REVIEW

Chemical upcycling of poly(ethylene terephthalate) waste: Moving to a circular model

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Abstract

The circular economy is a path that society, governments, and business must adopt to develop a viable and sustainable model for plastic production. Following the route guided by the United Nations and the new laws of the European Union, such as the Green Deal, it will be able to put an end to the great problem of this era, the inadequate treatment and management of plastic waste. On the plastics production ladder, poly(ethylene terephthalate) (PET) ranks fifth alongside polyurethanes, but only an average of 17% of total PET waste is recycled. Moreover, according to the latest survey made by Zero Waste Europe, most of this recycling source is used in low features applications through a downcycling process. There are mainly two ways for PET recycling, it can be done mechanically or chemically. On the one hand, mechanical recycling is easy to employ but presents some limitations as the properties of the final product decrease from the second cycle, whereas chemical recycling offers versatile procedures although it requires huge amounts of investment money. To address these drawbacks, diverse chemical recycling methods, specially aminolysis and glycolysis, were proposed as the promising way to obtain high added-value products. In this review, different updated state of the art works about recycling of PET were discussed, presenting the two forms for recycling PET waste, mechanical and chemical approach, and the reason of why is important to focus on the obtention of high-added value products in an upcycling process.

KEYWORDS

aminolysis, circular economy, glycolysis, mechanical recycling, PET waste, poly(ester-amide)s, polyurethanes, upcycling

1 | INTRODUCTION

Nowadays, one of society's main objectives is to adopt a sustainable way of life. This means changing the way we currently consume, produce, and behave, acting as a whole community, thinking globally rather than acting locally. To do so, the United Nations have recently established the 17th Sustainable
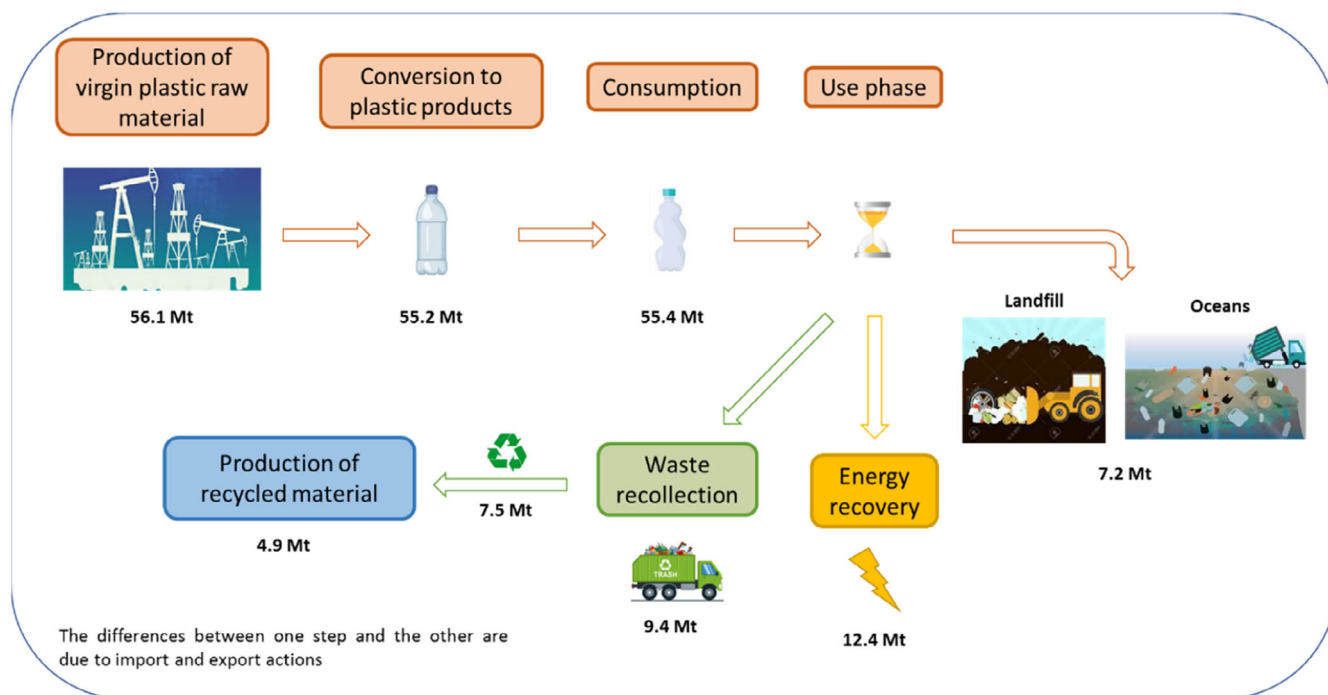
FIGURE 1 Cycle scheme of post-consumer plastic waste according to the Eurostat 2018 survey.[4]

Development Goals, a route to guide each country to that purpose.

In the case of plastic industry, a circular model must be adopted instead of present linear production. Currently, there are major difficulties in achieving this change in the production model. In this sense, on the one hand, emerging economies have little to no recycling infrastructure, leading to a worsening of the harnessing of plastic waste.[1] On the other hand, other developed economies, despite having better recycling infrastructures, continue to struggle to recycle.[2] It is therefore necessary to establish appropriate policies that generate an adequate framework to allow the development of systems with better treatment and management of plastic waste and evaluated in their entire life cycle (goal 12th Responsible Consummation and Production). While these political and economic considerations will play a crucial role in fostering model change, chemistry is expected to play a leading edge role. Therefore, polymer chemists will come up with pioneering solutions to introduce new recyclable plastic materials in the industry, more efficiency and durable, with the capacity to be reused as much as possible and, at the end, to be recycle again (goal 9th Industry, Innovation, and Infrastructure). It is also essential establish regulations for those products that end up in the oceans, forming the Plastic Garbage and affecting the Ocean Ecosystem (goal 14th Life Below Water).[3]

According to the last survey from Eurostat, 24.8% of plastic waste ends up in landfills and 42.7% is used for energy recovery, which produces undesirable greenhouse gases emissions. However, more than 30% of plastic debris has been properly recycled due to the implementation of a Circular Economic model in Europe. The *Circular Economy* is a closed system model that promotes the rules of the 6 "Rs of sustainability" (Reduce, Reuse, Recycle, Repair, Rethink, and Refuse) and the generation of a valuable material from waste, treating the waste as a valuable resource to produce useful, efficiency, suitable, affordable, high quality, and durable material that can be recycled as many times as possible to become sustainable and respectful with the environment (Figure 1).[4] In this way, the material value is maintained over time.

The Green Deal aims to encourage and manage this new path of circular production and responsible consumption of plastics by focusing on three main goals: making Europe the first climate-neutral continent by 2050, achieving that all plastic packaging placed on the EU market have to be reusable or recyclable by 2030, and banning single-use plastics as they are the principal debris on the coast and in the oceans. For instance, a very problematic polymer to recover from these locations is poly(ethylene terephthalate) (PET) because its density is higher than that of seawater, depositing the remains on the seabed. According to this European Directive PET-bottles must contain at least 30% of recycled material by 2030, and it must be minimize the amount of material needed through an eco-design of the PET bottle.[5] On the plastics production ladder, PET ranks fifth, next to

polyurethanes, quadrupling the production over 74 million tonnes between 2017 and 2021. PET is characterized for its excellent mechanical and thermal properties, its transparency and its higher permeability to moisture and oxygen, making the perfect candidate for drink bottles. PET also highlights for its low production price and its easily recollection in waste treatment as it is not use in multilayer products.[6] However, only an average of 17% of PET waste is recycled from bottles placed on the market, with a recovery rate of 31% from bottle to bottle. The other part of recycled PET goes to downcycled purpose, for instance, packaging uses 74% of recycled PET derived from bottles, leading to a lower manufacturing grade, and therefore carrying a loss in the circular bottle stream.[7] And what is more, only 14% of the global polyester market (fibers, single-use tray manufacturing, films, and strapping) is based on recycled polyester. For all these facts, new methods for recycling of PET must be studied.[8] In fact, several contributions have already been made in this aspect, allowing the thickness of the PET-bottles to be reduced.

