



UNIwersYTET WARSZAWSKI
WYDZIAŁ CHEMII



Experiment 24

Chemical recycling of poly(ethylene) terephthalate (PET)



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I. Basic information and biodegradable polymers.

Plastics have become commonly used materials in our everyday lives. The world production of plastics increased in the last ten years by 62%, simultaneously steel production decreased by 21% [1] and at present time global plastics production is about 130 mln tonn per annum. However, growing applications of plastics contributing to growing amount of solid wastes. In 2008, total generation of post-consumer plastic waste in EU-27, Norway and Switzerland was 24.9 Mt. Packaging is by far the largest contributor to plastic waste at 63%. Average EU-27 per-capita generation of plastic packaging waste was 30.6 kg in 2007. [2]

The traditional petroleum derived plastics are not biodegradable and accumulate in the environment. It would appear that application of biodegradable polymers in production of plastics may be alternative to recycling of plastics. Biodegradable plastics were first introduced in 1980s. The biodegradable materials can be prepared from petroleum derived polymers by addition to them antioxidants reacting under UV radiation inducing degradation of polymer chains by photo-oxidation. As additives hydroperoxides and transition metal complexes can be used. However biodegradability of such materials is still controversial and they should be rather considered as oxo-degradable plastics.

Polymers with hydrolysable backbones are sensitive to biodegradation under particular conditions. The most important example of such class of polymers are aliphatic polyesters used in packaging production (Figure 1 shows formula of the most important examples such polymers). They are extensively studied due their simple synthesis and versatility in application. Polylactide (*PLA*) is usually obtained from polycondensation of D- or L-lactic acid. (Figure 2) Because the biodegradation rate for PLA is relatively low (full biodegradation in few weeks) thus copolymers with others hydroxyacids have been developed. [2]

Chemical structure of poly(glycolic acid) (PGA), poly(lactic acid) (PLA), and poly(lactic-co-glycolic acid) (PLGA).

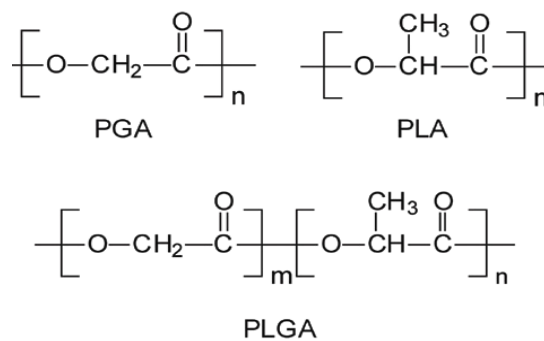


Fig. 1. Chemical structures of polymers and copolymers most commonly used in preparation of biodegradable materials.

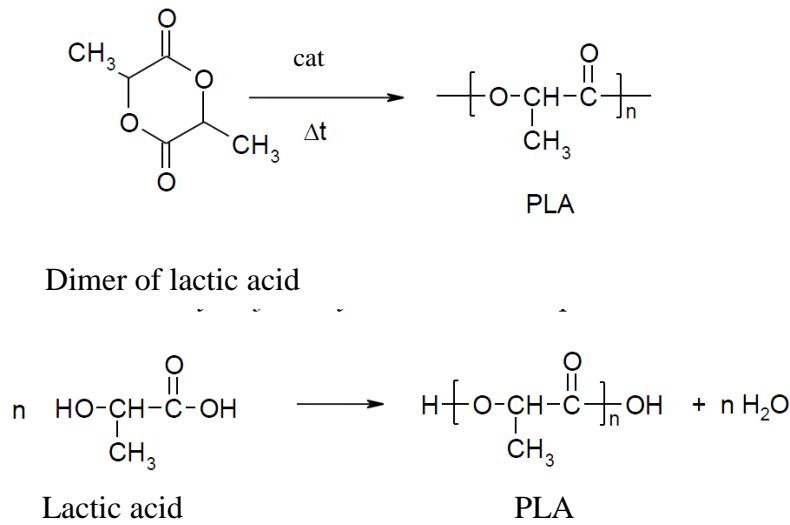


Figure 2 The possible routes of polylactide (PLA) synthesis.

In recent years biodegradable polymers obtained from renewable resources have attracted much attention. Natural biodegradable polymers called biopolymers (such as proteins, polysaccharides, starch and cellulose) can be extracted from renewable natural sources. However the obtained material required chemical modification to improve its mechanical properties. Thus many from the commercial available biodegradable materials based on biopolymers are in fact the mixture containing aliphatic polyesters as improving additive. (Table 1). This type of materials can be used in packaging production and usually is completely biodegradable during 70-80 days. (Figure 3) Microorganisms are able to consume these materials in their entirety, producing carbon dioxide and water as by-products. Then this kind of material is marked with special code as compostable. (Figure 4)

Table 1

Commercially available starch and blends with polyesters.[2]

Trade name	Company	Country
Mater-Bi [®] , Biocool [®]	Novamont	Italy
Solanyl [®]	Rodenburg Biopolymers	Netherlands
Ecofram [®]	National Starch	USA
Vegeplast [®]	Végémat	France
Biolice [®]	Limagrain	France
Biotech [®]	Biotech	Germany
Bioplast [®]	Biotec	England
Plantic [®]	Plantic Technologies	Australia



Figure 3. Decomposition process of plastic bottle (based on PLA) during 70-80 days.

a)



b)



Figure 4. a) The completely biodegradable bag made from composite thermoplastic starch and aliphatic polyesters and appropriate code for biodegradable materials.

In recent years another type of biodegradable polymers has been proposed. There are microbial polymers wholly biodegradable obtained from bacteria or transgenic plants with using biotechnological processes. These polymers are obtained by polymerization from monomers prepared by fermentation process or produced by range of microorganisms. For example Cargil Dow Polymers produced PLA from lactic acid obtained via starch fermentation by lactic bacteria.

