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Different methods for returning PET into the economic cycle: A review

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Abstract

Polyethylene terephthalate (PET) is a saturated polyester, which is widely utilized in the production of films, bottles, and fibers in terms of its excellent thermal stability, clarity, strength, and moldability. PET waste has increased as the manufacture and consumption of PET bottles have increased. Major environmental and financial problems have resulted from the disposal of PET bottle waste. Both clear PET bottles and colorful PET bottles are recycled using various methods. However, it is possible to recycle PET trash by chemically replicating the monomers, separating them, and creating new PET from them. Here, we review the synthesis, characterization, and different methods for PET recycling as well as the commercial exploitation associated with the recycling and re-use of them.

Keywords: *Polyethylene terephthalate (PET), Polyester, Recycling, Plastics, PET waste*

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1. Introduction

Polyethylene terephthalate (PET) is a group of polyester polymers which are used widely in everyday items, such as rigid and flexible packaging of foods and beverages. PET is a kind of strong, hygienic, and clear plastic with a lightweight and beneficial cost profile leading to meeting high-end application demands globally. It is used to make containers that can be warmed in an oven or microwave and is known as "Polyester" in the fabric business. In the 1930s, polyester was created for the first time as a synthetic fabric. In order to create industrial or clothing fibers, many of the PETs manufactured today are often combined with natural fibers like cotton and wool in the latter case. For example, fleece pullovers are made of PET fiber. In the early 1950s, the use of PET extended to packaging films. PET film is used as a carrier for films and magnetic tapes. PET bottle manufacturing process was developed in the 1970s. PET bottles were originally used for soft drinks, but their application for bottled water has gradually expanded. Besides, PET containers are resistant to attack by micro-organisms so they are preferred for the packaging of pharmaceuticals. One of the most important properties of PET is sustainability and recycling making it the most recycled plastic in the United States and worldwide. PET has a positive environmental effect despite being petroleum-based. On the one hand, it is less heavy and requires less fuel to transport than alternative container materials like glass and aluminum. Ongoing advances in technology continue to decrease the weight of PET containers and boost the energy efficiency of PET even more. For instance, a two-liter PET bottle weighed approximately 68 grams in 1980; today it weighs between 42 and 45 grams [1]. Owing to these favorable properties, PET is the most recycled plastic over other types of plastics because of the mentioned multiple advantages. It is already extensively employed in many different industries, particularly for creating artificial vascular scaffolds. It also has a wide range of distinctive qualities, including transparency, solubility, wrinkle resistance, exceptional barrier resistance, fatigue resistance, and high toughness [2]. According to the recycling international website, the distribution of PET packaging consumption worldwide is forecast to reach 20.8 million tons in the next five years [3] and it accounted for 34.6 percent of global PET just for bottled water packaging consumption in 2019 as illustrated in Figure 1 [4].

PET was first synthesized in the United States in the mid-1940s by DuPont chemists looking for polymers that could be used to make new fibers. DuPont later called these polyester fibers "Dacron" [5]. Technology was created in the early 1970s to enable PET to be stretch blow molded into sturdy, light, and unbreakable bottles. PET bottles were first invented in 1973 and quickly became popular. In 1977, the first PET bottles were recycled. PET is one of the most popular, adaptable, and tested materials in use today. PET resin is used to make almost all single-size and 2-liter carbonated soft beverages and water marketed in the United States, as well as more than half of the world's synthetic fibers. PET recycling is a developing industry because industrialized human society relies on plastic. Society can move towards a circular economy approach by recycling effectively and of high quality, thus protecting nature and the environment for future generations. The European Food Safety Authority under the European Recycling Regulation 282/2008, which went into effect in 2008, must separately certify every recycling procedure. (EFSA).For this evaluation process, EFSA has developed a conservative evaluation concept to protect consumers. Welle reported in 2013 that super-clean recycling is used for bottle-to-bottle recycling of PET and there is no risk at all for consumers, even when PET bottles are sporadically used for storing non-foodstuffs and when these end up in the PET recycling stream [6].

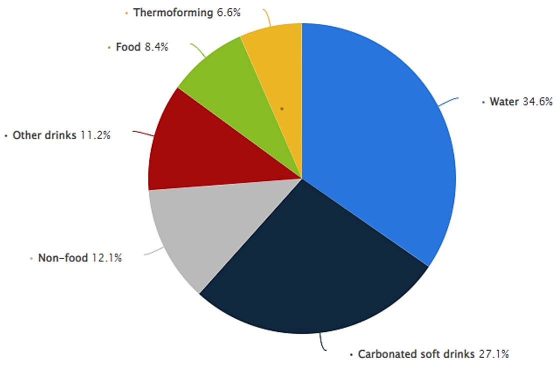

Figure 1. Global PET packaging consumption in 2019 [4].

