Chapter 1

INTRODUCTION: BACKGROUND LITERATURE

1.1 General

1.1.1 Plastic: History

The term “plastic” is derived from the Greek word “plastikos” meaning ‘fit for moulding’, and “plastos” meaning moulded. It refers to the malleability or plasticity of the material during manufacture, that allows it to be cast, pressed, or extruded into a variety of shapes - such as films, fibres, plates, tubes, bottles, boxes and much more. Parkesene is considered to be the first man-made plastic and it was patented by Alexander Parkes, in Birmingham, UK in 1857 [1].

Krische and Spitteler patented the manufacture of casein plastics [2]. This plastic was made in 1987 and is still in use in button industry. The formation process involves the reaction of casein and formaldehyde. The ability of formaldehyde to form resinous substances was observed by chemists as early as in the second half of the 19th century. First patent in the field of phenol-aldehyde resins for use as an ebonite substitute in
electrical insulation was awarded to Arthur Smith in 1899 (Patent 16274). In due course Leo Hendrik Baekeland discovered techniques of controlling and modifying the reactions so that more useful products could be made. The first of his 119 patents on phenol-aldehyde plastics was awarded in 1907 and the General Bakelite Company was formed in the United States in 1910. While celluloid was the first plastic material obtained by the chemical modification of a polymer, the phenolics were the first commercially successful fully synthetic resins [2].

The only plastic materials available by 1900 were shellac, gutta percha, ebonite and celluloid. The major growth period of the plastic industry has been since 1930. The decade 1930-1940 saw the initial industrial development of four major thermoplastics that are in use even today; ie polystyrene, polyvinylchloride, polyolefins and polymethylmethacrylate. Since all these materials can be formally considered as derivatives of ethylene, they have, in the past, been referred to as ethenoid plastics. However, the somewhat inaccurate term, vinyl plastics is usually preferred nowadays.

The discovery and development of polyethylene in 1931 by Fawcett and Gibson provides an excellent example of the importance of observation and follow up of any experimental result. Detailed investigation of the product showed that it is an excellent electrical insulator with very good chemical resistance. Nylon, developed as a fibre in the mid-1930s, by Carothers and his team of research workers for Du Pont was first used as a moulding material in 1941. Also, a patent was awarded to Kinetic Chemical Inc. in 1941 based on the discovery of polytetrafluoroethylene
Investigations on Advanced Oxidation Processes as potential environment friendly techniques for the degradation of plastic pollutants

by R. J. Plunkett. Materials such as polyethylene and polystyrene, originally rather expensive special purpose materials, were produced in large tonnages at low cost during the first decade after world war II.

In the mid-1950s a number of new thermoplastics with very valuable properties became available. High-density polyethylenes produced by the Phillips process and the Ziegler process were marketed. These were shortly followed by the discovery and development of polypropylene which was the first genuinely new large tonnage thermoplastic material developed since World War II. This is arguably the most important episode in the history of polymer science [2].

Somewhat more specialised materials were the acetal resins, first introduced by Du Pont, and the polycarbonates, developed simultaneously but independently in the United States and Germany. Further developments in high-impact polystyrenes led to the discovery of acrylonitrile butadiene styrene (ABS) polymers. In 1943 Ziegler was able to grow long hydrocarbon chains by linking a series of ethylene molecules onto aluminum alkyls. The reaction rate increased in presence of titanium tetrachloride. This has also opened up the possibility of forming high molecular weight materials.

1.1.2 Raw materials for plastics

Today, the plastic industry is heavily integrated with the oil industry. In fact a popular view is that it would not be possible to produce plastics if oil were not available. Before World War II, the most important class of thermoplastics, the cellulosic, was produced from vegetable sources, cellulose being an important constituent of vegetable matter. The furane
plastics were produced from waste oat husks. Nylons were also developed from this raw material. Henry Ford had experimented with soya bean plastics and several types of plastics had been derived from natural rubber. Early grades of polyethylene were obtained from sugar cane via molasses, ethyl alcohol and ethylene. Some of these processes are still in use but their relative significance has declined.

Until mid-1950s, the main raw material source for the European plastic industry was coal. Coal yields four products on destructive distillation: coal tar, coke, coal gas and ammonia. Coal is an important source of aromatic chemicals such as benzene, toluene, phenol, naphthalene and related products. From these materials, other chemicals such as adipic acid, hexamethylenediamine, caprolactam and phthalic anhydride could be produced eventually leading to such important plastics as the phenolic resins, polystyrene and the nylons. Reaction of coke with calcium oxide gives calcium carbide, which produces acetylene on treatment with water. Acetylene is an important starting point for the production of acrylonitrile, vinyl chloride, vinyl acetate and other vinyl monomers [2].

The development of the petrochemical industry is probably the greatest single contributing factor to the growth of the plastics industry. The two industries are having a remarkable degree of interdependence today. In the first instance, the growth potential of plastics stimulated research into the production of monomers and other intermediates from petroleum. As a result cheap and abundant intermediates became available and this in turn stimulated further growth of the plastics industry. This would not have been possible if the industry was dependent on coal alone.
Petrochemicals were also being used to produce ethylene dichloride, vinyl chloride, ethylene glycol, ethylene oxide and styrene. During World War II, the large synthetic rubber industry created in the United States used butadiene and styrene, the former entirely and the latter partly derived from petroleum. In the early days, polyethylene was produced from molasses via ethyl alcohol and ethylene. Today ethylene used for polymerisation as well as for other purposes, is obtained almost entirely from petroleum. With each succeeding year in the 1950s and 1960s there was a swing away from coal and vegetable sources towards petroleum for raw materials. Some such petroleum derived products include terephthalic acid, styrene, benzene, formaldehyde, vinyl acetate and acrylonitrile \[2\].

1.1.3 Chemistry, types, properties and uses of plastics

Plastics are organic polymers formed from thousands of small molecular units called monomers joining together by chemical bonds. The monomer units are usually from the petrochemical industry. In petroleum refinery, heavy crude oil is separated into lighter fractions by distillation process. Each fraction is a mixture of hydrocarbon chains, which differ in terms of size and structure of the molecules. The main fraction of oil that is used for plastic production is known as naphtha. In a polymerisation reaction, monomers like ethylene and propylene are linked together to form long polymer chains. These polymers differ in their properties, structure and size depending on the various types of basic monomers used.
There are two main methods for the manufacture of synthetic polymers. The first involves breaking the double bond in the original olefin by addition polymerization to form new carbon-carbon bonds, i.e., the carbon-chain polymers. For example, the fabrication of polyolefins, such as polyethylene (eqn. 1) and polypropylene, is based on this general reaction.

\[ n[CH_2=CH_2] \rightarrow [-CH_2-CH_2^-]_n \]  

The second process is the elimination of water (or condensation) between a carboxylic acid and an alcohol or amine to form polyester (eqn. 2) or polyamide [3].

\[ nCH_3COOH + nCH_3CH_2OH \rightarrow [-CH_2COOCH_2CH_2^-]_n \]  

\[ HOOCC_6H_4COOH + H_2NC_6H_4NH_2 \rightarrow [-OCC_6H_4CONHC_6H_4NH^-]_n \]  

Broadly speaking, plastics are of two kinds; thermoplastics and thermosetting plastics. Thermoplastics are products of the first kind of general reaction mentioned above. Thermoplastics have either linear or branched chain structures and there are no cross links. Since different polymer chains of thermoplastics are held together by weak van der Waals’ forces or dipole forces or hydrogen bonding, they soften on heating and stiffen again on cooling. Polyethylene (PE), Polyvinyl chloride (PVC), Polypropylene (PP), Polystyrene (PS) etc are examples. In thermoplastics, the backbone is solely built of carbon atoms which makes them resistant to degradation or hydrolytic cleavage of chemical bonds. Consequently, thermoplastics are considered as non-biodegradable.
plastics. Thermoset plastics are synthesized from the second kind of general reaction stated above. Thermosetting polymers have three dimensional cross linked structure and the neighbouring polymer chains are held together by strong covalent bonds. They are solidified after being melted (by heating). The process of changing from the liquid state to the solid state is irreversible [3]. Different from the linear structure of thermoplastics, thermoset plastics have a highly cross-linked structure [4-5]. Since the main chain of thermoset plastics is made of heteroatoms, they are potentially susceptible to be degraded by the hydrolytic cleavage of chemical bonds such as ester bonds or amide bonds [6]. Structures of the two types of plastics are given in figure 1.1.

