Methods of Recycling, Properties and Applications of Recycled Thermoplastic Polymers

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Abstract: This study aims to provide an updated survey of the main thermoplastic polymers in order to obtain recyclable materials for various industrial and indoor applications. The synthesis approach significantly impacts the properties of such materials and these properties in turn have a significant impact on their applications. Due to the ideal properties of the thermoplastic polymers such as corrosion resistance, low density or user-friendly design, the production of plastics has increased markedly over the last 60 years, becoming more used than aluminum or other metals. Also, recycling is one of the most important actions currently available to reduce these impacts and represents one of the most dynamic areas in the plastics industry today.

Keywords: plastics recycling; chemical recycling; environmental impacts; energy recovery

1. Introduction

Polymeric materials can be classified as thermosets and thermoplastics. Thermoset polymers refer to the irreversible polymerization and this type of polymer is cured by chemical reaction or heat and becomes infusible and insoluble material. Thermoplastics are made up of linear molecular chains and this polymer softens on heating and hardens when cooled [1–6].

Thermoplastic polymers are represented by a large range of plastic materials. There are three types of thermoplastic polymers:

- Crystalline thermoplastics, usually translucent with molecular chains which present a regular arrangement. Compared to other types, these polymers have more mechanical impact resistance. Examples of this type of polymers are polypropylene (PP), low-density polyethylene (LDPE), and high-density polyethylene (HDPE).
- Amorphous thermoplastics, usually transparent with the molecules arranged randomly. Examples of this type of polymers are polyvinyl chloride (PVC), polymethylmethacrylate (PMMA), polycarbonate (PC), polystyrene (PS), and acrylonitrilebutadiene styrene (ABS).
- Semi-crystalline polymers present combined properties of crystalline polymers and amorphous polymers. The representative polymers of this group are polyester polybutylene terephthalate (PBT) and polyamide Imide (PAI) [1,7–10].

These polymers present unique properties (physical, thermal and electrical) that make them suitable for many applications. The injection modeling process is the main technique of polymer processing which allows the fabrication of different kinds of parts, such as the computer mouse [11–15].

These plastic materials can be modeled into a variety of products for a wide range of applications due to the fact that thermoplastic polymers are inexpensive, lightweight and durable. In the last
decades, the production of plastics has increased significantly causing a big problem in the whole world regarding the discarded end-of-life plastics which are accumulated as debris in landfills and in natural habitats worldwide and by the management methods related to constantly growing resources of plastics. In the last years, the problem of recycled plastics was attempted to be solved by several methods (such as mechanical recycling or chemical recycling) leading to products ready to be used in determined conditions, in the most economic, ecological and rational way [16–23]. The purpose of this review is to present the advantages and disadvantages of thermoplastic polymers used in industrial applications, the processes used in the recycling and perspectives for a green bio-industry.

2. Recycled Thermoplastic Polymers

Due to the ideal properties of the thermoplastic polymers such as corrosion resistance, low density, high strength, and user-friendly design, plastic usage has become much higher than the usage of aluminum or other metals. For example, density is a very important parameter because it reveals information about the intrinsic strength of the construction that is supposed to be created, as in the case of flax reinforcement when PP and LDPE are the best choices (because of their low density) since its purpose is to produce a composite that is as light as possible. The glass transition temperature (Tg) is another characteristic that is very important when studying polymer mechanical properties, because the flexibility of amorphous polymers is reduced drastically when they are cooled below Tg. At these temperatures, there are no dimensional changes or segmental motion in the polymer. Also, the mechanical properties are very important in the case of thermoplastic polymers, mostly the tensile strength (important for their performance under stress) and tensile modulus (the resistance of the material to elastic deformation) [12,24–31]. The main thermoplastic polymers and their properties are presented in Table 1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Limits</th>
<th>Type of Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ (g/cm³)</td>
<td>Upper</td>
<td>PP  0.920</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>PP  0.899</td>
</tr>
<tr>
<td>Tg</td>
<td>Upper</td>
<td>−10</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>−23</td>
</tr>
<tr>
<td>σmax (MPa)</td>
<td>Upper</td>
<td>41.4</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>26</td>
</tr>
<tr>
<td>E (GPa)</td>
<td>Upper</td>
<td>1.776</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Also, the plastic manufacturing cost is lower due to its simple mass production (Figure 1). The main reasons which make the thermoplastic polymers used in various applications are:

- The thermoplastic polymers can be processed by several methods leading to various kinds of plastic products;
- They are used for a specific application several compounding, operating condition, additives, fillers, and reinforcements;
- Several manufacturing systems are used at this moment to produce plastic items with the lowest cost range [33–35].

