CHAPTER - 2

REVIEW OF LITERATURE OF PET WASTE RECYCLING

2.1. INTRODUCTION

Plastics have become an indispensable part of modern life. Cars, computers, bottles, telephone, clothing, packaging; no aspect of our society is untouched by plastics. With more and more plastics products, particularly plastics packaging, being disposed of soon after their use, the landfill space required by plastics waste is a growing concern because most plastics are not degradable and can stay as such for several hundred years. The plastics are too rare and valuable to be wasted. Thus, recycling of materials is rapidly developing discipline because of environmental awareness; need to conserve materials and energy, and growing demand to increase production economy. However, plastics are being recycled\(^{16}\) in various ways ever since their introduction over a hundred years ago but newer developments and applications requires essential development of technology for their recycling.

Out of different kinds of plastics available Polyethylene Terephthalate (PET) is a widely accepted and very popular packaging material\(^{17}\). It is a strong but lightweight form of clear polyester. British Calico Printers first developed PET for use in synthetic fibers in 1941. The patent rights were then sold to Du Pont and ICI who in turn sold regional rights to many other companies\(^{18}\). Although originally produced for fibers, PET began to be used for packaging films in the mid 1960s and then, in the early 1970s, the technique for blowing bi-axially oriented bottles was commercially developed.

PET is such a pleasant sounding acronym for a material that's gobbling up the packaging world. It is used for soft drinks and bottled water. The popularity of PET in packaging is mainly due to its good performance and relatively cheap cost. The growing appeal of PET packages springs from their positive environmental image, outstanding rigidity and clarity\(^{19}\). PET is
used in a wide range of electronics and interface applications such as membrane touch panels and touch screens\textsuperscript{20}. PET is also used in film capacitors for energy saving lamps\textsuperscript{21}. The growing use of PET has poised a concern on its disposal.

PET is non-biodegradable. Thus, it will create environmental hazards if disposed in landfills. Therefore, the only way of addressing the problem of disposal of post industrial and post consumer PET waste is through recycling\textsuperscript{22}. Recycling may be defined as any activity involving reclamation, recovery or reuse of materials or articles. It also extends the service life of plastics. A striking feature of PET, which is on the environmental side, is that it is fully recyclable. PET Bottle was patented in 1973\textsuperscript{23} and four years later i.e. in 1977, the first PET bottle was recycled and was turned into a bottle base-cup. Soon however, the fiber industry discovered the new material source and started using it for making textiles, carpets and non-wovens. Today, even though the "bottle to bottle\textsuperscript{24} recycling\textsuperscript{25} process is growing, the fiber market is still the major outlet for recovered PET.

PET occupies the top of the list of polymers to be recycled. This is due to its easy recycling by different ways, which, in accordance, give variable products that can be introduced as starting ingredients for the synthesis of many other polymers\textsuperscript{26}. Extensive studies\textsuperscript{27} degradation of PET waste\textsuperscript{28-45} have developed many processes of commercial importance in order to save the environment. PET is being recycled by various ways such as mechanical recycling methods\textsuperscript{46-48} namely floatation process, solution process etc. and chemical recycling methods namely hydrolysis\textsuperscript{49}, methanolysis, glycolysis\textsuperscript{50} etc.

Some of the recognized techniques have been reported in different research and review journals. Various processes such as hydrolysis\textsuperscript{51}, methanolysis and glycolysis have been employed to study the degradation of the main chain of PET by chain scission. But the disadvantage associated with these processes is that PET flakes are subjected to higher temperature and higher pressure which would change their morphological structure.
The hydrolysis of PET with water at 150-250°C under pressure in presence of a catalyst results in the reclamation of terephthalic acid and ethylene glycol monomer. Methanolysis of PET occurs at 160-240°C under the pressure of 20-70 atmospheres to give an excellent yield of monomers. Glycolysis of PET involves treatment of high molecular weight PET with an excess of glycol at 180°C in presence of a catalyst to produce hydroxyl-terminated short-chain fragments. These reactions are carried out at high temperature and high pressure and thus, consume a lot of energy.

Thus degradation of the PET waste at lower temperature is subject of research for development of processes/techniques to carry different reactions such as glycolysis, methanolysis, hydrolysis etc. at ambient temperature. The literature survey reveals that no attempt till now is made to carry out the recycling of waste at room temperature.

The degradation of the PET waste at lower temperature was investigated through ammonolysis and aminolysis by making use of liquor ammonia and aqueous methylamine respectively. Overtone & Haynes used methylamine to selectively separate amorphous and crystalline regions while characterizing the morphology of PET. Zeronian & Collins reported that certain organic amines and ammonia can diffuse into the fiber structure causing in-depth attack to weaken the fiber, the extent of which is proportional to the severity if the treatment. Kurita has suggested that aminolysis with 70% methylamine degrades PET fibers, increases percent crystallinity of the residue and decreases molecular weight. Mehta & Bell concluded on the basis of weight loss, crystallinity and molecular weight measurements on aminolyzed PET, that aminolysis procedure is effective in removing the amorphous phase selectively.

The main objective is to prepare the industrially useful chemical and products for industrial and domestic applications. For recycling and reuse of PET waste the chemical method of recycling will be used. The process of depolymerization will decompose the PET waste. An attempt has been made to synthesis Terephthalic dihydrazide by reacting PET waste with hydrazine mon
hydrate at room temperature avoiding tedious condition of high temperature and high pressure.

Thus, new monomers will be generated. The monomers so obtained will be characterized with the help of various conventional techniques. These new monomers after proper characterization will be converted into other industrially useful chemicals. These chemicals will be utilized in the development of products of various end uses such as plasticizer.

2.2. PREPARATION, PROPERTIES & APPLICATIONS OF POLYETHYLENE TEREPTHALATE (PET)

Polyethylene terephthalate (PET) is most common thermoplastic polyester and was first known as fiber\(^5^8\). It has the following chemical structure.

![PET Structure](image)

PET is a condensation polymer derived from terephthalic and (TPA) or dimethyl terephthalate (DMT) and ethylene glycol (EG)\(^5^9\) with the removal of water molecules and methanol respectively\(^6^0,6^1\) as shown in the following reaction:

Polyethylene terephthalate (PET) is formed by combining one molecule of TPA (terephthalic acid) or by combining one molecule of DMT (dimethyl terephthalate) and two molecules of EG (ethylene glycol) to from BHET (bishydroxyethyl terephthalate) which is polycondensed to from PET. Polymerization occurs by heating these systems, typically with an antimony catalyst and removing either water or methanol\(^6^2\).
Scheme 2.1 – Reaction scheme of PET synthesis.

But in the laboratory, PET is made by other reactions. Terephthalic acid and ethylene glycol can polymerize to make PET when it is heated with an acid catalyst. It’s possible to make PET from terephthoyl chloride and ethylene glycol. This reaction is easier, but terephthoyl chloride is more expensive than terephthalic acid, and it’s a lot more dangerous.

**The steps for the synthesis of PET are shown below as per Scheme 2.2**

![Scheme 2.2: Route for PET production](image)

Polyethylene terephthalate (PET) is a clear tough plastic with good gas and moisture barrier properties. PET is a wonder material that made the whole container pack world very transparent, glamorous and most
convenient. It has all the aesthetic appeal of breakage and other damages during transportation. It can be labeled, colored or printed on. Most of the traditional packs such as glass, tin and other plastic containers are replaced by PET because it exhibits some outstanding characteristics better than others such as:

- Unique appearance
- Food grade i.e. Non-toxic
- Chemical Resistance
- Good Creep resistance
- Impact Resistance: Unbreakable
- Recyclability

PET has proven to have the most excellent mechanical properties among the commodity polymers especially when utilized as film and fibres. It has a high glass transition temperature ($T_g$) of 85°C and has a high melting temperature ($T_m$) of 255°C.

