3rd SYMPOSIUM OF THE ASSOCIATION OF HELLENIC PLASTIC INDUSTRIES
“PLASTICS AND THE ENVIRONMENT”
National Research Foundation
Athens, November, 4th 2011

“Plastic Waste Management - How Can Hydro- and Oxo-Biodegradable Plastics Mitigate the Waste Burden?”

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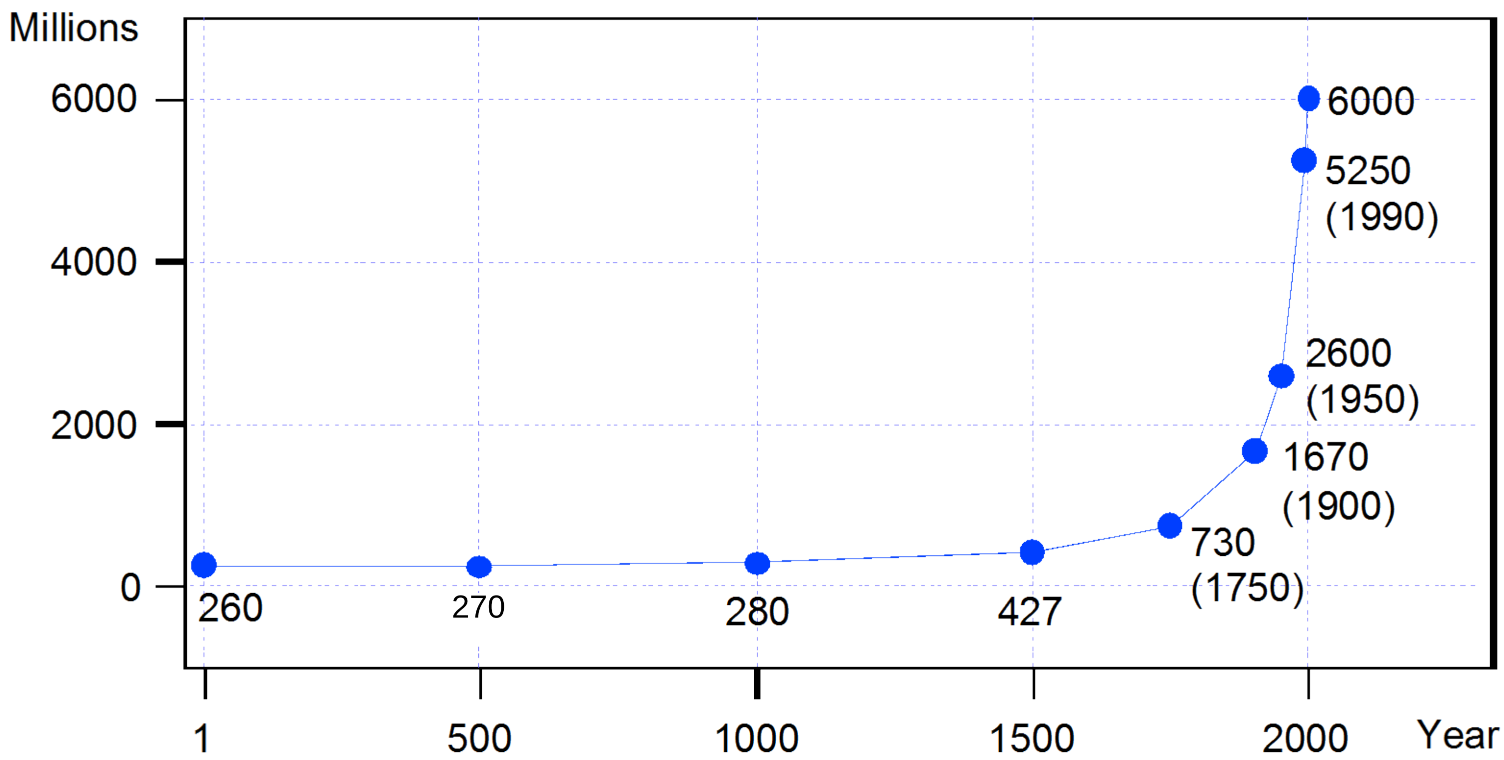
Presentation Outline

