## REVIEW

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# Research and progress of chemical depolymerization of waste PET and high-value application of its depolymerization products

Fan Cao,[a] Liyan Wang,*[a] Rongrong Zheng,*[a] Liying Guo,*[a] Yanming Chen[a] and Xin Qian[b]

PET (polyethylene terephthalate) has good transparency, corrosion resistance, gas barrier properties and mechanical properties, and is widely used in beverage bottles, fabrics, food packaging, tires, films, engineering plastics and other fields. With the rapid growth in demand and use of PET materials, the pollution of waste PET to the environment has become increasingly prominent. The recycling methods of waste PET mainly include primary recycling, mechanical recycling, chemical recycling, and energy recycling. The chemical recycling method is of great significance for solving environmental problems and reducing the plastic industry's dependence on petrochemical resources, and is an inevitable choice for realizing PET closed-loop recycling. In this paper, the chemical depolymerization methods of waste PET, the types of alcoholysis catalysts with the greatest possibility of industrialization, and the high-value application research of chemical recovery products are reviewed in order to have a good reference significance and promote the recycling and high-value utilization of waste PET.

## 1 Introduction

Polyethylene terephthalate, referred to as PET, is a saturated polyester obtained by the polycondensation of PTA (purified terephthalate) or DMT (dimethyl terephthalate) and EG (ethylene glycol),[1] It is a semi-crystalline thermoplastic resin, which is a saturated polyester that can be used to prepare chemical fibers and films. The production of traditional textiles has come from PET fibers since the mid-1940s, and it was not until the 1980s that PET was widely used to produce plastic bottles, and in 1987 its production exceeded 3 billion bottles. In recent years, with the development of science and technology, PET also has more types and is further used in a wider range of fields, such as high-strength fibers, films, coatings, auto parts, electronic devices, *etc.* It is closely related to our life, so the demand has been rising in recent years. Fig. 1 shows the proportion of global PET plastic production to various plastics production in recent years. PET is difficult to degrade under natural conditions, and the white pollution problem caused by it has attracted the attention of various countries. Generally speaking, plastics have a low recycling rate after use, however, PET is one of the materials with a higher recycling rate, and in 2017, nearly 57% of the PET bottles in the world were recycled in Europe.[2] Energy recovery of waste PET by incineration or pyrolysis is not feasible, because it will have adverse effects on

the environment and human beings, and high-value secondary raw materials cannot be obtained. Primary recycling has strict requirements on raw materials, while mechanical recycling is less efficient. The side reactions caused by the thermal degradation process will cause the physical properties of the recycled products to decline, change the color, and finally reduce the value of the products. Recycling is not a slogan or a marketing activity, but a need for a circular economy. At the same time, it is also the protection of the ecological environment by energy conservation and emission reduction, which is conducive to the realization of "carbon peaking" and "carbon neutrality".[3] Therefore, how to recycle waste PET and realize its high-value utilization has become an important problem for the majority of polymer workers.

*[a]School of Petrochemical Engineering, Shenyang University of Technology, Liaoyang 111003, China. E-mail: wangliyan0122@163.com*

*[b]Liaoning Shengda Environmental Resources Group Co., Ltd, Liaoyang 111003, China*



Fig. 1 The share of PET plastics in various plastics production.[4]

**Fig. 2** General thinking of waste PET degradation and high value application review.

The recycling process of waste PET is generally divided into four categories,[5] Namely primary recovery (re-extrusion), secondary recovery (mechanical), tertiary recovery (chemical), quaternary recovery (energy recovery). Primary recycling is the recycling of uncontaminated raw materials. It is a simple and low-cost process to recycle waste plastics into the factory. Secondary recycling is a mechanical recycling technology, mainly through a series of processes such as cutting, crushing, and melting. However, after repeated use, the strength of PET will decrease compared with the original, and the brittleness will increase, which will affect the quality of the product. In the end, it can only be downgraded and recycled.[6] Tertiary recycling refers to chemical recycling, in which polymers are degraded into monomers or oligomers. At present, the chemical recycling methods of waste PET polyester mainly include the following: (1) hydrolysis method; (2) methanol alcoholysis method; (3) ethylene glycol alcoholysis method; (4) alcohol-alkali combined depolymerization method; (5) ammonolysis; (6) other depolymerization methods. In the process of PET depolymerization into monomer recovery, it mainly includes hydrolysis to recover TPA (terephthalic acid),[7] methanol alcoholysis to recover DMT,[8,9] ethylene glycol alcoholysis to recover BHET (diethylene glycol terephthalate),[10] and ammonolysis to recover BHETA (bis(2-hydroxyethylene)terephthalamide).[5] Four-stage recovery refers to the recovery of energy, because most waste polyesters are derivatives of petroleum, which can recover heat during combustion. In this paper, the chemical depolymerization method of waste PET, the types of alcoholysis catalysts with the greatest possibility of industrialization, and the high-value application of chemical recovery products are reviewed, in order to provide reference and promotion for the high-value utilization of waste PET resources in green recycling. The general idea is shown in Fig. 2.

## 2  Chemical depolymerization of PET

PET can be degraded into oligomers and many important chemical production raw materials under the action of specific reaction conditions and degradation agents, which is based on the reversible equilibrium mechanism of polyesterification reaction.[11] Fig. 3 shows the chemical recycling process of waste PET.

### 2.1  Hydrolysis

The hydrolysis method refers to the hydrolysis of PET waste into ethylene glycol and TPA under certain acid–base conditions. The reaction is usually carried out at a temperature of 200–250 °C and a pressure of 1.4–2 Mpa for 3–5 hours to complete. Hydrolysis methods include acid hydrolysis, neutral hydrolysis, and alkaline hydrolysis.[12] Its principle is shown in Fig. 4.

**2.1.1  Neutral hydrolysis method.** Neutral hydrolysis refers to using water or steam to depolymerize PET without adding an acid-base catalyst, usually at a temperature of 250–300 °C and a pressure of 1.5–4.0 Mpa. The weight ratio of reaction feed PET to water is generally between 1 : 2 and 1 : 12. The neutral hydrolysis method can directly depolymerize PET into monomers for synthesizing polyester without producing acid–base waste liquid. It is an environmentally friendly process and has received more and more attention from researchers in recent years. There are two modes of neutral hydrolysis of PET, namely batch mode and continuous mode. In neutral hydrolysis, traditional catalyst systems such as metal salts are introduced to improve the reaction speed. However, due to the incorporation of a large amount of metal ions into the reaction medium, it is difficult to separate after the reaction, resulting in lower product TPA purity. The layered hydroxide has excellent anion exchange properties, and the layered hydroxide has a strong affinity for terephthalate ions, which enables TPA to enter the layered hydroxide and is easy to separate from the mixed liquid.