It is a simple long-chain polymer and its chemical inertness made it particularly suitable for packaging applications. PET offers good properties as a material of choice for various packaging, electronic and other applications. PET articles achieve improved toughness and other physical properties through molecular orientation resulting from stretching at temperatures slightly above its glass transition temperature ($T_g$).

Polyethylene terephthalate (PET) is a plastic material, which has found increasing applications within the packaging field. PET is used in a wide range of applications such as in beverage containers, especially water, wrapping materials, toys, automobile components, fibers and in many other products.

PET containers are lightweight and shatter resistant. The greater acceptance of PET as a packaging material is due to its toughness, clarity, capability of being oriented and reasonable cost, as well as the development of
high-speed bottle processing technology. PET bottles are an inevitable and ubiquitous fact of modern living. Most water bottles are sold in PET plastic bottles, because of their lightness and transparent nature.

As a result of the diversity of its applications in large volume consumer products, the total consumption of PET, although an engineering polymer, is comparable to that of a commodity polymer like HDPE, as indicated in Table 2.1

| S. No. | PET     | YEAR  
|-------|---------|-------
| 1.    | Fibers  | 8,500 | 11,157| 16,500|
| 2.    | Bottles | 1,200 | 2,460 | 4,200 |
| 3.    | Film    | 900   | 1,000 | 1200  |
| 4.    | Others  | 900   | 1,000 | 850   |
| 5.    | Total   | 11,500| 15,617| 22,750|

Thus, the average growth rate of PET consumption has been about 9°/c per year and the global annual consumption of PET is growing day by day. PET is being used in wide range of applications, which become waste only a short time after purchase. Thus, the waste generated from the short term uses ii packaging and allied industries requires special attention as it is considered major contributor to the growing environmental problem because of its being non-biodegradable and draws continuous criticism in society by mo environmental critics. The issue of its disposal today is a common concern and this has a range of environmental impacts.

To resolve these environmental and space problems caused by PE a management process should be adopted.

2.3. MANAGEMENT OF WASTE

Until recently, waste PET was disposed in landfills after their use. Economically, the best option is often landfill but this sort of disposal
creates environmental hazards and space problems because PET is not biodegradable and occupies a large volume. This could be solved through a sound program of recycling and reclamation, which could prove to be one of the key parameters for creating new products. Much plastic material is discarded as waste. Therefore, it is essential that we find means to recycle the materials in some form. In addition to reducing the amount of plastics waste requiring disposal, recycling plastic can have several other advantages such as:

- Reduced consumption of energy and raw materials.
- Reduced amounts of solid waste going to landfill.

According to an environment agency report, 80% of post-consumer plastic waste is sent to landfill and only 20% is recycled. Papers show that recycling is not only environmentally correct but also can be a source of income for producers of materials and final products. In India, the plastic industry is growing phenomenally. Plastics have use in all sectors of the economy - infrastructure, construction, agriculture, consumer goods, telecommunications, and packaging. But along with a growth in the use, a countrywide network for collection of plastic waste through rag pickers, waste collectors and waste dealers and recycling enterprises has sprung all over the country. It is estimated that India generates 5600 tonnes of plastic waste daily. Out of which more than 50% of the plastic waste generated in the country is recycled and used in the manufacture of various plastic products. Recycling of PET waste contributes to energy conservation since material produced from scrap sources requires much less processing energy than that from virgin sources.

The process of recycling could be successful only when continuous source of PET scrap is available. For mixed plastic recycling extruders are specially designed or are made compatible using the compatibilizer system, which are able to furnish the desired properties. Since the major packaging use of PET is in disposable bottles for soft drinks
& mineral water, even at 20% collection rate, about 1 million tons of PET bottle waste will be available for recycling.

The need for more PET recycling becomes more important due to the continuing expansion of the plastics industry and growing public concern over the use and disposal of plastics.

Unfortunately, the recycling rates for plastics have not kept pace with the increased level of production. As a result, waste plastic packaging and durable products represent a significant portion of the municipal solid waste stream. Packaging can create substantial environmental hazards because due to its short-term use and its manufacturing which consumes energy and natural resources and produces waste.

Over the last several decades, the process of recycling polymer waste has been attracting the attention of many scientists working on this issue. Polymer recycling is very important for at least two main reasons: firstly, to reduce the ever increasing volumes of polymer waste coming from many sources (from daily life packaging materials and disposables) and secondly, to generate value-added materials from low cost sources by converting them into valuable materials similar, to some extent, to virgin materials. Plastics are 100% recyclable via various routes.26

- Mechanical recycling: Plastics can be recycled several times into economically useful low cost products e.g.: Footwear, mats, etc.
- Chemical recycling: Plastics can be chemically recycled to recover monomer for reuse.
- Waste plastics are also recycled without sorting into synthetic lumber / wood products like rails, fencings, posts, benches and land scraping products.
- Thermal recycling: Plastics can be thermally recycled / incinerated to recover energy

### 2.3.1. SOURCES OF PET WASTE

STUDIES ON THE PHYSICO-CHEMICAL PROPERTIES & COMPATIBILITY OF POLYMERIC PLASTICIZERS WITH RUBBER AND PVC COMPOUND

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The major sources of PET waste are commercial, industrial, household, construction and hospital organizations.

Some other major sources of PET waste are those generated at various process stages in the production of polyester fibers and filaments, and post consumer bottle waste. Although the number of PET bottles is fewer than others, it is still an important source in the plastic waste stream as it is immediately added to the plastic waste stream after use. The used garments made from polyester fibers and filaments would potentially be a major source of PET waste.
The PET waste is also generated by desilvering industries and film manufacturers including x-ray and lithographic films where silver is collected and the remaining PET is discarded as waste. The PET waste is also generated in polyester staple fiber plant and film formation. In United States, approximately $0.3 \times 10^6$ t of PET bottles are produced annually. The current and projected Indian PET market scenarios are as shown in Table 1.2. These bottles and non-bottles PET are almost all discarded, although some 20 to 25% are recycled.

<table>
<thead>
<tr>
<th>Market Segment</th>
<th>2005</th>
<th>2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSD</td>
<td>20000</td>
<td>50000</td>
</tr>
<tr>
<td>WATER</td>
<td>20000</td>
<td>50000</td>
</tr>
<tr>
<td>EDIBLE OIL</td>
<td>6000</td>
<td>10000</td>
</tr>
<tr>
<td>JARS</td>
<td>12000</td>
<td>16000</td>
</tr>
<tr>
<td>SMALL BOTTLES</td>
<td>8000</td>
<td>13000</td>
</tr>
<tr>
<td>OTHERS</td>
<td>7000</td>
<td>8000</td>
</tr>
<tr>
<td>RETAIL/PROMOTIONAL</td>
<td>6000</td>
<td>8000</td>
</tr>
<tr>
<td>NON-BOTTLE</td>
<td>1000</td>
<td>10000</td>
</tr>
<tr>
<td>TOTAL</td>
<td>80000</td>
<td>165000</td>
</tr>
</tbody>
</table>

### 2.3.2. SEPARATION & IDENTIFICATION

One of the major problems in the management of plastic waste is separation of different kinds of plastic waste. PET marks the major plastic stream, which after recycling and reprocessing can be used as a new material and energy source etc but there are many types of Plastic. So for PET recycling to work and to make sorting and thus recycling easier, the
American society of plastics industry developed a standard marking code to help consumers identify and sort the main types of plastic\textsuperscript{82}. Plastic containers for consumer products are assigned a number between 1 and 7, out of which PET occupies the top position. This number will be found inside a recycling symbol, a triangle of arrows, on the containers.

The symbol with a number inside indicates the kind of plastic. Thus, PET bottles are easy to identify and segregate, and a significant business has developed in their collection and reprocessing.