- General Considerations on Polymeric Materials and Plastics. Nomenclature, Production & Consumption

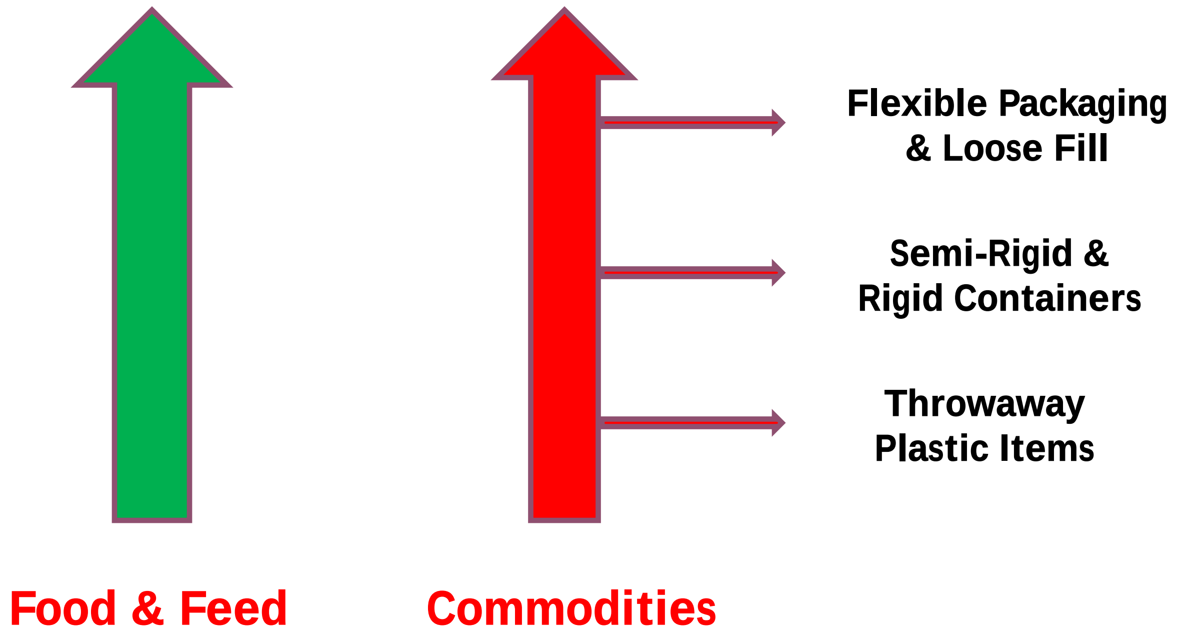
- Plastics from Fossil Fuel & Renewable Resources. What Will Be Next?

- Conclusive Remarks & Recommendations

Growth of World Population



Growing of Needs vs Growing of Population



Semantics on Plastic Nomenclature

- **PLASTICS**: Identify a wide family of various **man-made** finite & semifinite items obtained by processing of Polymeric Materials consisting of **monomeric units from monomers derived from fossil fuel feedstock**

- **BIOBASED PLASTICS**: Identify the family of **plastic items** obtained by **man-guided processing of synthetic polymeric materials** based on **Biotech Building Blocks** from Natural Feedstock including items obtained by processing of chemically **modified natural polymers** (Artificial) and blends of synthetic & natural polymers.