ZSM-5 based zeolites are simply recyclable and easily regenerable catalysts with Brønsted and Lewis acid sites. Kang *et al.*[13] used it for the hydrolysis of PET in neutral media to control the concentration of Brønsted and Lewis acid sites in ZSM-5 zeolite by changing the Si/Al ratio of the zeolite framework and counterion species. H⁺@ZSM-5-25 dominated by Lewis acid sites was used for the neutral hydrolysis of PET under microwave-assisted conditions. Compared with the catalyst-free

Fig. 3 Chemical recycling process of waste PET.



Fig. 4 Reaction formula for the degradation of PET by hydrolysis.

condition, the reaction initiation temperature was reduced and the activation energy was reduced by about 19 times, showing that Higher TPA yield. Finally, the H⁺@ZSM-5-25 catalyst maintained its catalytic activity after 6 cycles.

**2.1.2 Acid hydrolysis.** The acid hydrolysis of PET usually uses concentrated sulfuric acid as an additive, and sometimes inorganic acids such as nitric acid and phosphoric acid can be used to degrade PET in an acidic environment.[14]

Wang et al.[15] used a 70% $ZnCl_2/H_2O$ acid system and used $ZnCl_2$ as a catalyst to break the ester bond of the PET material, and finally degrade PET. The yield of TPA is as high as 98.31%, and the purity reaches 97.14%. This degradation system is easy to separate and reuse. The possible mechanism of zinc chloride catalyzing the hydrolysis of PET is proposed: first, $Zn^{2+}$ attacks the carbonyl oxygen on the main chain of PET, prompting the transfer of electron cloud to oxygen, and the oxygen in water is connected to the carbonyl carbon in a bimolecular nucleophilic manner, then one proton in the water molecule is transferred to

the oxygen of the ester group, resulting in the cleavage of the ester bond, and finally TPA and EG are obtained.

Semyonov et al.[16] partially hydrolyzed the PET bottle flakes by $HNO_3$ solution and DMF (N,N-dimethylformamide), and the carboxyl groups generated on the surface of the PET bottle were used as a linker for subsequent surface connection and nucleation. By adding $ZrCl_4$, free TPA and zirconium ions are compounded, and finally the organic metal frame material is grown on the surface of the PET bottle flake to prepare the mixed material frame (UiO-66). In this study, PET was simultaneously used as a source of TPA and as an organic ligand and support for assisted growth on the surface of MOFs. PET@UiO-66 showed excellent stability during the adsorption process, and the synthesized adsorbent had strong adsorption capacity for imidacloprid in water.

**2.1.3 Alkaline hydrolysis.** The alkaline hydrolysis method is generally carried out in KOH or NaOH solution with a concentration range of 1–6 mol $L^{-1}$, the reaction temperature is 200–250 °C, and the reaction can be completed in 3–5 hours at 1.4–2.0 Mpa. After acidification of the degradation products terephthalate and EG, relatively pure TPA was finally obtained.

Kosmidis et al.[17] added a phase transfer catalyst (quaternary ammonium salt) to the alkaline hydrolysis reaction of waste PET beverage bottles, and the yield of PTA was significantly improved. Using this method to depolymerize PET, the yield of PTA can reach more than 93%. At present, this method is not only applied to PET fibers, but also applied to the recovery of nylon 46 and nylon 66. The alkaline hydrolysis product is relatively pure and the reaction is relatively thorough, but the waste

Fig. 5  Photocatalytic depolymerization of PET.



Fig. 6  Methanol alcoholysis reaction formula.

lye after the reaction must be treated to avoid environmental pollution.

Mohsin et al.[18] used DMSO (dimethyl sulfoxide) and methanol as auxiliary solvents and sodium methoxide as catalyst to perform alkaline hydrolysis of PET under microwave irradiation. The use of auxiliary flux improves the solubility and dielectric constant of sodium methoxide, PET is completely hydrolyzed within 5 minutes, and the optimal reaction temperature is 60 °C.

Ügdüler et al.[19] studied two-step aqueous-alkali hydrolysis of different types of PET waste plastics under mild conditions (≤80 °C). Under optimal conditions (60 : 40 vol% EtOH : H$_2$O, 5 wt% NaOH at 80 °C) product yields of approximately 95% were achieved in less than 20 minutes. The products are EG and TPA. The results show that the PET degradation rate increases inversely proportional to the PET particle size.

Uekert et al.[20] used CdS/CdO$_x$ quantum dots (QDs) as photocatalysts under alkaline conditions to completely depolymerize PET under visible light irradiation. The depolymerization products are H$_2$, terephthalate and aliphatic high-value oxidation products. The separation of holes and photogenerated electrons occurs after the photocatalyst absorbs photons, and H$^+$ in water is reduced by photogenerated electrons to obtain clean energy H$_2$, as shown in Fig. 5.

## 2.2 Alcoholysis

Alcoholysis of PET is an important and effective method for recycling waste PET. The depolymerization of monohydric alcohols (mainly methanol) is called PET alcoholysis, and the alcoholysis of dihydric alcohols (mainly ethylene glycol) and polyols is called saccharolysis.

**2.2.1 Methanolysis.** The methanol alcoholysis method refers to the use of methanol to degrade PET waste into DMT and EG under certain reaction conditions,[21,22] The product can be directly used as raw material for producing polyester. Methanol alcoholysis needs to add a small amount of catalyst, and zinc acetate is generally used as the catalyst, which can improve the reaction speed. According to the different depolymerization reaction conditions, the degradation of PET by methanol alcoholysis can be attributed to the liquid methanol

alcoholysis method, the gaseous methanol alcoholysis method, and the supercritical methanol alcoholysis method. The reaction formula is shown in Fig. 6.

*2.2.1.1 Liquid methanol alcoholysis.* The liquid methanol alcoholysis conditions of PET are as follows: the temperature is 180–280 °C, the pressure is 20–40 atm, and zinc acetate, magnesium acetate, cobalt acetate and lead dioxide are used as catalysts. Methanol participates in the reaction in a liquid state, and in the reaction process, PET can be directly reacted with methanol or reacted with the reaction product ethylene glycol for further alcoholysis reaction. Usually the recovery rate of DMT is between 80% and 85%, and the products of methanol alcoholysis are usually separated and purified by crystallization or rectification.

