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Chemical degradation and recycling of polyethylene terephthalate (PET): a review

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Polyethylene terephthalate (PET) is one of the most common plastics, which is mainly used in food packaging and textiles. In recent years, the massive use of PET has led to the destruction of the ecological environment, and it is necessary to develop green, low-cost, and efficient recycling technologies to alleviate such problems. In this paper, we summarized the advantages and disadvantages of chemical degradation of PET in the past decade, including alcoholysis, hydrolysis, aminolysis and pyrolysis. Among them, several new catalysts have been applied to the depolymerization of plastics, such as ionic liquids, eutectic solvents, metal–organic frameworks and polyoxometalate, which not only shorten the reaction time, but also increase the yield of the product and the conversion of PET. This review emphatically introduced the conversion of PET and the yield of the product under different parameters, and clarified the direction of future research on the chemical degradation of PET.

Sustainability spotlight

In this paper, we summarized the advantages and disadvantages on chemical degradation of PET in the past decade. And this review emphatically introduced the conversion rate of PET and the yield of the product under different parameters, clarified the direction of future research on the chemical degradation of PET.

1 Introduction

Plastic is a composite material predominantly composed of synthetic polymers. Its widespread adoption over traditional

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materials can be attributed to its remarkable properties, such as resistance to corrosion, low density, cost-effectiveness, and excellent chemical and physical stability.[1] Plastics have become integral to various sectors, including textiles, medical devices, food packaging, construction, and transportation, among others.[2] Since the 1940s, certain countries began leveraging petroleum-based feedstocks for plastic production. Over time, as industrialization progressed and global populations expanded, the demand for plastics surged. Statistical data reveals that the global production of plastics reached 234 million tons in 2000 and 461 million tons in 2019,

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representing an approximate 40% increase over the two-decade period.[3,4] If this trend persists, global plastic production is anticipated to surpass 1 billion tons per year by 2025.

While plastics exhibit exceptional durability and stability, they are highly resistant to natural degradation processes, with degradation potentially taking hundreds of millions of years. During this prolonged degradation, a substantial release of toxic compounds occurs, significantly contributing to environmental pollution.[5] Numerous studies highlight the pervasive presence of plastic waste in marine environments, where it either floats on the ocean surface or accumulates on the seabed, gradually releasing pollutants into the ecosystem. This ongoing process poses severe risks to marine biodiversity and ecological balance.[6–10] Currently, approximately 9% of plastic waste is recycled, 12% is incinerated, and the remaining 79% accumulates in landfills or disperses into natural habitats.[4,11] Incineration of plastics results in the generation of hazardous air pollutants, including dioxins, furans, mercury, sulfur oxides, and polychlorinated biphenyls (PCBs), as well as residual ash that contaminates both water and soil.[12,13] Landfilling, on the other hand, involves the deposition of plastic waste into soil or underground voids, where it can leach into groundwater and adversely affect water quality and soil integrity.[14] Consequently, the development of efficient and sustainable recycling methodologies for plastic waste has become an urgent and critical focus in contemporary scientific research, particularly in the context of environmental chemistry and material science.

The main types of plastic are polyethylene terephthalate (PET), polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), polylactic acid (PLA), polycarbonate (PC), polyoxymethylene (POM), *etc.*[3] The most commonly used plastic is PET,[15] as shown in Fig. 1. It is a polyester formed by condensation of multiple ethylene glycol (EG) and terephthalic acid (TPA) through ester bonds, and is a semi-crystalline thermoplastic material,[16,17] usually identified by the "1" in various plastics.[18] There are generally three ways of synthesising PET: (1) esterification of terephthalic acid with ethylene glycol; (2) transesterification reaction of dimethyl terephthalate with ethylene glycol; (3) direct polycondensation reaction of bis(2-hydroxyethyl) terephthalate.[19,20]
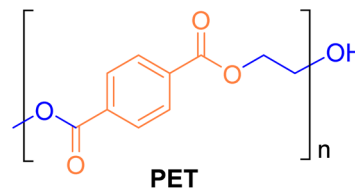

Fig. 1 Chemical structure of PET.

The primary application of PET is in food packaging, owing to its excellent transparency and corrosion resistance.[21,22] The most prevalent use is in the production of beverage bottles. As of January 2023, China's total PET bottle production has reached nearly 13 million tons, with a significant globally increase from over 41 million tons in 2014 to approximately 56 million tons by 2016. Alongside this growth in PET production, tens of millions of tons of PET plastic waste are generated annually, posing numerous environmental challenges. The accumulation of such waste has serious negative impacts on both the human environment and ecological systems.[23,24] Thus, there is an urgent need to develop environmentally friendly, cost-effective, and efficient recycling technologies to mitigate these adverse effects.

Currently, PET recycling methods are categorized into four types: primary, secondary, tertiary, and quaternary recycling.[25] Primary and secondary recycling are collectively referred to as mechanical recycling. The difference between the two types lies in the recycling process: primary recycling involves separation, sorting and purification, and there is minimal treatment of the material, it is re-used in its original form and for the same purpose, such a plastic bottle remains a plastic bottle after primary recycling. Secondary recycling, on the other hand, involves reprocessing the materials with a new purpose that reduces their properties. For example, plastic bottles get textiles after secondary recycling.[10] Tertiary recycling, or chemical recycling, involves the degradation of polymers into monomers or other polymeric structures *via* chemical reactions in the presence of reagents.[26] Quaternary recycling, or energy recovery, refers to the incineration of plastics to recover energy.[27,28]

There are generally three strategies for converting polymers into high-value chemicals: (1) depolymerization of polymers into monomers, oligomers, or other derivatives, followed by their recycling into high-value chemicals in a closed-loop system; (2) degradation of polymers into small molecules such as CO_2, CH_4, or CH_3OH, which are then upgraded into high-value chemicals; (3) direct conversion of polymers into high-value chemicals.[29] Recycling not only serves as a cornerstone of a circular economy but is also a critical requirement for environmental protection.

2 Chemical degradation of PET

To date, several chemical methods for the degradation of PET have been reported. As shown in Fig. 2, these methods include hydrolysis, alcoholysis, glycolysis, pyrolysis, aminolysis, and hydrogenolysis.[30–34] While these techniques have significantly

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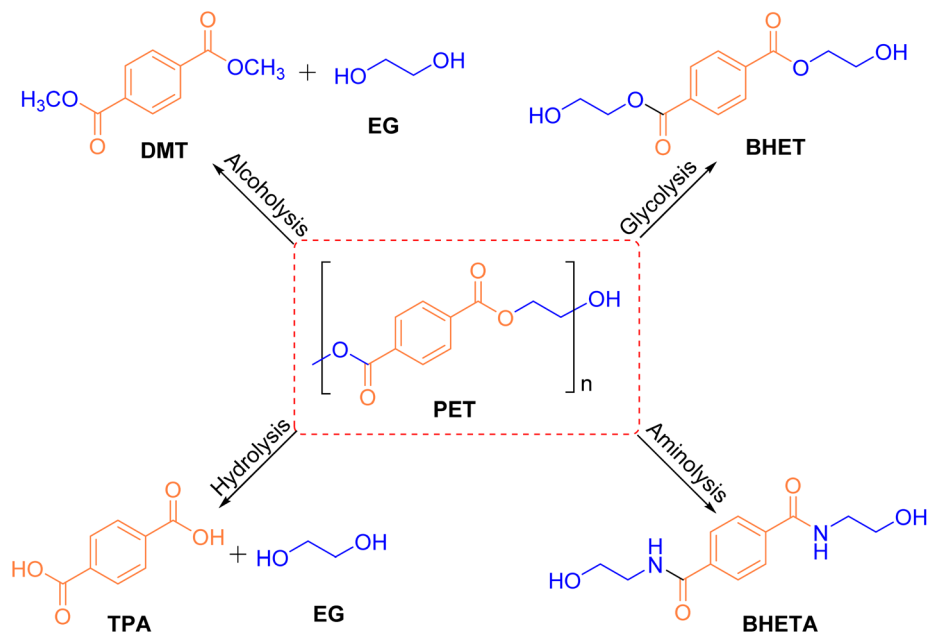
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Fig. 2 General reaction pathways for the chemical recycling of PET.

enhanced the efficiency of PET degradation, the development of low-temperature, low-energy, cost-effective, and highly efficient processes that can completely convert PET into high-value chemicals remains a critical challenge.[35]

2.1 Alcoholysis

Alcoholysis is considered a reliable and effective chemical method for PET degradation.[36] The solvents commonly employed in this process include alcohols such as methanol, ethylene glycol, and isooctanol. The primary products of alcoholysis are typically dimethyl terephthalate (DMT) and EG,[37,38] which can subsequently be converted into bis(hydroxyethyl) terephthalate (BHET) monomers. The reaction mechanism for methanolysis is depicted in Fig. 3.

2.1.1 Methanol as solvent. Methanol, a low-boiling alcohol, serves as an effective solvent in depolymerization reactions. The process requires the presence of Brønsted acids, Lewis acids, hydroxides, oxides, organic bases, and other co-solvents, which collectively enhance the yield of DMT. Hofmann[39] demonstrated that zinc(II) acetate can directly catalyze the depolymerization of PET in methanol, resulting in efficient degradation to yield DMT and EG. DMT, in particular, holds significant value as a key intermediate in chemical synthesis. In

the related study, researchers employed dichloromethane as a solvent, carrying out the reaction at 160 °C for 20 minutes. Nuclear magnetic resonance (NMR) analysis revealed that the yields of DMT and EG exceeded 95% under these conditions. However, when the reaction time was reduced to 10 minutes, the yield decreased to approximately 70%. Temperature and catalyst loading were also found to have a substantial impact on the reaction outcome. Specifically, no DMT was produced when the reaction temperature ranged from 120 °C to 140 °C, and the catalyst loading was set at 0.5 mol% (Table 1).

The Wang group[40] dispersed ZnO nanoparticles, prepared from $Zn(Ac)_2 \cdot 2H_2O$, into methanol and EG solutions to obtain methanol and EG dispersions of ZnO nanoparticles. These dispersions were utilized as pseudo-homogeneous catalysts in the methanol hydrolysis process. The effects of reaction parameters, such as the mass ratio of methanol to PET, reaction time, and temperature, on PET conversion and DMT yield were systematically investigated. It was observed that both dispersions exhibited excellent stability and transparency. Experimental results indicated that a PET conversion of 97% and a DMT yield of 95% were achieved after 15 minutes at 170 °C. Cho[41] and colleagues employed a strategy to convert waste PET into DMT at relatively low temperatures. By controlling moisture content and using K_2CO_3 as a catalyst, they facilitated PET
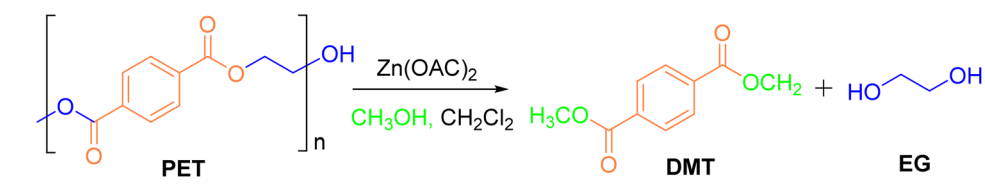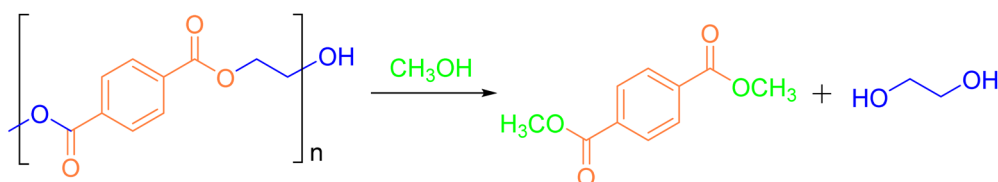

**Fig. 3** The reaction formula of methanol alcoholysis.

Table 1 The depolymerization of PET catalyzed by Zn(OAc)$_2$. Reproduced with permission.[39] Copyright 2020, European Chemical Society