**Figure 1.1:** Structure of thermoplastics and thermosetting plastics

Some common types of plastics, their resin identification code and uses are given in table 1.1 below [7].
### Table 1.1: Common plastics resin code, characteristics and applications

<table>
<thead>
<tr>
<th>Plastic Identification Code</th>
<th>Type of plastic polymer</th>
<th>Properties</th>
<th>Common Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate (PET)</td>
<td>Clarity, strength, toughness, barrier to gas and moisture.</td>
<td>Soft drink, water and salad dressing bottles; peanut butter and jam jars; small customer electronics.</td>
</tr>
<tr>
<td>PE-HD</td>
<td>High-density polyethylene (HDPE)</td>
<td>Stiffness, strength, toughness, resistance to moisture, permeability to gas.</td>
<td>Water pipes, hula hoop rings, five gallon buckets, milk, juice and water bottles; grocery bags, some shampoo/toiletry bottles. Blister packaging for non-food items; cling films for non-food use. May be used for food packaging with the addition of the plasticisers needed to make natively rigid PVC flexible. Non-packaging uses are electrical cable insulation; rigid piping; vinyl records.</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride (PVC)</td>
<td>Versatility, ease of blending, strength, toughness.</td>
<td>Blister packaging for non-food items; cling films for non-food use. May be used for food packaging with the addition of the plasticisers needed to make natively rigid PVC flexible. Non-packaging uses are electrical cable insulation; rigid piping; vinyl records.</td>
</tr>
<tr>
<td>PE-LD</td>
<td>Low-density polyethylene (LDPE)</td>
<td>Ease of processing, strength, toughness, flexibility, ease of sealing, barrier to moisture.</td>
<td>Frozen food bags; squeezable bottles, e.g. honey, mustard; cling films; flexible container lids.</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene (PP)</td>
<td>Strength, toughness, resistance to heat, chemicals, grease and oil, versatile, barrier to moisture.</td>
<td>Reusable microwaveable ware; kitchenware; yogurt containers; margarine tubs; microwaveable disposable take-away containers; disposable cups; soft drink bottle caps; plates.</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene (PS)</td>
<td>Versatility, clarity, easily formed</td>
<td>Egg cartons; packing peanuts; disposable cups, plates, trays and cutlery; disposable take-away containers.</td>
</tr>
<tr>
<td>ABS</td>
<td>Other (often polycarbonate or ABS)</td>
<td>Dependent on polymers or combination of polymers</td>
<td>Beverage bottles; baby milk bottles. Non-packaging uses for polycarbonate: compact discs; &quot;unbreakable&quot; glazing; electronic apparatus housings; lenses including sunglasses, prescription glasses, automotive headlamps, riot shields, instrument panels.</td>
</tr>
</tbody>
</table>
Plastic products have become absolutely necessary ingredients of modern living because of their properties like flexibility, toughness, durability, light weight, ease of fabrication, relatively low cost, ease of manufacture, versatility and imperviousness to water. Plastics are used in the manufacture of a wide range of products. Many traditional materials such as wood, stone, leather, paper, metal, glass, ceramic etc have been replaced by plastics. Applications of plastic to modern life are countless. It covers health, well being, shelter, transportation, sports, leisure activities etc. In developed countries, about one third of plastic is used in packaging and another one third in construction-related applications such as piping used in plumbing, vinyl sliding etc. Other uses include those in automobiles (up to 20% plastic), furniture and toys [3].

The energy requirement for the fabrication of plastic materials is comparatively less. The low density of plastic reduces the expenses for transportation and general handling. Complex parts can be moulded in one operation thereby work and material can be saved. Wide range of surface finish is possible for plastic goods. Good insulation property of plastics is useful for applications as thermal and electrical insulators [2].

The range of strengths, flexibilities, degrees of toughness as well as chemical and solvent resistances of plastic materials are wide and so are their range of applications. Many plastic materials posses photoconductivity, very low coefficient of friction to steel, high dielectric constant, high ultraviolet light transmission etc [2].
Worldwide production of different types of plastics during the period 1995-2010 is given in figure 1.2.

Figure 1.2: Statistics of the production of plastic from 1995-2010

The enormous quantity of plastics used world over is evident from figure 1.3 below:

Figure 1.3: The annual production of plastic worldwide
The per capita consumption of plastic in different geographical regions and its relation with the GNI is given in table 1.2.

**Table 1.2: Plastic consumption worldwide**

<table>
<thead>
<tr>
<th>Main World Areas</th>
<th>KG/CAPITA</th>
<th>GNI/CAPITA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe W,C,E</td>
<td>90</td>
<td>18000</td>
</tr>
<tr>
<td>Eurasia, Russia, others</td>
<td>14</td>
<td>1600</td>
</tr>
<tr>
<td>North America</td>
<td>145</td>
<td>32000</td>
</tr>
<tr>
<td>Latin America</td>
<td>22</td>
<td>3500</td>
</tr>
<tr>
<td>Middle East, incl.TR</td>
<td>20</td>
<td>2500</td>
</tr>
<tr>
<td>Africa, North&amp; South</td>
<td>13</td>
<td>2000</td>
</tr>
<tr>
<td>Other Africa</td>
<td>≤1</td>
<td>300</td>
</tr>
<tr>
<td>China</td>
<td>14</td>
<td>800</td>
</tr>
<tr>
<td>India</td>
<td>4</td>
<td>450</td>
</tr>
<tr>
<td>Japan</td>
<td>90</td>
<td>3500</td>
</tr>
<tr>
<td>Other Asia Pacific, rest</td>
<td>11</td>
<td>600</td>
</tr>
<tr>
<td>Total World</td>
<td>25</td>
<td>5200</td>
</tr>
</tbody>
</table>

The approximate quantity of plastics used over the years in various sectors of application is given in table 1.3.

**Table 1.3: Approximate quantity of different types of plastic used over the years (in ’000 tons)**

<table>
<thead>
<tr>
<th>Year</th>
<th>Adv. composites</th>
<th>Speciality</th>
<th>Engineering</th>
<th>Commodity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1979</td>
<td>1</td>
<td>60</td>
<td>950</td>
<td>8,000</td>
</tr>
<tr>
<td>1989</td>
<td>30</td>
<td>100</td>
<td>3,000</td>
<td>80,000</td>
</tr>
<tr>
<td>2000</td>
<td>90</td>
<td>300</td>
<td>6,500</td>
<td>90,000</td>
</tr>
<tr>
<td>2010</td>
<td>300</td>
<td>600</td>
<td>20,000</td>
<td>200,000</td>
</tr>
<tr>
<td>2020*</td>
<td>700</td>
<td>1000</td>
<td>40,000</td>
<td>700,000</td>
</tr>
</tbody>
</table>

*Estimated figures

The consumption pattern of plastics in various sectors of the Indian economy is shown in figure 1.4.
Figure 1.4: Plastic consumption pattern (India)

Being one of the fastest growing economies in the world, the production and consumption of plastic is growing very fast in India. Hence it is imperative that integrated measures are adopted to minimize the environmental hazards of plastics. These include, but are not limited to, minimization in the use of plastics and plastic products, recycling, reuse and safe disposal, education of the public on the hazards of plastics and the need for protecting the environment from plastics etc. In this context, investigations are in progress in many laboratories around the world on the development of appropriate technologies for the safe disposal of plastics [8-9]. In the current study, the application of Advanced Oxidation Processes (AOPs) and combination processes is examined in detail for the safe degradation and disposal of waste plastic materials.