Pham et al.[9] developed a new catalytic reaction system, to selectively convert PET to DMT using methanol solution. In the reaction system, K$_2$CO$_3$ was used as a catalyst, a mixture of methanol and polar aprotic solvent were used to achieve complete PET decomposition within 24 h under ambient conditions, and the methanolysis DMT yield reached 93.1% within 24 h. This method is characterized by high yield of DMT, good hydrolytic stability, and easy recycling of materials.

*2.2.1.2 Gaseous methanol alcoholysis.* As the name suggests, gaseous methanol alcoholysis refers to replacing liquid methanol with superheated steam methanol, passing it into the product of glycolysis in the form of bubbling, and mixing it with oligomers or BHET monomers undergo transesterification to remove esters and alcohol gases, because the self-polycondensation reaction of ethylene glycol will occur at a certain temperature. The reaction equilibrium is also forward due to the removal of product from the reactor with steam, promoting the reverse forward. This reaction is generally carried out under low pressure conditions and requires less equipment.

Gamble et al.[23] advocated a method suitable for various types of polymerization reactions and gaseous states, and individualized the decomposition of raw materials from the decomposition boiling point of the polymerizer, and made a deep understanding of various influencing factors. As methylated transport and solubility in the liquid decrease, the reaction will also decrease. Therefore, the influence of factors such as temperature and pressure on the gas–liquid reaction is more complicated than that in the homogeneous reaction (liquid methanol depolymerization).

*2.2.1.3 Supercritical methanol alcoholysis.* The supercritical methanol depolymerization method refers to the degradation of PET in a state higher than the supercritical state point of methanol. Under these conditions, the decomposition rate of PET is much faster than that of liquid methanol alcoholysis. Under the condition of no catalyst, PET can be depolymerized into monomers in a short time, and the depolymerization efficiency of PET can be greatly improved by using supercritical methanol to depolymerize PET. However, due to its harsh operating conditions and high process requirements, it is not widely used.

Liu *et al.*[24] conducted alcoholysis on waste PET under supercritical methanol conditions, and studied the effects of methanolysis temperature, time and the mass ratio of methanol to PET on the alcoholysis reaction. The optimal reaction conditions are: temperature 298 °C, time 112 min, mass ratio of MeOH to PET is 6, under these conditions the yield of DMT is as high as 99.79%.

**2.2.2 Glycol alcoholysis.** At present, among many PET polyester recycling methods, the process conditions of ethylene glycol alcoholysis method are becoming more and more mature, and some companies have realized commercial operation. Polyester monomer BHET and a small amount of oligomers can be obtained by alcoholysis with ethylene glycol. BHET can not only be used as a monomer for synthetic polyester materials, but also widely used in unsaturated polyester resins as a common monomer for synthetic polymer materials, and its added value is high. The depolymerization of this method is usually performed at a temperature of 180–250 °C and a pressure of 0.1–0.6 Mpa. The catalyst is generally acetate or solid super acid, and the addition amount accounts for about 0.1–2% of the mass of PET, and the reaction time is 6–8 hours. The reaction formula is shown in Fig. 7.

Fujita *et al.*[25] proposed an economical process for ethylene glycol depolymerization. The reaction temperature was 210–250 °C, and the feed ratio of ethylene glycol and PET was 1.3–2.0, under the protection of inert gas N$_2$. When this feed ratio is greater than 2.0, a large amount of ethylene glycol will dimerize under BHET catalysis, the consumption of ethylene glycol will increase, and the cost will also increase accordingly. At the same time, the ethylene glycol dimer produced will also lower the softening point of the PET produced by repolymerization. In addition, the particles are wetted by the ethylene glycol vapor produced by the reaction before being fed into the reactor, and the reaction is in a homogeneous state after entering the reactor, thus greatly increasing the reaction rate. Controlling
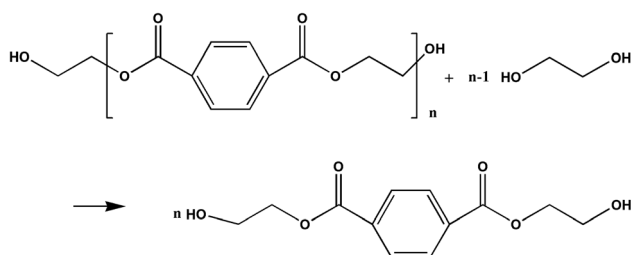
the ethylene glycol ratio both reduces ethylene glycol consumption and improves process economics.

Ghaemy *et al.*[26] used excess ethylene glycol and metal acetate as a catalyst to depolymerize waste PET under N$_2$ atmosphere and the boiling point of ethylene glycol was 197 °C, and it took 10 hours for all the depolymerization. The alcoholysis products were analyzed, and it was found that the main components of the depolymerization products were BHET (>75%), a small amount of dimers and trimers. Moreover, the study found that the content of oligomers in the alcoholysis products is mainly related to the mass ratio of PET and ethylene glycol, and as the ratio increases, the content of oligomers increases.

In addition, it is striking that Japan's Teijin Company creatively developed the regeneration process of PET ethylene glycol depolymerization/methanol transesterification in response to the problem of more oligomers in the ethylene glycol hydrolysis product, and realized a large-scale commercial production. This process consists of two-step reactions, ethylene glycol depolymerization and methanol transesterification. In the reaction, PET is first subjected to ethylene glycol alcoholysis to generate BHET, and the alcoholysis product is then transesterified with methanol. The process of transesterification with methanol can effectively depolymerize the oligomers that are not completely depolymerized in the ethylene glycol depolymerization process and convert them into DMT uniformly. The depolymerized monomer DMT can be melted and the purity of vacuum distillation can reach 99.99%, and the quality is stable. The process conditions are relatively mild, the reaction is easy to control, the safety is good and non-corrosive, and the total investment cost is low. However, it is necessary to add a catalyst with a higher content in the reaction, which brings great pressure to the purification of the product.

### 2.3 Ammonolysis

Ammonolysis of PET is usually carried out with primary amine aqueous solution, the more common ones are methylamine, ethylamine and ethanolamine. The polymer participating in the reaction is in the form of powder or fiber, and the aminolysis product is BHETA, the reaction temperature is usually 20–100 °C, anhydrous *n*-butylamine is also used as an aminolysis agent at 21 °C. The decomposition reaction of PET and amine-based molecules is shown in Fig. 8.

