How Mitigate the Environmental Impact of Plastics.

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The word plastic is derived from the Greek (plastikos) meaning capable of being shaped or molded.

- Plastics are a range of synthetic or semi-synthetic polymerization products that can be molded into a permanent object having the property of plasticity.

Properties of Plastics

- Resistant
- Durable
- Insulator
- Easy to produce
- Inexpensive

About 330 million tones of plastic is produced each year.
Plastics: Pollution and Recycle.

Relevant part of Plastics are building up in landfill or reach the see!!!

How to solve the problem:

1) Increase plastic recycling and/or
2) Use biodegradable plastics and/or
3) Use less plastics
4) Ban of same plastics.

EN13432 Standard

From December 2009 plastic bags were eliminated from retail trade in Italy and EU.

Resin Identification Coding System
### Plastic Wastes and Recycling Code

<table>
<thead>
<tr>
<th>Code</th>
<th>Code Type</th>
<th>Example of Inclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PETE</td>
<td>Polyethylene terephthalate (PET) soft drink bottles, mineral water, fruit juice containers and cooking oil.</td>
</tr>
<tr>
<td>2</td>
<td>HDPE</td>
<td>High-density polyethylene (HDPE) milk jugs, cleaning agents, laundry detergents, bleaching agents, shampoo bottles, washing and shower soaps.</td>
</tr>
<tr>
<td>3</td>
<td>PVC</td>
<td>Polyvinyl chloride (PVC) trays for sweets, fruit, plastic packing (bubble foil) and food foils to wrap the foodstuff.</td>
</tr>
<tr>
<td>4</td>
<td>LDPE</td>
<td>Low-density polyethylene (LDPE) crushed bottles, shopping bags, highly-resistant sacks and most of the wrappings.</td>
</tr>
<tr>
<td>5</td>
<td>PP</td>
<td>Polypropylene (PP) furniture, consumers, luggage, toys as well as bumpers, lining and external borders of the cars.</td>
</tr>
<tr>
<td>6</td>
<td>PS</td>
<td>Polystyrene (PS) toys, hard packing, refrigerator trays, cosmetic bags, costume jewellery, audio cassettes, CD cases, vending cups.</td>
</tr>
<tr>
<td>7</td>
<td>OTHER</td>
<td>Other plastics, including acrylic, polycarbonate, polyactic fibers, nylon, fiberglass. An example of one type is a polycarbonate used for CD production and baby feeding bottles.</td>
</tr>
</tbody>
</table>
Plastic Use: The Advantages and Limits.

- The energy requirements for PE bags is lower than paper.
- Plastics have several environmental advantages:
  - i.e. fuel saving in cars owing to the lower weight.
- Big convenience owing to adaptability to various needs.
- Substitution of plastics ⇒ big increase in package weight, cost, volume, energy consumed, but.....
- High environmental impact (not degradable) and micro-plastics!
Municipal Solid Waste - Material Type.

Container and Packaging MSW Data, 2007 (U.S. EPA 2008)

- Paper & Paperboard: 52%
- Plastic: 17%
- Glass: 15%
- Wood: 11%
- Steel: 3%
- Aluminum: 2%
Plastic Wastes.

> 25% of wastes in landfill are plastics (low degradation time > 50 years)

Even additives of plastic are a problem
  - i.e. responsible of 28% of all cadmium present

Low density increases the collection difficulties
  - 20,000 bottle = 1t of recycled plastic


In The EU, 2011

Published On October 31, 2013 In Plastic Waste
Total Plastic Wastes Collected after Use by Sector (2001) (weight %).

- Municipal solid waste: 66.9%
- Distribution & industry: 20.7%
- Automotive: 4.3%
- Electrical & electronic: 4.3%
- Building & construction: 2.7%
- Agriculture: 1.1%

Europa Total: 24,500,000 tons (~ 50%)
Plastics in the Household Waste Stream.

- Bottles: 27%
- Films: 23%
- Bags: 14%
- Other packaging: 21%
- Other: 15%

PET and HDPE are the most common types of plastics in the household waste stream.
Chinese Plastic Waste Imports ($10^3$ tons).

- **No more imported from 2015!!!**

Source: Ascon GmbH, CPPI
Municipal Waste are (IT - art. 184 comma 2):

1. Domestic waste, even bulky, produced from local and places used for residential dwelling;
2. Not dangerous wastes produced from local and places used for the one different from the N° 1 similar to municipal waste for quantity and quality;
3. Wastes coming from street sweeping;
4. Of any kind or origin placed on street and public areas or on street and private areas still subject to public use or on beaches, sea and lake and on the banks of rivers;
5. Vegetables coming from green areas, i.e. gardens, parks and cemeteries;
6. From exhumations and estumulatios and other waste from cemetery different from the ones of point 2), 3) and 5).
Heterogeneity:
• The CER Code provides 900 different types of waste (of which 408 are classified as dangerous waste)
• Product characteristics and different physical states
• Each year are synthetized about 2000 new substances, new materials, and new products
• Wastes composed by different materials
• Ex. plastics: complex polymeric materials (thousand of different types) with different characteristic involving all sectors both as products and as package

Hazard:
• Substances classified hazardous are more than 6000
• CER 408 waste type classified hazardous or contaminated by different substances
• Also in municipal waste there are hazardous wastes which, when not separated, contaminate the overall material.
Special Wastes.