The recycling and incineration are the usual aspects of recovery methods in the case of thermoplastic polymers. The incineration presents some problems like the production of toxic gases and the residue ash which contains lead and cadmium. The recycling presents advantages such as reduction of environmental problems and saving both material and energy [33,35,36].

![Collection → Separation → Manufacturing → Marketing](image-url)

Figure 1. The steps involved in thermoplastic polymers recycling.
The plastic can be degraded in the environment by four mechanisms: photodegradation, thermo-oxidative degradation, hydrolytic degradation, and biodegradation by microorganisms. The natural degradation of plastic begins with photodegradation due to the UV light from the sun which provides the activation energy required to initiate the incorporation of oxygen atoms into the polymer, leading to thermo-oxidative degradation. In this step, the plastic becomes brittle and its fracturing into smaller pieces until the polymer chains reach sufficiently low molecular weight to be metabolized by microorganisms. The microorganisms convert the carbon of the polymer chains to carbon dioxide or incorporate it into biomolecules, but this process will take at least 50 years [36]. So, a solution to these problems will be the recycling, because most commodity plastics are relatively stable, making monomer recovery poor.

2.1. Primary Recycling

The most popular process is represented by the primary recycling due to their simplicity and low cost. This process refers to the reuse of products in their original structure. The disadvantage of this process is represented by the existence of a limit on the number of cycles for each material [18,36,37].

2.2. Secondary Recycling or Mechanical Recycling

In this process, only the thermoplastic polymers can be used, because they can be re-melted and reprocessed into end products. The mechanical recycling does not involve the alteration of the polymer during the process.

This process is represented by a physical method, in which the plastic wastes will be formed by cutting, shredding or washing into granulates, flakes or pellets of appropriate quality for manufacturing, and then melted to make the new product by extrusion. Also, the reprocessed material can be blended with virgin material to obtain superior results. After the plastic is sorted, cleaned, dried and then directly processed into end products, the quantity of the waste plastic will be dramatically reduced (Figure 2). The disadvantages of this method refer to the heterogeneity of the solid waste and the deterioration of product’s properties in each cycle which occurs due to the low molecular weight of the recycled resin. It happens because of chain-scission reactions caused by the presence of water and traces acidic impurities and to avoid lowering molecular weight intensive drying is recommended, the use of chain extender compounds or reprocessing with vacuum degassing. Also, this method is relatively inexpensive but needs substantial initial investment [18,36].

![Figure 2](image_url). The steps involved in mechanical recycling.

2.3. Feedstock or Chemical Recycling

This process can be used with mechanical recycling as a complementation. Chemical recycling is defined as the process in which polymers are chemically converted to monomers or partially depolymerized to oligomers through a chemical reaction (a change occurs to the chemical structure of
the polymer). The resulted monomers can be used for new polymerizations to reproduce the original or a related polymeric product. This method is able to transform the plastic material into smaller molecules, suitable for use as feedstock material starting with monomers, oligomers, or mixtures of other hydrocarbon compounds [36,38].

The chemical reactions used for decomposition of polymers into monomers are:

- Hydrogenation
- Glycolysis
- Gasification
- Hydrolysis
- Pyrolysis
- Methanolysis
- Chemical depolymerization
- Thermal cracking
- Catalytic cracking and reforming
- Photodegradation
- Ultrasound degradation
- Degradation in microwave reactor.

The chemical recycling is not fully developed and for this reason, only a few companies are working on it because this method needs a lot of investment and expert personnel. At this moment, numerous methods are under investigation; for example, the gasification and pyrolysis method is under extensive research to establish the suitable conditions, and the processes that have reached commercial maturity at this moment are glycolysis and methanolysis [36,39–41].

For example, PET (polyethylene terephthalate) can be cleaved by some reagents, like water (hydrolysis), acids (acidolysis), glycols (glycolysis) or alcohols (alcoholysis). According to the reagent used, different products are obtained.