Entry	Catalyst loading [mol%]	MeOH [equiv.]	CH$_2$Cl$_2$ [equiv.]	T [°C]	t [min]	Yield of DMT [%]
1	1	46.2	17.4	160	20	98
2	1	46.2	17.4	160	15	81
3	1	46.2	17.4	160	10	75
4	1	46.2	17.4	140	20	<1
5	1	46.2	17.4	140	60	92
6	1	46.2	17.4	120	20	<1
7	1	69.4	17.4	160	20	<1
8	1	92.5	8.7	160	20	<1
9	1	46.2	26.2	160	20	98
10	0.75	46.2	17.4	160	20	76
11	0.5	46.2	17.4	160	20	<1
12	—	46.2	17.4	160	20	<1

decomposition with only methanol, achieving a PET conversion of 4.5% and a DMT yield of 3.6%. The process also generated by-products such as 1-(2-hydroxyethyl)-4-terephthalate methyl ester (HEMT) and monomethyl terephthalate (MMT). The catalytic efficiency was significantly enhanced by the addition of the non-polar proton co-solvent dimethyl carbonate (DMC). Optimal conditions involved molar ratios of catalyst, methanol, and moisture to PET repeat units of 0.2, 50, and 0.4, respectively, as well as a DMC to PET repeat unit ratio of 50 at 25 °C for 24 hours. The use of chlorinated methane solvents, such as dichloromethane (DCM) and chloroform, reduced by-product formation and improved DMT selectivity. Zhang[42] introduced aromatic boronic acids to facilitate the *in situ* capture of EG during the methanolysis of waste PET, yielding pure DMT and five-membered arylboronic esters (ABE) (Fig. 4). Arylboronic esters are valuable organoboron compounds that serve as intermediates for the synthesis of medicinal materials and natural products *via* coupling reactions. Without a catalyst,

yields of DMT and ABE were 8% and 10%, respectively, after 2 hours at 180 °C. To enhance yield, they adjusted the calcination temperature, catalyst loading, and the Mg/Al ratio in magnesium–aluminum layered double oxide (Mg–Al-LDO) catalysts, thereby introducing weak alkaline sites. Under optimal conditions, the conversion of PET reached 100%, with ABE and DMT yields of 96% and 99%, respectively. Furthermore, it was demonstrated that the Mg$_4$–Al$_1$-LDO catalyst could be recycled, highlighting its potential for sustainable chemical processes.

Lv[43] utilized low-cost, environmentally friendly sodium silicate (Na$_2$SiO$_3$·9H$_2$O) as an alkaline catalyst for the hydrolysis of PET to DMT. The reaction was conducted in an autoclave, with reaction parameters such as methanol quantity, reaction temperature, and catalyst loading systematically optimized. Catalyst activity was found to be related to its alkalinity, which could be modulated through calcination. The highest alkalinity was achieved at 300 °C for 2 hours, but maximum catalyst activity was observed after calcination at 400 °C. The optimal
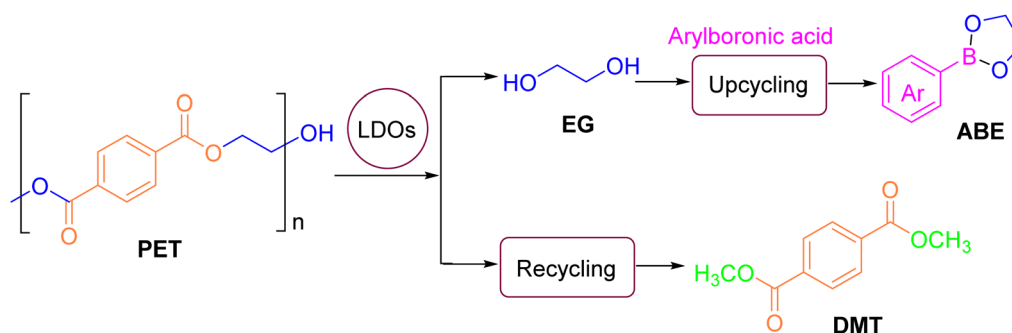
Fig. 4 Waste PET uncycling by *in situ* capturing EG with arylboronic acid in the methanolysis process. Reproduced with permission.[42] Copyright 2024, Elsevier Ltd.
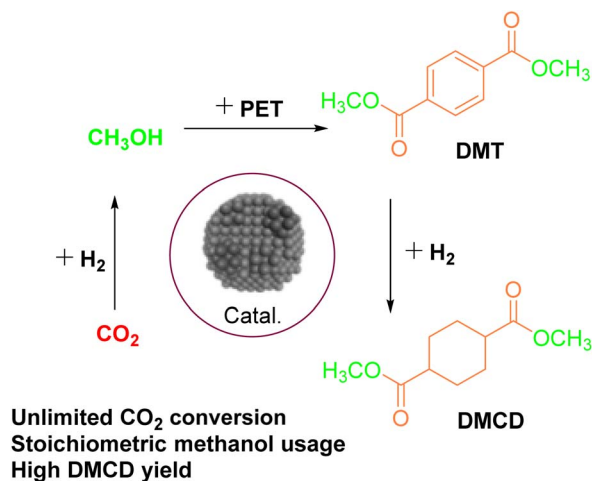
Fig. 5 One-pot catalytic system. Reproduced with permission.[44] Copyright 2021, Wiley-VCH GmbH.

conditions for complete PET degradation were a 5 wt% catalyst, a methanol-to-PET mass ratio of 5 : 1, and a reaction time of 30 minutes at 200 °C, yielding a DMT yield of 95%. To address the limitations of conventional PET degradation methods, Wang[44] proposed a one-pot catalytic system that combined CO_2 hydrogenation, PET methanol hydrolysis, and DMT hydrogenation. The system (Fig. 5) employed a $Cu_4Fe_1Cr_1$ catalyst to promote CO_2 hydrogenation and DMT conversion. It was observed that the presence of PET enhanced CO_2 hydrogenation, while H_2 generated from CO_2 reduction facilitated PET methanolysis. This process yielded valuable degradation products, including DMT, dimethyl cyclohexanedicarboxylate (DMCD), and para-xylene (PX). The yield of EG increased from 12.1% to approximately 88% when CO_2 and H_2 were used instead of excess methanol, demonstrating the synergistic effect of CO_2 hydrogenation and PET methanolysis. The use of a single hydrogenation catalyst for multiple reactions enhances efficiency and sustainability, converting waste PET and CO_2 into high-value chemicals. It is noteworthy that PET undergoes transesterification with excess methanol in the presence of an appropriate catalyst to yield DMT and EG. Both of these products can be reutilized in industrial polymerization processes. DMT, as a valuable chemical intermediate, can be repolymerized into new PET, thereby supporting sustainable production and the circular economy of polymer materials.

The Yu group[45] developed a CO_2–H_2-PET system for one-pot methanol decomposition by coupling CO_2 hydrogenation to methanol (CH_3OH) with PET methanolysis to DMT. In this system, Cu/ZnO served as the catalyst, and tetrahydrofuran (THF) was used as the solvent to dissolve PET particles. To enhance the yield of methanol from CO_2 hydrogenation, various alcohols, including ethanol (EtOH), *n*-propanol (*n*-PrOH), *n*-butanol (*n*-BuOH), and isopropanol (i-PrOH), were introduced. The results revealed that the ability of these alcohols to promote PET conversion followed the order: i-PrOH < *n*-BuOH < *n*-PrOH < EtOH. Although EtOH improved methanol yield, it also produced more by-products, resulting in a lower DMT yield.

Among the tested alcohols, i-PrOH was found to be the most effective, as it enhanced the yields of both methanol and DMT while minimizing by-product formation. Under optimal conditions, the PET degradation rate increased from 31.9% to 63.1%, and the DMT monomer yield reached 92.7%. Yin[46] explored the use of supercritical methanol to depolymerize PET into its monomers, DMT and EG. However, the harsh reaction conditions posed challenges for industrial application. To address this, the researchers introduced CO_2 to facilitate the supercritical methanolysis of PET and examined the effects of the methanol-to-PET weight ratio, reaction time, and initial CO_2 pressure on the DMT yield. Their findings demonstrated that increasing the methanol-to-PET ratio and prolonging the reaction time both led to higher DMT yields. It was further confirmed that the presence of CO_2 enhanced the supercritical methanolysis of PET by accelerating its depolymerization. This was attributed to the insertion of CO_2 into the PET molecular chain, which weakened intermolecular forces, thereby promoting chain cleavage. Under optimal reaction conditions (270 °C, methanol-to-PET mass ratio of 6 : 1, and 40 minutes reaction time), a DMT yield of 95% was achieved. Tanaka[47] proposed a novel method for PET degradation by capturing EG with DMC as a trapping agent to produce DMT at room temperature (Fig. 6). The method utilized the principle of transesterification as a reversible reaction, where the equilibrium was shifted toward the product side, thus increasing the DMT yield (Fig. 6a). During the reaction, ethylene carbonate (EC) was formed from EG and DMC. As a five-membered cyclic compound, EC exhibited high stability, which hindered the reverse reaction to DMC and EG (Fig. 6b). Simultaneously, methanol produced during the process further reacted with PET, facilitating PET decomposition through methanolysis (Fig. 6c). Initially, Tanaka's team ground post-consumer PET into powder and mixed it with 10 mol% lithium *tert*-butoxide (LiO*t*Bu) at 65 °C for 5 hours. However, this approach yielded only 18% DMT and 22% EG. The introduction of THF increased the yields, but they remained below 50%. Subsequent experiments revealed that substituting THF with DMC significantly improved the DMT yield, reaching 86%. This breakthrough enabled a deeper understanding of the depolymerization mechanism and prompted investigations into the effects of alkali metal alkoxide catalysts, the dosage of MeOH and DMC, and reaction time on DMT yield. Under optimized conditions, the DMT yield exceeded 90%, demonstrating the effectiveness of the strategy.

To develop an efficient and environmentally friendly system for PET methanolysis, Yan[48] synthesized a series of non-metallic deep eutectic solvent[49,50] (DES) catalysts composed of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). Among the synthesized catalysts, the 1,5-diazabicyclo [4.3.0]-5-nonene (DBN)/phenol catalyst exhibited the best catalytic performance with the added advantage of leaving no metal residues in the final product. FT-IR spectra revealed the formation of N–H–O hydrogen bonds between DBN and phenol, where the N–H group interacted with the carbonyl oxygen of PET, while the oxygen atom of phenol activated the hydroxyl (–OH) group in methanol. During the methanolysis of PET, one of
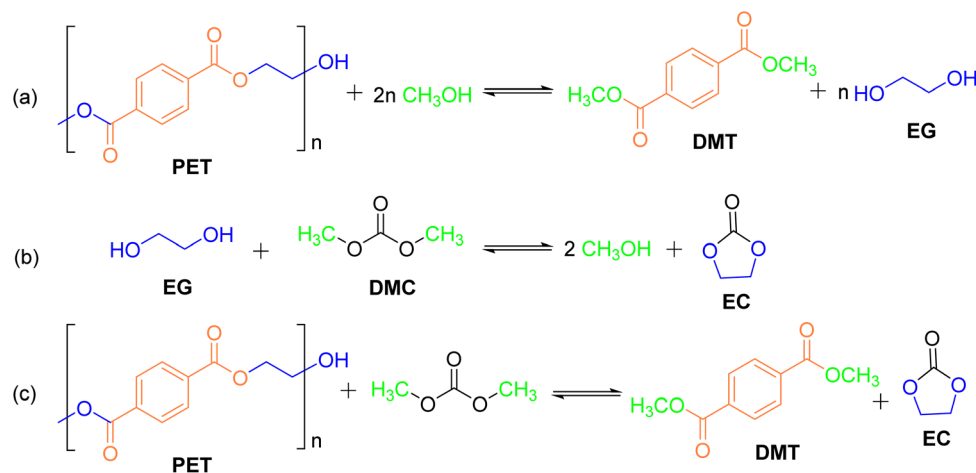
Fig. 6 General process of depolymerization of polyethylene terephthalate, (a) The products of the alcoholysis of PET are the compounds DMT and EG. (b) EC was formed from EG and DMC. (c) The methanol formed *in situ* further reacts with PET, and facilitates the overall PET methanolysis. Reproduced with permission.[47] Copyright 2021, The Royal Society of Chemistry.

the key products is EG. It was observed that when the reaction temperature exceeded 130 °C, the reaction time was extended to 90 minutes, or the catalyst loading was increased, the concentration of EG in the solvent rose. This shift in equilibrium favored the formation of by-products, specifically 2-hydroxyethyl methyl terephthalate (MHET) and BHET, thereby reducing the yield of DMT. To achieve optimal reaction conditions, the researchers identified that conducting the reaction at 130 °C for 1 hour, with a catalyst mass fraction of 5 wt% and a methanol-to-PET mass ratio of 3 : 1, resulted in complete conversion of PET. Under these conditions, a high DMT yield of 95.3% was achieved, demonstrating the efficiency of the DBN/phenol DES catalyst in PET methanolysis.