Saint Jude Polymers was the first company in the USA that set up a process to recycle PET bottles in 1976. In their process, the bottles were recycled into plastic straps and brush bristles, and a year later, the company began producing pelletized recycled PET for the general market. Later in the 1990s, with the availability of appropriate recycling techniques, the US Food and Drug Administration began issuing a "no objection letter" regarding the use of PET in food contact packaging applications [7]. In this review, we discuss PET synthesis, characterization, and recycling practices.

2. Synthesis procedure

Production of PET essentially involves four stages: (1) transesterification or direct esterification, (2) pre-polymerization, (3) melt polycondensation, and (4) solid-state polycondensation. A schematic diagram (Figure 1) shows the different stages.

The commercial PET resin production is from ethylene glycol (EG) and either dimethyl terephthalate (DMT) (Figure 2) or terephthalic acid (TPA). Both DMT and TPA are solids, the melting point is 140°C while TPA sublimes at 427 °C. In both processes, the intermediate bis-(2-hydroxyethyl)-terephthalate (BHET) monomer is first generated using either methanol (the DMT procedure) or water (the TPA procedure), and the BHET monomer is then polymerized with heat and a catalyst under decreased pressure to create PET resins. Both procedures may create PET with low and high viscosities.

A transesterification or a direct esterification process prepares BUET intermediate in which there are three main reversible reactions including ester interchange reaction, transesterification reaction, and polycondensation reaction [8]. Two Ziegler-Natta catalysts were employed by Bingquan et al. to speed up the polymerization of ethylene. After comparing the findings with those obtained using commercial catalyst N-catalyst (BRICI), they demonstrated that the Ziegler-Natta catalysts had higher activity, better hydrogen response, and better copolymerization performance for the ethylene polymerization process [9]. They study the effects of the catalyst on the kinetic behavior, hydrogen response, and copolymerization process. Solid-state polycondensation (SSP) is a method used for preparing bottle-grade chips. The traditional manufacturing SSP process is divided into two distinct plant portions. The melt phase process results in a product with a lower inherent viscosity that is appropriate for textile applications but not for bottle grade or other high molecular weight applications. In a solid-state polymerization section, the lower intrinsic viscosity material is further polymerized to bottle-grade intrinsic viscosity [10]. Recently, Vazquez-Duhalt et al. reported a simple and efficient method for producing PET nanoparticles at a large scale as shown in Figure 3. According to this method, the drink bottle is used as the initial material, and after grounding and sieving steps; it is dissolved in concentrated trifluoroacetic acid solution (TFA) stirring until complete dissolution. Then, it remains overnight in order to remove micro/nanoparticles. In the next stage, it is centrifuged and the supernatant is re-suspended in 0.5% sodium dodecyl sulfate (SDS) which finally is led to nanosized PET particles. This NanoPET suspension is long-lasting and can be dried if necessary. This method is a simple and effective means of creating PET nanoparticles. It is important to highlight that utilizing this method, it is possible to produce large amounts of materials without enduring any chemical changes [11].

Maslak et al. published a comprehensive report on PET precursors and potential degradation products as well as the structural analysis of possible degradation products and their ecotoxicological assessment. They investigated 11 chemicals from the PET precursors and potential breakdown products group. They predicted the in-silico drug-likeness and physicochemical

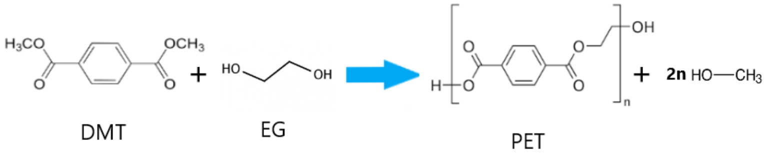

Figure 2. The commercial PET resin production.

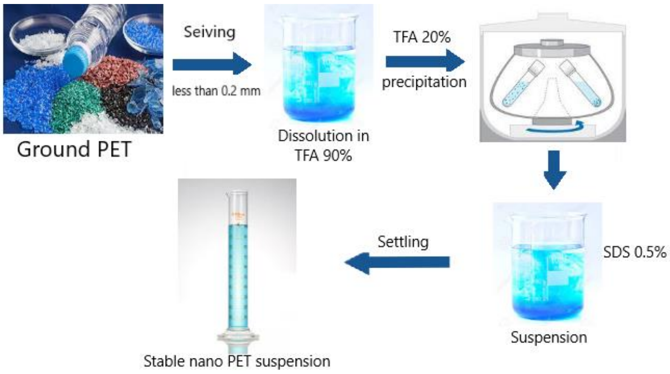

Figure 3. Synthesis of nanosized PET particles

properties of these compounds using different platforms; the results showed no antimicrobial properties even at 1000 mg/mL. The eco toxicological impact of the chemicals on marine microorganisms' PET trimer was one of the most toxic molecules tested on Allivibrio fischeri bacteria, with six of eleven PET-associated compounds found as toxic to aquatic microorganisms. In contrast, most of the compounds were not toxic to human lung fibroblasts. Only three of these compounds including PET monomer were toxic to nematode Caenorhabditis elegans at a high concentration of 500 mg/mL. PET dimer can be utilized as screening, identification, and characterization substrate for novel PET-depolymerizing enzymes (Figure 4) [12].

