

Scientific Symposium
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Titled



Recycling of waste Materials

إعادة تدوير المواد المستهلكة







* In 1862, Alexander Parkes introduced the world's first-ever man-made plastic, at the London International Exhibition. "Parkesine,"

It is a brand name for the first synthetic plastic • composed of Cellulose nitrate plasticized with Camphor. Parkesine was marketed as a substitute for Ivory. It was used for small objects, such as jewelry, buttons, fountain pens, and brush handles.

The world's first fully synthetic plastic was Bakelite, invented in New York in 1907, by Leo Baekeland, who coined the term "plastics".

Then a number of plastic and chemical innovations emerged in the period surrounding World War II.

- Polyethylene (PE) was created in England in 1933 and was a closely held state secret, as the lightweight plastic was used to insulate radar cabling, sufficiently lightening them to be placed on airplanes and giving Britain's planes a significant advantage against the Germans'.
- Polystyrene (PS) was created first as an alternative to diecast zinc, but quickly became a replacement for rubber in the copolymer of polystyrene and butadiene: styrenebutadiene rubber (SBR).
- . Nylon, which DuPont released for sale as synthetic silk hosiery in 1939 to much fanfare, was quickly rationed by the U.S. military for use in parachutes and ropes.

- A Dow chemist created expanded polystyrene (EPS) by accident in 1941 and the sturdy lightweight plastic became a useful thermal insulator and shockabsorber.
- Polypropylene, today one of the most used polymer in the world, got its start as a commodity in 1954, becoming a very useful polymer due to its adaptability.
- High-density PE (HDPE), today most commonly used to make plastic milk jugs, was developed during this period as well.
- PET was first prepared in England by J. Rex Whinfield and James T. Dickson of the Calico Printers Association during a study of phthalic acid begun in 1940

Today plastics are renowned for their sustainability, strength and design flexibility, finding unique and innovative applications in sectors ranging from healthcare and medicine, consumer technology, automotive, packaging, aerospace, building and construction and everything in between.

In the last few years, new disposal plastics waste of the non-biodegradable have been accumulated in the environment, which are very hazardous for the human lives and creating serious environmental problems and if this state is allowed to continued then either we have to stop the uses of polymers or the current non-degradable polymeric systems are either to modified to degradable one, or recycling their wastes as to save the environment from one side and to save the recovery plastics from other side.

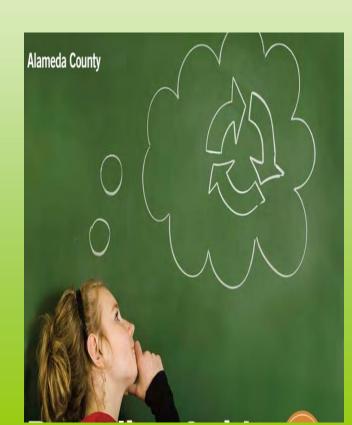


What is Recycling?

Recycling is the process of making or manufacturing new products from a product that has originally served its purpose. If these used products are disposed of in an appropriate, environmentally friendly way.

Recycling is beneficial in many ways including:

- 1-Recycling helps protect the environment.
- 2-Recycling conserves natural resources.
- 3-Recycling saves energy.



Polyethylene terephthalate(PET)



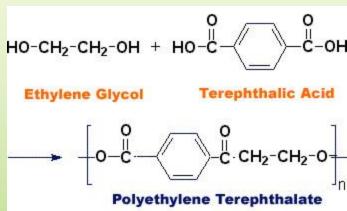


used in:

video and audio tapes, X-ray films, food packaging and especially of soft-drink bottles.