2.1.2 Use diols or polyols as solvents. In addition to its application in the synthesis of DMT using ethylene glycol, ethylene glycol can also serve as a solvent in the alcoholysis of PET, facilitating the conversion of BHET monomer. Glycolysis, a specific type of alcoholysis, typically employs diols (commonly ethylene glycol) as solvents.[51] The ester groups in PET undergo transesterification with the diols, yielding the primary product, BHET monomer,[52] which can subsequently be utilized as a feedstock for the production of recycled PET or other polymers. However, due to the relatively slow nature of PET glycolysis, the addition of auxiliary catalysts is necessary to accelerate the reaction. Catalysts employed in PET glycolysis include homogeneous catalysts, primarily consisting of ionic liquids,[53–55] deep eutectic solvents,[56] metal salts, and others. Heterogeneous catalysts, such as metals, metal oxides, metal–organic frameworks (MOFs),[57] carbonaceous compounds, and zeolites, are also commonly utilized in this process.[58,59]

2.1.2.1 Heterogeneous catalysts. MOFs are porous crystalline materials that have gained widespread application in various fields due to their biomimetic catalysis and biocompatibility.[60] General PET depolymerization is a process in which degradation occurs layer by layer, from the outermost layer to the innermost. Notably, Xia[61] proposed a strategy to achieve rapid

depolymerization by concurrently degrading both the outer and inner layers of PET. Traditional PET degradation proceeds from the outer layer to the inner layer, where the surface chains are depolymerized into shorter chains, which subsequently detach from the PET substrate to form oligomers. As the inner layer begins to degrade, oligomers from the outer layer gradually convert to monomers. The simultaneous degradation of the outer and inner layers transforms the PET particles from a dense structure to a flocculent one under high temperature and micro pressure, resulting in a multi-layer porous structure that significantly increases the contact area between PET and reactants, thereby enhancing the yield. In the course of research, two "Dawson"-type polyoxometalates (POMs) were synthesized. The first is α^2-$K_8P_2W_{17}O_{61}X(H_2O)\cdot16H_2O$ (X = Zn, Mn, Co, Ni, Cu), prepared in four steps with transition metal-substituted POM framework structures. Among these, the Zn- and Ni-substituted POM catalysts exhibited the best oligomer performance, although the Ni-substituted POM catalysts showed the lowest activity. Steric hindrance and catalyst activity are critical factors in PET degradation. The hydrolysis process is divided into three stages: the first stage (from the start to 3 minutes) is characterized by the expansion of PET and an increase in chain spacing, significantly enhancing the contact area between PET, the catalyst, and the solvent. In the second stage (approximately 10 minutes), BHET and oligomers begin to form. In the third stage (10–15 minutes), oligomers disappear and are converted to BHET. Under optimal conditions, PET is completely degraded, yielding a product with a 72.1% yield. The controlled degradation of PET has potential applications in the production process of PET–PLA copolymers, enabling sustainable recycling technology. The second catalyst is $K_{10}[M_4(H_2O)_2(PW_9O_{34})_2]\cdot H_2O$ (M = Zn, Mn, Cu, Ni, Co).[62] In this case, the transition metal active sites attack the C–O bond in PET, and the catalyst forms numerous hydrogen bonds between W–O and EG, facilitating rapid PET degradation. Characterization results of the catalyst and PET alcoholysis products revealed two

Table 2 Catalytic performance of different types of catalysts on PET alcoholysis. Reproduced with permission.[62] Copyright 2022, Elsevier Ltd[a]

Catalyst	Cat/PET (wt%)	PET : EG (w/w)	Temp (°C)	Time (min)	C_{PET} (%)	Y_{BHET} (%)
$Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$	0.5	1:4	190	40	100	84.5
$SiW_{11}Zn$	2.0	1:4	185	30	100	84.1
K_2CO_3/EG	4.2	1:5	180	120	100	88.0
[amim][ZnCl_3]	10.0	1:4	175	75	100	80.1
1,3-DMU/Zn(OAc)_2	5.0	1:4	190	20	100	82.0
[Dmin][Zn(OAc)_3]	16.7	1:4	180	90	100	67.1
[Bmim]_2[CoCl_4]	16.7	1:11.7	175	90	100	81.1
Urea	10.0	1:4	180	180	100	77.7
$K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot H_2O$	2.0	1:4	240	8	100	39.0
$K_{10}[Ni_4(H_2O)_2(PW_9O_{34})_2]\cdot H_2O$	2.0	1:4	240	8	100	48.9
$K_{10}[Cu_4(H_2O)_2(PW_9O_{34})_2]\cdot H_2O$	2.0	1:4	240	8	100	58.5
$K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2]\cdot H_2O$	2.0	1:4	240	8	100	86.0
$K_{10}[Zn_4(H_2O)_2(PW_9O_{34})_2]\cdot H_2O$	2.0	1:4	240	8	100	92.8

[a] Reaction conditions: PET (1.0 g), EG (4.0 g), cat (2.0 wt%), 240 °C, 8 minutes.

distinct weight losses between 30 °C and 800 °C, attributed to the presence of crystal water in the catalyst and the mass loss resulting from structural collapse. In the exploration of optimal conditions (Table 2), when the temperature ranged from 210 °C to 230 °C, the conversion and BHET yield reached 100% and 63.7%, respectively, with the BHET yield increasing to 92.8% upon further increasing the temperature to 240 °C. Within 3–10 minutes, PET was completely degraded at 5 minutes, and the BHET yield reached its maximum (92.8%) at 8 minutes. The amount of catalyst also significantly influenced the degradation yield; within the range of 0.5–4.0 wt%, the BHET yield first increased and then decreased, reaching its maximum value at a catalyst dosage of 2.0 wt%. Mechanistic studies on controlled

Fig. 7 ZIF-8 catalyzes the depolymerization process of PET. Reproduced with permission.[63] Copyright 2016, Springer Science, Business Media New York.

alcoholysis revealed that the formation of the flocculent structure in PET is a key factor in achieving controlled degradation.

Suo[63] synthesized metal–organic framework (MOF) catalysts ZIF-8, ZIF-67, and MOF-5 using $Zn(NO_3)_2\cdot6H_2O$, $Co(NO_3)_2\cdot6H_2O$, and 2-methylimidazole (Hmim) as raw materials, which exhibited high catalytic activity. Among these, ZIF-8 demonstrated higher activity than ZIF-67 and MOF-5, likely due to differences in the molar ratio of Hmim to metal in the catalyst. When the molar ratio was 2:1, PET could not be fully converted, and the yield of BHET reached only 47.73%. However, when the molar ratio increased to 4:1, both the conversion of PET and the yield of BHET improved significantly. Beyond a molar ratio of 4:1, the cavity of ZIF-8 became increasingly obstructed by Hmim, leading to a decrease in both conversion and yield. In the presence of ZIF-8 and EG, complete depolymerization of PET was achieved by reacting at 197 °C for 1.5 hours, resulting in a BHET yield of 76.75%. The depolymerization process is illustrated in Fig. 7.

Nguyen[64] et al. also utilized the metal–organic framework M-BDC (M = Cu, Co, Ni, and Zn) as catalysts for PET glycolysis. These frameworks, composed of benzene dicarboxylic acid (BDC) and the metals Cu, Co, Ni, and Zn, showed varying catalytic performances, with Zn-BDC exhibiting the best catalytic activity. The researchers further developed a deep neural network (DNN) model to optimize the parameters for PET depolymerization, finding that the error between experimental results and DNN model predictions was minimal (<1%). Under optimal conditions, the catalyst could be recycled three times, and the product BHET could also be converted into TPA. Maihom[65] demonstrated that PET glycolysis could yield MHET and BHET monomers using a Zn-supported MOF-808 metal–organic framework. Additionally, catalysts based on three tetravalent metals—Zn–Hf-MOF-808, Zn–Zr-MOF-808, and Zn–Ti-MOF-808—were synthesized, with Zn–Ti-MOF-808 exhibiting the lowest catalytic activity among the three. Sardon[66] reported that the yield of BHET could reach 88% when 1,3-dioxane was used as a co-solvent, EG as the solvent, and triazacyclodecene (TBD) as the catalyst, under reaction conditions of 65 °C for 1 hour. The study also demonstrated that a heterogeneous
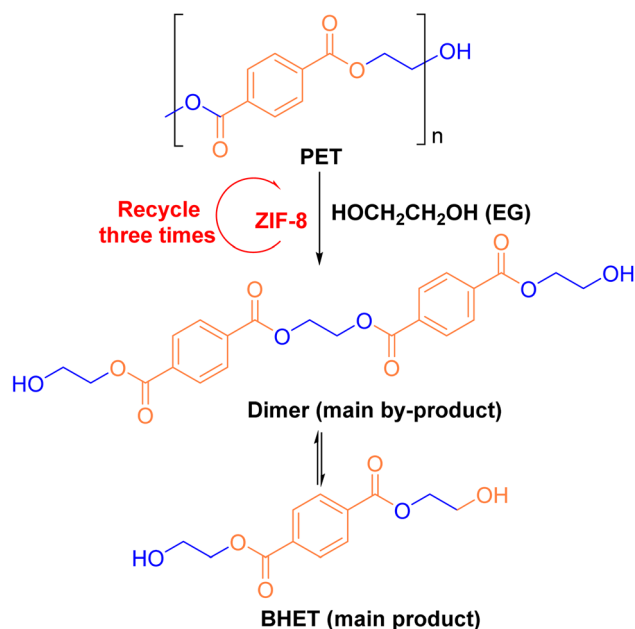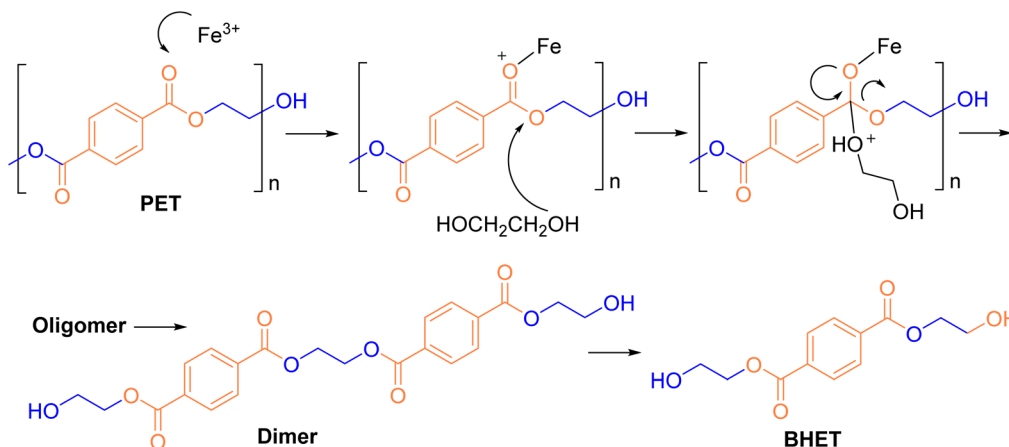
Fig. 8 Glycolysis mechanism of PET using Fe_2O_3 nanoparticles as catalysts. Reproduced with permission.[63] Copyright 2021, the Royal Society of Chemistry.

depolymerization process could be converted into a homogeneous one with the addition of an effective co-solvent. In recent years, nanomaterials have gained significant attention in various industries, including PET glycolysis. Numerous studies have shown that nanostructured heterogeneous catalysts can enhance the yield of BHET while maintaining the ability to be recycled. Kim[67] synthesized an Fe_2O_3@MoS_2 0D/2D nanocomposite catalyst for PET glycolysis, designed to strip MoS_2 and uniformly precipitate it on Fe_2O_3 nanoparticles within a Taylor–Couette flow reactor. The reaction mechanism is shown in Fig. 8. After optimizing reaction conditions, the conversion of PET and the yield of BHET reached 97% and 90%, respectively, at a temperature of 225 °C for 3 hours.