3. Characterization

PET is a thermoplastic that comes in two forms: amorphous (transparent) and semi-crystalline (opaque and white). It is resistant to mineral oils, solvents, and acids in general, but not to bases. Semi-crystalline PET is strong, ductile, stiff, and hard, but amorphous PET is more ductile. PET is very simple to process and recyclable for use in other goods. One of the most important characteristics of PET, intrinsic viscosity is dependent on the length of its polymer chains and is measured in deciliters per gram (dl/g). The longer the polymer chains, the more the entanglements between them, and hence the greater the viscosity. During polycondensation, the average chain length of a batch of resin can be adjusted [10]. The IR spectra are used for detecting trace chemical additives presented and related to polymer or bottle manufacture that could migrate from bottle to water. Figure 5 shows IR spectra for PET bottles in which two bands at 1340 cm-1 and 1370 cm^{-1} correspond to the ethylene units in different conformations, respectively [13]. DSC is another method used for detecting PET and results indicated that the bottleneck is practically amorphous with a crystallinity ratio not exceeding 14% and a glass transition temperature Tg of 72°C. Furthermore, there is not an exothermic peak on heating confirming the crystallization of PET in the stretched part of the bottle due to the blowing process [14]. According to Li et al., typical PET characteristics include high hardness, stiffness, and strength in thermoplastic, high dimensional stability, an extended temperature range for service from -40°C to 100°C, white color in the semi-crystalline state, and transparency in the amorphous state, as well as its resistance to heat and chemicals. Pet is not susceptible to stress cracking and is resistant to water, diluted acids, neutral and acidic salts, alcohol, ethers, oils, fats, aromatic and aliphatic

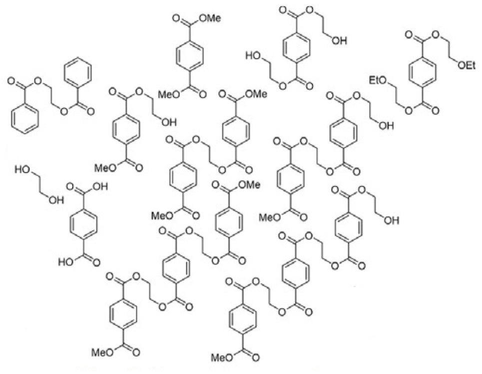

Figure 4. Synthetic model compounds and potential breakdown products pf PET.

hydrocarbons at room temperature. PET is not resistant to alkalis, superheated steam, phenols, esters, oxidizing acids, and chlorinated [10].

4. Methods of recycling

According to the extensive usage of PET, massive amounts of PET trash are generated each year, and reducing these amounts is an important part of any waste management strategy. Primary (re-extrusion), secondary (mechanical), tertiary (chemical), and quaternary (energy recovery) recycling are the four basic ways of recovering PET trash [15]. Chemical recycling of PET is included different methods, such as glycolysis, methanolysis, and hydrolysis. These processes led to the formation of raw materials or monomers of the polymers. Ethylene glycol and terephthalic acid are created as byproducts of hydrolysis, one of the crucial processes for recycling PET chemicals. There are three different types of hydrolysis: neutral hydrolysis, acid hydrolysis, and alkaline hydrolysis. However, the chemical recycling of PET has some disadvantages, such as requiring large-scale implementation to be cost-effectively viable, and attracting higher manufacturing costs than mechanical recycling with no economic incentive in terms of chemically reprocessed PET's higher production cost when compared to virgin PET, it has many advantages that can be listed as below:

- Disassembled PET scrap into monomers, oligomers, and other compounds,
- In comparison to other recycling technologies in the creation of indigenous raw materials, it only follows 'sustainability' principles. So, it requires no additional resources for PET manufacturing,
- It preserves the regenerated PET wastes' molecular weight [16],
- And tarnish yellowing of PET products does not arise during PET chemical recycling.