Special Waste are (art. 184 comma 3):

a) Wastes from farm and agro-industrial activities;
b) Wastes arising from activity of demolition/construction of buildings and hazardous wastes resulting from excavation activities;
c) Wastes from industrial manufacturing (except the petroleum coke used as fuel for production use);
d) Wastes from craftsmanship;
e) Wastes from commercial activity;
f) Wastes from service activity;
g) Wastes arising from recovery activity and waste disposal, from sludge produced by water purification and other treatment of water/wastewater and fume reduction;
h) Wastes arising from hospital activity;
i) deteriorated and obsolete machinery and equipment;
j) motor vehicles, trailers and the like out of use and parts thereof;
k) The fuel produced from waste (CDR - fuel derived from carbon wastes).
Recycling Classification.

Recycling
- Collection: plastics are labeled with a number
- Coding for plastics
  - 1 PET (polyethylenterephthalat)
  - 2 HDPE (high density polyethylene)
  - 3 Vinyl/PVC (polyvinylchloride)
  - 4 LDPE (Low density polyethylene)
  - 5 PP (Polypropylene)
  - 6 PS (Polystyrene)
  - 7 Others

- Treatment/Selection
  - Best economic is obtained when materials are selected
  - Plastics are mainly selected visually. However, plant for automatic selection based on visible/IR light adsorption are known and used.

- Definitions
  - Post consumer Material: Plastics collected by public organizations and processed in pellets for reuse.
  - Post industrial Materials: Plastics collected by firms (as scrap, splatter, waste, flakes, or packaging)
Turning waste into a resource is a goal the European plastics industry is committed to achieve to improve Europe’s resource efficiency.

This goal is impossible to achieve with 38% of plastics waste still going to landfill.

As such, landfill is a major hurdle that must be eliminated for such an ambitious goal to be reached.

Recycling and energy recovery are both complementary and necessary to achieve the zero plastics to landfill by 2020 goal.
Plastic Applications by Sectors and Type (2002).

Packaging
Building
Automotive
Electrical
Other

PE-LD/LLD  PE-HD  PP  PS/EPS  PVC  Styrene Copolymer.  PMMA  Artific. Fiber  Sost. Thermo.  PUR  PA
Plastics Demand by Market (2013).

Source: PlasticsEurope (PEMRG) / Consultic / ECEBD
European plastics converter demand by segments and polymer types (2016).

Source: PlasticsEurope (PEMRG) / Conversio Market & Strategy GmbH
Plastics Identification System (ISO 1043-1).

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS&lt;</td>
<td>Acrylonitrile/butadiene/styrene</td>
</tr>
<tr>
<td>ABS-FR&lt;</td>
<td>Flame-retardant ABS</td>
</tr>
<tr>
<td>EP&lt;</td>
<td>Epoxy</td>
</tr>
<tr>
<td>PA&lt;</td>
<td>Nylon (polyamide)</td>
</tr>
<tr>
<td>PA6&lt;</td>
<td>Nylon 6</td>
</tr>
<tr>
<td>PA66&lt;</td>
<td>Nylon 6/6</td>
</tr>
<tr>
<td>PBT&lt;</td>
<td>Polybutylene terephthalate</td>
</tr>
<tr>
<td>PC&lt;</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PE&lt;</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PE-LLD&lt;</td>
<td>Linear low-density polyethylene</td>
</tr>
<tr>
<td>PE-LMD&lt;</td>
<td>Low-medium den. polyethylene</td>
</tr>
<tr>
<td>PE-HD&lt;</td>
<td>High density polyethylene</td>
</tr>
<tr>
<td>PET&lt;</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>PS&lt;</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PS-HI&lt;</td>
<td>High impact polystyrene</td>
</tr>
<tr>
<td>PVC&lt;</td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td>SAN&lt;</td>
<td>Styrene/acrylonitrile</td>
</tr>
<tr>
<td>SI&lt;</td>
<td>Silicone</td>
</tr>
</tbody>
</table>
Materials Compatibility.

- The mingling of different polymers in the recycled stream makes recycling of plastics difficult.
- There is a need for separating plastic components into appropriate categories based on composition.

*Design consideration:*

- Use as few different types of materials as possible
- Ensure all materials can be easily separated from the primary plastics
- More than one type of plastics used should be compatible with one another.
## Materials Compatibility Chart.

<table>
<thead>
<tr>
<th>Matrix Material</th>
<th>PE</th>
<th>PVC</th>
<th>PS</th>
<th>PC</th>
<th>PP</th>
<th>PA</th>
<th>POM</th>
<th>SAN</th>
<th>ABS</th>
<th>PBTP</th>
<th>PETP</th>
<th>PMMA</th>
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<td>PE</td>
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</tr>
</tbody>
</table>

Key: ■ Compatible  ● Compatible with limitations  □ Compatible only in small amounts
○ Non compatible

Source: Adapted from Bras e Rosen, 1997.
Options for Plastics Recovery.

- **RECOVERY**
  - **MATERIAL RECYCLING**
    - MECHANICAL RECYCLING (Plastic Products)
    - FEEDSTOCK RECYCLING (Chemical feedstock's)
  - **ENERGY RECOVERY**
    - DIRECT INCINERATION (MSWI)
    - ALTERNATIVE FUEL (cement, power)

EU Directive 75/442/EC, Annex IIB
“Cycle-of-Life” of a Polymer.

- Selection/design of the polymer
- Synthesis of monomer
- Polymerization
- Post-polymerization manufacture and/or polymer blends
- Use
- Post-use
  - Recycle,
  - Energy recovery
  - Disposal (Landfill)
Life Cycle of Plastics in 2012 (EU-27+N/CH).

- **Plastic production EU-27**: 57 Mtonne

- **Converter demand EU-27**: 45-9 Mtonne
  - 60% long service life
  - 40% short service life

- **Consumer demand**: 45-9 Mtonne

- **Exports**
  - Post consumer plastic waste: 57 Mtonne
  - Recycling: 6.6 Mtonne (26.3%)
  - Energy recovery: 8.9 Mtonne (35.6%)

- **Imports**
  - Disposal: 9.6 Mtonne

**Conversion**
- 61.9% recovery
- 38.1% disposal
The service life of plastics products goes from less than 1 year to 50 years or more.

