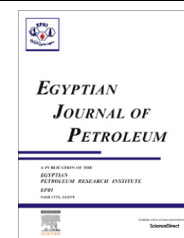




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REVIEW

Greener routes for recycling of polyethylene terephthalate



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Abstract The article reviews the different routes for recycling of polyethylene terephthalate. Chemical recycling processes are divided into six groups: methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis, and other methods. In a large collection of researches for the chemical recycling of PET, the primary objective is to increase the monomer yield while reducing the reaction time and/or carrying out the reaction under mild conditions. This article also presents the impact of the new recyclable catalysts such as ionic liquids on the future developments in the chemical recycling of PET.

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1. Synthetic polymers

The synthetic polymer industry represents the major end use of many petrochemical monomers such as ethylene, styrene, and vinyl chloride [1]. There are two main processes in the manufacture of synthetic polymers. The first involves breaking the double bond in the original olefin by additional polymerization to form new carbon–carbon bonds. For example, the fabrication of polyolefins, such as polyethylene and polypropylene, which is based on this general reaction. The second process is the elimination of water (or condensation)

between a carboxylic acid and an alcohol or amine to form polyester or polyamide [2].

Plastics are synthetic polymers that are divided into two groups: thermoplastics and thermo-set plastics [3]. Thermoplastics can be repeatedly softened and hardened by heating and cooling. In thermoplastics, the atoms and molecules are joined end-to-end into a series of long, sole carbon chains. These long carbon chains are independent of the others [4]. The structure in which the backbone is solely built of carbon atoms makes thermoplastics resistant to degradation or hydrolytic cleavage of chemical bonds. Consequently, thermoplastics are considered a non-biodegradable plastic. Examples of thermoplastics are polyethylene and polypropylene.

Thermo-set plastics are usually liquid or malleable prior to curing and designed to be molded into their final form. They are solidified after being melted by heating. The process of changing from the liquid state to the solid state is irreversible [3]. Distinguished from the linear structure of thermoplastics,

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thermo-set plastics have a highly cross-linked structure [3,2]. Since the main chain of thermo-set plastics is made of heteroatoms, it is possible that they are potentially susceptible to be degraded by the hydrolytic cleavage of chemical bonds such as ester bonds or amide bonds. Examples of this type are phenol-formaldehyde resin and polyurethane [5].

2. Polyethylene terephthalate (PET)

PET is semi-crystalline, thermoplastic polyester of characteristic high strength, transparency and safety [6]. For the manufacture of PET the intermediates, pure terephthalic acid (TPA) and ethylene glycol (EG), are derived from crude oil. When heated together the first product is a monomer bis(2-hydroxyethyl) terephthalate (BHET) mixed with low molecular weight polymers (oligomers). The mixture then reacts further, distills out excess ethylene glycol and forms the PET as shown in Fig. 1. At this stage, the PET is a viscous molten liquid. It is extruded, and water quenched to form a glasslike amorphous material. Some PET is also manufactured using technology based on the dimethyl ester of terephthalic acid (DMT).

The required high molecular weight PET is manufactured by a second polymerization stage carried out in the solid state at lower temperatures. This effectively removes all volatile impurities, like acetaldehyde, free glycols and water. The high molecular weight is essential for good mechanical properties providing stiffness, toughness and creep resistance while, at the same time, giving sufficient flexibility to resist bursting and breaking under pressure.

Once the polymer is formed it is very difficult to purify and for this reason the purity of the starting materials is the key factor. Vacuum distillation processes easily purify ethylene glycol while terephthalic acid is purified by repeated crystallization. Such high purity and high molecular weight materials are needed for food packaging applications.

Catalysts are used at extremely low concentrations to promote the reactions and ensure practical economics. The most common catalyst is antimony trioxide but salts of titanium, germanium, cobalt, manganese, magnesium and zinc are also used and small amounts remain encapsulated into the polymer matrix or in the polymer chain itself. However, in the laboratory, PET can be prepared by other reactions, such as the reaction of terephthaloyl chloride with ethylene glycol. This reaction is easier, but terephthaloyl chloride is more expensive than terephthalic acid, and it is more dangerous [7].

3. Importance of polyethylene terephthalate

PET has been traditionally employed in the production of textile fibers ever since the mid-1940s [8]. The PET bottle was patented in 1973 by Nathaniel Wyeth and began to be used popularly for the production of disposable soft drink bottles in the 1980s. In 1987, more than 700 million pounds of PET were consumed in their production [8].

The overall world production of polyesters was 25–30 million tons in 2000, this value increased to 55 million tons in 2012 and mostly consisted of polyethylene terephthalate (PET). Polyester consumption has increased substantially in fibers and molding resins due to the strong demand for textile

applications, as well as in food packaging and bottle markets for glass replacement [9].

Two PET grades now dominate the global market, i.e. fiber-grade PET and bottle-grade PET. These standard grades differ mainly in molecular weight or intrinsic viscosity (IV), respectively, optical appearance and the production recipes. The latter differ in the amount and type of co-monomers, stabilizers and metal catalysts, as well as colorants. Textile fiber-grade PET has a molecular weight of 15,000–20,000 g/mol, which refers to an intrinsic viscosity between 0.55 and 0.67 dL/g. PET fiber-grades for technical yarns such as tire cord have high molecular weights, with an intrinsic viscosity above 0.95 dL/g. Bottle-grade PET appears 'glass-clear' in the amorphous state. The average molecular weight ranges from 24,000 to 36,000 g/mol, which refers to an intrinsic viscosity between 0.75 and 1.00 dL/g. The standard bottle grade has an intrinsic viscosity of 0.80 dL/g. Other PET grades are manufactured for packaging films, as well as for the production of video and audio tapes. These PET types are often standard grades with an intrinsic viscosity of 0.64 dL/g. To reduce the sticking tendency of the final product, solid additives such as SiO₂ or clay with specific particle sizes and particle-size distributions are incorporated [10].

4. Recycling of waste polyethylene terephthalate

Recycling processes are the best way to economically reduce PET waste [11,12]. On the other hand, as the price of virgin PET remains stable, new and cheaper technologies for recycling PET give a benefit to the PET recycling industry by providing industry with relatively cheaper PET. The first recycling effort of post-consumed PET bottles in the world was in 1977 [13]. The major factor affecting the suitability of post-consumed PET flake for recycling is the level and nature of contaminants present in the flakes.