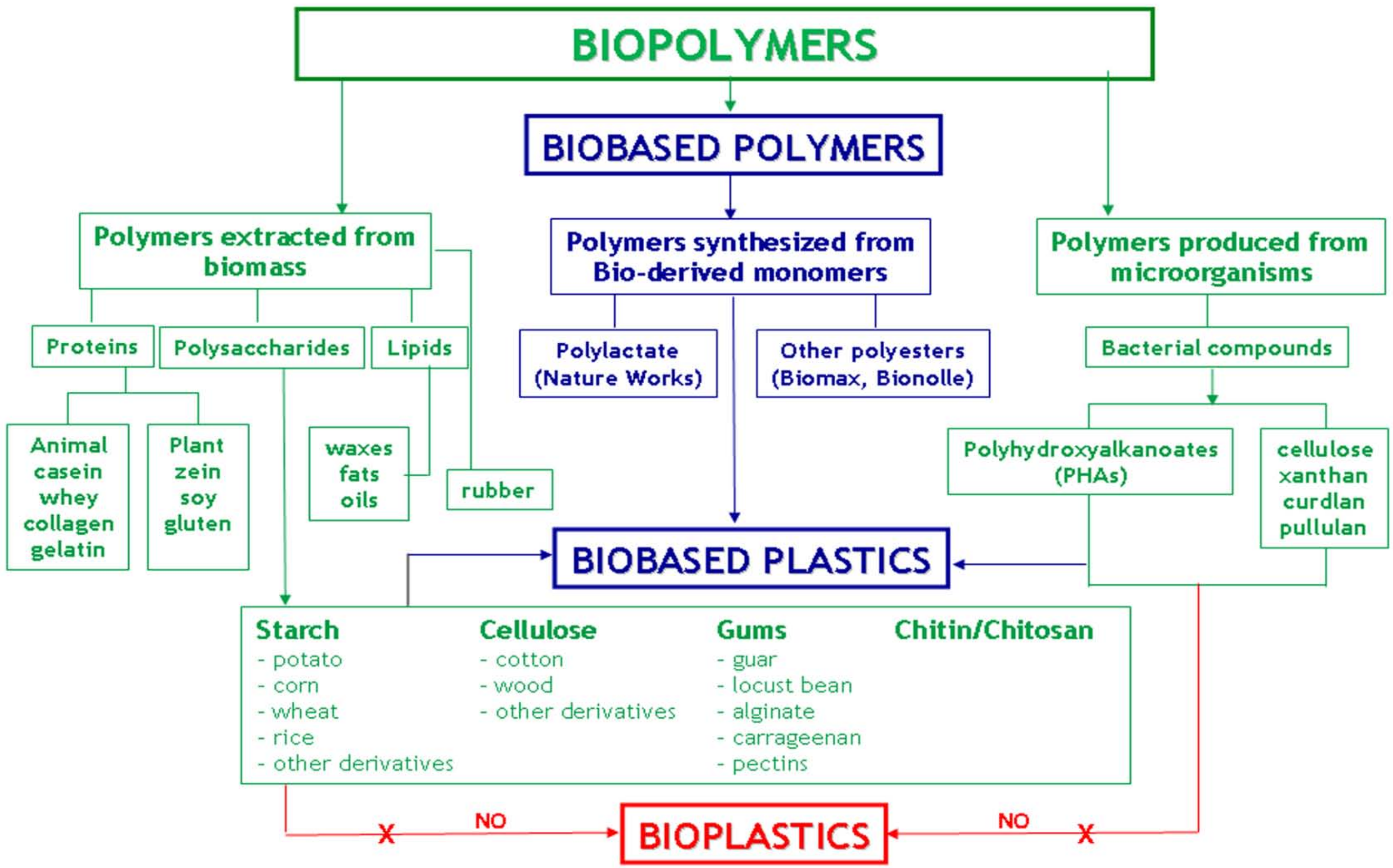
- **BIOPLASTICS**: should identify a family of plastic items **directly designed and produced by nature**

ASTM Definitions

BIODEGRADABLE: a degradable plastic in which the **degradation results from the action of naturally occurring micro-organisms** such as bacteria, fungi and algae.

COMPOSTABLE: a **plastic that undergoes biological degradation during composting** to yield carbon dioxide, water, inorganic compounds and **biomass.**
(Microbial combustion)

Natural & Derived Polymers & Relevant Plastics



Product overview and market projection of emerging bio-based plastics

PRO-BIP 2009

Final report

June 2009

Li Shen[1], Juliane Haufe, Martin K. Patel[2]

Group Science, Technology and Society (STS)
Copernicus Institute for Sustainable Development and Innovation
Utrecht University
www.chem.uu.nl/nws www.copernicus.uu.nl

commissioned by
European Polysaccharide Network of Excellence (EPNOE, www.epnoe.eu)
and
European Bioplastics (www.europeanbioplastics.org)