At present, the application of partial aminolysis reactions in the modification of PET has been found to produce fibers with specific processing properties. Lorusso *et al.*[27] explored aminolysis pathways using different amine-based materials, including EDA (ethylenediamine), TAEA (triaminotriethylamine), APTMS ((3-aminopropyl)trime-thoxysilane), TRIAMO ((3-trimethoxysilylpropyl)diethylenetriamine). The results showed that aminolysis with EDA and TAEA as reagents reduced the properties of PET, and the antibacterial properties of natural textiles treated with APTMS and TAEA-based reagents were improved. The use of aminosilane as a reagent as a protective layer can deposit a dense coating on the fiber. Compared with natural PET, APTMS-modified PET shows better wear resistance.
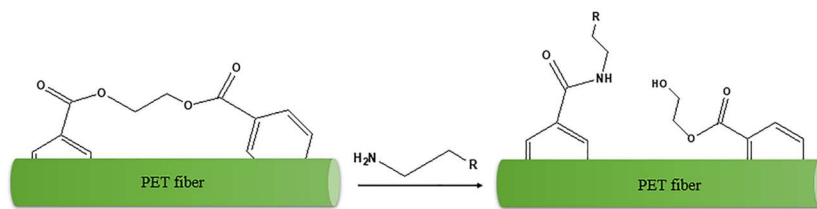


Fig. 7 Glycol alcoholysis reaction formula.

**Fig. 8** Decomposition reaction of PET with amine-based molecules.[27]

Leng et al.[28] used EA (ethanolamine) for the ammonolytic degradation of waste PET, and the product was BHETA. The PET additive obtained during the aminolysis process was added to CRMA (waste rubber powder modified asphalt), and it was found that the CRMA added with the waste PET additive was improved in terms of storage stability, rutting resistance and fatigue resistance. Improve the rotational viscosity of the modified adhesive, effectively optimize the engineering performance of the asphalt pavement.

Chan[29] uses DETA (diethylenetriamine) and TETA (triethylenetetramine) to aminolyze PET, and the obtained product is a water-soluble oligomer, which is cross-linked with EGDE (ethylene glycol diglycidyl ether) in water to obtain a hydrogel. The hydrogel shows the typical polyelectrolyte behavior of polycations, has good adsorption function for anionic dyes, and can be used as adsorbents in industrial dyes.

Teotio et al.[30] used ethylamine, n-butylamine and n-hexylamine as ammonolysis reagents to chemically recover N,N-dialkyl-1,4-benzenedicarboxamide, a product with a calorific value equivalent to coal, from waste PET bottles through ammonolysis without catalyst. The calorific value of this compound is theoretically comparable to that of solid fuel, and it can be used as a new type of propellant in the missile and aerospace industries in the future.

### 2.4 One-pot catalysis

Peking University Ma Ding et al.[31] cooperated with Xiao Dequan's research group at the University of New Haven to realize a new process of converting $CO_2$ and PET, two urgently needed wastes, into high-value chemicals through a series of reactions. Methanol is produced by hydrogenation of $CO_2$, and

DMT is obtained by alcoholysis of PET. DMT is hydrogenated in the same catalyst to produce high-value chemical products. Studies have shown that such a process can not only convert waste $CO_2$, but also consume the generated methanol in situ through the PET alcoholysis reaction, and the DMT product generated by PET depolymerization can be hydrogenated into DMCD (dimethyl cyclohexanedicarboxylate) or PX (paraxylene) by the same catalyst, thereby promoting the conversion of PET. The reaction mechanism is shown in Fig. 9.

### 2.5 Enzymatic hydrolysis

We all know that microorganisms play an important role in the material circulation of the ecosystem and the cleaning of pollutants. At present, the enzymatic hydrolysis method has become a very feasible and environmentally friendly way to treat PET. Since the 1990s, the application of microbial enzymes to degrade polymer materials has attracted people's attention.

Yoshida et al.[32] collected 250 environmental samples contaminated with PET flakes from PET bottle recycling points, including activated sludge, wastewater, soil, and sediment. Microorganisms that can use low crystallinity (1.9%) PET film as the main carbon source for growth—Ideonella sakaiensis 201-F6—were screened from the samples. The PETase (PET hydrolase) produced by this strain was incubated with (1.9%) PET at 30 °C for about 6 weeks. PET is degraded into two environmentally friendly monomers, BHET and MHET (mono(2-hydroxyethyl)terephthalate acid). A MHETase (MHET hydrolase) was also found in the study, which cooperates with PETase to hydrolyze MHET, the main intermediate product of PET, into TPA and EG. The degradation process is shown in Fig. 10.
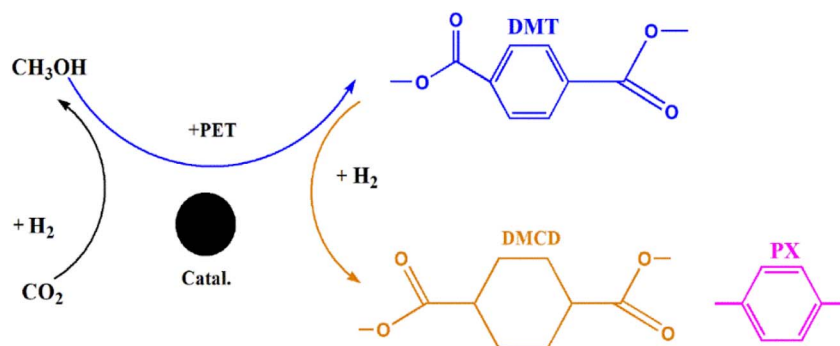


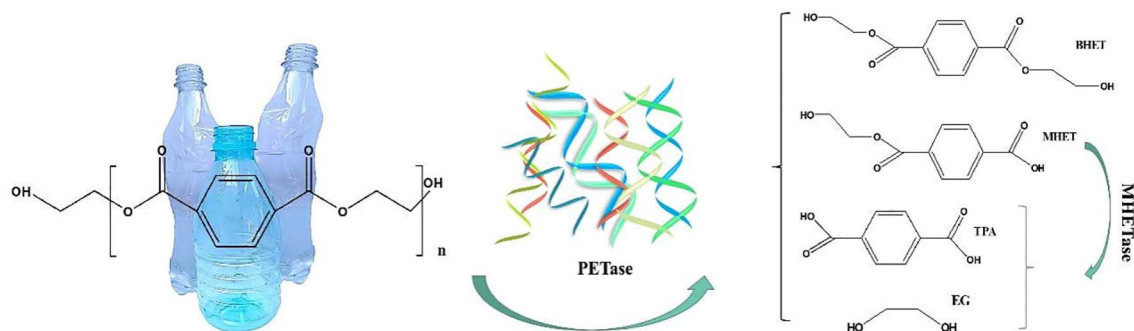**Fig. 9** Schematic diagram of one-pot catalysis.