Hydrolysis is a recycling method that involves a reaction of PET with water in an acid, alkaline or neutral environment, leading to total depolymerization into its monomers. The disadvantages of the hydrolysis method are represented by the high temperatures (between 200 and 250 °C), by pressures (between 1.4 and 2 MPa) and by the long time needed to complete depolymerization. This method is not widely used, because of the high cost. Hydrolysis of PET flakes can be carried out by:

- Alkaline hydrolysis, which uses an aqueous alkaline solution of NaOH or KOH, of a concentration of 4–20 wt %. In a study, PET from post-consumer soft-drink bottles was cut into small pieces and then subjected to alkaline hydrolysis. After that, an autoclave was used; the temperature ranged from 120–200 °C with aqueous NaOH solutions and at 110–120 °C with a nonaqueous solution of KOH in methyl cellosolve. Sulfuric acid was used to separate terephthalic acid (TPA) of high purity. It was reported that it was obtained about 2% admixture of isophthalic acid together with the pure 98% TPA and the activation energy calculated was 99 kJ/mol [42]. Also, it was demonstrated by alkaline hydrolysis the possibility of simultaneously recycling PET and PVC from PVC-coated woven fabrics [43].
- Acid hydrolysis used concentrated sulfuric acid and also other mineral acids like nitric or phosphoric acid. In several studies, it was reported that the depolymerization of PET powder from waste bottles using nitric acid was carried out at temperatures between 70 and 100 °C [44,45]. Also, it was reported the hydrolysis of PET using sulfuric acid (96 wt %) at room temperature (30 °C) [46].
- Neutral hydrolysis, using hot water or steam, high-pressure autoclaves at temperatures between 200 and 300 °C and pressures of 1–4 MPa. It was reported that this method is more effective at temperatures higher than 245 °C, with complete depolymerization taking place at 275 °C and its TPA yield being usually above 95% [42].
Of all these methods of hydrolysis, the neutral hydrolysis gets an increased interest because it is considered more environmentally friendly, but this method presents a main disadvantage namely that all mechanical impurities present in PET are left in the TPA, thus the product can be considered of lower purity than the product of acid or alkaline hydrolysis [41,42,47].

Chemical recycling of PET by glycolysis involves ethylene glycol insertion into PET chains to give bis(hydroxyethyl) terephthalate (BHET), which is a substrate for PET synthesis and other oligomers [41,48,49]. In a study, it was used for PET glycolysis several ionic liquids and basic ionic liquids as catalysts and it was observed that the basic ionic liquid, 1-butyl-3-methylimidazolium hydroxyl ([Bmim]OH), exhibits higher catalytic activity for PET glycolysis, compared with 1-butyl-3-methylimidazolium bicarbonate ([Bmim]HCO$_3$), 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and 1-butyl-3-methylimidazolium bromide ([Bmim]Br) [50]. In another study, it was found that the purification process of the products in the glycolysis catalyzed by ionic liquids was simpler than that catalyzed by traditional compounds (metal acetate) [51]. Also, Pardal, F. and G. Tersac reported that the reactivity order of different glycols varies according to the conditions of temperature and catalysis. The global reactivity depends on the chemical reactivity of the glycol and on its physicochemical properties such as the polarity of the reaction mixture and ability to solvate the solid polyesters [52].

Chemical recycling of PET by methanolysis involves PET degradation by methanol at temperatures between 180 and 280 °C and pressures from 2 to 4 MPa with the main products being dimethyl terephthalate (DMT) and ethylene glycol (EG). Yang, Y. and co-workers reported that the optimal depolymerization conditions refers to the temperature between 260 and 270 °C, the pressure of 9.0–11.0 MPa and the weight ratio (methanol to PET) from 6 to 8 [53]. After the main products are obtained, the DMT is purified by distillation to remove all of the physical contaminants and then it can be reused to produce PET [41,54]. Also, Kurokawa H and co-workers have reported that the rate of methanolysis strongly depends on the solubility of PET [55].

Polymers like PET produce mainly the monomers from which they have been produced. In comparison, polyolefins cannot be degraded with simple chemicals to their monomers due to the random scission of the C-C bonds. Polyolefin are a major group of thermoplastics used throughout the world in applications such as toys, containers, bags, film, battery cases, and electrical components [56].

