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A Review Study on Advancements in the Recycling Methods of Polyethylene terephthalate

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Recycling polyethylene terephthalate (PET) is of pivotal importance, as the bulk of PET waste generated is rising rapidly due to the wide variety of its applications. This has given rise to growing awareness and concern for the ever-increasing environmental pollution. To manage this waste, there has been significant improvement in various methods of polymer recycling, particularly in chemical recycling methods. This review provides an in-depth analysis of PET recycling methods including primary, mechanical, chemical, and energetic recycling. It also provides a detailed view of the effect of the new advanced catalysts on the future advancements in chemical recycling especially in glycolysis to improve the process efficiency and to make it economically feasible. Further, this article presents the alternative methods like nanotechnology as well as the utilization of enzymes for overcoming limitations of the prevailing methods and highlights the efforts made in these upcoming fields for enhancing the quality of the end product obtained by recycling PET waste.

1. Introduction

Polyethylene terephthalate is a thermoplastic polyester that is known for its transparency, lightweight, flexibility, good dimensional stability, and higher strength. It can vary from being semi-rigid to rigid as per the reaction conditions. It also has very good resistance to many solvents, moisture, oils, alcohols, and good barrier properties [1]. When ethylene glycol (EG) and terephthalic acid (TPA) are reacted, the product synthesized is polyethylene terephthalate (PET). The polymerization reaction takes place at high temperatures and low vacuum pressure. Due to the formation of long chains of polymer, the viscosity increases, and the reaction is terminated after achieving the desired chain length. At higher temperatures, PET begins to crystallize and becomes opaque and rigid. End products like trays and containers can be produced by this crystalline form. As it is a thermoplastic polymer, it can also be reheated more than once [2]. The entire procedure is explained in a simplified way in Figure 1, and the reactions are shown in Figure 2[3].

PET is used in a variety of applications right from bottles to textile fibers for fabrics. It is also utilized in the storage of different chemicals as it shows very good resistance to oils, alcohols, dilute acids, aliphatic hydrocarbons, etc.

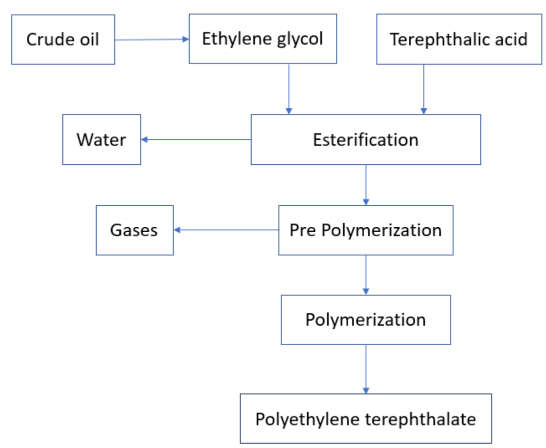

Fig 1. Manufacturing of PET

This extensive usage of PET products has led to the generation of substantial amounts of PET waste. PET is non-biodegradable due to its resistance against organic agents. Hence the voluminous waste production of PET is considered to be harmful to the environment. [4] About 40% of this plastic waste is generated from the use and throw packaging.

Every year, plastic waste weighing around 18 billion pounds is disposed of into the oceans by India alone. In India, 4, 41,962 tons of plastic waste was produced by 13 states in 2017-18. The manufacturing of PET resin in India is increasing exponentially with the rapid rise in demand. Nearly 1,450 kT of PET was produced in India despite the total capacity of 1,976 kT, which includes the export and domestic consumption, in the year 2015-16. Also, about 900 kT of PET is imported to India from different countries in a year having different quality grades. Around 96% of PET is utilized for making bottles, and nearly 80% of these bottles are recycled, hence, nearly 691 kT of the total plastic bottles are recycled in India. [5]

According to future trends, the significance of PET is going to continue to be on the rise especially due to the high market demand of this polymer with the growing economy. [6] People are now realizing that the environmental benefit increases with the improvement in the recycling rate. Because of this, there is a marked increase in the development of better techniques for PET recycling. Among the different techniques of recycling PET, the tertiary method has shown remarkable developments, specifically in hydrolysis, alcoholysis, and glycolysis reactions. As glycolysis is the simplest and most cost-effective amongst these processes, researchers have turned their attention towards the glycolysis of PET.