Plastics become waste at the end of their service life.

From production to waste, different plastic products have different life cycles and this is why the volume of collected waste cannot match, in a single year, the volume of production or consumption.
Landfill Bans Foster Higher Recycling Rates

Plastic post-consumer waste rates of recycling, energy recovery and landfill per country in 2016

- Recycling
- Energy Recovery
- Landfill
- Countries with landfill restriction implemented
Eco-Efficiency Concept.

Full LCA part aggregated:

- Energy
- Raw Materials
- Emission
- Tox & risk potential

Pilot trials, working facilities

Cost Impact

Relative Environmental Impact

- Good eco-efficiency
- Low eco-efficiency
Eco-efficiency of Packaging Waste Management Options (European Context).

Relative environmental Impact vs. Relative cost graph, showing different recycling scenarios:
- Landfill
- Now
- 15% recycling
- 25% recycling
- 35% recycling
- 50% recycling

The graph illustrates the trade-off between environmental impact and cost for various recycling percentages.
Selected Automotive Applications.

<table>
<thead>
<tr>
<th>Size</th>
<th>small</th>
<th>medium</th>
<th>big</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mirror Housing (finisher)</td>
<td>Lamp (finisher)</td>
<td>Air system</td>
<td>Washfluid Tank+liquid (lid)</td>
</tr>
<tr>
<td>Plastics</td>
<td>ABS Group (ind. Total mirror)</td>
<td>PC Group (incl. Total lamp)</td>
<td>PP Group (incl. dashboard)</td>
</tr>
</tbody>
</table>

- Big, medium and small parts
- Individual parts or in assembly
- Different types of plastic
Eco-Efficiency: Recovery of a Bumper (PP).

*) assuming 100% recycled is used in the same application = ideal case
Eco PowerMate PC of NEC.

- 100% recycled plastic
- Virtually no dangerous material
- Use 1/3 of typical energy for a PC
- Equipped with a 900MHz Crusoe processor, 20GB hard disk, and 15-in. monitor.
E-Paper, E-Ink, E-Newspaper.

- E-Ink – available in different format
- 160 pixels/inch; variable dimensions
- Readiness and flexibility similar to paper
- Luminosity 5x and uses 99% less power than a LCD.
Plastics in Electrical & Electronic – Significant Increase.

Consumption in ktons

Consumption in Europe: 2.0 million tons

Year


1949 1483 1054 843 411

General

IT telecom

Waste categories of collected WEEE in EU28, 2012

Data source: Eurostat (env.waselee), 2015.

Includes: Mechanical recycling  
Feedstock recycling  
Chemical recycling

Non included: energy recovery

### Table

<table>
<thead>
<tr>
<th>Case</th>
<th>Recycling</th>
<th>With energy recovery</th>
<th>Landfill</th>
<th>Pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(PE)</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>1(PET)</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>2(MIX1)</td>
<td>+++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>2(MIX2)</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>2(MIX3)</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>2(MIX4)</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+++</td>
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<tr>
<td>3(PE)</td>
<td>+++</td>
<td>++</td>
<td>+</td>
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<td>3(PP)</td>
<td>+++</td>
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<td>3(PS)</td>
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</tr>
<tr>
<td>3(PET)</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>3(PVC)</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>

- **XXX** best option
- **XX** intermediary option
- **X** worst option
- Option not assessed
### Packaging & Packaging Waste Directive 94/62/EC (proposal amendment 2013/0371 (COD)).

<table>
<thead>
<tr>
<th></th>
<th>94/62/EC</th>
<th>Revision (2)</th>
<th>Revision (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deadline</td>
<td>30 June 01</td>
<td>31 Dec 08</td>
<td>4 Nov 13</td>
</tr>
<tr>
<td>Overall recov</td>
<td>50-65%</td>
<td>Min 60%</td>
<td></td>
</tr>
<tr>
<td>Overall recycl</td>
<td>25-45%</td>
<td>Min 55-80%</td>
<td></td>
</tr>
<tr>
<td>Glass recycl</td>
<td>Min. 15%</td>
<td>Min. 60%</td>
<td></td>
</tr>
<tr>
<td>Paper recycl</td>
<td>Min. 15%</td>
<td>Min. 60%</td>
<td></td>
</tr>
<tr>
<td>Metals recycl</td>
<td>Min. 15%</td>
<td>Min. 50%</td>
<td></td>
</tr>
<tr>
<td>Plastics recycl</td>
<td>Min. 15%</td>
<td>Min. 22.5%*</td>
<td>Reduction light plastic</td>
</tr>
<tr>
<td>Wood recycl</td>
<td>-</td>
<td>Min 15%</td>
<td></td>
</tr>
</tbody>
</table>

*22.5 % by weight for plastics, counting exclusively material that is recycled back into plastics

**60% recovery of packaging plastics (lightweight plastics)
Difficult Materials to Recycle.

Thermosetting Plastics (epoxide, polyimides, polyesters)
- The recycling of thermosetting plastics is more difficult because these materials cannot be easily remolded or reformed.
- Some thermosetting are milled and then added to pure material before reworking as filler materials.

Rubber (natural or synthetic BN, SBR, etc.)
- When vulcanized, it becomes an highly crosslinked material.
- Contains further a variety of other fillers and additives.
- Most waste rubber are end use tires, which are not biodegradable.
- Waste tire can be used as fuel in some industrial applications, but they generate polluting emissions.

