CHAPTER 1

INTRODUCTION

INTRODUTION

Plastics are the main sources of non-biodegradable solid wastes, disposal of which is a major problem, although they make up only 6-7% by weight of the total solid waste. Furthermore, they occupy large amounts of space thus reducing the capacity of landfill areas and causing environmental pollution.

This problem of plastic waste management; can be overcome by recycling plastic waste through collection, separation, cleaning and reprocessing it into more useful products **[Cornell 1993]**.

Poly (ethylene terephthalate) "PET"; has been known for many years simply as a textile fiber forming material. The main growth now observed in the PET market is due to films, bottles, sheets and coating products, which, came into existence in the 1970s **[Giannotta 1993].** PET was first prepared by Whinfield and Dickson in 1946, and commercially introduced in 1953 as a textile fiber. It has become one of the most important thermoplastics in world production because of its excellent mechanical properties, good thermal properties and cost. PET is semi-crystalline saturated polyester produced from terephthalic acid (TPA) and ethylene glycol (EG) **[Whinfield and Dickson 1946].** PET products are characterized by high strength, transparency, and safety. PET is widely used in the manufacture of soft-drink bottles for replacing poly (vinyl chloride) and glass bottles. However, because it is difficult to dispose of PET bottles in nature, the disposal of a large number of PET bottles has caused serious environmental problems **[Albertson 1993], [Montaudo 1993].** Since the green revolution movement established in the 1980s, researchers have begun to focus on

recycling and management of plastic wastes **[Jabarin 1987]** and **[Edge 1993].** Today, PET bottles have become one of the most valuable and successfully recyclable materials. PET finds major applications in food packaging of pharmaceuticals, textiles, hardware, electrical components for office and industrial use, and as X-ray films, because of its excellent physical, mechanical, chemical, thermal, optical and barrier properties. Food packaging contributes approximately 66% to the waste stream and potentially creates the biggest problem regarding waste management **[Scheirs 1998].** A very important feature of PET, decisive in the choice of its wide application in the manufacture of packaging for the food industry, is that it does not have any side effects on the biology of human beings. It should be; pointed out that PET does not create a direct hazard to the environment but because of its substantial fraction (by volume) in the waste stream and its high resistance to atmospheric and biological agents, it seen as a noxious material **[Paszun 1997].** Recycling has become a necessity over the years to reduce the amount of waste generated, environmental pollution, to conserve petroleum and for economic reasons.

Recycling technique, such as reprocessing with virgin resin, blending and pyrolysis of waste plastics, recycling through solutions, chemical reactions, are being followed the world over **[Brydson 1995], [Adak 1997]** and **[Scheirs 1998].** The phenomenal growth of the plastics industry has seen the emergence of greater quantities of scrap plastic. This recycling by reprocessing within the industry has continued to grow with the increasing use of thermoplastics and the increasing amount of clean uncontaminated plastic scrap available. PET is one of the most important recyclable polymers, a quality that has made it easier to earn consumer acceptance over the other packaging polymers.

PET accounts for 8% by weight and 12% by volume of the world's solid waste **[Sivaram 1997].** Because it is not appropriate to dispose of waste PET by land-filling, alternative methods of recycling of waste PET including five main approaches have been proposed, namely: physical, primary, secondary or mechanical, tertiary or chemical, and quaternary recycling **[Papaspyrides 1996].** Physical recycling of PET consists of the collection, separation, digestion, and granulation of polymer waste and then introducing into production. The products made with these procedures usually do not meet high quality standards **[Fransco et al. 1994].**

Recycled PET (R-PET) mainly used as melt-spun fibers in the fashion market as fleece sweaters, sports bags, backpacks, athletic wear, egg cartons and tennis ball cans **[Armstromg 1995]**. The other uses include blow-molded containers for household chemicals/detergents, multilayered bottles **[Griffin 1996]**, insulation foams, automotive parts **[Anon 1996]**, packaging film and polyesters **[Rebeiz 1994].**

Primary recycling refers to the "in-plant" recycle of the scrap material of controlled history. This process remains the most popular as it ensures simplicity and low cost, dealing, however, only with the recycling of clean uncontaminated single-type waste **[Collins 1991]**.
Secondary or Mechanical recycling includes two main approaches.

i) To separate the polymers from their, contaminants and then segregate them into generic types, one or more of which is then recycled into products produced from virgin or primary recycled material.

ii) To separate the polymers from their associated contaminants and remelt them as a mixture without segregation **[De Winter 1992].** The processes involved include, size reduction (granulators, shredders), separation, cleaning, drying, and compounding. The main disadvantage of this type of recycling is the deterioration of product properties in every cycle **[Paci 1998].**

Tertiary or chemical recycling defined as the process leading in total depolymerization to the monomers, or partial depolymerization to oligomers and other chemical fractions. Post-consumer condensation polymers (such as polyamides, polyesters, and polyurethane) are very sensitive to solvolytic chain cleavage and can be recycled **[Chen 1991]**, **[Yoshioka et al 1994]** and **[Debruin et al 1995]**. Chemical recycling of PET, which includes methanolysis, hydrolysis, glycolysis, aminolysis, ammonolysis, and degradation, or cracking, provides a very potent way to recover raw materials, such as terephthalic acid and ethylene glycol or oligomer, and some other useful small molecules. Chemical recycling of wasted PET products will thus be a more resourceful and valuable way **[Paszun 1997] and [Scheirs 1998].**

Quaternary recycling refers to the recovery of plastic's energy content. Incineration aiming at the recovery of energy is currently the most of effective way to reduce the volume of organic materials. Although polymers are actually high-yielding energy sources, this method has been widely accused as ecologically unacceptable owing to; the health risk from airborne toxics such as dioxins.

1.1 Recycling of PET by Glycolysis

Glycolysis involves the insertion of ethylene glycol (EG) (or diethylene glycol (DEG) and propylene glycol (PG)) in PET chains to give bis (hydroxyethyl) terephthalate (BHET) and its oligomers, which are a precursor for synthesis of new materials. Kinetics of glycolysis reaction of PET has been studied by and reviewed by several investigators. **[Baliga and Wong 1989],[Jojnson and Teeters 1991], [Lee 1994], [Bisio 1994],** and **[Brandrup 1996].**

Glycolysis of PET actually yields the "true" monomer used in the past for the polyester condensation, namely BHET, along with respective oligomers (n=2-10). The main advantage of this method is that it can easily integrate into a conventional PET production plant and the recovered BHET can blend in with fresh BHET. However, there is always a risk of contaminants. On the other hand, the main disadvantage is that reaction products are not discrete chemicals but BHET along with higher oligomers, which are difficult to purify with conventional techniques.