melting point of ~260°C





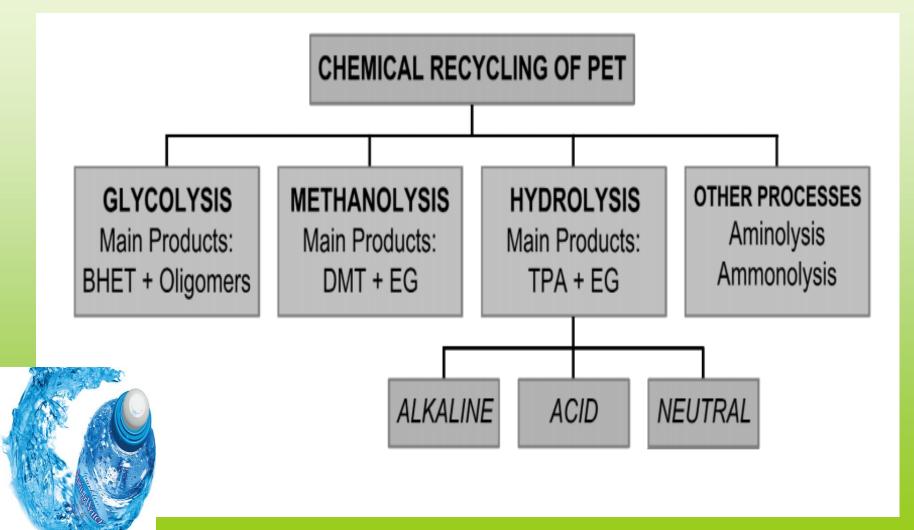


PET polymer can be recycled by four methods as follows:

- **1-Primary recycling** is one of the oldest methods used for recycling of PET polymer it is a re-extrusion method, such recycling process deal with uncontaminated scrap materials and only with one type of waste polymer, and to be original polymer.
- **2-Secondary recycling** or mechanical recycling include cleaning the waste polymer and mechanically reprocessing it to granules by grinding and the extrusion by heat and reforming. But the problems are in each time of its recycling the heterogeneity of the solid waste will increase and the degradation products during extrusion process by heating will complicated.
- **3-Tertiary recycling** or chemical recycling it is depolymerization process of PET to the monomers, or partial depolymerization to oligomers and other chemical substances, through transformation of the PET polymer chain by means of solvolytic chain cleavage .Cleavage of the polymer chain is by some reagents such as water, alcohol, acids, glycols and amines It is a reversible polycondensation reaction ,to its monomer or oligomer and the resulted materials will be reused as raw material for high quality chemical products.

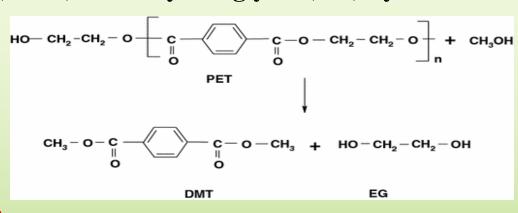
PET Chemical-Recycling Techniques





The two important tertiary or chemical recycling methods are: Methanolysis method:

The chemical degradation of PET polymer to dimethyl terephthalate(DMT) and ethylene glycol (EG) by methanol





Glycolysis method:

The following, ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), propylene glycol (PG) or dipropylene glycol (DPG) and others are used as a solvent to produce bis (2-hydroxy ethyl) terephthalate (BHET) and other PET glycolyzates which can be used to manufacture unsaturated resin polyurethane foams, copoylyesters, acrylic coatings and hydrophobic dyestuffs.

Other chemical recycling methods are:

1- Hydrolysis method include depolymerization of PET polymer by hydrolysis method by the addition of water in acidic ,alkaline or neutral environment and terephthalic acid (TPA) and ethylene glycol (EG) are produce.



2- Ammonolysis method include the reaction of PET waste with anhydrous ammonia in an ethylene glycol environment and terephthalamide will produce.

4-Quaternary recycling (energy recovery by incineration).

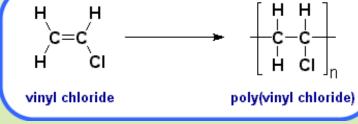
Incineration of the plastic waste and recover its energy content is represent the quaternary recycling. It is applied when the waste is toxic and hazardous to handle or when its collection, sorting and separation is difficult or economically not useful .