There are three main sectors where biodegradable polymers have been introduced medicine, packaging and agriculture. Table 2 illustrates main applications of biodegradable polymers.

Nevertheless at present time only a few groups of the biodegradable materials are of market importance. The main reason is their price, which is not yet competitive with

petroleum derived polymers. Another problem is influence of these polymers on environment. It worth noting that landfilling of this type of materials causes increasing greenhouse gases emission.

Table 2

Some applications of biodegradable polymers.[2]

Product	Society	Composition	Applications
Mater-Bi [®]	Novamont (Italy)	Starch and polyester	Collection bags for green waste, agricultural films, disposable items.
Polynat [®]	Roverc'h (France)	Rye flower (80%)	Disposable items, flower containers
Ecofoam [®]	American Excelsior Company (USA)	Starch	Wrapping plastics
Biopol [®]	Goodfellow (Great Britain)	PHB/PHV	Razors, bottles
Eco-pla [®]	Cargill Dow (USA)	PLA	Sanitary products, sport clothes, conditioning and packaging
Bio-D [®]	Cirad (France)	Proteins extracted from cotton seed	Agricultural films
Ecoflex [®]	BASF (Germany)	Co-polyester	Agricultural films
Eastar Bio [®]	Eastman (Great Britain)	Co-polyester	Agricultural films
BAK 1095 [®]	Bayer (Germany)	Polyester amide	Disposable items, flower containers

II. Plastic recycling legislation in European Union

Directive 94/62/EC of the European Parliament and of the Council of 20 December 1994 on packaging and packaging waste promotes the recovery and incineration at waste incineration plants with energy recovery and recycling of packaging waste. [3] This document has two the main goals protect the environment and ensure the functioning of the internal market.

Additionally European Commission prepared a voluntary identification system - (97/129/EC) - for packaging, which established that:

“the numbering and abbreviations on which the identification system is based, indicating the nature of the packaging material(s) used” The use of this system is voluntary for plastics.

Numbering and abbreviations are as follows:[4]

Table 5: EC voluntary scheme for plastics identification		
Material	Abbreviations	Numbering
Polyethylene Terephthalate	PET	1
High density polyethylene	HDPE	2
Polyvinyl chloride	PVC	3
Low density polyethylene	LDPE	4
Polypropylene	PP	5
Polystyrene	PS	6
Others	Unallocated	7-19

According to requirements of European Commission from 1999 should be recovered 50-65 % (weight) of plastic wastes. Germany was the first country which introduced obligatory regulations for the recovery and recycling of packaging materials. The Duales System Deutschland (DSD) was introduced in 1991 and this is the most effective recovery system in the Europe. The introducing of this system caused decreasing of weight of producing of package by 14% and increasing of recycled plastics by 86%. Another country which has recently introduced a regulation concerning disposal of household packages is France. Here importers and manufacturers of packaging materials are held responsible for contributing to the recovering of these materials. In the most countries in European Union management system plastic wastes is based on the same assumptions. Generally currently, existing legislation in European Union provides for the promotion of recycling and the reduction of incineration and landfilling of unseparated wastes.

In 2001 Poland as European Union Member State has introduced two laws that are implementation of Directive 94/62/EC. On the basis of these laws manufacturers of packaging materials are responsible for indicating the nature of packaging materials and their partially recovering, the price of recovery should be included in the product price. Moreover this law introduces the rule of sustainable development, it means development which allows that human needs can be meet not only in the present, but also for generations to come. Additionally establishes that the offender of pollution bear the cost of pollution (Dz. U. Nr 75, poz. 493- "Ustawa szkodowa"). Besides for facilities of recovering of especially dangerous wastes (for example automotive battery) deposit fee was introduced. The deposit fee is included in price of product and will be returned after returning used product to appropriate storage place.

III. Plastic recycling methods

There are three main methods for recovery plastics from the wastes:

Mechanical recycling

Feedstock recycling

Energy recovery

The type of chosen method depends on the properties of polymers. Other type of recycling must be used for thermoplastics and another for thermosets. Because thermoplastics are plastics which undergo a softening when heated to a particular temperature, can repeatedly soften and melt if enough heat is applied and hardened on cooling, so that they can be made into new plastics products. Examples are polyethylene, polystyrene and polyvinyl chloride, among others. Thermosets can melt and take shape only once. They are not suitable for repeated heat treatments; therefore after they have solidified, they stay solid. Examples are phenol formaldehyde and urea formaldehyde resins.

Mechanical recycling

Mechanical recycling of plastics refers to processes which involve the reprocessing of plastic was by melting, shredding or granulation. The obtained material is called recycle and has form of pellets, granules, flakes, etc. The mechanical recycling involves the following stages: separation of plastics, washing to remove dirt and contaminants, crushing, extrusion by heat and reprocessing into new plastic goods. It should be noted that this type of recycling is limited only to thermoplastics. Besides some difficulties are related with application of this type of recycling on the large scale. Polymer materials must be accurately separated by resin type because the presence of other polymers in polymer matrix can dramatically change the properties and application of obtained recycled material can be not possible. For example small amount of polyvinyl chloride (PVC) in recycled polyethylene terephthalate (PET) significantly decreases its commercial value due worse properties of such material. Moreover processing of materials made from the same polymer but with different colour leads to the material with undesirable grey colour. Additionally most of polymers can partially degrade during their use under influence of ultraviolet radiation, oxygen, ozone and other factors therefor recycled polymers exhibit worse mechanical properties in comparison with virgin polymers, and can be applied for less demanding applications. For example recovered car bumpers can be processed in mechanical recycling into car carpets. It worth to note that mechanical recycling is widely applied in automotive industry.