4.1. Contamination

Contamination of post-consumed PET is the major cause of deterioration of its physical and chemical properties during re-processing [14]. Minimizing the amount of these contaminants leads to better PET quality [15]. Post-consumed PET is contaminated with many substances such as the following:

4.1.1. Acid producing contaminants

The most harmful acids to the post-consumed PET recycling process are acetic acid, which is produced by poly(vinyl acetate) closures degradation, rosin acid and abietic acid that are produced by adhesives and hydrochloric acid that is produced by poly(vinyl chloride) (PVC). The acids act as catalysts for the chain scission reactions during post-consumed PET melt processing [16]. Paci and La-Mantia [17] reported that the presence of PVC (as little as 100 ppm) would increase post-consumed PET chain scission due to the catalytic effect of hydrogen chloride evolving during the degradation of PVC.

4.1.2. Water

Water reduces molecular weight (MW) during post-consumed PET recycling through a hydrolysis reaction. Moisture contamination should be below 0.02% to avoid the

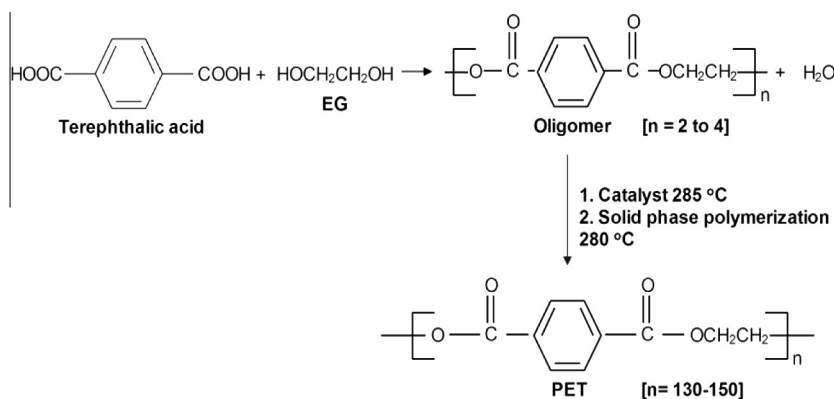


Figure 1 Manufacture of PET as described in [7].

MW reduction. Most water content comes from the flake washing process but can be reduced substantially by proper drying [18].

4.1.3. Coloring contaminants

Fragments of colored bottles and printed ink labels cause undesirable colors during processing. Enhancement of sorting and washing processes in bottle recycling may reduce coloring contaminants [18].

4.1.4. Acetaldehyde

Acetaldehyde is present in PET and post-consumed PET. It is a by-product of PET degradation reactions. [18]. Stabilizers such as 4-aminobenzoic acid, diphenylamine and 4,5-dihydroxybenzoic acid are added to PET in order to minimize the amount of the generated acetaldehyde [19].

4.1.5. Other contaminants

The public use of PET bottles for storing other substances such as detergents, fuel, pesticides, etc, could be a health hazard if traces of these substances remain after post consumed PET recycling. The increase of people's awareness of the danger of storing the materials affecting public health has minimized the amount of these contaminants significantly [20].

4.2. Classification of PET recycling

There are four distinct approaches to the recycling of post-consumer PET materials:

- (1) Primary recycling involves the use of pre-consumer industrial scrap and salvage.
- (2) Secondary recycling involves physical reprocessing, for example grinding, melting and reforming.
- (3) Tertiary recycling involves subjecting waste PET to chemical treatment whereby its components are isolated and reprocessed for use in manufacture.
- (4) Quaternary recycling in which the energy content of the plastics waste can be recovered by incineration [7].

4.2.1. Primary recycling: pre-consumer industrial scrap and salvage

It is the recycling of clean, uncontaminated industrial scrap. The recycled scrap or waste is either mixed with virgin material to assure product quality or used as second grade material [21,22].

4.2.2. Secondary recycling: physical reprocessing

It is the mechanical recycling of post-consumed PET, which passes through different steps such as contaminant removal, drying and melt reprocessing.

4.2.2.1. Steps of physical reprocessing. **4.2.2.1.1. Contaminant removal.** The removal of contaminants from post-consumed PET is a vital step in the mechanical recycling process of PET. Contaminant removal consists of several processes in which post-consumed PET bottles are sorted, ground and washed. The sorting process is separating PET bottles from PVC, polyethylene and other plastic containers [23].

After sorting, post-consumed PET is ground into flakes in order to be easily reprocessed. PET flakes are washed following grinding. There are two ways in which post-consumed flakes are washed [18]:

- (1) Aqueous washing which consists of two steps; a hot wash with 2% NaOH solution and a detergent at 80 °C followed by a cold wash with water only.
- (2) Solvent washing for which tetrachloroethylene (TCE) has been reported to be suitable for washing PET flakes.

4.2.2.1.2. Drying. Drying is regarded as an essential step in post-consumed PET recycling. Minimizing the moisture content of post-consumed PET flakes reduces the hydrolytic degradation effect [24].

4.2.2.1.3. Melt reprocessing. PET flake can be readily reprocessed into granules by conventional melt extrusion [18]. Extrusion of PET flakes at 280 °C with the presence of above-mentioned contaminants reduces the MW due to degradation reactions [25].

4.2.2.2. Advantages. Compared to chemical recycling routes, physical recycling of PET by melt reprocessing is relatively

simple, requires low investments, utilizes established equipment, is flexible in terms of feedstock volume and has little adverse environmental impact.

4.2.2.3. Disadvantages.

- (i) The major problem encountered in melt reprocessing of any PET is the reduction in melt viscosity, which is caused by thermal and hydrolytic degradation.
- (ii) Melt reprocessing can generate cyclic and linear oligomers, which can affect the final product properties such as printability or dyeability [26].
- (iii) Contaminants such as PVC, poly vinylidene chloride (PVDC), glues, ethylene-vinyl acetate (EVA), paper, etc. generate acidic compounds, which catalyze the hydrolysis of the PET's ester linkages during thermal reprocessing [27].
- (iv) A major obstacle in the recycling of post-consumer PET is the yellowing of the polymer. The color is due to intramolecular cross-linking and oxidation reactions. Yellowing is a significant problem for PET that is reused in bottle production.

4.2.3. Tertiary recycling: chemical recycling

Chemical recycling involves the transformation of polymer chain. The polymer backbone under the recycling process is degraded into monomer units (i.e. depolymerization), or randomly ruptured into larger chain fragments (i.e. random chain scission) with associated formation of gaseous products.