Composite Materials based on Plastics.
- A composite is a combination of two or more different materials that results in a superior (often stronger) product.
The Recycling Process.

Primary Processing
  Plant internal recycling

Secondary or physical processing (mechanical recycle)
  - Milling and washing
  - Refusing and reforming

Tertiary or chemical processing (chemical recycle)
  - Depolymerization
  - Purification of regenerated chemicals

Cannot be used substances which are not normed!
Complex technologies are required for Plastic recycle:

- Complete identification of plastics (codes or analytical!)
- Method of Label removal, metal covering, adhesives, or insulating foam (if recycled)
- Separation of rubber and other elastomers from plastics with similar density
- Separation of metal sheets
- Identification and removal of potentially dangerous materials (battery, mercury relays, soldering alloy based on beryllium copper and lead)
- Control of plastic additives and fillers.
### Plastic Selection by Sector.

<table>
<thead>
<tr>
<th>Packaging Commerc.</th>
<th>Packaging Industry</th>
<th>post consumer house</th>
<th>Automotive</th>
<th>Electrical electronic</th>
<th>Agriculture</th>
<th>Building</th>
</tr>
</thead>
</table>

#### COLLECTING AND RECYCLING SYSTEMS

- Energy recovery
- Selected materials recycling
- Mixed material recycling

- **Depending on use**
  - Recycling of mixed materials
  - Recycle of selected materials
  - Energy recovery

- **Depending on material**
  - Plastics related to use sector
  - Plastics focused on materials

**COLLECTION AND CLASSIFICATION**

- Packaging Commerc.
- Packaging Industry
- Post consumer house
- Automotive
- Electrical electronic
- Agriculture
- Building

Environmental and health impact assessment, focusing on the most significant environmental impact indicators (e.g. energy use, heavy metals to water, CO₂ emissions)
Contribution to the reduction (-) or increase (+) of GWP compared to landfill (kg CO₂eq per kg).

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Collection/sorting</th>
<th>Treatment</th>
<th>Process</th>
<th>Landfill</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottle recycling</td>
<td>0.1</td>
<td>0.54</td>
<td>-1.27</td>
<td>-0.31</td>
<td>-0.95</td>
</tr>
<tr>
<td>Film recycling</td>
<td>0.1</td>
<td>*</td>
<td>-0.48</td>
<td>-0.36</td>
<td>-0.74</td>
</tr>
</tbody>
</table>

Italian Legislation have introduced eight «Consorzi di filiera» with reference to specific commercial categories.

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>Website</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNA</td>
<td>Consorzio nazionale acciaio</td>
<td><a href="http://www.cna.it">www.cna.it</a></td>
</tr>
<tr>
<td>CIAL</td>
<td>Consorzio imballaggi alluminio</td>
<td><a href="http://www.cial.it">www.cial.it</a></td>
</tr>
<tr>
<td>COMIECO</td>
<td>Consorzio recupero e riciclo degli imballaggi a base cellulosica</td>
<td><a href="http://www.comieco.it">www.comieco.it</a></td>
</tr>
<tr>
<td>RILEGNO</td>
<td>Consorzio nazionale recupero e riciclaggio degli imballaggi di legno</td>
<td><a href="http://www.rilegno.it">www.rilegno.it</a></td>
</tr>
<tr>
<td>COREPLA</td>
<td>Consorzio nazionale per il recupero degli imballaggi di plastica</td>
<td><a href="http://www.corepla.it">www.corepla.it</a></td>
</tr>
<tr>
<td>COREVE</td>
<td>Consorzio recupero vetro</td>
<td><a href="http://www.coreve">www.coreve</a></td>
</tr>
<tr>
<td>COBAT</td>
<td>Consorzio recupero batterie</td>
<td><a href="http://www.cobat">www.cobat</a></td>
</tr>
<tr>
<td>COOU</td>
<td>Consorzio obbligatorio oli usati</td>
<td><a href="http://www.coou">www.coou</a></td>
</tr>
</tbody>
</table>
CO.RE.PLA is a national consortium for collection, recycling, and recovery of plastic package wastes. Start in 1997 to coordinate the following processes:

- Plastic waste collected by municipal services
- Collection of secondary and tertiary plastic containers
- Selection of types of used packages
- Recycle and recover wastes from collected packages.
- Organize the sale of plastic recycled.
Recycling System Organization (It).

- Producers
- Importers
- Fillers
- CONAI
- Municipality
- CO.RE.PLA
- Selection Unit
- Recycling plants
- Energy recovery unit
- Municipal operators
- Private operators
- Collection programs
- Transformed materials

Financial flow
Material flow
Consortium Composition and Headquarters.

<table>
<thead>
<tr>
<th>CATEGORY</th>
<th>MEMBER NUMBER</th>
<th>% SECTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEEDSTOCK PRODUCTORS</td>
<td>97</td>
<td>91</td>
</tr>
<tr>
<td>PACKAGING PRODUCTORS</td>
<td>1902</td>
<td>86</td>
</tr>
<tr>
<td>PACKAGING USERS</td>
<td>26</td>
<td>35</td>
</tr>
<tr>
<td>RECYCLING COMPANIES</td>
<td>45</td>
<td>80</td>
</tr>
</tbody>
</table>

18 Selection centers

47 Collection centers

A grid of 50 centers for secondary and tertiary packaging of plastic.
Amount and Costs of Recycling.

[Graph showing amount of recycling in kilotons (kt) and liters per kilogram (L/kg) for the years 1996 to 2000.]

- Package recycle HH
- Package recycle I&T
- Energy recovery
- Total recovery

- Cost of a Kg
Plastic Recycling.