Feedstock recycling

Feedstock recycling another called chemical or tertiary recycling is decomposition of polymers with using chemicals or under influence of heat to obtain monomers (chemical depolymerization), fuels or industrial chemicals. Chemical depolymerization is limited to condensation polymers such as polyesters, polyamides, phenol formaldehyde resin, polyacetals, polyurethanes. The most often chemical depolymerization is used for poly(ethylene) terephthalate (PET) recycling. Figure 5 shows the main reactions using in chemical depolymerization of PET glycolysis, methanolysis and hydrolysis.

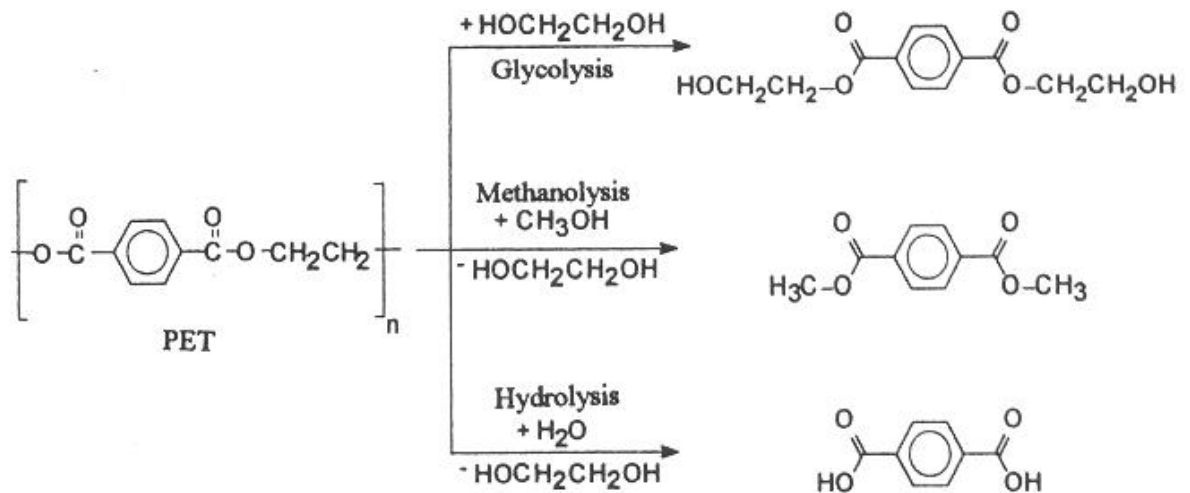


Figure 5. Depolymerization of PET into monomers by different solvolysis methods. [6]

Besides chemical depolymerization into feedstock recycling are classified such processes as hydrogenation, gasification, thermal treatments and catalytic cracking and reforming. (Figure 6)

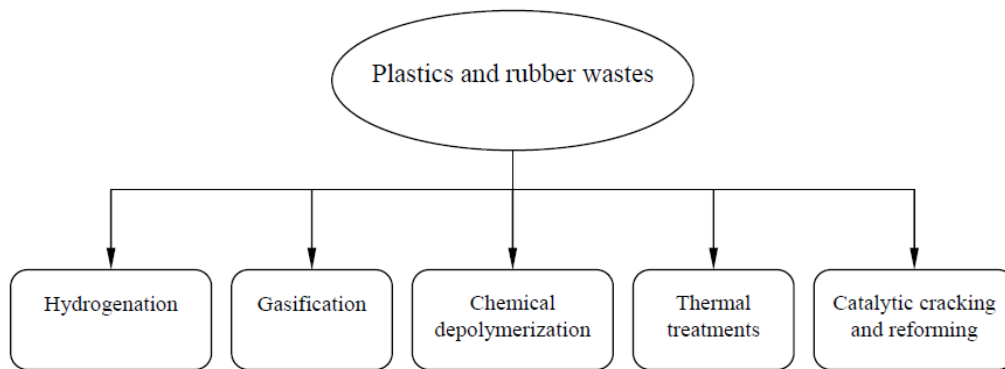


Figure 6. Alternatives for the feedstock recycling of plastics and rubber wastes (Aguado and Serrano 1999) [4].