Investigation and growth of the application of a glycolysis product have been the main field of interest for researchers. Future trends include development in nanotechnology, which makes high performance possible with lesser amounts because of its large surface-area-to-volume ratio. In the case of biopolymer products like mixed PET and PLA bottles, the segregation of the mixture in the post-consumer plastic waste stream is strenuous and has higher economical demand when carried through this conventional method. [7] Overall, the sole aim of recycling PET is to decrease the hazardous environmental effect it owes to its non-biodegradable nature.

2. Methods of PET recycling

Polyethylene terephthalate is one of the most desirable materials to recycle and comes second after aluminum in terms of the residual value for recycled materials [3]. Due to this, PET recycling has been one of the most lucrative and extensively used among polymers. The three major factors to be considered while recycling PET are the collection of used PET products, the different processes involved in methods of recycling, and the market for the final recycled products. There are four widely used techniques to recycle PET which are-

Property	Value
Melting Point	> 240 ^{0}C
Polyvinyl chloride content	< 50 ppm
Polyolefin content	< 10 ppm
Water content	<0.02 wt.%
Dye content	<10 ppm
Metal content	<3 ppm
Yellowing index	<20

Table 1. Property requirements for the recycling of PET waste [8]

(i) Primary recycling which uses pre-consumer industrial scrap (ii) Secondary recycling which involves mechanical processes (iii) Tertiary recycling which includes utilization of chemicals for treatment (iv) Quaternary recycling which involves incineration for energy recovery of the waste. 'Zero Order' recycling method for direct reuse of waste products is also practiced. [2]

2.1. Primary recycling

The primary recycling method, also known as pre-consumer industrial scrap, is one of the oldest methods for PET recycling. In this process, waste scraps with comparable properties are recycled in-plant. The first stage of this technique is cleaning followed by the removal of any contaminants from the product. Then it is blended with new raw material to obtain desired properties and quality of the end product. Thus, this method is simple and cost-effective but is suitable only for uncontaminated waste materials or for materials with very low levels of contamination.

Besides, this method is useful for only one type of waste material and is therefore not favored by many. [9]

2.2. Secondary Recycling

Mechanical recycling, also termed secondary recycling, is the technique in which many processes are used to turn the plastic waste into a useful form. The first stage includes several steps for the removal of contaminants from the waste which is then undergoing melt extrusion in the later stage for reprocessing into granules.
Secondary recycling can be categorized into two: the first category includes turning the plastic waste into a granular form. It is then blended with the virgin material to obtain the same original end product. In the other type, the pellets are used to produce a variety of materials instead of utilizing the pellets to make the same end product. Figure 2 shows the steps involved. [3]

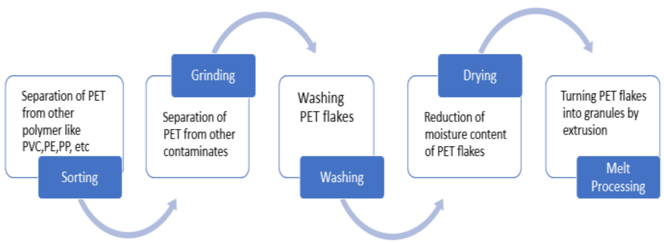

Fig 2. Mechanical Recycling Process

The removal of impurities consists of three vital processes namely in sorting, grounding, and washing. In the sorting step, the bottles are separated from other products. In the next stage that is grinding, the bottles are ground into flakes. These flakes are then washed by either of the two methods that is a hot washing in 2% aqueous NaOH solution containing detergent at a temperature of 80 °C which is followed by cold washing mostly with water or by washing with a solvent such as tetrachloroethylene which is the most favorable solvent for washing flakes. [3] The next crucial step is drying as it reduces the moisture content of PET flakes, which results in the reduction of the effects of hydrolytic degradation. The last stage is melt processing which turns the flakes into valuable granules by extrusion process. Two methods are used for this purpose, a direct one that turns PET flakes directly into fibers by an extrusion process, and the second method which consists of the formation of pellets by reprocessing of PET flakes followed by their melt extrusion into fibers. [10]

When compared to the tertiary recycling methods, secondary recycling is not only relatively straightforward, cost-effective, flexible but also causes very little harm to the environment. [11] But the major disadvantages of this process include the complex nature of waste and deterioration in properties with every cycle which makes recycling difficult. In the presence of even a trace quantity of acidic impurities during the preprocessing step, hydrolytic degradation can result in a decrease in the molecular weight of the material. Furthermore, the formation of cyclic oligomeric products can also take place which affects properties like dyeability or printability of the end product. Also, there is a possibility of yellowing of the product due to oxidative reactions and intramolecular crosslinking which drastically affect the final product.

