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Catalytic depolymerization of polyester plastics toward closed-loop recycling and upcycling

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Plastic waste is globally ubiquitous and ecologically harmful, but it can be recycled as an abundant carbon source to alleviate worldwide heavy dependence on fossil resources and reduce CO_2 emissions. Therefore, research into the chemical recycling of plastic waste has become a critical and pressing area. Compared with polyolefins, polyesters, as represented by PET and PLA, can easily achieve selective depolymerization to their corresponding monomers due to the presence of weaker ester bonds, thus favoring their closed-loop recycling and upcycling. However, comprehensive reviews on this important topic remain scarce, especially from the standpoint of re/upcycling. In this review, we present significant progress in the catalytic depolymerization of different polyesters, including biodegradable polyesters and nonbiodegradable polyesters, and discuss the key factors that limit the efficacies of the different methods and formidable challenges towards closed-loop recycling and upcycling. Such insightful discussion may benefit the further development of advanced strategies to address the problems with the increasing polyester plastic wastes and stimulate their efficient recycling to value-added chemicals and materials.

1. Introduction

Today, plastics are used in almost all products. Consequently, plastic waste has become a globally ubiquitous and ecological threat.[1] In 2020, global annual plastic waste production was about 367 million metric tons (Mt), and the total plastic waste is predicted to reach 12 000 Mt by 2050.[2,3] Currently, less than 10% of plastic waste is recycled, with about 10% incinerated and the remaining 80% sent to landfill or randomly discarded in the environment.[4] But landfill and incineration do not solve the problem of unsustainable plastics and ultimately contribute to environmental pollution by releasing substances such as greenhouse gases. Moreover, accumulating and poorly biodegradable plastic pollution is a serious global environmental problem, especially the bioaccumulation of micro- and nanoplastics in living organisms throughout the food web.[5–7] Current consumption patterns of plastics have led to a large amount of plastic waste (*e.g.*, packaging materials), which is becoming a major contributor to environmental pollution in solid waste streams. Clearly, plastic recycling is an urgent global issue concerning carbon neutrality and environmental remediation.[8,9]

Plastics are currently recycled through primary, secondary, tertiary, and energy recycling methods (Fig. 1).[10–12] Primary recycling refers to the reprocessing of plastic, to produce a product that serves the purpose identical to the original plastic.[10] For example, new polyethylene terephthalate (PET) bottles can be manufactured from recycled PET bottles. Secondary recycling refers to the physical processing of plastic waste and reuse, also known as mechanical recycling, but the value of recycled plastic products typically declines, with different use cases.[13,14] For example, recycled low-molecular weight PET is used in fibre production. Mechanical processes such as sorting, grinding, cleaning, and extrusion are involved in both primary and secondary recycling methods, but mechanical reprocessing results in thermal and mechanical degradation of the polymers to varying degrees, therefore, the number of cycles of primary and secondary recycling is limited by polymer degradation.[10,13] The incineration of plastic waste, also known as energy recycling, can partially recover energy in the form of heat. Although this method does not require recycling, CO_2 and other harmful gases are released during combustion, with significantly less energy generated by the burning of plastics compared with the energy saved by recycling plastics.[15] Therefore, instead of benefitting the economy, the incineration of plastic waste will exacerbate environmental pollution and resource consumption. Chemical recycling, or tertiary recycling, is the process of breaking down plastic waste into chemicals through chemical reactions,

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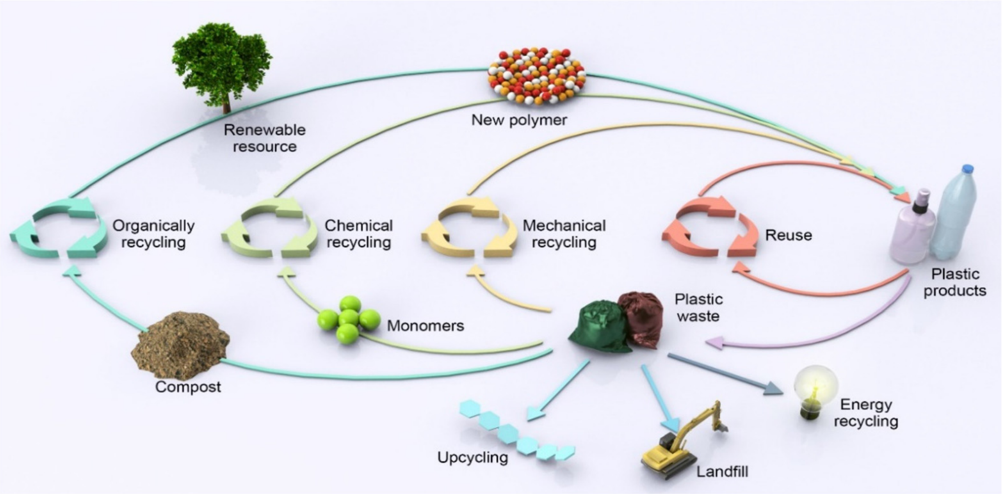

Fig. 1 Recycling routes of polyester plastics.

which can be either used to produce the same plastics with virgin-like material properties (*i.e.*, closed-loop recycling) or other useful materials (*i.e.*, upcycling).

It is important to position plastic wastes as low-cost, abundant raw chemical materials and consider them as the beginning rather than the end of value chain.[16] To this end, high-purity monomers or chemicals obtained from chemical depolymerization of plastic wastes can be recombined into new plastics *via* closed-loop recycling or other value-added products *via* upcycling.[11] Primarily, it is difficult to adapt the design of traditional polyolefins into closed-loop recycling. Polyolefins (Fig. 2), such as polyethylene (PE), polypropylene (PP), and polystyrene (PS), are the most widely used petroleum-based polymer materials, with a global market size of USD 240 billion in 2020. Generally, polyolefin monomers are joined by C–C bonds, with the monomer skeleton structure also composed of C–C bonds. Thus, the selective recovery of monomers by polyolefin depolymerization is challenging under moderate reaction conditions, as the bond energies of the different C–C bonds are basically the same.[11,17] Although some recent advances have been made in polyolefin depolymerization, with the capture of fuel additives such as alkanes and aromatics through the catalytic pyrolysis of waste polyolefins, this cannot solve the recycling issue.[17,18] Therefore, there is still a need to produce new plastic from non-renewable resources including petroleum and coal.[19] Moreover, if plastic waste is converted to fuel, the carbon atoms in the plastic will still end up in the atmosphere, which is not conducive to carbon neutrality in terms of carbon footprint.

Compared with polyolefins, polyesters can be more easily depolymerized to their monomers *via* highly selective breakage

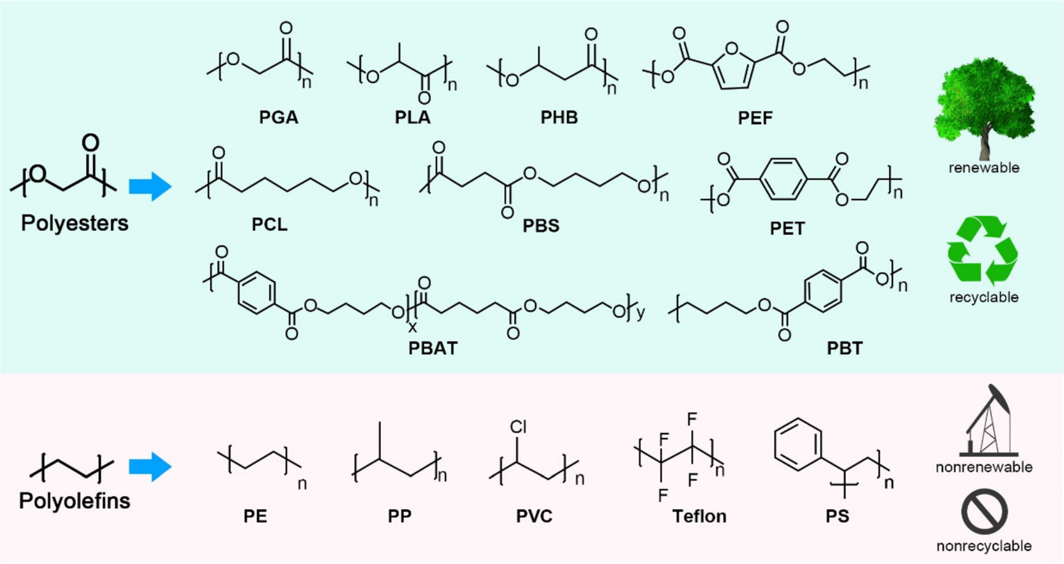

Fig. 2 Comparison between polyesters and polyolefins.

of the ester bonds.[20–23] More importantly, most polyesters, such as poly(lactic acid) (PLA), poly(3-hydroxybutyrate) (PHB), polycaprolactone (PCL), poly(ethylene-2,5-furandicarboxylate) (PEF), and PET, can be produced from a variety of sources, including non-renewable and renewable resources, and have become more attractive due to their good thermal and mechanical properties, processing versatility, and degradability (Fig. 2).[24–27] Among these, PET is the most important and abundant one, and is widely used as thermoplastic polymers with excellent properties, including thermal stability, transparency, high strength, low density, chemical resistance and low cost.[28] PBT and PEF are structurally and functionally similar to PET, and possess unique advantages in physicochemical properties.[29,30] For example, PBT can be a viable substitute for the crystalline thermoplastics (*e.g.*, PE and nylon) because of its lower melting point, lower strength and stiffness, lower glass transition temperature, and better impact resistance. More significantly, aliphatic-based polyesters are known as biodegradable plastics and prone to be degraded by natural microorganisms to water and dioxide. Among the biodegradable plastics, PLA is a promising industrial thermoplastic with the highest market share.[29] Nowadays, polymer blending techniques have been used for PLA modification to improve its biodegradation rate and toughness for different applications.[31] Polyhydroxyalkanoates (PHAs) are naturally synthesized by biological methods, and have attracted widespread interest in biomedical applications because of their excellent biodegradability and biocompatibility.[32,33] PHB, as a target molecule from plant cells, is the simplest of PHAs. Aliphatic co-polyesters such as PBA, PBSA, PBAT, and PCL are also biodegradable and available from non-renewable and renewable resources, and are commercial thermoplastic polyesters with excellent manufacturing performance, flexibility, and toughness.[34,35]

Taken together, polyesters, as represented by PET and PLA, are important polymer materials, and their market size is rapidly growing with promising potential to replace polyolefins and use for preparing electronics, food and beverages, healthcare, and consumer goods.[36–39] Therefore, it is important to study the catalytic depolymerization of waste polyester plastics toward closed-loop recycling and upcycling. Recently, a number of comprehensive reviews on plastic recycling have appeared.[10,11,24,28,40,41] However, most previous reviews have mainly focused on summarizing the depolymerization methods of polyesters with less attention to the correlation between their depolymerization and re/upcycling. Meanwhile, the corresponding challenges still need to be clearly discussed, especially from the standpoint of closed-loop recycling and upcycling. In this review, we will summarize the significant progress in the catalytic depolymerization of various polyesters, and discuss the key factors limiting the efficacies of these methods and the formidable challenges in closed-loop recycling and upcycling. Such insightful discussion may benefit the further development of advanced strategies to address the problems of increasing amounts of waste polyester plastics. In addition, this review can also be used as a helpful guide for the recycling and upcycling of polycarbonate, polyurethane, polyamide, polyether, and other polyester-like polymers with easily decomposable chemical bonds.

2. Closed-loop recycling

Various technologies have been reported for the degradation of polyester, including gasification, pyrolysis, hydrogenolysis, enzymolysis, hydrolysis, and alcoholysis.[16,42] While gasification, hydrogenolysis and pyrolysis can efficiently decompose plastics into chemicals or fuel additives, their products are difficult to use directly to synthesize new polyesters, making it difficult to achieve closed-loop recycling.[43–45] Although chemical reagents are not required in pyrolysis, most pyrolysis processes require harsh reaction temperatures, which can easily lead to side reactions such as monomer dehydration and racemization.[46,47] Hydrogenolysis uses hydrogen to depolymerize polyesters and produce saturated alcohols and alkanes in the presence of costly noble metal catalysts, which also rely on harsh reaction conditions and toxic reagents, and are not suitable for closed-loop recycling.[48] Therefore, in view of closed-loop recycling, alcoholysis, hydrolysis, and enzymolysis will be mainly discussed below due to their capability to selectively cleave ester bonds to the corresponding monomers.