**Fig. 10** PETase degradation process of PET.

PETase (IsPETase) from *Ideonella sakaiensis* reported that PETase has the highest activity under mild conditions, low thermal stability limits enzymatic degradation ability, Using the structural information of IsPETase, Son *et al.*[33] developed a rational protein engineering strategy and screened several IsPETase variants with high thermal stability to enhance the degradation activity of PET.

Moog *et al.*[34] used the photosynthetic microalga *Phaeodactylum tricornutum* combined with the PETase enzyme from *Ideonella sakaiensis* and found that at 21 °C and saline conditions, PETase was still active on industrial PET chips, with the degradation products being BHET and TPA. This study demonstrates the potential of the diatom system for bioremediation of PET-contaminated seawater.

# 3 PET chemical depolymerization—types of alcoholysis catalysts

The alcoholysis of PET is a very slow process if no catalyst is added, and the type of catalyst is directly related to the effect of alcoholysis. Therefore, research on ethylene glycol alcoholysis catalysts has also attracted much attention in recent years. Novel, efficient and environmentally friendly are the new requirements for catalysts.[35] At present, the catalysts used for the alcoholysis of ethylene glycol include metal salt catalysts, ionic liquid catalysts, and titanium-based catalysts. The relatively novel catalysts include nano-ZnO catalysts, carbon-based solid catalysts, and mesoporous catalysts.

## 3.1 Metal salt catalyst

The earliest catalyst used for the alcoholysis of metal acetate PET. From the perspective of the reaction mechanism, both alcoholysis and polycondensation are essentially transesterification reactions based on the $A_{AC}2$ nucleophilic substitution reaction mechanism. It is only due to the control of the reaction conditions that the main direction of the reaction is different.

Ghaemy *et al.*[26] conducted a more detailed study on four metal acetate catalysts. When depolymerizing PET with ethylene glycol, zinc acetate, manganese acetate, cobalt acetate and lead acetate were used as catalysts respectively, and found

that the reaction temperature was 198 °C, the molar ratio of PET to ethylene glycol is 1 : 8.5, and the catalyst dosage is 1%, the recovery rate of monomers depolymerized with zinc acetate as catalyst can reach 75%. The activity order of the measured catalysts is: $Zn^{2+} > Mn^{2+} > Co^{2+} > Pb^{2+}$. Since metal salts contain heavy metal ions, they are easily soluble in ethylene glycol, which puts a lot of pressure on the purification of the product and easily causes heavy metal pollution. Therefore, we should explore more green catalysts.

Esquer and García[36] studied the order of activity of other metal-based catalysts, in metal chlorides: $Co^{2+} > Mn^{2+} > Zn^{2+}$; in metal sulfates: $Zn^{2+} > Ni^{2+} > Cu^{2+} > Fe^{2+}$.

## 3.2 Ionic liquid catalyst

Ionic liquid is a green catalyst that can replace heavy metal salt catalysts. It is a salt with a melting point lower than 100 °C, which is suitable for low temperature and low pressure conditions and does not emit toxic substances in the environment, and has certain stability. After the reaction, it can also be recycled and reused.

The good catalytic performance of ionic liquids originates from the synergistic catalysis of acid and base.[37] The anion in the system can act as a Brønsted base to form a hydrogen bond with the hydroxyl group of EG, and the electronegativity of the hydroxyl oxygen of EG is enhanced, making the carbonyl carbon of PET more easily attacked; the metal ion or cation has Lewis acidity that can activate the carbonyl oxygen of PET.

Wang *et al.*[38] used ionic liquids to catalyze the degradation of PET. The study found that at a temperature of 180 °C and a reaction time of 6 hours, PET could be completely degraded. Temperature is a crucial factor in the reaction process. Compared with traditional metal salt catalysts, ionic the liquid is easier to separate and purify the product. After that, they analyzed the reaction mechanism. The kinetic study showed that the activation energy of this reaction was 232.79 kJ mol$^{-1}$. In addition, it was found that the depolymerization catalytic activity of the ionic liquid remained after the depolymerization was completed. Can be used multiple times.

Yue *et al.*[39] synthesized [Bmim]ZnCl$_3$ and [Bmim]MnCl$_3$, and studied their catalytic effect on the depolymerization of PET ethylene glycol. Because of the addition of zinc and manganese elements, the catalytic activity of the ionic liquid was further

improved, indicating that there is a synergistic catalytic effect between the two. At 190 °C, the weight ratio of catalyst to PET is 0.05, the reaction is 2 hours, the PET conversion rate is 100%, and the BHET yield can reach 71.2%. Although it is environmentally friendly to use ionic liquids as catalysts to depolymerize waste polyesters, the basic ions contained in ionic liquids are expensive and complex, resulting in high degradation costs.

Sun *et al.*[40] developed a low-cost, biocompatible ionic liquid, [Ch]$_3$[PO$_4$]. It can play a dual role in the dissolution and alcoholysis of PET. Under the condition of 180 °C, the reaction time is about 4 hours, the conversion rate of PET is about 100%, and the yield of BHET is about 60.6%.

### 3.3 Titanium catalyst

In essence, ethylene glycol depolymerization and polycondensation of PET is essentially a transesterification process, Therefore, in theory, it may be feasible to use the same catalyst to catalyze two reactions efficiently. This may be a feasible and worth exploring experiment, which avoids the separation of catalysts and is beneficial to the continuous operation of the whole process. But in fact, due to the different roles of different metal elements in catalysis, it is not easy to achieve efficient and directional catalysis of two reactions by one element at the same time. Since the activity of titanium-based catalysts can be changed by adjusting the coordination number and ligand structure, if different catalytic mechanisms are integrated into one catalyst at the same time, whether it can make it show better catalytic effect in both alcoholysis and polycondensation reaction.

Based on the above thinking, Wang Shaobo of Donghua University designed and synthesized sodium ethylene glycol titanate, and explored its catalytic performance. The results show that the use of ethylene glycol sodium titanate as a catalyst is very suitable for ethylene glycol alcoholysis regeneration catalysis, and the prepared rPET is basically consistent with the original structure of PET. Moreover, titanium-based catalysts are also relatively green and environmentally friendly catalysts.

### 3.4 Nano ZnO catalyst

For a homogeneous catalyst, it will eventually remain in the product after alcoholysis and seriously affect the quality of the product, and the separation from the product is also complicated. Contact and mass transfer process between catalysts. Therefore, it is very urgent to develop a catalyst with low temperature, high efficiency and easy recovery.