2.3. Tertiary Recycling

Tertiary or chemical recycling involves advanced processes that break down plastic material into different products which can be further purified by different methods. As discussed previously, PET is a polyester containing an ester group that can undergo different chemical reactions resulting in the synthesis of different products as shown in Figure 3. [4] As chemical recycling ensues the creation of different raw materials from the PET waste including the original reactant for PET, this method is the most acceptable one as per the fundamentals of sustainable development.[12] In this method, the waste is treated with different chemicals to obtain monomers and a mixture of products like Terephthalic acid (TPA), dimethyl terephthalate (DMT), various glycols, bis (2-hydroxy ethyl) terephthalate (BHET) as well as a variety of liquids, gases, fuels, etc.[13].

The major important advantage of this method over others is that the molecular weight and intrinsic viscosity of the PET material are conserved. [14] Also, we can recycle very complex and highly contaminated waste as per the desired requirements. [15] The necessary properties like workability, printability, and dyeability of the final product

can be obtained for the required grade without the yellowing of the product. However, as chemical reprocessing requires higher costs and advanced equipment, the manufacturing cost of the end product is significantly more especially when compared to the products made entirely with virgin raw materials.
The important depolymerization process in chemical recycling involves the reaction of waste with different reagents like acids, alkalis, and water in hydrolysis; alcohols majorly methanol and ethanol in alcoholysis process; various glycols and salts in case of glycolysis; amines in aminolysis and ammonia during ammonolysis. The use of some hybrid processes like glycolysis hydrolysis, alkaline hydrolysis extrusion, etc. has also been reported. [16]

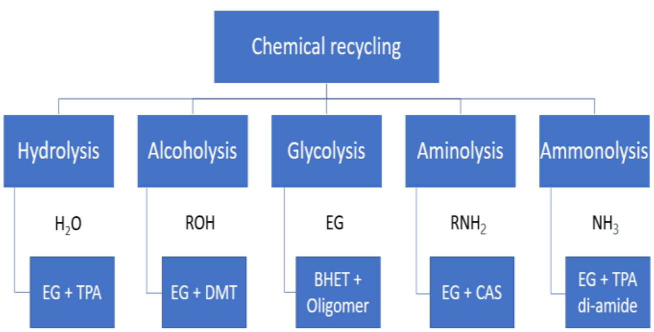

Figure 3. Classification of the chemical recycling methods centred upon the products of each reaction. BHET bis (2hydroxyethyl) terephthalate; DMT dimethyl terephthalate; TPA terephthalic acid; EG Ethylene Glycol; CAS 1,4-diisocyanatobenzene.

2.3.1. Hydrolysis

Hydrolysis is a process of recycling PET waste by reacting in an acidic, alkaline, or neutral atmosphere with water PET, resulting in its complete depolymerization in the favorable conditions into its monomers. This is one of the most significant chemical recovery strategies. [2] As water is a weak nucleophile among the depolymerizing agents, hydrolysis is sluggish when compared to glycolysis and methanolysis. The hardship of recovering monomers is another downside of hydrolysis, which involves multiple steps to obtain the necessary purity.

2.3.1.1 Acidic Hydrolysis

Using distilled sulphuric acid (H_2SO_4) as well as other mineral acids like phosphoric or nitric acid, acid hydrolysis is often carried out. The addition of condensed sulphuric acid made it achievable at the synthesis level to prevent elevated pressure and temperature. It was observed that almost complete depolymerization happens no sooner at the temperature of 900ºC than at a concentration of sulphuric acid of over 80 percent. The reaction speed decelerates very fast below 76 mph. At temperatures of 600ºC and less, the volume of unreacted PET often increases dramatically. However, the immense corrosivity of the reaction system is due to presence of concentrated sulfuric acid (H_2S0_4) and the production of vast amounts of aqueous wastes and inorganic salts are a major downside of PET hydrolysis. [16] Waste PET bottles can be degraded by using nitric acid at a temperature range of 70–100ºC and pressure range of about 7 to 13 MPa for a reaction time of 72 hours. [17] This process also results in the synthesis of oxalic acid and other value-added products along with primary reaction products. This is beneficial as their cost is higher than that of ethylene glycol and terephthalic acid.