- **Plastic Waste**
- **Post consume recycle**

Year:
- 1996
- 1997
- 1998
- 1999
- 2000

'000 ton:
- 0
- 500
- 1000
- 1500
- 2000
- 2500
- 3000

**Graph Description:**
- The graph illustrates the recycling of plastic waste from 1996 to 2000.
- The y-axis represents the amount of scrap in '000 tons.
- The x-axis represents the years from 1996 to 2000.
- Two categories are shown: Plastic Waste and Post consume recycle.
Recycling Progress in UE.

'000 tons

(= 11% post-user waste)

- Mechanical Recycling
- Forecast Potential MR
- Feedstock Recycling
Treatment of Total Plastic Packaging Waste by EU-27, 2007-9 (%).

- Recycle
- Energy/recovery
- Incineration
Practical Development in the Recovery of Plastic Wastes

- Automatic Selection (labeling/identification)
- Integral Treatment MSW
- Identification of best practices for mechanical recycling*
- Carbon substitute (plastics/paper)
- Recycling Processes with Solvent (PVC, PO)
- Recycle as monomer (PET, nylon)
- Recycle of other materials (PVC, mixed)
The Recycling of Plastics is Carried out in a Five Step Process.

Step 0 - Plastics collection
This is done through roadside collections, special recycling bins and directly from industries that use a lot of plastic.

Step 1 - Manual and/or mechanical sorting
At this stage nails and stones are removed, and the plastic is sorted into three types: PET, HDPE and 'other'.

Step 2 - Chipping
The sorted plastic is cut into small pieces ready to be melted down.

Step 3 - Washing
This stage removes contaminants such as paper labels, dirt and remnants of the product originally contained in the plastic.

Step 4 - Pelleting
The plastic is then melted and extruded into small pellets ready for reuse.

Step 5 – Packaging. Recycled plastic is put into containers for packaging and labeled with information on type of material, density and melt index.
Sorting by Optical Sensor.
Steps for “Bottle to Bottle”.

1. **Collection/Sorting**
2. **Baled Bottle**
3. **Grinding Washing**
4. **Flake**
5. **Cleaning Process**
6. **BTB Pellet**
Features of Mechanical Recycling.

Different plastics not compatible
Properties can deteriorate
Closed loop recycling is limited:

- PVC windows ➞ windows
- PET bottles ➞ fiber applications
- PP bumpers ➞ plant pots
- PE food contact film ➞ garbage bags
- PE film ➞ pipes
- PP closures ➞ non-critical car parts
Potential limitations:

- Processing specifications
- Color, odor, food contact considerations
- Substitution ratio
- Price vs. virgin material

Future trends:

- Improved sorting technologies
- Vinyloop process
- Other solvent processes
- Wood composites
Final Uses of Recycled HDPE Bottles.

- Bottle: 29%
- Pipes: 18%
- Film, Coatings: 7%
- Garden: 11%
- Injection Molding: 8%
- Furniture: 9%
- Other: 18%
Market of PVC Composites (Kton/anno – 2017).

- cables: 23%
- films: 15%
- coatings: 16%
- floor: 18%
- Plastisol: 10%
- others: 18%

Total: 4091 Kton composites/year
The process of PVC Mechanical Recycle uses a solvent to separate PVC from fibers or other materials.

The process operates in a close cycle.

Batch process:
- Dissolution
  - PVC precipitation
  - Solvent recycle

PVC Recovering as PVC Composites able to be Converted in final products.
Summary of PVC Recycling Process.

1. Feeding
2. Milling
3. Dissolution
4. Solution PVC/Solvent
5. Additives
6. Precipitation
7. Ve
8. PVC
9. Insolubles
10. Drying
11. Solvent recovery
12. Final drying
13. PVC
14. Air
15. Water
Steps in the PVC Recycling Process.

1. **Debaling** → **Bottle singulation** → **Metal diversion** → **Bottle separation** → **Bottle pre-washing** → **1st Stage grinding**
2. **2nd Stage grinding**
3. **Intensive washing** → **Gravimetric separation** → **Pre-drying** → **PVC flakes removal** → **Metal parts removal** → **2nd Stage grinding**
4. **Second stage drying** → **Dust removal** → **Bühler Process** → **PET Pellets**

**Legend:**
- Grinding & washing
- Contamination removal
- Upgrading
In the Ring Extruder the material is initially degassed in the solid-state.
World Polyester Demand.

- Fiber: 1992-2012: 7%
- PET Resin: 1986-2012: 18-10%
- Total: 1986-2012: 9-7%

- Volume KMT:
  - 1986: 0
  - 1991: 10,000
  - 1996: 20,000
  - 2001: 30,000
  - 2006: 40,000
  - 2011: 50,000

- Specialties
- Film
- PET Resin
- Fiber
Recycle/Regeneration of Polyesters
(Polyethylenterephthalate - PET).

Raw Materials for PET Monomers

Production of Ethylene Glycol (EG)

\[
\ce{H2C=CH2 + O2 \xrightarrow{Ag} \ce{HO-\triangle-\ce{HO}} \xrightarrow{\text{H2C-CH2}}} \]

Temperature 175-225 °C.
Pressure 1500-3000 kPa (15-30 Atm)

Production of PTA and DMT

- PTA = terephthalic acid
- DTM = methyl terephthalate

Temperature 150-200°C.
Pressure 500 psi (ca. 35 bar)
Production of EG Monomer.

\[
\text{CH}_2=\text{CH}_2 + \text{O}_2 \xrightarrow{\text{Ag cat.}} \text{HO-CH}_2-\text{CH}_2-\text{OH} \quad (70-80\%) + \text{CO}_2 + \text{H}_2\text{O}
\]

- H\text{O}
  - excess 10:1
  - Acid catalyst

90%

+ diglycols (9 %) + telomers (1%)

Oxygen is used in the first stage, both reactions are exothermic; EO is recovered from water, then distilled. The crude glycol mixture is further fractionated.
Polyester Chemistry - Esterification of PET.