However, in India this method of separation of products at the time of manufacturing is not being used. These codes below are called the SPI resin identification system, developed by the American Society of the Plastics Industry in 1988. Table 1.3 shows different kinds of numbers i.e. codes to be mentioned on the product.

Pregranulation color separation being practiced by PET bottle recovery processors generally results in purer recycled products and a simpler process with less complicated separation.

Table 2.3: SPI resin identification coding system

<table>
<thead>
<tr>
<th>Recycling no.</th>
<th>Abbreviation</th>
<th>Polymer name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PETE or PET</td>
<td>Polyethylene Terephthalate</td>
</tr>
<tr>
<td>2</td>
<td>HDPE</td>
<td>High-Density Polyethylene</td>
</tr>
<tr>
<td>3</td>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
</tr>
<tr>
<td>4</td>
<td>LDPE</td>
<td>Low-Density Polyethylene</td>
</tr>
<tr>
<td>5</td>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>6</td>
<td>PS</td>
<td>Polystyrene</td>
</tr>
</tbody>
</table>
The packaging waste of PET bottles and containers in crushed from may contain other material such as PE, PP, PVC and paper. Therefore, these different materials need to be separated and then cleaned of other contaminants such as adhesives and coatings. Since clear PVC bottles are also used for packaging of liquids. Thus, there is a possibility of mixing PET and PVC bottle flakes.

These two polymers have comparable density and therefore, cannot be readily separated by floatation techniques. A chemical embrittlement process may have to be incorporated for separating these two polymers from mixed plastics. Furthermore, it is desirable to segregate the PVC and PET bottles prior to crushing these into flakes because at PET extrusion temperature, PVC degrades, generating hydrochloric acid that can damage the screw, barrel and other processing machinery.

### 2.3.3. CLEANING AND SEGREGATION OF PET WASTE

There are three types of PET waste generated in the solid waste stream:

- Post industrial waste
- Post consumer waste
- Polymerization waste

Postindustrial waste is clean and is amenable to ready collection and segregation. Post-consumer waste is generated by consumers. Another category of PET waste is the polymerization waste, which is in the form of lumps and is termed as hard waste. Hard waste is contaminated with degraded polymer and oligomer. It also must be ground to smaller particles for recycling.

Post consumer waste comprised of bottles, films, threads and fabrics are generally contaminated with other plastics and additives, such as dyes, pigments. These are reclaimed from households, directly from garbage
bins, junk shops etc. Post consumer waste is collected for recycling rather than discarded after serving their initial purpose. The collected waste is sorted to enhance quality and then baled to reduce storage and shipping costs. The sorted waste is cleaned and processed into end products. Post consumer waste is dirty and this dirt or contaminations in waste will lower down the quality of the material for recycling. Although the steps taken to recycle post consumer waste may vary from operation to operation but typically involve the washing and conversion into flakes.
The retrieval and recovery of these wastes are illustrated in the flow as shown in Scheme 1.2.

**Scheme 1.2: System of recovery and processing of PET waste**

2.4. RECENT DEVELOPMENTS IN RECYCLING OF PET WASTE

PET recycling technologies have been advancing for more than a decade. There is a widespread recognition of recycling technologies for PET waste, which has given a way to solve the landfill problem. Though earlier, most commercial recycling systems depended on some floatation or hydrocyclone system to separate PET from other plastic material\(^\text{130}\) but now, economic and ecological friendly alternative systems have been developed.
New technologies, today, have minimized the problem of contamination in recycled products and have allowed the recycling industry to produce very pure recycled PET.

P.G. Schmidt has reported the structural studies of polyethylene terephthalate. James E. Thomson also describes an x-ray diffraction method for the determination of % crystallinity in oriented films and fibers of PET. Extensive studies on thermal, chemical and catalytic photolytic degradation of PET waste have developed many processes of commercial importance in order to save the environment. Polyethylene terephthalate (PET) can be recycled in two ways i.e. mechanically and chemically. The recent advances made in the recycling of PET waste are discussed in the forthcoming sections.

2.4.1. MECHANICAL RECYCLING

Mechanical recycling refers to processes, which involve the melting, shredding or granulation of waste plastics.

Plastics must be sorted prior to mechanical recycling. It is the simplest and currently most effective route where in wash and dry systems are adopted for recycling PET bottles. The automatic plant features x-ray based sorting to ensure that PVC contamination is kept to less than 20ppm even when as much as 2% of the incoming bottles are made from PVC.

In the wet recycling system, after the bottles have been ground up, the pieces of paper label are removed by air filtration. Then the remaining material is separated by water filtration. Since PET material and aluminum are heavier than water, they will sink, while the lighter base cup material floats to the top and can be siphoned off. In the dry recycling system, the various materials are separated by air which removes the paper and also separates the lighter base cup material, the PET material and aluminum.
Some methods of separation of plastics, metals and labels are described in next section from 2.4.1.1 to 2.4.1.4.

**Flow chart of Mechanical Recycling**

2.4.1.1. FLOTATION PROCESS

At present, the recycling of plastic materials is mostly done using homogeneous polymers. A separation from a municipal collection of plastics is necessary before recycling operations. If mixed plastics are being recycled, they are sorted in a floatation tank, where some types of plastic sink and others float. The easiest way of separation is by flotation in water\(^92\), i.e. the separation of the different plastics based on the different densities with respect to water. By using this method, generally two fractions are obtained from municipal post-consumer wastes: a light fraction (floating on water) and a heavy fraction. This means that all the plastic materials are separated in a "light fraction" mostly of polypropylene and polyethylene and in a "heavy fraction" mainly of polyvinyl chloride (PVC) and polyethylene terephthalate (PET)\(^{93-94}\).

In this process, most PET is reclaimed by a system that separates polyethylene terephthalate (PET) and high-density polyethylene (HDPE) by
their difference in density. It includes step that granulates or grinds the PET bottles cryogenically, because adhesive contaminants are embrittled at cryogenic temperatures whereas PET is not. Then screening removes the fine powder from the coarser PET flakes, and produces clean recycled PET free from adhesives for commercial use.

2.4.1.2. WATER BATH / HYDROCYCLONE PROCESS

In this process, bottle components are substantially separated before granulation. Color-sorted crushed bottles from the bale move continuously through a hot water bath maintained at 70-100°C wherein the PET bottle shrinks. As a result, high-density polyethylene base cups, labels and many of the polypropylene cups can be separated from PET bottles. The bottles and the base cups are granulated separately and washed. After washing and rinsing, the PET Hakes in a water medium move through a hydrocyclone to remove any residual polyethylene (PE) and adhesives. Finally, the cleaned and dried recycled PET passes through a metal detector to ensure the absence of aluminum.

2.4.1.3. SOLUTION / WASHING PROCESS

Color-sorted crushed bottles are first thoroughly washed in a hot solution containing a non-caustic cleaning agent. After washing, the base cups are removed mechanically and label materials are removed by filtration. The clean PET obtained is granulated into flakes. Dried recycled PET passes through a metal detector to ensure the absence of aluminum. The washing solution can be reused after filtration if the concentration of cleaning agent is maintained and if, it is free of contaminants.

2.4.1.4. SOLVENT / FLOTATION PROCESS

An interesting reclamation method is solvent process as demonstrated for polyethylene and polyacrylate in which the polymers are dissolved in a solvent, filtered and re-precipitated by a non-solvent. The process includes a number of floats / sink steps and uses chlorinated solvents. Water floatation step
separates polyethylene (PE) and some labels from color-sorted polyethylene terephthalate bottles.

The chlorinated solvents dissolve the adhesive and float HDPE and remaining label materials whereas the last float/sink step separates clean PET from aluminum. Finally, the solvents are removed and recovered in a closed distillation system and the adhesive- free PET is dried.

2.4.2. CHEMICAL RECYCLING

Chemical recycling\textsuperscript{96-98} is the process used to break down polymeric waste into simpler substances subsequently depolymerizes to produce virgin materials\textsuperscript{99-100}.