2.3.1.2. Alkaline Hydrolysis

The alkaline hydrolysis of PET is done by using a reagent such as the solution of strong bases like sodium hydroxide or potassium hydroxide at a concentration of about 4-20 weight %.[3] The products obtained from this reaction are disodium or dipotassium terephthalate chloride ($TPA\text{-}Na_2$ or $TPA\text{-}K_2$) and ethylene glycol. The recovery of ethylene glycol which is obtained as a product is done by distillation at temperatures up to 340^0C.

By the use of a strong mineral acid like concentrated sulphuric acid, the mixture can be neutralized to obtain terephthalic acid in the pure form. Temperature range of $210\text{-}250^0C$ and pressure of about 1.4 to 2 MPa is provided for a reaction time of 3 to 5 hours. [18] Remarkable yield can be obtained by performing the reaction at a temperature of 200^0C and with the use of aqueous NH_3 solution as a reagent. The reactivity of sodium hydroxide aqueous solutions and various sodium oxides in different alcohol solutions with PET were contrasted by Namboori and Haith. [19] They concluded that among all the reagents tested, sodium ethoxide in ethanol was the most reactive whereas; aqueous solution of sodium hydroxide had comparably lower reactivity. Alkaline hydrolysis can also be carried out by using phase transfer catalysts such as tri octyl methyl ammonium bromide which acts as the lipophilic group. Thanks to this application of phase transfer catalysts, it has become possible to ease the conditions of a PET hydrolysis reaction even at temperatures below 100^0C. [20]

2.3.1.3. Neutral Hydrolysis

Neutral hydrolysis of PET is carried out at temperatures in the region of 200 to 300ºC in high-pressure autoclave reactors and at pressures range of 1 to 4 MPa using an excess of water. [3] Temperatures of more than 245^0C are generally selected for this process as the reaction rate is better when PET is in molten form rather than in solid state. Neutral hydrolysis is preferred over acidic or alkaline because this process results in the formation of significantly lesser amounts of inorganic salts and thus is more environmentally favorable in nature. However, the purity of products obtained can be substantially lower as the impurities present in PET remain in terephthalic acid. [16]

2.3.2. Alcoholysis

Alcoholysis is the high temperature ($180\text{-}280^0$C) and pressure (2-4 MN/m2) transesterification reaction of an alcohol with PET accelerating to generate N, N-dimethyltryptamine, and ethylene glycol as monomers. This process is generally carried out using an organometallic catalyst. [12] Methanol for methanolysis is a widely used alcohol, but ethanol and others can also be used as a digestive medium. Currently, methanolysis is successfully used in fiber waste, scrap bottles and used films. [4] In this case, the waste produced during the manufacture of PET may be conveyed directly to the process of alcoholysis and can be reused to create the polymer in this manner.

If the mechanism is disrupted by water, it poisons the catalyst and forms different azeotropes. Deactivation of catalysts is also of utmost importance to prevent transesterification of dimethyltryptamine with ethylene glycol into diethylene glycol terephthalate and PET. The structure of the substance is a mixture containing DMT as the main product along with glycols, derivatives of phthalates, and alcohols. [12] This mixture of complex compounds makes it wasteful and very tedious for isolation and refining, thus making the techniques of hydrolysis and glycolysis more superior.

2.3.3. Glycolysis

Glycolysis occurs because of a transesterification reaction of PET wastes with excess glycol within the temperature range of $180\text{-}240^0$C and at higher operating conditions in the presence of a variety catalyst along with solvents. Glycols result in breakage of ester linkages to produce products like various oligomers. [2] The most widely employed catalysts include organometallic salts of metals like zinc, lead, magnesium as well as zeolites, ionic liquids, and other chemicals. Products formed by glycolysis can also be further used to produce various other polymers like polyester polyols, unsaturated polyester resins, polyurethanes as well as urethane oil varnishes and softeners. [24] Therefore, it is one of the widely studied and extensively used methods of chemical recycling of PET waste.