Du *et al.*[41] studied the effect of nano-ZnO dispersions as catalysts for alcoholysis of PET. For the first time, methanol and ethylene glycol dispersions of ultrafine ZnO nanoparticles were used as pseudo-homogeneous catalysts for alcoholysis of PET. The reaction equation is shown in Fig. 11. The as-prepared ZnO nanoparticles had a uniform size of 4 nm and were stable in dispersion for 6 months. The ultra-small-sized nanocatalysts can easily enter the porous framework of PET, react quickly, and effectively improve the yield of DMT monomers. Experiments show that the ZnO nanocatalysts are efficient, easy to recycle
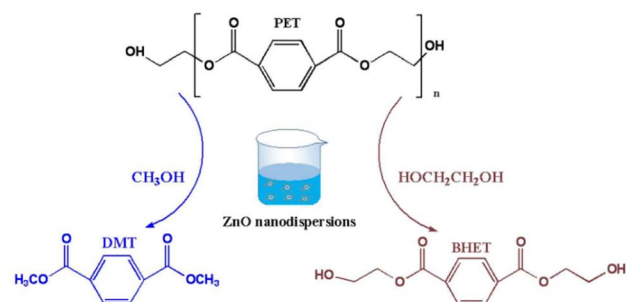


**Fig. 11** Nano-ZnO dispersion catalyzed depolymerization of PET.

and reuse, environmentally friendly and sustainable. Therefore, it can be foreseen that this nanocatalyst may be a promising strategy for the chemical depolymerization of PET.

### 3.5 *Camellia oleifera* shell carbon C–SO$_3$H based solid acid catalyst

There are many kinds of crops in China. As an important crop in southern China, *Camellia oleifera* has been continuously expanded in recent years, and many by-products are produced during the processing, such as *Camellia oleifera* shells. At present, we have not made reasonable use of *Camellia oleifera* shells. As biomass materials have recently entered people's field of vision, can it be used as a catalyst for depolymerization of PET?

Liu *et al.*[42] used *Camellia oleifera* shell as raw material, and successfully prepared carbon-based solid acid catalyst after washing, carbonization and sulfonation. Under the electron microscope, the structure of the treated Camellia oleifera shell was observed to be compact and orderly, while the untreated original Camellia oleifera shell structure was loose and disordered. The experiment found that the best preparation conditions of the catalyst were the impregnation ratio of 1 : 1, the impregnation concentration of 2 mol L$^{-1}$, the sulfonation temperature of 160 °C, and the alcoholysis product of carbon-based solid acid as the catalyst was BHET monomer, and the recovery rate was 68%.

### 3.6 Mesoporous catalyst

Generally, the product BHET obtained by catalyzed glycolysis of PET has a slight color, which also leads to the subsequent production of repolymerized PET (rPET) with a darker color. rPET with poor chromaticity cannot be used for the production of high-quality products. In order to obtain BHET with good chromaticity, it is necessary to design a catalyst to efficiently catalyze the degradation of PET to prepare colorless BHET.

Yao *et al.*[43] combined the advantages of homogeneous catalysts and heterogeneous catalysts and prepared a mesoporous catalyst supported by SBA-15 by ultrasonic impregnation method, which could enter the reaction center and be easily recovered after the reaction. At a temperature of 197 °C and a mass ratio of EG to PET of 4 : 1, the catalyst completely

depolymerized PET after 1 hour. The highest yield of BHET was 91.0%, and the recovered BHET also had good chromaticity.

### 3.7 Metal organic frameworks (MOFs) catalysts

Metal–organic frameworks are a new type of coordination polymers with periodic multi-dimensional network structure assembled by metal ions and multidentate organic ligands such as nitrogen and oxygen.[44] It is a microcrystalline porous material with the properties of inorganic materials and carbon-based materials. MOFs have well-defined structures, high specific surface area, and more active sites, and compared with amorphous catalysts, crystalline catalysts with well-defined structures are more favorable for the catalytic process. In new research fields, MOFs show excellent performance in catalysis, storage, adsorption, *etc.*, and have broad application prospects.[45]

In addition, since the solid catalyst has good thermal and chemical stability, it is easy to separate from the reaction mixture and can effectively avoid contaminating the product. Based on the above characteristics, MOFs can be used as catalysts for PET glycolysis.

Suo *et al.*[46] prepared three metal–organic framework catalysts (ZIF-8, ZIF-67, MOF-5) and used them in the alcoholysis of PET. It was found that ZIF-8 had the highest catalytic activity among these catalysts. When this catalyst was used, the PET chips could be completely depolymerized within 1.5 hours at 197 °C, and the products were mainly BHET monomers. After that, the ZIF-8 catalyst was recovered three times and three experiments were carried out. It was found that the catalyst activity remained unchanged and could be recycled for many times.

Wu *et al.*[47] used (Zr-MOF) UiO-66 to degrade waste PET under hydrogen or argon conditions, and the degradation products obtained MMT (mono-methyl terephthalate), TA (terephthalic acid), which were the equation is shown in Fig. 12. It was found that higher yields could be obtained under hydrogen conditions. In addition, the PET degradation reaction is not affected by the presence of polyethylene and polypropylene pollutants, and the dyed PET is degraded to obtain a white product.

These findings suggest that MOFs catalysts have broad application prospects, which will play a role in realizing a circular polymer economy as catalysts designed to guide next-generation polymer degradation.
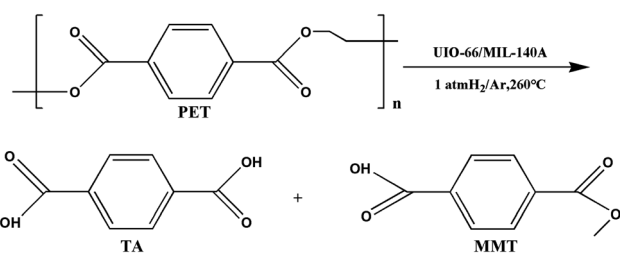


Fig. 12 Reaction formula for PET degradation catalyzed by MOFs.

# 4 Functional utilization of PET chemical depolymerization products

PET can obtain DMT, PTA, BHET, EG and other monomers through chemical depolymerization, $H_2$ (ref. 20) or other chemicals, We can add some modified components to the product to develop and prepare its downstream products, so as to achieve the purpose of recycling waste polyester. The main products include PU (polyurethane), UPR (unsaturated polyester), PET copolyester, DOTP (plasticizer), alkyd resin, epoxy resin, FPR (fiber reinforced plastic), *etc.*

### 4.1 Preparation of polyurethane

Polyurethane elastomers are widely used in fibers, adhesives, coatings, synthetic leather, high-performance elastomers and other fields, and are one of the six major synthetic materials (PE, PP, PVC, PS, PET, PU). At present, countries in the world are in short supply of fossil energy, and the price of chemical raw materials is rising. The reaction of PET depolymerization products with aliphatic carboxylic acids can generate polyester polyols, which can then be used to synthesize polyurethane foams. For example, the reaction of BHET monomers with polyisocyanates can produce polyurethane foams with good thermal stability. Such reactions are flexible and variable, and the synthesized materials are also used to prepare various functional materials. At the same time, the properties of polyurethane materials prepared by mixed alcoholysis products have wider adaptability than commercial products in all aspects.