2.1 Alcoholysis of polyesters

For polyester alcoholysis, methanolysis, *i.e.*, using methanol as the solvent, compared with ethanolysis and glycolysis, exhibits the higher reactivity, due to the smaller steric hindrance and stronger nucleophilic ability of methanol, and thus it is widely reported in the depolymerization of polymers.[49–55]

Collinson *et al.* reported the methanolysis and ethanolysis of PLA over the $Zn(OAc)_2$ catalyst at the boiling point of the solvent, showing 70% methyl lactate and 21% ethyl lactate yields, respectively, under reflux conditions for 15 h.[56] Zn–N-heterocyclic carbene alkoxide complexes ($[(S, C_{NHC})ZnCl(OBn)]_2$ and $[(O, C_{NHC})ZnCl(OBn)]_2$) can also efficiently depolymerize PLA to methyl lactate and oligomers in methanol at room temperature through extensive transesterification reactions.[57] Magnesium and calcium alkoxides were also found to be efficient for the depolymerization of PLA, and 89% conversion of PLA and 86% yield of ethyl lactate (2.05 L) were achieved under the optimized reaction condition.[51]

Basic organic molecules, typically nitrogenous bases, have also been used in methanolysis. By employing triazabicyclodecene (TBD) as an organocatalyst, Leibfarth *et al.* reported PLA depolymerization in a methanol and methylene chloride mixture *via* rapid and quantitative transesterification, obtaining an optimal 95% yield of methyl lactate in only 2 min.[58] Zinck *et al.* also used TBD and anhydrous toluene to depolymerize PLA to form oligomers with a tunable microstructure at 105 °C.[59] Moreover, commercial-grade PGA resin obtained complete PGA depolymerization in only 30 min at 120 °C.[58] In addition to TBD, Alberti *et al.* found that organic bases such as 4-dimethylaminopyridine (DMAP), triethylenediamine

(DABCO), and diazacyclodecene (DBU) could serve as effective catalysts for the methanolysis of PLA to methyl lactate.[60] Besides, they also used methanol as the only solvent, obtaining efficient PLA depolymerization at a relatively high temperature of 180 °C with a monomer yield of above 99% in 10 min. Brønsted acidic ionic liquids (ILs) of 1-butyl-3-methylimidazolium hydrogen sulfate ([BMim]HSO_4) and 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([MimPS]HSO_4) were reported in PLA depolymerization, and obtained 87.9% and 88.7% yields of methyl lactate at 115 °C, respectively.[41,63] [MimPS]HSO_4 was found to effectively catalyze PHB methanolysis with an 83% yield of methyl 3-hydroxybutyrate at 140 °C.[64] In addition, the Lewis acid of ferric chloride ($FeCl_3$) showed efficient catalytic performance in the methanolysis of PLA waste (Table 1, 87.2%).[65] Moreover, Fe-containing magnetic IL (1-butyl-3-methylimidazolium tetrachloroferrate, [BMim]$FeCl_4$) was found to exhibit high reactivity, catalyzing PLA methanolysis at 120 °C with 94.6% yield of methyl lactate, and PHB methanolysis at 140 °C achieved 94.6% yield of methyl 3-hydroxybutyrate.[66,67] Furthermore, the Brønsted–Lewis acidic IL of 1-(3-sulfonic acid)-propyl-3-methylimidazole ferric chloride ([MIMPS]$FeCl_4$) was found to be effective for the methanolysis of PHB with a yield of 87.4% for methyl 3-hydroxybutyrate under optimal conditions.[68] In addition, the combination of acidic ILs and alkaline ILs was reported in the conversion. For example, 1-butyl-3-methylimidazolium acetate-promoted zinc acetate (2[BMim][OAc]-$Zn(OAc)_2$) effectively co-catalyzed the methanolysis of PLA with an optimal methyl lactate yield of 92%.[69] In addition to imidazole-cation-derived ILs, imidazole-anion-derived ILs have been synthesized and used in the alcoholysis of polyester. For example, 2-methylimidazolium-anions and DBU cations ([HDBU][2-MeIm]) showed an efficient catalytic performance in the depolymerization of PLA, PHB, PC, and PET at relatively low temperatures, with optimal yields of 87, 33, 96, and 75%, respectively, for methyl lactate, methyl 3-hydroxybutyrate, bisphenol A, and dimethyl terephthalate.[50] Moreover, replacing the anion with acetate and propionate ([HDBU][AA] and [HDBU][PA]) further enhanced the catalytic performance in PLA depolymerization.[70]

For PET depolymerization, methanolysis is also an efficient method, in which methanol attacks the ester bond (180–280 °C, 2–4 MPa) in PET and undergoes transesterification to produce dimethyl terephthalate (DMT) and ethylene glycol (EG).[28] Kumazawa *et al.* reported this reaction in supercritical methanol with a final DMT yield of 97% at 300 °C.[86] Zhang *et al.* also reported on the methanolysis of PET in a high-performance manner under sub-supercritical conditions

Table 1 Alcoholysis results of biodegradable polyesters using different catalysts

Catalyst	Solvent	Polymer	T^a (°C)	t^a (h)	Conv.^{a} (%)^a	Yield$_m$ ^{a} (%)	Ref.
$Zn(OAc)_2$	MeOH	PLA	64.7	15	—	70	56
$Hf(OiPr)_2$	MeOH/CH_2Cl_2	PLA	25	24	—	75	61
$Mg(OEt)_2$	EtOH	PLA	200	1	89	86	51
$Zn(HMDS)_2$	MeOH	PLA	25	2	—	99	62
$Zn(HMDS)_2$	MeOH	PHB	25	24	—	93	62
TBD	EtOH/CH_2Cl_2	PLA	—	0.03	100	>95	58
DMAP	MeOH	PLA	180	0.16	—	97	60
[Bmim]HSO_4	MeOH	PLA	115	3	90.2	87.9	41
[MimPS]HSO_4	MeOH	PLA	115	3.5	97.5	88.9	63
[MimPS]HSO_4	MeOH	PHB	140	3	91.2	83.7	64
$FeCl_3$	MeOH	PLA	130	4	96.0	87.2	65
[Bmim]$FeCl_4$	MeOH	PLA	120	3	99.3	94.6	66
[Bmim]$FeCl_4$	MeOH	PHB	140	3	94.1	85.0	67
[MimPS]$FeCl_4$	MeOH	PHB	140	3	98.5	87.4	68
[Bmim]OAc	MeOH	PLA	115	3	97.2	92.5	41
[Bmim]OAc/$Zn(OAc)_2$	MeOH	PLA	110	2	97	92	69
[HDBU][2-MeIm]	MeOH	PLA	70	1	100	87	50
[HDBU][AA]	MeOH	PLA	100	5	100	91	70
$Zn(OAc)_2$	EG	PET	196	3	—	85.6	71
$K_6SiW_{11}ZnO_{39}$	EG	PET	185	0.5	100	84	72
[Bmim]OH	EG	PET	190	2	100	71.2	73
$[Bmim]_2[CoCl_4]$	EG	PET	175	1.5	100	81.1	74
[Bmim]$ZnCl_3$	EG	PET	190	2	100	83.3	75
[Ch][OAc]	EG	PET	180	4	98.2	85.2	76
1,3-DMU/$Zn(OAc)_2$	EG	PET	190	0.33	100	82.0	77
Urea/$ZnCl_2$ DES	EG	PET	170	0.5	100	82.8	78
Mn_3O_4@SiO_2	EG	PET	300	1.3	—	90	79
$ZnMn_2O_4$	EG	PET	260	1.3	100	92.2	80
Fe_3O_4	EG	PET	300	1	100	90	81
MnO_2/HGO	EG	PET	200	0.16	100	100	82
Fe_3O_4@SiO_2@[mim][$FeCl_4$]	EG	PET	180	24	100	100	83
CHTs	EG	PET	196	0.83	—	81.3	84
CeO_2 NPs	EG	PET	196	0.25	98.6	90.3	85

[a] *T*: reaction temperature, *t*: reaction time, conv.: conversion, yield$_m$: monomer yield.

(200 °C, 3.5 h) without catalysts.[87] Furthermore, Kurokawa *et al.* reported that aluminium triisopropoxide (AIP) may facilitate the methanolysis of PET, but the yields of DMT and EG were strongly dependent on the solubility of PET, with 88.5% DMT and 87.2% EG produced in 20 vol% toluene/methanol mixture at 200 °C.[88] Mckeown *et al.* used a simple organocatalyst (tetramethylammonium methyl carbonate) for the transesterification of polyesters, such as PLA, PCL, PET and PEF.[89] In addition, a nano-dispersed ZnO was prepared as a pseudo-homogeneous catalyst and employed for the methanolysis of PET, resulting in 97% DMT after only 15 min at 170 °C.[90] However, although methanolysis is effective and promising, it is still not considered to be the best solution for the closed-loop recycling of PET, most likely related to its currently industrial production that is based on terephthalic acid (TPA) and bis(2-hydroxyethyl) terephthalate (BHET). The recycled DMT from PET methanolysis requires an additional transesterification or hydrolysis process to form BHET or TPA for the next PET reproduction, reducing the economic benefits of methanolysis.

Glycolysis is a simple method for commercial PET recycling worldwide, involving the transesterification of PET with an abundance of glycol at temperatures between 100 and 300 °C. The glycolysis agents include ethylene glycol, propylene glycol, diethylene glycol, and 1,4-butanediol.[67] Among them, EG, due to its low toxicity and low vapor pressure, as well as the ability of the recovered BHET to repolymerize into new polyesters, represents the most attractive and commonly used agent for PET glycolysis.[71,91] In the catalytic mechanism, the initial diffusion of EG into the polymer causes it to swell. Subsequently, a nucleophilic attack by free electrons on the oxygen of EG with the carbonyl carbon of the PET ester results in the formation of a new C–O bond with EG and breakage of the ester C–O bond.[90] Next, the degradation of PET will be gradual, beginning with PET oligomers, then transitioning to BHET dimers, and finally to BHET monomers.[28,92]

Table 2 Hydrolysis of polyesters using different catalysts

Catalyst	Polymer	T^a(°C)	t^a (h)	Conv.^{a} (%)	Yield$_m$ ^{a} (%)	Ref.
—	PHB	200	6	100	84	101
—	PET	265	2	100	~100	102
—	PLLA	250	0.25	100	90	103
H_2SO_4	PHB	70	0.5	100	50	104
H_2SO_4	PHB	200	2	100	73.9	43
$Zn(OAc)_2$	PET	265	—	100	100	105
H_2SO_4	PET	135	5	—	90	106
H_2SO_4/H_3PO_4	PET	140	2.3	100	97.8	107
HNO_3	PET	98	2.3	87.4	87.3	108
HZSM-5	PET	230	0.67	100	100	109
NaOH	PET	99	2.5	—	85	110
$NaOH/Na_2SO_4$	PET	150	1.5	98.5	98.5	111
KOH	PET	200	1	—	98	112
KOH	PET	160	0.5	92.2	90.9	113
KOH/TOMAB	PET	95	1	—	84	114
KOH/TBAI	PET	90	0.67	100	100	115
NaOH/PTC	PET	90	1	—	99	116
NaOH/ethanol	PET	80	0.33	—	95	117
NaOH	PLLA	180	0.33	100	100	118

[a] *T*: reaction temperature, *t*: reaction time, conv.: conversion, yield$_m$: monomer yield.