However, there are still some drawbacks accompanying the glycolysis process. It is very difficult to completely remove additives, dyes, catalyst residues and other impurities from the end product. [25] Further purification is extremely necessary for the synthesis of high-quality PET end products suitable for use in food and pharmaceutical industries. [26] However, due to the variety of catalysts, synthesis of a myriad of products with the desired properties is possible. Thus, glycolysis proves to be an economically flexible process and is currently the most successful option of PET recycling.

2.3.3.1. Solvent-assisted glycolysis

In the solvent assisted glycolysis process, PET is degraded by glycols along with a solvent like xylene which serves as the reaction medium. Initially, the solvent acts as a medium to enhance the mixability of the mixture containing glycol and PET. When PET is glycolysis with ethylene glycol, xylene as a solvent and zinc acetate as the catalyst, the yield of product BHET obtained is better than that of glycolysis without xylene. [27] Ethylene glycol readily dissolves in PET between the temperature range of 170°C and 225°C but only frugally dissolve in xylene. The products obtained from the reaction are, however, readily soluble in xylene. Thus, as the reaction proceeds, the equilibrium is shifted in the forward direction that is for degradation of PET to glycolysis products like BHET. By this process, higher yields of products can be achieved but as the solvents used can have adverse effects on the environment, further investigations in this process are currently very restricted. [28]

2.3.3.2. Supercritical glycolysis

By the supercritical glycolysis method, PET is degraded with the use of glycols like ethylene glycol at pressure and temperature conditions beyond the critical state of the used glycol. Such conditions have previously been investigated in hydrolysis as well as alcoholysis methods of recycling but have only recently been explored in the field of glycolysis technique. [28] This method could prove to be beneficial as along with being environmentally favorable, it also eliminates the requirement of catalysts to be used which might involve complicated processes for segregation from the products obtained. However, higher operating conditions required might complicate the process when compared to other methods.

2.3.3.3. Catalyzed glycolysis

Uncatalyzed glycolysis of PET requires higher operating conditions along with a much longer process duration for the formation of the desired end products. Therefore, catalytic glycolysis is one of the widely studied methods of improving the glycolysis rate. Metal-based catalyst mostly used for transesterification reaction is the widely used catalyst.

The rate of glycolysis reaction is dependent on various factors including the ratio of PET to glycol used, the type and loading of catalyst required, and the required reaction conditions which involve the temperature and pressure ranges. Furthermore, the reaction of PET producing BHET is reversible. Therefore, it is extremely important to conduct the reaction at optimum conditions as any disturbance in equilibrium can result in a backward shift which is not at all desirable. [28]

2.3.3.3.1. Metal salts

Metal acetates are one of the first reported among the metal salt catalysts used for glycolysis reaction of PET. Polyester polyols were produced from PET waste first by using zinc acetate as catalyst. Metal salts catalysts are very successful in quickening the rate of reaction. But they can have a catalytic effect on the reaction only below the temperature of 245 °C. Due to mass transfer limitations, any increase in the rate is restricted above this temperature. As a result, in order to overcome this limitation, there was a need to develop a modern catalyst for glycolysis. Titanium (IV) phosphate has been introduced recently as a catalyst which shows faster glycolysis at the temperature of 200°C, for reaction time of 150 minutes and catalyst to PET w/w ratio of 0.003. The products obtained by this catalyzed reaction include about 97.5% BHET, which was drastically more than that obtained by using zinc acetate, which only provided 62.8 % BHET. [31]

Furthermore, zinc and lead are considered to be heavy metals that can have extremely adverse effects on the environment. Thus, efforts have been made to develop and introduce milder catalysts which are less harmful. By utilizing milder alkalis as well as sodium carbonate, monomer yield comparable to those obtained by involving metal acetate catalyst can be produced. [32] Other chemicals like lithium hydroxide, potassium, and sodium sulfate and glacial acetic acid, etc. can also be utilized for similar yields. [33] The BHET monomer produced by this reaction can be further utilized to make dyes and softeners which could be used in the textile industry. [34]