**Step growing polymerization - Polycondensation**

\[
\begin{align*}
\text{250 °C, Basic catalysis} & \quad \text{HO-CH}_2\text{-CH}_2\text{-OH} - \text{H}_2\text{O} \\
\text{2n CH}_3\text{OH} & \quad \text{n CH}_3\text{O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-} \\
\end{align*}
\]

**Interexchange between Esters - Transesterification**

\[
\begin{align*}
\text{Low Temp.} & \quad \text{HO-CH}_2\text{-CH}_2\text{-OH} \\
\text{- 2n CH}_3\text{OH} & \quad \text{n CH}_3\text{O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-} \\
\end{align*}
\]

Relevant use of energy, low emissions: \(\sim 0.7 - 3.9 \, \text{g/kg product}\); most emissions are reduced through optimization of cooling towers.
PTA Technology Preferred (Amoco).

Polyethylene terephthalate Capacity

![Graph showing the introduction of PTA technology and the increase in capacity from DMT and PTA over time. The graph highlights a significant increase in capacity from 1995 onwards, marked by the introduction of PTA technology.](https://example.com/gra.png)
PET Manufacture Process.

Suspension Preparation

PTA → Glycol → Catalyst

Esterification

Pre-condensation

Polycondensation

PET Fused or pellets
Intrinsic Viscosity (IV) and Molecular Weight (MW).

<table>
<thead>
<tr>
<th>IV</th>
<th>Grade of PET</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>Fibre Grade</td>
<td>29,000</td>
</tr>
<tr>
<td>0.60</td>
<td>Filament Grade</td>
<td>36,000</td>
</tr>
<tr>
<td>0.70</td>
<td>Bottle Grade (Low IV)</td>
<td>47,000</td>
</tr>
<tr>
<td>0.80</td>
<td>Bottle Grade (Med IV)</td>
<td>57,000</td>
</tr>
<tr>
<td>0.90</td>
<td>Bottle Grade (High IV)</td>
<td>67,000</td>
</tr>
<tr>
<td>1.0</td>
<td>Tyre Cord Grade</td>
<td>78,000</td>
</tr>
</tbody>
</table>

**Higher IV**
- Increases strength (pressure containers)
- Increases stress crack resistance (pressure containers)
- Reduces crystallization rate (clear preforms)

![Graph showing the relationship between Intrinsic Viscosity and Molecular Weight](image)

- **Solid Starting**
- **Melt phase**

Intrinsic Viscosity (dL/g)

Molecular Weight

0.00 0.25 0.50 0.75 1.00

0 20000 40000 60000 80000 100000
Chemical Recycling of PET.

Three main routes to the chemical recycling of PET:

**Glycolysis**

The conditions used are more «mild» than methanolysis or hydrolysis, but is less effective to treat waste colored and/or mixed materials. The products are commonly oligomers which can be used to make fresh PET, or as precursor of polyurethane foams or unsaturated polyesters.

**Hydrolysis**

Need drastic conditions, in particular as concerns T and P owing to the low wettability of PET. When carried out in basic media (saponification), the reaction is easier and allow to obtain salts of terephthalic acid from which PTA can be recovered by acidification. High capital investments are needed because of the high number of operations and the drastic conditions of the process, which however allows to treat colored and/or mixed wastes.

**Methanolysis**

Consists in a transesterification (commonly base catalyzed) and need drastic operative conditions. dimethylterephthalate (DMT) is the final product, useful in the direct preparation of PET, and can treat colored or mixed samples.
Polyester Regeneration.

Glycolysis \[ R = \text{CH}_2\text{CH}_2\text{OH} \] \( 100-180^\circ\text{C} \) \( 100-200\text{ kPa} \)

Hydrolysis \[ R = \text{OH} \] \( 160-350^\circ\text{C} \) \( 340-1000\text{ kPa} \)

Methanolysis \[ R = \text{CH}_3 \] \( 260-300^\circ\text{C} \) \( 340-650\text{ kPa} \)
Petretec Process (Dupont) for Polyester Regeneration.

- PET Wastes
  - Contaminated PET
    - Landfill/Comb.
    - Mechanical Recycle
  - PET for Recycling
    - DMT Temp >220°C
    - Solution PET / DMT
      - METHANOLYSIS REACTOR
        - CH$_3$OH, 260-300°C, 340-650 kPa
          - DMT + Ethylene Glycol
            - excess CH$_3$OH
              - Column to Remove Methanol
                - CH$_3$OH
      - DMT + Ethylene Glycol
        - azoetrope
          - Distillation
            - MPT
      - MPT / Ethylene Glycol
        - Ethylene Glycol / MPT
          - Pure DMT
Teijin e Aies Co. Processes.

Input of used PET bottle flakes

Hopper

Methanol

H₂O

Ester exchange

DMT separation/refinement

PTA production

EG

Liquid state polymerization

Solid state polymerization

Resin for PET bottles

Depolymerization

BHET

EG

BHET Refinement (decoloration/Distillation, etc.)

PET resin

BHET

HO-CH₂CH₂-OOC - COO-CH₂CH₂-OH

DMT

H₃COOC- COOCH₃

EG

HO-CH₂CH₂-OH

Attilio Citterio

Post-Consumer PET Bottle Collection in Europe.

![Graph showing the collection rate of PET bottles in Europe from 2006 to 2014. The collection rate is measured in % (rhs) and the graph indicates a steady increase in PET collection over the years.]
Decontamination at Flakes Level.