The chemical recycling is carried out either by (i) solvolysis or by (ii) pyrolysis, where solvolysis involves the degradation by solvents including water, and pyrolysis involves the degradation by heat in the absence of oxygen or air, or vacuum. Chemical recycling yields monomers, petroleum liquids and gases. Monomers are purified by distillation and drying, and used for manufacture of polymers [7].

Chemical recycling processes for PET were implemented nearly parallel to the manufacture of the polymer on a commercial scale [28].

4.2.3.1. Solvolysis. Solvolysis process is divided as follows: (1) Hydrolysis, (2) Aminolysis, (3) Ammonolysis (4) Methanolysis and (5) Glycolysis.

4.2.3.1.1. Hydrolysis. It involves the hydrolysis of post-consumed PET to TPA and EG. A growing interest in this method is connected with the development of PET synthesis directly from EG and TPA, which eliminates methanol from the technological cycle [14]. The main disadvantage of this method is the use of high temperature (200–250 °C) and pressure (1.4–2 MPa) as well as long time needed for complete depolymerization. Commercially, hydrolysis is not widely used to produce food-grade recycled PET, because of the cost associated with purification of the recycled TPA. Hydrolysis of PET can be carried out as (1) alkaline hydrolysis, (2) acid hydrolysis and (3) neutral hydrolysis [7].

4.2.3.1.1.1. Alkaline hydrolysis

Alkaline hydrolysis of PET (Fig. 2) is usually carried out with the use of an aqueous alkaline solution of NaOH, or KOH of a concentration of 4–20 wt% [29]. Pitat et al. [30] have

patented a method of PET alkaline hydrolysis by an 18 wt% solution of NaOH. The most advantageous results are achieved at a PET: NaOH weight ratio of 1:20, at about 100 °C in 2 h. Lazarus et al. [31] described a process allowing the recovery of TPA and other monomeric components from PET/polyamide 6 polymeric mixtures. Namboori and Haith [32] compared the reactivity of NaOH aqueous solutions, as well as solutions of sodium tert-butoxide in tert-butanol, sodium isopropoxide in isopropyl alcohol, sodium methoxide in methanol, and sodium ethoxide in ethanol with PET. They have demonstrated that, sodium ethoxide in ethanol is the most reactive and an aqueous solution of sodium hydroxide is the least reactive. Oku et al. [33] reported the addition of an ether (such as dioxane or tetrahydrofuran) as a mixed solvent with an alcohol (methanol or ethanol) accelerated the reaction. The time for complete reaction (>96%) of solid PET with NaOH in methanol at 60 °C was 40 min with dioxane as a co-solvent and 7-h without dioxane.

PET hydrolysis in a non-aqueous alkaline solution involves the hydrolysis of post-consumed PET using alkaline hydrolysis in non-aqueous ethylene glycol solution [34]. Benzaria et al. [35] described an interesting process, in which the depolymerization was carried out in a mixer-extruder with the use of solid sodium hydroxide at temperatures of 100–200 °C. Collins and Zeronian [36] have demonstrated that NaOH solutions in methanol react with PET significantly faster than analogous aqueous solutions.

A phase transfer catalyst has been reported to catalyze the alkaline hydrolysis of PET [37]. The phase transfer catalyst (PTC) undergoes an ion-exchange reaction with the inorganic salt in the aqueous phase and forms an ion pair, which can cross the solid-liquid interface due to its lipophilic nature. In the organic phase, this ion pair undergoes a nucleophilic displacement reaction with the organic reagent to form the product. The new ion pair returns to the aqueous phase and the cycle continues. However, when strong inorganic bases are present the process is not as clear-cut [37]. The use of PTC has been proposed for the alkaline hydrolysis of PET, in order to carry out the reaction in mild experimental conditions, i.e.,

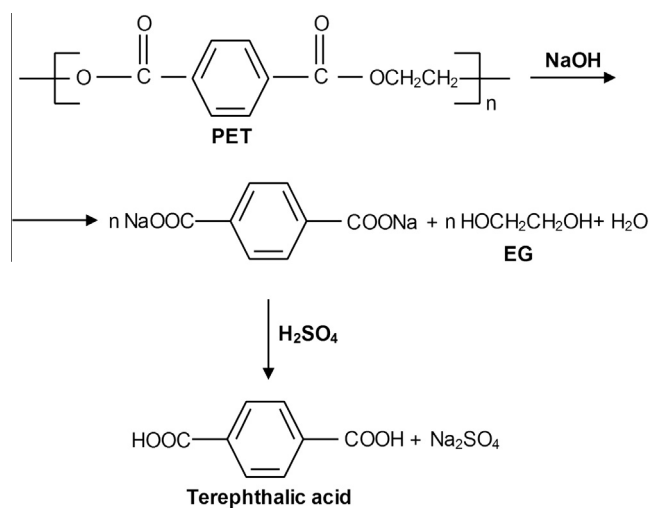


Figure 2 Alkaline hydrolysis of PET using NaOH or KOH as described in [29].

atmospheric pressure and temperatures below 100 °C. The method had been applied in PET fibers as well as Nylon 46 and Nylon 66 fibers. Very good results were obtained for the depolymerization of PET and the yield in terephthalic acid was as high as 93% [38].

4.2.3.1.1.2. Acidic hydrolysis

Acid hydrolysis is performed most frequently using concentrated sulfuric acid as shown in Fig. 3, although other mineral acids such as nitric or phosphoric acid have also been employed. In order to avoid high pressures and temperatures in the reaction vessel, a concentrated sulfuric acid (14.5 M) has been proposed by Puzstaszeri, Brown, O'Brien and Sharma [39–41]. However, the process becomes very costly due to the need to recycle large amounts of concentrated H₂SO₄ and the purification of EG from the sulfuric acid. TPA recovery from PET scrap material in concentrated sulfuric acid at 60–93 °C has been also described [40]. In another patent, the production of pure TPA was described by acid hydrolysis of PET in a 90 wt% H₂SO₄ solution at 85–90 °C [41].

A substantial drawback of PET hydrolysis by concentrated sulfuric acid is the high corrosiveness of the reaction system and the generation of large quantities of inorganic salts and aqueous wastes [42]. Yoshioka et al. [43] also described a process for the depolymerization of PET powder from waste bottles using nitric acid (7–13 M) at 70–100 °C for 72 h. TPA and EG were produced and the resultant EG was simultaneously oxidized to oxalic acid. The proposed method had the advantage of resulting in value-added products such as oxalic acid, which is more expensive than TPA and EG.