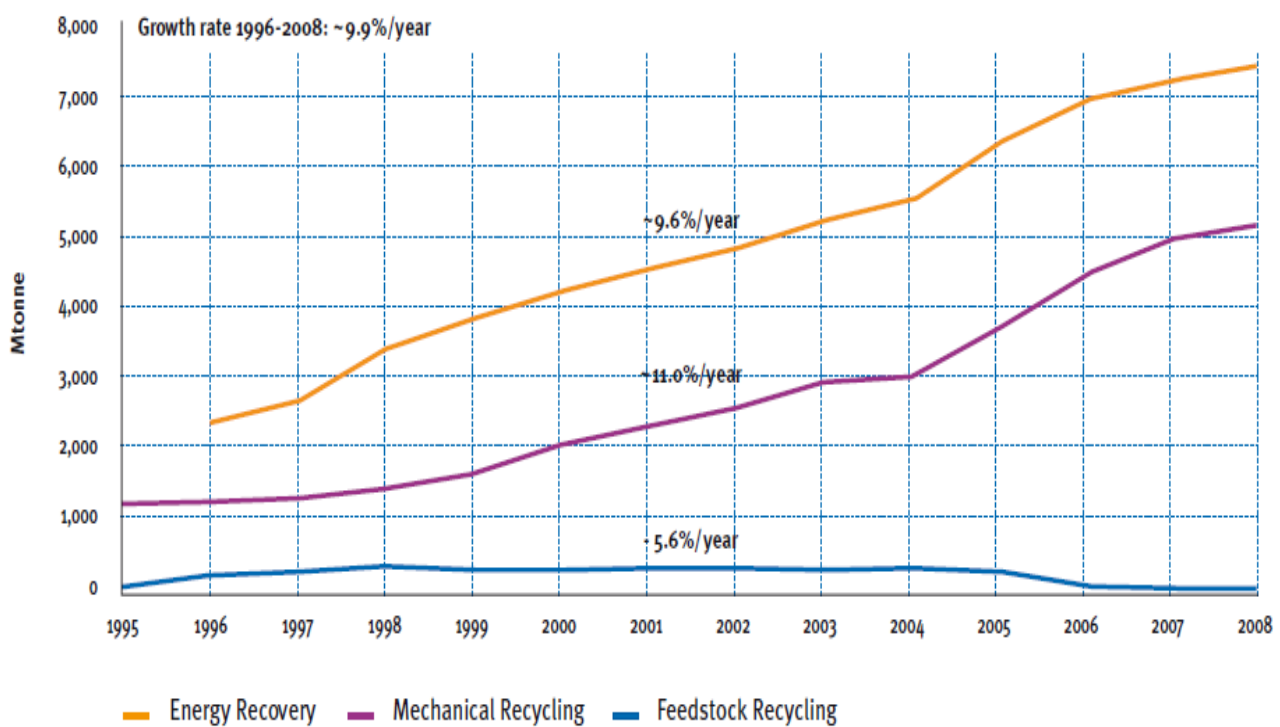


Figure 7. Plastic recovery options in EU-15, 1996-2008. [2]

Nowadays, feedstock recycling is limited mainly from economical point of view and contribution of this type of recycling into global plastic waste management is very small. (Figure 7) Moreover the factors which determine the profitability of alternative feedstock recycling methods are the

degree of separation required in raw wastes, the value of the products obtained, and the capital investments in the processing facilities. After initial modest growth and stabilization between 1995 and 2005, feedstock recycling dropped to near negligible amounts after 2005 due to a combination of technological and economic reasons. (Figure 7)

Energy recovery from plastics

At present energy recovery is a major contribution to the global plastic recovery. (Figure 7) The combustion of plastics in the incineration plant allows to transform chemical energy into heat or electricity. Plastic wastes are valuable fuel due to a relatively high heat capacity in comparison with other typical fuels. (Table 3)

Table 3

Heat capacity of plastics and some other materials. [4]

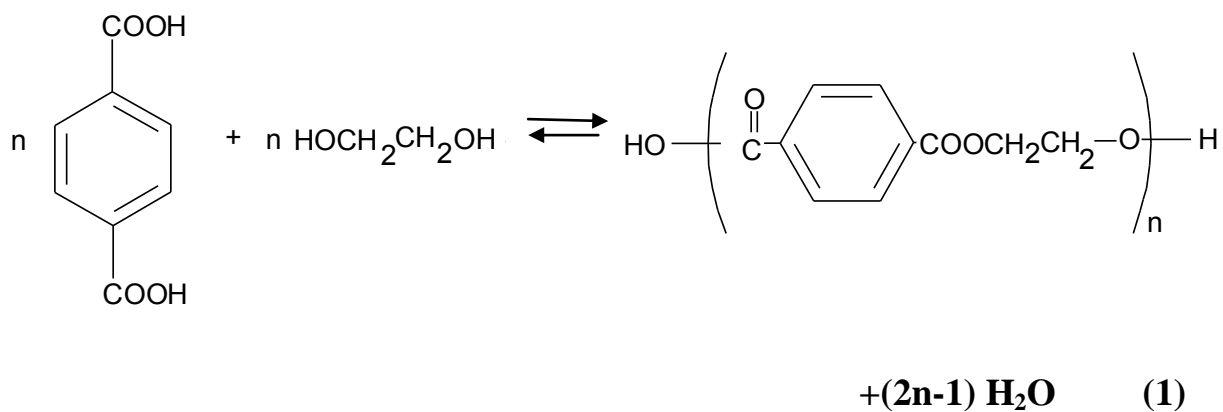
Material	Heat capacity [MJ/kg]	Material	Heat capacity [MJ/kg]
PVC	18	Heavy fuel oil	41
PE	27	Coal	26
PET	46	Natural gas	36 *
PS	41	Milled peat	10
ABS	35	Paper	17

* Unit MJ/m³ (0 °C)

It should be noted that polyvinyl chloride PCV and other polymers containing chlorine can not be combusted in typical incineration plants because extremely toxic dioxines and furanes are obtained.

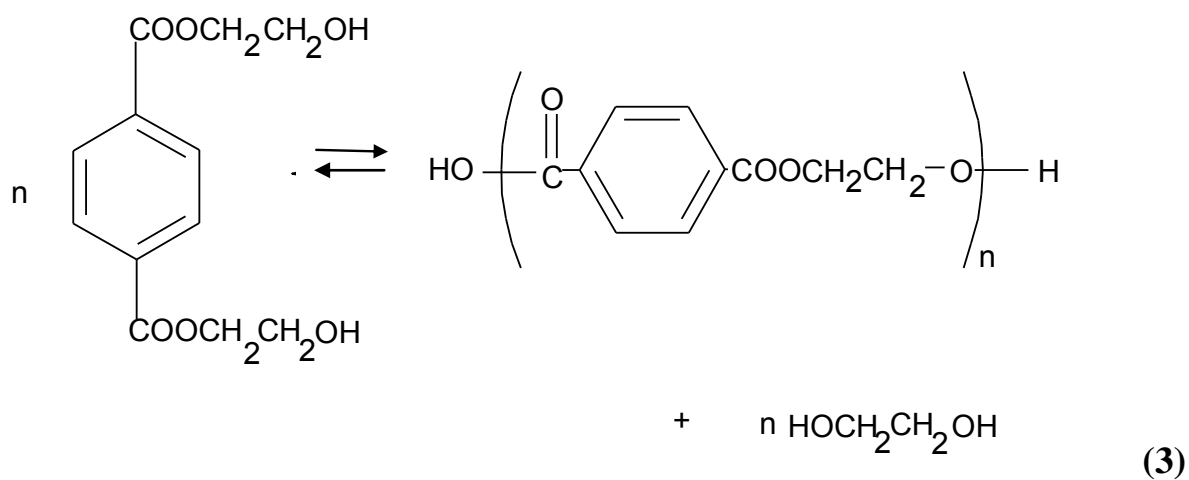
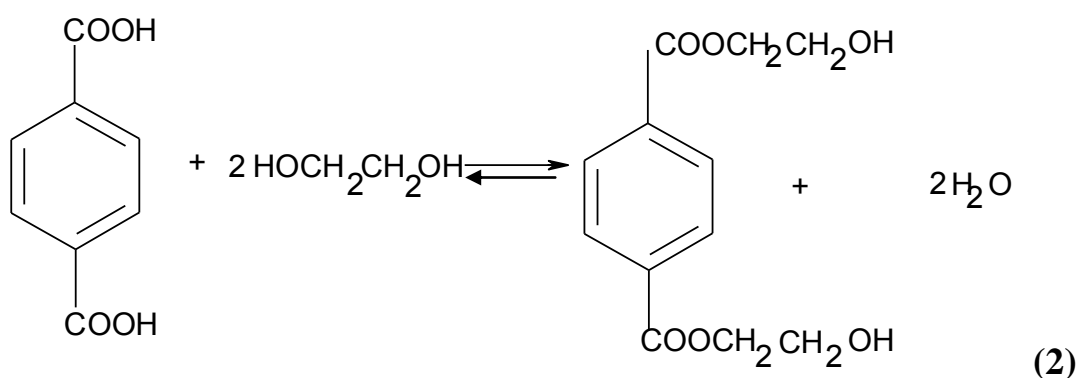
IV. Synthesis of poly(ethylene) terephthalate (PET)