Acid and base catalysts have also been found with high activity in PET glycolysis (Table 2), which can be classified as homogeneous and heterogeneous catalysts depending on whether they are soluble in EG. Metal acetates are the most commonly used homogeneous catalysts for PET glycolysis, such as $Zn(OAc)_2$, $Mn(OAc)_2$, $Co(OAc)_2$, and $Pb(OAc)_2$. For example, $Zn(OAc)_2$ can reach the equilibrium state of PET glycolysis in 3–5 h with an optimal BHET yield of 66.9%.[71,93] Chen *et al.* found that the combined use of $Zn(OAc)_2$ and microwave irradiation shortened the equilibration time to 35 min at the same reaction temperature, with the BHET yield of 78% at equilibration.[94] In addition, metal chlorides, metal carbonates, metal bicarbonates, and metal sulfates have been used to catalyze PET glycolysis, though they were less catalytic than $Zn(OAc)_2$.[91,95] Organic bases such as TBD are also efficient in catalyzing the glycolysis of PET. The corresponding TBD calculation and experimental results show that the hydrogen bonds between TBD and the carbonyl oxygen in PET can cause PET to become activated, thus facilitating PET depolymerization.[96] Sardon *et al.* reported on a protic ionic salt (TBD : MSA (1 : 1)) formed by an equimolar quantity of TBD and methanesulfonic acid (MSA), which could completely depolymerize PET in less than 2 h with a 91% yield of BHET.[97] The protic ionic complex could be recycled at least 5 times and remained stable up to >400 °C. Under mild conditions, the transition-metal-substituted polyoxometalates (POMs) of $K_6SiW_{11}MO_{39}(H_2O)$ ($M = Zn^{2+}$, Mn^{2+}, Co^{2+}, Cu^{2+}, and Ni^{2+}) also showed excellent catalytic activities in PET glycolysis.[72,98] Zhang *et al.* conducted PET glycolysis over a $K_6SiW_{11}ZnO_{39}$ catalyst at a low catalyst/PET molar ratio (0.13%) and a high PET/EG weight ratio (1 : 4), and the yield of BHET was found to be more than 84% under atmospheric pressure at 185 °C for 0.5 h.[72] Moreover, the same research team reported on multiple transition metal Zn-substituted polyoxometalates ($Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$) with more active sites, which could obtain complete PET conversion and 84.5% BHET yield at 190 °C for 40 min with a lower catalyst/PET molar ratio (0.018%) and high PET/EG weight ratio (1 : 4).[98] Among the imidazolium-based ionic liquids, metal-containing ionic liquids such as $[BMim]_2[CoCl_4]$, $[BMim]_2[ZnCl_4]$, and $[BMim]_2[ZnCl_3]$ were found with better thermal stability and higher performance than traditional metal catalysts and metal-free ionic liquids such as [BMim]Cl, [BMim]Br, $[BMim]HCO_3$, $[BMim]H_2PO_4$, and $[BMim]HSO_4$. This could be attributed to the strong interactions between the ester bond and the metal ions, causing the ester bonds to break more easily.[73–75,99,100] In addition, a series of choline-based ionic liquids without metals have been developed for the glycolysis of PET, and under the optimum conditions (180 °C, 4 h), choline acetate ([Ch][OAc]) performed better in the glycolysis of PET, with a BHET yield of 85.2%.[76] The promotion may be ascribed to the formation of hydrogen bonds between EG and [Ch][OAc]. Furthermore, deep eutectic solvents (DESs), such as urea/$ZnCl_2$ and 1,3-dimethylurea/$Zn(OAc)_2$ have been developed with good glycolysis performance under mild reaction conditions with corresponding BHET yields up to 83 and 82%, respectively.[77,78]

Compared with the homogeneous catalysts, the heterogeneous catalysts can be readily extracted from the reaction system, thus they have attracted increasing attention in PET glycolysis. Imran *et al.* investigated PET glycolysis over supported metal oxides, in particular Mn_3O_4@SiO_2 nanocomposites, and obtained a high BHET yield of over 90%.[79] Imran *et al.* further compared the catalytic performance of ZnO, metal oxide spinels, and mixed metal oxide spinels, and found that $ZnMn_2O_4$ with a larger surface area and higher acidity afforded a BHET yield of 92.2% at 260 °C.[80] They also reported that superparamagnetic γ-Fe_3O_4 nanoparticles, as a catalyst that can be readily restored, were efficient for PET glycolysis to BHET in more than 90% yield at 300 °C in 1 h.[81] However, most of these oxide catalysts required high reaction temperatures (>250 °C) to achieve the complete depolymerization of PET. To address this problem, efforts have been made in developing efficient oxide catalysts for PET glycolysis at lower temperatures. Nanoporous MnO_2/HGO nanosheets with a substantial surface area were prepared by the oxidation etching method and demonstrated a complete BHET yield of 100% within a brief 10 min at 200 °C, but required a substantial weight ratio of EG : PET (18.5 : 1) to drive the depolymerization reaction.[82] Paramagnetic ionic liquid-coated SiO_2@Fe_3O_4 nanoparticles (Fe_3O_4@SiO_2@[mim][$FeCl_4$]) were also used as catalyst for PET glycolysis with nearly 100% BHET yield over 12 consecutive reaction cycles at 180 °C for 24 h. Interestingly, the catalyst was readily recovered magnetically without tedious separation or purification processes.[83] Chen *et al.* investigated the Mg–Al hydrotalcite catalyst which, upon calcination at 500 °C, with a Mg/Al molar ratio of 3, showed 81.3% yield of BHET at 196 °C in 50 min, although it tended to deactivate in the recycling tests.[84] Recently, Wang *et al.* reported that ultrafine CeO_2 nanoparticles with rich oxygen defects afforded 90.3% BHET yield in 15 min at 196 °C, but their activity also decreased after 3 cycles.[85]

The polyester alcoholysis by the above catalysts follows a similar reaction mechanism (Fig. 3). Typically, polyesters are first dissolved or swelled in alcohol. Then, the catalyst's cation interacts with –C═O in the polyester ester, enhancing the carbonyl carbon's electro-positivity. The anion reacts with the H atom in the –OH group of alcohol at the same time, forming the transition state of the six-membered ring. As a result, the O in the –OH group of alcohol will be more electronegative, making it easy to attack the carbonyl carbon in the ester. Thus, the central carbon's hybridization has shifted from sp^2 to sp^3, creating a tetrahedral middle. Next, the original ester bond (–C–O–) is broken as the hydrogen atom leaves alcohol and electrons on the oxygen atom transfer to form C═O again.[68]

Overall, methanolysis is very efficient for the depolymerization of polyesters such as PLA, and the obtained products can be used directly for the synthesis of lactone or lactide which could be used for the ring-opening polymerization (ROP) reaction to produce new polyesters. Glycolysis is the most attractive method for PET recycling, and the corresponding monomeric products can be reused to produce plastics. Catalysts reported for alcoholysis consist of organometallic complexes, organic bases, ionic liquids, and heterogeneous oxide catalysts.

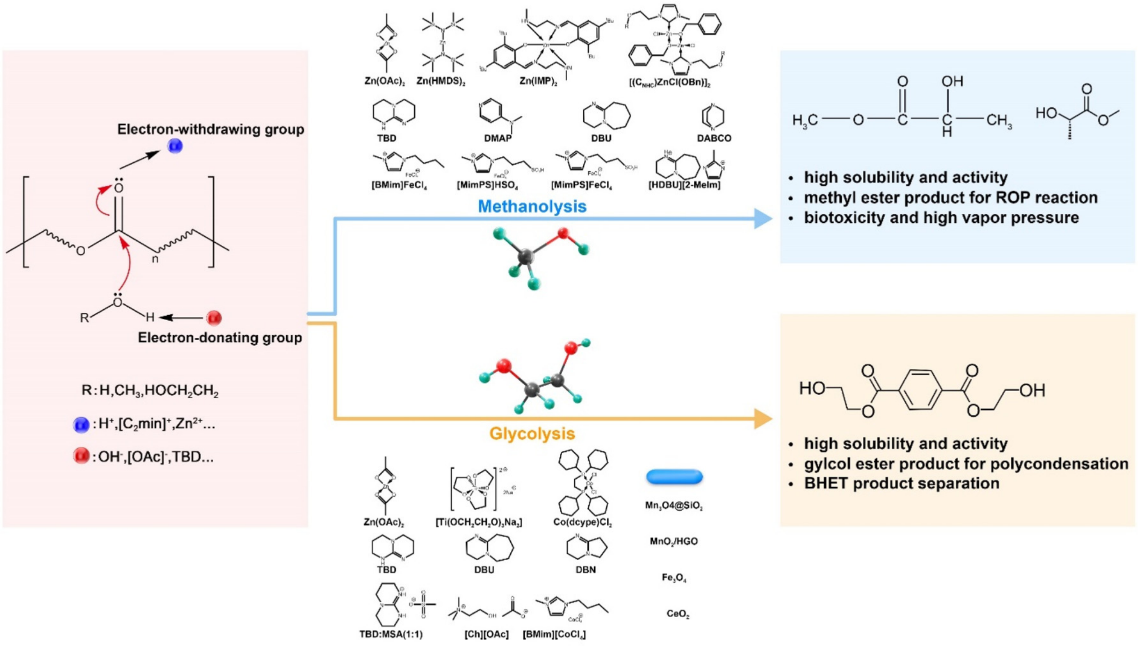

Fig. 3 Proposed catalytic mechanism for the depolymerization of polyester in alcoholysis.[68]

However, many challenges still limit their future development and application. Firstly, the homogeneous catalysts are difficult to separate and recover from the alcoholysis system after reaction, and most heterogeneous catalysts exhibit relatively low activity in polyester depolymerization. Clearly, more efficient and green catalysts need to be developed, for example, based on the Earth-abundant and nonnoble metals or oxides. Secondly, alcohols are susceptible to forming ethers under the catalysis of acids. Although methanol is better suited to polyester depolymerization, its biotoxicity and high vapor pressure can cause potential environmental pollution and safety problems. For PET glycolysis, the BHET product is highly soluble in EG solution, leading to the notorious separation problem after the reaction (Fig. 3).

2.2 Hydrolysis of polyesters

Hydrolysis of polyesters refers to the depolymerization of polyesters into monomers in acidic, alkaline, or neutral aqueous solutions (Table 2). However, the hydrolysis of ester bonds in water generally has a higher activation energy than alcoholysis, leading to higher depolymerization temperatures.[1] In addition, most polyesters are insoluble in water due to the high degree of polymerization and crystallinity, as well as strong hydrophobicity. Therefore, using solid acids to catalyze polyester hydrolysis is relatively difficult because the catalyst cannot effectively contact with polyester.

The simplest polyester hydrolysis process is carried out in neutral aqueous solutions, which, however, require a high reaction temperature (200–400 °C) due to the strong hydrophobicity and rigid structure of the polymer. Saeki *et al.* found that PHB could undergo autocatalytic hydrolysis under sub-supercritical conditions without any external catalysts, in which carboxylic acid from hydrolysis also further catalyzes the hydrolysis of PHB.[101] The results showed that the yield of 3-hydroxybutyric acid (3HB) decreased from 84% at 200 °C to 30% at 220 °C, possibly due to the influence of side reactions such as racemization and decomposition at high reaction temperatures. Campanelli *et al.* tested the breakdown of liquefied PET in an abundance of water at temperatures exceeding 250 °C and found that PET was fully depolymerized to TPA in 2 h.[102] Moreover, the neutral hydrolysis of PLA in sub-supercritical water was investigated, and 90% lactic acid yield was obtained in 20 min at above 250 °C.[103] Neutral hydrolysis can avoid the use of acid/base reagents. However, the high-temperature and high-vacuum reaction conditions are harsh, which will cause side reactions and reduce the selectivity of the monomers. As a result, current polyester hydrolysis reactions are mainly under acid or alkali catalysis.