4.2.3.1.1.3. Neutral hydrolysis

Neutral hydrolysis is carried out with the use of water or steam. In spite of this, the pH of the post reaction mixture amounts to 3.5–4.0, which according to Michalski [44] is caused by the formation of TPA monoglycol ester during the reaction. The process usually runs at a pressure of 1–4 MPa at temperatures of 200–300 °C [45]. The ratio by weight of PET to water is from 1:2 to 1:12 [46].

It has been confirmed that PET hydrolysis proceeds significantly faster in the molten state than as a solid; therefore, it is advantageous to carry out recycling using this method at temperatures higher than 245 °C [47].

An undoubted advantage of neutral hydrolysis is its high ecological purity, and therefore growing interest in this technology can be expected. Its drawback is that all mechanical impurities present in the polymer are left in the TPA; thus, the product has a considerably worse purity than the product of acid or alkaline hydrolysis [48].

4.2.3.1.2. Aminolysis. The aminolysis of PET yields diamides of TPA, which is known as bis(2-hydroxy ethylene)terephthalamide (BHETA) as shown in Fig. 4. There are no known reports concerning the utilization of this process on a commercial scale in PET recycling. However, it is known that partial aminolysis has found its application in the improvement of PET properties in the manufacture of fibers with defined processing properties [49]. In the majority of PET aminolysis processes described, the polymer was in the form of powder or fibers. The reaction was usually carried

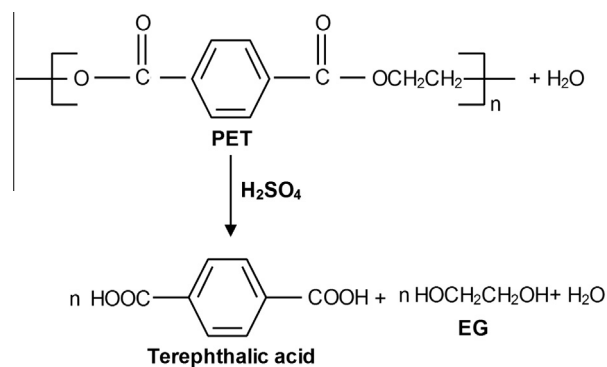


Figure 3 Depolymerization of PET using H₂SO₄ as described in [40].

out using primary amine aqueous solutions, most frequently methylamine, ethylamine, and ethanolamine in the temperature range of 20–100 °C. Anhydrous *n*-butylamine was also applied as an aminolytic agent at a temperature of 21 °C [49].

Shukla and Harad [50,51] have used ethanolamine for the aminolysis of PET waste materials in the molar ratio 1:6 (PET:ethanolamine) under reflux in the presence of different catalysts for time periods varying up to 8 h. The catalysts, namely glacial acetic acid, sodium acetate and potassium sulfate, were used in concentrations ranging between 0.3% and 1.5% by weight of polymer. Zahn and Pfeifer [52] carried out aminolysis of PET with solutions of hydrazine, benzylamine, ethylene diamine, hexamethylene diamine, piperidine and aniline. They obtained different reaction products as the diamides of terephthalic acid, which do not possess any potential for further chemical reactions. Tawfik and Eskander [53] investigated the aminolysis degradation of PET waste by ethanolamine (EA) in the presence of dibutyl tin oxide (DBTO) as a catalyst. Spychaj et al. [54] described the chemical degradation of waste PET with polyamines, such as diethylenetriamine, triethylenetetramine, and their mixtures, as well as mixtures of triethylenetetramine and *p*-phenylenediamine or triethanolamine, and the characteristics of the products.

4.2.3.1.3. Ammonolysis. Terephthalamide is produced by the action of ammonia on PET in an ethylene glycol environment as shown in Fig. 5. Very good results were obtained from the ammonolysis of PET waste from postconsumer bottles; the process was carried out under a pressure of about 2 MPa in a temperature range of 120–180 °C for 1–7 h. After the reaction was completed, the amide produced is filtered, rinsed with water, and dried at a temperature of 80 °C. The product has a purity of not less than 99%, and the yield is above 90% [55].

A low-pressure method of PET ammonolysis, in which the degradation agent is ammonia in an ethylene glycol environment, is also known. The process is catalyzed by zinc acetate in a quantity of 0.05 wt%, conducted at a temperature of 70 °C and a ratio of PET-NH₃ of 1:6 terephthalamide was produced with a yield of about 87% [55].

4.2.3.1.4. Methanolysis. Methanolysis actually involves the degradation of PET by methanol at high temperatures and high pressures with the main products being dimethyl terephthalate (DMT) and ethylene glycol (EG) as shown in Fig. 6. Methanolysis of PET flakes is usually performed at temperatures between 180 °C and 280 °C and pressures from 2 to

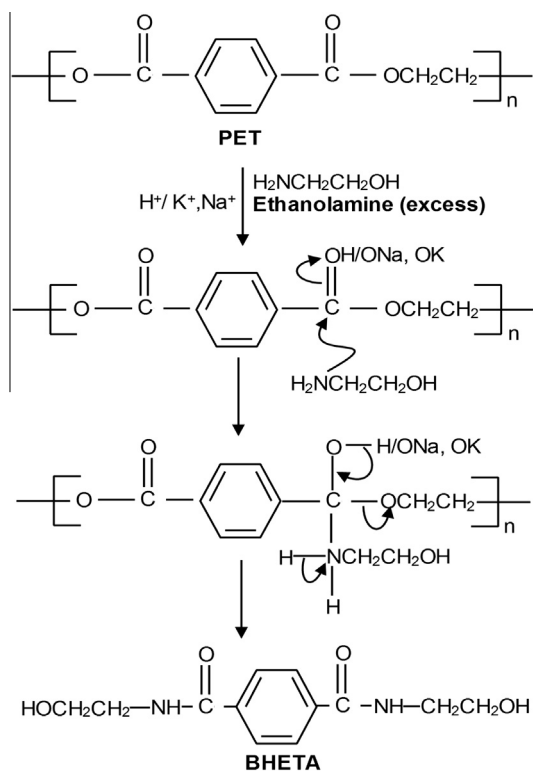


Figure 4 Aminolysis of PET as described in [50].