The chemical process for converting certain plastic wastes back to raw materials is known as depolymerisation\textsuperscript{101-103}. Several commercial processes exist to recover synthesis monomers from plastics by depolymerisation\textsuperscript{104-107}. These processes must be very efficient with very high yields of monomers and little waste; the resulting end products can then be used to make new plastics that may be indistinguishable from the initial or virgin polymers.

Chemical recycling\textsuperscript{151-156} is drawing attention because of limit in materials recycling and elevated cost in the treatment of waste. It is not as expensive as mechanical recycling, but not as economical as using waste plastic as feed stock.

Post consumer polyethylene terephthalate (PET) bottles have been recycled into fiber and sheet products. There has been a growing need, however, for a chemical recycling\textsuperscript{157} process. In this process, post consumer polyethylene terephthalate (PET) bottles are recycled into monomers that can be used as feedstock for the recycled production of PET bottles for beverages\textsuperscript{158}.
Different methods used for chemical recycling\textsuperscript{159} of polyethylene terephthalate (PET) are shown in Scheme 1.3.

\begin{center}
\begin{tikzpicture}
\node (methanol) at (0,0) {Methanol tank};
\node (pet) at (5,0) {PET production};
\node (petwaste) at (0,-3) {PET waste};
\node (methanol2) at (5,-3) {DMT Tank};
\node (eg) at (2.5,-1) {EG tank};
\node (depol) at (2.5,-3) {Depolymerization};
\node (separation) at (2.5,-5) {Separation};
\node (eg2) at (2.5,-7) {EG};
\node (pet3) at (5,-7) {DMT};
\node (petwaste2) at (0,-7) {PET waste};
\draw[->] (methanol) -- (pet);
\draw[->] (methanol) -- (petwaste);
\draw[->] (methanol2) -- (petwaste2);
\draw[->] (methanol) -- (eg);
\draw[->] (methanol2) -- (pet3);
\draw[->] (pet) -- (eg2);
\draw[->] (petwaste) -- (depol);
\draw[->] (petwaste2) -- (depol);
\draw[->] (depol) -- (separation);
\draw[->] (separation) -- (petwaste2);
\draw[->] (separation) -- (pet3);
\end{tikzpicture}
\end{center}

\textbf{Flow chart of Chemical Recycling}

Chemical recycling\textsuperscript{160-163} leads to the formation of raw materials (monomers)\textsuperscript{164-167} from which the polymer is made of. In this way the environment is not surcharged and there is no need for extra resources (monomers) for the production of polyethylene terephthalate (PET). Various techniques employed for chemical recycling of PET waste have been reviewed in the forthcoming sections from 1.4.2.1 to 1.4.3.

\textbf{2.4.2.1. HYDROLYSIS}

An important method of chemical processing of PET waste is hydrolysis, which yields terephthalic acid and ethylene glycol. Hydrolytic depolymerization of PET was reported by Yalcinyuva & Kamal et. al.\textsuperscript{168-169} Broun et.al.\textsuperscript{170} and Tustin et.al.\textsuperscript{171} have reported the method for recovering terephthalic acid\textsuperscript{172} and ethylene glycol. Doerr\textsuperscript{173} have suggested the process for minimizing formation of low molecular weight oligomers in the hydrolytic depolymerization of PET. Campanelli & Cooper\textsuperscript{174-175} have studied the
catalyzed hydrolysis of PET and they have also suggested the kinetics of high
temperature hydrolytic depolymerization of PET.

Socrate & Vosa\textsuperscript{176} have studied the continuous process for the recovery
if terephthalic acid from waste polyethylene terephthalate. Michalski\textsuperscript{177-179} has
suggested the hydrolysis of PET in closed system. Pusztaszeri\textsuperscript{180} have also
reported the method for recovery terephthalic acid from PET scrap. Pitat et.al.\textsuperscript{181}
have reported the methods for processing of PET waste by hydrolysis.

The processes\textsuperscript{182-184} can be performed as neutral hydrolysis, acid
hydrolysis and alkaline hydrolysis, which are discussed below in the sections
1.4.2.1.1. to 1.4.2.1.3.

2.4.2.1.1. NEUTRAL HYDROLYSIS

Hydrolysis of PET waste with water at 150-250°C under pressure in
presence of a catalyst results in the reclamation of terephthalic acid and
ethylene glycol monomer was investigated by Genta M. et. al.\textsuperscript{185} and
Achilis D. S. et. al.\textsuperscript{186}, respectively. The reaction takes 4 hours to complete.
The contaminants are removed from the hot reaction solution containing the
crude acid by means of pressurized filtration through a suitable filter.
Terephthalic acid is purified and crystallized giving an almost theoretical yield.
The filtrate contains ethylene glycol but not enough to be recovered. Hydrolysis
behaviour of PET was also evaluated by Hsuan & Koerner\textsuperscript{187} in water (pH=7)
and Michalski\textsuperscript{188} have utilized the PET waste by hydrolysis in neutral
environment.

The hydrolytic depolymerization of molten polyethylene terephthalate
(PET) waste was investigated by Guclu G.\textsuperscript{189} et. al. in neutral water using a 2-L
stirred pressure reactor at temperatures of 250, 265, and 280°C\textsuperscript{190}. The main
products of the reaction were found to be terephthalic acid, ethylene glycol, and
diethylene glycol. The effect of zinc catalysts on the hydrolytic
depolymerization of polyethylene terephthalate (PET) melts in excess water has
also been reported by Goje & Thakur\textsuperscript{191}. 
Hydrolytic depolymerization of PET (polyethylene terephthalate) waste in excess of water was also studied using a 0.5-L stirred high-pressure autoclave at temperatures of 100, 150, 200, and 250°C and at 200, 300, 400, 500, 700, and 800 psi (pounds per square inch) pressure\textsuperscript{192}. Polyethylene terephthalate (PET) waste was successfully decomposed in a steam atmosphere too, yielding an amount of terephthalic acid predicted from the chemical formula of PET by Campanelli & Cooper\textsuperscript{193}. The tedious condition of the reaction i.e. high temperature and high pressure make the process economically not viable. Furthermore, the ethylene glycol cannot be recovered efficiently.

2.4.2.1.2. ACID HYDROLYSIS

With sulphuric acid\textsuperscript{194,195}, the reaction is completed within minutes but purification of terephthalic acid is required to remove dyes, pigments or other impurities. Yoshika et.al.\textsuperscript{196} proposed the degradation of polyethylene terephthalate powder from waste bottles at atmospheric pressure in 3-9 M sulphuric acid below 150-190°C for 12 hrs to clarify the mechanism for a feedstock recycling process and terephthalic acid (TPA) and ethylene glycol (EG) were produced.

The depolymerization reaction of PET with water in an acid (H$_2$SO$_4$) environment happens according to the following reaction:

\[
\text{PET} + 2n\text{H}_2\text{O} + n\text{H}_2\text{SO}_4 \rightarrow n\text{HOCH}_2\text{CH}_2\text{OH} + n\text{C}_6\text{H}_4\text{COOH} + 2n\text{H}_2\text{O}
\]
The detailed mechanism of acid depolymerization is as under

\[
\begin{align*}
\text{C-O} & \quad + \quad \text{H}^+ \\
\rightarrow \quad \text{C-O} & \quad + \quad \text{OH} \\
\rightarrow \quad \text{C-O} & \quad + \quad \text{HO}^-
\end{align*}
\]

Kumar & Rao\textsuperscript{197} have conducted the experiments of cylindrical shaped pellets in 13M nitric acid at 80, 90, and 100°C respectively. Also, an experiment was conducted with a waste PET bottle sheet in 9.5 M nitric acid at 100°C and terephthalic acid is obtained. Hydrolysis reaction of PET waste powder in HNO\textsubscript{3} was investigated by Mishra et. al.\textsuperscript{198} in batch process at 88-120°C temperature and 1 atm pressures. Particle size ranging from 50-512.5 µm and reaction time 30-200 min required for hydrolysis of PET were optimized. Terephthalic acid (TPA) and ethylene glycol (EG) remain in liquid phase. This process is commercially possible and several have been proposed to process post-consumer recycled PET but ethylene glycol cannot be recovered in this case.