Challa **[Challa 1960]** found that the glycolysis rate was important in determining the maximum extent of polymerization..Chen et al. **[Chen et al 1991]** illustrated the kinetics of the glycolytic depolymerization of PET in pressure reactor at temperatures between 190 and 240°C. They found that the depolymerization of PET was dependent on the pressure, temperature, and EG/PET ratio. They also demonstrated that the glycolysis rate was second order with respect to the EG concentration. More recent, Campanelli et al. **[Campanelli et al 1994]** studied the kinetics of the glycolysis depolymerization of PET in a pressurized reactor at temperatures between 245 and 275°C. They concluded that

the glycolysis rate was first order with respect to ethylene glycol concentration for initial time concentration.

Moreover, the behavior of EG acting as both the reactant and the catalyst in the glycolysis reaction investigated. Glycolysis of PET carried out with ethylene glycol at three different ratios of PET waste to glycol. The glycolyzed products could be readily polyesterified by reacting with adipic acid, to give polyester polyols with low acid number. Kinetics of polyesterification of the glycolyzed product made from 62.5% ethylene glycol (EG) and 37.5% waste investigated further at different hydroxyl to carboxyl ratios. The kinetic results of the polyesterification of glycolyzed PET waste were compared to the polyesterification of pure diols, namely ethylene glycol and BHET with adipic acid. The reactions follow second order kinetics at 170°C and the rate of polyesterification of the mixed diol system from PET waste lies intermediate between those of the pure diols, namely, EG and BHET. Ethylene glycol exhibited the highest reactivity the kinetic plots of the mixed diols from PET waste at 200°C were nonlinear, and thus the reaction may not follow second order kinetics. The nonlinearity explained in terms of the different reactivity of the different diol species in the reaction mixture **[Vaidya and Nadkarni 1988].**

Vaidya and Nadkarni **[Vaidya and Nadkarni 1989]** found that, after 8h of reaction at 200°C with PET/EG (w/w) ratios of 62.5:37.5, 50:50, 37.5:62.5, the amount required for complete depolymerization to BHET is ~ 32 g EG for 100 g of PET. While with a PET/EG molar ratio of ~1:5, almost pure BHET can obtain. On the other hand, Baliga and Wong **[Baliga and Wong 1989]** had employed a PET/EG molar ratio of 1:4 and had been able to attain a maximium hydroxyl value (HV) of

(HV) of 375 mg KOH/g for oligomeric products under similar conditions. On the other hand, from the preliminary experiments, it was observed that with low amounts of EG to PET, as PET/EG (w/w) of 62.5:37.5, a significant depolymerization had occurred and special heavy mixing equipment would be necessary in industrial applications to avoid degradation reactions. While at high EG amounts there is no such problem, but a high oligomers as intermediates obtained at the initial stages of glycolysis proceeds so swiftly to obtain BHET and dimer (97% of reaction) occurs in the first hour **[Vaidya and Nadkarni 1988].**

Orbay et al. **[Orbay et al 1998]** illustrated that the glycolysis of PET waste EG or PG in xylene was attempted at temperatures between 170 and 245°C. Best results were obtained from glycolysis with EG at 220°C, which yielded 80% mol BHET monomer and 20 % mol dimer fractions in quite pure crystalline form.

Much effort have been devoted to improve depolymerisation procedures in order to make chemical recycling of PET more rapid as well as less sensitivity to the contaminants that may be present in post-consumer waste. The rapid depolymerisation had achieved by melting PET with preheated reagents or using supercritical conditions **[Sato et al 1998].**

Using of microwave irradiation as the source of heating in glycolysis of PET waste was investigated to achieve complete PET solubilization in approximately 5min. The glycols used as solvolysis reagents and a number of basic inorganic compounds examined as potential catalysts **[Krzan 1999].**

Ikladious **[Ikladious 2000]** studied the depolymerisation of PET waste by glycolysis at different weight ratios of PG at 200°C and in the presence of zinc acetate as a catalyst. He found that the glycolyzed products consisted mainly of dimer and trimer of bis-hydroxy propyl terephthalate and no monomer detected. It was clear that the dimer/trimer ratio increased with increasing ratio of PG from 40 to 60 wt%.

Shukla **[Shukla 2002]** studied the depolymerization of PET with ethylene glycol in the presence of different catalysts, using two conventional catalysts such as zinc and lead acetate, and two alkalis catalyst such as sodium carbonate and sodium bicarbonate. The resulting monomer BHET was characterized by thin layer chromatography. The results showed that, the qualitative and quantitative yields of the monomer obtained with alkalis as catalysts were most comparable with the conventional heavy metal catalysts.

1.2 METHANOLYSIS OF PET

Methanolsis, actually, is the degradation of PET by methanol at high temperatures and high pressures which produces dimethyterephthatae (DMT) and EG as the main products. Methanolysis is currently successfully applied to PET scrap including scrap bottles, fiber waste, used films, and plant waste. The main advantage of this method is that an installation of a methanolysis unit can be located in the polymer production line, since the DMT produced has a product quality identical to virgin DMT. Also, EG and methanol can be easily recovered and recycled. In this way, waste PET arising in the production cycle utilized and the monomers recovered can reuse in the

manufacture of a full valuable polymer **[Marathe 1980], [Bisio 1994] [Socrate 1995], [Brandrup 1996]** and **[Paszun 1997].** Disadvantage of this method, is the high cost associated with the separation and refining of the mixture of the reaction products (glycols, alcohols, and phthalate derivatives). If water enters into the process, it poisons the catalyst and forms various azeotropes. However, the main disadvantage is associated with the trend of all new PET production processes to use terephthalic acid (TPA) instead of DMT produced by hydrolysis to TPA adds a considerable cost in the methanolysis process **[Paszun 1997]** and **[Scheirs 1998].**

Methanolysis has been attempted by Lotz et al. **[Lotz 1967]** stated that, the PET was completely (more than 99%) depolymerized to DMT and EG by reacting molten PET with methanol at 210°C in the absence of a catalyst. Sako et al. **[Sako et al 1997 and 1998]** proposed a new process of methanolysis by treating PET with supercritical methanol. In this process, PET can be completely depolymerized to DMT, EG, and oligomer above 300°C at 11MPa for 30 min without a catalyst.