In order to achieve all the objectives mentioned above, different PET waste recycling methods were proposed, focused on obtaining high-added value products, which could later be used to obtain other polymeric materials with advanced performance. For this purpose, in the present review, different ways of recycling PET have been critically addressed, pointing out the advantages and disadvantages of each one of them. Furthermore, the use of functional monomers derived from chemical recycling of PET for obtaining other polymers and their applications in different sectors has been evaluated. In the end, the strategies outlined in this manuscript have been developed to move from a linear production process to a circular model, taking the EU Sustainable Development Goals as a reference.

The efficiency of recycling processes (mechanical and chemical) begins with the sorting and pretreatment process of PET waste. Contaminated PET waste streams can decrease the recycling efficiency of these residues, even affecting the quality of the final product, due to undesired secondary decomposition reactions. Although many different types of sorting processes are currently available and are currently being studied for optimization,[9] this review will focus on methods of recycling PET waste after sorting has been completed.

2 | RECYCLING APPROACHES

During the last 20 years, different recycling methods of PET have been developed to adopt a sustainable production system which are indeed consistent with the concept of Circular Economy. Currently, four routes for the treatment of PET waste can be distinguished: the *recycling of pre-consumer material*, which is clean, uncontaminated and single-type waste, has been rejected due to presented defects on the design (primary recycling); the *mechanical recycling* in which the PET has to be separated from the other plastics and be cleaned before obtaining recycled PET (secondary recycling); *chemical recycling* that consists on the depolymerization of PET to attractive monomers or oligomers that could be used in the repolymerization of PET or in the synthesis of other alternative products (tertiary recycling); and finally the *energy recovery* through the incineration of the organic material (quaternary recycling).[10]

In the primary recycling, the pre-consumer PET waste can be treated by mechanical or chemical recycling. However, mechanical recycling is currently the most widely used recycling approach since the required infrastructures are actually the same as those for conventional production, and they also eluded the precedency problem of the plastic waste and the separation and cleaning procedure.[6,11]

The PET recollection and sorting processes are characterized by its easy separation from other polymers by hand picking or automatic systems, and then by color separation since mechanical recycling only admits light blue and transparent PET bottles, which is indeed the main drawback and forces to downcycling of discarded PET waste. According to the Zero Waste Europe survey, Deposit Return Schemes have demonstrated to improve collected material system in terms of quantity and quality.[12] Despite this fact, it is still necessary to remove the impurities and those contaminations from food packing by super-clean recycling process, dealing with the harsh restrictions on the use of recycled PET for food packaging when this waste does not come from the same origin. Moreover, no control of the additive status is necessary due to the outstanding properties of PET, such as good permeability, antioxidant behavior and flexibility.[6]

The *mechanical recycling* is indeed the easiest method to imply in the industry as they use the same infrastructure as the production from virgin materials. They also reduce the economic loss for all the plastic shrinkage that are obtained through the production process. In addition, by including this pre-consumer waste in recycling, the problem of precedence of plastic waste is also avoided and the separation and cleaning procedure is not necessary.[6] Nevertheless, mechanical recycling requires a prior separation of the rest of the polymers from the post-consumer plastic waste, and then they must be cleaned to avoid contaminations of the container content during recollection process (food, chemicals, etc.).[13] Subsequently, they are reduced in size and introduced into

melt extrusion, avoiding the modification of the basic polymer during the process and undergoing chain scission, some by-products (carbon dioxide, water and carboxylic acid or aldehyde end groups) are formed, and undesired side-reactions (such as intramolecular crosslinking or oxidation reactions) take place, which leads to the loss of transparency (yellowing).[14] During the mechanical recycling of PET by extrusion at 280 °C, thermal and hydrolytic degradation reactions responsible for molecular weight reduction and intramolecular crosslinking occur.[15] According to Bergeret et al.,[16] hydrolytic reactions occur in areas such as the feeder and die ("strongly oxygenated" zones) while crosslinking occurs in the middle of the reactor ("poorly oxygenated" zones). Both types of side reactions are closely related to the geometry and size of the extruder (such as feeder and die sections and screw length). These side-reactions lead to a reduction in molecular weight and intrinsic viscosity. Therefore, it has been pointed out that mechanical recycling processes need to preserve these parameters (molecular weight and viscosity) in order to continue to be used for applications requiring high viscosity or high molecular weight.[17]

The main inconvenience of this recycling approach is the reduction of PET properties after each mechanical recycling cycle, decreasing the polymer elasticity and viscosity, so after several cycles this recycled polymer ends up in landfills due to the loss of the material value of the polymer.[18] To compensate this fact, in the industry the mechanical recycled PET stream is mixed with the pristine material.[19] According to governmental organizations, the percentage of recycled PET in bottles will increase considerably in the coming years, reaching 30% by 2030. It is therefore necessary that mechanical recycling methods become increasingly effective and succeed in minimizing the adverse effects of reducing the properties of the material after it has been recycled.[5]

On the other hand, the *chemical recycling* needs new infrastructures and implies a change in the production process, normally linked to a considerable economical investment.

In contrast to mechanical recycling, chemical recycling of PET is currently at an earlier stage of development, causing most of the existing technologies on the market to be mainly in a pilot scale. Indeed, industrial efforts focused on glycolysis are showing promising commercial viability on a larger scale.[20] On the other hand, the use of aminolysis technologies beyond the laboratory scale has not been reported. Literature reports point out that toxicity or the high price of the chemicals required for aminolysis are disincentivizing the study of this approach on a larger scale. Under this framework, three main factors determine the profitability of chemical recycling of PET: (1) the degree of separation required in the raw wastes, (2) the value of the obtained products, and (3) the required capital investment in the facilities.[8] However, chemical recycling approaches offer new ways to obtain versatile products and achieves the incorporation of more plastic waste independently of their source and use. They also provide the possibility of producing other high-added value products, such as polyurethanes, polyamides, and other polyesters.[21] This recycling strategy seems to have valuable potential for the treatment of complex plastic waste, such as multilayer systems and composites materials.[6,22] Thus, this solution could be applied in the industry with minimum cost and high benefits, keeping the quality as the original product and without mixing with pristine material.

Chemical recycling is carried out by the degradation of PET with a solvent (solvolysis) or with heat (pyrolysis), yielding to monomers and by-products, or petrol liquids and gases which can later be used in the synthesis of new products of interest, respectively.[23] The main products of thermal cracking of PET without using a catalyst are terephthalic acid and benzoic acid, and when a zeolite is applied as catalyst aromatic hydrocarbons can be obtained as products.[24]

For solvolysis, depending on the type of solvent/reactant used, four divergent routes can be distinguished: *Hydrolysis* in which PET is depolymerized by water in different media (alkaline, acid and neutral) to get its essential monomers terephthalic acid and ethylene glycol; *Alcoholysis* in which an alcohol is employed obtaining ethylene glycol and terephthalate ester; *Aminolysis* to produce monomers, like bis-hydroxyethylene terephthalamide (BHETA), by amine application; and *Glycolysis* where another glycolyzed monomer, such as bis-hydroxyethylene terephthalate (BHET), is produced by using of a glycol product.[25] For all of them, the PET waste could come from several sources, such as the ocean trash, landfill debris or the PET scrap that cannot be recycled again by the mechanical approach (Figure 2).