1.1.4 Environmental issues related to plastics

The ‘white pollution’ caused by plastic wastes is a major environmental problem. Disposal of plastic wastes is a serious environmental issue due to their recalcitrant nature. The accumulation
of plastic products in the environment adversely affects animals or/and humans and is called plastic pollution in general [10]. The main reason for the accumulation of plastic is its short-term and often single use. These wastes are not properly managed and are ultimately disposed off in unauthorized dumping sites or burnt in the open [11]. Evidences show that substantial quantities of plastic waste are polluting marine and other habitats [12]. This is a small component of the waste by weight but is huge in terms of volume due to the physical nature of the material.

Plastic pollutants are classified into micro- (between 2 µm and 5 mm), meso- (between 5mm and 20 mm), or macro-debris (larger than 20 mm) [13-14]. Yet another classification is as primary and secondary. Primary plastic pollutants are in the original form while the secondary plastics are resulting from the degradation of primary plastics [15]. Figure 1.5 is a typical unauthorized dumping site which is only a tip of the iceberg.

Figure 1.5: Accumulation of plastic wastes
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The very same qualities that make plastic durable and attractive to manufacturers and consumers alike make it harmful to our health and environment. Plastic does not decompose biologically and this leads to a steady increase in the accumulation of plastic waste in our surroundings. These discarded non biodegradable wastes have become a major waste management challenge. Around 50% of non degradable materials are plastics or plastic related. It is estimated that a foam plastic cup will take 50 years, a plastic beverage holder will take 400 years, a disposable diaper will take 450 years and a fishing net will take 600 years [16] for complete degradation. When plastics are used, recycled or disposed off, harmful chemicals are released. More than 90% of the wastes found on the beaches around the world are plastic or plastic related.

Toxicity due to pure plastic as such is less since they are insoluble in water and are biochemically inert. Plastic products are blended with a variety of organics or additives, which serve as fillers, plasticisers, lubricants, anti-aging agents, flame retardants, pigments etc. Some of these added materials can be toxic. The amount of additives in plastic ranges from 0% (in polymers used to wrap foods) to more than 50% (for certain electronic applications). Many of the environmental issues associated with plastics are compounded by the additives [17]. For example adipates and phthalates are often added as plasticizers to brittle plastics like polyvinyl chloride [18]. Traces of these additives may leach out of the product leading to many health issues. Phthalates present in PVC can leach out of products as they are not chemically bound to the plastic matrix [19-20]. Bisphenol A(BPA) and phthalates are found in many plastic products including food packaging, perfumes, cosmetics,
Introductio

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are accidentally produced during the preparation of some chlorinated polymers like PVC [11].

Thousands of animals and birds are killed every year from plastic litter as they often mistake plastic waste for food. These plastic wastes stay in their stomach without digestion. The animals and birds are then unable to eat any real food and this situation ultimately kills them. A typical scene is shown in figure 1.6.

![Figure 1.6: Animals eating plastic, mistaking for food.](image)

Pollution due to plastic may directly or indirectly affect human health in many ways. The monsoon flooding in Mumbai city in the year 2005 was the indirect result of large accumulation of plastic bags in the gutters and drains leading to clogging. This blocked the rainwater flow through the underground systems leading to massive flood and death of thousands of people. Similar incidents are reported from Bangladesh and many other countries in the third world [28]. Education and outreach programs, stringent laws and policies, government and private enforcement etc are some of the major initiatives needed for successful prevention of plastic pollution [26].
1.2 Disposal methods

Disposal of plastic waste is an important environmental challenge. Unscientific disposal results in the formation of even more harmful chemical pollutants such as benzene, dioxins, etc which release harmful toxins into air and water bodies. Some of the disposal methods in use are shown in figure 1.7.

![Disposal Methods Diagram]

Figure 1.7: Commonly used disposal methods for plastics

1.2.1 Recycling

From the waste management perspective, the three R’s—reduce, reuse and recycle are widely advocated to manage the quantities of plastic, especially plastics packaging [29]. Plastic recycling is the process of recovering scrap or waste plastic and reprocessing the material into useful products, sometimes completely different in form from their original state. Recycling and reuse of plastics are gaining importance as a
sustainable method for plastic waste disposal. Unfortunately, plastic is much more difficult to recycle than materials like glass, aluminum or paper. A common problem with recycling plastics is that they are often made up of more than one kind of polymer and/or there may be some sort of fibre added to it (a composite). Products made of a single polymer are easier and more efficient to be recycled than composite items, films and mixed wastes. As a consequence, it is not very easy to recycle a substantial proportion of the packaging plastics in a typical shopping basket using the currently available technology [29]. When plastic is melted during the recycling process, it breaks down and releases the chemicals used in the production process. Resulting air pollution causes skin and respiratory problems from exposure to and inhalation of toxic fumes, especially hydrocarbons and residues. The problem is more acute in the case of PVC. Heating and reheating of plastic for recycling also degrades it, resulting in downcycling. Plastic bottles, for example, are made into carpet, fleece, plastic lumber and other products that cannot be recycled again. Recycling and re-utilization of waste plastics lead to reduction of the use of virgin materials. This in turn results in lesser use of energy and thus reduction in carbon dioxide emissions.

Economically, in some cases, plastics recycling may be profitable. However, a number of factors can complicate the practice of plastics recycling, such as the collection of the plastics waste, separation of different types of plastics, cleaning of the waste and possible pollution from the recycling process. A further complicating factor is the low-value nature of most of the products that can be manufactured from recycled plastics. Reusing plastic is preferable to recycling as it uses less energy
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and fewer resources. At present our consumption of fossil fuels for plastic production is linear, from oil to waste via plastics. It is essential to take a more cyclical approach to material usage, though achieving this goal is complex [29].

Plastic polymers require complex processing to be recycled as each type melts at different temperatures and has different properties. Hence careful separation is necessary. Moreover, most plastics are not properly compatible with one another. Polyethlene terephthalate (PET) and high density polyethylene (HDPE) bottles have been proven to have high recyclability and are taken by most curb side and drop-off recycling programs. The growth of bottle recycling has been facilitated by the development of processing technologies that increase product purities and reduce operational costs. Recycled PET and HDPE have many uses and well-established markets. In contrast, the potential of recycling polyvinyl chloride (PVC) bottles and other materials is limited. A major problem in the recycling of PVC is the high chlorine content of raw PVC (around 56 percent of the polymer's weight) and the high levels of hazardous additives added to the polymer to achieve the desired material quality. As a result, PVC requires separation from other plastics before mechanical recycling.

We cannot escape from the toxins that are released when recycling takes place irrespective of the location, since toxins don't stay local. Once emitted into the environment, dioxins, for example, can travel vast distances via air and ocean currents which make them a global contaminant. In spite of many such disadvantages, ‘recycling’ option is viewed as the preferred route for plastic disposal because of its broad
public appeal and comparatively less environmental hazards [11]. However, even the best technology available today for plastic recycling is not without harmful effects on human and environmental health. Hence reducing the use of plastics is the best option for our health and environment. The recycling message is simple; both industry and society need to regard end-of-life items, including plastics, as raw materials rather than waste.

1.2.2 Incineration

Incineration is a waste treatment process that involves the combustion of organic substances present in waste materials. Incineration and other high-temperature waste treatment systems are described as "thermal treatment". Incineration converts the waste into ash, flue gas, and heat. The ash is mostly formed by the inorganic constituents of the waste, and may take the form of solid lumps or particulates carried by the flue gas. The flue gases must be cleaned of gaseous and particulate pollutants before they are dispersed into the atmosphere. In some cases, the heat generated by incineration can be used to generate electric power.

When incinerated, plastic releases high amounts of fossil carbon into the atmosphere as CO₂. Burning plastic in incinerators releases toxic heavy metals and chemicals. They also produce a variety of toxic discharges to the air, water, and ground that are significant sources of powerful pollutants, including dioxin (common name for a group of ~ 25 chemicals) and other chlorinated organic compounds. Garbage incinerators and medical waste incinerators are two of the largest sources of dioxin
according to the U.S. Environmental Protection Agency. It is a toxic waste product formed when waste containing chlorine is burned or when products containing chlorine are manufactured. Dioxins are among the most potent synthetic chemicals which can cause cancer and harm our immune and reproductive systems even at very low concentrations.