Coating compositions were also derived by Sayre et. al.\textsuperscript{199} from the acidolysis of polyethylene terephthalate where polyethylene terephthalate was utilized as a raw material for producing the film forming resin\textsuperscript{200, 201} for such coatings.

2.4.2.1.3. ALKALINE HYDROLYSIS

The process is also known as saponification with alkali\textsuperscript{202}. Shukla & Mathur\textsuperscript{203} have studied the treatment of PET waste with aqueous as well as
alcoholic solution of NaOH\textsuperscript{204} and at varying temperature for different durations of time by Kosmidis et al.\textsuperscript{205}.

Mishra et al.\textsuperscript{206} have also studied the depolymerization of PET in aqueous sodium hydroxide solution\textsuperscript{207}, undertaken in a batch process at 90-150°C and 1 atm by varying PET particle size in the range of 50-512.5 μm. Reaction time was also varied from 10-110 min to explore effect of particle size of PET and reaction time on batch reactor performance. Particle size of PET and reaction time required were optimized. Disodium terephthalate (TPA salt)\textsuperscript{209} and ethylene glycol (EG) remain in liquid phase.

![Chemical Structure](image)

The ester group in PET can be cleaved by aqueous sodium hydroxide (4-20 %). The reaction is slow, and is accelerated by amines. Amines bring down the saponification temperature and also the time of treatment. Namboori\textsuperscript{209-210} studied the effect of sodium hydroxide on PET fibers and reported that alkaline hydrolysis\textsuperscript{211} proceeds linearly with respect to time at constant temperature. He also studied the steric effects in basic hydrolysis of PET waste. The use of alcoholic solution of alkali as well as the use of additives like cationic surfactants to aqueous alkaline bath has been suggested to accelerate the hydrolytic action on PET by Shukla et al.\textsuperscript{212} and Ibrahim\textsuperscript{213}. Shukla & Hedao et al.\textsuperscript{214} have revealed that the rate of hydrolysis of PET fiber is enhanced by adding certain additives like ethylenediamine to the aqueous solution of sodium hydroxide.
Chemical recycling of polyethylene terephthalate (PET) flakes to terephthalic acid (TPA) and oxalic acid was investigated by Yoshika T. et.al.\textsuperscript{215} through simultaneous hydrolysis and oxygen oxidation in concentrated NaOH. The depolymerization of polyethylene terephthalate (PET) flakes carried out in a potassium hydroxide solution was also reported by Wan Kao et. al.\textsuperscript{216}.

Polyethylene terephthalate taken from post consumer soft-drink bottles was subjected to alkaline hydrolysis after cutting it into small pieces by Karyannidis et. al.\textsuperscript{217} The reaction took place in an autoclave at 120-200°C with aqueous NaOH solutions and at 110-120°C with a nonaqueous solution of KOH in methyl Cello solve. The disodium or dipotassium terephthalate received was treated with sulfuric acid and terephthalic acid (TPA) of high purity was separated. The 1H NMR spectrum of the TPA revealed an about 2% admixture of isophthalic acid together with the pure 98% TPA.

Schwartz et. al.\textsuperscript{218} have reported a method for treating polyesters comprises combining discrete particles of a polyester with an alkaline composition such that the alkaline composition coats the polyester particles. The particles are then heated in an environment that is at least substantially free of water. The method can be effectively used in cleaning, decontaminating and even increasing the intrinsic viscosity of polyester materials.

\textbf{2.4.2.2. METHANOLYSIS & ALCOHOLYSIS}

The most popular method of utilizing polyester waste\textsuperscript{219,220} is to convert ii into dimethylterephthalate\textsuperscript{221,224} by high-pressure methanolysis. In methanolytic depolymerization of PET, as reported by Yang Y. et. al.\textsuperscript{225}, clean post consumer PET flakes are mixed with methanol in a chemical process under heat and pressure through which PET is converted back into its raw materials namely dimethyl terephthalate and ethylene glycol which can then be purified, mixed with virgin raw materials and re-reacted to produce PET. In this process\textsuperscript{226}, PET is mixed with methanol and if required, a catalyst
can be added like zinc acetate, manganese acetate, cobalt acetate etc. and heated at 160-240°C for less than an hour under a pressure of 20-70 atm to get an excellent yield of monomers. Michel$^{227}$ have studied the methanolysis of PET waste using methanol vapour.

Alcoholysis of PET waste is supposed to take place according to the following reaction:

\[
\text{PET} + \text{CH}_3\text{OH} \rightarrow \text{DMT} + \text{EG}
\]

Depolymerization of polyethylene terephthalate (PET) in supercritical methanol was investigated by Goto M. et. al.$^{228,229}$ to develop a chemical recycling process for waste plastics. A batch reactor was used at 573 K and the estimated pressure of 20 MP for a reaction time of 2-120 min. PET decomposed to its monomers, dimethyl terephthalate (DMT), and ethylene glycol (EG), by Genta M. et. al.$^{230}$ through methanolysis in supercritical methanol.

Depolymerization of polyethylene terephthalate (PET) waste by methanolysis$^{231}$ using zinc acetate in the presence of lead acetate as the catalyst by Mishra & Goje$^{232}$ was carried out at 120-140°C in a closed batch reactor. Optimal percentage conversion of PET waste was 97.8% at 120°C and 100% at 130-140°C for the optimal reaction time of 120 min. Methanolysis of PET waste in the presence of aluminium isopropoxide catalyst has also been investigated by Kurokawa et. al.$^{233}$ Aluminium triisopropoxide (AIP) prompted the methanolysis of polyethylene terephthalate$^{234}$ to form monomers namely dimethylyterephthalate (DMT) and
ethylene glycol (EG), in an equimolar ratio. Mansour & Ikladious\textsuperscript{235} have also investigated the depolymerization of PET waste using 1, 4-Butanediol and triethylene glycol in presence of zinc acetate as catalyst. Another lab procedure involving the chemical recycling of PET is described through transesterification reaction by Donahue, Exline & Warner\textsuperscript{236}. The process involves the synthesis of dibenzyl terephthalate from PET waste was also reported by refluxing in benzyl alcohol at atm pressure in the presence of a catalyst.

Gamble et. al.\textsuperscript{237} have described a process for the depolymerization of polyethylene terephthalate into component monomers using a reactor in which the polyethylene terephthalate is a discontinuous phase which contacts a continuous phase of superheated methanol vapor. The present invention provides a process for converting polyester to its component monomers. Monomer making method of polyethylene terephthalate rate which adds methanol was also reported by Ishiara et. al.\textsuperscript{238}

2.4.2.3. GLYCOLYSIS

Glycolysis\textsuperscript{239,240} is the breakdown of the ester linkages by a glycol, resulting in oligomers or oligoester diols/polyols with hydroxyl terminal groups. Treatment of polyethylene terephthalate (PET) with an excess of a glycol results in a transesterification reaction. In this process, the reduction of a high molecular weight PET to short chain fragments is accomplished by heating PET with a glycol\textsuperscript{241}.

Omrani et. al.\textsuperscript{242} have glycolysed post consumer PET waste at different reaction times and different weight ratios of 37.5 to 62.5 % PET by using propylene glycol (PG) in presence of a catalyst under nitrogen purge. The glycolysis of polyethylene terephthalate waste fibers was also reported by Shukla & Harad\textsuperscript{243} using excess ethylene glycol in the presence of different chemicals namely glacial acetic acid, lithium hydroxide, sodium sulfate, and potassium sulfate. Good yields (> 60%) of the monomer bis (2-hydroxyethylene
terephthalate) were obtained using these chemicals as depolymerization catalysts.