Currently, the main drawbacks of chemical recycling are related to their drastic reaction conditions (high pressure and/or high temperature), because these conditions could affect the chemical composition of the obtained polymer and the price of the recycled product could increase. This last issue produces the loss of material value of the polymeric material, and as a consequence causes its exclusion from the recycling cycle. In addition, one should also consider the economic issue because it could prevent its application on a large scale.[18,26] For instances, in alcoholysis supercritical methanol can be applied in order to reduce reaction times, although high temperatures (240–320 °C) and high pressures (20 MPa) cannot be avoided.[27] In the neutral hydrolysis the ethylene glycol (EG) must be purified by distillation, and high

FIGURE 2 Scheme of chemical recycling types of poly(ethylene terephthalate) (PET) waste and the different origin of these debris
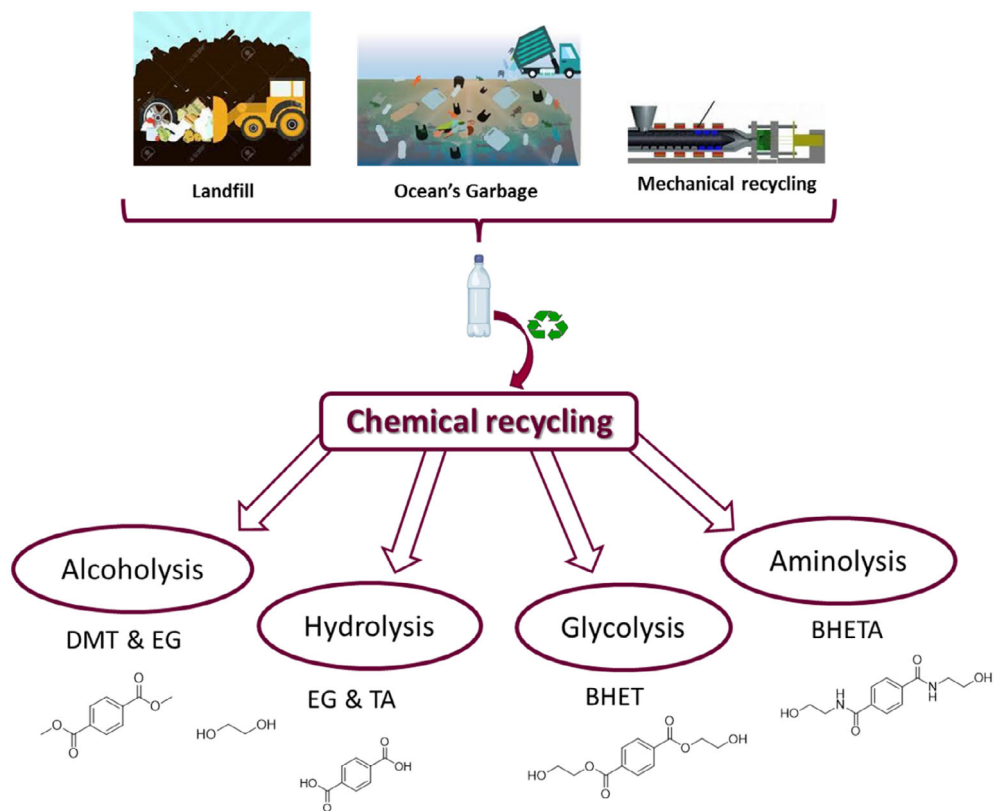
temperatures (140–190 °C) and pressures (4 MPa) are required.[28] The acid hydrolysis follows similar path to the neutral case, with the difference of performing the solvolysis in an acidic medium (using nitric or sulfuric acids as catalysts). Owing to the reduction in pH, solvolysis reaction times can be reduced and purification of the tereftalic acid (TPA) can be favored.[29] In the alkaline hydrolysis, the reaction conditions are analogous to the acidic version, with strong bases like potassium hydroxide or sodium hydroxide acting as catalysts and obtaining EG and terephthalate salts as final products, which are then neutralized with strong acids to obtain TPA.[30] Glycolysis and aminolysis also require higher temperatures (180–220 °C) resulting in a monomer that can be applied in the PET repolymerization process or can be used to synthesize other polymers, such as polyurethanes, polyamides, and polyesters, for a different purpose than the original one.[31]

To these difficulties, we must add the problem of traceability and the loss of mechanical and thermal properties, both in mechanical and chemical recycling, as they are not able to obtain high molecular weight products.[22] Currently, the combination of both processes is being considered, where first mechanical recycling would be carried out and then, once this process can no longer be applied on PET waste, recycling will be carried out by chemical means. Therefore, both processes would be complementary to each other.[4]

Taking into account the latest studies mentioned above,[31] chemical recycling by solvolysis is presented as a viable solution to the current shortage in the production of raw materials, that reduces dependence on the petroleum. In this way, it would be possible to maintain the value and improve the sustainability of PET-based materials, even upcycling discarded waste to obtain new materials with advanced performance.[32] For this reason, new ways have continued to be developed to overcome these drawbacks in PET recycling.

2.1 | Aminolytic route

The aminolysis procedure is generally characterized by the use of aliphatic amines, since they present better nucleophilic character respect to alcohol counterparts. The general scheme of aminolysis of PET to obtain aminolyzed monomers is depicted in Figure 3.

The work developed by Shukla et al. is the first example of aminolysis of PET waste with the final goal of producing high-added value products. In that work, an aminolysis-type route from PET fibers and soft drink bottles was proposed, using an excess of ethanolamine in the presence of different catalysts (glacial acetic acid, potassium sulphate and sodium acetate) and different catalyst loading (between 0.3% and 1.5% by polymer weight).
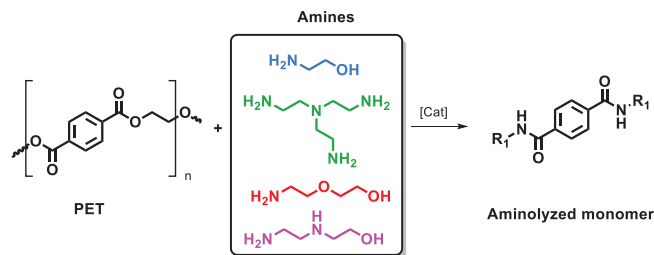
FIGURE 3 Reaction scheme for poly(ethylene terephthalate) (PET) depolymerization with various amines

Their final goal was getting BHETA monomer due to its high potential and versatility, since it could be used to prepare new polymer materials for different applications. These authors observed that the yield of BHETA was higher employing PET fiber waste (91.1%) than for the bottle waste (83.2%), making a strong difference when no catalyst was applied (52% yield). The reason for this difference in the yields between PET fibers and plastic bottles was attributed to the molecular weight and its chain distribution.[33]

The use of BHETA as a new high value-added feedstock has been very widespread, for the preparation of other polymers such as polyurethanes. Early work focused on the insertion of BHETA as *chain extenders*. Shamsi's group[34] observed that BHETA-polyurethanes showed better performance as adhesives with respect to commercial ones. Later, Aslzadeh et al.[32] evaluated that the introduction of BHETA motifs in polyurethane coating formulations led to an increase in toughness and stiffness, due to the formation of hydrogen bonds through amide groups. Conversely, these authors found that the thermal stability of those polyurethanes decreased with increasing BHETA content within the hard segment.