Many of these toxins enter the food supply and become more concentrated as they move up through the food chain. In addition to air and water emissions, incinerators create toxic ash—or slag—which contains heavy metals, dioxins, and other pollutants. This toxic ash must be landfilled and the pollutants present in the ash can then leach into groundwater.

Despite being an attractive technological option for waste management, combustion-based processes are subject of intense debate around the world. In the absence of effective controls, harmful pollutants may be emitted into the air, land and water which may adversely influence human health and environment [30].

1.2.3 Landfills

A large portion of the plastic waste is buried under ground, in landfills and some often end up littering streets and countryside via open dumping (quite unfortunately). In landfills, leachate is produced when water picks up toxins as it seeps through the trash. Although this toxic leachate is expected to be collected in landfills and to be safely disposed off, it also leaks into ground and surface water, releasing pollutants into the environment and causing health risks for humans and wildlife. It is often difficult to find adequate places to build landfills. Plastic products
are not easily biodegradable and remain in landfills, without breaking down or changing composition. The buildup of plastic waste in landfills is simply not sustainable. Plastic wastes, including packaging, electrical equipment and scrap from old vehicles, are major components of both household and industrial wastes. Our capacity for disposal of waste in landfill is finite and in some locations landfills are at, or are rapidly approaching, capacity [14,31]. It has also been suggested that because of the longevity of plastics, disposal by landfill may simply be storing problems for the future [14,29]. For example, plasticizers and other additive chemicals have been shown to leach from landfills [32].

1.2.4 Construction of roads

The government has made it mandatory for road developers to use waste plastic along with bituminous mixes for road construction wherever possible to overcome the growing problem of disposal of plastic waste in India’s urban centers. Road developers are encouraged to use waste plastic along with hot mixes for constructing bitumen roads within 50 km of periphery of any city that has a population of over five lakh. India generates ~5.6 million tonne of plastic waste annually. As per a study by the Central Pollution Control Board, 60 large cities in India generate over 15,000 tonne of plastic waste every day. Delhi generates close to 7,000 tonne of waste every day, of which over 10 per cent is pure plastic. This cannot be disposed of even through waste-to-energy plants because of environmental reasons [33].
The following types of waste plastic can be used in the construction of rural roads:

- Films (Carry Bags, Cups) thickness up to 60 micron (PE, PP and PS)
- Hard foams (PS) (any thickness).
- Soft Foams (PE and PP) (any thickness).
- Laminated plastics of thickness up to 60 micron (Aluminium coated also) such as packing materials used for biscuits, chocolates, etc.,
- Poly Vinyl Chloride (PVC) sheets or Flux sheets should not be used in any case.
- Plastic roads are presumed to have the following advantages.
  - Strength of the road increased (Increased Marshall Stability Value)
  - Better resistance to water and water stagnation
  - No stripping and no potholes.
  - Increased binding and better bonding of the mix.
  - Increased load withstanding property
  - Decrease in the overall consumption of bitumen.
  - Reduction in pores in aggregate and hence less rutting and ravelling.
  - Low maintenance cost.
  - Increased road life period.
  - No leaching of plastics [34].
Disadvantages of plastic roads are:

1) Toxics present in the co-mingled plastic waste would start leaching during the road laying process. In the presence of chlorine containing plastics, noxious HCl gas will be released.

2) After the road laying the first rain may trigger leaching, as the plastics will merely form a sticky layer (mechanical abrasion).

3) The components of the road, once it has been laid, are not inert.

The use of plastic waste for road construction seems to be a good solution for the environmental issues caused by plastic. The advantages and disadvantages of the method has been widely discussed. But still a comprehensive final view on the environmental effects of using plastic waste for road construction is not available. The main reason is that the effects were studied only for a limited period of time. Effects of such trials will be clear only after a long time period. To be used in the construction process, the plastics waste (bags, cups etc) made out of PE, PP and PS must be cut into a size between 2.36mm and 4.75mm using shredding machine. Converting plastic into small particles can cause major environmental issues in future because the natural degradation of plastic will take more than thousand years. The plastic particles may slowly get into the environment and will remain in the air/water/soil. Inhaling of this contaminated air can cause serious allergic issues and may lead to skin diseases and even cancer.
1.3 Degradation of Plastics

Irreversible degradation has been proposed by various investigators as viable option to reduce the environmental issues caused by plastic. Major degradation methods are:

- Thermal degradation
- Ozone-induced degradation
- Biodegradation
- Advanced Oxidation Processes

1.3.1 Thermal Degradation

Under normal conditions, photochemical and thermal degradations are similar and are classified as oxidative degradation. Thermal reactions occur throughout the bulk of the polymer sample, whereas photochemical reactions occur only on the surface [35]. The depolymerization reaction in thermal degradation need not be initiated at terminal end of the macromolecule. Instead, imperfections in the chain structure (initiator fragment or a peroxide or ether link) form a weak link from where depolymerization starts. A large number of addition polymers depolymerize at elevated temperature. Thermal degradation above 200°C leads to chain scission and largely depends on impurities like unsaturation sites, head-to-head units, etc. [36]. Polyolefins are known to be sensitive to thermal oxidation, due to the impurities generated during their manufacture at high temperatures [37].

Thermal degradation of polymers consists of two distinct reactions, which occur simultaneously. One is a random scission of links, causing a molecular weight reduction of the raw polymer, and the other is a chain-
end scission of C-C bonds, generating volatile products [38-40]. Thermal
degradation of the polymers follows either chain end degradation (Eqs. 4
and 5) or random degradation route (Eq. 6) as shown below:

\[ M_n \rightarrow M_{n-1} + M \] .........................................................(4)

\[ M_{n-1} \rightarrow M_{n-2} + M \] .........................................................(5)

\[ M_n \rightarrow M_x + M_y \] ..................................................................(6)

\[ n = x + y \]

where M represents the monomer.

The chain end degradation starts from the end of the chain and
successively releases the monomer units. This type of degradation route is
also known as depolymerization reaction. Such reactions are the opposite
of the propagation step in addition polymerization and occur through free
radical mechanism. Random degradation occurs at any random point
along the polymer chain. This is reverse to polycondensation process
where the polymer degrades to lower molecular weight fragments but
practically no monomer is liberated. For random degradation to occur, the
polymer chain does not necessarily require to have any active site [41].
The addition of a catalyst lowers the temperature of decomposition,
improves the quality of products obtained from pyrolysis of plastic wastes
and also enable a given selectivity to a certain product to be achieved.
Solid acid catalysts, such as zeolites, favour hydrogen transfer reactions
due to the presence of many acid sites. The access of molecules to
reactive sites on the catalyst is limited to the pore size as well as the
growth of end products inside the pores. Therefore, zeolite catalysts may
produce molecular sieving and shape selectivity [42]. Garforth et al [43]
have investigated catalytic degradation of polyolefins using TGA as a potential method for screening catalysts and have found that the presence of catalyst led to a decrease in the apparent activation energy. For polymer degradation, different types of catalysts have been reported in the literature [44–45]. These include Pt-Co and Pt-Mo supported over SiO₂ [46], zeolite catalysts and non-zeolite catalysts, transition metal catalysts (Cr, Ni, Mo, Co, Fe) on supports such as Al₂O₃, SiO₂, zeolite etc.