4 MPa [18]. Methanolysis is currently and successfully applied to scrap bottles, fiber waste, used films and plant waste [28].

Alcoholysis of PET with trimethylol propane in the presence of zinc acetate as a catalyst was reported to give products that, when mixed with PVC, could result in PVC plastisols [56,57]. There are known examples of using arylsulfonic acid salts as the catalyst for methanolytic degradation of PET [58]. The principal elements of the installation used in the batch method of methanolysis are autoclave, crystallizer, centrifuge, and a system for the melting and distillation of the DMT obtained [59]. Gruschke et al. [60] reported that PET was completely (more than 99%) depolymerized to DMT and EG by reacting molten PET with methanol at 210 °C in the absence of a catalyst. Sako et al. [61] proposed a new process of methanolysis by treating PET with supercritical methanol. In this process PET can be completely depolymerized to DMT, EG, and oligomers above 300 °C at 11 MPa for 30 min without a catalyst.

The main advantage of this method is that an installation of methanolysis can be located in the polymer production line,

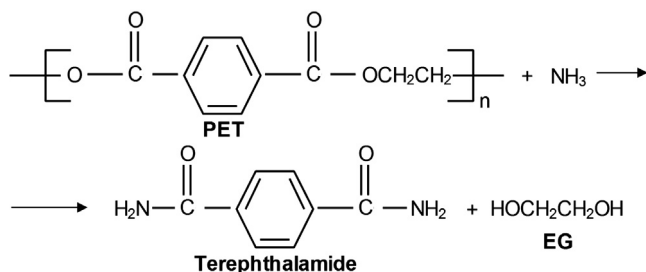


Figure 5 Ammonolysis of PET as described in [55].

since the DMT produced has a product quality identical to virgin DMT. In addition, ethylene glycol and methanol can be easily recovered and recycled. In this way, waste PET arising in the production cycle is used and the monomers recovered can be re-used in the manufacture of a full value polymer [57].

Disadvantages of the method include the high cost associated with the separation and refining of the mixture of the reaction products (glycols, alcohols and phthalate derivatives). If water perturbs the process, it poisons the catalyst and forms various azeotropes. However, the main disadvantage is associated with the trend of all of the new PET production processes to use TPA instead of DMT as the raw material. The conversion of the DMT produced by hydrolysis to TPA adds considerable cost to the methanolysis process [57].

4.2.3.1.5. *Glycolysis*. The glycolysis reaction is the molecular degradation of PET polymer by glycols, in the presence of trans-esterification catalysts, where ester linkages are broken and replaced with hydroxyl terminals [7] as shown in Fig. 7.

Glycolysis of PET was first described in a patent in 1965 [62]. In the late 1980s a number of further PET glycolysis patents were issued [63]. The variables affecting the rate of glycolysis of PET have been studied in detail [64,65]. PET degradation is carried out most frequently using ethylene glycol [66], diethylene glycol [67], propylene glycol and dipropylene glycol [68].

Studies on the kinetics of PET glycolysis have shown that glycolysis without a catalyst is very slow and complete depolymerization of PET to BHET cannot be achieved. It also yields an end product that contains significant amount of other oligomers in addition to the BHET monomer. This results in difficulty in recovering the BHET monomer when it is the desired product. Thus, research efforts have been directed toward increasing the rate and BHET monomer yield by developing highly efficient catalysts and other techniques, and optimizing the reaction conditions (e.g. temperature, time, PET/EG ratio, PET/catalyst ratio) [69].

There are four distinct methods for the glycolysis of post-consumer PET materials:

- (1) Solvent-assisted glycolysis
- (2) Supercritical glycolysis
- (3) Microwave-assisted glycolysis
- (4) Catalyzed glycolysis

4.2.3.1.5.1. Solvent-assisted glycolysis

It involves the degradation of PET by ethylene glycol in the presence of solvent as a reaction medium. Güçlü et al. [70] added xylene in the zinc acetate catalyzed PET glycolysis reaction, and obtained BHET yield that was higher than that without xylene. The main objective of xylene was initially to provide mixability to the PET-glycol mixture. At temperatures between 170 °C and 225 °C, EG dissolves sparingly in xylene while it dissolves readily in PET. Meanwhile, the glycolysis products are soluble in xylene. Therefore, as the reaction progressed, the glycolysis products moved from the PET-glycol phase to the xylene phase, shifting the reaction to the direction of depolymerization.

Further investigations may have been prevented by the reason that organic solvents are harmful to the environment and massive use of these solvents is not a very attractive idea [71].

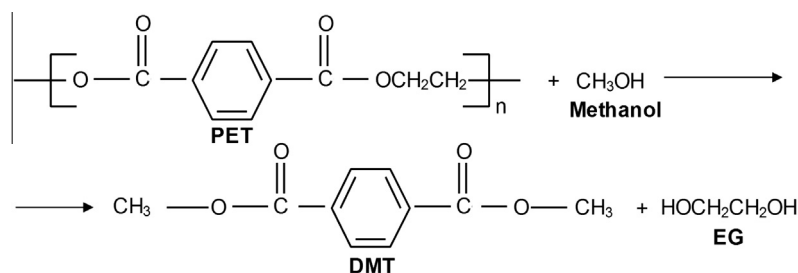


Figure 6 Methanolysis of PET as described in [28].

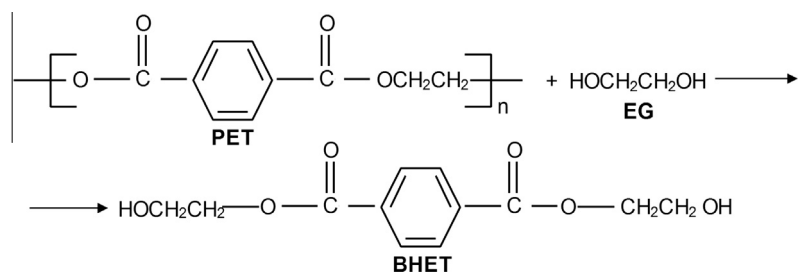


Figure 7 Glycolysis of PET as described in [7].

4.2.3.1.5.2. Supercritical glycolysis

Supercritical glycolysis involves the degradation of PET by ethylene glycol at a temperature and pressure above the critical point of ethylene glycol. The use of supercritical conditions has been explored earlier in PET hydrolysis and methanolysis, but only recently for glycolysis [72]. The main advantage of the use of supercritical fluids in a reaction is the elimination of the need of catalysts, which are difficult to separate from the reaction products. It is also environmentally friendly.