The BHETA moiety has also been inserted into the soft segments of the polyurethanes.[35] This has required the prior preparation of a polyol containing BHETA within its structure by the ring-opening reaction of ε-caprolactone and using BHETA as initiator (Figure 4).

This BHETA-functionalized polycaprolactone (PCL) could subsequently be used as a soft segment for the production of biodegradable polyurethanes. Since the chemical environment of the BHETA residue within the soft segment is different from its hard counterpart, the behavior of the aminolyzed monomer could vary considerably. In fact, the insertion of reactive molecules into the hard or soft segment leads to polyurethanes with different properties and performance.[36] Biodegradability tests yielded very promising results independently of the molecular weight of the soft segment used.

In other aminolytic recycling approaches, various amines were used to generate new monomers of interest.

In this regard, 3-amino-1-propanol was used to carry out aminolysis of PET bottles in the presence of sodium acetate as catalyst, leading to bis-(3-hydroxypropyl) terephthalamide (BHPTA),[37] a monomer similar to BHETA. This amide was also introduced into the soft segment of polyurethanes, through the formation of a PCL-based bearing BHPTA motif. The results demonstrated that the functionalized polyol conferred high impact resistance to the polyurethane, which together with the scratch resistance, hardness and flexibility provided by BHPTA, made this polymer an excellent sustainable candidate for coating.

Other amines used to chemically recycle PET by an aminolysis process were N-(aminoethyl)ethanolamine[38] or other polyamines such as diethylenetriamine or triethylenetetramine.[39] Despite several amine groups, the chemical recycling conditions were still drastic (190 °C) but with shorter times (30 min) and using zinc acetate as catalyst. Because polyamines were used, the aminolyzed PET products were led to the formation of PET-derived hydrogels. These revalorized hydrogels were employed as dye absorbents, providing an attractive solution to water pollution caused by industrial dyes.

As part from the synthesis of polyurethanes or hydrogels, the aminolyzed PET monomers could be also used for the production of other polymers such as poly(ester-amide)s. The research group of Elsaeed and Farag used BHETA and different long-chain diacids to produce curable unsaturated poly(ester-amide)s. These authors demonstrated that the curing time of these curable polymers was reversibly proportional to the chain length of diacids.[40]

2.1.1 | Aminolysis by sustainable procedures

Currently, there is an emerging investigation line to incorporate *sustainable procedures* in the chemical recycling of PET waste by different approaches. To achieve shorter reaction times, performing the synthesis under milder reaction conditions (low temperatures, atmospheric pressures, no metal catalyst, etc.) and, at the same time, improving yields and conversion rates, these miscellaneous approaches have been proposed as more sustainable alternatives to conventional methods in the chemical recycling of PET by aminolytic route.[41]

The first example in the recycling of PET applying *microwave radiation* was proposed by Shukla and Harad, who developed this alternative method to the conventional one.[33] As part from performing the reaction at lower reaction times (4 min), the process becomes economically viable since the aminolyzed monomer (BHETA) yields were higher than 90% and common and
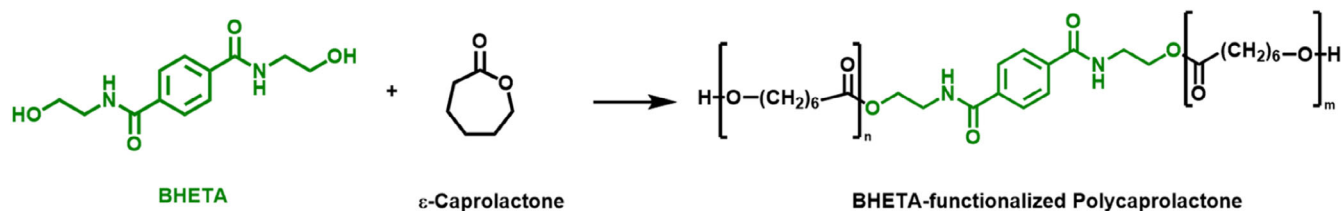
FIGURE 4 Synthesis of polycaprolactone bearing bis-hydroxyethylene terephthalamide (BHETA) motif by ring opening of ε-caprolactone

cheap catalysts can be employed, such as sodium acetate, sodium bicarbonate and sodium sulphate.[42] Later, Bäckström et al. shown a way to recycle PET by a sustainable aminolysis methodology applying microwave radiation with different amines. The main advantages of this microwave-assisted depolymerization were the strong reduction of reaction times (<15 min), the absence of catalyst and solvent and the final product was obtained in "one-pot" reaction. The aminolyzed terephthalamide-monomers were then used for several purposes.[43]

Ionic liquids (ILs) are another sustainable option for developing a green methodology for depolymerization of PET waste. It is well-known that these ionic compounds exhibited unique features, such as thermal stability, non-volatility, and low flammability. In the study of Shukla and co-workers, BHETA was obtained by applying imidazolium-based ionic liquids and an excess of ethanolamine, varying time periods up to 120 min and the concentration of diverse ionic liquid solvents. Moreover, it was demonstrated that the reaction could also be performed under microwave irradiation in the presence of various catalysts (lead acetate, sodium acetate, sodium bicarbonate, and sodium sulphate).[44]

Related to ionic solvent, *deep eutectic solvents (DESs)* are used as an alternative to ionic liquids due to their similar characteristics, as well as their lower cost, easier synthesis, little toxicity, and higher biodegradability. They are simply made by combining quaternary ammonium salts (choline chloride) with either hydrogen bond donors (urea) or Lewis acids (zinc chloride). These kinds of catalysts have been demonstrated to be effective for the degradation PET waste, achieving higher yields and shorter reaction times under milder reaction conditions.[45]

The use of *sunlight* as a clean and renewable energy source is another alternative to develop an environmentally friendly procedure for PET waste aminolysis. In this line, Tawfik and co-workers proposed a new methodology to perform the aminolysis of PET waste by applying sunlight energy. Although reaction conditions were mild (atmospheric pressure, low-cost catalysts), reaction times were very long (21 days). The BHETA obtained through this sustainable route was employed in anticorrosive

paint formulations. By performing the corresponding corrosion test, it was shown that BHETA was a perfect candidate for anticorrosive paints, as it hardly affected the physical and mechanical properties of the films, as well as improving the adhesion to the steel substrate.[46]

2.1.2 | Aminolysis by organocatalysts

With the aim of avoiding the classical catalysts based on heavy metals, such as tin or bismuth various *organocatalysts* have been proposed as sustainable approach of recycling PET-waste. For instance, at the University of the Basque Country, conjugated salt of 1,5,7-Triazabicyclodec-5-ene:Methanesulfonic acid (TBD: MSA) or 1,8-Diazabicyclo [5.4.0]undec-7-ene:benzoic acid (DBU:BA) were employed in an upcycling aminolytic process of PET waste to obtain different terephthalamide diols. These attractive monomers could be further used as possible precursors in the production of poly(ester amide)s. The advantages of these organocatalysts were their chemoselectivity, reducing the energy required in the chemical recycling procedure, and strong H-bonding motifs. The reaction conditions in the depolymerization were evaluated, showing the best results were reached with 20 eq. of the amine species, TBD:MSA (0.1 eq.) as catalyst and performing the reaction at 180 °C. In addition, different aminoalcohols were used in order to study the depolymerization kinetics, exhibiting higher reaction rate with smaller alkyl chains. Finally, linear poly(ester amide)s with low to moderate molecular weights (up to 10 kg mol^{-1}) were obtained by applying the DBU:BA catalyst and under moderate conditions. This work perfectly exemplifies how, through a correct eco-design, plastic waste can be creatively reused, with the possibility of using a multifunctional diol for crosslinked materials (Figure 5).[47]