Škerget et al. used sub- and supercritical water (SubCW and SCW) to study the hydrolytic depolymerization of colorless and colored bottles in a batch reactor at temperatures from 250 to 400 °C, with a reaction period of 1–30 minutes. Primary and secondary products were generated during the hydrolysis of PET waste (Figure 5). This method led to obtaining TPA in high yield and purity on one hand and the other hand, the determination of chemicals such as IPA, acetaldehyde, 1,4 dioxane, and CO_2 in the concentration of secondary reaction products generated during the degradation of PET waste. Furthermore, in these reaction conditions, TPA was decarboxylated, producing the significant chemical benzoic acid. The findings indicated that method might be scaled up, the plastic monomers recycled, and value-added chemicals extracted for use in the chemical industry in addition to producing new plastics [17].

The ultrasmall ZnO nanodispersion was used as a pseudo homogeneous catalyst in the alcoholysis of PET by Wang et al. which demonstrated that in high temperatures (170°C), the conversion of PET improved PET conversion and DMT yield up to 95 percent and after a short period of time. They found that compared to PET glycolysis, PET methanolysis had a quicker response time (1/4) and greater activity (4.7 times). According to the findings, pseudo homogeneous ZnO nanocatalysts are very effective, recoverable, and reusable, making the process more sustainable and ecologically benign. Therefore, it is possible that this pseudo homogeneous nanocatalyst could be a promising technique for depolymerizing PET chemically [18].

The mechanical process is another way for recycling of the post-consumption plastic goods that involve the collection, handling, sorting, densification, shredding, melting, and granulation steps. This procedure is further divided into two types: primary recycling, which includes waste from manufacturing companies, and secondary recycling, which results in new items with inferior qualities to the originals [19]. By altering PET-based multilayer packaging materials, Edeleva et al. increased the possibility of mechanical recycling of PET. They created a thermoformable multilayer food packaging system using modified polyethylene terephthalate (PETM) for the outer layer that is suitable for hot-fill applications and can be recycled in a traditional waste stream. It is an amorphous co-polyester with a high glass transition temperature; thus, high thermal stability and transparency and 1,4-cyclohexylene was selected as the inner layer that consists of dimethanol-modified polyethylene terephthalate (dimethanol-modified PET), which is allowed to be recycled in a PET stream. The product exhibited some favorable properties including high thermal stability that make it applicable for hot-fill

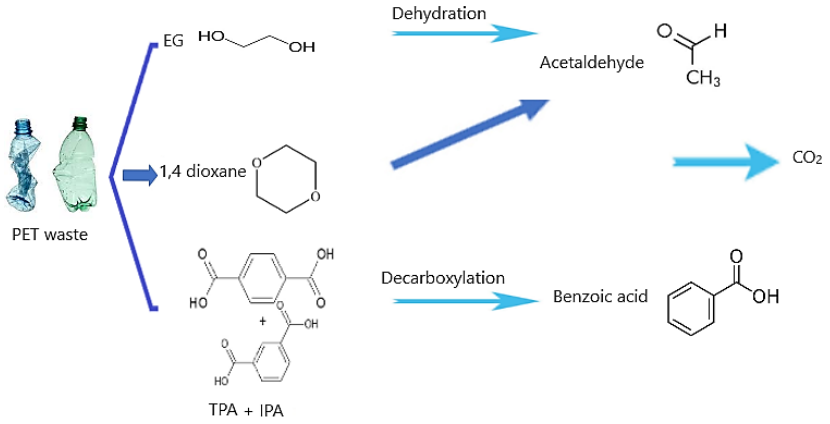

Figure 5. Potential pathways for PET

food packaging applications and high transparency as well as excellent recyclability [20].

Biocatalytic hydrolysis is another method for recycling PET and returning them to the circular plastics economy. The majority of the produced plastic waste is burnt or winds up in landfills or in the ocean and only roughly 9% of it is recycled [21], so researchers focused on thermostable polyester hydrolases such as lipases and cutinases from both fungal and bacterial origin as promising catalysts for the hydrolysis of PET [22]. Enzymes have previously shown their versatility when it comes to the modification and degradation of PET. Biocatalytic PET recycling, an emerging technological prospect, promises to be a more ecologically beneficial recycling option than traditional recycling, with the aim of replacing the single-use paradigm of plastic with a circular economy [23].

5. Conclusion

PET bottles are becoming more popular, and the number of post-consumer PET bottles is rising in tandem. Recycling PET bottles into new valuable chemicals are becoming increasingly significant, both commercially and environmentally. A clearer consensus can be created to guide future efforts for PET recycling and highlight the primary problems in investigating and deploying of PET breakdown processes. The public, environmental groups, governments, and corporate leaders all demand long-term solutions for plastic pollution, which has become a worldwide problem. Utilizing multiple described approaches has the potential to considerably boost productivity in large-scale industrial operations, enhance catalytic performance, and promote reusability for long-term applications. Furthermore, the separation and purification of depolymerized products can have a significant impact on the technology's profitability.

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