Poly (vinyl chloride)(PVC)



used in:

Construction, clothing, electrical cable insulation, inflatable products



melting point of ~100-260°C





Rigid PVC has great potential importance to building industry since it has excellent resistance to weathering. It is economic polymer. Therefore, PVC is used for making pipes for drainage and guttering. Window frames, acid recovery plants and for handling hydrocarbons are other important uses of PVC due to its very good resistance to chemicals. Also PVC used for making bottles for consumable liquids (like edible oil, squashes, wine and vinegar) for liquids of household use (mineral water, cosmetics and detergents).

Plasticized PVC is used as an insulating material. Because it is washable and has greater abrasion resistance therefore it is used in hand bags, bathroom curtain, kitchen upholstery and for seats upholstery in vehicles. Toys, packaging items, tubes, pipes and hoses, leather cloths, moulded objects, sheet, films, containers, footwear, belting etc.

Recycling of Poly (vinyl chloride) PVC Waste •

On account of wide consumption of poly (vinyl chloride) as one of the most commonly used thermoplastic materials due to its low cost and high performance, combined with the wide range of products that can be obtained from different processing conditions and techniques, which make PVC a universal polymer and the result was rapid growth of the PVC wastes, and the quantity of used PVC items entering the waste stream is gradually increased as progressively greater numbers of such PVC products

Methods of recycling PVC

* Energy –recovery techniques which consist of the energy recovery from the wastes by incineration

The problem is the formation of toxic compounds and pollutants in both air emissions and solid waste residues which can be released into the environment. In addition, the high content of chlorine in PVC polymer which yields large amounts of HCL during thermal decomposition, beside formation of some toxic compounds such as toxic dioxins and furans. HCL is believed to be linked to the formation of acid rain and corrosion of incinerator tubes.

* Mechanical recycling of PVC

The conventional mechanical recycling processes include separation grinding and feeding of ground product into the conversion equipment without any changes in the chemical composition of the material.

* Chemical recycling of PVC

The chemical or feedstock recycling is based on the idea of breaking up polymer waste to the basic chemicals by means of heat, chemical agents and catalysts.

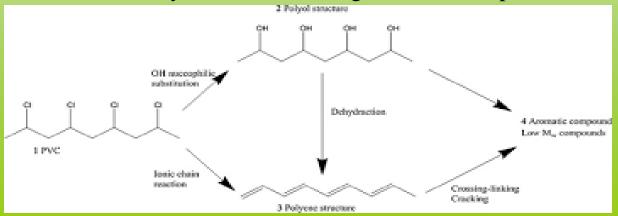
The chemical recycling methods include:

Dehydrochlorination and dechlorination of PVC

materials.

Wet-treatment processes for both the dehydrochlorination and the dechlorination of PVC are more suitable for recycling of PVC than the thermal dehydrochlorination of PVC, where the thermal degradation of PVC results in almost complete dehydrochlorination above 260oC, but the process lead to the production of some toxic

Recently, dechlorination of PVC was employed efficiently using NaOH /ethylene glycol (EG) solution where done at atmospheric pressure and the procedure take advantage of the high boiling point of EG (196 oC). The processes of dehydrochlorination of PVC waste which was achieve by wet processes have been improved by the substitution of water by ethylene glycol (EG) .The use of EG allows the process to be carried out at atmospheric pressure due to its high boiling point, and due to the reduced polarity of the solvent, the diffusion of the hydroxide containing solution is improved



Low density polyethylene (LDPE)