Poly(ethylene) terephthalate belongs to the group of linear aromatic polyesters produced in polycondensation of terephthalic acid with ethylene glycol.

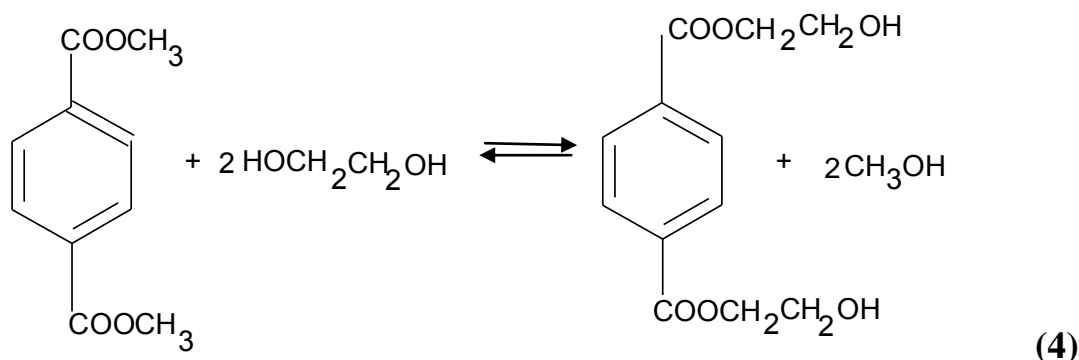


Polycondensation can be performed in three ways:[5]

1. One-step synthesis esterification between terephthalic acid (TPA) and ethylene glycol (with equimolar ratio) according to equation (1) rarely used on industrial scale due low yield
2. Two step synthesis: esterification between bis-(2-hydroxy)ethyl terephthalate (BHET) and ethylene glycol according to equation (2) and next polycondensation of BHET according to equation (3):



3. Two-step synthesis: transesterification of dimethylterephthalate (DMT) with ethylene glycol according to equation (4) and next polycondensation of BHET according to equation (3).



Because DMT is better soluble in ethylene glycol than BHET the yield of reaction (4) is higher than yield of reaction (3).

Synthesis of PET is performed in presence of catalysts such as cobalt(II) acetate, zinc acetate, calcium acetate or antimony oxides.

V. Properties and applications of PET

Poly(ethylene) terephthalate abbreviated as PET is thermoplastic polyester which can exist as an amorphous form (transparent with density $d=1.33\text{g/cm}^3$) and as semi-crystalline form (opaque or white with density $d=1.445\text{ g/cm}^3$ [5]). The melting point of this polymer can be in range $252 - 264\text{ }^\circ\text{C}$ depending on the molecular weight. This is transparent, tough material which has a good gas and moisture barrier properties, and high resistance to the most organic solvents.

Because of excellent properties poly(ethylene) terephthalate found wide practical application mainly in manufacture of synthetic fibers (textile obtained from this fiber is called polyester) and food packaging such as beverage bottles and frozen food trays that can be heated in a microwave or conventional oven. The plastic bottles made from PET can be used for a variety of foods and beverages, including alcohol, salad dressing, pickled food and soft drinks. Other applications of PET include X-ray and other photographic films, magnetic tape, and food packaging films. In addition it's chemical inertness allows to use this material in chemical sector mainly for chemicals storage.

The world production of PET in 2002 was 26 million tons which is expected to rise to 58 million ton in 2012 (Kloss J et al, 2006 & Shukla SR, 2009). This make up about 18% of world polymer production. The largest part of production is used in fibers manufacture (about 60%) and on the second place in bottle manufacture (about 30%). [8] Figure 8 illustrates global uses of PET.