1.3.2 Ozone-induced degradation

The presence of ozone in the air, even in very small concentrations, markedly accelerates the aging of polymeric materials [47]. This process in saturated polymers is accompanied by the intensive formation of oxygen-containing compounds, by impairment of the mechanical and electrical properties of the specimens [48]. Exposure of polymers to ozone results in the rapid and consistent formation of a variety of carbonyl and unsaturated carbonyl products based on aliphatic esters, ketones, and lactones as well as aromatic carbonyl associated with the styrene phase. This follows a more gradual formation of ether, hydroxyl and terminal vinyl groups with time and concentration [49]. The reactions of ozone with polymers occur with main chains containing C-C bonds, aromatic rings or saturated hydrocarbon links. The reaction proceeds through unstable intermediates such as the bipolar ion or peroxo radicals, which can isomerize, degrade or cause decomposition of macromolecules [50]. Ozone normally attacks the unsaturation in the unsaturated polymers and this reaction generally occurs in three principal steps. The first step is a cycloaddition of ozone to the olefin double bond to form ozone-olefin adduct referred to as the ‘primary ozonide’. This is an unstable species.
because it contains two very weak O-O bonds. The second step is the decomposition of the primary ozonide to carbonyl compounds and a carbonyl oxide. The carbonyl oxide is considered to be the key intermediate in the C-C bond ozonolysis mechanism. The third step is the fate of the carbonyl oxide, which depends on its source, as well as the environment [51-54].

The effects of ozone (O\textsubscript{3}) gas exposure at various concentrations and treatment times on structural, mechanical and barrier properties of polyethylene and polyamide films were investigated by Ozen et al [55]. The results showed that O\textsubscript{3} treatment caused formation of oxygen-containing functional groups and degradation of polymeric chains in polyethylene films and significantly increased the \(-\text{C-N-}\) stretch observed at 1125 cm\textsuperscript{-1} in the FT-IR spectra in polyamide films.

Ozen et al [55] have studied the effect of ozone exposure on structural and mechanical properties of packaging films. The study showed that ozone treatment has affected the PE and polyamide films in different ways. Formation of oxygen-containing functional groups are responsible for the degradation of polymeric chains in PE films and increase in the -C-N- stretching in polyamide.

1.3.3 Biodegradation

Biodegradation is biochemical transformation of compounds by microorganisms. According to ASTM standard D-5488-94d biodegradation is defined as ‘‘process which is capable of decomposition of materials into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms’’.

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Mineralization of organic compounds yields carbon dioxide and water under aerobic conditions, and methane and carbon dioxide under anaerobic conditions. Abiotic hydrolysis, photo-oxidation and physical disintegration of polymers may enhance biodegradation of polymers by increasing their surface area for microbial colonization or by reducing molecular weight [56].

Biological degradation is chemical in nature but the source of the reacting chemicals is from microorganisms. These chemicals are of catalytic nature e.g. enzymes. The susceptibility of the polymers to microbial attack generally depends on enzyme availability, availability of a site in the polymers for enzyme attack, enzyme specificity for that polymer and the presence of coenzyme if required [57].

Biodegradation of polymers occurs through four different mechanisms: solubilization, charge formation followed by dissolution, hydrolysis and enzyme-catalyzed degradation [58-59].

A good review about the degradation of plastics by microorganisms was done by Gnanavel et al [60]. Plastics are biodegraded, (a) in wild nature under aerobic conditions (CO₂, water are produced), (b) in sediments & landfills under anaerobic conditions (CO₂, water, methane are produced) and (c) in composts and soil under partial aerobic & anaerobic conditions. The plastics which were studied are polyethylenes, polyvinyl chloride, polyesters, polyepsilon lactone, polylactic acid, polyurethane, polyvinyl alcohol, nylon, polyester-polyurethane etc. Bacterial and fungal species are used widely for degradation. Many strains of *Pseudomonas spp* are reported in this respect. The organisms
which degrade the hydrocarbon in plastics and use them as carbon source can be employed.

Review by Leja et al [61] covers polymer biodegradation and biodegradable polymers. Biodegradation processes of xenobiotics such as aromatic compounds, plastics (PVA, polyesters, polyethylene, and nylon), and polymer blends (Starch/Polyethylene, Starch/Polyester, and Starch/PVA) are described. Information about biodegradable polymers such as mixtures of synthetic polymers and substances that are easily digestible by microorganisms (chemically modified starch, starch-polymer composites, thermoplastic starch, and biodegradable packing materials), synthetic materials with groups susceptible to hydrolytic microbial attack (polycaprolactone) and biopolymesters (poly-β-hydroxyalkanoates) is also provided. This review has covered many major aspects about the natural and synthetic polymers, their types, uses and degradability.

Zheng et al [62] reviewed the technological advancement made in the development of more easily biodegradable plastics and the biodegradation of conventional plastics by microorganisms. Additives, such as pro-oxidants and starch, are incorporated in plastics to make them biodegradable. Recent research has shown that thermoplastics derived from polyolefins, which were generally resistant to biodegradation in ambient environment, are biodegraded following photo-degradation and chemical degradation. Thermoset plastics, such as aliphatic polyester and polyester polyurethane, are easily attacked by microorganisms directly because of the potential hydrolytic cleavage of ester or urethane bonds in their structures. Synthetic polyolefins are inert because their backbones
consist of only long carbon chains [63] which are non-susceptible to degradation by microorganisms.

Yoon et al [64] isolated mesophilic bacterium capable of biodegradation of low-molecular-weight polyethylene (LMWPE). This rod-shaped gram negative bacterium was identified as *Pseudomonas sp. E4*. The biodegradability decreased with increase in molecular weight.

Sangale et al [65] consolidated most of the available literature on the biodegradation of polythene and considered that the cheapest, eco-friendly and acceptable method is microbial degradation. The microbes release extracellular enzymes such as lignin peroxidase and manganese peroxidase which degrade the polythene.

Bhardwaj et al [66] also reviewed the literature on microbial degradation of polymers and concluded that microbial enzymes provide one of the most powerful tools for the degradation of plastics.

Müller et al [67] tested the decay characteristics of three common types of shopping bag polymers in sea turtle gastrointestinal fluids (GIF): standard, degradable and biodegradable plastic. The biodegradable bags showed mass losses between 3 and 9% in 49 days.

Biodegradation studies on polyethylene and polypropylene plastic showed that pre-treated polymers degrade more easily than untreated polymers [68]. Degradation is more facile with starch and cellulose blended polymers. Study on cell surface hydrophobicity and the effect of addition of surfactants showed an important role for surface film formation which is a prerequisite for biodegradation.
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Evaluation of the biodegradability of natural and synthetic polyethylene done by Nanda et al [69] with three different Pseudomonas sp. demonstrated that natural polyethylene plastic bags containing 6% vegetable starch, biodegraded faster compared to the synthetic ones. Best degradation was observed with Pseudomonas sp. from sewage sludge dump. Pseudomonas sp. isolated from textile effluents drainage site was less effective and the lowest activity was shown by Pseudomonas sp. from household garbage dump.

1.3.4 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs), are a set of processes designed to remove contaminants in water and waste water by oxidation through reactions involving highly reactive hydroxyl radicals (•OH) [70]. AOPs under appropriate conditions can reduce high concentration of contaminants to minute quantities and thus significantly bring COD and TOC down. AOPs are called the water treatment processes of the 21st century [71]. Usually AOPs involve a specific subset of processes that involve O₃, H₂O₂, and/or UV light. Reactive free radicals in particular •OH, are generated by irradiation with different high energy sources. These reactive oxygen species (ROS) are the strongest oxidants that can be applied in water and can virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed. Once formed, •OH reacts nonselectively with the contaminants which will be quickly and efficiently fragmented and converted into small inorganic molecules.
•OH is the second strongest oxidizing species after fluorine with a relative oxidation power of 2.8 eV. This nonselective primary oxidant is capable of readily attacking or degrading almost all recalcitrant organic compounds and converting them to less harmful intermediates and end products [72].

Figure 1.8 illustrates some special characteristics of •OH that make AOP a powerful method for the removal of refractory compounds.