The reaction of polyethylene terephthalate (PET) waste powder with ethylene glycol\textsuperscript{244} was carried out in a batch reactor at 2 atmospheres of pressure and a 220°C temperature by Goje & Mishra\textsuperscript{245}. Further, Troev & Grancharov\textsuperscript{246} investigate that the degree of depolymerization of PET waste was proportional to the reaction time and to increase the yield of the monomers an external catalyst was introduced. Polyethylene terephthalate (PET) waste was depolymerized by ethylene glycol (EG), diethylene glycol (DEG) and propylene glycol (PG) in the presence of a novel catalytic system of titanium (IV)-phosphate. Chen et al.\textsuperscript{247} found that the depolymerization of PET fiber proceeds faster in the presence of titanium (IV)-phosphate compared with compounds traditionally used in this process. These experiments can also be carried out in excess ethylene glycol (EG) and polyethylene terephthalate oligomer in the presence of zinc acetate as catalyst at 190°C. It was found that the catalyst concentration increased the glycolysis rate.

Investigations on catalytic glycolysis of PET waste were reported by Kao & Chang et al.\textsuperscript{248}. Wang & Chen\textsuperscript{249} have studied the kinetics of glycolysis of PET waste with Bisphenol-A. Chemical recycling of waste PET to produce terephthalohydroxamic acid (TPHA) and terephthalohydrazide (TPHD) was proposed by Yamaye M. et. al.\textsuperscript{250} through the decomposition of...
PET pellets to the corresponding oligomeric mixture in boiling ethylene glycol, followed by its treatment with hydroxylamine and hydrazine. The reaction of PET with ethylene glycol was also examined in a pressure reactor at temperature above 245°C by Campenelli & Cooper. The process of depolymerization of PET resin by EG glycolysis under pressure is also investigated by Chen, Ou, Hu & Lin. The kinetics of this pressurized depolymerization of PET resin was also discussed. It was found that the rate of depolymerization is dependent of temperature, pressure, and concentration ratio of EG to PET. The rate of depolymerization is proportional to the square of EG concentration and faster than that under atmospheric pressure. Glycolyzed products under pressure consist of the PET monomer, BHET, and oligomers, mostly dimer and trimer.

The monomer bis (2-hydroxyethyl terephthalate) (BHET) was obtained with high purity and significant yield by depolymerization of waste polyethylene terephthalate (PET) by Xi, Lu & Sun. The glycolysis reaction was carried out at 196 °C with a weight ratio of ethylene glycol (EG) to PET from 0.5 to 6; weight ratio of catalyst to PET from 0 to 1.5% and time of 1-5 h in the presence of zinc acetate as a transesterification catalyst. A process for removing contaminants from material containing polyethylene terephthalate ("PET") which has been embrittled by mixing material containing PET with ethanediol having a temperature at or about the boiling point of ethanediol for a predetermined period of time was given by West et. al.

Hall et.al. have reported that polyester is depolymerized by methanolysis and methanol is recovered in a process that uses methyl benzoate and/or p-methyltoluate as an azeotropic agent while the methanol is present. Accordingly, there is provided a process for depolymerizing polyester, involving a step of treating the polyester with methanol at elevated temperature in a zone to provide a mixture, followed by one or more steps for recovering dimethyl terephthalate (DMT) and glycol, and including a second step of
recovering methanol from the mixture resulting from first step. Chilukuri\textsuperscript{256} have invented a process for the conversion of polyethylene terephthalate waste to polyalkylene terephthalate useful as engineering thermoplastic, which comprises reacting Polyethylene terephthalate powder with a diol containing 3-12 carbon atoms in the liquid phase in the presence of a catalyst at a temperature in the range 180\textdegree-270 °C under reduced pressure and inert atmosphere. West et.al.\textsuperscript{257, 258} have reported the conversion of decontaminated crushed polyethylene terephthalate to decontaminated PBT without requiring a catalyst by mixing with 1,4-butandiol under reduced pressure, transetherifying at 120-190 °C, distilling off ethandiol and tetrahydrofuran under sub-atmospheric pressure. Salsman et.al. have reported an adhesive or coating composition comprising a reaction product of terephthalate polymer and mixture of glycols in the presence of a glycolysis catalyst.

2.4.2.4. AMINOLYSIS / AMMONOLYSIS

Spychaj et.al\textsuperscript{259} describes the chemical degradation of waste polyethylene terephthalate (PET) with polyamines or triethanolamine. They also reported that the solvolysis of polymer ester bonds was caused by diethylenetriamine, triethylenetetraamine, their mixtures, as well as mixtures of triethylenetetraamine and p-phenylenediamine or triethanolamine. Awodi et.al.\textsuperscript{260} have reported the aminolysis of polyethylene terephthalate. Blackmon, Fox & Shafer\textsuperscript{261} have also suggested the process for converting PET scrap to diamide\textsuperscript{262} monomers.

Collins & Zeronian\textsuperscript{263} have analyzed the molecular weight distributions of aminolysed PET using gel permeation chromatography. Ellison et. al.\textsuperscript{264} have reported

The physical properties of PET fibres degraded by aminolysis whereas Farrow et. al.\textsuperscript{265} have studied the degradation of PET by methylamine through infrared and x-ray methods. Papoola suggested the aminolytic degradation of PET and mechanism of the reaction.
The term chemical recycling of plastics describes a family of plastics recycling processes that convert solid plastic materials into smaller molecules (chemical intermediates). These chemical intermediates are suitable for use as feedstock for the production of new chemicals and plastics. The term chemical recycling is most often applied to the depolymerization of certain condensation or addition polymers back to monomers. Examples of these types of plastics are polyesters (e.g. PET used in soda bottles), polyamides (e.g. the nylon used in carpeting), and polyurethanes (e.g. the foam in automobile seats).

2.4.3. RECYCLING OF PET WASTE BY OTHER PROCESSES

Various researchers have made efforts to recycle PET waste by other processes \(^266-271\) i.e. biodegradation, solvolysis, aminolysis, enzyme degradation, thermal degradation \(^272\), pyrolysis \(^273\) etc. Me Mohan et.al. \(^274\) have reported the degradation studies of polyethylene terephthalate (PET).

The penetration of new markets by polyester fibers has emphasized the need for increased stability of the polyester toward a variety of degradative reactions. Extensive studies of the nature of the thermal, hydrolytic, oxidative, and radiation-induced degradation reactions have been reported \(^275\). Bottle grade virgin PET (polyethylene terephthalate) resin was investigated through five consecutive injection-molding steps to stimulate recycling cycles by Donini & Maria \(^276\). Degradation of polyethylene terephthalate waste in nitrobenzene at 170°C has also been reported by Gaylord & Rosenbaum \(^277\).

Polyester (i.e. the aromatic polyethylene terephthalate), despite its oxygen content is degradation resistant probably because it has rigid, rod-like chains \(^278\). Potential biodegradability of polyethylene terephthalate was also investigated by Kint & Guerra \(^279\). They reported the hydrolytic degradation of polyethylene terephthalate (PET) under bioenvironmental conditions. Most of the papers published so far on this subject have been focused on the hydrolysis of PET at high temperatures. Although some authors claim to enhance the biodegradation properties of this aromatic polyester by copolymerization with readily hydrolysable aliphatic polyesters, no clear and satisfying
conclusions can yet be formulated. Poly (ethylene terephthalate-co-lactic acid), poly (ethylene terephthalate-co-ethylene glycol), and poly (ethylene terephthalate-co-e-caprolactone) block and random copolymers are the modifications mainly investigated for biodegradable applications. The hydro degradability and biodegradability of PET, PET copolymers and PET blends are detailed in this review. Effect of infections on the degradation of polyethylene terephthalate implants was also studied by Gumargalieva et. al\textsuperscript{280}. The macro kinetics of degradation of polyethylene terephthalate (PET) prostheses removed from patients was investigated.