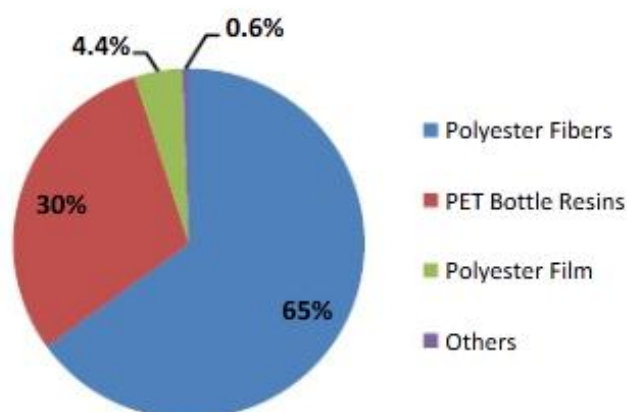


Figure 8. Global uses of PET. [9]

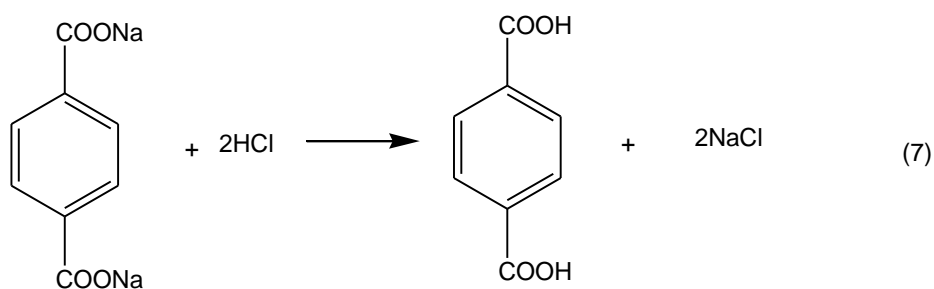
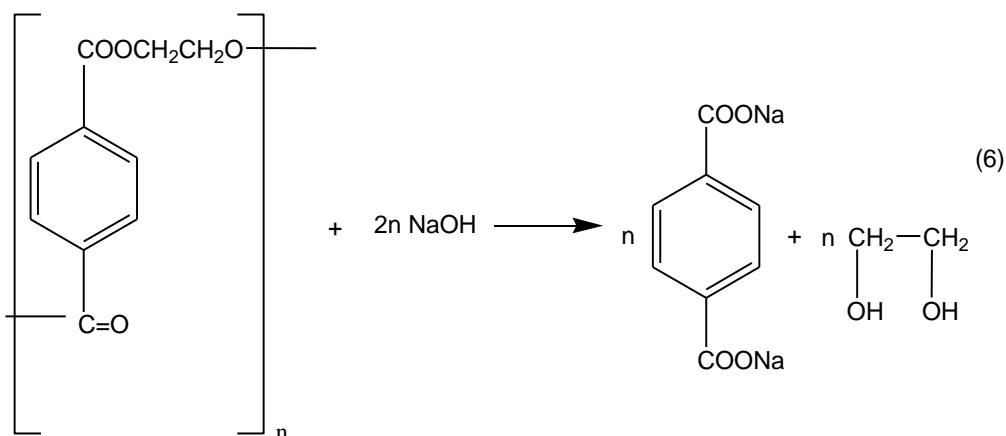
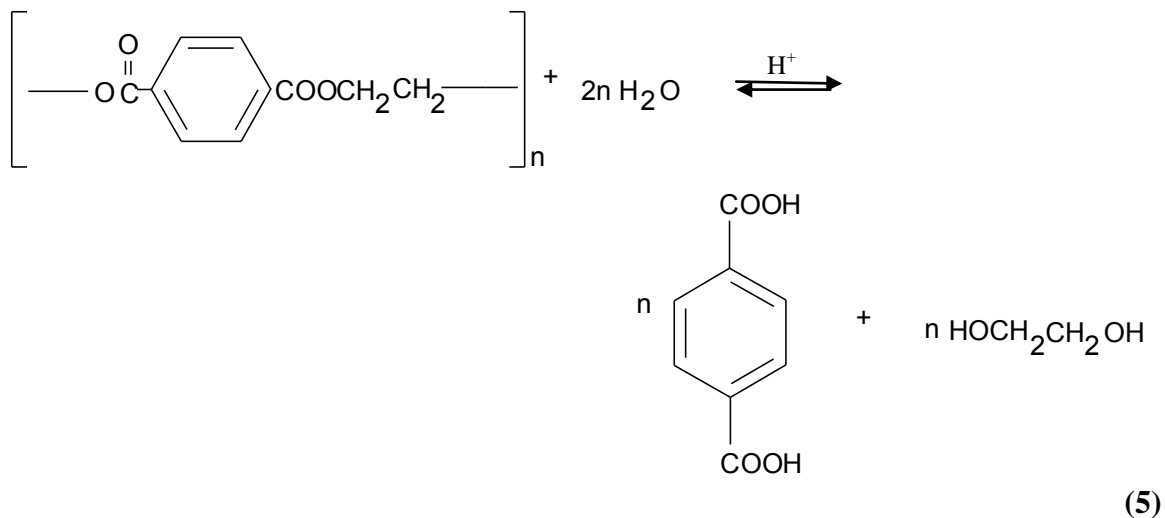
Post-consumer PET products, especially bottles are responsible for create large streams of solid wastes, they are not hazard to the environment, but are being concerned due to their substantial volume. Additionally their high resistance, non-biodegradability and poor photo degradability are a serious problem related with environmental protection. Thus recycling of PET has received a great deal of attention in the last years.

VI. Chemical recycling of waste PET

The bottles are the major source of waste PET. They usually contain paper labels, acrylic glue to paper labels and the pigments. Thus mechanical recycling leads to recyclate with worse properties. Despite this PET recyclate is commercially available and some firms, inter alia Coca-Cola, have chosen this method of recycling. Chemical recycling of PET is possible as results of presence of reactive functional ester group in molecule and includes chemolysis of the polyester with an excess of reactants such as water in hydrolysis, glycols in glycolysis, amines in amminolysis.