Figure 1.8: Special characteristics of •OH

AOPs are generally classified as homogeneous or heterogeneous based on the nature of the medium in which the process takes place. Homogeneous processes are further subdivided into processes that use energy and that do not use energy (see figure 1.9).
Figure 1.9: Classification of Advanced Oxidation Processes
1.3.4.1 Homogeneous AOPs

Homogeneous AOPs generally employ Ultraviolet (UV) radiation, Ultrasound (US), electrical energy etc for the degradation of compounds. Processes based on this include \( \text{O}_3/\text{H}_2\text{O}_2/\text{UV}, \ \text{UV/}\text{H}_2\text{O}_2, \ \text{O}_3/\text{UV}, \ \text{Photo-Fenton}, \ \text{O}_3/\text{US}, \ \text{H}_2\text{O}_2/\text{US}, \ \text{Electro-Fenton} \) etc and their combinations.

1.3.4.2 Heterogeneous AOPs

In Heterogeneous AOPs, catalysts are employed for the enhancement of the degradation of compounds. Here the contaminants are present in the aqueous phase, while the catalyst is in the solid phase. The catalyst accelerates the degradation process through the formation of electron-hole pairs on irradiation with an appropriate energy source. The photo-generated holes and electrons are responsible for the oxidation and reduction processes, respectively. Relevant details are discussed later in this chapter.

1.3.4.3 General mechanism of AOP

Oxidation is defined as the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant), which has a higher affinity for electrons. These electron transfers result in the chemical transformation of both the oxidant and the reductant, in some cases producing chemical species with an odd number of valence electrons. These species, known as radicals, tend to be highly unstable and, therefore, highly reactive because one of their electrons is unpaired. Oxidation reactions that produce radicals tend to be followed by additional oxidation reactions between the radical oxidants and other reactants (both organic and inorganic) until thermodynamically stable oxidation products are formed.
The ability of an oxidant to initiate chemical reactions is measured in terms of its oxidation potential. The most powerful oxidants are fluorine, hydroxyl radicals (’OH), ozone, nascent oxygen etc. The oxidation potential of some of the common oxidants are given in table 1.4.

Table 1.4: Oxidation potential of common oxidizing agents.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Oxidation species</th>
<th>Oxidation potential, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fluorine</td>
<td>3.06</td>
</tr>
<tr>
<td>2</td>
<td>Hydroxyl radical</td>
<td>2.80</td>
</tr>
<tr>
<td>3</td>
<td>Sulphate radical</td>
<td>2.60</td>
</tr>
<tr>
<td>4</td>
<td>Atomic oxygen</td>
<td>2.42</td>
</tr>
<tr>
<td>5</td>
<td>Nascent oxygen</td>
<td>2.42</td>
</tr>
<tr>
<td>6</td>
<td>Ozone</td>
<td>2.07</td>
</tr>
<tr>
<td>7</td>
<td>Persulphate</td>
<td>2.01</td>
</tr>
<tr>
<td>8</td>
<td>Hydrogen peroxide</td>
<td>1.77</td>
</tr>
<tr>
<td>9</td>
<td>Perhydroxyl radical</td>
<td>1.70</td>
</tr>
<tr>
<td>10</td>
<td>Permanganate</td>
<td>1.68</td>
</tr>
<tr>
<td>11</td>
<td>Hypobromous acid</td>
<td>1.59</td>
</tr>
<tr>
<td>12</td>
<td>Hypochlorous Acid</td>
<td>1.49</td>
</tr>
<tr>
<td>13</td>
<td>Hypochlorite</td>
<td>1.49</td>
</tr>
<tr>
<td>14</td>
<td>Hypoiodous acid</td>
<td>1.45</td>
</tr>
<tr>
<td>15</td>
<td>Chlorine</td>
<td>1.36</td>
</tr>
<tr>
<td>16</td>
<td>Chlorine dioxide</td>
<td>1.27</td>
</tr>
<tr>
<td>17</td>
<td>Oxygen(molecular)</td>
<td>1.23</td>
</tr>
<tr>
<td>18</td>
<td>Bromine</td>
<td>1.09</td>
</tr>
<tr>
<td>19</td>
<td>Iodine</td>
<td>0.54</td>
</tr>
</tbody>
</table>

The end products of complete oxidation (ie, mineralization) of organic compounds are carbon dioxide (CO₂), water (H₂O) and salts.

These reactive species are generated through ozonation [73], Fenton process, Fenton-like process [74-76], photochemical oxidation,
electrochemical oxidation [77-78], H₂O₂/UV, UV/O₃ [79-80], photocatalytic oxidation [81-82], sonolysis etc. Precise, pre-programmed dosages, sequences and combinations of these reagents are used under appropriate reaction conditions in order to obtain a maximum yield of reactive free radicals, in particular •OH. The mechanism of AOPs essentially consists of three parts:

1) Formation of •OH

2) Initial attacks on target molecules by •OH and their breakdown to fragments

3) Subsequent attacks by •OH until ultimate mineralization

The hydroxyl radicals attack organic chemicals by radical addition, hydrogen abstraction and electron transfer as follows (R represents the reacting organic compound):

\[ R + \cdot OH \rightarrow ROH \quad : \text{Addition} \]
\[ R + \cdot OH \rightarrow R' + H_2O \quad : \text{Abstraction} \]
\[ R + \cdot OH \rightarrow R^+ + OH^- \quad : \text{Electron transfer} \]

Subsequent steps involving •OH as well as ROS formed during the course of the reaction, lead to further reaction and eventual mineralisation.

The AOPs have both advantages and disadvantages which have to be taken into consideration while selecting the process for specific type of pollutants. The advantages include:
Effective removal of contaminants that are resistant to conventional treatment and the complete mineralization of organic compounds into H\textsubscript{2}O and CO\textsubscript{2}.

- Low selectivity and wider application potential.
- High reaction rate.
- Major disadvantages include:
  - High consumption of reagents, especially H\textsubscript{2}O\textsubscript{2} wherever it is a reagent.
  - Homogeneous Fenton-based AOPs generate contaminated intermediate products which require secondary treatment.
  - Radical scavenging by interfering compounds reduces effectiveness of AOP.
  - The most widely investigated AOP in environmental decontamination is photocatalysis, in particular due to the possibility of using sunlight as the source of irradiation. Hence the technique is discussed in detail below.

### 1.3.4.4 Photocatalysis

In photocatalysis light is used to activate the catalyst which can modify the rate of a chemical reaction without itself getting consumed in the chemical transformation. The wavelength at which the reaction takes place depends on the nature of the processes and photochemical characteristics of components. The wavelength range of various photoprocesses are shown in figure 1.10.
Depending on whether the catalyst is dissolved in the reaction system or remain suspended, photocatalysis can be classified into homogeneous and heterogeneous processes.

1.3.4.1 Homogeneous Photocatalysis

In homogeneous photocatalysis, the catalysts are in the same phase as the reactants and they are uniformly distributed within the reaction medium. Therefore, the reaction takes place within the liquid. Homogenous photoprocesses for pollutant degradation include O$_3$/UV, H$_2$O$_2$/UV, O$_3$/H$_2$O$_2$/UV, Fenton and Photo-Fenton [83-84]. The most widely used transition metals as homogeneous catalysts in Fenton and O$_3$-based AOPs are Fe$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, Mn$^{2+}$, Mn$^{3+}$, Mn$^{4+}$, Ti$^{4+}$, Cr$^{3+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ etc [83-92]. Some of the major homogeneous catalytic processes are shown in table 1.5.
Table 1.5: Summary of the major homogeneous photocatalytic processes.