Cevher and Sürdem[48] depolymerized PET bottle waste with ethylene glycol and ethanolamine, and the depolymerization products were BHET and BHETA. In the process of preparing PU, castor oil and boric acid were added to improve the adhesion of PU, and finally a polyurethane adhesive was synthesized.

Commonly used polyurethanes have a wide variety of excellent properties and are well suited for ventricular assist devices, but they exhibit low stability in biological environments. Gawlikowski *et al.*[49] prepared polyurethane by copolymerizing PET with dimerized linoleic acid. The obtained product showed excellent biocompatibility and chemical stability, and could be used in cardiac prostheses in the future.

Zhou *et al.*[50] used NPG (neopentyl glycol) and DPG (dipropylene glycol) to depolymerize waste PET bottles through glycolysis in the presence of *n*-butyl titanate catalyst, respectively, and the depolymerized products were then synthesized into new aqueous polyurethane dispersions. The results showed that the urethane obtained by two steps of alcoholysis and synthesis had lower crystallinity and increased heat resistance.

### 4.2 Synthetic unsaturated polyester

PET is formed by esterification and polycondensation of saturated dibasic acid (terephthalic acid) and dihydric alcohol (ethylene glycol).

Generally, when PET polyester is used to prepare unsaturated polyester, glycolysis is used. The monomer or low-

molecular polymer obtained by alcoholysis can be used as raw material for the production of unsaturated polyester. Dibasic acid, acid anhydride or acid chloride can be polycondensed according to a certain feeding ratio to obtain unsaturated polyester.[51] Its performance is superior to the *ortho*-type general unsaturated polyester obtained by polycondensation of saturated dibasic acid or anhydride, unsaturated dibasic acid or anhydride and dihydric alcohol.

Duque-Ingunza *et al.*[52] obtained high yields of BHET using excess EG for glycolysis of PET waste particles in the presence of $Na_2CO_3$ as a catalyst. The alcoholysis product BHET is polycondensed with maleic anhydride to form unsaturated polyester resin. After adding styrene monomer, methyl ethyl ketone peroxide is used as initiator and cobalt octoate is used as catalyst to obtain unsaturated polyester through cross-linking reaction.

Kárpáti *et al.*[53] optimized glycolysis and designed a one-pot depolymerization–polycondensation reaction to produce unsaturated and saturated polyesters. The ratios of ethylene glycol/adipic acid and butane-1,4-diol/adipic acid were used to adjust the system for PET depolymerization. The results of the study show that diacids can be used in the PET solvolysis process, and that increasing the proportion of diacids leads to an increase in the molecular weight of the resulting oligomers, unsaturated polyesters are dissolved in styrene, and cross-linking and molding are characterized by DMA.

Abdullah and Ahmad[54] used ethylene glycol for alcoholysis of waste PET, and the synthesized UPR was blended with 0.3% coconut fiber to prepare coconut fiber reinforced composites. Phosphorus-based flame retardant is added to the material, and the treated fiber composite material exhibits excellent flame retardant and mechanical properties.

### 4.3 Synthetic PET based copolyester

PET-based copolyester is a product synthesized by adding modified components, namely depolymerization monomers, to conventional polyesters by copolymerization. The reaction changes the chain structure and chain length of the molecule, thereby changing the properties of macromolecules. The application range of polyester materials.

El Mejjatti A. *et al.*[55] carried out end-group carboxylation of ε-caprolactone oligomers with succinic anhydride under the catalysis of 4-dimethylaminopyridine to obtain double carboxyl-terminated caprolactone oligomers. The BHET obtained by alcoholysis and this oligomer were copolymerized under the catalyst of tetrabutyl titanate to form an elastic copolyester PET-PCL with amorphous multi-block characteristics.

Ben *et al.*[56] used stannous octoate as a catalyst to copolymerize PET alcoholysis product BHET with ε-caprolactone (ε-CL) at a temperature of 220 °C for 6 hours. A series of P(ET-CL) copolyesters were synthesized with the mass ratio of BHET/ε-CL ranging from 90/10 to 10/90. Copolyesters with a mass ratio of 30/70 to 60/40 show random microstructures, other copolyesters show some block copolymer characteristics, such copolyesters incorporating aliphatic segments are biodegradable sex.

### 4.4 Preparation of plasticizers

DOTP (diisooctyl terephthalate) is a plasticizer with excellent performance, which can be obtained by depolymerizing waste PET with isooctyl alcohol. It was researched and developed by Eastman Chemical Company of the United States in 1976. It is widely used in the production of polyvinyl chloride, vinyl chloride, and other thermoplastic products, as well as in the manufacture of films, artificial leather, wire and cable insulation materials, sheets and other plastic products. It has excellent anti-fog and cold resistance, and can be used as a lubricant for precision instruments and an additive for lubricating oils. Due to the recent shortage of PTA raw materials, China needs to import a large amount from abroad every year, so we can use waste polyester as the raw material for DOTP production.

There are two production methods for preparing DOTP from waste PET, namely direct method and indirect method.

(1) In the indirect method, the waste polyester is converted into TPA by alkali hydrolysis and acidification and neutralization, and then the iso-octanol of equimolar mass is esterified under the action of a catalyst to obtain DOTP. The intermediate process of this reaction is complicated and the product yield is low, but the product quality is high.

(2) Direct method, in the presence of an appropriate amount of catalyst, the waste polyester is directly reacted with iso-octanol. The transesterification reaction is carried out under high temperature and normal pressure until the acid value of the reactant is reduced to the acceptable level. The method is characterized by simple process and high product yield, but oil, pigments, dyes, additives, *etc.* in the waste will affect the quality of the product, so the requirements for waste polyester are higher.

As shown in Fig. 13, using waste PET and isooctanol as raw materials, under the action of a catalyst (a combination of zinc acetate and tetrabutyl titanate) and EG, the depolymerization reaction and the transesterification reaction are completed in one step. The produced crude DOTP products go through a series of technological processes to obtain qualified DOTP products.