2.3.3.3.2. Heterogeneous catalyst

Homogeneous catalysts are very effective concerning their activity in the glycolysis reaction. But they present certain drawbacks, the major one amongst which is the problem of separation of catalyst from the end products obtained. Due to this, there is a need for an additional unit operation such as distillation which can complicate the process. [35] Due to this, heterogeneous catalysts like zeolites can be utilized as they have comparable catalytic activity. Zeolites have more surface area due to mesopores and micropores that also provide various active sites for the reaction to take place. Other catalysts like solid acids can also be utilized as they are non-corrosive and can be easily separated by filtration along with the lesser forms of additional waste products. However, these catalysts need higher operating conditions and there is no remarkable improvement concerning yield when compared to other homogeneous catalysts. As a result, there is an urgent need to introduce a better catalyst for the efficient breakdown of PET wastes with increased yield. [25]

2.3.3.3.3. Ionic liquid catalyzed glycolysis

Ionic liquids present an interesting solution to the problem of catalyst removal faced by homogeneous catalysts. Ionic liquids are basically salts present in the liquid state with melting point of less than 100 ℃. As there is more charge distribution in larger unsymmetrical ions, the melting point of these liquids can even be below 0℃. These liquids having some interesting features like good thermal stability, low flammability, and non-volatile nature. [36]

But the major benefit of ionic liquids over traditional catalysts is the simplified purification process to obtain the reaction products. Thus, these liquids could be extremely favorable for the glycolysis process of PET waste. Acidic, basic, and neutral are the major three varieties of ionic liquids available. Acidic liquids can be used only below the temperatures of 180 ^{0}C, as beyond this temperature they become unstable. [37] On the other hand, the production of basic ionic liquids is complicated and expensive, but they provide higher rates of PET depolymerization. Neutral liquids are synthesized by a simple process; they are stable at higher temperatures and are the most eco-friendly of the three. They can be synthesized by integrating metals on ionic liquids. For example, metals acetates can be added to these ionic liquids to form catalysts like 1-butyl-3-methylimidazolium acetate with copper acetate and 1-Butyl-3-methylimidazolium acetate with zinc acetate. 100% breakdown of PET is possible by using this catalyst at 180 ℃ after the reaction time of about 8 hours. [38] Another catalyst 1-butyl-3 methylimidazolium bromide proves to be the best catalyst with respect to PET conversion and in straightforwardness and economics of synthesis. [37]

2.3.4. Aminolysis

When amines are reacted with Polyethylene terephthalate, the corresponding diamines of ethylene glycol and terephthalic acid are obtained as products. The translation of PET into ethylamine, methylamine, dimethylamine, and trimethylamine, as products shows a close reaction rate. Out of these, the maximum product yield of monomers is obtained by using triethylamine. [40] Aminolysis of PET with ethanolamine results in the synthesis of bis(2-hydroxylethyl) terephthalamide (BHETA) which can further undergo reactions to produce value added secondary products. Though this process has been studied by conducting the reaction with a variety of amines solutions namely hydrazine, benzylamine, piperidine, hexamethylenediamine, aniline and piperidine, it has not yet been successfully applied on a commercial level. [33]

For enhancing the properties of PET in fiber production method, partial aminolysis of PET has been carried out using methylamine, ethylamine, butylamine, ethanolamine and triethylenetetramine at a temperature range of about 20-100ºC. The reaction can be conducted in a gas phase or in an aqueous solution. [45] The products obtained by this process can potentially be used as synthon for the synthesis of polyurethanes particularly, rigid polyurethane foams. [46]

Reactants	Reactant Ratio (w/w)	Catalyst used	Catalyst /PET Ratio (w/ w)	Temp (°C)	Time (min)	Conversion of PET (%)	Yield of BHET (%)	References
EG/PET	4:1	Zinc acetate	0.0033	196	120	100	76.7	(Lima et al., 2017) [39]
EG/PET	4:1	Titanate Nanotubes	0.0033	196	120	100	82.6	(Lima et al., 2017) [39]
EG/PET	10:1	(Mg-Zn)-Al layered double hydroxide	0.01	190	180	100	90	Eshaq and Elmetwally (2016) [40]
EG/PET	5.63:1	SO42-/ZnO-TiO2	0.0033	180	180	100	91.9	Zhu et al. (2012) [41]
EG/PET	2.45:1	Na2CO3	0.01	196	60	75	78.8	Lopez-Fonseca et al. (2011) [42]
DEG/ PET	9:1	Potassium acetate (K(OAc)2)	0.01	210	180	100	93.94	Raheem and Uyigue (2010) [43]

Table 2. Glycolysis of PET waste using different catalysts.