In this sense, the following works demonstrated the possibility of introducing plastic waste in very strict sectors through careful eco-design. Indeed, in the medical sector, new applications have emerged using secondary raw material such as PET waste. Tan et al. presented new
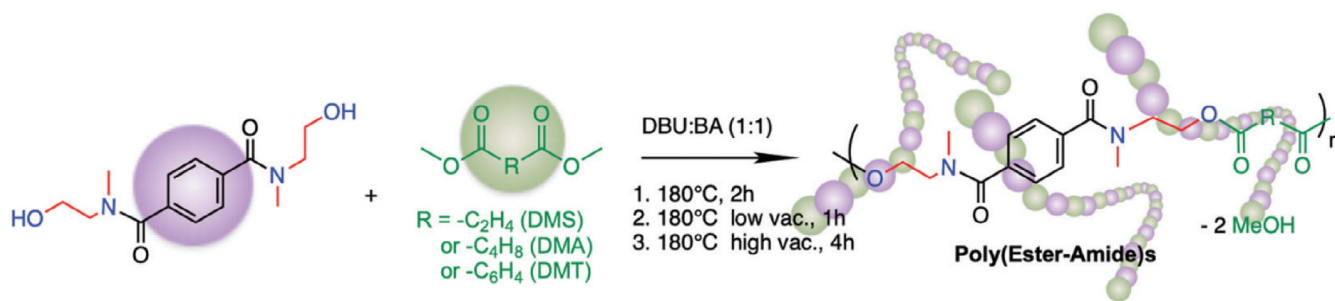
FIGURE 5   Synthetic route for preparation of poly(ester-amide)s by organocatalysis. Copyright 2020, the Royal Society of Chemistry.[47]
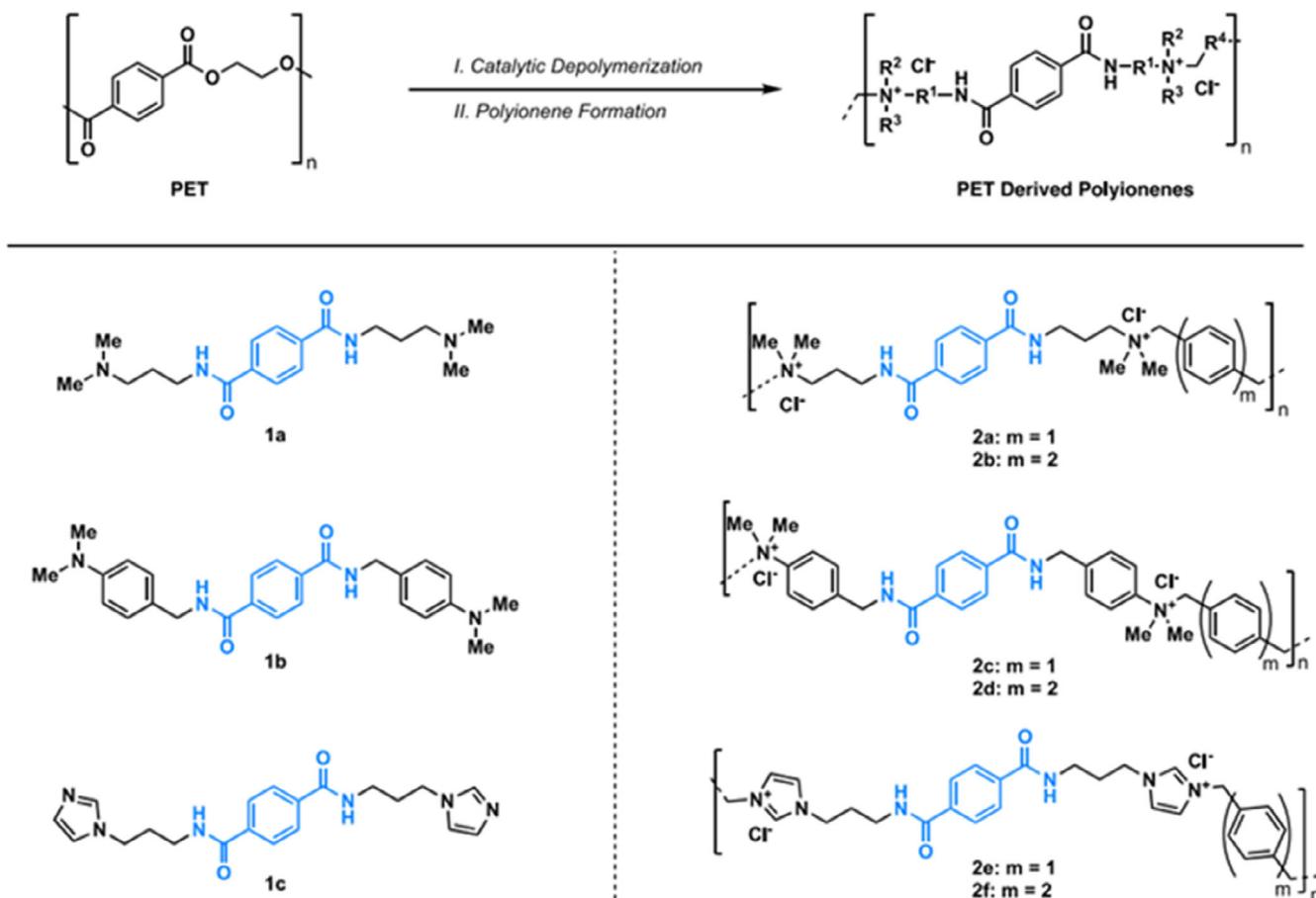

FIGURE 6   Preparation of antimicrobial cationic polyionenes from poly(ethylene terephthalate) (PET) residues via aminolysis. Copyright 2019, American Chemical Society.[48]

strategies for the construction of macromolecular antimicrobial compounds to address the problem of bacterial resistance. They developed a catalyst- and solvent-free depolymerization of PET residue via aminolysis. The corresponding aminolyzed products were then employed for the formation of antimicrobial *cationic polyionenes*. The aminolytic process consisted of a simple polyaddition polymerization with lower temperatures and shorter times rates (e.g., 120 °C for 2 h). In this case, the depolymerization monomers along with α,ω-tetramethyldiamines and

p-xylylene dichloride dissolved in N,N-dimethylformamide, were combined under nitrogen at 85 °C to obtain the polyionenes. These polymers are characterized by their sustainable synthetic procedures and a good association and integration into cell membrane due to the amphiphilic character. The formed polyionenes were shown to exhibit high potency against a broad spectrum of pathogenic microbe analysis (Figure 6).[48]