Aluminium tri-isopropoxide (AIP) promoted the methanolysis of PET to form monomers, DMT and EG. The methanolysis at 200°C in methanol with an AIP catalyst gave DMT and EG in 64% and 63% yields, respectively. Using a toluene/methanol mixed solvent with maximum yields, 88% for DMT and 87% for EG increased the yields. These results indicated that the rate of methanolysis was strongly dependent on the solubility of PET. The results of gel permeation chromatography (GPC) analysis suggested that the methanolysis of PET in the absence of the catalyst proceeded via three steps. In the first step, the depolymerization occurred at a tie molecule connecting PET

crystals and the chain length shortened to about 30% of length. The shortened chain depolymerized to oligomers in the second step. The GPC curve of the oligomers tailed to low molecular weight, clearly indicating that the depolymerization took place at random positions on the polymer chain. The third step includes the depolymerization from the oligomers to the monomers, promoted only in the presence of the AlP catalyst **[Kurokawa et al 2003].** AlP serving as a Lewis acid catalyst promote transesterification of dialkylcarbonates with phenol **[Illuminati 1976].**

In addition, Halacheva demonstrated the preparation of oligoester polyols by alcoholytic destruction of PET with DEG **[Halacheva 1995].**

1.3 HYDROLYSIS OF PET

Hydrolysis is another method of PET waste chemical processing leading to terephthalic acid (TPA) and ethylene glycol (EG). The growing interest in this method is connected with development of new factories for PET synthesis directly from TPA and EG. In this way, the production of methanol eliminated from the technological cycle. Commercially, hydrolysis is not widely used to produce food-grade recycled PET because of the cost associated with purification of the recycled TPA. Hydrolysis of PET flakes can be carried out as (a) alkaline hydrolysis, (b) acid hydrolysis, and (c) neutral hydrolysis, **[Bisio 1994], [Brandrup 1996], [Paszun 1997] and [Scheirs 1998].**

- **ALKALINE HYDROLYSIS**

Alkaline hydrolysis of PET is usually carried out with the use of an aqueous alkaline solution of NaOH, or KOH of a concentration of 4-20 wt%. **[Paszun 1997]** The reaction products are EG and the terephthalate salts, e.g. TPA-Na_2. The mixture was heated up to 340°C to evaporate and recover the EG. Pure TPA can be obtained by neutralization of the reaction mixture with a strong mineral acid (e.g. H_2SO_4). The process runs for 3-5h at temperature ranged from 210 to 250°C, under pressure of 1.4-2 MPa. **[Alter 1986].**

The best results of PET alkaline hydrolysis were achieved using an aqueous ammonia solution at 200°C **[Datye 1984].** Alkali decomposition of PET in non-aqueous solution had been reported by Oku et al. **[Oku et al 1997]** The addition of an ether (such as dioxane or tetrahydrofuran) as a mixed solvent with an alcohol (methanol or ethanol) accelerated the reaction rate. The time for complete reaction (>96%) of solid PET with NaOH in methanol at 60°C was 40 minute and 7h without dioxane. Moreover, Oku et al. reported that, the pellets of PET were heated in anhydrous ethylene glycol with NaOH at 150°C for 80 min or 180°C for 15 min to produce disodium terephthalate (Na_2-TPA) and EG. The reaction system is simple; no water and no extra reagent other than NaOH and EG used. The main advantage of the alkali hydrolysis method is that it can tolerate highly contaminated postconsumer PET such as magnetic recording tape, metallized PET film, or photographic film (x-ray). The process was relative simple and less costly than methanolysis **[Scheirs 1998].**

In addition, the hydrolytic depolymerization of PET with alkaline hydroxide examined by Kao et al **[Kao et al 1998].** The results

investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The presence of water facilitated the alkaline hydrolysis of PET; however, the presence of metal acetates decreased the hydrolysis rate. The activation energy for alkaline hydrolysis of PET, determined by the thermograms, was in good agreement with the value obtained from the experiments in a batch reactor.

Through hydrolytic degradation of PET, various oligomers are formed, which can be detected using chromatographic techniques, which were rather expensive. This process finally leads to a strong decreased in strength of PET fibers. A much faster identification of the characteristic degradation products can be achieved through ***matrix assisted laser desorption ionization mass spectrometry*** (MALDI-MS). The principle of this method was already well known especially in the lower molecular mass range (<10,000 Dolton), MALDI-MS exhibits the highest mass resolution and the best conditions for the formation of intact ions. Therefore, only the oligomeric degradation products used investigating the degradation behavior of PET by this method **[Zahn 1957], [Bruck 1958], [Heidemann 1965], [Mori 1971]** and **[Weidner 1995 and 1996].**

In addition, Weidner **[Weidner et al 1997]** studied the hydrolytic degradation of technical PET, which was investigated by means of different methods such as size-exclusion chromatography (SEC), viscometry, light-scattering, thin-layer chromatography, end-group titration, and MALDI-MS. The long-term degradation simulated by exposing PET filament yarns to aqueous neutral conditions at 90°C for 18 weeks. As expected, an ester scission process leads to form acid terminated oligomers (H-$[GT]_m$-OH) and T-$[GT]_m$-OH and ethylene

glycol terminated oligomers (H-[GT]$_m$-G), where G is an ethylene glycol unit and T is a terephthalic acid unit. Additionally, the scission of the ester bonds during the chemical treatment led to a strong decrease in the number of cyclic oligomers ([GT]$_m$).

Alkaline hydrolysis was also described by Karayannids et al. **[Karayannids et al 2002].** They reported that, the reaction took place in an autoclave at 120-200°C with aqueous NaOH solutions and at 110-120°C with a non-aqueous solutions of KOH. The disodium or dipotassium terephthalate received was treated with sulfuric acid and terephthalic acid (TPA) of high purity was separated. The ^{1}HNMR spectrum of the TPA revealed an about 2% admixture of isophthalic acid together with the pure 98% TPA. The purity of the TPA obtained tested by determining its acidity and by polymerizing it with ethylene glycol by using tetrabutyl titanate as catalyst. A simple theoretical model developed to describe the hydrolysis rate. This method is very useful in recycling of PET bottles and other containers because nowadays TPA was used to replace dimethyl terephthalate (the traditional monomer) as the main monomer in industrial production of PET.