![Bar chart showing concentrations of various compounds in different samples.

- Trichloroethane
- Toluene
- Chlorobenzene
- Phenylcyclochlorohexane
- Benzophenone

Samples:
- Masterbatch
- Pellets B
- Preform B
- Bottle B

Concentration (ppm)
Bottle PET Recycling into New Products.
Final Uses of PET Recycled from Bottles for Food.

Energy saving: PET/RPET = 24
Products Made with Recycled PET.
How Plastics in Computers are Recycled.

1. **CRT Monitor**
   - Body (plastic)
   - Cathode ray tube
   - Chassis and other remaining parts

2. **Desktop PC**
   - Body (steel)
   - Cable
   - Unit (Hard disk drive, power cable, etc.)
   - Printed circuit board
   - Chassis and other remaining parts
   - Front panel, mouse, keyboard

3. **Recycling Process**
   - Crush
   - Solid fuel
   - Glass
   - Copper, steel and other metals
   - Steel
   - Steel, aluminum and other metals
   - Rare metals (Gold, silver and other metals)
   - Steel, aluminum and other metals
   - Solid fuel
   - Dust

Result: Recycle

- Quality of the raw material
- Single stream collection
- Long term vision
- Reliable partners and long term contracts
- Transparency
- Sustainability
- Markets will become more volatile, but the world needs more secondary fibres
- End of waste directive
- Fair Trade and Free Trade
- Quality Standards.
Biodegradable Plastics.

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”

http://iscamap.chem.polimi.it/citterio/education/course-topics/
Bio-plastics and Biodegradable Plastics.

The word “bio-plastics” is often used confusingly. However, bio-plastics consist of either **biodegradable plastics** (i.e., plastics produced from fossil materials) or **bio-based plastics** (i.e., plastics synthesized from biomass or renewable resources). The inter-relationship between biodegradable plastics and bio-based plastics is shown in Figure 1. Polycaprolactone (PCL), and poly(butylene succinate) (PBS) are petroleum based, but they can be degraded by microorganisms. On the other hand, poly(hydroxybutyrate) (PHB), poly(lactide) (PLA) and starch blends are produced from biomass or renewable resources, and are thus biodegradable. Despite the fact that polyethylene (PE) and Nylon 11 (NY11) can be produced from biomass or renewable resources, they are non-biodegradable. Acetyl cellulose (AcC) is either biodegradable or non-biodegradable depending on the degree of acetylation. Starch, cellulose, chitosan and other polymers from nature are classified as natural polymers.
Biodegradable Plastics.

Several types of plastics are biodegradable:

1. **Biopolymers** (polymers made by living organisms or from natural precursors) having bonds breakable by biological systems)
   - Polyhydroxyalkanoates, polyaminoacids, polyglycerols, etc.

2. **Photodegradable Plastics** (chemical stability and material durability) is reduced by additives or via appropriate preparative methods).

3. **Synthetic biodegradable plastics** : prepared by inclusion of starch, cellulose, etc., on synthetic polymer during manufacture
Polymeric Biomaterials Used for Bioapplications.


Degradable Polymers

- Chemical Degradation
  - Hydrolysis
    - Hydrolysable polymers
  - Photo-chemistry
    - Photo sensible additives
    - Photo sensible copolymers
  - Oxidation
    - Oxidable Polymers

- Biological degradation
  - Aseptically
    - Reabsorbing polymers
  - Microbiological
    - Biodegradable polymers
  - Biodegradable additives

- Physical degradation
  - Mechanical
    - All polymers
  - Thermal
    - All polymers
Photodegradable Polyethylene.
Biodegradation Mechanism.

To cell level

extracellular enzymatic breaking

polymer \rightarrow \text{oligomers \rightarrow monomers} \rightarrow \text{intracellular metabolism} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Biomass}

Endocellular enzymes can react only with molecules that are penetrated in the cell: small or long hydro-soluble molecules.
The only norm which actually refers to biodegradation is NF EN 13342. Four Criteria of acceptance are indicated:

- **Composition**: maximum amount of volatile solids and heavy metals
- **Biodegradability**: > 90% of reference substance amount evaluated simultaneously, this must shows a biodegradation >70% in 45 days
- **Time of test limited to 6 month**
- **Disintegration**: less than 10% of residues of >2 mm size in 3 month
- **Quality of final compound**: performance >90% of starting
Biodegradable End of Life. Composting?

- Wood
- Cellulose diacetate
- Aliph./arom. Copolyester
- Polyester-amides
- Newspaper
- Cellulose paper
- Aliphatic (co)polyester
- Medium chain-PHA
- Polycaprolactone
- Polylactide
- Proteins
- PHBV "Biopol"
- TPS blend
- Thermoplastic Starch (TPS)

Composting time (months)
Differences between PLA and PP.

Compared with common petroleum-based polymers such as polypropylene (PP), advantages of PLA include high strength and high modulus, in addition to being a biodegradable renewable resource. Disadvantages of PLA include low resistance to conditions of high heat and humidity, low heat distortion temperature (HDT), low flexibility, and long mold cycle time.

A main focus of research is to improve durability of PLA, mainly related to fast hydrolysis under high humidity conditions.

The table shows:

<table>
<thead>
<tr>
<th>Property</th>
<th>PLA</th>
<th>PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural Modulus</td>
<td>5000</td>
<td>125</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>125</td>
<td>40</td>
</tr>
<tr>
<td>HDT (°C)</td>
<td>200</td>
<td>20</td>
</tr>
<tr>
<td>Elongation % (Yld)</td>
<td>20</td>
<td>5000</td>
</tr>
<tr>
<td>Impact Strength</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

PLA possesses higher strength than PP, but inferior heat resistance and impact strength.
Global Production Capacity of Bioplastics.