Another example in medical treatment that demonstrates the high potential of these secondary raw
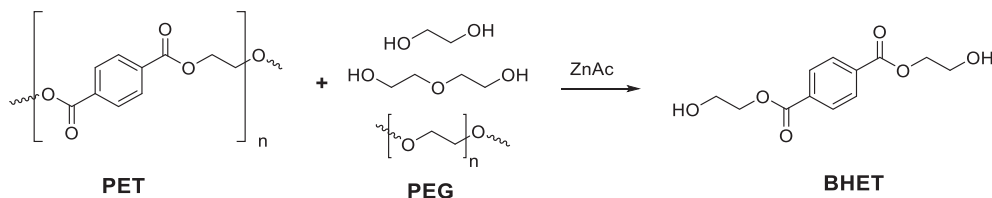
materials was developed by Natarajan and co-workers, in which the aminolytic method of PET waste was applied to synthesis biodegradable poly(ester amide)s for bone tissue regeneration (osteogenesis). This class of biocompatible polymers showed a buffering effect and a cellular response similar to those of proteins caused by the presence of amide bonds. According to the proposed methodology, aminolyzed monomer BHETA and dicarboxylic acids were used for the synthesis of these biodegradable polymers, to face the problem of non-biodegradable materials employed in engineering scaffolds in recent days. In addition, the chemical structure of BHETA confers rigidity to the material, a useful quality in bone engineering. Regarding the mechanical properties, the higher the content and length of the dicarboxylic acid group in the chain, the higher the elasticity of the polymer, providing the buffering effect so sought after in osteogenesis. The degradation and release of this material was also conditioned by the length of the dicarboxylic acid group, decreasing with increasing acid content in the chain. Moreover, the viability tests carried out confirmed the cytocompatibility of these polymers, essential for medical applications.[49]

Forming composites materials was another way of performing an upcycling process of PET waste. Using transesterification reaction, More et al. proposed the synthesis of poly(ester-amide) resins mixing BHETA with modified oil fatty acid. By combining renewable resources and waste material, these poly(ester-amide) resins were applied for coating on mild steel panels, as they presented excellent thermal and mechanical properties. The selected fatty acid chain provided flexibility to the structure due to its aliphatic nature, while the aromatic benzene ring and the amide of BHETA were the responsible for the stiffness, hardness, and strength of the coating. Furthermore, all the coated films were unaffected by acid, alkali, and solvent in terms of adhesion and presented good resistance to acid, although a loss of gloss occurred in an alkaline environment.[50]

2.2 | Glycolytic route

Glycolysis is a method within PET chemical recycling that provides useful monomers and is characterized by

the use of glycols of different lengths to depolymerize the polymer. BHET is the most predominant glycolyzed monomer, due to the fact that a different range of new high value-added products could be obtained.[51] The most common procedure consists of the use of ethylene glycol as reagent, together with PET residues, and the presence of a catalyst, such as zinc acetate stands out as the most commonly used (Figure 7).

Other polyol oligomers can be obtained by the application of different and less common glycolyzed reagents, such as trimethylolpropane, pentaerytheritol[52] or ethylene carbonate.[53]

For the glycolysis of PET waste, different glycols could be used. For instance, using ethylene glycol, propylene glycol, diethylene glycol, and triethylene glycol (TEG) in the presence of zinc acetate as catalyst (1% wt) at 190–220 °C led to glycolyzed monomers. The potential of these products could subsequently be used to obtain unsaturated polyester resins. The mechanical properties of these resins were comparable with those obtained conventionally from virgin material. Regarding flexibility, there was a notable difference between the resins formed with diethylene glycol and triethylene glycol with respect to those with polyethylene glycol, the latter being less flexible due to the higher ether content. On the contrary, polyethylene glycol resins offered better results in tensile strength and hardness.[54]

Unsaturated polyester resins had also been produced by the combination of oligo-cellulose and glycolyzed products of PET waste, with TEG, maleic anhydride and different catalyst depending on the resource, $SnCl_2$ catalyst for the PET and H_2SO_4 catalyst for the cellulose waste. The introduction of cellulose oligomers into the formulations of those polyesters enhanced crystallinity and improved thermal stability of the resins compared to the pristine materials.[55]

Torlakoğlu and Güçlü applied the general PET glycolysis procedure to produce short oil alkyd resins for coatings purpose, using phthalic anhydride, glycerin, coconut oil fatty acids and PET-based alkyd resin. Furthermore, the resins showed similar properties to conventional products, such as physical and chemical film properties, thermal oxidative degradation resistance, and gelation time.[56]

Another example in the resins type sector is the application of glycolyzed products as modifiers in the

synthesis of urea-formaldehyde resins with the aim to upgrade these materials. These modifiers were able to involve effectively in the resin network structure, which led to better adhesion strength in the dry state and to improve their moisture resistance after immersion in water.[57]

These glycolyzed monomers have also been used in other polymeric materials such as epoxy resins or polyurethanes. These materials can also be employed as coatings due to their high adhesion ability. Macijauskas and Jankauskaite developed a different method to obtain epoxy resin and polyurethanes for this purpose. To do so, they initially depolymerized PET residue with propylene glycol under nitrogen atmosphere at 200 °C, yielding oligoester diols with low molecular weight. They then used these diols to produce epoxy resin with epichlorohydrin (by a ring opening reaction), or to form polyurethane with aliphatic isocyanate. The epoxy resin shown poor coating properties probably due to the high percent of starting components that could be extracted after cross-linking reaction, whereas the polyurethanes cured effectively, leading to the formation of coatings with great mechanical properties.[58]

The reuse of PET waste has also been included in other sectors, such as rigid polyurethane foams. Luo et al. depolymerized PET waste with crude biobased glycerol, at different weight ratios to produce functionalized polyols and using titanium isopropoxide (0.5% wt) as a catalytic agent. Those polyols were synthesized by a continuous two-step method: (1) glycolysis of PET waste heated at 230 °C under nitrogen atmosphere, (2) series of reactions (transesterification, and condensation) of glycolyzed PET products at 200 °C under vacuum. With the corresponding characterization techniques, it was shown that the higher the crude glycerol content, the lower molecular weight of the polyol. Subsequently, polyurethane foams were mainly obtained using foaming reagent (water) and prepolymers based on diphenylmethane diisocyanate (MDI). A clear relationship was demonstrated between the glycerol content, and the final properties of the polyurethane foams, showing an increase in cream time, growth time, gel time, density, and compressive strength when more glycerol was added. On the contrary, the foam cell size and its thermal stability decreased with increasing glycerol content in the polyols chains[59] (Figure 8).

Similar results were obtained in the work of Kirpluks et al., in which the synthesis of polyols from glycolyzed PET products were used to produce high-density rigid polyurethane foams for automotive application.[60] These foams were characterized by their smaller cell size and cell size distribution, as well as better mechanical and thermal properties. The latter were due to the

introduction of aromatic structures into the polyurethane polymer matrix.