- **ACID HYDROLYSIS**

Acid hydrolysis performed most frequently using concentrated sulfuric, nitric, or phosphoric acid. In order to avoid high pressures and temperatures in the reaction vessel. However, the process proves very costly because of the need to recycle large amounts of concentrated H_2SO_4 and the purification of EG from the sulfuric acid.

Yoshioka et al. **[Yoshioka 1994 and 1998]** proposed an acid hydrolysis of PET waste powder in relatively dilute sulfuric acid (<10M) and the reuse of the sulfuric acid by recovery methods such as dialysis. However, this requires long reaction times (5h) and an increase in the reaction temperature (150°C). Yoshioka et al. also described a process for the depolymerization of PET powder from waste bottles by using nitric acid (7-13M) at 70-100°C for 72h. TPA and EG were produced and the resultant EG was simultaneously oxidized to oxalic acid. The proposed method had the advantage to produce valuable-added products such as oxalic acid, which is more expansive than TPA and EG. However, the process of acid hydrolysis also induced other problems, such as corrosion of equipment and difficult separation of liquid products from the acid waste of strong acids.

- **NEUTRAL HYDROLYSIS**

Neutral hydrolysis is carried out with the use of hot water or steam. The process usually runs in high-pressure autoclaves at temperature 200-300°C and pressure 1-4 MPa and with excess water **[Paszun 1997]** and **[Scheirs 1998].** The TPA and EG produced from this method have high purity. Several researchers **[Campanelli 1993 and 1994], [Weidner 1997] [Kao 1998]** and **[Launay 1999]** have studied the kinetics of the hydrolytic depolymerization of PET under neutral conditions. In comparison to acid and alkaline hydrolysis, neutral hydrolysis has the main advantage that the amounts of inorganic salts, which were difficult to dispose of, can be avoided. Therefore, it can be considered as more environmental friendly and growing interest in this technology. Its main drawback was that all mechanical impurities present in PET

left in the TPA, thus the product can be consider of lower purity than the product of acid or alkaline hydrolysis.

The main problem encountered in neutral hydrolysis was employment of large excess of reactants such as water as well as high temperatures and pressures. In case of neutral hydrolysis, it was found that the large amount of water was required (ratio of 5/1 to 20/1 water/PET (w/w) **[Vaidya and Nadkarni 1987]** and **[Campanelli 1993].**

Yalcinyuva et al. **[Yalcinyuva 2003]** proposed a simultaneous glycolysis and neutral hydrolysis of PET waste. The reaction has been carried out at 170 and 190°C with constant amount of ethylene glycol (EG) and increasing amount of water, in the presence of xylene. The organic solvent made it possible to employ very low amounts of reactants as well as application of lower temperatures and pressures in contrast with previous methods, yielding intermediates suitable for PET or other polymeric materials. These intermediates were characterized by measuring acid value (AV) and hydroxyl value (HV) as well as by differential scanning calorimetry (DSC). A water soluble crystallizable fraction with high purity, consisting of mono 2-hydroxy ethyl ester of terephthalic acid (monohydroxyethylterephthalate, MHT) monomer has been obtained with significant yield.

Yalcinyuva et al. **[Yalcinyuva 2003]** also described the neutral hydrolysis of PET waste, which has been carried out with different amounts of water and different catalysts and in the presence of xylene. The organic solvent made it possible to employ very little amounts of water, lower temperatures and pressures and providing concentrated ethylene glycol (EG) solutions in contrast with previous methods,

yielding intermediates suitable for PET preparation. These intermediates characterized by FTIR spectroscopy, acid value (AV), and hydroxyl value (HV) and viscosity average molecular weight (M_V) measurements.

1.4 AMINOLYSIS AND AMMONOLYSIS OF PET

Aminolysis is the reaction of PET with different amine aqueous solutions to yield the corresponding diamides of TPA and EG. There are no available reports for the utilization of this process in a commercial scale. However, partial aminolysis has found its application in the improvement of PET properties in the manufacture of fibers with defined processing properties. The amines used include methylamine, ethylamine, and ethanolamine in the temperature range of 20-100°C. Degradation with triethanolamine gives different ester products and taking into consideration the presence of functional hydroxyl and amine groups, the products may constitute potentially as raw materials for the synthesis of polyurethanes, mainly rigid polyurethane foams **[Spychaj 1998].**

Ammonolysis is the reaction of anhydrous ammonia with PET to produce a terephthaliamide. This can be converted to terephthalonitrile and further to other chemical substances. The reaction is carried out with post consumer PET bottles at 120-180°C and pressure of about 2 MPa for 1-7h **[Spychaj 1998].**

1.5 THERMAL AND PHOTO DEGRADATION OF PET

It is well known that the thermal degradation of the plastic waste, such as PS, PVC and PET, causes serious pollution problems, which convert waste plastics to useful hydrocarbons. Murata and Makino **[Murata and Makino 1975]** studied the thermal degradation of polyethylene (PE) and polypropylene (PP) in a reactor equipped with a feeder for the plastics. PE and PP were easily degraded without carbonaceous residue above 445°C and 410°C, respectively, yielding hydrocarbons with a carbon number ranging from 1 to 30. Ng et al. **[Ng et al 1995]** investigated the thermal cracking of a high-density PE and obtained results similar to those of Murata and Makino. There are many studies on the pyrolysis of PVC. PVC was dechlorinated in the temperature rang from 573 to 653K, and then the remaining carbon chains were decomposed above 653K. **[Anderson 1961], [Chang 1974], [Kuroki et al 1976], [Farr 1986], [Ishihara 1989], [Songip et al 1993 and 1994], [Wu et al 1994],** and **[Bisi et al 1994].**

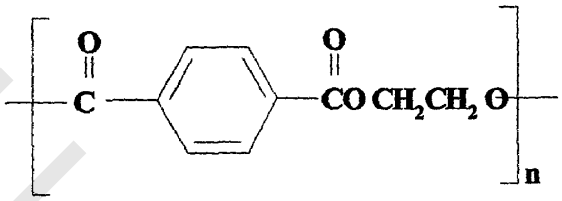
The aromatic linear polyester PET, as with most synthetic polymers, undergoes complex physicochemical transformations after its polymerization. Some degradative processes may be induced by thermal, chemical, or irradiative agents encountered during processing or when in normal use. Consequently, various aspects of the mechanisms and kinetics of degradation of PET, have long been of interest **[Marshall 1953], [McMahon et al 1959]** and **[Goodings 1961].**