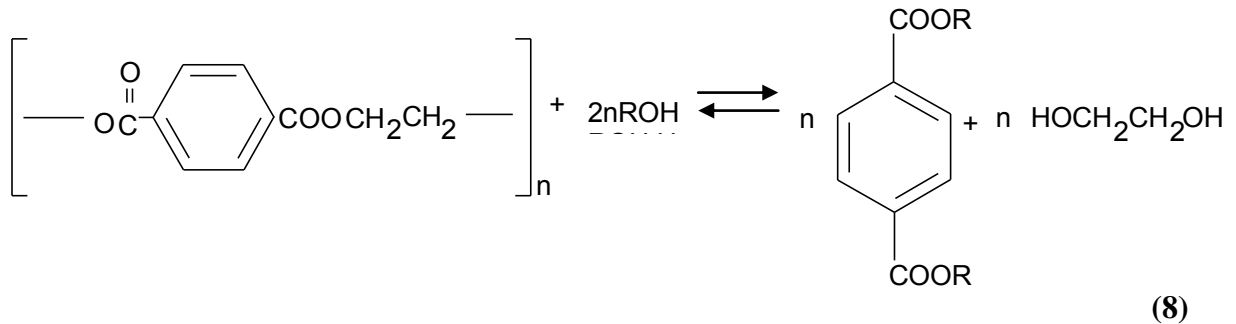
Hydrolysis

Hydrolysis can be carried out in an acid, alkaline or neutral environment. In neutral environment terephthalic acid is obtained according to equation (5). In alkaline environment salt of terephthalic acid is obtained (equation (6)) which can be transformed to acid (equation (7)).

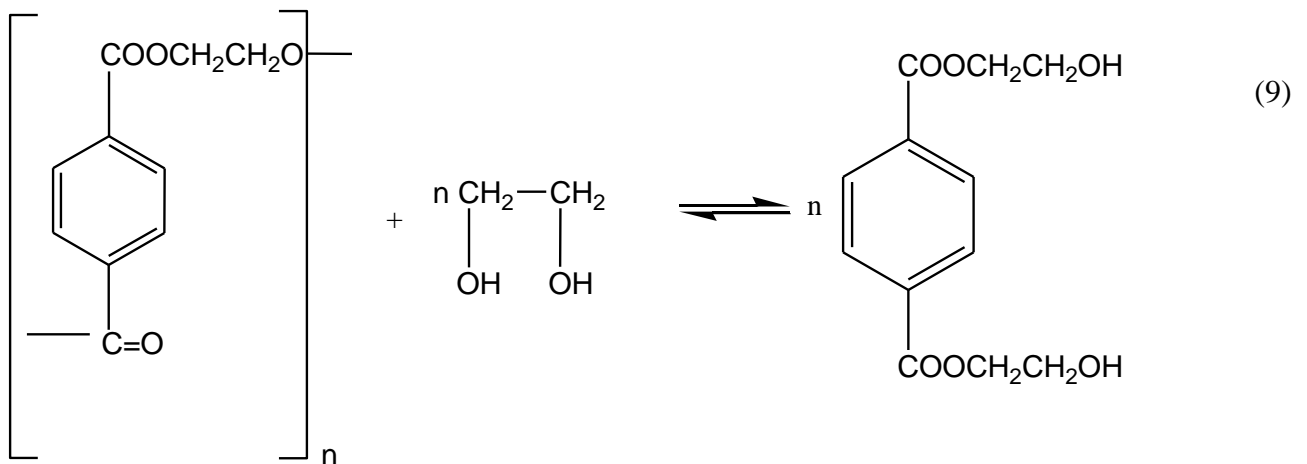


1. Alcoholysis:

General equation for alcoholysis is the following:



The most widely used are methanolysis with using methanol CH_3OH to produce dimethyl terephthalate (DMT) with glycol as by product and glycolysis with using ethylene glycol to produce BHET (equation (9)).



Glycolysis can be carried out using different glycols not only ethylene glycol, also propylene glycol, 1, 4-butanediol and triethylene glycol, diethylene glycol (DEG), dipropylene glycol (DPG), glycerol (Gly) and etc. But the most valuable is glycolysis BHET because can be used not only as monomer in PET synthesis but also in many other synthesis as reactant (Figure 9).

This process can be carried out to obtain the oligomers which can be used as a starting material in the manufacture of unsaturated polyesters, vinyl ester resins, epoxy resins, alkyd resins and polyurethanes.