In the work of Ghaderian et al. the same effect of propylene glycol/PET ratio (1:1, 2:1, 2.5:1) was observed, as its increased, in terms of hydroxyl numbers, led to the decrease in viscosity of the glycolyzed product and molecular weight. Afterwards, rigid polyurethane foams were prepared by mixing those upcycled polyols, and water as the blowing agent, with MDI-prepolymer. In addition, the final properties of these rigid foams derived from upcycled polyols achieved a density, compressive strength, modulus, thermal stability, and thermal conductivity similar to those of conventional foams. On the other hand, density had an inverse behavior with the cell size, when the first increased the latter decreased under the same formulation foams conditions.[61]

Polyurethane foams are thermolabile and flammable materials with a high flammability index due to their low density, porous structure, and large specific surface area. In order to solve this drawback, Li et al. proposed a method in which recycled PET monomer (BHET) was introduced into flame-retardant rigid polyurethane foams. The insertion of dimethyl methylphosphonate (DMMP) as the flame retardant led to fireproof foams. The authors appreciated an effect on the foam properties when higher amounts of the flame retardant were used, increasing the porosity and decreasing the compression properties and density of the foam, which led to the rupture of the cell walls along with the formation of big cells. Moreover, the BHET structure improved the thermostability and decomposition temperature of rigid polyurethane foams.[62]

Glycolyzed monomers have also shown their potential in other applications, being able to be incorporated into water-dispersed polyurethanes. This type of polyurethane is increasingly demanded by today's society, since the use of organic solvents is discarded, and water is introduced into their formulations. As a result, adverse impacts caused by volatile organic compounds are minimized.[63] In this way, Cakic and co-workers aimed to obtain water-dispersed polyurethane formulations using isophorone diisocyanate, the polyol resulting from the glycolysis of PET with glycols (propylene glycol, triethylene glycol and poly(ethylene glycol)) in different ratios, dimethylol propionic acid as a potential ionic center for water dispersibility, and ethylenediamine as a chain extender. The aromatic part of the polyester would confer higher stiffness to the polyurethane chain but lower thermal stability. The length of the glycols also influenced the chain properties, lowering stiffness when the glycol content increased. On the other hand, film adhesion and gloss made these materials excellent
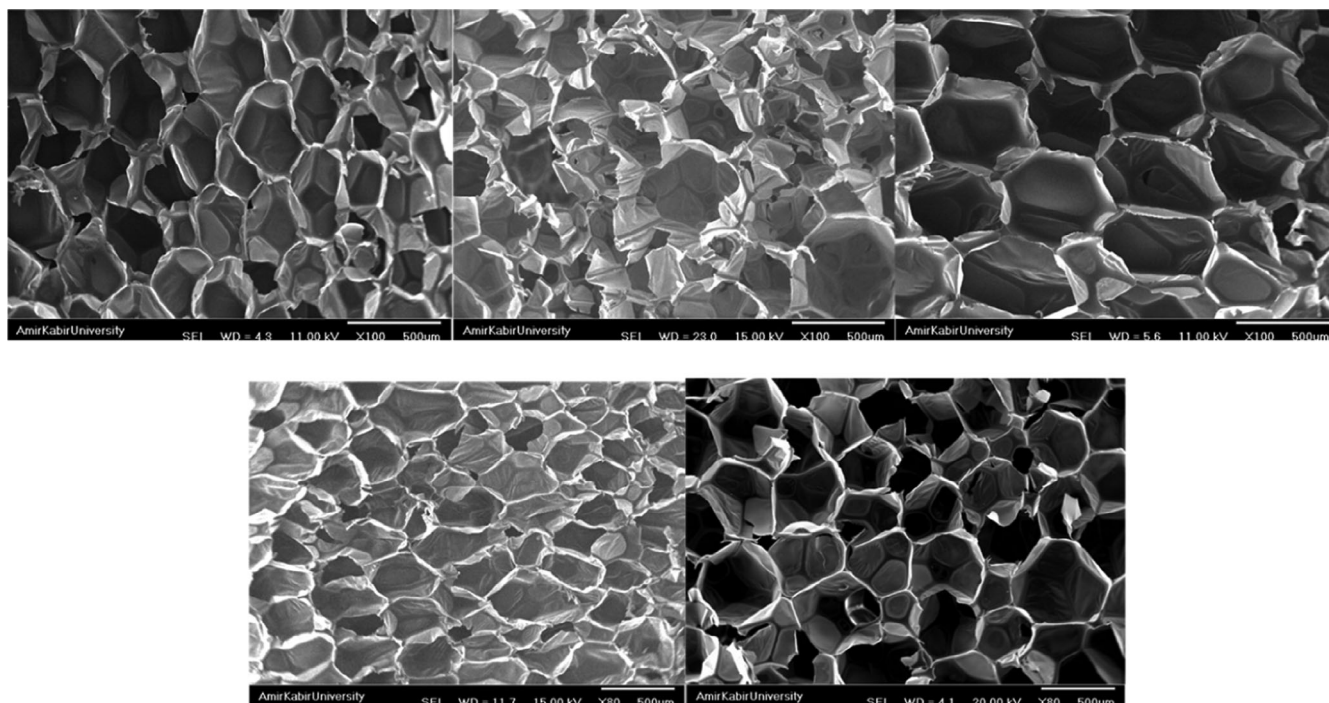
FIGURE 8   Different foams obtained by applying oligomers from poly(ethylene terephthalate) (PET) glycolysis.[59] Copyright 2014, Springer Nature

candidates for applications in civil engineering, metallic or polymer coatings.[64]

2.2.1 | Glycolysis by sustainable procedures

Based on the Principles of Green Chemistry, some research projects focused on the application of alternative reaction conditions in the chemical recycled of PET, such as employing different catalytic systems, developing microwave-assisted technology, using green and biodegradable solvents like ionic liquids or DESs, and exploring supercritical methods.[65] Chemical recycling processes for PET catalyzed by ILs or DESs holds few advantages over classical catalytic agents, such as the reaction could proceed at lower pressures, easy recovery of catalyst, catalyst reusability and product purification.[20] Therefore, the principles of Green Chemistry addressed through these approaches would be: Innocuous solvents and auxiliaries, Energy efficient by design, catalytic rather than stoichiometric reagents, Analytical methodologies for pollution prevention and Inherently safer processes. The use of ionic liquids as catalysts in PET glycolysis processes has been extensively addressed in previous work.[66] In fact, in spite of their high initial cost, ionic liquids have become increasingly attractive tools for green chemistry because of their low volatility and recyclability.[67] However, regarding biodegradability the general behavior is more

disparate, while the choline-based ionic liquids are completely biodegradable for concentrations up to 50 mg/L,[68] the imidazolium derivatives showed a wide range of toxicities.[69] The PET glycolysis using *ionic liquids* was first addressed by Wang et al. in 2009, investigating the influence on the conversion parameters and selectivity of the reaction by applying 1-butyl-3-methylimidazolium chloride as an ionic liquid specie.[70] Subsequently, other examples were proposed based on the adjustable physical and chemical properties of ionic liquids.[71] Regarding the nature of ionic liquids, it has been described that in glycolysis PET, the catalytic activity of Lewis acids was more efficient than their basic counterparts.[72]

Another environmentally friendly example is *DESs*,[73] they were mostly applied as solvents rather than catalyst, although they show strong H-bond interaction with the reagents and coordination action with metal ions. Wang and co-workers proposed a new series of urea/metal salts to be used as catalyst and DESs in the PET depolymerization process. The high catalytic activity was attributed to the coordination bonds formed between metal ions and ethylene glycol, as well as the synergetic catalysis of H-bonds formed between urea and ethylene glycol. Moreover, this method was proved to be energetically efficient, showing high PET glycolysis conversions and reaching higher selectivity values (up to 83%) in shorter reaction time under mild conditions compared to the conventional catalysts.[74]

On the other hand, supercritical fluids can also be considered as a sustainable way to perform PET glycolysis using supercritical ethylene glycol. These kinds of solvents were useful in the chemical recycling process due to their environmentally friendly nature, high solvent density and solubility, high kinetic energy, and high diffusion and reaction rate.[75]

