarbonate (PC), obtaining the valuable molecule bisphenol A (BPA) [54].

PC is a polymer derived from fossil sources with a wide range of applications, including food packaging and the manufacturing of compact disks [55]. In the work of Song et al., different ChCl-based DESs with acidic or alkaline properties were prepared and used to catalyze PC methanolysis with the best catalytic performance shown by ChCl/urea [33]. Using this eutectic mixture as a catalyst, under the optimal reaction conditions [4.0 g PC, m(DES):m(PC) = 0.01:1, n(methanol):n(PC) = 5:1, reaction temperature 130 °C for 2.5 h], PC conversion and yield of BPA were 100% and 99.8%, respectively. BPA product was easily isolated from the reaction mixture via a simple filtration and extraction process. Moreover, the DES was recycled and reused for PC depolymerization for five consecutive cycles without any significant decrease in PC conversion and BPA yield.

Based on DFT calculations, a plausible mechanism for this ChCl/urea-catalyzed PC methanolysis was suggested.

As shown in Scheme 14, the eutectic mixture could improve the nucleophilicity of the oxygen atom in methanol by promoting its attack on the carbonyl of the polyester, thus allowing the decomposition of the polymer into BPA and DMC.



Scheme 14. PC methanolysis catalyzed by ChCl/urea DES.

In addition, kinetic studies revealed that methanolysis of PC was a pseudo-first-order reaction with an activation energy of 141.47 kJ mol^{-1} [54].

4.3. DES-Mediated PolyButylenes and PolyLactic Polymers Degradation

In recent years, poly(butylene adipate-co-terephthalate) (PBAT) has attracted much interest as a biodegradable polymer with applications in food packaging [56], although its biodegradation speed was slow.

In 2023, Meng and coworkers, in order to obtain a novel bio-based packaging material with high biodegradation speed, developed a blended system composed of PBAT, starch, and the ChCl/Gly deep eutectic mixture (100/30/10) (Figure 4) [57].

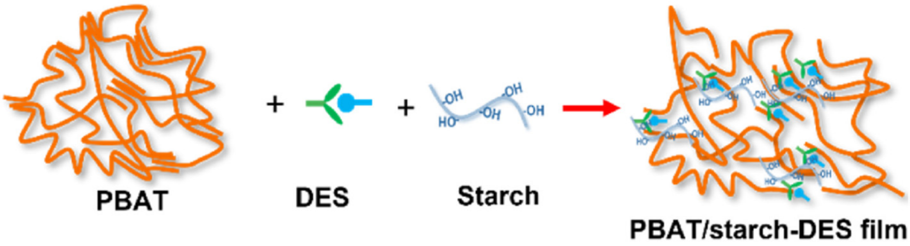


Figure 4. Schematic depiction of PBTA/starch/DES films as reported in the work of Meng and coworkers [58]. Adapted with permission from Ref. [57]. 2023, Elsevier.

The authors found that the eutectic mixture ChCl/Gly (1:2 mol/mol) acted as a plasticizer, accelerating the degradation of PBAT/starch films. It was suggested that the presence of the eutectic mixture could help the starch chain to interact with PBAT, thus improving the hydrophilic character of PBAT/starch blends, in favor of the adhering of hydrophilic microorganisms that, with their enzymes, degrade PBAT into low molecular weight fragments.

In a composting test using kitchen waste, the reduction in molecular weight PBAT/starch/DES films was about 50% faster than PBAT films [57].

The increasing development and adoption of biodegradable plastics hold great promise for a more sustainable and eco-friendly future.

The biodegradation process of polymers can be influenced by various physicochemical parameters such as morphology, crystallinity, hydrophilicity, and molar masses. Polymers with high degrees of crystallinity degrade slower as crystallites are less accessible to enzymes and water. On the other hand, polymers with high hydrophilic character are preferred for better interaction with bacteria and enzymes that can catalyze the hydrolysis of the polyester chains. Lower molecular weight is also favorable for faster degradation, especially under composting and abiotic aqueous conditions. Of note, also multiphase morphologies can favor biodegradation through the creation of peculiar pathways for bacteria and enzyme activities.

In this context, the work of Massardier et al. introduces a new application of DESs in polymer degradation [58]. The authors demonstrate that a blend of poly(butylene succinate) (PBS) and polylactic acid (PLA) and ChCl/Gly (PBS/PLA/DES) exhibits higher weight losses and faster fragmentation compared to a PBS/PLA blend under conventional conditions.