Source: Bioplastic EU
Capacity Bioplastic Production in 2011 by types.

- Others: 0.4%
- Bio-PA: 1.6%
- Bio-PE: 17.2%
- Bio-PET 30: 38.9%
- PLA: 16.1%
- Biodegradable Polyesters: 10%
- Biodegradable Starch Blends: 11.3%
- Regenerated Cellulose¹: 2.4%
- PHA: 1.6%
- Others: 0.5%

Total: 1,161,200 metric tonnes

Biobased/non-biodegradable: 58.1%
Biodegradable: 41.9%

Source: Bioplastic EU
Thermal Poly(aspartate) as a Biodegradable Alternative to Poly(acrylate).

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”

http://iscamap.chem.polimi.it/citterio/education/course-topics/
Scale consists of insoluble inorganic compounds such as calcium carbonate, calcium sulfate, and barium sulfate.

Scaling induces:

- reduced water flow though pipes,
- reduced heat transfer in boilers and condensers,
- pump failures
Antiscalants.

- Prevent scale formation entirely or
- Permit the scale to be deposited in such a way that it is easily removed by the fluid flowing along the pipe or heat transfer surface.
- Antiscalants complex with the cations present in water to prevent formation of the insoluble inorganic solids.

Per es.:

\[
\text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{CaCO}_3(s)↓
\]

\[
\text{Ca}^{2+}(aq) + \text{EDTA}^{4-}(aq) \rightleftharpoons [\text{CaEDTA}]^{2-}(aq)
\]
Polyacrylate (PAC) is one of the most common scale inhibitors.

- PAC is a polyanion, i.e. a polyelectrolyte.

**Polyelectrolytes:**
- Are polymers with bound positive or negative charges
- Are also called macroions or polyions
- Can be polyanions or polycations
- Are generally water soluble polymers if their structure is linear
Synthesis of Polyacrylic Acid and Conversion to Polyacrylate.

- Radical Initiation
- PM controlled by termination agents by atom transfer (weak C-H, S-H or O-H bonds, ethers, alcohols, tiols, etc.)

- Crosslinking (through a tridimensional lattice) slow down the H⁺/Na⁺ exchange
PAC as an Antiscalant or Dispersant.

- Polymeric antiscalants are generally low molecular weight polymers.
- Polymeric dispersants consist of higher molecular weight fractions.
- Dispersants do not stop the formation of scale, but instead are able to keep the scale particles suspended in the bulk fluid by imparting a negative charge to the particles.
- PAC comprises 5% of many laundry detergent formulations because of its dispersant properties.
Crosslinked PAC.

- A crosslinked form of the sodium salt of polyacrylic acid is used as a superabsorbent material in diapers and other personal hygiene products.
- Crosslinked PAC has a great affinity for water, but is unable to dissolve and will instead swell in aqueous solution.
- Because of the presence of the charged groups on the polymer chain of a polyelectrolyte, the polymer will be highly expanded in aqueous solution.

\[ R_g = f (\text{pH}, C_s) \]
Attilio Citterio

Forces on Mica Surface
(Mg$^{2+}$, pH = 8, PAA = 10-50 ppm).

**Steric force**

**Interconnection force**

$pH = 8$

50 ppm

10 ppm
Forces on Mica Surface
(Ca$^{2+}$, pH = 8, PAA 10 ppm).

Compact flakes
Crosslinking Agents.

Low molecular weight compounds having more reactive centers (almost 3) able to form a tridimensional knot in the lattice of polymer. Typical are:

- polyalcohols (polyols: tri and tetra OH) for polycondensation reaction to give polyesters
- polyol acrylates (for radical polymerization - crosslinking agents)

\[
\text{HO-CH}_2\text{C-R}
\]
\[
\text{HO-CH}_2\text{C-R}
\]
\[
\text{HO-CH}_2\text{C-R}
\]
\[
R = \text{H}, \quad R = \text{alkyl} \quad R = \text{CH}_2\text{OH}
\]

Trimethylolpropene triacrylate
PAC and the Environment.

- PAC is nontoxic and environmentally benign, **but it is not biodegradable.**
- Because it is widely used for many applications, it poses an environmental problem from a landfill perspective.
- When PAC is used as an antiscalant or a dispersant, it becomes part of wastewater.
- PAC is nonvolatile and not biodegradable, so the only way to remove it from the water is to precipitate it as an insoluble sludge.
- The sludge must then be landfilled.
Substitute: Thermal Polyaspartate.

- The Donlar Corporation developed an economic way to produce thermal polyaspartate (TPA) in high yield and with little or no waste products.
- Polyaspartate is a biopolymer synthesized from L-aspartic acid, a natural amino acid.
- Polyaspartate has similar properties to the polyacrylates and so it can be used as a dispersant, or an antiscalant, or a superabsorber.
- Polyaspartate is biodegradable.
Synthesis of Thermal Polyaspartate.

Aspartic acid

\[
\text{Aspartic acid} \xrightarrow{\text{heat}} \text{Polyaspartate}\]

\[
\begin{align*}
\text{NaOH} & \quad \text{30\% legame } \alpha \\
\text{70\% legame } \beta & \quad \text{Polyaspartate}
\end{align*}
\]
TPA as Alternative to Polyacrylates.

TPA is marketed and sold as:

- a corrosion and scale inhibitor,
- a dispersing agent,
- a waste water additive,
- a superabsorber, and also as
- an agricultural polymer. (As an agricultural polymer, TPA is used to enhance fertilizer uptake by plants. Less fertilizer is added to the soil and the environmental impact from fertilizer run-off is reduced).