The Choi group[68] developed a method to rapidly insert the alkali cation K^+ into MnO_2 to prepare a catalyst for PET glycolysis, resulting in an ultra-thin manganese dioxide nanosheet (e-MON) with a two-dimensional structure, which is also recyclable. In the study, reaction conditions were optimized by varying the reaction time, temperature, and catalyst amount. Ultimately, a catalyst concentration of 0.01 wt% was used to achieve complete depolymerization of PET *via* continuous reaction at 200 °C for 30 minutes, resulting in a 100% yield of BHET. Wang[69] coordinated the KH550 modifier with CeO_2 to form defect-rich CeO_2 nanoparticles (NPs) with a very small size (2.7 nm). The cerium ions in CeO_2 exist in two valence states, Ce^{3+} and Ce^{4+}, with Ce^{4+} being reduced to Ce^{3+} during the glycolysis process, thereby enhancing the degradation efficiency of PET. The CeO_2 NPs catalyst achieved 98.6% PET conversion and 90.3% BHET yield after a 15 minutes reaction at 196 °C. Glycolysis can also be applied to PET-containing textiles. For instance, Yu[70] synthesized a new heterogeneous catalyst, Zn-MCM-41-25, by using Si/Al with a Zn to molar ratio of 25. Zn-MCM-41-25 demonstrated good catalytic activity in the depolymerization of waste PET textiles. Under optimal conditions, with 8% Zn loading, 5% catalyst dosage, an EG/PET mass ratio of 6, and a reaction temperature of 200 °C for 1 hour and 45 minutes, 100% PET conversion and an 81.4% BHET yield were achieved. Hydrogen bonding and coordination were identified

as key factors for rapid alcoholysis. Shen[71] developed a green, new catalyst—titanium phthalate (Ti-PA)—by gradually adding $Ti(OiPr)_4$ to phthalic acid over 12 hours at 90–120 °C, followed by washing with ethanol and drying to obtain a white powder. Ti-PA can decompose into TiO_2, CO_2, and H_2O at high temperatures. Used as a catalyst in EG for the hydrolysis of waste PET, Ti-PA demonstrated good catalytic activity. Response surface methodology[72] indicated optimal conditions at 0.86% Ti-PA dosage, 13.7 mL EG, and a reaction time of 3.98 hours at 191 °C. The Yu group[73] synthesized an orderly octahedral titanium benzoate (Ti-BA) catalyst by using benzoic acid (BA) and titanium ester *via* a hydrothermal method. The Ti-BA catalyst achieved a BHET yield of 90.01% at 217 °C for 3.3 hours, with an EG/PET mass ratio of 3.59 and a catalyst dosage of 2% by weight. The efficient degradation of PET was attributed to the synergistic effect of titanium ions and EG in the catalyst, enhancing its catalytic performance. Titanium was chosen for its biocompatibility and catalytic activity. Ti-BA exhibited good hydrolysis resistance and was easily recoverable. The Zhai group[74] synthesized acetylacetone titanium oxide $[TiO(acac)_2]$ by reacting acetylacetone and isopropyl titanate in a three-necked flask. The catalyst, a pale yellow powder, demonstrated good stability, as evidenced by FT-IR analysis showing the chelation of the C=O bond in acetylacetone with titanium atoms. The hydrolysis of waste PET was conducted using $[TiO(acac)_2]$ as a catalyst and EG as a solvent under optimal conditions: 3 g of PET, 0.467% catalyst, 13.5 mL EG, and a 3.77 hours reaction at 200.5 °C, yielding 96.41% BHET. Lu[75] designed and synthesized the novel bisidazole cationic zinc eutectic solvent catalyst $[C_2(Mim)_2][OAc]_2$-$2Zn(OAc)_2$ to catalyze the degradation of PET in EG. The catalyst demonstrated good catalytic activity, with a synergistic effect between $[C_2(Mim)_2]$$[OAc]_2$ and $Zn(OAc)_2$. The catalyst led to 100% PET conversion and 85.2% BHET yield. Fang[76] investigated the use of neopentyl glycol (NPG), dipropylene glycol (DPG), and polypropylene glycol (PPG) for PET degradation to obtain a series of alcoholytic products. It was found that the alcoholysis activity of DPG was lower than that of NPG and EG. The study also observed

that small molecule alcohols could convert PET into oligomers, dimers, and trimers, with higher temperatures enhancing alcoholysis activity. Thus, glycolysis can serve as an environmentally friendly method for PET degradation and contribute to the synthesis of waterborne polyurethane. Shaver's research[77] focused on the sustainable recycling of plastic cards, commonly made from thermoplastic composite materials containing PET. Using ethylene glycol-modified polyethyl terephthalate (PET-G) as an alternative thermoplastic, Shaver's group developed a strategy for converting polyester components in plastic cards into monomer units and then polymerizing them to form complex laminate materials, preserving the performance of the plastic cards. This strategy promotes the recycling of plastic cards and supports the circular economy. In addition to diols, polyols can also serve as solvents for PET degradation. Chen[78] used the ionic liquid [Bmim]Cl and isooctanol (2-EH) to catalyze the degradation and conversion of PET into dioctyl terephthalate (DOTP). The preparation strategy for the ionic liquid is shown in Fig. 9.

The alcoholysis of PET in various ionic liquids (ILs) is presented in Table 3. Zinc acetate (ZA), a solid that is poorly soluble in alcohols and ionic liquids and easily separable, was used as the catalyst in this experiment. The reaction conditions included a reaction time of 5 hours, an IL : 2-EH : PET mass ratio of 2 : 2 : 1, and a catalyst/PET mass ratio of 1.2%. PET was found to be completely depolymerized, with a yield of 93.1% for dioctyl terephthalate (DOTP). This method resulted in a shorter reaction time compared to traditional ionic-free liquid alcoholysis reactions, and the ionic liquids could also be reused. The alcoholysis of PET using methanol, polyol (mainly EG), and polyols as solvents leads to the main products of DMT and BHET. The addition of an appropriate amount of catalyst or co-solvent during the reaction can accelerate the reaction rate, improving the conversion of PET and the yield of the product. In recent years, the development of catalysts, such as ionic liquids,[79] deep eutectic solvents,[80,81] and metal oxides,[60] has greatly facilitated the degradation of waste PET.

2.1.2.2 Homogeneous catalysts. Homogeneous catalysts exhibit high depolymerization efficiency; however, they are challenging to recover after the reaction and separation.[4,82] Llopis[83] used a large amount of EG to perform glycolysis of solid

Table 3 The alcoholysis of PET in different ILs. Reproduced with permission.[78] Copyright 2014, Elsevier Ltd[a]

IL	Degradation rate of PET (%)	Yield of DOTP (%)
—	1.7	1.2
[Amim]Cl	56.1	42.4
[Bmim]Cl	57.3	43.2
[Bmim]Br	46.2	37.3
[Bmim]NO$_3$	10.5	6.5
[Hmim]CF$_3$SO$_3$	5.2	3.7
[Bsmim]HSO$_4$	28.6	20.5
[Bmim]BF$_4$	4.3	3.1
[Bmim]PF$_6$	3.7	2.2

[a] Reaction conditions: reflux temperature, 4 h, weight ratio of ionic liquid : 2-EH : PET 2 : 2 : 1.

PET at various times and temperatures, without the use of catalysts, and observed the depolymerization process. Initially, EG diffuses into the PET particles and attacks the amorphous regions, which is a heterogeneous process, followed by a homogeneous process, generating oligomers and the monomer BHET, with yields exceeding 97%. However, this process is slow and time-consuming, and the addition of a catalyst can accelerate the reaction rate. Compared to traditional catalysts, ionic liquids serve as green catalysts that minimize product residues. The Shuangjun group[84] synthesized a series of Lewis acidic ionic liquid (LAILs) as catalysts, using 1-hexyl-3-methylimidazole chloride ([Hmim]Cl) and metal oxides (CoCl$_2$, FeCl$_3$, ZnCl$_2$, CuCl$_2$) in the presence of dichloromethane for 8 hours, followed by evaporation. Experimental results showed that [Hmim]CoCl$_3$ catalyzed the complete conversion of PET in 4 hours, while [Hmim]ZnCl$_3$ only required 1.5 hours, indicating its high reactivity. However, when the reaction time was 4 hours, the yield of BHET catalyzed by [Hmim]ZnCl$_3$ was lower than that of [Hmim]CoCl$_3$, due to the formation of by-products from the high activity of [Hmim]ZnCl$_3$. Furthermore, the hybrid catalyst of [Hmim]ZnCl$_3$ and [Hmim]CoCl$_3$ achieved an 87.1% BHET yield from PET conversion, which was higher than the yield from using a single ionic liquid catalyst. Barikani[85] and colleagues synthesized a cobalt based ionic liquid
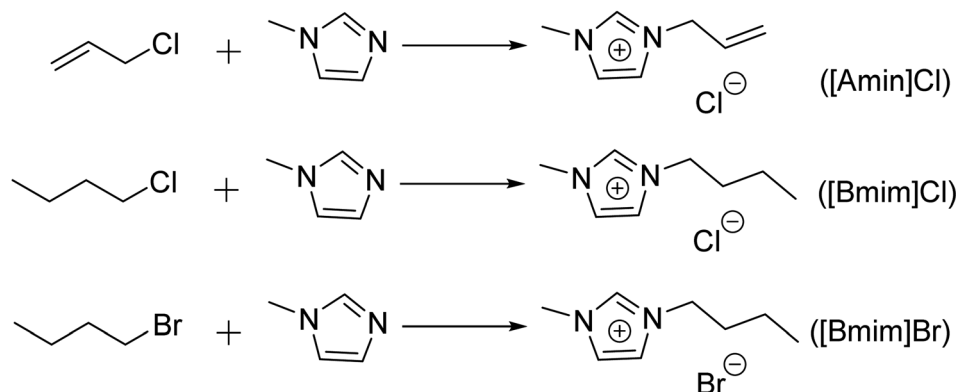

Fig. 9 Preparation strategies for ILs. Reproduced with permission.[78] Copyright 2014, Elsevier Ltd.

functionalized graphene (rGO[TESPMI]$_2$CoCl$_4$) and explored the effects of reaction temperature, time, catalyst dosage, and EG dosage on PET depolymerization. They found that when the catalyst dosage ranged from 0.05 to 0.15 g, the yield of BHET increased, but it decreased when the dosage exceeded 0.15 g. The yield of monomer gradually increased between 150 °C and 190 °C and stabilized around 180 °C. Reaction time also played a role in the conversion rate of PET, and the yield and selectivity of BHET increased between 1–3 hours, but began to decrease after 4 hours. The optimal reaction conditions were identified as follows: 1 g of PET, 0.15 g of catalyst, 14 g of ethylene glycol, and a reaction temperature of 190 °C for 3 hours. Under these conditions, PET conversion reached 100%, and the BHET yield was 95.22%. Furthermore, the catalyst maintained good activity after 5 consecutive uses. Zhang[86] synthesized a TPA-based ionic liquid as a catalyst for PET glycolysis. The carboxyl group in TPA and the hydroxyl group in EG can form hydrogen bonds that promote transesterification. After screening various catalysts with different cations and anions (Table 4), the results showed that 1-ethyl-3-methylimidazole terephthalate ([EMIm]$_2$TPA) exhibited excellent catalytic activity, which remained unchanged after 15 uses. After 106 minutes of reaction under the influence of the catalyst, PET was completely converted, and the BHET yield reached 83.6%. The repolymerization of BHET into recycled PET (r-PET) led to less yellowing, and [EMIm]$_2$TPA significantly reduced by-products, improving the color quality of r-PET.