The polymer pellets were subjected to a drying process in an oven set at 70 °C for 12 h. Afterward, the pellets were combined with additives and fed into a DSM microextruder, which operated at 190 °C for 3 min.

Two types of polymer blends were used in this work: the PBS/PLA (60:40 wt ratio) as a reference and the PBS/PLA/DES (60:40:1 wt ratio) blend to observe the DES influence on degradation. The pellets were molded into dumbbell-shaped specimens and transformed into thin films with a thickness of 0.2 mm through a compression process at 210 °C, and these were utilized for biodegradation experiments.

Polymeric films of PBS/PLA and PBS/PLA/DES were then exposed to different environments: abiotic hydrolysis (conducted at 58 °C in deionized water and in an alkaline solution), composting (conducted at 58 °C in open containers), soil burial (conducted at room temperature in open containers) and humid atmosphere (conducted in a closed transparent chamber with humidity-saturated air at room temperature).

The study demonstrated that the PLA dispersed phase in the PBS matrix forms larger domains in the presence of DES compared to the neat PBS/PLA blend. The addition of DES resulted in a decrease in molar mass values, similar mechanical properties, and a decrease in thermal stability for the PBS/PLA/DES blend. Degradation tests also revealed an improved degradation tendency of the PBS/PLA blends when ChCl/Gly DES is present, which enhances chain scissions and is supposed to work as a compatibilizer between the two phases (interfacial agent).

5. Deep Eutectic Solvents Degradation of Other Polymers

5.1. Treatment of Rubber Tires with DES

When dealing with the environmental issues derived from polymeric materials, a special case is represented by rubber tires.

Roughly half of a tire's composition is made up of rubber, and the worldwide output of rubber materials has reached nearly 30×10^9 kg in recent years [59]. The tire manufacturing industry is the primary consumer of rubber, accounting for 65% of global production, and generates substantial volumes of rubber waste. As a result, the recycling of rubber is often referred to as tire recycling.

Every year, approximately 1.5 billion tires are disposed of, and they can contain as much as 90% of vulcanized rubber, a material known to be very hard to recycle or reprocess due to its crosslinked structure [60].

In 2019, the groups of Walvekara and Khalid explored for the first time the effect of ChCl-based DESs in the devulcanization of ground tire rubber [61].

In particular, the authors investigated the use of three DES (namely ChCl:urea, ChCl:$ZnCl_2$, and $ZnCl_2$:urea) as a medium in the thermochemical-ultrasonic devulcanization of ground tire rubber (GTR). The effects of DES content and time were explored toward the GTR devulcanization at a temperature of 180 °C.

All the experiments were performed as follows: GTR were added to various DES mixtures at mass ratios of 1:20, 1:30, and 1:40, with a total mixture weight of 50 g, to ensure optimal devulcanization surface contact. The rubber and DES mixtures were first sonicated in a water bath at 37 kHz for 1 h. Afterward, they were heated on a hotplate stirring at 180 °C and 300 rpm for variable periods of time (5, 15, and 30 min). Treated samples were subsequently washed with ultra-pure water, filtered, and dried in an oven at 70 °C overnight.

Based on several advanced spectroscopic analyses (EDX: Energy Dispersive X-ray, FT-IR: Fourier Transform Infrared Spectroscopy, FESEM: Field Emission Scanning Electron Microscope) and many other analytic techniques, the authors concluded that a higher level of devulcanization could be correlated to the increasing thermal exposure and to rubber/DESs mass ratio. Both aspects lead to a significant reduction in the crosslink density of devulcanized rubber. In particular, the Horikx analysis revealed selective devulcanization of sulfidic bonds while the polymeric chains remained intact, as confirmed by FTIR analysis. The FESEM investigation showed an increase in the surface roughness of devulcanized polymers, thus indicating a high degree of plasticity and mobility of polymeric chains.

Additionally, a strong correlation was found between a high soluble fraction and the degradation of main chains, indicating that low-viscosity solvents are preferable for efficient chemical transport during the devulcanization process.

Among the studied DESs, ChCl:urea exhibited the most rapid and extensive devulcanization, followed by $ZnCl_2$:urea and ChCl:$ZnCl_2$ DESs.