Utrecht
The Netherlands

Footnote in Pro-BIP Executive Summary

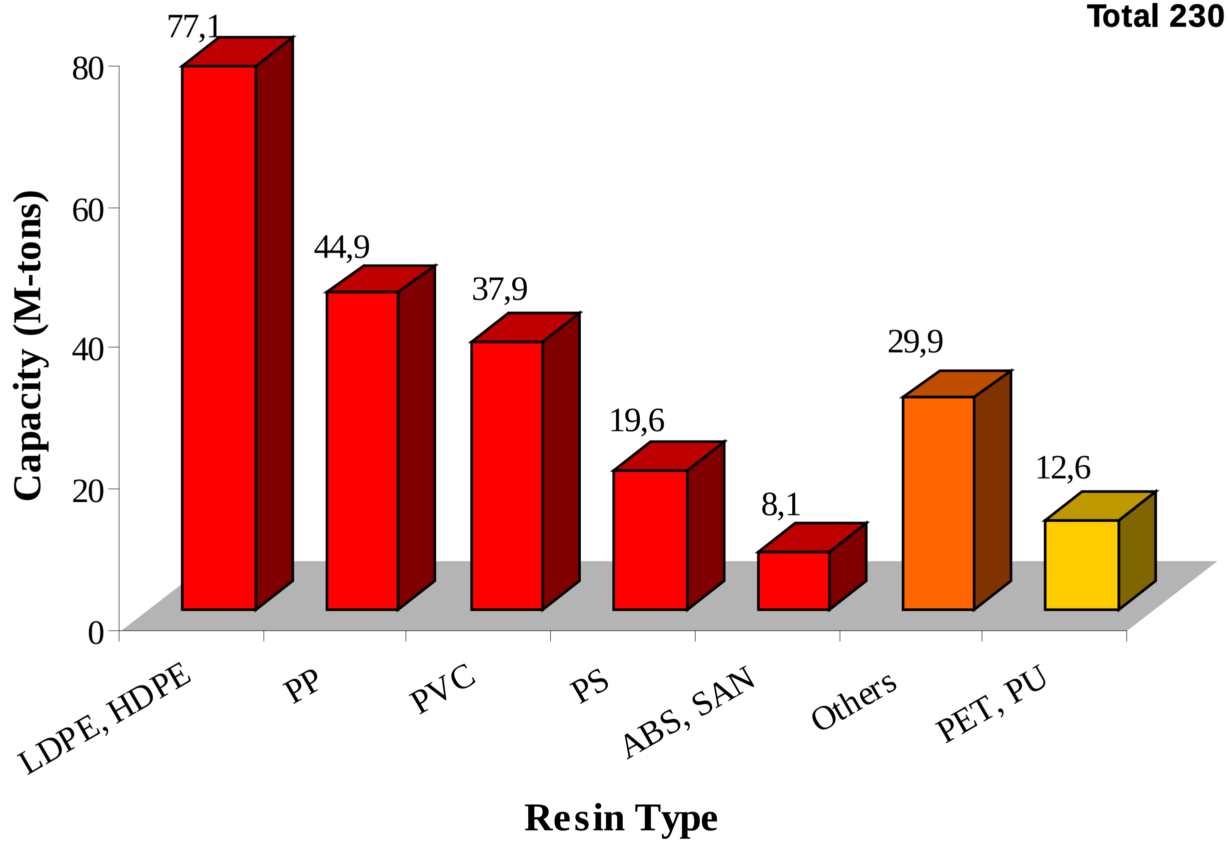
- The subject of this study is ***bio-based plastics***. In this report, bio-based plastics are defined as **man-made or man-processed organic macromolecules derived from biological resources and for plastic and fibre applications** (without paper and board).[1]

[1] In this report, the term "*bioplastics*" is avoided due to its ambiguity: it is sometimes used for plastics that are bio-based and sometimes for plastics that are biodegradable (including those representatives that are made from fossil instead of renewable resources).