Yu *et al.* investigated the hydrolysis of PHB by sulfuric acid (H_2SO_4) and found that neither 3HB nor crotonic acid (CA) was detected in acid solutions (0.1–4 N H^+) at 70 °C, while PHB could be completely decomposed in concentrated H_2SO_4 solutions (80–98 wt%) with CA and 3HB yields of 90% and 2%, respectively.[104] Therefore, 3HB was an intermediate with a volcano yield curve with the reaction time, and the optimal yield was about 50%. Bonartsev *et al.* investigated the hydrolysis reaction kinetics of PLA, PHB, and their derivatives in phosphate buffer at 37 °C and 70 °C.[119] Interestingly, the total molecular weight of PHB remained unchanged at the initial stage of hydrolysis, but the atomic force microscopy (AFM) characterization showed macromolecule splits. Due to the large size and hydrophobicity of the PHB fragments, diffusion from the polyester matrix to the aqueous media remained difficult at the initial stage. During the second stage, the PHB molecular weight decreased gradually, and at a critical mass, the PHB fragments dissolved in the aqueous medium. Li *et al.* studied the conversion of PHB to 3HB and CA monomers under hydrothermal conditions, and found that 3HB and CA further dehydrated and decarboxylated to propylene and CO_2 at 200 °C in H_2SO_4 solution (0.5 mol L^{-1}) for 2 h (Fig. 4a).[43]

$Zn(OAc)_2$ and other metallic salts with Lewis acidity were also frequently used for PET hydrolysis.[105] However, these Lewis acids could undergo significant hydrolysis under hydrothermal conditions. For example, $Zn(OAc)_2$ could be partially hydrolyzed to form acetic acid and zinc hydroxide. Currently, the acid catalysts used in PET hydrolysis mainly consist of strong Brønsted acids, such as sulfuric acid (H_2SO_4), nitric acid (HNO_3), and phosphoric acid (H_3PO_4). Mancini *et al.* investigated the acid hydrolysis of post-consumer PET by using a H_2SO_4 solution (7.5 M), reaching 90% TPA conversion in 5 h at 135 °C.[106] However, with increasing H_2SO_4 concentration, the EG yield decreased, as the strong dehydration effect of H_2SO_4 could lead to the carbonization of EG.[120] To reduce the carbonization degree, H_3PO_4 was used to replace a part of H_2SO_4, thereby reducing the sulfuric acid concentration and increasing the EG yield.[107] Using HNO_3 instead of H_2SO_4 as an acid catalyst for hydrolysis offered the characteristics of oxidation side reactions. For example, during PET hydrolysis, HNO_3 could oxidize the resulting EG into a value-added oxalic acid, which was detrimental to the closed-loop recycling of PET.[108] Interestingly, it was reported that introducing Na_2SO_4 into the reaction solution could minimize the oxidation of nitric acid, leading to a higher EG yield through the ionic exchange reactions which protected EG during its recovery.[28,108,111] To understand the Brønsted acid-catalyzed hydrolysis mechanism of PET, Yoshioka *et al.* proposed a widely accepted shrinking-core model (Fig. 4b).[120] The kinetic studies revealed that the hydrolysis reaction took place on the PET powder's surface, influenced by the formation and expansion of pores and cracks, thus indicating that the apparent reaction rate was directly proportional to the concentration of esters and sulfuric acid.

PET materials have strongly hydrophobic and rigid structures, resulting in insufficient contact with solid acids; therefore, PET hydrolysis has been rarely conducted using solid acids. Recently, Cha *et al.* reported a microwave-assisted hydrolysis method to depolymerize PET into TPA by using ZSM-5-based zeolites as simply recoverable and facilely regenerable catalysts.[109] 100% TPA yield could be obtained after only 40 min by using the H^+@ZSM-5-25 catalyst, and above 90% TPA yield was still maintained after 6 consecutive cycles. In particular, spent catalysts could be simply regenerated into new catalysts after annealing at 823 K for 6 h.

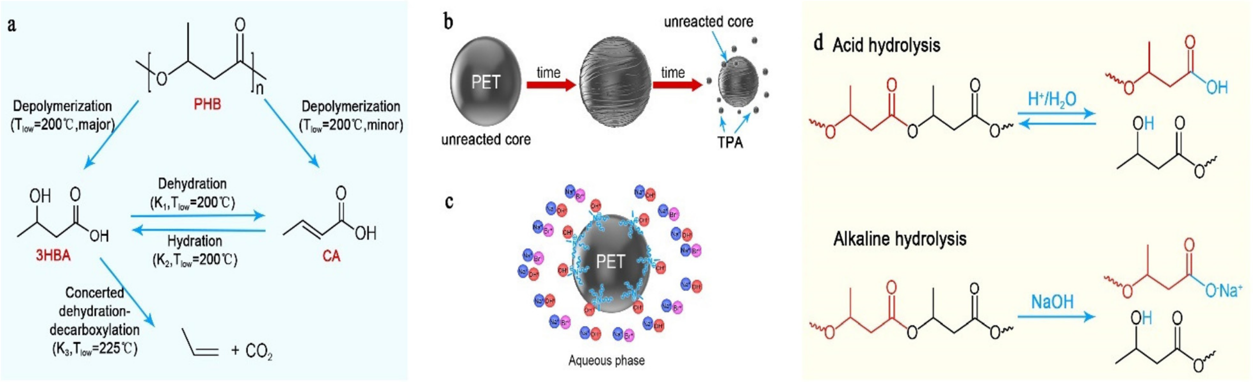

Fig. 4 (a) Proposed reaction network for PHB-to-propylene conversion,[43] (b) proposed shrinking-core model for the hydrolysis of PET over Brønsted acids,[120] (c) hydrolysis mechanism over alkaline catalysts and surfactants,[115] and (d) the hydrolysis mechanism in acid and alkaline solutions.[43]

Alkaline hydrolysis with inorganic base catalysts is another commonly used method to hydrolyze polyesters. Yagihashi *et al.* reported the recovery of L-lactic acid from poly(L-lactic acid) (PLLA) in a dilute aqueous NaOH solution (0.6 mol L^{-1}) at 160 °C for 60 min, and showed that PLLA almost completely converted to L-lactic acid without the formation D-lactic acid.[118] Accordingly, the components solubilized from PLLA mainly consisted of L-lactic acid, suggesting that the degradation reaction was controlled by the dissolution of products on the polyester surface rather than by a chemical reaction. Tsuji *et al.* investigated the hydrolysis of PLLA films in 0.01 M NaOH at 37 °C and found that hydrolysis mainly occurred in the amorphous region *via* the surface erosion mechanism.[121] Bonartsev *et al.* investigated the effects of molecular weight and morphology on the hydrolysis of PLA, PHB, the PHB–PLA blend, and the copolymer PHBV (20% of 3-hydroxyvalerate) at 37 and 70 °C.[119] The results showed that compared with high molecular weight polymers, the low molecular weight polymers had a higher degradation rate, and the hydrolysis activity of polyester decreased with the increasing hydrophobicity. Therefore, the degradation was enhanced according to PHBV < PHB < PHB–PLA blend < PLA. Yu *et al.* investigated the proportion of PHB precipitate that was broken down into soluble monomeric substances in a sodium hydroxide solution at 70 °C.[104] The results indicated that alkaline concentration was an important factor affecting PHB alkaline hydrolysis. The overall PHB degradation rate was found to be less than 5% at low concentrations of NaOH (0.1–0.4 mol L^{-1}), reaching 70% when the NaOH concentration increased to 4 mol L^{-1}. Moreover, a mechanism study suggested that the formation of crotonate did not occur through 3HB dehydration following the hydrolysis or dehydration of 3-hydroxyl groups prior to hydrolysis, but rather through the transient arrangement of a 6-membered ring comprising two adjacent 3HB units. Wan *et al.* carried out the depolymerization of PET flakes in a KOH solution at 120–160 °C and the ester linkage on the solid PET surface reacted with KOH in the solution, forming EG and terephthalic potassium salt.[114,122] Interestingly, a number of surfactants as phase-transfer-catalysts have been found to significantly promote the alkaline hydrolysis of PET, such as trioctylmethyl ammonium bromide (TOMAB) and tetrabutyl ammonium iodide (TBAI).[114–116] Hasan *et al.* reported on the alkaline hydrolysis of PET under microwave irradiation in the presence of quaternary ammonium salt and TBAI, with 99% of TPA obtained under the optimal conditions (10% NaOH, 60 min, 200 W power, and 3% wt./wt. TBAI and PET).[115] In this reaction, there exists a solid organic phase and an aqueous phase, so the phase transfer catalyst might work following an interfacial mechanism.[115,116] As shown in Fig. 4c, at the interface of the organic and aqueous phases, metal carbanion was created, and then surfactants were used to separate the species from the interface into the organic phase, creating reactive intermediates. As a result, the ester linkage in the PET macromolecule could be more easily attacked by the OH^- ion to accelerate the depolymerization. The formed terephthalate anion then returned to the aqueous phase in the form of disodium salt.[114] However, the addition of surfactants generally made the separation and recovery process more difficult. In addition to surfactants, Meester *et al.* found that the addition of ethanol to water could also promote PET alkaline hydrolysis, achieving approximately 95% TPA yield under the optimal condition (60 : 40 vol% EtOH : H_2O, 5 wt% NaOH, 80 °C, 20 min).[117] Recently, Wang *et al.* also reported a two-step alcoholysis and hydrolysis strategy for the efficient and selective depolymerization of PET-like polymers by a catalyst system composed of K_3PO_4/ethanol with a high degradation efficiency (>95%) under mild degradation conditions (110–130 °C).[48]

Although polyesters can be hydrolyzed into soluble products in both acids and bases, their tolerance to protons and hydroxyl anions was found to be significantly different (Fig. 4d). Taking PHB as an example, monomeric hydrolysis is rare in acid solutions of 0.1–4 mol L^{-1}. Conversely, hydroxyl anions have the ability to effectively target the PHB backbone at alkali concentrations between 0.1 and 4 mol L^{-1}.[104] These hydroxyl anions have the ability to diminish the energy barrier of ester bond breakage, resulting in similar activation energies for the saponification and biodegradation of PHB.[109] When an ester bond is broken down into carboxylic acid and alcohol in an alkaline solution, the hydroxyl anions will draw out protons from the acid and create carboxylate ions with a negative charge, which will be thermodynamically advantageous for nucleophilic substitution or re-esterification of the resulting alcohol and acid. Because hydroxyl anions can serve as a reagent rather than a catalyst, in this case, a high alkali concentration will promote the hydrolysis of polyester.[1,104] However, in acidic solutions, protons will act as catalysts for hydrolysis and esterification.[43,101] Thus, the polyester hydrolysis process yields a combination of carboxylic acid and alcohol, which can be further esterified with protons, and the hydrolysis step is preferred in concentrated acid solutions.

In summary, water is a green and inexpensive solvent for the hydrolysis of polyesters to monomers, and some challenges in this hydrolysis method need to be addressed for its application. Firstly, inorganic acids and bases are generally homogeneous and dissolve in water during the reaction, making product separation difficult and potentially causing serious environmental pollution. Secondly, owing to the weak nucleophilic ability of water molecules compared with alcohol molecules, the hydrolysis activity of polyesters is lower, and thus requires higher temperatures to achieve efficient depolymerization. Meanwhile, some polyester monomers are susceptible to side reactions (*e.g.*, dehydration, decomposition, and racemization) at high temperatures, further lowering their selectivity. Thirdly, although inorganic bases (*e.g.*, NaOH and KOH) can facilitate polyester hydrolysis, they will neutralize the carboxyl groups in the products to generate corresponding carboxylic salts during hydrolysis. As a result, alkali hydrolysis will not only deactivate the catalyst, but also requires the neutralization of the products, which will increase the operational cost of product separation and purification as well as waste discharges.