He[87] synthesized four ionic liquids containing organophosphorus groups, namely [P4444]For, [P4444]Ace, [P4444]Pro, and [P4444]But, using tetrabutyl phosphonium hydroxide and four carboxylic acids (formic acid, acetic acid, propionic acid, and butyric acid) as raw materials. Among these, [P4444]Ace exhibited good glycolytic activity on waste PET and demonstrated excellent thermal stability. After 120 minutes at 195 °C, PET conversion reached 100%, but the yield of BHET was relatively low, at only 37.8%. When the temperature was increased to 200 °C, the PET conversion remained stable, and the BHET yield improved to 40.8%. The optimal catalyst amount was found to be 15 wt%. The mechanism of [P4444]Ace-catalyzed PET depolymerization was further investigated, revealing that [P4444]Ace formed a new chemical bond with the hydroxyl

group in EG, which accelerated PET depolymerization. Sert[88] studied the glycolysis of PET using EG in the presence of five different DES catalysts. The best catalytic effect was observed with a DES synthesized from potassium carbonate and EG, which achieved an 88% yield of BHET at 180 °C, with an EG/DES ratio of 15 and a DES/PET ratio of 6. While many studies have reported on the use of homogeneous catalysts, several disadvantages persist, such as difficulty in catalyst separation, low selectivity, and low product purity.

2.2 Hydrolysis

In addition to alcoholysis, hydrolysis can also be used for the chemical degradation of PET, and it is considered one of the most efficient methods for PET degradation.[89] The reaction formula for PET hydrolysis is shown in Fig. 10. The general products of PET hydrolysis are TPA and EG, which are the basic monomers of synthetic PET. Since the resulting TPA is of high purity, it can be purified and then regenerated into PET, contributing to material recycling. PET hydrolysis is classified into three categories: acid hydrolysis, alkaline hydrolysis, and neutral hydrolysis.[16] Several factors influence the hydrolysis process, including temperature, reaction time, concentration of acid or base, and the type and concentration of the catalyst.

2.2.1 Acid hydrolysis. Acid hydrolysis is most commonly carried out using concentrated sulfuric acid, nitric acid, or phosphoric acid.[89] For example, Islam[90] used 80% v/v aqueous sulfuric acid for PET acid hydrolysis and found that after 30 minutes of reaction at 100 °C, PET was completely converted, and the yield of TPA reached over 95%. The hydrolysate, prepared from H$_2$SO$_4$ and distilled water, yielded consistent quantities and quality of the product after four cycles. Over these cycles, the stock solution of TPA gradually changed from bright white to grey-white, while the original hydrolysate, initially colorless, became brown to brown-black as the reaction progressed. This color change was attributed to the by-products, such as glycerol or dissolved TPA, formed during the reaction. This study presents a sustainable method to convert waste PET into a valuable commodity. However, using strong acids like hydrochloric acid, nitric acid, and sulfuric acid has several disadvantages. These acids are not recyclable, and their use generates large amounts of strong acid wastewater, significantly increasing production costs.[89] Therefore, the development of recyclable and reusable catalysts for PET hydrolysis is crucial. In recent years, researchers have developed catalysts that are easier to recover and recycle. For example, Hu[89] used TPA as an acid catalyst to promote PET hydrolysis, since TPA is a basic building block of PET. This avoids unnecessary separation processes and the generation of large amounts of wastewater. TPA, being easily recyclable, can maintain its activity after multiple uses. In Hu's study, the purity of the prepared TPA reached 99%, and its activity remained unaffected after 8 repeated uses. The hydrolysis mechanism involves the ionization of the carboxyl group in TPA in water, producing hydrogen ions that react with the carbonyl group in PET to form a carbocation and a hydroxyl group. The carbocation then undergoes nucleophilic attack by water, leading to the formation of TPA and EG. The optimal

Table 4 Effect of the cationic and anionic structure of ILs on PET glycolysis. Reproduced with permission.[86] Copyright 2023, American Chemical Society[a]

Entry	Catalyst	Conversion of PET (%)	Yield of BHET (%)
1	—	3.3	0
2	[EMIm]$_2$TPA	99.8	73.9
3	[PMIm]$_2$TPA	97.8	71.8
4	[BMIm]$_2$TPA	97.4	70.8
5	[BMMIm]$_2$TPA	92.4	62.9
6	[EMIm]$_2$IPA	98.4	70.5
7	[EMIm]$_2$PA	96.6	69.0

[a] Reaction conditions: 5.0 g of PET, 20.0 g of EG, and 0.25 g of ILs, reacting for 120 min at 190 °C.
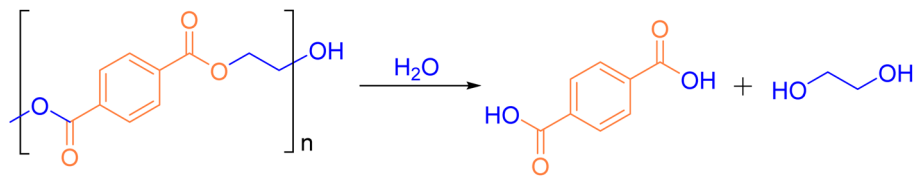
Fig. 10 Reaction formula for the degradation of PET by hydrolysis.

conditions for the reaction were: TPA concentration of 0.1 g mL^{-1}, a PET : H$_2$O mass ratio of 1 : 8, 2.5 g of PET, a reaction temperature of 220 °C, and a reaction time of 180 minutes, achieving 100% PET conversion and a 95.5% TPA yield. Abed-soltan[91] investigated a series of hydrophobic aryl sulfonic acids as catalysts for PET hydrolysis. Compared to H$_2$SO$_4$, p-toluenesulfonic acid monohydrate (PTSA), 2-naphthalenesulfonic acid (2-NSA), and 1,5-naphthalenedisulfonic acid tetrahydrate (1,5-NDSA) exhibited higher catalytic activity. At a catalyst concentration of 4 M and 150 °C, these three catalysts required less time than H$_2$SO$_4$ to degrade PET to TPA, with yields exceeding 90%. The study also evaluated the contact angle of the catalyst solution on PET film, finding that the catalyst exhibited good wettability on the PET surface, which positively impacted the hydrolysis efficiency (Fig. 11).

The Neaţu group[92] used sulfonic acid-modified Ti$_3$C$_2$-MXene as a solid acid catalyst for PET hydrolysis. MXene, a two-dimensional (2D) metal carbide–nitride material, was functionalized with –SO$_3$H groups, which were immobilized between the MXene layers. Characterization revealed that the higher the initial concentration of sulfonic acid, the greater the number of sulfonating groups and the larger the interlayer spacing. Initially, at 180 °C for 4 hours, no PET conversion was observed, and the conversion was low at 12 hours. However, after 24 hours, nearly 100% of PET was hydrolyzed into TPA and EG, with the TPA yield reaching approximately 99%. In addition to these sulfonic acids, Alba-Rubio[93] demonstrated that poly(4-styrenesulfonic acid) (PSSA), a reusable and recyclable acid catalyst, could also catalyze the hydrolysis of PET to TPA and EG. Their experiments measured the effects of parameters such as catalyst concentration, time, and temperature. They found that the activity of PSSA was higher than that of H$_2$SO$_4$, and the hydrophobic polystyrene backbone in PSSA improved its wettability, resulting in a smaller contact angle on the PET surface. This, in turn, increased the reaction rate and shortened the reaction time. However, the relatively high cost of PSSA is a concern, as it significantly increases the degradation cost. Hu[94] used the recyclable and inexpensive strong acid p-toluenesulfonic acid (PTSA) as a catalyst for PET hydrolysis. The study revealed that the reaction system contained more hydrogen, which enhanced hydrolysis. Scanning electron microscopy (SEM) images showed morphological changes in PET during hydrolysis catalyzed by PTSA. The hydrolysis occurred on the surface of PET, and as the reaction progressed, small pores formed on the surface, allowing the solution to penetrate the material and accelerate the hydrolysis. X-ray
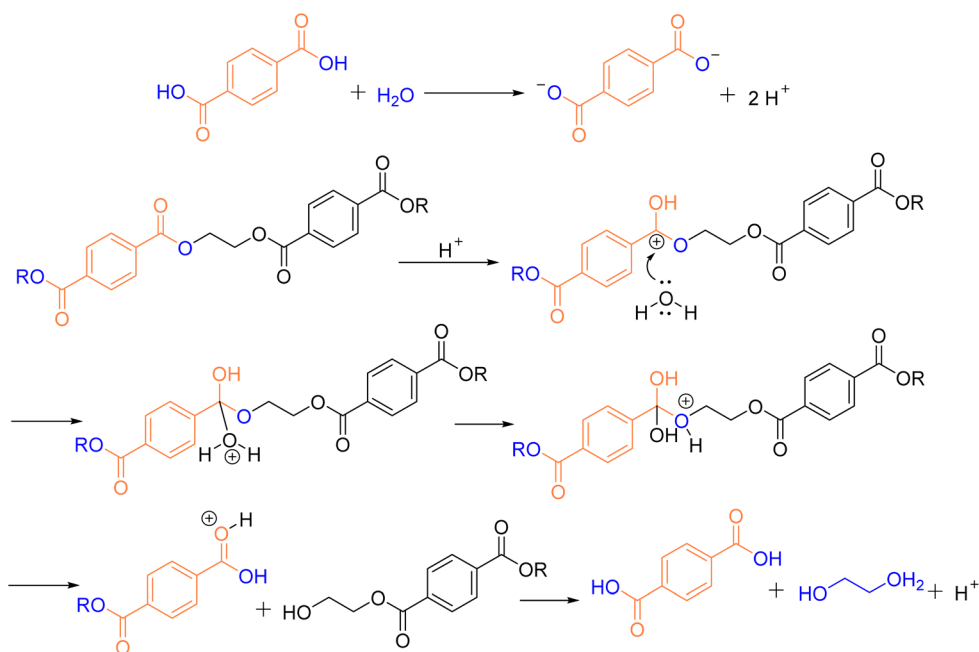

Fig. 11 PET hydrolysis mechanism with TPA as an acid catalyst. Reproduced with permission.[89] Copyright 2021, Elsevier Ltd.

diffraction (XRD) and NMR analysis detected no stray peaks in the TPA spectrum, confirming the high purity of the product. Under the conditions of 80% PTSA concentration and a mass ratio of 20 : 1 to waste PET at 150 °C, nearly 100% PET was degraded to 96.2% TPA within 90 minutes. Moreover, after five consecutive cycles, the recovered PTSA maintained its hydrolysis catalytic efficiency. The recovered PTSA was in the same form as the fresh PTSA (a white powder), and its purity reached 96.6%. The yield of TPA obtained by R-PTSA catalysis remained in the range of 95.2% to 97.7%.

2.2.2 Alkaline hydrolysis. Alkaline hydrolysis is typically carried out using strong alkalis such as sodium hydroxide or potassium hydroxide,[95] but these are not environmentally friendly or economical. Green catalysts are offering new approaches for PET hydrolysis. Attallah[96] adopted a mixture of choline chloride containing 10% sodium hydroxide and methyl cresol to form a DES as a catalyst. The optimization of PET depolymerization conditions was carried out using the Box–Behnken design (BBD), considering parameters such as DES volume, NaOH concentration, and microwave (MW) irradiation time, as shown in Table 5. The response surface diagram generated from the independent variables and PET depolymerization data revealed that PET depolymerization was correlated with the weight loss, carbonyl index, and crystallinity of PET, with PET weight loss being the key factor. The results showed that as the concentration of DES increased and the MW irradiation time was prolonged, the PET weight loss rate, carbonyl index, and crystallinity all increased, leading to better PET depolymerization. Compared to traditional hydrolysis, the reaction time was reduced to 90 seconds, achieving 84% PET depolymerization and 91.55% TPA monomer conversion. While alkaline degradation of PET reduces energy consumption, it still

Table 6 Degradation of PET under different reaction condition. Reproduced with permission.[97] Copyright 2023, Elsevier Ltd[a]

Entry	KOH concentration (g mL^{-1})	Temperature (°C)	Time (min)	Degradation rate (%)
1	0.02	80	60	73.87
2	0.05	80	60	95.31
3	0.05	80	180	99.37
4	0.1	80	60	98.32
5	0.2	80	60	100.00
6	0.2	70	60	98.59
7	0.2	60	60	96.22
8	0.2	50	60	78.05
9	0.2	80	90	100.00
10	0.2	80	30	97.61
11	0.2	80	15	87.85
12	0.2	80	5	46.07

[a] Reaction solvent: ethanol aqueous solution with a concentration of 90 vol%.

requires a large amount of acid to neutralize the terephthalate, leading to the precipitation of TPA.