<table>
<thead>
<tr>
<th>AOP Technology</th>
<th>Brief Description</th>
<th>Major Reactions</th>
</tr>
</thead>
</table>
| **O$_3$/UV** | Hydroxyl radicals are generated when UV light is applied to ozonated water. Destruction of organic compound occurs by hydroxyl radical reactions, coupled with direct photolysis and oxidation by molecular ozone. | O$_3$ + H$_2$O + hv → H$_2$O$_2$ + O$_2$  
2O$_3$ + H$_2$O → 2'OH + 3O$_2$  
'O' + Pollutants → Oxidation By-products |
| **H$_2$O$_2$/UV** | This process involves the formation of hydroxyl radicals by the photolysis of H$_2$O$_2$ and subsequent propagation reactions. The photolysis of hydrogen peroxide occurs when UV radiation (hv) with wavelength less than 400 nm is applied. The process requires relatively high dose of H$_2$O$_2$ and longer UV-exposure time. | H$_2$O$_2$ + hv → 2'OH  
H$_2$O$_2$ → H$_2$O + ½O$_2$  
'O'+H$_2$O$_2$ → HO$_2$ + H$_2$O  
HO$_2$ + H$_2$O$_2$ → 'OH+ H$_2$O + O$_2$  
HO$_2$+$^\cdot$HO$_2$ → 'OH+ HO + O$_2$  
2'OH → H$_2$O$_2$ |
| **O$_3$/H$_2$O$_2$/UV** | When O$_3$ and H$_2$O$_2$ are simultaneously present in water, they react to form hydroxyl radicals. These hydroxyl radicals can oxidize most dissolved organic matter to form various intermediates. In the presence of UV, more hydroxyl radicals are generated leading to the mineralization and effective destruction of contaminants. | H$_2$O$_2$ + H$_2$O → H$_2$O' + HO$_2$'  
O$_3$ + H$_2$O$_2$ + hv → O$_3$ + 'OH + HO$_2$'  
O$_3$ + HO$_2$ → 'OH + 'O$_3$ + O$_2$  
'O$_3$ + 'O$_2$' → 'O$_3$ + O$_2$  
'O$_3$ + H$_2$O → 'OH + OH + O$_2$ |
| **Photo Fenton** | Fenton reagent is a mixture of ferrous iron (catalyst) and hydrogen peroxide. The photo Fenton process (H$_2$O$_2$/Fe$^{2+}$/UV) involves the HO' formation through photolysis of hydrogen peroxide (H$_2$O$_2$/UV) and Fenton reagent (H$_2$O$_2$/Fe$^{2+}$). In the presence of UV irradiation, the ferric ions (Fe$^{3+}$) formed are photocatalytically converted back to ferrous ions (Fe$^{2+}$), with formation of an additional equivalent of hydroxyl radicals. The hydroxyl radicals formed react with organic species, promoting their oxidation. | Fe$^{2+}$+ H$_2$O$_2$ → Fe$^{3+}$+ OH$^-$ + 'OH  
Fe$^{3+}$+ H$_2$O$_2$ → Fe$^{2+}$ + .O$_2$ + 2H$^+$  
Fe$^{3+}$+.O$_2$ → Fe$^{2+}$ + O$_2$  
'O' + pollutants → oxidation product |
1.3.4.2 Heterogeneous photocatalysis

Here the catalyst and reactants are in different phases. Heterogeneous photocatalysis appears to be a promising solution for the degradation of pollutants in water [93]. This treatment nonselectively degrades pollutants in the presence of catalysts (mostly semiconductor material) and UV radiation (wavelength ranging from 320 to 400 nm), visible light or solar radiation [94-99].

Most common heterogeneous photocatalysts are transition metal oxides and semiconductors which have unique characteristics. TiO$_2$, ZnO, ZrO$_2$, CdS, MoS$_2$, Fe$_2$O$_3$, WO$_3$ and ZnS are among the semiconductors used as heterogeneous photocatalysts for environmental waste treatment [94,100-104]. Among them, ZnO and TiO$_2$ have been widely investigated because they offer several advantages, such as effectiveness under ambient conditions, low cost, commercial availability, low toxicity and photochemical stability compared to others. Besides, the morphology of TiO$_2$ allows easy electron transfer and stabilizes charge separation. As a result, the recombination of photogenerated carriers is prevented. Based on literature, it can be concluded that heterogeneous systems are highly influenced by types and characteristics of catalysts, pH of the treatment system, light intensity, type of pollutant, concentration of oxidants, presence of ionic species and type of intermediates.

Hydroxyl radicals are produced with the help of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) and/or catalysts (e.g. titanium dioxide). The photocatalytic procedure is particularly useful for removing biologically
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toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents and volatile organic compounds in waste water [105].

1.3.4.2.1 Semiconductors as Photocatalysts

Semiconductors are crystalline or amorphous solids which behave as insulators at absolute zero but conduct electricity at normal temperatures. According to band theory there is only a small gap between the filled valence band (VB) of electrons and empty conduction band (CB) of semiconductor materials. At absolute zero since the electrons occupy their lowest possible energy level, the conduction band will be empty and the semiconductors will behave as perfect insulators. Since the energy gap is small in semiconductors at normal temperatures excitation of some electrons from the VB to CB can take place and electricity is conducted. This thermal excitation of electrons at normal temperature depends on the energy gap between VB and CB. Conductivity of semiconductors increases with increase in temperature. Si and Ge are the most commercially used semiconductors. Figure 1.11 shows the band structure of insulators, conductors (metals) and semiconductors.

![Diagram of Energy bands of insulators, conductors and semiconductors](image)

**Figure 1.11:** Energy bands of insulators, conductors and semiconductors
Introduction: Background Literature

Semiconductors are of two types; intrinsic and extrinsic semiconductors. Intrinsic semiconductors are pure semiconductors having small energy gap between filled valence band and empty conduction band. Extrinsic semiconductors are obtained by adding proper trivalent impurities like Ga, Al, B etc or by adding pentavalent impurities like P, As etc to the intrinsic semiconductors. This process called doping improves the conductivity of semiconductors. Figure 1.12 shows the band structure of undoped and doped semiconductors [106].

![Band structure of semiconductors](image)

**Figure 1.12:** Energy bands of pure, n-type and p-type semiconductors

Many metal oxides such as TiO₂, ZnO, ZrO₂, Fe₂O₃, WO₃ etc and sulphides such as CdS and MoS₂ can act as semiconductor materials and are suitable for photocatalysis for the degradation of organic and inorganic pollutants [107-110]. These semiconductors possess characteristics such as suitable band-gap energies, stability towards photo-corrosion, nontoxic nature, low cost, and physical characteristics that enable them to act as
catalysts. Figure 1.13 lists the energy levels of some semiconductor materials, which are used for photocatalytic reactions [111].

![Energy level diagram for typical semiconductors](image)

**Figure 1.13:** Energy level diagram for typical semiconductors

When a semiconductor is irradiated with photons of energy equal to or greater than its band gap energy (3.2eV in the case of TiO\(_2\) as well as ZnO) the photons are absorbed and electron-hole pairs are created [92,112]. These electrons and holes can either recombine or migrate towards the surface participating in several redox reactions eventually leading to the formation of Reactive Oxygen Species (ROS) such as \(\cdot\)OH radicals and H\(_2\)O\(_2\). These transitory ROS can initiate and promote a number of reactions which end up in complete mineralisation of the pollutants into harmless products such as CO\(_2\), water and salts. The principle of semiconductor photocatalysis can be represented as in figure 1.14.
Introduction: Background Literature

Investigations on Advanced Oxidation Processes as potential environment friendly techniques for the degradation of plastic pollutants

Figure 1.14: Schematic diagram illustrating the principle of Semiconductor photocatalysis

The basic reactions taking place are:

SC (Semiconductor) + hv → h⁺ + e⁻ ............................................. (10)

h⁺ + e⁻ → Heat (Recombination) ................................................. (11)

h⁺ + OH⁻ →'OH .................................................................(12)

h⁻ + H₂O →'OH + H⁺ ...........................................................(13)

Scavenging of conduction band electrons

e⁻ + O₂ → O₂⁻ .................................................................(14)

Formation of multiple peroxide species

H⁺ + O₂⁻ → HO₂⁻ ...............................................................(15)

HO₂⁻ + e⁻ + H⁺ → H₂O₂ ..........................................................(16)

Pollutant + ROS (H₂O₂, O₂⁻, HO₂⁻, ·OH etc) →

Intermediates → H₂O + CO₂ + Salts ...........................................(17)
1.3.4.2.2 Typical photocatalytic studies on plastic materials

Numerous studies have been reported on the application of photocatalysis for the removal of chemical and bacterial pollutants from water. These are summarised in many excellent reviews. Detailed account of these findings is beyond the scope of this chapter and is hence not reviewed here. Studies on the application of photocatalysis for the degradation and removal of plastic and plastic products are very few. Some of the important studies in this context are summarised below.