In early work, semi-quantitative methods were used to investigate the products of thermal decomposition of PET and the kinetics was studied

by melt-viscosity techniques. It is now believed that the thermal decomposition process of PET in inert atmosphere can be represented by the reaction scheme.

$$A_1 \xrightarrow{\Delta} A_2 \xrightarrow{\Delta} A_3$$

Where A_1 is the polymer (PET) with the structure



The primary degradation process was attributed to a random scission of ester links in the main chain; yielding A_2 which, has been shown to be a mixture of monomeric terephthalic acid and vinyl ester oligomers **[Marshall 1953], [Goodings 1961], [Luderwald 1979]** and **[Bendas 1981].** Because the end-groups in PET are predominantly hydroxyl-esters, trans-esterification of the vinyl esters formed on degradation and lead to the rapid production of low molecular weight volatile fragments with consequent weight loss. The volatiles (A_3) have been shown to be mostly HCOOH, CH_3COOH, CO, CO_2, C_2H_4, H_2O and CH_4 **[Fann 1996], [Edge et al 1996]** and **[Tate 1996].**

Jenekhe **[Jenekhe 1983]** investigated the kinetics of the thermal degradation of PET employing differential kinetics models and rapid computer analysis of thermogravimetric weight-loss data. It was shown that the rate of degradation, activation energy, and pre-exponential factor depend strongly on heating rate whereas the order of reaction,

found to be one remains unchanged. Estimates of low temperature (<300°C) isothermal kinetics, and hence isothermal stability of PET films, from non-isothermal kinetics were shown to be similarly dependent on the heating rates employed in dynamic thermogravimetry. The observed variation of kinetic parameters with heating rate attributed to the coupling of physical transport processes with chemical processes.

The thermal degradation of PET occurred through intramolecular backbiting lead to cyclic oligomers of up to three units in size. And chain scission through a C–H hydrogen transfer reaction, lead to vinyl ester and acid end-groups **[Luderwald 1976], [Foti 1984],** and **[Montaudo 1993].** Villain and coworkers **[Seo 1991]** and **[Villain 1994]** found that the aliphatic end-groups were more susceptible to thermal degradation. PET has also been found to be more susceptible to hydrolysis in the presence of 0.007%, water. The rate of chain scission at 280°C was found to be double that of dry material.

Takao et al. **[Takao et al 1997]** demonstrated that the PET waste can be successfully decomposed in a steam atmosphere, yielding an amount of terephthalic acid predicted from the chemical formula of PET. It was found that the steam accelerated the hydrolysis of PET, yielding terephthalic acid and oxygenated compounds such as aldehyde and ester with less 1% carbonaceous residues. The amount of carbonaceous residue decreased with an increase in the fraction of steam in the carrier gas and was about 16% in nitrogen steam and below 1% in steam. The amount of terephthalic acid predicated from the chemical formula of PET (about 87%) recovered at about 723K in a carrier gas containing 70% steam and 30% nitrogen. Kinetic equations were proposed by considering both the hydrolysis and thermal pyrolysis of PET.

Chiu and Cheng **[Chiu and Cheng 1999]** investigated thermal degradation and catalytic cracking reactions of PET at atmospheric pressure. The extent of PET thermal degradation is little affected by the particle size, but tremendously affected by temperature. In PET catalytic cracking reaction, copper (II) chloride was the most active among tested catalysts. It reduced the carbonaceous residues and increased the percentage weight loss of PET about 3.5 times in comparison with thermal degradation at the same reaction conditions. Considering the weight loss of catalyst itself during the reaction, copper (II) chloride was still the most effective. Mixing catalysts and PET by impregnation demonstrated higher cracking ability than physical mixing. The results of PET catalytic cracking over copper (II) chloride demonstrated that the effect of temperature on the percentage weight loss was similar to thermal degradation but shortened cracking time. The optimal catalyst-to PET ratio was 0.1%. The catalytic cracking has some advantages over thermal degradation (non-catalytic) such as increasing the cracking ability of plastics, shortening the cracking time, and reducing the proportion of solid residue in final products. Finally, it can report that, the catalytic cracking more efficient and economical way to recycle waste PET than the non-catalytic process

Hay and Holland **[Hay and Holland 2002]** proposed the thermal degradation of two commercial, PET samples and two laboratory prepared polyesters, poly (ethylene isophthalate) poly (diethylene glycol terphthalate), was studied using thermogravimetry and thermal analysis-Fourier transform infrared spectroscopy. The commercial PET samples copolymerised with diethylene glycol and isophthalic acid groups in different proportions, and their thermal stabilities found to differ. Through a study of the thermal degradation of poly (diethylene

glycol terephthalate) and poly (ethylene isophthalate), it was found that diethylene glycol and isophthalate units promoted thermal degradation through increased chain flexibility and more favorable bond angles, respectively. The thermal degradation of all the polyesters tested lead to the formation of non-volatile residue. Infrared spectroscopic analysis indicated that the residue consisted almost exclusively of interconnected aromatic rings.

Samperi and colleagues **[Samperi et al 2004]** studied the isothermal degradation of PET conducted at the temperature range of 270-370°C, in order to simulate the reactions that take place during the processing of PET under inert atmosphere (N_2). The structural characterization of the reaction products was performed by mass spectrometry and by ^{1}HNMR analysis. The result indicates the formation of cyclic oligomers that decompose at higher temperature. The proposed tools could not detect vinyl ester terminated oligomers, whereas the formation of anhydride containing oligomers was well apparent.