M. Patel et al. 2009

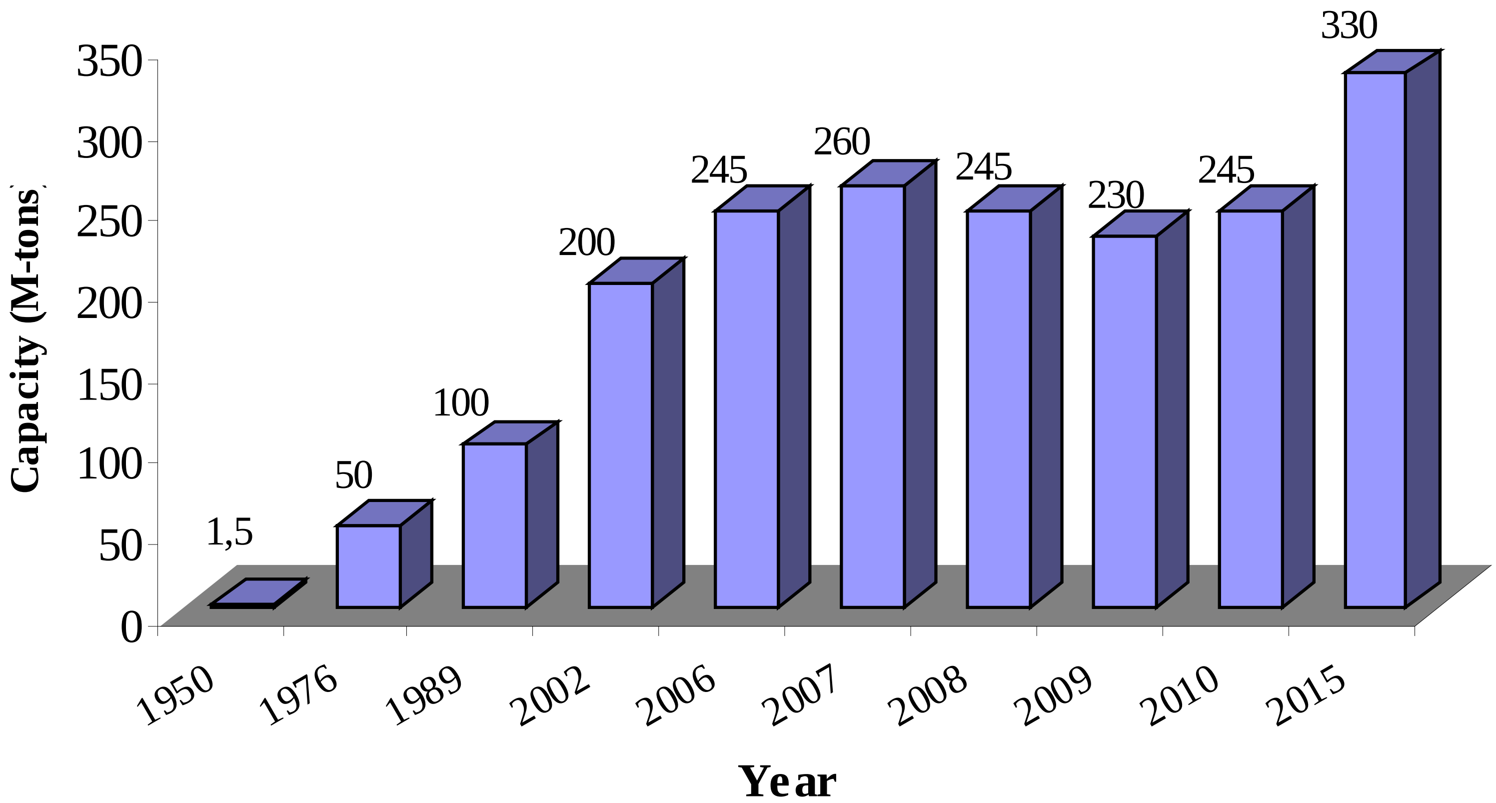
Global Plastic Production by Resin Type: 2009