2.3 Enzymolysis of polyesters

Enzymolysis uses the microbial enzyme system to degrade the polyester polymers, has mild reaction conditions, low energy consumption, good selectivity and environmental friendliness. Thus, many efforts have been recently reported in the discovery of hydrolytic enzymes that can efficiently degrade polyesters, and make it become a viable recycling strategy.[123]

Biodegradable aliphatic polyesters could be degraded and mineralized through natural microorganisms, and eventually convert to carbon dioxide and water. However, there are many factors that still influence the biodegradation process, including the properties of polyester (*e.g.*, molecular weight, crystallinity and impurity), microbial factors (*e.g.*, strain type, number of bacteria and enzymatic properties), and environmental factors (*e.g.*, temperature, humidity, pH and oxygen concentration).[124] Even widely used PLA, as an example, takes a long time to fully degrade in ambient conditions. Currently, PLA biodegrades by anoxic composting, which typically requires a composting temperature of about 60 °C and humidity of about 50%.[7,125,126] In addition, most biodegradable polyesters are expensive; if they are biodegraded to carbon dioxide and water after one single use, this will waste significant resources and energy, and cause potential harm to environment. Thus, more attention should be paid to enzymatic strategies for the purpose of closed-loop recycling, but few are being reported. Yakunin *et al.* reported that two microbial carboxyl esterases (ABO2449 and RPA1511) were discovered to be capable of effectively breaking down PLA into lactic acid monomers, dimers, and larger oligomers, instead of CO_2, as the end products.[127] Myburgh *et al.* reported that the yeast *Saccharomyces cerevisiae* was equipped with a fungal cutinase-like enzyme (CLE1) which effectively catalyzed the enzymolysis of various PLA materials, resulting in the liberation of 9.44 g L^{-1} lactic acid from 10 g L^{-1} PLA films.[128]

For aromatic polyesters, such as PET, although they are naturally nonbiodegradable, recent studies showed that the PET enzymolysis is feasible toward closed-loop recycling. Müller *et al.* demonstrated PET can be depolymerized by a hydrolase (TfH) from the actinomycete *Thermobifida fusca.*[129] Yoshida *et al.* reported a novel bacterium, *Ideonella sakaiensis* 201-F6, with an activity up to 120 fold of TfH (Fig. 5a).[130] Tournier *et al.* used computer-aided enzyme engineering to produce a thermostable leaf-branch compost cutinase (LCC), showing a 90% PET conversion in less than 10 hours at 65 °C (Fig. 5b).[131] Later, Alper *et al.* used a structure-based machine learning algorithm to engineer a robust and active FAST-PETase that can completely hydrolyse the untreated post-consumer-PET in 1 week, with a TPA yield of 94.9% at 30–50 °C.[132] Similarly, Bell *et al.* obtained an evolved thermostable HotPETase (T_m = 82.5 °C) with the highest T_m among the active IsPETase derivatives.[133] PET is known to be a semi-crystalline compound, and its amorphous region is more flexible at its glass transition temperatures (T_g, 65–71 °C), making it easier for enzymes to contact and react.[134]

As to the enzymatic mechanism, Guo *et al.* proposed a PETase catalytic pathway based on microbe *Ideonella sakaiensis* (Fig. 5c).[135,136] PETase adopts the canonical α/β hydrolase fold, strictly conserved catalytic triad S131-h208-D177, involving nucleophilic groups (*e.g.*, serine), catalytic groups (*e.g.*, aspartic acid) and alkaline groups (*e.g.*, histidine).[137] The enzyme's apo-form creates a slight opening for the binding of the substrate to the protein surface, exhibiting different conformations of the W156 side chain. When the enzyme binds PET, the carbonyl group of the 1st benzene ring is oriented towards the core of the substrate binding cleft through a nucleophilic assault, while the oxyanion hole aligns the ester linkage to stabilize the intermediate. The conventional method of cutinase entails the formation of an intermediate acyl enzyme, which is then subjected to a subsequent nucleophilic attack by a water molecule. Once the ester bond is severed, the residual benzoic acid group of the product forms a broad, level surface that can be conveniently piled up in front of the W156 side chain. Afterwards, the product is rotated and moved away from its original stacked T-position before it is released.[136]

Enzymolysis is superior in terms of its high selectivity, involving a large number of weak non-covalent interactions

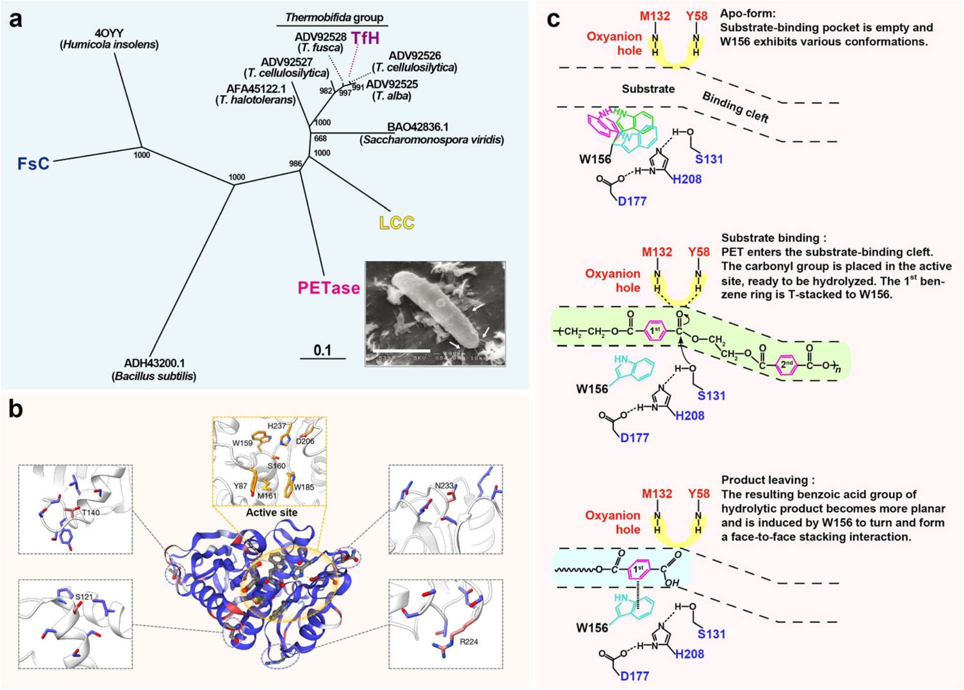

Fig. 5 (a) Unrooted phylogenetic tree of known PET hydrolytic enzymes,[130] (b) WTPETase protein structure rendered by the output of MutCompute,[131] and (c) possible catalytic mechanism of PET enzymolysis.[136]

between substrate and enzyme that essentially impart stability and flexibility to the large molecules.[138] Thus, when a polyester interacts weakly with a flexible enzyme, this may facilitate the mass transfer and depolymerization of the polyester chain.[139–141] In addition, the short covalent connection between the enzyme and the substrate can trigger the substrate to perform the induced fit, thus promoting the catalytic depolymerization.[131,139,142,143] However, challenges such as unbalanced enzyme–substrate interactions, low thermostability, low efficiency at high temperatures, and inhibiting intermediates, still hamper its further applications.[134]

3. Upcycling of polyesters

Different from closed-loop recycling, upcycling aims to chemically recycle or modify plastic waste to produce new products with higher market values, including small-molecule chemicals and polymer materials. For making small-molecule chemicals, like closed-loop recycling, upcycling also requires the complete depolymerization step. However, the target product is not the original monomer, but new high-value-added chemicals. Upcycling to materials is derived from incomplete depolymerization of polyesters, and involves the controlled degradation and post-functionalization of polyesters to obtain new materials with enhanced properties.[16] Unlike polyolefins, polyesters, such as epoxy resins, polyurethanes, and unsaturated polyesters, have active functional groups for targeted deconstruction and subsequent reconstruction into new materials with improved properties.[144] Thereby, the upcycling of plastic waste is a multidisciplinary approach that involves various depolymerization methods and techniques.[145]

3.1 Hydrolysis/alcoholysis/enzymolysis of polyesters

Li *et al.* reported that the process of upcycling poly (3-hydroxybutyrate) (P3HB) into value-added polymerizable monomers, followed by polymerization towards degradable and recyclable polymers through four steps, including the efficient conversion of P3HB into ethyl 3-hydroxybutyrate (HBEt), selective ring-opening with CHO, cyclization to form the new bicyclic monomer 4-methyloctahydro-2*H*-benzo[*b*][1,4]dioxepin-2-one (4-MOHB), and its ROP, is made easier (Fig. 6a).[146] Wang *et al.* developed an alternative cyclization-depolymerization strategy for integrating upcycling and closed-loop recycling of aliphatic polyester poly (*p*-dioxanone) (PPDO) by using an acidic ionic liquid as a catalyst/solvent bifunctional agent at a relatively low reaction temperature of 120 °C (Fig. 6b).[147] In addition, they used an "amino-alcoholysis" strategy to upcycle the poly (bisphenol A carbonate) (BPA-PC) into BPA monomers and chiral 2-oxazolidinone chemicals *via* ZnX_2-catalyzed depolymerization by chiral amino alcohols under mild conditions (25 °C, 3 h).[148] Wang *et al.* found that the "polymer to polymer" approach enabled the recycling of PLA plastic waste from its end-of-life to new high-quality PLA materials (Fig. 6c). During depolymerization, organometallic complexes and organic bases were employed for selective methanolysis, while new lactide monomers were added to the repolymerization process to obtain new polyester with a higher molecular weight.[149]

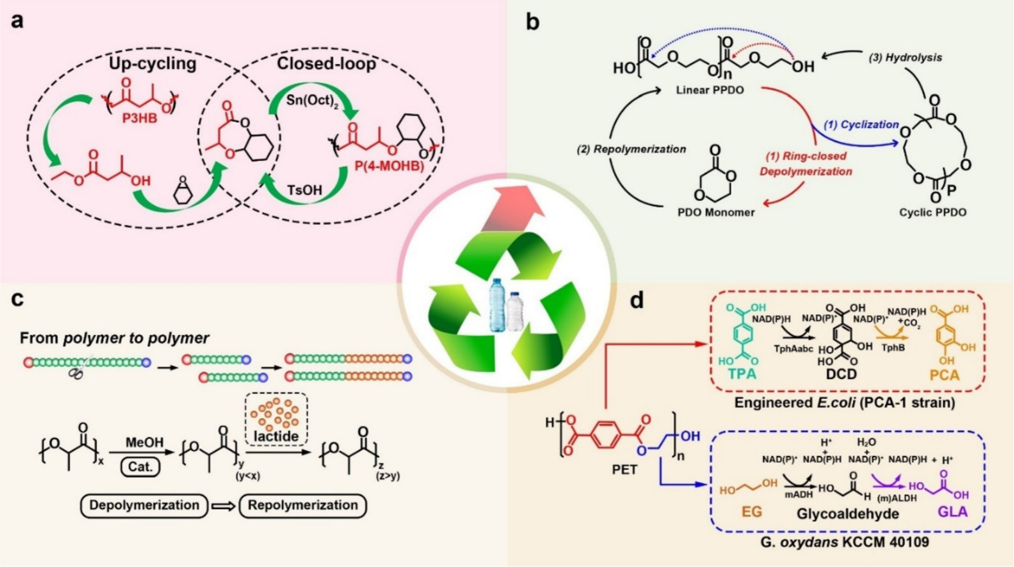

Fig. 6 (a) The upcycling of P3HB based on alcoholysis method,[146] (b) the upcycling of PPDO based on hydrolysis method,[147] (c) the upcycling of PLA based on methanolysis method,[149] and (d) the upcycling of PLA based on enzymolysis methods.[152]

The combination of hydrolysis/alcoholysis and bio-mediated transformation is also a promising strategy for upcycling polyester waste into new chemicals and polymers. O'Connor *et al.* reported three strains capable of accumulating medium chain length PHAs from PET hydrolysate, namely, GO16 (*Pseudomonas putida*), GO19 (*Pseudomonas putida*), and GO23 (*Pseudomonas frederiksbergensis*).[150] Narancic *et al.* used GO16, a metabolically versatile *Pseudomonas umsongensis*, for the upcycling of PET hydrolysate into biodegradable polyester PHAs *via* microbial cultivation.[151] Kim *et al.* investigated a one-pot chemobioprocess of PET depolymerization, first by depolymerizing PET into a glycolysis slurry on a biocompatible betaine catalyst, then by using *IsPETase* and *IsMHET* for enzymatic hydrolysis to produce TPA and EG, and finally through bioconversion to protocatechuic acid and glycolic acid (Fig. 6d).[152,153] Wallace *et al.* upcycled the PET-derived monomer terephthalic acid into value-added small-molecule vanillin using a novel engineered *Escherichia coli.*[154] Recently, Kunjapur *et al.* used an ω-transaminase from *Chromobacterium violaceum* (cvTA) to efficiently catalyze amine transfer to potential PET-derived aldehydes, such as terephthaladehyde from TPA and 4-formylbenzoic acid from MHET, to form monoamine *para*-(aminomethyl) benzoic acid (*p*AMBA, 70 ± 8% yield) or diamine *para*-xylylenediamine (*p*XYL, 69 ± 1% yield), both of which are valuable building blocks for polymeric materials and pharmaceuticals.[155]

Value-added materials can also be obtained from targeted deconstruction and subsequent reconstruction of PET upcycling. Szilagyi *et al.* produced desirable metal–organic frameworks (MOFs) with a Uio-66 topology by first depolymerizing PET into terephthalic acid, followed by subsequent purification and MOF synthesis.[156] Beckham *et al.* demonstrated that PET could be upcycled into long-lifetime fibre-reinforced plastics *via* combination with renewably sourceable monomers.[157] In the work, glycolyzed PET was obtained from controlled diol deconstruction by using titanium butoxide, which was reacted with renewably sourceable monomers, such as olefinic diacids and olefinic monoacids, to produce a series of unsaturated polyesters or diacrylic polymers. Similarly, Abdelaal *et al.* documented the transformation of PET waste into unsaturated polyester through the utilization of PET controlled glycolysis and subsequent interaction with maleic anhydride.[158] Pitet *et al.* employed PET wastes in combination with a bioderived dimer fatty acid to fabricate engineering-grade segmented thermoplastic copolyesters through solvent-free melt polycondensation.[159] Clearly, these examples of progress show that upcycling based on closed-loop recycling methods is efficient and promising. This strategy can be further improved by further improving the catalyst activity and stability and product separation efficiency as well as preventing the side reactions of solvents.