5.2. Use of DESs in the Treatment of Polyurethane (PU)

To date, only one example of polyurethane (PU) degradation in DES was reported in the literature by Deng et al. In this work, ChCl/urea (1:2) was found to be very effective for the degradation of polyurethane (PU) into high added-value monomers such as polycarbonate diol (PCDL) and *o*-toluidine [62].

Among all the chemical bonds and functional groups of PU, there are carbamate, urea, and ester functions, which are notoriously completely and non-selectively cleaved in the solvolysis processes. The ester bonds cleavage, and in particular the carbonate bonds hydrolysis in the polycarbonate-containing PU, is undesirable, being PCDL high added value polymers.

Controlled degradation of the copolymer for the possible recovery of the different fractions is desirable, and it could be carried out through the selective cleavage of the carbamate and urea bonds without breaking the carbonate bonds.

In the PU model used in this work, a soft segment of polycarbonate diol (PCDL) containing the carbonate bonds was bonded to one hard segment of 3,3′-dimethylbiphenyl−4,4′-diyl diisocyanate (TODI).

In a typical experiment, 5 g of the PU elastomer and 50 g of the DES solution were used, and the obtained mixtures were analyzed by using ^{13}C NMR, ^{1}HNMR, and MALDI-TOF-MS techniques.

The combination of these spectroscopic techniques confirmed the cleavage of the carbamate and urea bonds, while the carbonate bond hydrolysis in the PU depends on the reaction conditions.

The degree of PU degradation is less than 35.4% after 10 h at 140–150 °C, while it increases considerably up to 100% at higher T (160–180 °C). The PU/DES ratio was also investigated, observing an increase in PU conversion from 1:5 to 1:30 in the temperature range of 140–180 °C.

Under optimized reaction conditions, the complete degradation of PU (5 g) was obtained using 50 g of DES (urea/ChCl = 2/1), by heating at 170 °C and at atmospheric pressure for 8 h, with a PCDL yield of 57.4%. After the reaction, the mixture was cooled to room temperature and filtered. The residue was formed by unreacted PU and PCDL (57.4%), while the filtrate mainly consisted of DES and *o*-toluidine (16.9%).

FT-IR, ^{13}C NMR, and ^{1}H NMR analyses confirmed the chemical stability of DES under the optimized reaction conditions. Then, by monitoring the PU degradation degree and the PCDL yield in each reaction cycle, it was found that the DES system could be recycled up to 8 times, with a constant degradation ratio and a PCDL yield decrease of about 5.8%.

This result indicated the great potential of the DES system as an efficient catalyst for green and controllable PU degradation.

6. Conclusions

DESs have attracted increasing attention in almost all fields of chemistry due to their biological compatibility, tunability, low toxicity, easy preparation, low cost, etc. [63–65].

In recent years, a high number of studies have been carried out on the chemical recycling of PET, PU, PEF, PC, PLA, and other widely used polymeric materials in the presence of DES as catalysts or as reaction medium. Interestingly, very good performances were reported in most cases by using these novel neoteric solvents in greener solvolysis processes, also in combination with microwave irradiation (MW), Lewis acid catalysts, biocatalysts, with the obtainment of fine chemicals or high value-added products (monomers, other polymers, etc.).

PET treatment is one of the most studied processes, by hydrolysis, glycolysis, and aminolysis reactions with traditional heating or microwaves.

It has been observed that microwaves contribute to the structural modifications of the morphology and crystallinity of PET by increasing the degradation efficiency compared to thermal treatment alone.

In many cases, it is possible to make the whole process greener by recovering the solvolysis monomers through simple work-ups that do not use traditional VOC solvents. However, large volumes of water are required in most cases for the recovery or purification of monomers such as MHET, BHET, TPA, or other functionalized derivatives like BHETA and MHETA.

Combined methodologies with enzymes or other reagents have also been investigated, offering interesting perspectives in the next future for the development of green technologies of polymer up-cycling and for their use as new raw materials for the production of new high-added-value products.

In the near future, a higher number of processes that use DESs as catalysts for the degradation of plastics from fossil origin (e.g., PU) or from bio-based sources such as PC, PLA, or PEF are expected to be published in the literature, in order to reduce the environmental impact of chemical processes and redesign the future towards greener solutions.

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