Imran et al. [72] investigated the use of EG in its supercritical state at 446.7 °C and 7.7 MPa. Supercritical process was carried out at 450 °C and 15.3 MPa, and the results were compared with those from the subcritical processes carried out at 350 °C and 2.49 MPa, and 300 °C and 1.1 MPa. Compared to the subcritical process, the BHET-dimer equilibrium was achieved much earlier for supercritical process: a maximum BHET yield of 93.5% was reached in 30 min. Disadvantages of the method include the high temperature and pressure needed to carry out the process.

4.2.3.1.5.3. Microwave-assisted glycolysis

Beyond eco-friendly catalysts, Pingale and Shukla [73] extended their study to the use of unconventional heating source of microwave radiations. The employment of microwave radiations as heating source drastically decreased the time for the completion of reaction from 8 h to just 35 min. However, it did not increase the BHET monomer yield. The use of more efficient catalyst along with microwave irradiation heating may be able to increase the BHET yield while decreasing the reaction time.

Cho et al. [74] studied the non-aqueous glycolysis with microwave irradiation in the presence of alkali catalyst to reduce the reaction time and develop economically feasible treatment process. The results indicated that the alkali concentration and the irradiation time were main factors in

determining the treatment efficacy. The irradiation time was important since it affected the system temperatures. Chaudhary et al. [75] studied the preparation of polyester polyols from PET by reacting with diols of different molecular weights (62–1500) under microwave irradiation in the presence of zinc acetate (0.5%, w/w). The reaction time required for glycolysis could be significantly reduced (30 min) by the use of microwave as compared to the conventional thermal glycolytic process, which requires a minimum of 8–9 h to reach the same level of depolymerization.

4.2.3.1.5.4. Catalyzed glycolysis

Glycolysis without a catalyst is an extremely sluggish process. There has been a strong interest in the development of highly active transesterification catalysts for the depolymerization of PET to BHET. The most studied method of increasing the glycolysis rate is catalysis. PET glycolysis is considered a trans-esterification reaction. Thus, trans-esterification catalysts have been applied to increase the reaction rate of PET glycolysis, with metal based catalysts being the most popular.

Helwani et al. [76] have listed all the catalysts that have been used before in other trans-esterification reactions. Fig. 8 shows the reaction mechanisms of glycolysis with metal-based catalyst [71]. A free electron pair on the EG oxygen initiates the reaction by attacking the carbonyl carbon of the ester group of the polyester. The hydroxyethyl group of ethylene glycol then forms a bond with the carbonyl carbon of the polyester breaking the long chain into short chain oligomers and finally BHET.

The rate of glycolysis reaction depends on a number of parameters including temperature, pressure, PET/EG ratio, and the type and amount of catalyst. Also, the transformation of dimer to BHET monomer is a reversible process. Prolonging the reaction after the equilibrium of the two is attained will cause the reaction to shift backwards, increasing the amount of dimer at the expense of the BHET monomer. It is thus

important to know the optimum conditions of the glycolysis reaction. With metal based catalysts (Fig. 8), the metal forms a complex with the carbonyl group, facilitating the attack of EG on PET leading to the formation of BHET. A number of glycolytic depolymerization processes have been reported with different catalysts and different reaction conditions [71].

4.2.3.1.5.4.1. Metal salts

The oldest reported catalysts for PET glycolysis are metal acetates. Zinc acetate was first used in the synthesis of polyester polyols from PET waste [77].

In 1989, Chujo et al. [65] investigated the use of metal acetates (zinc, manganese, cobalt, and lead) as catalysts. They reported that zinc acetate showed best results in terms of the extent of depolymerization reactions of PET. They also observed that the equilibrium between the BHET monomer and dimer was reached after 8 h of reaction with the temperature at 190 °C. This may be considered as the beginning of PET glycolysis catalyst research as several researches followed later. Ghaemy and Mossaddegh [78] verified the results obtained by Baliga and Wong, and the order of activity of the catalysts ($Zn^{+2} > Mn^{+2} > Co^{+2} > Pb^{+2}$). The kinetics of the glycolysis of PET was studied using zinc acetate catalyst at the same temperature, and it was found that the equilibrium between the BHET monomer and the dimer was reached after two hours, as opposed to 8 h [79].

Meanwhile, Chen [80] studied that of manganese acetate and found out that the best glycolysis condition for the same temperature was the reaction time of 1.5 h with 0.025 mol/kg PET. Xi et al. [81] investigated the optimum condition of the reaction at 196 °C. They reported that a 3-h reaction with EG/PET weight ratio of 5, and catalyst/PET weight ratio of 0.01 can be effective in the glycolysis of PET.

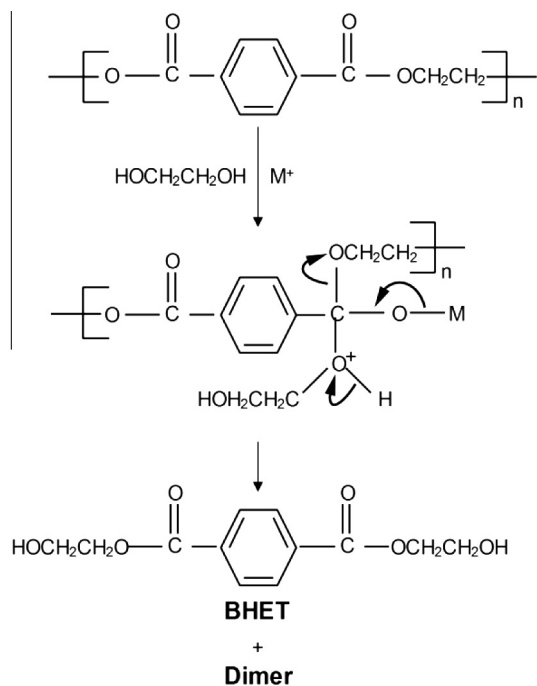


Figure 8 The reaction mechanisms of glycolysis using metal-based catalyst as described in [71].