3.2 Ammonolysis/aminolysis of polyesters

Upcycling of polyester can also be performed by aminolysis or ammonolysis, involving the electrophilic attack of polyesters by amines or ammonia, more thermodynamically favorable than hydrolysis and alcoholysis.

Harad *et al.* used ethanolamine (EA) with a 1 : 6 ratio of PET : EA under reflux conditions (180 °C) and yielded bis(2-hydroxyethylene) terephthalamide (BHETA).[160] Fukushima, *et al.* used TBD as the organic catalyst and various amines as the depolymerization media for the aminolysis of wastes PET (Fig. 7a), yielding a versatile library of functional terephthalamides with great potential as building blocks for high-performance materials.[37] Specifically, bis-amine-functionalized terephthalamides are desired monomers for highly thermostable polymers such as polyamides, polyimides, polyurethanes,

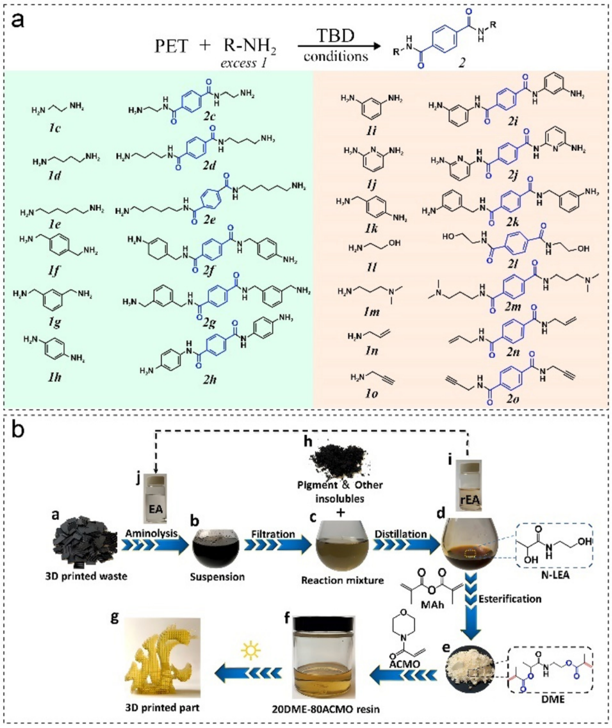

Fig. 7 (a) Terephthalamides are produced through the organocatalytic aminolysis of PET,[37] and (b) schematic upcycling process from FDM 3D printed PLA waste to MSLA 3D printed photocurable resins.[162]

and polyureas.[161] Zhang, *et al.* used 2-aminoethanol for aminolysis of PLA to *N*-lactoyl ethanolamine, which was then isolated and purified to react with dimethylaminopyridine (DMAP) to synthesize dimethacrylate ester (DME), a new 3D printing material with a tensile strength of 58.6 MPa and a Young's modulus of 2.8 GPa (Fig. 7b).[162] Recently, Ma *et al.* treated PLA with a simple ammonia solution over Ru/TiO_2 and achieved a 94% selectivity to alanine at 140 °C, transforming PLA into lactamide and then further into ammonium lactate at higher temperatures.[163] The final product alanine is one of the most important amino acids, and is widely used in food, forage, and pharmaceutical applications.

The ammonolysis method facilitates the homogeneous distributions of functional groups on polyester fabrics. Lorusso *et al.* synthesized zwitterionic polymer brushes through the chemical modification of PET in an attempt to modify its hydrophobicity by the controlled insertion of amide moieties.[164] In the work, the PET fabric was prefunctionalized by surface ammonolysis with diethyl amine, and then immobilized in the bromoisobutyryl bromide and TEA mixture to produce zwitterionic brushes by atomic transfer radical polymerization. Karpati *et al.* carried out ammonolysis of PET with an epoxy hardener isophoron-diamine as the solvent, and obtained 90% yield of the terephthalamide-diamine product over zinc acetate catalyst.[165] Moreover, the raw aminolysis product could be further used as a cross-linking agent for epoxy resins without purification.

In summary, on the basis of ammonolysis/aminolysis, polyester can be upgraded to numerous nitrogen-containing chemicals and materials, a process worthy of further development. However, compared with water and alcohol as solvents, amines and ammonia are toxic and have high vapor pressures, which cause potential pollution and corrosion concerns.

3.3 Reductive and oxidative upcycling

Reductive and oxidative upcycling of polyesters generally involves their depolymerization and subsequent reduction and oxidation reactions.

Lactic acid can be converted to a series of small molecules with high industrial values by hydrogenation and oxidation reactions, as shown in Fig. 8a, including dehydrating to acrylic acid, condensing/dehydrating to 2,3-pentanedione, decarbonylating/dehydrating to acetaldehyde, reducing to 1,2-propanediol, oxidizing to pyruvic acid, hydrodeoxygenating to methyl propionate, and ammonizing to alanine.[161] Therefore, PLA depolymerization and lactic acid conversion can be efficiently coupled, and PLA waste can be upcycled to produce many value-added chemicals. Ma *et al.* recently reported the valorisation of waste PLA for the production of methyl methacrylate (Fig. 8b). The PLA is initially transformed into methyl propionate using an α-MoC catalyst in a methanol solution, and then the resulting methyl propionate is combined with formaldehyde to create methyl methacrylate (81% conversion, 90% selectivity), an essential monomer of polymethyl methacrylate that is used in paints, coatings, and adhesives.[166] Furthermore, under the same reaction conditions, PGA and PCL were successfully converted into methyl acetate with a 94% yield and methyl hexanoate with a 79% yield, respectively.[166]

PET composed of aromatic monomers is an ideal resource for the production of aromatic compounds.[167] 1,4-Benzenedimethanol is an essential component in the manufacture of pesticides, perfumes, and dyes, and can be obtained directly from PET hydrogenolysis. Clarke *et al.* tested a series of ruthenium(II)-catalysts bearing tridentate aminophosphine ligands for PET hydrogenolysis, and at 110 °C, 73% 1,4-benzenedimethanol was yielded using the ethylenediamine variant of the ruthenium(II)-sulfoxide complex in a 50/50% mixture of THF and anisole.[168] By using two ruthenium(II)-complexes bearing tridentate phosphine ligands for PET hydrogenolysis in the presence of $HNTf_2$ (1 mol%), Klankermayer *et al.* obtained high PET conversion (>99%) and 1,4-benzenedimethanol selectivity (>86%) under optimal conditions (140 °C, 100 bar H_2 for 16 h) for a variety of commercial PET sources, such as bottles, yoghurt pots, and sports jersey (Fig. 8c).[169] Feghali *et al.* reported two efficient organocatalysts, $B(C_6F_5)_3$, and $[Ph_3C^+, B(C_6F_5)_4^-]$, for the reductive depolymerization of PET in an Et_3SiH and CH_2Cl_2 mixture, and obtained 1,4-phenylenedimethanol *via* hydrogenolysis and hydrosilyation cascade reactions.[170] However, the use of toxic, costly, and homogeneous chemicals in these methods made them difficult to separate and recycle, and potentially causes serious environmental pollution. To overcome the limits of homogeneous cat-

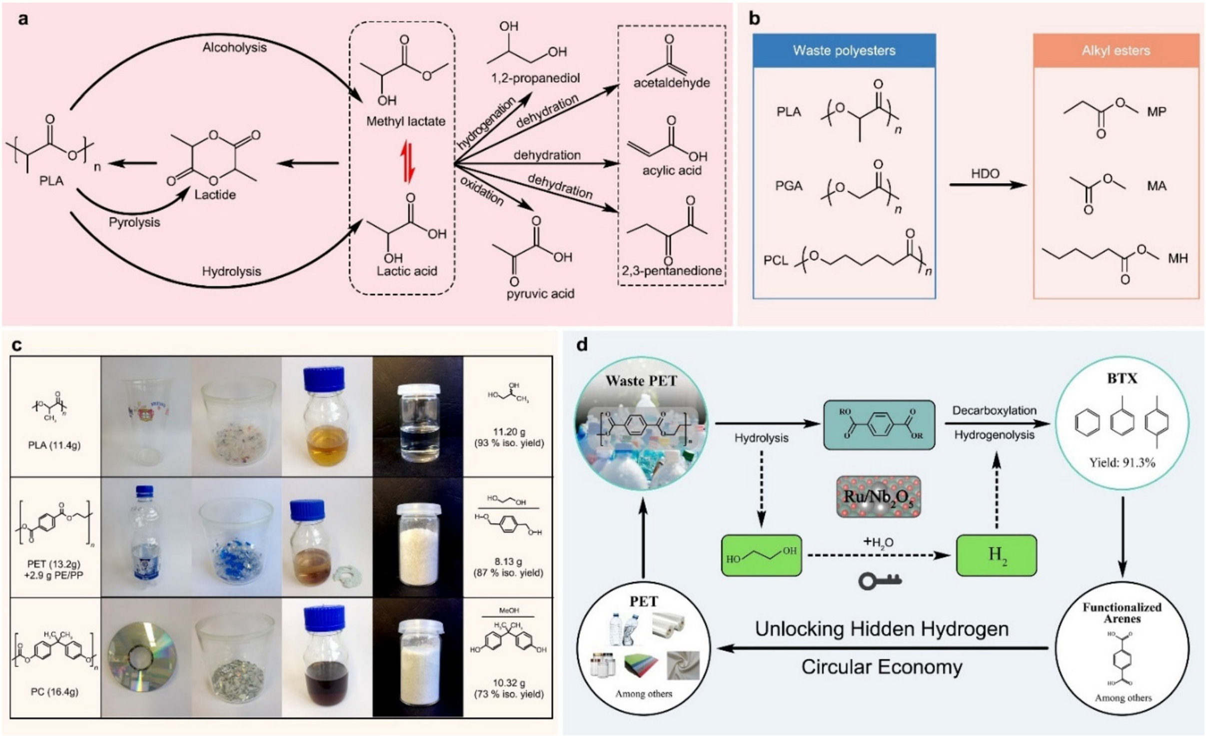

Fig. 8 (a) Lactic acid as a platform molecule for the synthesis of chemical intermediates,[161] (b) upcycling of polyesters *via* hydrodeoxygenation (HDO),[166] and (c and d) upcycling waste PET to 1,4-phenylenedimethanol[169] and aromatic products.[173]

alysts, heterogeneous catalysts have also been recently reported for the selective reductive depolymerization of PET. By using CuFeCr catalysts derived from layered double hydroxides (LDHs), Ma *et al.* performed the co-transformation of PET and CO_2, involving hydrogenation of CO_2 to methanol, PET methanolysis, and subsequent dimethyl terephthalate hydrogenation.[144,171] Yan *et al.* achieved a 95.2% overall yield of arenes and cyclic hydrocarbons on a Ru/Nb_2O_5 catalyst by transforming aromatic plastic wastes with C–O and C–C linkages into arenes in hydrogen.[172] Ru/Nb_2O_5 was also applied to H_2-free conversion of PET into toluene and *p*-xylene, instead of decarboxylation into benzene (Fig. 8d),[173] where no external H_2 was added, and the EG unit in PET acted as a hydrogen resource.[167]