The Xu group[97] selectively cleaved the C–O bonds in PET using a high-concentration 90 vol% ethanol aqueous solution, which resulted in the formation of small pores on the PET surface, thereby increasing the contact area for the reaction. Under low temperature and short reaction time conditions, KOH catalyzed the conversion of PET into dipotassium terephthalate (TPA-2K). TPA-2K is insoluble in the reaction system, facilitating separation, but it dissolves in water, forming a clear and transparent solution. TPA is obtained after neutralization with a small amount of acid. The concentration of KOH significantly influenced the degradation rate, as shown in Table 6. Additionally, the concentration of ethanol played a crucial role in the separation of the product. After 15 minutes of dehydrolysis at 80 °C, white powder and undepolymerized PET were observed. When the reaction time was extended to 1 hour, the degradation rate reached 73.87% with a KOH concentration of 0.02 g mL^{-1}. The conversion of PET increased to 100% when the KOH concentration was raised to 0.2 g mL^{-1}. Characterization analysis revealed that the tensile vibration of the C–O bond gradually decreased and eventually disappeared with the extended reaction time. This alcohol–water-based coupling system significantly accelerates the degradation of PET, and the separated TPA can be directly recovered without affecting its hydrolytic activity.

Sun[98] also used the alcohol–alkali hydrolysis method to produce TPA, using ethylene glycol and weak alkali sodium bicarbonate as the reaction media. First, they conducted optimization experiments by increasing the reaction temperature from 150 °C to 200 °C. The maximum TPA yield (94%) was achieved at 180 °C, while the TPA purity remained consistent at 98% throughout the process. The reaction temperature was maintained at 60–75 °C, and the mass ratio of NaHCO$_3$ to PET was increased from 0.8 to 1.1, resulting in a yield of 90.9%. The final ratio of 1 : 1.1 was chosen because the excess NaHCO$_3$ could neutralize the basic hydrolysate TPA. During the

Table 5 Experimental matrix and observed responses for PET depolymerization in BBD. Reproduced with permission.[96] Copyright 2021, American Chemical Society[a]

	Independent variable			Dependent variable		
Run	X_1 (mL)	X_2 (s)	X_3 (wt%)	Y_1 (%)	Y_2 (%)	Y_3 (%)
1	35	60	5.5	34.63	4.19	32.35
2	25	60	10.0	63.32	3.73	44.67
3	25	90	5.5	46.00	3.25	35.26
4	15	90	1.0	9.50	3.75	42.38
5	25	90	5.5	47.30	3.26	35.85
6	35	90	1.0	11.15	4.45	36.54
7	15	60	5.5	49.30	3.25	43.67
8	25	120	10.0	82.37	3.21	46.52
9	25	60	1.0	7.64	3.02	38.60
10	35	120	5.5	52.66	5.06	39.17
11	35	90	10.0	68.21	4.19	43.44
12	15	90	10.0	87.68	2.92	48.45
13	25	120	1.0	10.84	5.00	37.73
14	15	120	5.5	56.20	3.84	38.17
15	25	90	5.5	48.00	3.33	34.80

[a] X_1: volume of the DES, X_2: MW irradiation time, X_3: concentration of NaOH. Y_1: percentage weight loss of PET, Y_2: PET carbonyl index, Y_3: PET crystallinity index.

experiment, it was observed that when the V_{EG}/m_{PET} was 10/3, the yield of TPA remained stable as the amount of EG increased, the ratio of V_{water}/m_{PET} was tested in the range of 20/3 to 60/3, with the highest TPA yield occurring at 40/3, after which the yield began to decline. Finally, infrared and thermogravimetric analyses confirmed that the target product was pure TPA. Under optimal conditions, 98% of PET was successfully converted into TPA with a purity of 97%. This combination of alcoholysis and hydrolysis offers a promising method for degrading PET waste. Thielemans[99] used methanol potassium hydroxide (KMH) solution to degrade cut PET flakes into TPA. Spectroscopic analysis (FTIR) revealed that alcohol did not act as a reactive substance but rather as a medium for the alkaline catalyst. Experimental results showed that the conversion of PET flakes reached 100% after 4 minutes at 100 °C, while complete conversion was achieved in just 1 minute at 140 °C. They also observed a temperature-dependant competitive relationship between methanolysis and hydrolysis: high temperatures favored hydrolysis, whereas low temperatures favored methanolysis.

2.2.3 Neutral hydrolysis. The main advantage of neutral hydrolysis over acid and alkaline hydrolysis is that it avoids generating large amounts of inorganic salts, which are challenging to treat, making it a more environmentally friendly method.[100] However, a key disadvantage lies in the presence of residual impurities in TPA under industrial conditions and a lower TPA yield compared to acid and alkaline hydrolysis. In recent years, the development of new technologies has significantly improved TPA productivity. Savage[101] conducted extensive research on PET neutral hydrolysis, aiming for rapid hydrolysis of PET within 1 minute. The temperature, pressure and PET consumption were identified as the main factors influencing TPA yield. PET hydrolysis was carried out and compared under three conditions: saturated liquid ($T = 311$ °C),

compressed liquid ($T = 200$ and 260 °C) and supercritical water ($T = 400$ °C). At 10 MPa with a PET-to-water mass ratio of 1/10 for 30 minutes, the yield in saturated liquid was the highest, exceeding 80%. In contrast, under the same conditions, the yield in supercritical water reached only 74%, as a secondary reaction occurred, promoting the monomer's decomposition. When the temperature of compressed liquid was raised from 200 °C to 260 °C under constant pressure for 30 minutes, the Y_{TPA} increased from 2% to 60%. Although the decomposition rate of solid PET is slower, the TPA yield in saturated steam was slightly higher than that in saturated liquid. These experimental results provide valuable insights for future experimental research. In the synthetic textile industry, PET is one of the most widely used polymers.[102] However, during the production, PET is often blended with other different polyesters to manufacture textiles,[103] significantly increasing the complexity of its degradation. Sun[104] addressed this issue by first decolorizing textiles using ethylene glycol steam, followed by neutral hydrolysis with 2 wt% catalyst Zn(OAc)$_2$ at 210 °C and 1.7 MPa for 4 hours. The resulting TPA was purified under reduced pressure and polymerized to produce r-PET (Fig. 12). The TPA yield reached 99.9%, and the repolymerized r-PET exhibited properties comparable to those of virgin PET.

Currently, methods used for decolorizing non-ferrous waste textiles include the redox method, the electrochemical method, and the ozonation method, etc.[95,105] However, the processing conditions for these methods are often harsh and negatively impact the final product. The decolorization method developed by the research group promotes the sustainable development of the textile industry, while neutral hydrolysis enables the closed-loop utilization of polyester resources within the industry. Many researchers have identified ZSM-5 zeolite as an effective catalyst for the degradation of PET.[106] Cao[107] employed supercritical carbon dioxide (SCCO$_2$), which exhibits both swelling and
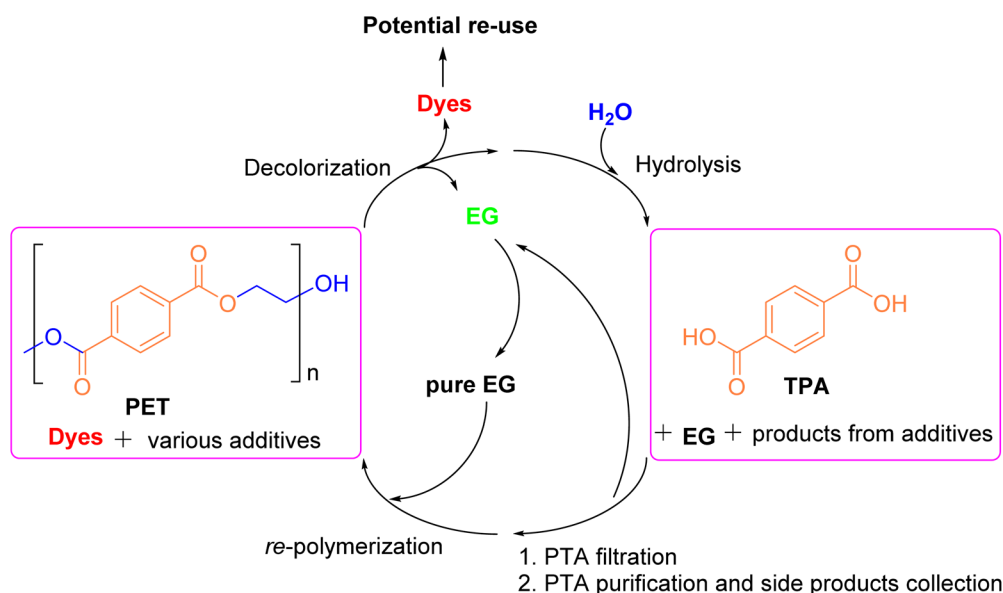

Fig. 12 A closed-loop route for recycling waste polyester textiles that includes pre-decolorization, neutral hydrolysis, PTA purification, and chemicals recovery. Reproduced with permission.[104] Copyright 2024, Elsevier Ltd.

crystallization effects on PET, in the presence of ZSM-5 zeolite to achieve efficient neutral hydrolysis. The effects of SCCO$_2$ and ZSM-5 zeolite on PET depolymerization under varying pressures and temperatures were studied. It was observed that the swelling effect of SCCO$_2$ facilitated PET hydrolysis, whereas its crystallization effects hindered hydrolysis. SCCO$_2$ exhibited a dual role in the PET hydrolysis process, occurring in two stages: the swelling stage and the PET hydrolysis stage. Once the CO$_2$ concentration reached a specific level, PET expanded to a loose state, after which hydrolysis proceeded efficiently. The Škerget[100] group explored the use of subcritical and supercritical water in high-pressure, high-temperature batch reactors to degrade both colorless and colored PET waste. The pathways for PET waste treatment under subcritical and supercritical water conditions are illustrated in Fig. 13. Their results showed that TPA crystals obtained from colorless PET waste under subcritical conditions were light yellow, while those obtained under supercritical conditions appeared light brown. For colored PET waste, the presence of additives and dyes led to the formation of black solids in the final product. The degradation of both colorless and colored PET under subcritical conditions at 250 °C for 10 minutes revealed that more than half of the PET remained undegraded, resulting in the lowest TPA yield. However, when the reaction time was extended to 30 minutes and the temperature was increased to 300 °C, the degradation efficiency reached its maximum. At this point, the TPA yield for colorless PET and colored PET was 90.0% and 85.0%, respectively.

Researchers[108] have also explored the use of marine components for neutral hydrolysis of PET, utilizing seawater as the reactant. In this approach, the salts naturally present in seawater (chlorides, bicarbonates, sulfates and bromides) act as catalyst. The final products are a mixture of solid TPA and sodium terephthalate dissolved in water, with all TPA precipitating upon the addition of H$_2$SO$_4$. Experimental results indicated that the depolymerization time and salt concentration in seawater had no significant effect on the reaction rate; temperature was identified as the primary factor controlling the depolymerization rate. The study also demonstrated that, in any seawater worldwide, PET would take approximately 162 years to fully depolymerize at a constant temperature of 30 °C. However, incorporating additional factors, such as microbial and physical degradation, could reduce the total degradation time of PET by 10–20%.

The above research demonstrates that each of the three hydrolysis methods (acid, alkaline, and neutral) has its own advantages and limitations. In acid and alkaline hydrolysis, the use of acid or alkali catalysts effectively increases the hydrolysis rate. Still, acid–base catalysts are difficult to recycle, leading to resource waste and higher production costs, while also generating significant amounts of strong acid or alkali wastewater. Neutral hydrolysis, on the other hand, avoids these environmental and economic issues. Currently, all three methods can achieve a PET conversion rate exceeding 90%. Future research should focus on developing more efficient and sustainable acid–base catalysts, as well as identifying optimal neutral conditions to further enhance the efficiency and sustainability of hydrolysis-based PET recovery.