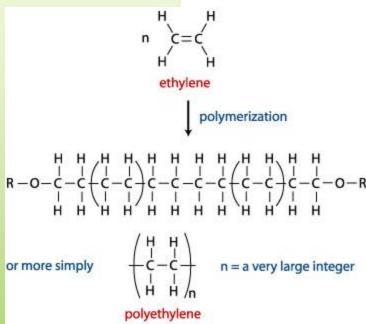


used in:

plastic bags, flexible containers







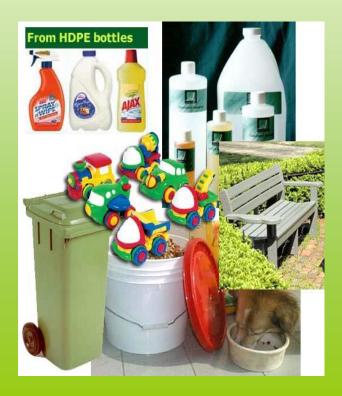
melting point of ~120°C

High density polyethylene (HDPE)





used in:
piping, automotive fuel tanks, bottles, toyes
melting point of ~130°C









Poly propylene(PP)





used in:

food containers ,battery cases, bottle crates, automotive parts and fibers



Figure 1: Chemical structure of polypropylene







melting point of ~160-165°C



Polystyrene(PS)

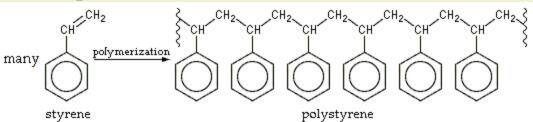


used in:

dairy product containers, tape

cassettes, cups and plates



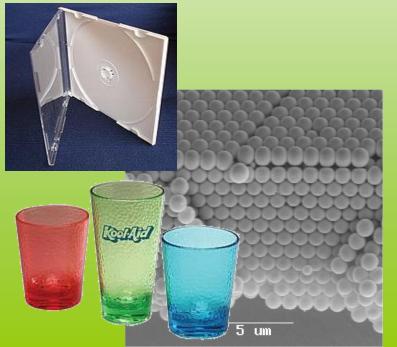








melting point of ~185°C



Recycling of Polyolefins and Polystyrene: HDPE ,LDPE, PP and PS



The low resistance of polyolefins and polystyrene to biological attack is related to its hydrophobicity, water repellency and high molecular weight and the lack of their functional groups recognizable by microbial enzymatic systems. all of these Properties limit their applications.

- The main important methods used for recycling of plastics waste are; mechanical recycling, burning to generate energy, and chemical recycling to convert them into intermediates, or by converting the plastics waste to their monomers.
- 1-Mechanical method
- 2-Pyrolysis or incineration methods

Thermal treatment of polyolefins and polystyrene wastes by pyrolysis or incineration is a more attractive alternatives. However ,the composition of Plastics in incineration process is usually said to generate high temperature that shortens the lifetime of furnace. Further, combustion converts the plastics into carbon dioxide, water, and other compounds such as dioxin that sometimes are harmful .Pyrolysis which converts waste plastics into fuel or useful hydrocarbon is also recognized as a very useful approach.

3-Dissolution/ reprecipitation methods
 Dissolution/ reprecipitation method based on the principle that polymers, can be dissolved in solvents with similar values of the solubility parameter



4-Chemical Oxidizing methods

Chemical oxidation polyolefins and polystyrene under thermal influence will create new functional groups along the polymer chains. Thermal oxidation of polymers will degraded their chains into short segments beside the functional groups occurrence. Polymer structure has significant influences on chine oxidation and fragmentation processes

5-Catalytic degradation methods

Thermal degradation of polyolefins and polystyrene with catalytic degradation of waste polymers produces high-quality fuels with the narrow distribution of a molecular size. In addition, the operation at a lower temperature reduces energy requirement. Another positive effect of catalyst on the degradation, is the increasing in the yields of valuable lighter hydrocarbons and its better quality. Magnesium oxid (MgO), calcium oxid (CaO), barium oxid (BaO), zeolite (HZSM5), active C, titanium dioxide (TiO2), chromium oxide(Cr2O3), iron oxid(Fe2O3), cobalt oxide (Co3O4), copper oxide (CuO) and zinc oxide (ZnO) catalyst separately were found active for recycling of 955 polyolefins and polystyrene



Recycled plastic is used to make a lot of new things!