Zhang & Wang have studied the biodegradability of polyethylene terephthalate fiber. The degradation of polyethylene terephthalate (PET) fiber by microbes and lipase was studied. Although the biodegradation ratio of PET fiber was still weak, with SEM micrographs and HPLC analysis it is demonstrated that microbes and lipase could act on the PET fiber and there were some cracks on the surface of the fiber. Polyethylene terephthalate (PET) taken from post consumer soft drink bottles can also be subjected to solid-state polycondensation after cutting into small pieces or after dissolution in trifluoroacetic acid, trifluoroacetic acid/dichloromethane mixture (50/50%, v/v) or nitrobenzene\textsuperscript{281, 282}.

Smith & Oliver\textsuperscript{283} have reported the enzymatic degradation of polymers. Specimens of C-labeled polyethylene terephthalate has been synthesized and exposed, in vitro, to a number of enzyme solutions. Polyethylene terephthalate was found to be affected by esterase and papain, although in different ways, but not by trypsin or chymotrypsin. This indicates that some nominally stable polymers are susceptible to degradation by enzymes under some circumstances although the amount of degradation is small. Acetaldehyde (AA) generation behavior of polyethylene terephthalate (PET) has also been investigated by Shukla et. al\textsuperscript{284} in terms of its relationship to changes in various processing
Enzymatic and microbial degradability of polyethylene terephthalate (PET) and PET co polyesters containing 30 mol% of either 5-nitroisophthali units (PET\textsubscript{70}NI\textsubscript{30}) or nitroterephthalic units (PET\textsubscript{70}NT\textsubscript{30}) was investigated by Marques & Calvo et. al.\textsuperscript{285} in laboratory cultures. Two commercial fungal Lipage, two bacteria from environmental isolates, and two collection lilamentous fungi were tested. The topography of the polymer surface exposed to degradation was characterized by interferometry-confocal microscopy techniques. Biodegradation was estimated by optical and electron microscopy observation, and gel permeation chromatography. Evidence of biodegradation including roughness enhancement, swelling and decrease of the weight-average molecular weight, was only obtained for the case of PET\textsubscript{70}NT\textsubscript{30} cultured with Aspergillus niger. Differences in surface textures were found to be crucial to determine the positive response of this copolyester to biodegradation.

Post-use polyethylene terephthalate (PET) is a valuable fuel, with high content (23 MJ/kg), equivalent to that of soft coal. Its incineration with energy recovery, whether alone on as a constituent of municipal solid waste, is therefore energetically sound\textsuperscript{286}

Ladasiu, Choudhury & Dutta\textsuperscript{287} studied the bulk chemical changes occurring in the polymer during thermo-oxidative degradation using proton nuclear magnetic resonance (\textsuperscript{1}H NMR). Diethylene glycol (DEG) is incorporated into polyethylene terephthalate (PET) during industrial synthesis in order to control crystallisation kinetics. DEG is known to be a weak point in the thermal degradation of PET, which is problematic during the recycling of the polymer. Studies on the thermal decomposition of the model polymer poly (diethylene glycol terephthalate) (PDEGT) have been reported by Lecomte & Liggat\textsuperscript{288} and were performed using TG, DSC, TVA and spectroscopic techniques. They revealed degradation behaviour with two distinct steps, where the first step initiates some 100 K below the
degradation temperature of PET. The second step is similar to the behaviors of PET.

Studies on thermal degradation of polyethylene terephthalate were also reported by Villian F. et al.289.

The pyrolysis of PET waste has also been investigated by Thithivat Subebasang290 et al. in the presence and absence of red phosphorous. They reported the conversion of polyethylene terephthalate into a highly cross-linked polymer of terephthalic acid, in a sealed vial over the temperature range of 300-400°C. Processing of heterogeneous plastics waste by pyrolysis in Germany is proposed as alternatives to combustion291-292. All polymers have high heat content so that incineration with energy reclamation offers a way of winning back some value from polymer wastes where the level of contamination or degree of mixing makes any other process economically unattractive. Pyrolysis of polymers in fluidised beds293 yields heating oils with calorific values of around 45 MJ kg⁻¹. Mixed plastics have a calorific value of around 37 MJ kg⁻¹.

Omrihi & Mamizadeh294 have reported the recycling PET from bottles has also been carried out by different extrusion methods. Under optimized processing conditions, a virgin polyethylene terephthalate (PET), recycled PET and a mixture of virgin and recycled PET295. Gurudutt et. al.296, 297 have also reported the production of dope dyed fibers starting from the PET bottle waste.

Vaidya & Nadkarni298-302 have reported the preparation of unsaturated polyesters from PET waste along with the kinetics of polycondensation. Watanabe et. al.303 have also reported the manufacturing of polyesters from PET waste. Bai et. Al304 have reported the one step production of dioctyl phthalate plasticizer by using PET waste material.

Brennan305 have reported the preparation of novel aromatic mixtures from PET waste and alkylene oxides. Carlstrom et. al.306 has reported that waste PE1 an be turned into useful PUR polyols. Kato &
Shibata\textsuperscript{307} have reported the reclamation of waste PET for coatings. Ostrysz et al.\textsuperscript{308} have reported the preparation of polyvinyl chloride plasticizer from PET waste bottles. Paszun &Spychaj\textsuperscript{309} have reported the recycling of PET waste to obtain cross-linking agents.

Solvolysis is an established method for the recycling of polyethylene terephthalate (PET). Carta, Cao & D'Angeli\textsuperscript{310} have reviewed an interesting method of PET recycling, i.e. chemical recycling; it is based on the concept of depolymerizing the condensation polymer through solvolytic chain cleavage into low molecular products which can be purified and reused as raw materials 'the production of high-quality chemical products. Andrej Karzen\textsuperscript{311} instigated the use of microwave radiation as the energy source in PET solvolysis reactions, and the conditions that govern its effectiveness. The main advantage of microwave use is short reaction times, between 4 and 10 min, in which complete PET degradation is achieved. Solvolysis reagents used were methanol, propylene glycol, and polyethylene glycol 400.

A polyethylene terephthalate depolymerization and purification process was given by Murdoch et al.\textsuperscript{312}, which comprised: conducting acetolysis on recyclable polyethylene terephthalate to form terephthalic acid and ethylene glycol diacetate; reacting said terephthalic acid with methanol to form dimethyl terephthalate; and reacting said dimethyl terephthalate with said ethylene glycol diacetate under transesterification and polycondensation conditions.

A process for preparing adhesives from polyethylene terephthalate was disclosed by Bathe et al.\textsuperscript{313}, which comprises reacting trimellitic acid polyester ether with polyethylene terephthalate to prepare a nonlinear copolymer with cross-linking characteristics suitable for use as an adhesive either as a hot-melt adhesive or as a pressure-sensitive adhesive. Another method to work-up waste material of polyethylene terephthalate (PET) in solid form and having a high initial viscosity for multivalent reuse and to recondense it to a high viscosity was given by Unger et al.\textsuperscript{314}. Brownscombe et al.\textsuperscript{315} have invented a
process for recycling a mixed polymer recycle stream containing polyester polymers, particularly polyethylene terephthalate (PET) typically in the form of carbonated soft drink or other containers. This novel process includes the steps of contacting the mixed polymer recycle stream with a solvent which selectively dissolves the PET; separating the selective solvent containing PET from the residual mixed polymer; cooling the selective solvent to precipitate the PET; and removing the selective solvent from the precipitated PET.