2.3 Aminolysis

At present, studies on the aminolysis of PET remain limited in the literature. Generally, PET is depolymerized using ethanolamine as a solvent, producing bis(2-hydroxyethylene) terephthalic acid (BHETA). Tian[109] employed ethanolamine to depolymerize PET sheets treated with acetic acid for swelling, resulting in the high-value product BHETA. The optimal swelling temperature was identified as 60 °C, achieving a degradation rate of 99% and an expansion rate exceeding 75% within 30 minutes. Further investigations on the effects of temperature and reaction time revealed that PET did not dissolve below 60 °C, whereas complete dissolution occurred at 70 °C, with the degradation rate reaching 99%. While shorter reaction times left undepolymerized PET in the product, excessively long reaction times increased experimental costs. Therefore, the optimal reaction time was determined to be 4 hours, yielding the highest PET conversion. This method offers a low-cost approach to PET depolymerization, as it does not require catalysts to produce valuable monomers. Ghorbantabar[110] conducted experiments using monoethanolamine and PET at a ratio of 5:1 at 160 °C for 2 hours to obtain BHETA. Samples were analyzed at regular intervals using FTIR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and elemental analysis (CHN) to obtain the corresponding calibration curves and calculate the PET conversion. DSC results demonstrated that as BHETA production gradually increased, its intensity peak rose correspondingly while the PET peak diminished. TGA analysis conducted between 25 °C and 800 °C revealed PET weight loss in the 339 °C to 484 °C range, consistent with PET degradation. BHETA reached its maximum value at 40 minutes, after which the yield remaining relatively
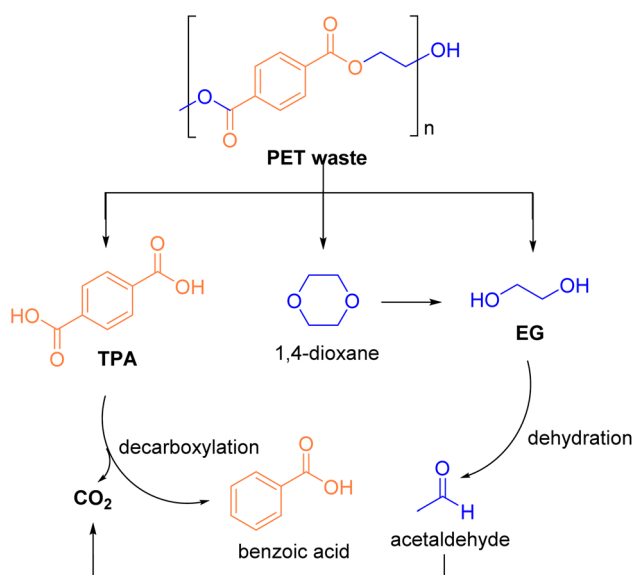

Fig. 13 Potential pathways for PET waste under sub- and supercritical water. Reproduced with permission.[100] Copyright 2020, Elsevier Ltd.

stable thereafter. These analyses confirmed the reliability of DSC and TGA for calculating conversion. Sivamurugan[111] was continuously stirred with a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$ in 50 mL of distilled water for 15 minutes, and then ethylenediamine was added dropwise to obtain a white precipitate, and the catalyst Sn-doped ZnO nanoparticles were obtained after filtration, washing and drying. The treated PET was cut into small pieces, and the solvent ethanolamine and catalyst were added for degradation to obtain BHETA. The study examined the effects of different amounts of Sn in the catalyst and the ratio of PET and ethanolamine on the products were emphatically discussed. The yield of undoped Sn can only reach 83%, 0.5 mol%, 1.0 mol%, and 2.0 mol% of Sn doped in ZnO nanoparticles, and the yield gradually increases, and the maximum yield can exceed 95%. At a ratio of PET to ethanolamine was 1 : 20, the BHETA yield reached the maximum of 94%, and the yield remained relatively unchanged when the ratio was further increased. Notably, the Sn-doped ZnO nanoparticle catalyst demonstrated recyclability, retaining its performance over seven cycles without yield loss. The poor hydrophilicity in the structure of PET fibers leads to static electricity the formation and low moisture absorption. In addition to PET, PVC is one of the most widely used plastics. More[112] investigated the synthesis of PVC plasticizers using BHETA, an aminolysis product of PET. Ethanolamine served as the solvent, while zinc acetate and sodium acetate were used as catalysts for PET depolymerization to obtain BHETA. The study explored the effects of PET and ethanolamine, catalyst selection, concentration and reaction time on PET degradation efficiency. Results in Table 7 (1–5) showed that it can be concluded that the yield can reach approximately 69% when the ratio of PET to ethanolamine is 1 : 4, and the influence of reaction time and catalyst selection is continued to be discussed under these conditions, Table 7 (6–9) finally determines the optimal conditions for PET. Subsequently, BHETA and heptanoic acid were catalyzed using 0.5% w/w sulfuric acid to synthesize a plasticizer (Fig. 14). Compared with DOP, a commonly used PVC plasticizer, the synthesized plasticizer exhibited superior compatibility and performance with PVC, offering enhanced application properties.
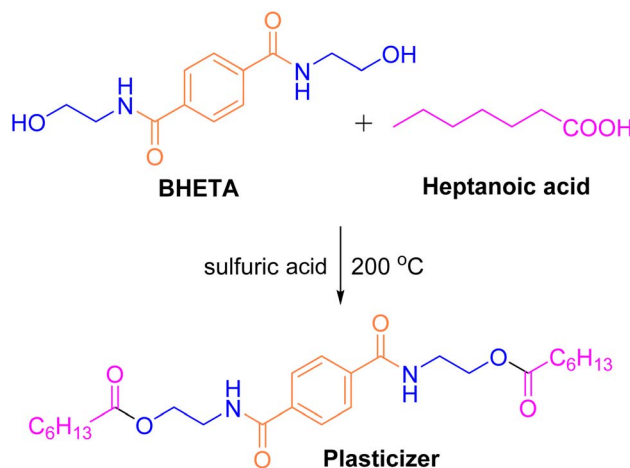

Fig. 14 Synthesis of plasticizer from bis(2-hydroxyethyl)terephthalamide (BHETA). Reproduced with permission.[112] Copyright 2013, Iran Polymer and Petrochemical Institute.

In addition to ethanolamine, other amines like liquid ammonia and aliphatic polyamines, such as 1,3-diaminopropane (DAP), ethylenediamine, diethyltriamine (DETA), triethyltetramine (TETA), are also used for the aminolysis of PET. These polyamines from intermediates with PET that can react with other substances to produce valuable chemicals or industrial materials. Haque[113] used PET fragments and DAP in a round-bottom flask, method A was reacted at 100 °C for 4 hours and then at room temperature for 20 hours, method B was reacted at 110 °C for 24 hours, and method C was reacted at 130 °C for 24 hours. Method C is a yellow-green liquid with the product of the monomer N^1,N^4-bis(2-(((E)-2-hydroxybenzylidene)amino)propyl)terephthalamide. Finally, the monomer N^1,N^4-bis(2-(((E)-2-hydroxybenzylidene)amino)propyl)terephthalamide generated by method C was condensed with salicylaldehyde in ethanol to obtain a yellow solid Schiff base and a yellow colloidal liquid condensation product, with yields of 25% and 62%, respectively, as shown in Fig. 15. Kang[114] has developed a low-cost, low-energy, and environmentally friendly depolymerization method that does not require the addition of catalysts and solvents. In this method, the gas–solid reaction occurs under certain temperatures conditions, along with specific ratios of PET to anhydrous ammonia and stirring rates. The colorless PET undergoes ammonolysis to produce white or gray powder, which was identified as terephthalamide (TP) after characterization and analysis. Temperature was found to be the key factor influencing PET degradation. Within the temperature range of 40–110 °C, the yield and purity of TP increased, but when the temperature reached 120 °C, carbonization occurred, resulting in the conversion of TP powder into a black solid and negatively affecting both purity and yield of TP. Experimental verification based on the optimal conditions predicted by Response Surface Methodology (RSM) and Box-BBD (18.5 g PET, reaction at 115 °C for 7.5 hours) showed that the yield and purity of TP could reach 87.34% and 94.5%, respectively.

Table 7 Degradation of PET under different reaction condition. Reproduced with permission.[112] Copyright 2013, Iran Polymer and Petrochemical Institute[a]

Entry	Catalyst	PET : ethanolamine	Time/h	Yield/%
1	Sodium acetate	1 : 1	1	62.15
2	Sodium acetate	1 : 2.5	1	65.23
3	Sodium acetate	1 : 4	1	69.56
4	Sodium acetate	1 : 5.5	1	70.66
5	Sodium acetate	1 : 7	1	71.19
6	Sodium acetate	1 : 4	2	74.17
7	Sodium acetate	1 : 4	3	74.93
8	Sodium acetate	1 : 4	4	75.03
9	Zinc acetate	1 : 4	3	81.16

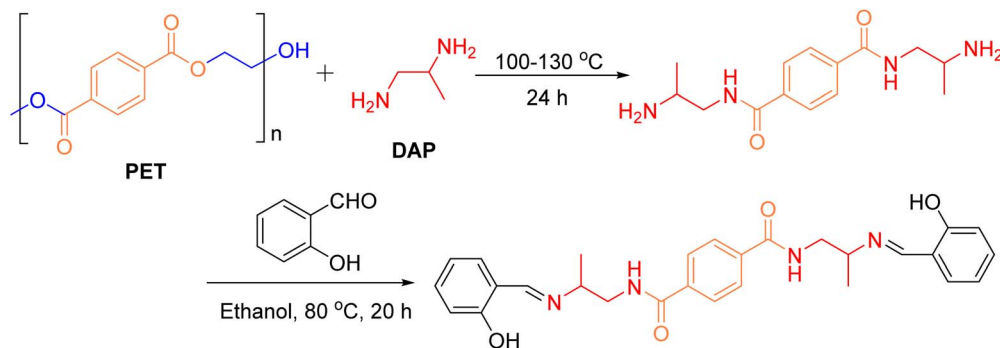[a] Reaction conditions: temperature = 60 °C, catalyst = 1.5 wt%.

Fig. 15 PET is converted to Schiff base after aminolysis.

Zhang[115] diluted and concentrated ethylenediamine to perform aminolysis with PET fibers, introducing NH_2 groups into the PET molecules, which enhanced the hydrophilicity of the PET fibers. The hydrophilicity was assessed by measuring the absorption of water droplets by the PET fibers. The adsorption time decreased with increasing ethylenediamine concentration, and remained constant when the concentration exceeded 150 g L^{-1}. While 70 °C was the intrinsic and optimal temperature for the reaction, temperatures above 70 °C led to the volatilization of ethylenediamine, causing a concentration effect. Due to the moderate reaction temperature and low ethylenediamine concentration, the treated PET fibers showed no significant degradation and retained their integrity. Zinchenko[116] reported the reaction of PET with DETA and TETA, followed by crosslinking with ethylene glycol diglycidyl ether (EGDE) to produce hydrogel materials. The water solubility of the ammonolysis products of PET was critical for the preparation of hydrogels. The reaction was conducted at 190 °C, with a PET and DETA ration of 1 : 3 for 30 minutes, resulting in the water-soluble product 13PD, which allowed for the complete depolymerization of PET. Mass spectrometry analysis revealed that 13PD was primarily a mixture of dimers composed of three DETA molecules and two terephthalic acid units. This product was then cross-linked with EGDE at 50 °C to form a transparent 13PD hydrogel, which exhibited a high degree of swelling compared to other hydrogels. This approach not only addresses environmental pollution concerns but also offers a promising solution for the industrial production of hydrogels.