2.3.5. Ammonolysis

The degradation of polyethylene terephthalate by using ammonia is called ammonolysis. Similar to glycolysis, different metal acetates can be used as catalysts in this method. According to studies conducted, zinc acetate was the most efficient among these catalysts. Potassium acetate and sodium acetate produced comparable results. [47] When ammonolysis of PET bottles is carried out for 1 to 7 hours at 120-180^{0}C using 0.5% of zinc acetate as catalyst, terephthalamide and ethylene glycol are obtained as products. Generally, a pressure of 2 MN/m^2 is applied but the process is also possible under lower pressures. The amide thus synthesized is filtered, rinsed with water, and then dried at a temperature of 80^{o}C. The resultant product has a purity of about 99% and yield of reaction is more than 90%. [48] Furthermore, terephthalamide is an intermediate product which can be used for the manufacture of terephthalonitrile. This compound can further undergo hydrogenation and can be converted to p-xylylene diamine or 1, 4-bis (amino-methyl) cyclohexane. [12]

2.4. Quaternary recycling

Today, there are several polymer nanofibers including those made with polymers like polyvinyl chloride (PVC), polyvinyl alcohol (PVA), polycaprolactone (PCL), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), and polypropylene (PP). These nanomaterials have been used in various fields including textile industries, medicine, the manufacture of integrated circuits, water treatment by catalysis, in improving battery performance, and others. However, the research about the application of cementitious materials has been limited. In the construction industry, fibers and microfibers made with carbon, Quaternary recycling, or energetic recycling are used whenever the collection, sorting, and separation of waste material are complex or not cost-effective, or when handling of the materials to be recycled is hazardous. As recycling cycles of polymers are limited, products that no longer harbor the desired properties are recycled by this process. Incineration is utilized to recover the energy content from the waste material. The PET waste is reduced to water and gases like carbon dioxide at a very high temperature preferably in the presence of air. The heat energy obtained from this is utilized to produce electricity for industrial and domestic buildings and also for turbine generators. But energetic recycling can produce airborne harmful chemicals like dioxins. [2] Therefore, despite being the origin of energy, this technique is not acceptable from an ecological point of view. Owing to this recognized risk of environmental pollution, the incineration of plastic is not very frequently used as a technique for managing waste. However, incineration plants in some European countries, which can capture toxic combustion products, are being developed as a possible solution to this problem.

3. New Developments in PET Recycling

We have discussed various methods of Recycling PET plastic (RPET), but the current methods still have their limitations. Hence advancement in methods to recycle PET more efficiently is the need of the hour. The existing recycling techniques are not as useful because PET containers contain contaminants like food particles.

3.1. Nanotechnology

Unfortunately, RPET has limited use since the recycling process causes a detrimental change in the material properties including mechanical and thermal properties, electrical conductivity, among others. Consequently, it is necessary to identify alternatives to reduce this effect. One possible option is to synthesize a composite material of RPET with another polymer. [49] Among the wide range of available polymers, polyacrylonitrile (PAN) is a good candidate considering the following characteristics: it improves the mechanical properties, has a high melting point, it is non-toxic, has a good chemical stability and it is technically viable to produce fibers. To produce composite materials, PAN has been combined with methylammonium lead triiodide (MAPbI3), polyvinylidene fluoride (PVDF), selenium disulfide (SeS2), graphene oxide (GO), and iron oxide (FeO), among others. With these precursors, nanomaterials such as nanoparticles, thin films and nanofibers have been synthesized. Nanofibers have some remarkable properties including high surface to volume ratio, good mechanical and thermal properties, high aspect ratio, light weight, etc. Special attention has been paid in the last decade to nanofibers due to these properties which can be extremely advantageous.