Goje and Mishra [82] also studied the optimum conditions of PET glycolytic depolymerization at 197 °C, and they reported 98.66% PET conversion with the reaction time of 90 min and PET particle size of 127.5 μm . Dayang et al. [83] later used the products from PET glycolysis catalyzed by zinc acetate to make thermally stable polyester resin via polyesterification with maleic anhydride and crosslinking with styrene. The synthesis of unsaturated polyester resin actually dates back to 1964 [84]. Campanelli et al. [85] studied the reaction of polyethylene terephthalate melts with ethylene glycol in a pressure reactor at temperatures above 245 °C. A kinetic model proposed for the initial period of the reaction was found to be consistent with experimental data. It was found that internal catalysis by ethylene glycol does not play an important role in the glycolytic depolymerization of PET. In 2003, Troev et al. [86] introduced titanium (IV) phosphate as a new catalyst. They reported that glycolysis in the presence of the new catalyst was faster compared to that with zinc acetate. Their data showed that at 200 °C, 150 min reaction time and 0.003 catalyst/PET weight ratio, the glycolyzed products from titanium (IV) phosphate catalyzed reaction consisted of 97.5% BHET, which was significantly higher than that of zinc acetate, which was 62.8%.

Since lead and zinc are heavy metals known to have negative effects on the environment, Shukla and Kulkarni [87] started to develop milder catalysts that are comparatively less harmful to the environment. They started with mild alkalies, sodium carbonate and sodium bicarbonate, and reported that the monomer yields were comparable with those of the conventional zinc and lead acetate catalysts [87]. They also reported glacial acetic acid, lithium hydroxide, sodium sulfate, and potassium sulfate to have comparable yields with those of the conventional heavy metal catalysts [52]. They recently used the recovered BHET monomer to produce useful products such as softeners and hydrophobic dyes for the textile industry [88]. López-Fonseca et al. [6] also used these eco-friendly catalysts in their study of catalyzed glycolysis kinetics. The latest catalysts that Pingale and Shukla [73] developed are inexpensive and readily available metal chlorides, wherein zinc chloride reportedly gave the highest BHET yield equal to 73.24%. The catalytic activity with these homogeneous catalysts is highly effective in the glycolysis of PET. However, they have several drawbacks, such as the catalyst cannot be easily separated from the reaction mixture because most of these catalysts are soluble in ethylene glycol; thus, required an additional unit operation (distillation) in the chemical process. It has also been noted that the zinc salts do not increase the glycolysis rate at temperatures above 245 °C, which limits their usage at the moderately high temperatures applied to decrease the overall reaction time, the catalysts could not be recycled and reused, the existence of side reactions, and the purity of products [85].

4.2.3.1.5.4.2. Heterogeneous catalysts

Shukla et al. [88] reported new addition to their set of eco-friendly catalysts in the form of zeolites. Zeolites have been used as catalysts in other reactions before, and their catalytic activity can be credited to their large surface area in mesopores and micropores that provide numerous active sites. Their result, however, showed that the BHET yield did not deliver

any significant improvement from the other catalysts they previously reported.

Imran et al. [89] studied the catalytic glycolysis of post-consumed PET in the presence of metal oxides that were impregnated on different forms of silica support [silica nanoparticles (SNPs) or silica microparticles (SMPs)] as glycolysis catalysts. The reactions were carried out at 300 °C and 1.1 MPa at an EG-to-PET molar ratio of 11:1 and a catalyst-to-PET-weight ratio of 1.0% for 40–80 min. Among the four prepared catalysts ($\text{Mn}_3\text{O}_4/\text{SNPs}$, ZnO/SNPs , $\text{Mn}_3\text{O}_4/\text{SMPs}$, and ZnO/SMPs), the $\text{Mn}_3\text{O}_4/\text{SNPs}$ nanocomposite had the highest monomer yield (>90%). This high yield may be explained by the high surface area, amorphous and porous structure, and existence of numerous active sites on the nanocomposite catalyst [89]. Imran et al. [90] also studied the catalytic glycolysis of post-consumed PET in the presence of novel mesoporous metal oxide spinel catalysts. ZnO (hexagonal), metal oxide spinels (Co_3O_4 and Mn_3O_4), and mixed metal oxide spinel (ZnMn_2O_4 , CoMn_2O_4 , and ZnCo_2O_4) catalysts were synthesized via the precipitation or co-precipitation method. The results revealed that the catalyst that yielded the highest amount of BHET (92.2 mol%) under reaction conditions (260 °C and 5.0 atm) was zinc manganite tetragonal spinel (ZnMn_2O_4), which has tetrahedral Zn^{+2} ion and octahedral Mn^{+3} ion coordination with the spinel crystal structure.

Park et al. [91] investigated the catalytic glycolysis of post-consumed PET using graphene oxide (GO)–manganese oxide nanocomposite (GO– Mn_3O_4) which was synthesized using ultrasound method, the glycolysis of PET was carried out in a stainless steel batch-type autoclave reactor at 300 °C and 1.1 MPa for 80 min. The highest monomer yield of 96.4% was obtained with the nanocomposite containing the lowest amount of Mn_3O_4 , while PET glycolysis with the Mn_3O_4 without GO yielded 82.7% BHET.

Chen et al. [92] studied the depolymerization of PET by ethylene glycol (EG) in the presence of Mg–Al hydrotalcites and their corresponding mixed oxides as solid base catalysts. Mg–Al hydrotalcites with different Mg/Al molar ratios were prepared by coprecipitation process, Mg–Al mixed oxides obtained by the calcination of hydrotalcites exhibited higher catalytic activity for the glycolysis of PET. Furthermore, Mg–Al mixed oxides calcinated at 500 °C with Mg/Al molar ratio of 3 offered the highest catalytic activity for the glycolysis of PET.

More recent three series of solid catalysts including $\text{SO}_4^{2-}/\text{ZnO}$, $\text{SO}_4^{2-}/\text{TiO}_2$ and $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$ were investigated for the glycolysis of PET which have exhibited high thermostability, superacid property and high catalytic activity. The solid acids have many advantages over homogeneous acids, such as non-corrosive, easy separation by filtration, and less waste production through recycling [93]. However, these catalysts require higher temperature and pressure. Thus, developing new catalysts that can effectively degrade the PET wastes into high-pure monomer BHET under the relatively mild condition is significantly important. Ionic liquids as promising catalysts have been reported that they could be used in the degradation of polymer. The special properties of ionic liquids make it easy to separate the catalyst from the solid glycolysis products. Thus, ionic liquids seem to be a promising catalyst for the depolymerization of PET.