In a parallel study, Samperi and colleagues investigated the isothermal degradation of poly (butylene terephthalate), PBT. In spite of, the two aromatic polyesters are structurally quite similar, but the results showed that the presence of the butylene unit in PBT was apparently able to induce significant changes in the isothermal degradation of PBT compared to PET **[Samperi et al 2004].**

Photodegradation is another method of the PET degradation. Some researchers considered PET photodegradiation. Ben et al. **[Ben et al. 1998]** investigated that Titanium dioxide thin films which have been deposited on PET by r.f. magnetron sputtering in argon–oxygen mixtures. The characteristics of the coatings investigated by X-ray

diffraction, scanning electron microscopy, and Rutherford backscattering spectrometry, infrared and UV–visible spectroscopy. The deposited films were found to be amorphous or crystalline, depending on the process parameters. The microstructure was variable within a wide range, from compact to porous and columnar. The O/Ti atomic ratio was found to increase with the total pressure. This increase was correlated with the incorporation of hydroxyl groups. The stresses determined by the bending beam method were compressive and increase with the kinetic energy of the sputtered particles. The variations of the optical constants (refractive index, extinction coefficient and optical band-gap energy) were related to microstructural and composition evolutions. PET photodegradation showed that the photooxidation rate was strongly dependent on the coating properties, and reached its lowest value when the sputtering parameters combine a moderate pressure (1.5 Pa) and a high r.f. power (>1.9 W cm^{-2}).

In addition, Guillaume et al. **[Guillaume et al. 2002]** demonstrated the chemiluminescence's of the polyester, poly (ethylene-co-1,4-cyclohexanedimethylene terephthalate). (PECT) had been determined and related to that from PET. The aliphatic backbone in PECT and PET was found to play a dominant role in controlling the behavior of the chemiluminescence (CL) emission and can be related to the nature of the hydroperoxidation sites. The CL emission and its profile were also found to be highly dependent upon the thermal and UV oxidative history of the material. Hydroperoxide sites formed during oxidation were found to be responsible for the thermally induced CL. Thermal oxidation of the polymer as measured by hydroperoxide concentration was also shown to be directly related to CL intensity and can predict the behavior of antioxidants.

Fechine and coworkers **[Fechine et al. 2002]** explained the weathering behavior PET. Samples produced by bi-axial extrusion were exposed in the laboratory for periods of up to ~1100 h. Films produced with different types of stabilizers (a ultraviolet absorber, carbon black and a mixture of TiO_2 and $BaSO_4$) were tested for mechanical properties and by UV-visible spectroscopy, titration, size exclusion chromatography and Fourier transform infrared spectroscopy. The results indicated that the unstabilized films were very susceptible to degradation, causing a large deterioration in mechanical properties and reduction in molecular weights of the stabilizers used; the UV absorber was shown to be the most effective. Furthermore, Fechine et al. **[Fechine et al. 2004]** investigated the surface of photograted PET. The results indicated that the unstabilized films were very susceptible to degradation, causing a large deterioration, especially in surface layers. The presence of an ultraviolet light absorber effectively reduced the formation of carboxyl end-groups at the surface as well as in the bulk of the films. In the case of samples with UV absorber, the fluorescence data showed a barrier imposed by this additive in the formation of the monohydroxy-terephthalate. Scanning electron microscopy of rupture surfaces showed that film ductility was highly reduced after exposure.

1.6. BIODEGRADATION OF PET

One of the possible solutions for environmental problems may be the development of biodegradable plastics to be used in packaging. Furthermore, agriculture and clinical uses are also waiting for the arrival of environmentally degradable polymeric films and sheets able to compete in price with conventional indestructible materials. Finally, biodegradable and biocompatible polymers with good mechanical

properties will be very welcome in the biomedical field. Because of simplicity and low cost, modification of well-established polymers appears to be the most promising approach in the development of novel biodegradable plastic materials.

- ***Polymer degradation*** is a deleterious change in the properties of a polymer due to a change in the chemical structure.
- ***A biodegradable polymer*** is a polymer in which the degradation happens in the bulk and at the surface, and is mediated; at least partially by a biological system.
- ***A bio-absorbable polymer*** is a polymer that; can be assimilated by a biological system.

Although PET is innocuous for the human body, it is looked on as; a noxious material due to its prominent presence in the waste streams and its high resistance to atmospheric and biological agents. However, time-controlled degradation of the polyester by the environment would be highly desirable for certain applications such as food packaging, and farming consumable and biodegradable biomaterials. Furthermore, according to toxicity data by Verschueren **[Verschueren 1996]** the breakdown products of the degradation of PET (ethylene glycol and terephthalic acid) were known to have very low acute toxicity to bacteria, algae, crustaceans, fishes and mammals, which means they can be bio- assimilated.

Biodegradation is known for enzymes that able to fasten the hydrolytic degradation of certain polyesters derived from natural products such as

poly (glycolic acid) "PGA", poly (lactic acid) "PLA" and poly (α-hydroxy alkanoates). Other synthetic polymers susceptible to degradation by micro-organisms are poly (ethylene glycol) "PEG" and poly (ω-caprolactone) "PCL". All of them are commonly recognized as, easily degradable polymers. Although these aliphatic polymers frequently described as 'truly' biodegradable, in practice the bio-assimilation step normally preceded by a biotic hydrolysis, giving monomeric and oligomeric products that are accessible to microorganisms.

Conversely, PET, is generally considered non-biodegradable. Smith et al. **[Smith et al. 1987]** synthesized specimens of ^{14}C-labeled PET and exposed them to several enzyme solutions. The polymer affected in a small extension by *esterase* and *papain*, apparently by different kinetics, but not by *trypsin* or *chymotrypsin*. These observations indicated that nominally stable PET is susceptible to biodegradation under certain conditions. Nevertheless, too much effort has devoted to increase the vulnerability of PET to biodegradation. The strategy based on making PET more susceptible to chemical hydrolysis, thus favoring biodegradation, has scarcely used.

Tietz and coworkers **[Tietz et al. 1992, and 1995]** prepared a modified PET for compo-stable products such as disposal nappies and rubbish bags capable of disintegrating in 4 days. The compound contains 5-sulphoisophthalate units, which are much less resistance to hydrolysis due to the activating effect exerted by the strong electron-with-drawing substitute. Aside from this rare but interesting example of modification, the approach almost unanimously applied consists of incorporating

units comprising well-recognized bio-hydrolysable polymers in the PET chain, either by polymer-polymer transesterfication or by copolymerization of the appropriate set of co-monomers.

Whereas PET, undergoes extremely small changes *in vivo* and resist fungal and enzymatic degradation. A Co-polyester contain one lactic acid unit for every three ethylene terephthalate units was shown to be biodegradable and has been suggested as an aorta implant, **[Schwertassek 1970 and 1972], [Leonard 1972], [Tokiwa et al. 1976 and 1977],** and **[Rudakova 1979]** by modification of PET with glycolic acid and lactic acid. Niekraszewicz **[Niekraszewicz 1993]** obtained biodegradable, cheap, and environmentally safe polymeric materials. These co-polyesters were prepared by ester-ester exchange between PET and PGA or PLA, and by polycondensation of PET with the cyclized dimers of these β-hydroxycarboxylic acids.