Total 230 M-tons



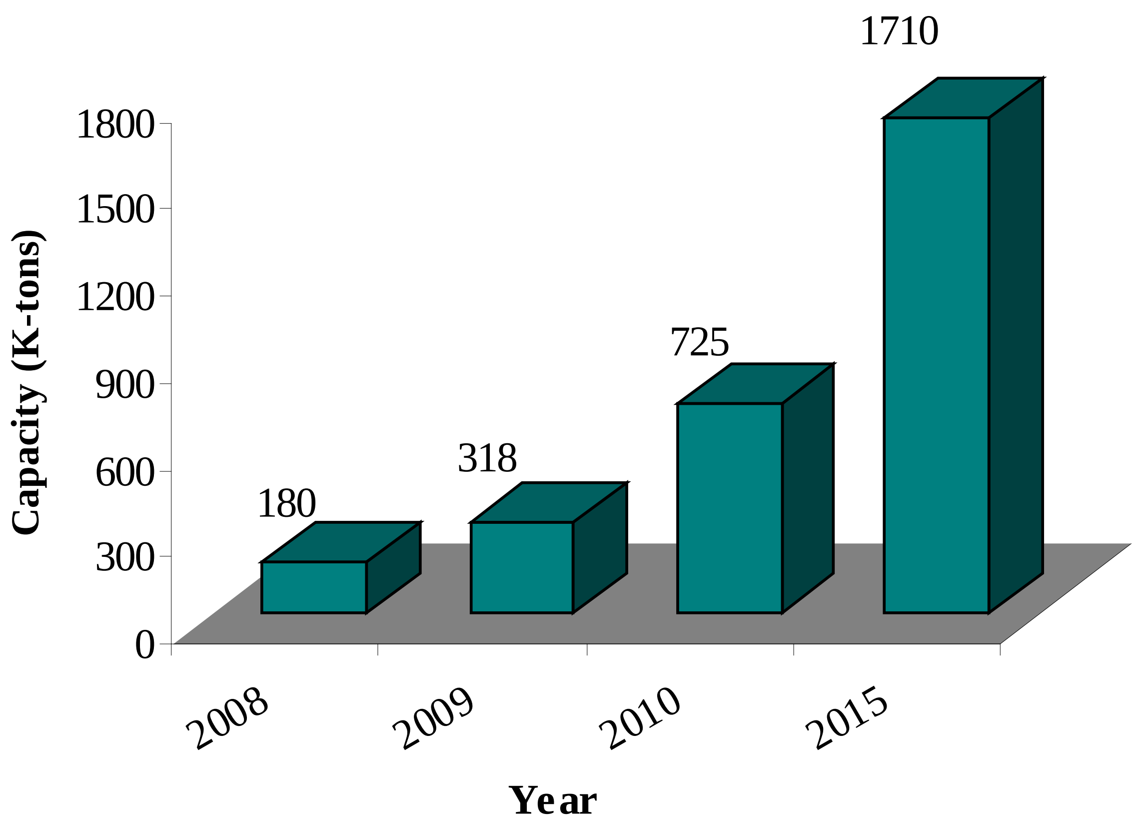
Source: www.cipet.gov.in, ***"Plastic Industry- Statistic"***