Liu *et al.*[57] used subcritical and supercritical isooctanol as raw materials to study the reaction of PET alcoholysis to prepare DOTP. The results showed that the optimal process conditions for the preparation of DOTP by alcoholysis of PET were as follows: the reaction temperature was 573 K, the mass ratio of isooctanol and PET was 1 : 4, the reaction time was 3 hours, the degradation rate of PET was 100%, and the yield of DOTP was 97%. This method does not use catalysts such as strong acids in traditional processes, is green and environmentally friendly, and DOTP is easy to separate.

Zhou *et al.*[58] used 2-EH (2-ethyl-1-hexanol) as solvent and ChCl-based DESs (choline chloride-based deep eutectic solvent) as catalyst, at a temperature of 180 °C for 1 hour, the molar ratio of PET to 2-EH was 1 : 5, and under the condition of 5% ChCl/$Zn(Ac)_2$, the conversion rate of PET was 100%, and the yield of DOTP was 84.7%. Moreover, the catalyst in this process is cheap, less toxic and easy to prepare.

**Recovery of Isooctanal**



**Fig. 13** DOTP made from waste PET.

## 4.5 Preparation of alkyd resin

Alkyd resin is a functional polymer material, which is widely used in the coating industry. It has good flexibility, adhesion, gloss, and is cheap and easy to obtain raw materials, which can be used in industrial coatings such as paints and varnishes.[59–62] In recent years, as countries around the world pay more and more attention to environmental regulations, environmentally friendly alkyd resins have become a breakthrough.

E. Ikladious et al.[63] used PET alcoholysis products, polyacids and hyperbranched polyesters to study the synthesis of medium oil alkyd resins using linseed oil and sunflower oil fatty acids. The effects of polyol functionality, alcoholysis products, and lipid fatty acid types on membrane properties and thermal properties were investigated. The study found that all alkyd resin samples began to decompose when the temperature was greater than 200 °C, which was just suitable for the processing requirements of most conventional coating applications, and provided a candidate material for environmentally friendly and inexpensive industrial coatings.

## 4.6 Preparation of epoxy resin

Atta et al.[64] used DEA (diethanolamine), DEG (diethylene glycol), TEA (triethanolamine), and TMP (trimethylol propane) on waste PET at a temperature of 210 °C and the catalyst was manganese acetate. Depolymerization, the depolymerization product is combined with epichlorohydrin to prepare diglycidyl and tetraglycidyl epoxy resins. The resulting resins were cured with different molar ratios of 1-(2-aminoethyl) piperazine as curing agent. The data show that cured epoxy resins based on glycolytic oligomers of PET and DEA have excellent chemical resistance as organic coatings for exterior coatings of ship bottoms, trunks.

Macijauskas et al.[65] studied the use of waste PET bottles to produce raw materials for compositions with high adhesion. Polypropylene glycol is used for alcoholysis of PET waste, and the reaction product is oligoester. The epoxy resin is obtained by reacting oligoester with epichlorohydrin, and the polyurethane is obtained by the reaction of alcoholysis PET and high-content aliphatic isocyanate. It was found that these two compositions can be used to form coatings with high mechanical properties.

Çam et al.[66] used EG to degrade waste PET bottle flakes, added epichlorohydrin to the degradation product to synthesize epoxy resin, and modified the epoxy resin with melamine formaldehyde resin and urea formaldehyde as modifiers. Epoxy resin has good water resistance and adhesion.

## 4.7 Preparation of fiber-reinforced plastics

A. Rorrer et al.[67] combined single-use carbonated beverage bottles with renewable-sourced monomers to produce high-value FRP (fiber-reinforced plastic). First, the bottle is cut into thin strips after removing the label and cap. Ethylene glycol or 1,4-butanediol is used as a solvent, and titanium butoxide is used as a catalyst to alcoholyze PET. The alcoholysate is then reacted with monomers from renewable sources to production of UPE or diacrylic polymers. These polymers were then dissolved in reactive diluents (acrylic and methacrylic acid) containing free-radical initiators to form resins, which were coated on woven fiberglass mats and reacted to produce various rPET-FRPs. The market price of upgraded FRP is 5–8 times higher than that of PET flakes, which not only provides an economic incentive for the recycling of waste PET, but also saves 57% of the total supply chain energy compared with standard oil-derived FRP, and reduce greenhouse gas emissions by 40% and promote sustainable development.

## 5 Conclusion and outlook

PET can be widely used as fiber and plastic in various fields, which brings convenience to people, but also causes serious white pollution problems due to the accumulation of a large number of wastes in the natural environment, and also causes a large amount of waste of petrochemical energy. With the improvement of people's awareness of environmental protection, the recycling of waste polyester has become a very popular topic. In several chemical depolymerization schemes, the

hydrolysis process is relatively mature, and the product purity is high, but the acid and alkaline hydrolysis are corrosive to the production equipment, and the waste liquid needs to be treated. Reducing the acid and alkali concentration is the direction of future research. The methanol alcoholysis method has been gradually abandoned due to its harsh reaction conditions, but the method of DMT to prepare high-value products by transesterification is still worth exploring. Ammonolysis requires a more economical and feasible route to change the status quo due to the complex product purification and low added value of the product. Ethylene glycol alcoholysis method has moderate reaction conditions, low energy consumption, and the depolymerization product BHET can be used in high value to prepare polyurethane, unsaturated polyester, coating film-forming substances, plasticizers, etc., so as to achieve carbon emission reduction and PET green closed-loop recycling. Personally, this method is theoretically the best choice for realizing large-scale industrialization, and has considerable environmental, social and economic benefits.

In order to achieve the "double carbon" goal and the sustainable development of materials, the recycling of waste PET can be developed from the following aspects. (1) Advocate garbage classification, and fundamentally carry out garbage pretreatment first. (2) The recycling of polyester should be application-oriented, develop theories and methods based on degradation and preparation of new products, and strive to achieve green environmental protection and reduce energy consumption in the recycling process. (3) Balance the development of physical recycling, chemical recycling, physical–chemical and biological recycling methods, and enrich the existing recycling system. (4) Improve the substitutability of recycled products and the market acceptance of depolymerization products, and gradually realize the industrialization of various technologies. In addition, the government should also give certain support to promote the healthy and efficient development of PET recycling technology.

## Author contributions

Conceptualization, Fan Cao and Liyan Wang, writing-original draft, Fan Cao, Liyan Wang, Rongrong Zheng, Yanming Chen, Liying Guo and Xin Qian, writing-review & editing, Rongrong Zheng and Liying Guo.

## Conflicts of interest

The authors declare that they have no conflicts of interest. The funding sponsors had no role in the design of the study; in the analyses, writing of the manuscript, and the decision to publish the results.

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