Tokiwa and coworkers **[Tokiwa et al. 1981, 1990 and 1994]** synthesized copolyesters of PET and poly (ε-caprolactone) "PCL" by transesterification upon mechanical blending at 270°C in the presence of a catalyst, and subjected them to biodegradation by *Rhizopus delemer* and *Rhizopus arrhizus* lipases. The susceptibility of PET/PCL co-polyesters to enzymatic hydrolysis was found to depend largely upon the composition of the copolymer. Thus, biodegradability increased gradually with the extension of the transesterification reaction, so that co-polyesters, which found at the early stages of the reaction were quite resistant to enzyme attack. Because hydrolysis decreased as the content of aromatic units increased, it was assumed that the rigidity of the aromatic ring depresses biodegradability by lipases. In contrast, Jun et al. **[Jun et al. 1994]** prepared these co-

polyesters in a similar manner and investigated their degradation when exposed to *Pseudomonas lipase* at pH = 7.0 by gel permeation chromatography and ^{1}HNMR. It was striking to observe that PCL incorporated into PET was resistant to *Pseudomonas lipase* in spite of that the homopolymer was readily degraded by this enzyme. Chiellini et al. **[Chiellini et al. 1996]** also evaluated the biodegradability of transesterified PET/PCL blends and observed that copolymers with intermediate compositions acted as compatibilizers, allowing for complete miscibility of PET and PCL. It was concluded that the higher the amount of incorporated PCL segments, the higher the susceptibility of these copolyesters to hydrolysis.

Khemani **[Khemani 1997]** synthesized biodegradable foamable aliphatic-aromatic polyesters by condensation polymerization of dimethyl terephthalate, dimethyl glutarate, 1, 4-butanediol and pentaerythritol as cross-linking agents, in the presence of titanium isopropxide.

Negata et al. **[Negata et al 1996]** prepared PET copolymers with non-polyester compounds such as poly (ethylene glycol) "PEG" and poly (butylenes glycol) "PBG" by melt polycondensation of dimethyl terphthalate and ethylene glycol containing 10-40% of the polyether. The biodegradability was estimated by weight loss of copolymer films in buffer solution with and without lipase at 37°C. Degradation slightly favored by the presence of enzymes and increased with content in glycol, a result that correlated to the amount of absorbed water and the content in ester linkages between PET and polyether segments. The weight loss of copolymers containing PBG units was much lower than that undergone by copolymers prepared with PEG.

Reed and Gilding **[Reed and Gilding 1979 and 1981]** reported the preparation and biodegradability of a series of copolymers of PET/poly (ethylene oxide) "PEO" for use in surgery. They found that *in vitro* degradation occurred by hydrolysis of ester linkages and that it was accelerated by the addition of enzymes. David et al. **[David et al. 1999]** studied that the various derivatives of terephthalic acid (TPA) and 2,6-naphthalene dicarboxylic acid (NDA), which have been degraded in the presence of various strains of micro-organisms. These compounds include the dimethylesters (TME and NDME), the ethylene glycoldiesters (TGE and NDGE) and the corresponding ethylene glycol polyesters (PET and PEN). The terephthalic acid derivatives were not degraded by a pure strain of nonsporulating gram-positive bacteria isolated from industrial compost for household refuses although this microorganism efficiently mineralizes aliphatic polyesters. The naphthalene dicarboxylic acid and derivatives did not allow growth of various *Pseudomonas* strains, which assimilate naphthalene, and some of its simple derived compounds. Therefore, isolation of microorganisms degrading these aromatic acids and ester derivatives performed using an enrichment technique. Garden soil or compost used as sources of microorganisms. Schnabel and coworkers **[Schnabel 2002]** demonstrated that the bacterial thermoplastic polyesters poly (3-hydroxyalkanoate) PHAs produced by the fermentation of renewable materials, such as sugars or molasses. The pure homopolymer, PHB, and pure copolymer (3-HBP-CO-HV) (88:12) were brittle materials. PHB or PHB/V mixed with other biodegradable materials to improve their mechanical properties. The blends were ductile polymers with plastic deformation. They were biodegraded in aerobic tests, under compost conditions in soil and water, and many pores to be found on

the surface. The blends degraded more easily in the aerobic test, i.e. in the river water and compost, than in the soil. The results showed that all kinetic data best conformed to the zero order biodegradation model with a low biomass specific maximum substrate utilization rate of 0.168 mg COD/mg VSS day reflecting the slow biodegradability of the waste water even after 99% removal of oil and grease.

1.7 Converting PET Waste into Useful Products

PET is one of the most important recyclable polymers, a quality that has made it easier to earn consumer acceptance over the other packaging polymers. Recycled PET (R-PET) is mainly used as melt-spun fibers in the fashion market as fleece sweaters, sports bags, backpacks, athletic wear, egg cartons and tennis ball cans. The other uses include blow-molded containers for household chemicals/detergents, multilayered bottles, insulation foams, automotive parts, packaging film and polyesters. Rossi et al. **[Rossi et al. 2003]** investigated the breaking down of recycled PET into its chemical building blocks using glycolysis. The main objective is to produce a polyester polyol for the polyurethane industry from recycled PET and to compare the properties with that of a virgin resin. Robin and coworkers **[Robin et al. 1998]** reported on the glycolysis of PET that leads to oligomers diols that were polycondensed with caprolactone. The obtained diols extended with hexamethylene diisocyanate to obtain polyurethane. In certain conditions, the polyurethanes were very miscible with PVC, leading to acceptable mechanical characteristics for blend. Chen et al. **[Chen et al. 2001]** reported on the glycolysis of recycled PET that can be used to the produce of BHET monomer. BHET has been widely used in the

production rigid or flexible polyurethanes. Billiau et al. **[Billiau et al. 2002]** used the recycled polyol oligomers for rigid polyurethane foam manufacture. The polyol molecular structure built on three diacidic moieties and three glycolic moieties in various proportions. Viscosity, foaming agent compatibility and storage stability were the most relevant physicochemical properties. The own effect of each structural unit was also investigated through some more homogeneous panels of polyols. Lack of storage stability appears when the proportions of constitutive PET units in glycolic and acidic moieties overcome critical values.