2.4 Pyrolysis

Chemical degradation of PET can also be achieved through pyrolysis, a process where PET is depolymerized into valuable fuel products by heating at high temperatures in the presence of an inert gas. This method is one of the most effective ways to recover fuel products.[117] The pyrolysis oil produced by pyrolysis includes various components such as alkanes, naphthenes, aromatics, *etc.*, which are the primary components of petroleum.[118] Other byproducts of pyrolysis include simple molecules like benzene dicarboxylic acid, benzoic acid, H_2, CO, CO_2, CH_4, *etc.*, which can be utilized in industrial applications. Kwon's group[119] analyzed the gaseous and liquid products of PET pyrolysis in the presence of ultra-high purity CO_2 and N_2. From

thermograms (TG) and differential thermograms (DTG) it was found that approximately 86% of the waste PET was decomposed within the temperature range of 380–670 °C. At 900 °C, about 14 wt% of PET remained, indicating that the mass decay and pyrolytic conversion of waste PET were consistent. Afterwards the group also investigated the concentration of pyrolysis products (H_2, CH_4, CO) as a function of temperature. Under N_2 conditions they monitored that the concentration of H_2 increased with temperature between 300–750 °C. However, above 750 °C, dehydrogenation occurred, causing the concentration of H_2 to decrease. The concentration of CO_2 remained unaffected by dehydrogenation, as evidenced by the similar concentration profiles of H_2 and CH_4 during pyrolysis. The mass balance indicated that liquid products accounted for 21.6 and 13.3% of the total pyrolysis products of waste PET under N_2 and CO_2 conditions, respectively, while gaseous products accounted for 63.8% and 71.5%, respectively. The study also demonstrated that CO_2 facilitated the transfer of carbon from liquid (oil) to gas (natural gas). Pyrolysis oil consists of multiple components such as benzene derivatives, PAHs, linear hydrocarbons and acids. Further analysis reveals that CO_2 inhibits cyclisation and aromatization during pyrolysis, notably with a decrease in benzoic acid content and a decrease in acidity. Overall, Eilhann's pyrolysis of waste PET to increased levels of gaseous products and inhibition of the acidic product benzoic acid using CO_2 as the reaction medium provides a new environmentally friendly process for the degradation of waste PET. Shahi[120] catalyzed the pyrolysis of PET using Lewis Brønsted acid-site catalysts, leading to the generation of solid, liquid and gaseous products. The effects of various parameters on the conversion rates were analyzed. The solid products primarily consisted of terephthalic acid and benzoic acid, while the gaseous products were mainly some alkane gases. The optimum conditions for the highest PET conversion were found to be 430 °C and a catalyst/polymer ratio of 1 : 10. Increasing the catalyst amount resulted in a decrease in solid product content and an increase in gaseous products, with the color of the solid products changing from yellow to colorless. Higher temperatures also increased the yield of gaseous products, primarily CH_4, C_2H_6 and C_2H_4. Diaz-Silvarrey[121] employed an environmentally friendly SZ catalyst to catalyze PET pyrolysis. The catalyst, consisting of zirconium chloride octahydrate and
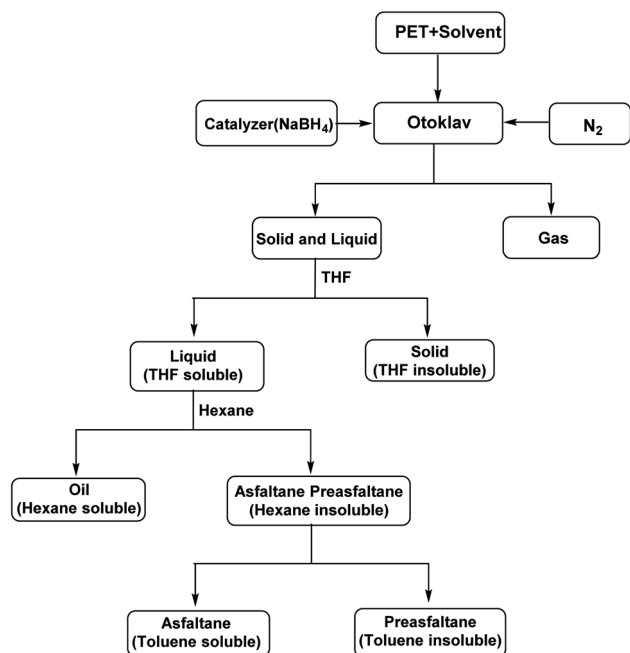
Fig. 16 Flow chart of the pyrolysis experiments. Reproduced with permission.[123] Copyright 2019, *IOP Conference Series: Earth and Environmental Science*.

ammonium sulphate, is strongly acidic. The results indicated that temperature had the greatest effect on PET conversion, with higher temperatures increasing the yield of gaseous products. In addition, the mass ratio of catalyst to PET also had an effect on the conversion of PET, with a more pronounced effect at higher temperatures. Increasing the mass ratio of catalyst to PET from 0 to 1 : 10 at 450 °C increased the gas product content by 3%, whereas at 600 °C the gas product content increased by 29%. However, SZ catalyst deactivation occurred at temperatures above 400 °C, leading to a reduction in catalyst acidity and activity due to clogging of the pores. This deactivation occurred twice in the 100–700 °C interval, with the catalyst's active sites decreasing at 525 °C, necessitating increased loading to maintain degradation to light hydrocarbons. The optimal conditions for the pyrolysis of PET to obtain

benzoic acid and gaseous products using SZ catalysts were found to be a catalyst loading of less than 10 wt% and a temperature below 525 °C. Straka's group[122] used low-temperature slow pyrolysis to produce solid fuels with higher and lower calorific values as well as valuable chemicals like paraformaldehyde, ethylene glycol, benzoic acid and benzoates. The results showed that after activation at a heating rate of 40 °C min^{-1} up to 200 °C, the waste PET could be completely pyrolyzed into oils (paraformaldehyde, glycol, benzoic acid and benzoates) and gases (CO, CO_2) by heating at a rate of 25 °C min^{-1} up to 400 °C. Olam's group[123] used sodium borohydride ($NaBH_4$) as a catalyst and hydrogen donor for PET pyrolysis and the experimental flow is shown in Fig. 16. As can be seen in Table 8. The total conversion increased from 15.2% to 55.3% and the liquid + gas yield rose from 6.9% to 28.6% as the reaction temperature increased from 325 °C to 400 °C in the presence of the catalyst. In the absence of the catalyst, the total conversion also increased substantially with higher temperatures, from 325 °C to 425 °C. Regardless of the presence of catalyst, total conversion and the yield of liquid + gas are also low at low temperatures, and high temperatures promote total conversion and the yield of liquid + gas. Overall, $NaBH_4$ can increase both the total conversion and the yield of liquid + gas from PET during the pyrolysis process.

Ben[106] investigated the pyrolysis of PET under N_2 with ZSM-5 zeolite and $NiCl_2$ as catalysts, focusing on the liquid phase products of PET pyrolysis as well as the effects of temperature and catalyst dosage on product yield. The yield of waxy products decreased from approximately 60 wt% to around 10 wt% while the gas yield increased from about 20 wt% to about 69 wt% with the gradual increase in ZSM-5 zeolite dosage at 450 °C. A similar trend was observed at 600 °C, indicating that ZSM-5 zeolite could enhance the gas yield and reduce the waxy product yield. Substituting $NiCl_2$ as the catalyst also enhances the gas yield and reduces the waxy product yield. A comparison of the ^{13}C NMR spectra of the waxy products with and without the ZSM-5 zeolite catalyst showed that ZSM-5 zeolite had the ability to deoxygenate the carbonyl groups and aliphatic C–O bonds in the products. Furthermore, using $NiCl_2$ as a catalyst reduced the content of aliphatic C–O in the wax products and promoted the decomposition of alkyl, alkoxy and branched alkanes on the

Table 8 Char yields and total conversions obtained in the pyrolysis of the PET. Reproduced with permission.[123] Copyright 2019, *IOP Conference Series: Earth and Environmental Science*

Entry	Sample amount (wt as used)	Catalyst concentration ($NaBH_4$, wt%)	Temperate (°C)	Char yield (wt%)	Total conversion (wt%)	Oil + gas (wt%)
1	30.00	3	325	84.8	15.2	6.9
2	30.00	3	350	75.0	25.0	12.9
3	30.00	3	375	56.7	43.3	9.2
4	30.00	3	400	44.7	55.3	28.6
5	30.00	3	425	48.2	51.8	44.6
6	30.00	—	325	90.6	9.4	0.1
7	30.00	—	350	84.7	15.3	1.1
8	30.00	—	375	66.5	33.5	4.1
9	30.00	—	400	49.5	50.5	18.7
10	30.00	—	425	46.9	53.1	43.7

aromatic ring. Lee[13] chose Pd/C, a stable and low-cost catalyst, to pyrolyze disposable plastic bottles primarily composed of PET. During the pyrolysis process, attention was given to the inhibition of harmful substances, such as polycyclic hydrocarbons and biphenyl derivatives, that could be produced. The analysis of the pyrolysis oil revealed that it consisted of polycyclic compounds, biphenyl derivatives and polycyclic amine compounds, with biphenyl derivatives including biphenyl-4-carboxylic acid, p-terphenyl, and terphenyl. They also examined the role of Pd catalyst to PET ratio in the PET pyrolysis process and found that there was no significant difference in the amounts of polycyclic hydrocarbons and biphenyl derivatives of the pyrolysis products between a Pd/PET ratio of 0.01 and non-catalytic conditions. However, the concentration of polycyclic hydrocarbons and biphenyl derivatives of the pyrolysis products decreased at 800 °C when the Pd/PET ratio was increased to 0.05. Small amounts of Pd did not significantly affect the concentrations of polycyclic hydrocarbons and biphenyl derivatives as pyrolysis products, but the concentrations increased at high temperatures or increased catalyst amounts because Pd catalyst promotes ring-opening reactions at the catalyst sites during the pyrolysis of PET, and high temperatures promote free radical reactions. It was also found that the production of amine compounds decreases with an increase in catalyst content. This not only inhibits the production of harmful substances, but also enhanced the yield of valuable compounds, providing a novel approach to the degradation of PET.

3 Summary and outlook

PET is one of the most widely used plastics, commonly found in everyday items such as water bottles, films, textiles, etc. Despite its widespread use, its special properties make it difficult to degrade, leading to significant plastic waste. Chemical recycling, on the other hand, provides an efficient method to address this issue by converting PET into valuable chemicals. This paper reviews various methods of chemical degradation, including alcoholysis (and glycolysis), hydrolysis, ammonolysis and pyrolysis. Among these methods, alcoholysis frequently uses methanol as a solvent, though other solvents such as ethanol and isooctanol, along with polyols, can also be used to produce DMT and EG, as well as BHET monomers. Glycolysis is a specialized form of alcoholysis that typically employs diols (such as ethylene glycol) as solvents, and can depolymerize PET to form BHET monomer using both homogeneous and heterogeneous catalysts. Hydrolysis involves both acid–base and neutral hydrolysis methods, which break down PET into TPA and EG. Neutral hydrolysis is considered simpler and more environmentally friendly compared to acid–base hydrolysis. Aminolysis, though less explored, is another promising method for chemical recycling, often using ethanolamine as a solvent to produce BHETA. Pyrolysis is a thermal degradation process in which PET is converted into simpler molecules by high-temperature heating. Key factors affecting the conversion of PET in pyrolysis include temperature and catalyst usage. The application of new technologies, such as ionic liquids, deep eutectic solvents and metal–organic frameworks, can accelerate the reaction rate and enhance the conversion and yield of PET degradation products. Other parameters, such as whether to add catalyst, different temperatures, times, solvents and their dosages, etc., also play a critical role in determining the products of PET degradation. Based on these published studies, significant potential remains for further advancing PET degradation technologies.

In the future, efforts should focus on clarifying specific degradation goals and continuing to develop chemical degradation technologies. This includes the creation of greener solvents or catalysts for alcoholysis, further exploration of neutral hydrolysis to reduce the costs and waste associated with acid–base hydrolysis, and the use of a broader range of amine compounds for ammonolysis. Additionally, enhancing the yield of desired substances in pyrolysis through the discovery of new catalysts will be key. Ultimately, the goal is to achieve sustainable recycling of waste PET, contributing to the reduction of plastic pollution.

Data availability

This is a review article. All the data reported here can be found in the cited papers in the Reference section.

Author contributions

Z. Q. Guo contributed to original draft preparation and writing—reviewing and editing. J. Wu contributed to conceptualization and writing—original draft preparation. J. H. Wang helped in conceptualization, writing—reviewing and editing. All the authors discussed and approved the current version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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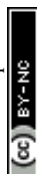
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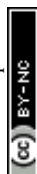
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