Chemical recycling uses a chemical process like pyrolysis which refers to the degradation of the polymeric materials by heating in the absence of oxygen. In a study, it was demonstrated that the oil and gaseous fractions recovered by pyrolysis of PP presented an aliphatic composition with a great potential to be recycled back into the petrochemical industry as a feedstock for the production of new plastics [39]. Achilias, D. and co-workers studied the recycling of LDPE, HDPE and PP by both a dissolution/reprecipitation technique (mechanical recycling) and pyrolysis (chemical/feedstock recycling). It was observed that mechanical recycling leads to high recovery of pure polymer with the disadvantage of using large amounts of organic solvents, while chemical recycling resulted to be the most promising technique. In the case of pyrolysis, a higher decomposition in PP, followed by LDPE and finally HDPE, was observed and also it was reported that the less crystalline or more branched polymers are less stable in thermal degradation [57].

The degradation of PS in various supercritical solvents (benzene, toluene, ethylbenzene) at 310–370 °C and 6.0 MPa pressure was studied. It was reported that PS had been successfully depolymerized; toluene was more effective than other solvents for the recovery of styrene from PS. Also, the highest yield of styrene was obtained from PS in toluene at 360 °C for 20 min [58].

2.4. Energy Recovery or Quaternary Recycling

This method refers to the recovery of the plastic’s energy content. The most effective way to reduce the volume of organic materials which involves the recovery of energy is represented by incineration. This method is a good solution because it generates considerable energy from polymers, but it’s not ecologically acceptable because of the health risk from airborne toxic substances, for example,
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Among the above recycling techniques, the only one acceptable according to the principles of sustainable development is chemical recycling, because this method leads to the formation of the monomers from which the polymer is made [36,41,59–61]. Also, the advantages and challenges of the techniques are presented in Table 2.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Challenges</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical recycling</td>
<td>Cost-effective, efficiency, well-known</td>
<td>Deterioration of product’s properties, pre-treatment</td>
<td>[18,62]</td>
</tr>
<tr>
<td>Chemical recycling</td>
<td>Operational for PET, simple technology</td>
<td>Mainly limited to condensation polymers</td>
<td>[41,57,62]</td>
</tr>
<tr>
<td>Energy recovery</td>
<td>Generates considerable energy from polymers</td>
<td>Not ecologically acceptable</td>
<td>[36,59]</td>
</tr>
</tbody>
</table>

3. Applications of Recycled Thermoplastic Polymers

Numerous waste materials are generated from manufacturing processes or municipal solid wastes every year. Due to the fact that solid waste management represents a big problem to the world, the waste utilization has become an attractive alternative to disposal. In 2012, according to the European Association of Plastics Recycling and Recovery (EPRO), 5.4 m tonnes were recycled, 34.7%, of all the plastic packaging waste [63,64]. One such waste is plastic, which is currently used in various applications presented in Table 3.

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Product Identification Code (SPI)</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>PETE</td>
<td>Drink bottles, detergent bottles, clear film for packaging, carpet fibers</td>
<td>[64]</td>
</tr>
<tr>
<td>PVC</td>
<td>V</td>
<td>Packaging for food, textile, medical materials, drink bottles</td>
<td>[65]</td>
</tr>
<tr>
<td>HDPE</td>
<td>HDPE</td>
<td>Detergent bottles, mobile components, agricultural pipes, compost bins, pallets, toys</td>
<td>[56,64]</td>
</tr>
<tr>
<td>PP</td>
<td>PP</td>
<td>Compost bins, kerbside recycling crates</td>
<td>[18,64]</td>
</tr>
<tr>
<td>PS</td>
<td>PS</td>
<td>Disposable cutlery</td>
<td>[66]</td>
</tr>
<tr>
<td>LDPE</td>
<td>LDPE</td>
<td>Bottle, plastic tubes, food packaging</td>
<td>[56,67]</td>
</tr>
<tr>
<td>Others *</td>
<td>OTHER</td>
<td>Containers</td>
<td>[68]</td>
</tr>
</tbody>
</table>

* Other plastics, including polylactic acid, acrylonitrile butadiene styrene, nylon and polycarbonate.