The application of *microwave-assisted technology* in the chemical recycling process offers a broad number of advantages over conventional heating, such as instantaneous and rapid heating with high specificity and noncontact technique. PET glycolysis can be considered an energy intensive process, implying high temperature and extended time periods, whereas the microwave aided glycolytic process had showed lower apparent activation energy and high reaction rates. This was the case of Chaudhary et al., reaching excellent yields in short reaction times (30 min) compared to the 8–9 h of the conventional heating process.[76] Pingale and Shukla demonstrated that microwave irradiation was very effective in the PET waste depolymerization reaction by glycolysis approach, achieving short reaction times, improving BHET yield and allowing substantial energy conservation.[77] In addition, microwave-assisted can be employed for upcycling PET residue to obtain high added-value products, like polyurethane foams. Aiemsaart et al. studied the thermal and morphological properties of polyurethane foams were based on glycolyzed PET products, MDI, and different catalysts under microwave irradiation. It was observed that all foam samples exhibited similar thermal behaviors and showed closed-cell structure. In contrast, the morphology of the foams varied depending on the catalyst used, with a more uniform cell distribution observed.[78] On the other hand, Roy et al. developed a microwave-assisted glycolysis method with the aim to produce flexible polyurethane and polyisocyanurate foams using oligoesters synthesized by polycondensation of low molecular weight diols, from PET waste depolymerization, with aliphatic diacids. These diacids were introduced into the soft segment of the polymer chain, whose chain length contributed to the flexibility of the foam. Additionally, all foams exhibited uniform cell dimensions and improved thermal stability due to the introduction of aromatic rings from the glycolyzed PET polyol structure.[79]

Hoang et al. proposed another sustainable method by applying microwaves as an energy source to obtain rigid polyurethane foams with the addition of a flame retardant, (triphenyl phosphate [TPP]). The recycling reaction took place in the presence of diethylene glycol and catalyzed by zinc salts during 80 min. In the second part of the synthesis, the foam formulation followed the conventional procedure using water as blowing agent. The reagents used were mainly MDI-prepolymers and recycled PET polyol together with TPP, which additionally contributed to improve the compatibility between the polyol and isocyanate. Due to the presence of aromatic groups from PET waste, the thermal stability was increased, and the flammability of these foams was also improved. On the other hand, TPP also influenced the final properties of the foam, decreasing the density and cell size, which implied a higher compressive strength in terms of higher tensile strength and lower deformation. Moreover, TPP could behave as a plasticizer, providing greater flexibility to the soft segment of the polyurethane.[80]

Finally, it should also be noted that the eco-friendly chemical recycling of PET waste has also been addressed through other sustainable approaches, such as electrochemical methods[81] or the use of specific enzymatic systems (esterases or lipases).[82]

2.2.2 | Glycolysis by sustainable organocatalysts

Organocatalysts were also an alternative option for chemical recycling of PET waste compared to metal-based approaches. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is commercially available catalyst, and its organocatalytic performance was based on effective hydrogen bonding. It is also highlighted for its efficient energy consumption, atom economy, and accessibility, along with its shorter reaction times under catalyst loadings.[83] The TBD moiety was also used as a salt (TBD:MSA) to catalyze PET glycolysis, efficiently (90% BHET) and rapidly (less than 2 h) (Figure 9). The high versatility of this salt was demonstrated because it could be reused for at least 6 catalytic cycles and was also able to regenerate PET from the glycolyzed monomer.[84]

As discussed in PET recycling by aminolysis, a correct eco-design allowed the reutilization of secondary raw materials and their reinsertion in different sectors such as the biomedical sector. In this sector, BHET was widely used for the synthesis of polyurethanes with the aim to prepare blends with alginate for sustained protein delivery, preventing hemolysis. The depolymerization procedure and the synthesis of polyurethanes followed general methods described above.[85] Subsequently, these polyurethanes were blended with sodium alginate and then cross-linked with calcium chloride to get a pH-sensitive gastrointestinal protein with excellent biocompatibility. Furthermore, the ratio between the two types of polyols (BHET and polyethylene glycol, PEG) in the polyurethane samples established the inhibition effectivity, showing maximum protection against hemolysis when the BHET/PEG proportion was higher. In the case of swelling and hydroxyl values, the higher

FIGURE 9 Poly(ethylene terephthalate) (PET) depolymerization with ethylene glycol by organocatalysts. *Source*: Adapted from information found in References 83,84
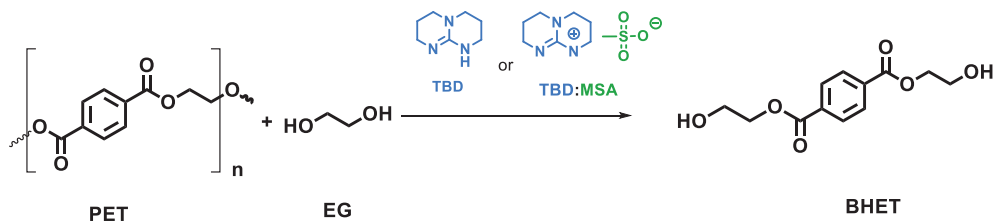
PEG content, the better the results. Moreover, the hydrophilic ability of PEG was indeed essential to gain better encapsulation and sustained release of the drugs.[86]

Apart from biomedical sector, there are other areas where BHET can also be used in addition to coatings and foams. For instance, they can be converted into urethane oils with physical properties comparable to those of commercial products by applying common reagents such as ethylene glycol, diethylene glycol, poly(ethylene glycol) 200, glycerine and toluene diisocyanate.[87] In this context, Saravari et al. followed the same idea and developed a method to produce urethane oils with different compounds, like soybean oil, to form monoglycerides and diglycerides. The isocyanate content correlated with viscosity, molecular weight, and drying time, with the first two increasing and the latter decreasing as the percentage of isocyanate increased. On the other hand, urethane oil films showed good hardness, high adhesion, and excellent water and acid resistance, but lower flexibility and poorer wear resistance compared to commercial products.[88] BHET was also employed in the production of bifunctional acrylic and allylic monomers as crosslinking agents.[89]

3 | CONCLUSIONS

In this review, different PET recycling methods have been revised, exposing the advantages and drawbacks of each of them, taking into account the Sustainable Developments Goals as well as the main problems of PET circularity. It is a fact that the only and best way to solve the inadequate treatment and management of PET waste is by integrating a circular production model, combining the two types of recycling methods and improving the recollection system.

As the mechanical approach for recycling PET residues cannot afford an infinity number of cycles, chemical recycling procedures were proposed as an alternative, in which glycolysis and aminolysis became the perfect candidates to address the economic issue linked to this process by producing high-added value materials.

Rigid polyurethanes and polyisocyanurate foams, unsaturated polyester and epoxy resins along with others examples of high-added value polymers were obtained

from the glycolysis of PET waste. In addition poly(ester amide)s, polyurethanes, composites, and others materials that were produced in the upcycling aminolysis method.

The chemical recycling procedures were carried out under drastic reaction conditions such as high temperatures and pressures, long reaction times, and heavy-metal based catalysts. These conditions hindered the implementation of these recycling procedures to the industry. Despite of these issues, the final products exhibited good mechanical, thermal and chemical properties, which implied a prospective future of revalorization materials. Furthermore, sustainable reaction conditions were presented as promising paths in these recycling systems, employing eutectic solvents, organocatalytic agents, or microwave-assisted technology.

In summary, high-added value products of good quality and excellent properties were obtained by upcycling process of PET waste, with the aims of developing circular production models and addressing the drawbacks of plastic waste treatment and management.

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