3.4 Photolysis and electrolysis of polyesters

Photolysis refers to the breakdown of polymer chains through the breaking of their ester bonds with the combination of UV radiation and oxygen. At present, photosensitizers or photosensitive functional groups have been designed for introduction in the polyester materials, which will help the waste absorb energy from UV radiation to break polymer bonds, reduce molecular weight, and undergo enzymatic hydrolysis by microorganisms.[174–177] Loyo *et al.* studied the photolysis of PLA materials, and found that calcium oxide additives contributed to the photolysis process of PLA, where it was hypothesized that the surface of calcium oxide nanoparticles may take up active hydroxyl groups, which contribute greatly to the free-radical reaction and accelerate the photolysis of PLA.[174] However, this is rarely reported in the re/upcycling of polyester. Chen *et al.* recently reported that *via* efficient solar-thermal catalysis for recycling, various polyesters were recycled to form high-value-added monomers, and the BHET yields dramatically increased from 27 to 82% when the illumination time was prolonged from 1 to 4 h.[178]

Coupling alkaline hydrolysis and electrocatalysis has also been performed for upcycling PET waste into terephthalate and formate in an H-type cell, where different electrocatalysts were examined, such as $CuCo_2O_4$/Ni foam,[179] CuO nanowire,[180] and $CoNi_{0.25}P$/NF.[181]

3.5 Other upcycling methods

PET can also be used to prepare certain special carbon-based materials *via* high-temperature treatment. Topuz *et al.* reported the valorization of PET wastes to produce nanofibrous adsorptive membranes for application in oil removal, in which PET wastes were dissolved first in a trifluoroacetic acid solvent and then electrospun into nanofibrous membranes.[182] Zhang *et al.* reported the mechanochemical extrusion of PET waste into porous carbon materials with a surface area of up to 1001 $m^2\ g^{-1}$.[183] PET and the pore-directing additives were first mixed and cyclically extruded in a twin-screw extruder, then carbonized under an inert atmosphere, and subsequently treated with hydrofluoric acid to remove additives, resulting in a porous carbon material. Yuan *et al.* pretreated PET wastes using physical and chemical activation methods to convert the

PET waste into value-added porous carbons for CO_2 capture.[184] Nunes *et al.* used PET waste to produce a high-performance porous membrane using the no-solvent-induced phase separation method.[185] Furthermore, Lee *et al.* demonstrated that the incorporation of carbon fibers into PET could practically upgrade the mechanical properties of the mixed plastics.[186]

Ladewig *et al.* showed that PLA waste could be utilized for the synthesis of lactate-containing metal organic frameworks (MOFs) of ZnBLD, which maintained the chiral separation ability and exhibit great potential for application.[187] Yang *et al.* investigated a two-step extrusion process for the re/upcycling of PHB to plasticized PLA.[188] In the process, the initial step involved subjecting PHB to thermal degradation in an extruder at a temperature of 220 °C, resulting in the formation of PHB oligomers (1600 Da) equipped with functional end-groups that could be subsequently covalently attached to the PLA chains, thereby introducing flexibility into the system.

4. Insights into challenges and strategies

Clearly, the closed-loop recycling and upcycling of polyesters proceeds by their selective depolymerization, which requires efficient breaking of their crystalline structures and ester bonds to form oligomers and monomers. To address this issue, we next try to analyse the key challenges and tentatively propose the corresponding strategies.

4.1 Catalysts

As discussed above, for polyester depolymerization, catalysts play essential roles in facilitating the selective breaking of ester bonds under mild conditions.

At present, organic, inorganic and enzymatic catalysts are used for polyester depolymerization. Among them, inorganic acids and bases as homogeneous catalysts are effective in polyester depolymerization, but they encounter problems associated with their separation and recycling, and also serious environment pollution. Organic acids and bases are not so active and the post separation is also challenging. Organic/inorganic metal salts work well in catalyst–substrate interaction and catalysis, but their stability and separation are also problematic. Ionic liquids could play the roles of catalysts and solvents, thereby providing high activities. However, they are frequently synthesized by sophisticated methods with relatively high costs and difficulty in separation from homogeneous systems. Hydrolases are generally biosynthesized by microorganisms. They have unique flexible biological structures that induce substrates for adsorption and catalysis. In particular, enzymatic catalysts have high specificity and can obtain high selectivity to monomers at low depolymerization temperatures. However, most enzymes are expensive, thermally unstable, and easily inhibited by products. In addition, the efficiency of enzymolysis is still low with unsatisfactory monomer concentrations in the products. Heterogeneous catalysts can be readily separated from the reaction solutions, but have low efficiency in their contact with polyester substrates. Thereby compared with homogeneous catalysts, they require higher reaction temperatures, and are susceptible to deactivation by blockage or poisoning of active sites, leaching or sintering of catalytic species, and so on.

Accordingly, the design of catalysts should consider the accessibility and efficiency of the active sites and their stability along with ease of separation from the reaction solutions. For homogeneous catalysts, it may be useful to solve the separation issue by changing their solubility under different conditions, such as temperature and pH.[189] While it is difficult to make the heterogeneous catalysts dissolvable, some process enhancers could be applied to improve the mass transfer efficiency, such as quaternary ammonium salts.[115]

In fact, enzymatic degradation is itself a natural behaviour, inspiring the design of chemical catalytic systems. For instance, the enzymolysis of cellulosic biomass is being engineered. During the process, the cellulose is generally degraded into oligosaccharides and disaccharides by the synergistic effect of endoglucanases and exoglucanases, and then hydrolysed to glucose by β-glucosidase (Fig. 9a).[190,191] Mimicking this enzymatic system, we may design depolymerization catalysts with multiple sites to work synergistically, considering the different stages of processing polymers from macromolecules to small molecules. At present, polyester enzymolysis is usually carried out at the glass transition temperature of polyesters, at which the amorphous regions of polyesters are more flexible for contacting catalysts. Therefore, the design of chemical catalytic systems should consider the reactivity and selectivity at around the glass transition temperatures of polyesters. In addition, enzyme activity and specificity not only come from the active sites, but also from the physicochemical structures and surface groups of the enzymes. For cellulase, its molecular structure consists primarily of two regions: the first region is the carbohydrate-binding module that can absorb and bind with polysaccharide substrates, and the other one is the catalytic domain with an open cleft complementary to the substrate form (Fig. 9b). Therefore, coupling the adsorption and catalytic regions can also be adopted when designing chemical catalysts. Recently, Pickford *et al.* employed a thermostable form of leaf compost cutinase (LLC) to fabricate synthetic fusion constructs of LCC with five type-A carbohydrate-binding modules (CBMs), which facilitated the enzyme–substrate interaction and ultimately achieved 97% PET conversion (Fig. 9c).[192] Perras *et al.* reported an ordered, mesoporous shell/active site/core catalyst architecture with benefits like processive enzymes, which can improve the polymer–surface interactions and the translocation of the macromolecules (Fig. 9d).[18]

4.2 Solvents

Solvents play a significant role in polyester depolymerization and re/upcycling, not only for dissolving the polymers, but also for promoting the reactions.

Whatever methods are used to degrade the polyesters, the primary step is to break their crystalline structures and the pro-

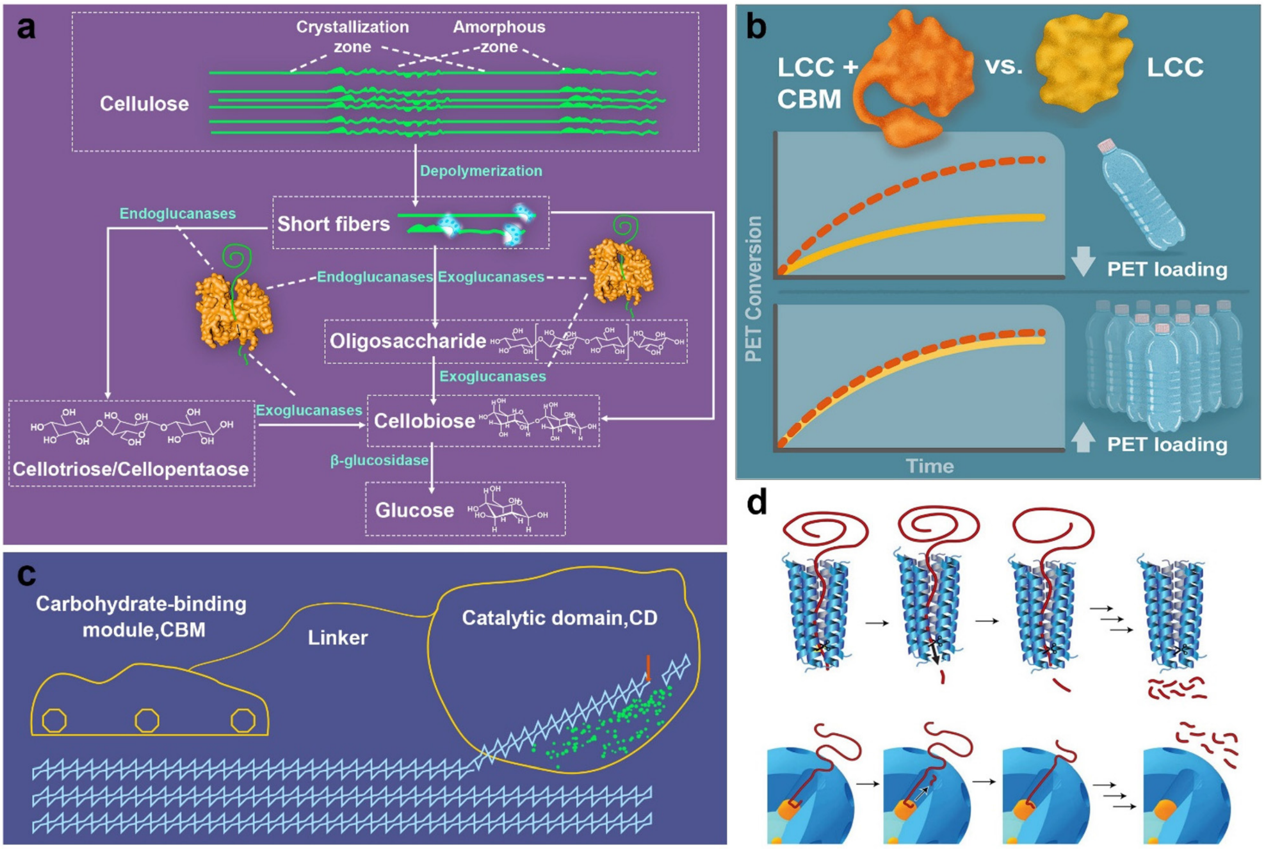

Fig. 9 (a) Enzymatic hydrolysis of cellulose, (b) cellulase structure, (c) binding modules in enzymatic PET hydrolysis,[192] and (d) catalytic upcycling of PE processive mechanism.[18]

tective polymer layers, making them accessible to catalysts. The solvents can be typically divided into good and poor solvents. In a so-called poor solvent, the attraction between the polymer chains is stronger than that between the chains and the solvent, the polymer tends to contract or phase separation occurs, and consequently does not easily mix with the solvent. Differently, in a good solvent, the attraction between the polymer chains is weaker, so the polymer chains tend to stay away from each other, leading to polymer swelling and dissolution. As shown in the phase diagram of a polymer solution (Fig. 10), at the temperature of θ, the phase diagram is divided into two parts: the lower part is the poor solvent region and the upper part is the good solvent region. The solid line in the diagram reveals that the phase separation of polymer solution occurs, and the dotted line shows the cryogenic boundary of a semi-thin good solvent. Clearly, polymer depolymerization requires the selection of a good solvent and appropriate reaction conditions to cause the polymer to swell and dissolve. High activity of polyester alcoholysis at room temperature was reported in the presence of alcohol and CH_2Cl_2, which can dissolve the polyester first, transforming a heterogeneous reaction into a homogeneous reaction.[61,193] Notwithstanding the toxic and environmental concerns over CH_2Cl_2, this confirms the strategy, which can be advanced actually by choosing greener solvents for the polyester depolymerization.