Abdel-Azim and coworkers; **[Abdel-Azim 1998]** synthesized different glycolysed oligomers by depolymerization of PET, in presence of manganese acetate as a catalyst. Diethylene glycol (DG), triethylene glycol (TG), propylene glycol (PG), mixtures of DG/TG, and DG/PG used for glycolysis. The glycolysed products were reacted with maleic anhydride (MA) to prepare a series of unsaturated polyesters (UP) having different molecular weights. These polyesters dissolved in styrene monomer and their curing behavior investigated and compared with the curing behavior of UP made from virgin materials. The effect of activator and initiator concentrations on the curing characteristics of the recycled resins was studied. The mechanical properties and the hardness of the cured resin measured and correlated to their molecular structure.

Suh et al. **[Suh et al. 2000]** reported the preparation of the unsaturated polyester (UP) based on the glycolyzed PET with propylene glycol (PG), diethylene glycol (DEG) and their mixture. They have studied the influence of glycol compositions on the chemo-rheological behavior and the mechanical properties of the glycolyzed PET. The gel time of

UP was delayed with increasing DEG contents. The tensile modulus decreased and toughness of cured products increased with increasing DEG contents due to the flexibility of ether linkage in DEG unit.

Viksne et al. **[Viksne et al. 2000]** demonstrated the recycling of PET through glycolysis with EG and PG mixtures and DEG. The glycolyzed products were reacted with maleic anhydride and mixed with styrene or tri ethylene glycol dimethacrylate (TGM) monomers to get unsaturated polyesters (UP) suitable for producing of varnishes and paints. The curing behavior of UP resins in the presence of different initiators was studied by means of differential scanning calorimetry (DSC). The processing characteristics like viscosity, exotherm temperature of curing, compatibility of UP resins with monomers investigated with respect to the type and amount of reactive monomers and initiators. The main properties (hardness; impact resistance elasticity) of varnish and paint coating were determined.

Rabeiz and Fowler **[Rabeiz and Fowler 1991]** investigated the mechanical and durability properties of polymer concrete (PC) made with the resins, which produced from recycled PET. The properties of PC using resins based on R-PET were compared to those PCs made from virgin materials. Resin using R-PET offer the possibility of a lower source cost for forming useful PC based products. In addition, the recycling of PET in PC would help to alleviate an environmental problem and would save energy. Potential applications for such PC material include recast components; repair materials for Portland cement concrete, bridge, wall, and floor overlays.

Nilgun et al **[Nilgun et al 2000]** proposed a new generation of block copolymers starting with depolymerized PET by glycolysis with some oligomeric diolos, alpha, omega – dihydroxy poly (dimethyl siloxane)s,

hexylene glycol, poly(ethylene oxide) glycols, and ethylene glycol used as diols. The dihydroxy-terminated products containing a terephthalyl group and oligomeric diols used to prepare macroinitiators (MI). These MIs were used to polymerize the styrene monomer.

Kawamura et al. **[kawamura et al. 2002]** considered the R-PET as a condensation polymer composed of ethylene glycol (EG) and terephthalic acid (TPA), they tried to use these derivatives in coating resin syntheses. Polyesters for powder coatings synthesized from R-PET in place of EG and TPA showed the same structure and characteristics as conventional polyester synthesized from ordinary EG and TPA monomers. An alkyd resin for ambient temperature curing coatings was synthesized from R-PET as a substituent for EG and phthalic anhydride (PA). After modifying its monomer composition, it finally showed the same characteristics as the original resin. The use of R-PET in alkyd and polyester resin syntheses provide beneficial means for mass consumption of R-PET.

Saint and coworkers; **[Saint et al. 2003]** demonstrated the synthesis of thermoplastic elastomer compounds by direct copolyesterification of reactive oligomers of PET, and poly (tetramethylene oxide), PTMO. PET was glycolysed to synthesis hydroxytelechelic oligomers of PET. Hydroxytelechelic PTMO modified to synthesis carboxytelechelic oligomers. The chemical structures of these oligomers were investigated by ^{1}HNMR and size exclusion chromatography. Multiblock poly (ester-ether), then obtained by polyesterification of the hydroxytelechelic and carboxytelechelic oligomers, using different catalysts and different reaction conditions. The thermal and thermomechanical behavior of the synthesized poly (ester-ether)

investigated by differential scanning calorimetry and by dynamic mechanical analysis, and showed a thermoplastic elastomer behavior.

Atta **[Atta 2003]** studied the preparation of aromatic epoxy resin by glycolysis of PET with different ratios of diethanolamine and triethanolamine and manganese acetate as a catalyst. P-Phenylenediamine and diaminodiphenylether used as curing agents. The curing reactions and thermal properties of cured aromatic epoxy resins investigated. Curing and post cure peaks observed in dynamic DSC thermograms. The cross-linked network was thermally stable up to 470°C. Preliminary tests indicate that the resins exhibit superior adhesion properties.

Rene et al. **[Rene et al 2003]** examined that PET was alcoholized with EG to synthesize hydroxytelechelic oligomers of PET. On the other hand, commercial hydroxytelechelic polyepsilon-caprolactone modified in order to synthesize carboxytelechelic polyepsilon-caprolactone. Multiblock copolyesters then synthesized by polyesterification of hydroxytelechelic PET and carboxytelechelic polyepsilon-caprolactone oligomers, using several catalysts and different reaction conditions, which had been linked with the average molecular weight of the obtained block copolyesters. It appeared that residual distannoxane species coming from glycolysis step were best catalyst for polyesterification reaction.

Luciana et al. **[Luciana et al. 2004]** reported that thermally sprayed coatings were increasing in importance as protection against corrosion and wear. PET powder deposited on 1020 steel by low-velocity flame spray technology. A potential application of this coating was to provide protection against corrosion in automobile fuel tanks, which were nowadays made of lead-tin-coated steel. In spite of the good properties

presented by the lead-tin-coatings, environmental cost restrictions had limited. PET powder was obtained from post-consumer beverage bottles. It was observed that the temperature attained by the PET during the deposition significantly affects the characteristics and properties of the coating. Chemical and structural changes of PET due to the thermal spray processing investigated by FTIR spectroscopy, differential scanning calorimeter and viscosity analysis. The corrosion resistance of the coating was evaluated by total and partial immersion testes in gasoline, diesel oil and alcohol.