4.2.3.1.5.4.3. Ionic liquid catalyzed glycolysis

An ionic liquid (IL) is a salt in the liquid state that has a melting point lower than 100 °C. The melting point of large, unsymmetrical ions, whose charge can be distributed over a large volume, is low and hence the melting point of the IL can be far below 0 °C. Common table salt, NaCl, contains small, single-atom ions, and its melting point is therefore as high as 801 °C [94]. Scientists are deeply interested in ILs because of their unique features, such as the strong solvent power for organic and inorganic compounds, thermal stability, nonvolatility, electrochemical stability, and low flammability [95–97]. In the last decade, ionic liquids have been widely used in extraction [98], catalysis [99], electrochemistry [100], and organic synthesis [101,102].

Recently, Wang et al. [103] reported that ionic liquid could catalyze the glycolysis of PET. The main advantage of ionic liquids over conventional catalysts like metal acetates is that the purification of the glycolysis products is simpler. They studied the catalytic glycolysis of PET under atmospheric pressure at reaction temperatures ranging from 160 to 195 °C for glycolysis times of 5–10 h. 100% conversion of PET was achieved after 8 h at a temperature of 180 °C, with the 1-butyl-3-methylimidazolium bromide ([Bmim][Br]) being the best catalyst in terms of PET conversion and ease and cost of preparation. They concluded that the BHET purity from their method was high. They did not, however quantitatively measure the BHET yield from their experiment. After this, they extended their research by investigating the reusability of the ionic liquid catalysts and kinetics of the PET degradation by ionic liquid alone. They concluded that the catalysts could be used repeatedly, the degradation reaction is first-order with activation energy equal to 232.79 kJ/mol, and it can potentially replace the traditional organic solvents used in PET degradation [103].

Yue et al. [104] studied the glycolysis of PET using several ionic liquids such as 1-butyl-3-methylimidazolium bicarbonate, 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium bromide. The basic ionic liquid, 1-butyl-3-methylimidazolium hydroxyl ([Bmim]OH), exhibited high catalytic activity for the glycolysis of PET under optimum conditions of m(PET):m(EG): 1:10, dosage of [Bmim]OH at 0.1 g (5 wt%), reaction temperature 190 °C and time 2 h [103].

Wang et al. also [105] studied the glycolysis of PET using imidazolium-based Fe-containing ionic liquid, 1-butyl-3-methylimidazolium tetra-chloroferrate ([Bmim]- FeCl_4). This magnetic ionic liquid exhibited higher catalytic activity for the glycolysis of PET, compared with FeCl_3 or ionic liquid, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). However, the main monomer product is very easy to be stained by Fe-containing ILs and needs to be washed by a large amount of deionized water, which not only increases the water consumption but also causes the loss of monomers [105].

Wang et al. [106] studied a series of 1-allyl-3-methylimidazolium halometallate ionic liquids in the catalytic glycolysis of PET that exhibited higher catalytic activity under mild reaction condition, compared to the traditional catalysts. Yue et al. [107] reported that [Bmim][ZnCl_2] could behave as an efficient catalyst for the depolymerization of PET in ethylene glycol.

Our group investigated the glycolysis of polyethylene terephthalate using 1-butyl-3-methylimidazolium acetate

([Bmim][OAc]) as a catalyst [108]. Using [Bmim][OAc] (1.0 g) with 20 g of EG and 3.0 g of PET, it is found that only 3 h of glycolysis at 190 °C is sufficient for the conversion of PET to reach 100% and the yield of BHET to reach 58.2%. The synergistic effect of the cation and anion in the Lewis base ionic liquid [Bmim][OAc] facilitates the attack of the oxygen in ethylene on the carbon cation of the ester group. The acetate-based ionic liquid [Bmim][OAc] might have the potential to substitute traditional compounds to catalyze the glycolysis of PET in industrial production, as it could be reused up to six times. The kinetics of the reaction was first-order with an activation energy of 58.53 kJ/mol [108].

Our group also studied the glycolysis of polyethylene terephthalate using 1-butyl-3-methylimidazolium acetate-promoted copper acetate ($\text{Cu}(\text{OAc})_2\text{-[Bmim][OAc]}$) and 1-Butyl-3-methylimidazolium acetate-promoted zinc acetate ($\text{Zn}(\text{OAc})_2\text{-[Bmim][OAc]}$) as catalysts [109]. Under the optimal conditions of 1.0 g of catalyst with 20 g of EG in the presence of 3.0 g of PET at 190 °C after 3 h of glycolysis, complete PET conversion was achieved using $\text{Cu}(\text{OAc})_2\text{-[Bmim][OAc]}$ and $\text{Zn}(\text{OAc})_2\text{-[Bmim][OAc]}$, and the yield of bis (2-hydroxyethyl) terephthalate (BHET) reached 53.95% and 45.6%, respectively. They could be used six times without a significant loss of catalytic performance. The PET glycolysis mechanism was investigated, and the results show that a hydrogen bond is formed between the carbonyl oxygen of metal acetate and the C2–H on an imidazolium ring of [Bmim][OAc]. As a result, the metal acetate changes from a bidentate to a unidentate coordination structure. Simultaneously, this change promotes the coordination of the carbonyl oxygen in the PET molecule with the metal atom of the metal acetate, which facilitates the attack of the oxygen atom in the hydroxyl of ethylene glycol on the carbon cation of the ester group in the coordinated PET molecule. The reaction kinetics for $\text{Cu}(\text{OAc})_2\text{-[Bmim][OAc]}$ and $\text{Zn}(\text{OAc})_2\text{-[Bmim][OAc]}$ was first-order with an activation energy of 56.4 kJ/mol and 53.8 kJ/mol, respectively [109].

5. Conclusion

Since the discovery of PET and the start of PET chemical recycling in 1950s that attracted great interest from the research community, PET glycolysis has gone a long way, back when zinc acetate was first used as a catalyst until when ionic liquid catalysts have been finally utilized. Studies have already dealt with most of the problems dealing with PET glycolysis, including impracticability of the reaction due to long reaction times, low yields, undesirable conditions, and pollution obstacle. Researchers have developed catalysts to increase the reaction rate, catalysts that can be recycled and reused, a method that does not require catalysts, and many others.

However, PET recycling is still far from its summit. However, researchers have found ways to solve each problem separately; there is still no way to solve them all simultaneously. The main issue that stands now is to deliver an efficient environmentally friendly way to chemically recycle PET. This may be an opportunity for researchers to try to develop efficient and highly selective catalysts that can be recovered and reused.

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