3.1. Recycled Polymers for Food Industry

The big problem with these recycled polymers refers to the possibility of contamination of virgin material and from contamination during the previous use of packaging and during production processes. The contamination of these materials may be of a chemical or microbiological nature [16]. Also, the Food and Drug Administration (FDA) has announced that their concerns with the use of recycled plastic materials in food-contact are related to:

- contaminants found in the post-consumer material which may appear in the final food-contact product made from the recycled material;
- recycled post-consumer material not suitable for food-contact use may be incorporated into food-contact packaging;
For example, the reused plastics can be contaminated by pollutants and the pollutants may migrate into the packaged goods in the next life of the material. The following methods are recommended to avoid migration of potential contamination:

- Packaging washing (only if it is used in the same way as before);
- Plastic depolymerization (the monomers are purified efficiently and the produced polymer is as pure as those made from conventional monomers, but this method is expensive);
- Using materials which consist of a few layers; the first layer made from a recycled plastic, the second layer that comes into contact with the product is made from virgin material (act as a functional barrier because it is reducing the migration of the contaminants from the recycled plastic into the packaged food). An example of this method is PET; the removing of all contamination from bottles is expensive, so to obtain a plastic with purity required for products which have direct contact with foods is very hard and for this reason PET is used as the outer layer in multilayered containers with the inner layer (virgin material) acting as a functional barrier [16].

Other important factors in the case of the interactions between packaging plastics and product depend on the sorption properties and on the diffusion behavior which is specific to certain polymer types or individual plastics. So, the inertness of the polymer is the basic parameter which determines the possibility for closed-loop recycling of packaging plastics. It was reported that the polymers which present a better inertness and are more appropriate for being reused in packaging applications are poly (ethylene naphtholate) (PEN), PET, and rigid PVC; followed by PS, HDPE, PP and LDPE which presents much lower properties for this type of application [70].

3.2. Recycled Polymers for Indoor Applications

Due to the growth of the number of home electrical appliances from the last years, several environmental risks were associated with these appliances. So, to avoid these risks many countries have introduced recycling systems. For example, the European Union has established three directives on electrical and electronic equipment: 2002/95/EC on restrictions on the use of certain hazardous substances in electrical and electronic equipment; 2002/96/EC on waste electrical and electronic equipment and 2005/32/EC on the eco-design of energy-using products [71].

In recent years, it was observed that electronic waste encompasses a broad and growing range of electronic devices ranging from large household appliances like air conditioners, refrigerators, and consumer electronics for computers and cellular phones. Also, it was reported that the recycling yield has increased since system implementation. The recycling yield rate, the weight of recycled materials divided by the total weight of collected appliances, has gradually increased to more than 70%. For indoor applications, the only used plastics are those in which recycling is from high-grade plastic. For example, polypropylene and polystyrene are recycled and they are used in the back-cabinets of TVs, flow fans, balancers of washing machines, base frames, dewatering tanks and protection nets of air conditioners. Also, polypropylene products are recycled in fresh food cases of refrigerators and water tanks of washing machines [71–75].

4. Perspectives for a Green Bio-Industry

The total production of plastics in 2015 was more than 322 million tons/year, which will increase to 400 million tons in 2020; according to PlasticsEurope, in 2015, global plastic’s production grew by 3.4% compared to 2014. The increasing consumption of polymer products in various fields generates a lot of waste materials, which equates to more than 12% of the urban solid waste stream. Therefore, the world is confronting a crisis, due to the generation of huge amounts of plastic waste by industries and householders; hence, an increasing attempt has been made to cope with waste polymers, due to
Recycling polymers are inexpensive, lightweight and durable which make them suitable to be molded into a variety of products that can find use in a wide range of applications. In the last 60 years, the production of plastics has increased significantly causing a big problem in the world. This review aims to provide an updated survey of the main recycled polymers and the recycle methods of thermoplastic polymers. Also, the main applications of thermoplastic polymers based on categorization by the Society of the Plastic Industry (SPI) and the new perspectives with reference to these polymers are presented. This study reveals that the recycling process is the best technique to treat waste polymer products in comparison with the old-style methods (combustion of waste polymers or burying underground) which lead to negative influences on the environment via the formation of dust, fumes and toxic gases.

Conflicts of Interest: The author declares no conflict of interest.

References