Global Plastics Production: 1950-2015



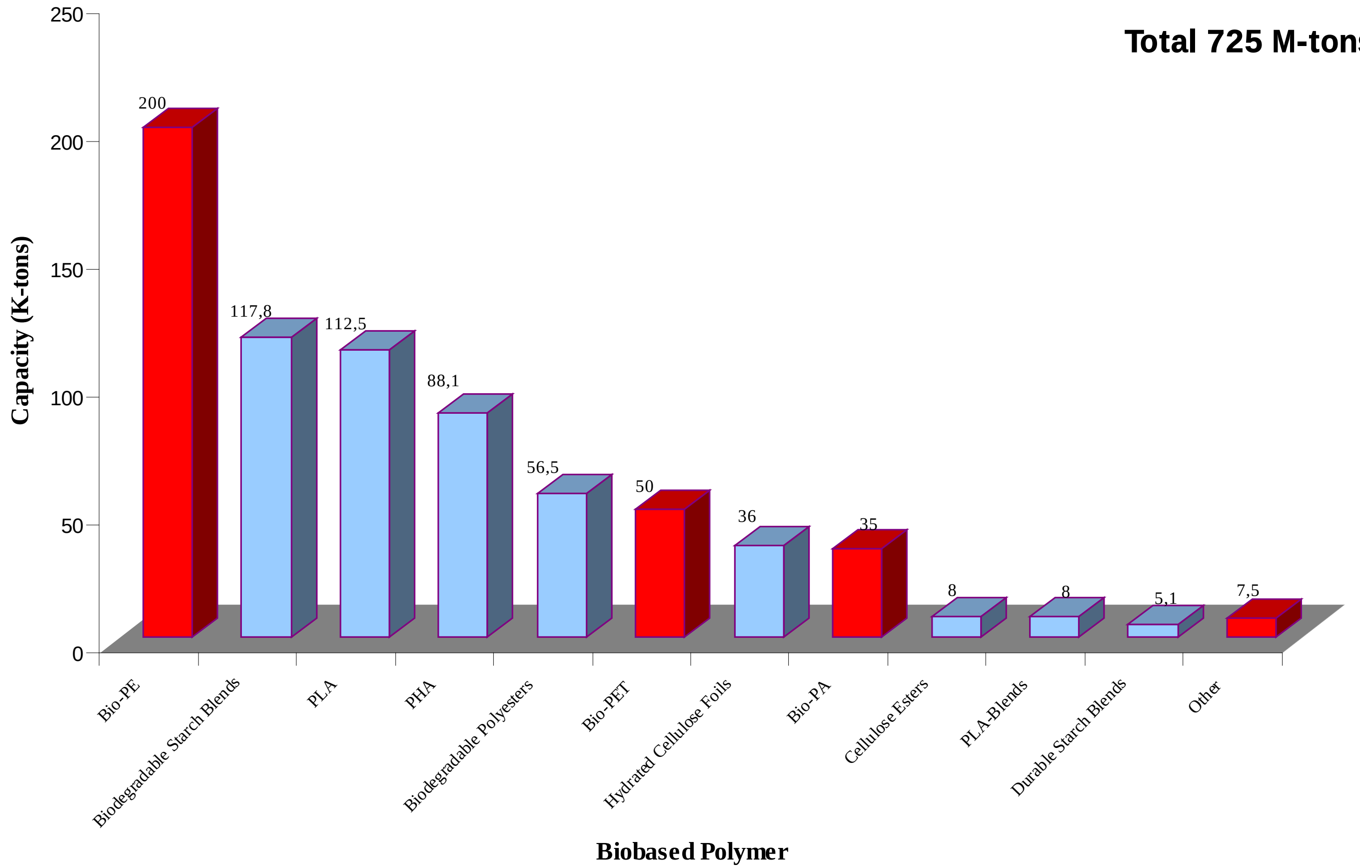
Source: www.plasticseurope.com: [1] *"I "Compelling Facts"*- Statistic on 2008 Production; [2] *"Plastics-The Facts 2010"*- Statistic on 2009 Production; [3] www.gtai.com: Trade & Invest, *"The Plastic Industry in Germany"*, Issue 2010/2011.

Global Production Capacity of Biobased Polymers: 2008-2015



Source: press@european-bioplastics.org, ***"Bioplastics - Statistic on Plastic Production"*.**

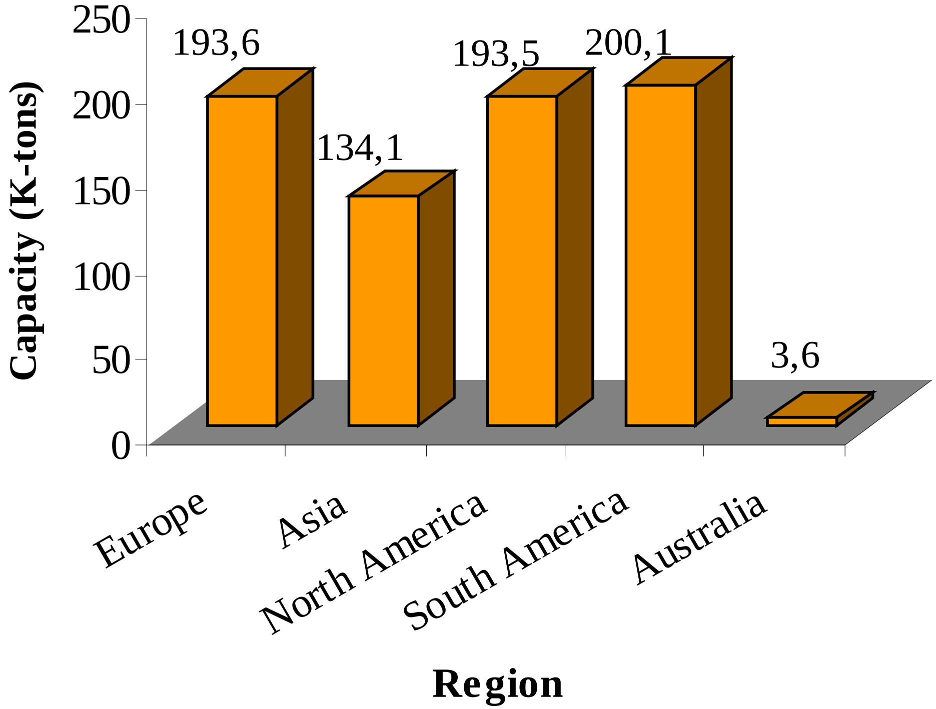
Global Biobased Polymer Production Capacity by Type: 2010