Ghatta et.al. have suggested a method for recycling polyethylene terephthalate beverage bottles comprising the removal of the contaminants with the use of supercritical carbon dioxide. The recycled material is placed in an autoclave and treated with carbon dioxide at a temperature greater than 31°C and a pressure greater than 50 bars. A process of recovering components such as ethylene glycol and dimethyl terephthalate from scrap polyester was proposed by Gamble et. al.

2.5. MAJOR PROBLEMS IN COMMERCIALIZATION OF AVAILABLE TECHNOLOGY

The recycling of post-consumer PET waste for use in plastic bottles as well as in several other applications presents various problems.

Various technical and non-technical complexities which come across during recycling of PET waste are as follows:

Post-used plastic, plastic material arising from products that have undergone a first full service life prior to being recovered. PET, the biggest source of plastic waste, presents a number of challenges in recycling because of its collection.

- Municipal waste has always been land filled without any previous classification.
- The plastic industries have increased exponentially resulting in landfills being full of plastic materials.
• A major concern during the reprocessing of PET is to remove all the contaminants that can catalyze the hydrolysis of PET. The presence of water giving hydrolytic chain cleavage is an important obstacle to repetitive recycling.

• Adhesive is the most troublesome contaminant in recycling and reuse of PET waste.

• Cleaning agents as caustic soda or an alkaline detergent, though aid in the removal of labels, must be avoided as they may get entrapped in the PET granules and may create problems in further processing.

• Recycling may degrade physical and rheological properties by shear and heat, grinding, cutting, in extrusion and molds.

• Cost of investment in capital equipment for recycling is also a big problem.

• Lower viscosity of PET scrap material compared to the virgin resin makes blow molding and thermoforming difficult, which could be overcome by increasing the molecular weight by recondensation in the solid state.

• Recycled plastics are considered low performance materials because their properties decrease with recycling.

  Difficulty in recycling mainly comes in because identification codes for bottles and other containers are lacking in India due to trade secret, high cost of the material and difficulty in the procurement of the same, yet it is being recycled by small units in the unorganized sectors.

  The future for recycling of PET is exciting even after serious problems in collecting, converting and marketing waste plastics and is bound to become practical, profitable and gradually integrated into the economic main stream.
2.6. APPLICATIONS OF PRODUCTS DEVELOPED FROM PET WASTE

Protection of our environment is now a global priority. With increasing application and decreasing prices, PET became the symbol of disposability in consumerism and hence an inevitable object of concern in the relatively recent heightened public awareness of environmental issues.\(^{324}\)

There is a widespread recognition today for recycling of PET and this offers exciting prospects for developing new end-use markets for post-consumer recycled PET.

Different options for products obtained from chemical recycling of PET are:

- Regeneration of base monomers, namely, MEG, PTA or DMT.
- Glycolysis of PET with MEG into the monomer, BHET (bis-hydroxy-ethylene-terephthalate) and other oligomers, followed by polycondensation into PET for pelletization or for direct melts spinning into fibers.
- Decomposition of PET with propylene glycol and reaction of the decomposition product with maleic anhydride to form "unsaturated polyesters" for fiber reinforced composites.
- Decomposition of PET with glycols, followed by reaction of the hydroxyl terminated products with dicarboxylic acids, for producing "polyester polyols" for polyurethane foam or elastomeric products.

At present, plastic bottles made from PET are the most commonly recycled Post consumer plastic products.\(^{325}\) Plastics made from polyethylene terephthalate waste are again washed and melted. These can be cooled into beads or into very fine thread-like material. These can be used to make carpets or fleeces, or the filling for duvets and jackets.\(^{326,327}\) Bottle grade PET waste can also be converted into spinnable chips and spun into filaments.
A new process for producing the high molecular weight of aramid polyamide from waste polyester bottles with diamines has also been proposed.

Many reviews have been reported on recycling and reuse of PET waste. McDonald reviewed the worldwide market of PET in terms of market development; capacity, production and consumption while the economy of recycling high processes for PET waste have been reviewed by Atkins. Maslowski Edward et al. All reviewers some technological aspects of direct processing of PET waste into fibres model study for the recycling of the interior upholstery plastic parts of end-of-life cars has also been carried out by reprocessing the homogenized scraps of an upholstery farm. The investigated scraps contained recycled polyethylene terephthalate, as one of the main component. The use of recycled and recyclable Pet plastic for food packaging was also discovered.

The recycled plastic from PET bottles, the kind often used for beverages like soda and juice, is not typically used to make new bottles. The plastic is used to make other products, like carpeting, polyester fabric and plastic strapping. The mechanical properties and structural applications of various polymer concrete systems from unsaturated polyester resin based on recycled PET waste have been evaluated by Rebeiz et. al. Resins using recycled PET offer the possibility of a lower source cost of materials for making useful polymer concrete products and this helps to solve the solid waste problem posed by the plastic, and saves energy.

Post consumer PET bottles are mainly recycled into textiles (or garments), carpets and sheets. Pricing news is also good for processors looking for recycled material. However, high-quality products, such as new drink bottles or textile fibres are also being manufactured from recycled PET - an important step towards improving quality and lowering costs in the plastics recycling sector.
About 7% of world's PET consumption is used in non-bottle applications such as sheets, foamed board etc. These applications can use recycled PET i.e. RPET. Because of its clear advantage, the use of PET is increasing. Its not just an excellent material for the production of bottle, its characteristic allow its use to be extended beyond its initial applications, which is resulting in the development of a number of markets for recycled PET\textsuperscript{38}. Thus, the on-going efforts to promote recycling of post consumer PET waste will continue. The use of recycled products in newer applications will gain momentum whereas the existing market for recycled products is simultaneously expanding.

2.7. LIMITATIONS OF DEVELOPED RECYCLING TECHNOLOGIES

There are several technical barriers to be overcome in mechanical recycling. It is in the nature of waste products that they are dirty and mixed. It takes time, energy and money to undo this degradation. Mechanical recycling is often discussed but it is limited by the need to separate and clean used plastics prior to recycling\textsuperscript{39} because the packaging waste of PET bottles and containers may contain other materials such as PE, PP, PVC, and paper. Therefore, these different materials need to be separated and then cleaned of other contaminants such as adhesives and coatings.
Chemical recycling methods usually employed such as glycolysis, hydrolysis, methanolysis etc. are effective but not much significant. Some major drawbacks of present recycling technologies are:

The acid hydrolysis of PET waste involves the use of strong inorganic acids such as nitric acid or sulfuric acid. The hydrolysis step gives crude TPA, which has to be purified through formation of its sodium salt. However, this process excludes any possibility of regeneration of MEG and is costly due to the necessity to construct a plant made of highly expensive corrosion-resistant material, in addition to the problems associated with large acid consumption. Therefore, this is not a preferred process for PET waste recycling.

The saponification process combines the steps of depolymerization and formation of sodium salt of TPA. It involves reaction at about 180°C for 4 to 6 hours in presence of concentrated alkali (NaOH), followed by neutralization by hydrochloric acid to obtain pure, crystalline Terephthalic acid. This process also is not environment friendly or cost effective.

In conversion of PET waste into dimethyl terephthalate (DMT), which was the major raw material for producing PET, involves the depolymerization of waste in a large quantity of methanol in the presence of a catalyst at high pressure (20-25 kg/cm²) and temperature (180°C) for 3 to 5 hours. The process is cumbersome, involving a large number of unit operations, such as crystallisation, filtration, distillation, besides being hazardous due to the use of a explosive chemical like methanol.

Glycolysis of PET waste involves hydrolytic degradation of polyester waste in excess MEG at high temperatures for extended period in the presence of a catalyst such as acetates of Zn, Mn, Co, Na or Ca. The reaction conditions are required to be optimized to control the amount of BHET vs. higher oligomers and the formation of DEG as a byproduct.

Therefore a recycling methodology should be developed which could provide a better solution to these limitations.