Today, there are several polymer nanofibers including those made with polymers like polyvinyl chloride (PVC), polyvinyl alcohol (PVA), polycaprolactone (PCL), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), and polypropylene (PP). These nanomaterials have been used in various fields including textile industries, medicine, the manufacture of integrated circuits, water treatment by catalysis, in improving battery performance, and others. However, the research about the application of cementitious materials has been limited. In the construction industry, fibers and micro-fibers made with carbon, PP, nylon, cellulose, PVA, and PAN have been used to improve the mechanical properties, durability, and drying shrinkage of cementitious materials. [50] Some studies have reported the use of PVA nanofibers, carbon nanofibers (CNF), and PET nanofibers. However, nanomaterials can be extremely difficult to manipulate and also have much higher costs, especially when compared to conventional materials. Thus, the evolution in the field of nanomaterials applications has been limited. Nevertheless, the benefits of nanotechnology far outweigh its drawbacks, making it an extremely promising alternative for PET recycling.

3.2. Enzymatic degradation of PET

Polyethylene terephthalate can contain amorphous and semicrystalline structures according to the thermal processing conditions. The flexibility of amorphous structures in PET increases after reaching the glass transition temperature and these sections are subjected to hydrolysis reaction by polyester hydrolase. Therefore, it is favorable to perform an enzymatic degradation reaction above the glass transition temperature of PET using thermostable biocatalysts. Ethylene glycol and terephthalic acid are obtained as the main products when polyester hydrolase reacts with amorphous PET. Two main compounds namely (2-hydroxyethyl) terephthalate (BHET) and mono-(2-hydroxyethyl) terephthalate (MHET) are synthesized as intermediate products in this process. By further subjecting these intermedial compounds to hydrolysis reaction, it is possible to synthesize the basic raw materials for PET that is ethylene glycol and terephthalic acid as well.

Two polyester hydrolases namely lipase and cutinase which are both obtained from fungal and bacterial sources are currently the most promising catalysts for this process. These hydrolases, especially cutinase, have been developed to sliver the ester bonds present in plant-based polyester compounds. As a result, their behaviour against PET, a synthetic polymer, is usually very minimal for a biocatalytic reaction to take place. There have been efforts to enhance the activity as well as thermostability of these hydrolases either by protein engineering or by structural interpretation of enzymes. This has resulted in the fabrication of highly active biocatalysts which has ultimately led to an improved understanding of their mechanism. [51] Overall, the enzymatic degradation of PET is a quite promising process which is also an environmentally favorable alternative to the standard methods of recycling PET.

Conclusion

Since Polyethylene terephthalate is small in weight, its feedstock is easily available and inexpensive, and the energy required for processing and packaging PET for consumer goods is the lowest for other commodities, even the poorest of the poor can afford PET products for mass consumption. This has culminated in the single-use of mass consumption PET products and, as a result, a substantial amount of those products was dumped into the garbage. There has been a comprehensive analysis of traditional and exemplary PET recycling, with a particular focus on chemical processes. Main recycling, but involving uncontaminated scrap, is easy and low cost and only works with single-type waste. A mechanical method with the benefit of ease, low cost, versatility, and less environmental impact was secondary recycling. This approach had problems with molecular weight reduction, as well as a drop in intrinsic viscosity during the process. Hydrolysis, alcoholysis, and most notably, glycolysis are involved in tertiary recycling. This method is one of the most commonly studied chemical recycling processes for PET. A long way has gone through this process. The glycolysis of PET is still far removed from its height. The key issues to be tackled in the future are the production of eco-friendly catalysts that produce lower yields than those that are not so eco-friendly (e.g., metal oxides). For an effective, sustainable, environmentally friendly, long response time and less energy-intensive way of chemically recycling PET, researchers have produced catalysts that are environmentally sustainable, recyclable, and reusable; a process that does not require catalysts, and many others to increase the rate of reaction and the yield of BHET monomer synthesized.

There may be several more methods of breaching the barriers, and alternatives may be found shortly with the rapid development of innovations such as nanotechnology. The biggest challenge now facing us is to have an efficient, sustainable, environmentally friendly, and less energy-intensive way of chemically recycling PET. There may be several more methods of breaching the barriers, and alternatives may be found shortly with the rapid development of innovations such as nanotechnology. Industries now shift towards biodegradable polymers synthesized from sources derived from naturally occurring monomers such as vegetable oils, biomass, etc. Nevertheless, waste plastics, particularly in countries where feedstocks of hydrocarbons are scarce and expensive, should be considered valuable resources. To address this issue, effective technologies, regulations, and waste management practices should be implemented based on the socioeconomic component of the region. PET recycling, though, is still far from its peak; an inexpensive and environmentally safe way to compost PET chemically is still unexplored.

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