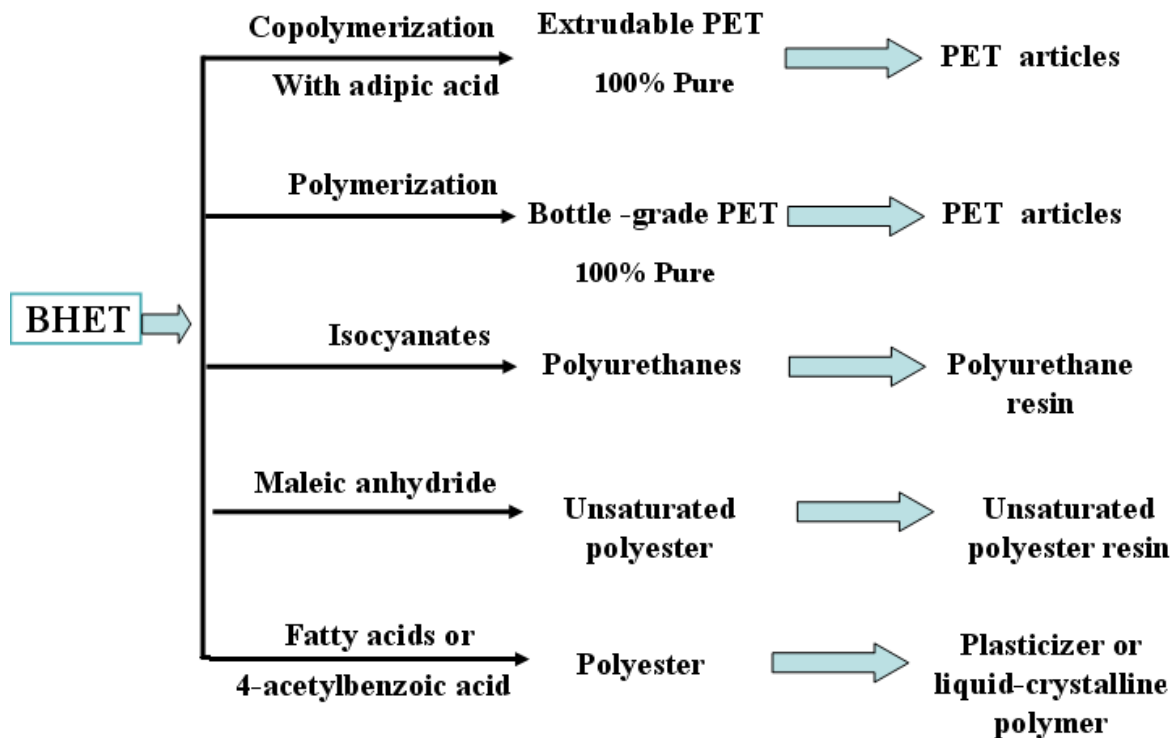
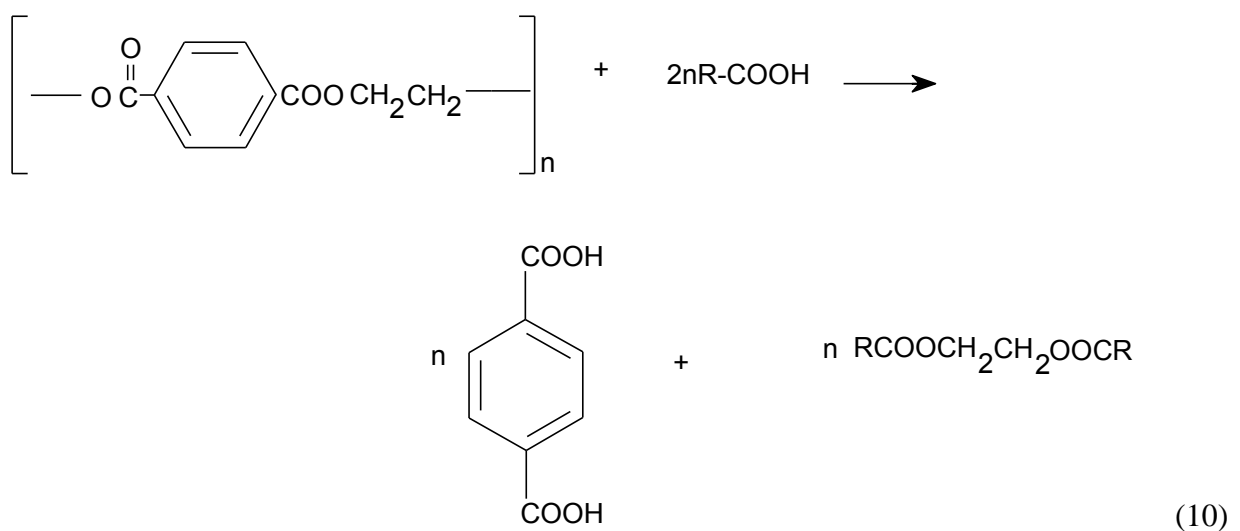


Figure 9. Using of BHET (glycolysis product of PET waste) to obtain other materials. [8]

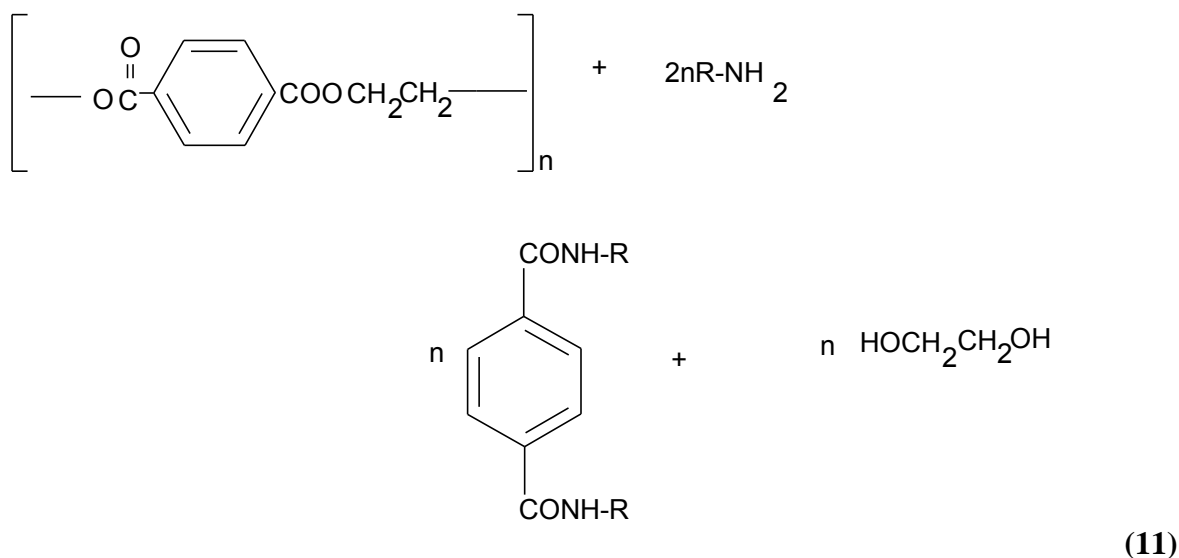
2. Acidolysis:

Acidolysis is carried out with carboxylic acid at high temperature to obtain terephthalic acid TPA and esters as by product according to equation below:



3. Aminolysis:

Aminolysis can be carried out using various amines, such as ethanolamine, benzylamine, hexamethylenediamine, aniline, methylamine hydrazine monohydrate and some polyamines. Catalysts such as lead acetate, glacial acetic acid, sodium acetate and potassium sulfate are usually used to facilitate the reaction.



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