A good review on mechanistic implications of plastic degradation was done by Singh et al [113]. This review covers studies on the degradation of different types of plastics, including photo-oxidative degradation, thermal degradation, ozone-induced degradation, mechanochemical degradation, catalytic degradation and biodegradation along with relevant mechanisms.

Zhao et al [114] studied solid-phase photocatalytic degradation of polyethylene plastic under UV and solar light radiation by measuring the weight loss. The weight loss rate was much higher for PE-TiO$_2$ samples than for pure PE. The study concluded that CO$_2$ and water are the main products of photocatalytic degradation of PE plastic.

Studies on the solid-phase photocatalytic degradation of polystyrene (PS) plastic with TiO$_2$ as photocatalyst in the ambient air under ultraviolet light irradiation showed that the weight loss rate was much higher for the PS-TiO$_2$ (TiO$_2$ incorporated in PS) than for pure PS sample [115]. The solid-phase photocatalytic oxidation of PS was initiated by reactive oxygen species generated on irradiation on TiO$_2$ surface.
Asghar et al [116] studied comparative photocatalytic degradation of polythene films with undoped and metal (Fe, Ag, and Fe/Ag mix) doped TiO$_2$ nanoparticles under different environments such as UV radiation, artificial light, and darkness. About 14% of weight loss is reported under UV irradiation with Fe/Ag mix doped TiO$_2$ nanoparticles. Similar results were observed under artificial light [household energy saver bulb of TORNADO 24 watt] with Ag doped TiO$_2$ nanoparticles in 300 hrs. Weight reduction was not observed under darkness. Results showed that polythene-TiO$_2$ compositing with metal doping is capable of enhancing the degradation of polythene plastic under light irradiation.

Photocatalytic degradation of TiO$_2$ incorporated polyethylene film exposed to visible white light and ultraviolet light has been investigated by Nair et al [117]. They observed that photodegradation of PE depended on the size of TiO$_2$ particles. PE film containing TiO$_2$ nanoparticles had more weight loss than that containing industrial TiO$_2$ in UV light while reverse is the case under sunlight. This is attributed to the composition of TiO$_2$; ie industrial TiO$_2$ was mostly anatase while nano TiO$_2$ was a mixture of anatase and rutile.

Ohtani et al [118] also conducted similar studies. They observed that, during photodegradation the transparent film of ‘TiO$_2$ incorporated’ PE turned white together with decrease in weight. The tensile strength also was reduced after irradiation. The study shows that the effect of photoirradiation is more in the amorphous region of the film which resulted in photooxidation to produce small voids. These voids result in decrease of light transmission in the visible region.
Solid phase photocatalytic degradation of polyethylene plastic with copper phthalocyanine (CuPc) modified TiO$_2$ photocatalyst was investigated by Zhao et al [119]. The study shows that the weight loss in the case of PE-(TiO$_2$/CuPc) samples is much higher than PE-TiO$_2$ samples. This is because in the case of PE-TiO$_2$, the photo degradation of PE mainly happens on the surface whereas in the case of embedded TiO$_2$/CuPc enough ‘OH is generated in the interior also to photo degrade more of the PE.

Solid phase photocatalytic degradation of PS plastic over copper phthalocyanine (CuPc) sensitized TiO$_2$ was investigated under fluorescent light radiation in the air by Shang et al [120]. The system has shown better photocatalytic degradation than PS over TiO$_2$. Higher charge separation efficiency of TiO$_2$/CuPc catalyst results in the generation of more ROS and that in turn leads to better degradation of PS.

Solid-phase photocatalytic degradation of polyethylene–goethite composite film under Ultra Violet (UV)-light irradiation was investigated by Liu [8]. The polyethylene–goethite (PE–goethite) composite film was prepared by embedding the goethite into commercial polyethylene. The photodegradation of the modified PE plastic was determined by monitoring its weight loss, Scanning Electron Microscopic (SEM) analysis and FT-IR spectroscopy. The weight of PE–goethite sample steadily decreased and led to a total 16% reduction in 300hrs under UV-light intensity of 1mW/cm$^2$.

Solid phase photocatalytic degradation of polyethylene (PE) plastic with goethite modified by boron(B) under UV-Vis light irradiation was
investigated by Liu et al [121]. Under UV light the PE-B-Goethite combination gave better degradation than in visible light.

Solid-Phase photocatalytic degradation of a Poly(vinyl chloride)-TiO$_2$ nano composite Film with Bismuth Oxyiodide (BiOI) as catalyst was investigated in ambient air at room temperature under UV light irradiation by Yang et al [122]. The degradation was monitored by weight loss, SEM and FT-IR spectroscopy. The PVC-BiOI/TiO$_2$ nanocomposite film exhibited higher photocatalytic degradation activity compared to the PVC-TiO$_2$ nanocomposite film, the PVC-BiOI nano-composite film or the pure PVC film. Due to the interaction between p-type BiOI and n-type TiO$_2$ in the BiOI/TiO$_2$ composite, the PVC-BiOI/TiO$_2$ nanocomposite film has shown higher photocatalytic degradation activity.

Another novel idea is the preparation of photocatalytically degradable nanohybrid hyperbranched poly(3-caprolactone)-TiO$_2$ (HPCL–TiO$_2$) by integrating the polymer with TiO$_2$ nanoparticles [123]. The composite is found to degrade faster under irradiation by UV light.

The solid-phase photocatalytic degradation of polyvinyl chloride (PVC) films by tungstophosphoric acid (HPW) was investigated by Zhang et al [124] based on the unique redox property of the heteropolyacid. PVC films doped with HPW (1.5, 2.0 wt.%) were prepared and their photocatalytic degradation was carried out under irradiation with UV light of wavelength 254nm and visible light above 300nm. The photocatalytic activity was determined by weight loss monitoring and SEM analysis. HPW-doped PVC showed highly enhanced photodegradation. Comparison of the photodegradation of PVC by boric acid and such acid
catalysts implied that the high photocatalytic activity of HPW-doped PVC film was due to the unique redox property of HPW, rather than its acidity.

Li et al [125] carried out the photocatalytic degradation of polyethylene (PE) plastic directly under sunlight irradiation with polypyrrole (PPy), TiO₂ and (PPy/TiO₂) nanocomposite as photocatalysts, prepared by sol-gel and emulsion polymerization methods. The degradation efficiency was determined by weight loss monitoring, Gel Permeation Chromatography (GPC), Atomic Force Microscopy (AFM) and FT-IR analysis. It was reported that PPy/TiO₂ exhibited much higher reactivity than TiO₂ or PPy, ie, 35.4% weight loss for PPy/TiO₂ versus 11.7% for PPy and 3.2% for TiO₂ in 240 hr.

Degradation of PVC by Fenton reaction followed by biological decomposition was investigated by Mackulak et al [126]. Low molecular weight fragments like trans-1,2-dichloroethene, cis-1,2-dichloroethene, trichlororoethene, tetrachloroethene etc are formed by the Fenton pretreatment. Digestion of these fragments by anaerobic microorganisms, resulted in slow mineralisation.

Photo assisted Fenton degradation was found to efficiently mineralize polystyrene and sulfonated polystyrene materials [127]. Sulfonate groups were capable of rapidly binding the cationic Fe(III) catalyst.

Some of the most important studies reported in literature on the application of photocatalysis for the degradation of plastic wastes are summarised above. Most of the studies are on developing biodegradable
plastic for the future by incorporating special materials in the plastic matrix. However, the equally important issue of safe disposal of plastic waste getting accumulated today is not seriously addressed. The present study is an attempt to explore the potential of heterogeneous semiconductor oxide mediated photocatalysis for the degradation of plastic waste littered around us. The possibility of using the relatively simple technique of Fenton reaction and its combination with light for the degradation of different types of plastics is also examined. The quantity of waste plastics generated in a typical lower middle class village community in central Kerala is also verified by physical survey as an eye opener to the gravity of the plastic menace.

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