On the other hand, solvents can also promote the polyester depolymerization. Breaking the ester bonds involves essentially nucleophilic substitution. Therefore, the selection of nucleophilic reagents is important in polyester depolymerization and re/upcycling. Fig. 10 also shows some nucleophilic reagents classified by different nucleophilic elements. O-based reagents include water, alcohols, glycols, and carboxylic acids, which form new C–O bonds when the nucleophiles attack carbonyl carbon with the O-atom.[194] However, these processes are generally reversible, and there is the need to tune reaction conditions to shift the reaction equilibrium. N-based nucleophilic reagents, including ammonia and amines, can efficiently form C–N bonds through N-atom nucleophilic attack on the carbonyl carbon. C-based nucleophilic reagents, such as hydrogen cyanide, alkynes, and Grignard reagents, can easily form C–C bonds. S-based nucleophilic reagents, such as hydrogen sulfide, thiol and sodium bisulfite, can form S–C bonds, which are also reversible due to a small energy difference between S–C and C–O bonds. Based on the properties of these reagents, they can be chosen for the closed-loop recycling or upcycling of polyesters.

4.3 Closed-loop recycling and upcycling

To study the closed-loop recycling of plastic wastes, their sources and industrial synthetic processes need to be preferen-

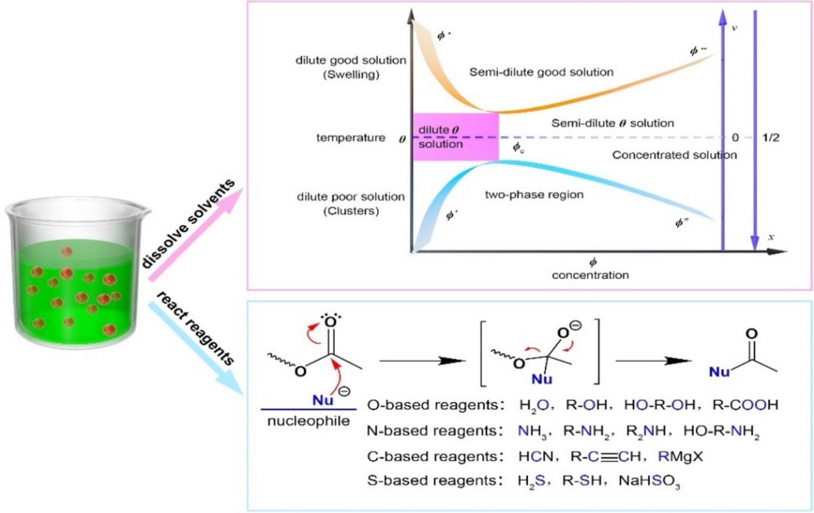

Fig. 10 Solvent role in for dissolving the polymers and nucleophilic substitutions to the acyl group of polyesters.

tially considered, which provide the directions for choosing and designing their depolymerization methods. As shown in Fig. 11, two reaction routes are available to produce PET industrially. The first route involves the melt polycondensation of bis(2-hydroxyethyl) terephthalate (BHET) with ethylene glycol (EG) as a byproduct, and the second one involves the melt polycondensation of a mixture of terephthalic acid (TPA) and EG with water as a byproduct. At present, most biodegradable polyesters are synthesized by the ring-opening polymerization (ROP) of lactones or lactides, and corresponding acid and ester monomers cannot be directly repolymerized to targeted high-molecular polymers (Fig. 11). Taking PLA as an example, it is difficult to obtain high-molecular PLA by the direct polycondensation of lactic acid recycled from PLA depolymerization. Commercially, PLA is prepared by the ROP of lactide, which can maintain the properties of the functional groups of the monomers without releasing small molecules (*i.e.*, H_2O and CH_3OH) in milder polymerization conditions and achieve the higher molecular weights. Similarly, the chemical recycling of PCL, PGA, PHB, and other polyesters with ROP requirement has not been well performed in a closed loop.[40] Therefore, if the plastic waste can be selectively depolymerized to lactone or lactide intermediates, the closed-loop recycling will be more technologically and economically viable.

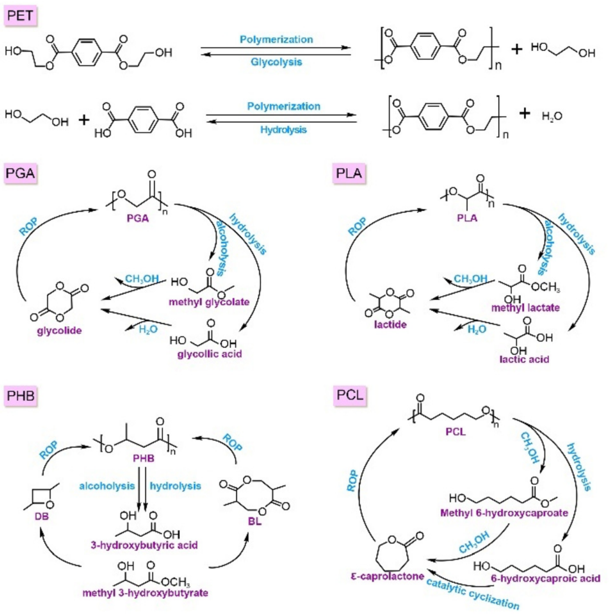

Fig. 11 Proposed closing-loop recycling routes of representative polyesters.

Upcycling is an open-loop method with production of value-added chemicals and materials from plastic wastes. Thus, in order for it to be highly efficient, a combination of innovative depolymerization chemistry, breakthroughs in catalyst science, new bio/chemotechnologies and analytical characterization capabilities, novel approaches to separation science and waste management, and thorough economic and life-cycle assessments are necessary.[195] In comparison with the aforementioned closed-loop recycling, upcycling has been rarely studied, and the resulting chemicals and materials are still limited, relative to the large volume of plastic wastes.[16] Meanwhile, upcycling may involve heteroatoms to build new molecular structures, but this often requires the use of toxic chemicals. Consequently, the expenses, energy consumption, and ecological effects linked to the upcycling methods should not exceed those of manufacturing the same items from fresh materials obtained from the closed-loop recycling process (Fig. 12).

4.4 Chemical recycling and upcycling of mixed plastics

Polymers are often blended together, combined with small-molecule additives, or physically and chemically bound to other plastics to improve their performances; however, this

Fig. 12 Potential future development of upcycling.

creates difficulties and challenges when it comes to recycling. To some degree, the recycling issues are closely related to their classification and separation. Therefore, polymer products should be easily identified so that they can be initially classified, sorted, and processed by later consumers and recyclers. Therefore, it is now necessary to separate plastics from waste mixture streams using a variety of techniques, including manual sorting, sieving, gravity sorting, magnetic sorting, photoelectric sorting, and rebound sorting, based on differences in the size, density, magnetism and photoelectric properties of plastic particles. In addition, the chemical recycling of mixed plastic wastes is comprehensive, and has to be addressed by different approaches (Fig. 13).

Currently, the chemical depolymerization and monomer recovery of mixed plastics are challenging.[48] To our knowledge, only a few literature reports are available on the chemical recycling of mixed plastics. For hybrid of PLA and PET plastics, Collinson *et al.* developed a stepwise depolymerization strategy by taking advantage of the different reactivities to alcoholysis of the two plastics over zinc acetate. Hence, PLA could successfully undergo alcoholysis into lactate esters, while PET showed no reactivity under the same conditions due to its lower degradation, which facilitated post-separation.[56] Sardon *et al.* also found that the protic ionic salt TBD: MSA catalyst could catalyze the selective and sequential depolymerization of PET and bisphenol A-based polycarbonate (BPA-PC), due to the energetic differences between BPA-PC and PET during glycolysis.[196] These methods provide a stepwise depolymerization strategy suitable for mixed polyesters with significant differences in intrinsic depolymerization activity.[197] Therefore, it is necessary to develop integrated methods compatible with different plastics degradation characteristics.

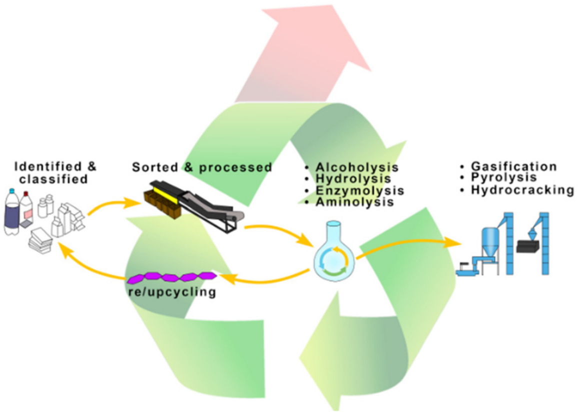

Fig. 13 Proposed strategies for chemical recycling and upcycling of mixed plastic wastes.

In cases where monomers are difficult to recycle from the mixtures of blended plastics, they can be considered for conversion, although not in an energy- or atom-economical way, into fuel additives (Fig. 13). One such method is gasification, and the plastic is partially oxidized at high temperatures to yield syngas (CO and H_2) as the main product. Secondly there is pyrolysis, which is performed at high temperatures to thermally decompose mixed plastics to pyrolysis oil and gas products in the absence of oxygen. Thirdly, hydrocracking of plastic mixtures with hydrogen *via* catalytic hydrogenolysis at elevated temperatures forms saturated alcohols and hydrocarbons. In brief, these processes do not have specific requirements for the compositions of the plastic wastes and allow for recycling of a wide range of feedstocks.

5. Conclusions

Polyesters are very important polymers with excellent properties and large market shares, and thus the development of chemical recycling methods provides a viable solution to the efficient utilization of polyester wastes towards the global goal of carbon neutrality. This review has provided a comprehensive overview of the progress made in the depolymerization of polyesters and their recycling applications, demonstrating their practicality. However, there still need to be large improvements in terms of efficiency, versatility and cost. To address these problems, in this review, the key limiting factors and relevant challenges have been discussed, and then some strategies have been tentatively proposed for the closed-loop recycling and upcycling of polyester wastes.

Currently, the main chemical depolymerization methods include hydrolysis, alcoholysis, enzymolysis, and ammonolysis. Hydrolysis uses green water solvent, but the hydrolysis activity is lower and thus requires higher reaction temperatures. Differently, methanolysis and glycolysis show superior depolymerization activities, but they are prone to side etherification reactions. Homogeneous catalysts have been largely used with high depolymerization efficiency, but their separation and recycling after reaction are difficult. Solid catalysts encounter low activity and stability, although they can be readily separated from the reaction solutions. Enzymolysis is highly selective under green and mild reaction conditions, but with low efficiency and the use of costly enzymatic agents. Aminolysis is of an excellent choice for upcycling, but the use of toxic and expensive chemicals should be considered.

These problems are closely related to the crystalline structures of polyesters and their accessibility to catalytic sites.

These are the key factors that limit the depolymerization of polyesters to the corresponding oligomers and monomers. As such, the following suggestions are worth considering. Firstly, it is very critical to choose green solvents not only for efficiently dissolving or swelling polymers, but also for improving the activity and selectivity in polyester depolymerization. Secondly, the development of efficient catalysts is still the central issue for the depolymerization and recycling of polyesters, particularly based on cheaper and nontoxic metals, instead of toxic metals (*e.g.*, Zn, Bi, Sn, and Cr). Meanwhile, it is worth designing enzyme-mimetic catalysts for higher efficiency and selectivity. Thirdly, the chemical recycling and upcycling of mixed plastic wastes is a comprehensive problem and should be addressed by multidisciplinary approaches. More process enhancers can be introduced to the depolymerization processes to improve the efficiency of the depolymerization and subsequent reactions of polyesters, such as photochemical, electrochemical, microwave-assisted and mechanochemical approaches.

Conflicts of interest

There are no conflicts to declare.

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