Source: press@european-bioplastics.org, *"Bioplastics- Statistic on Plastic Production"*.

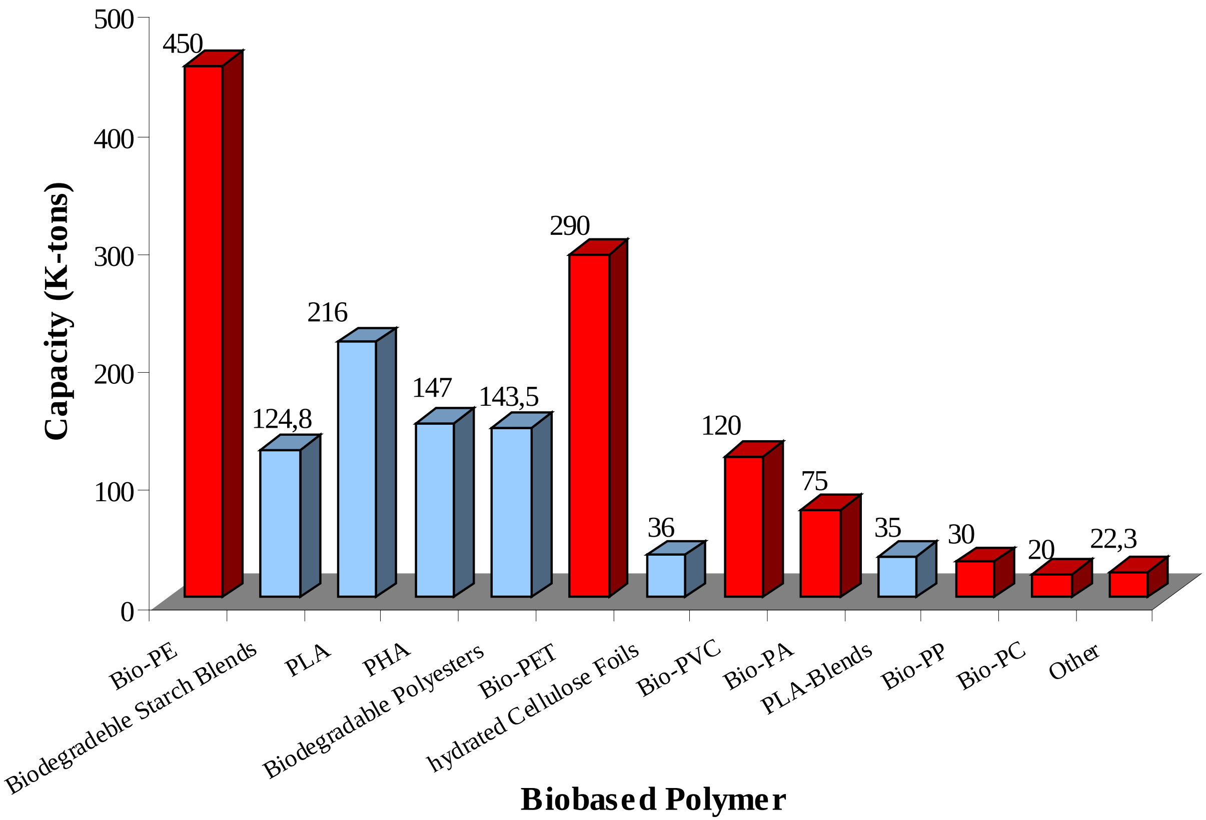
Biobased Polymer Production Capacity by Region: 2010

Total 725 M-tons



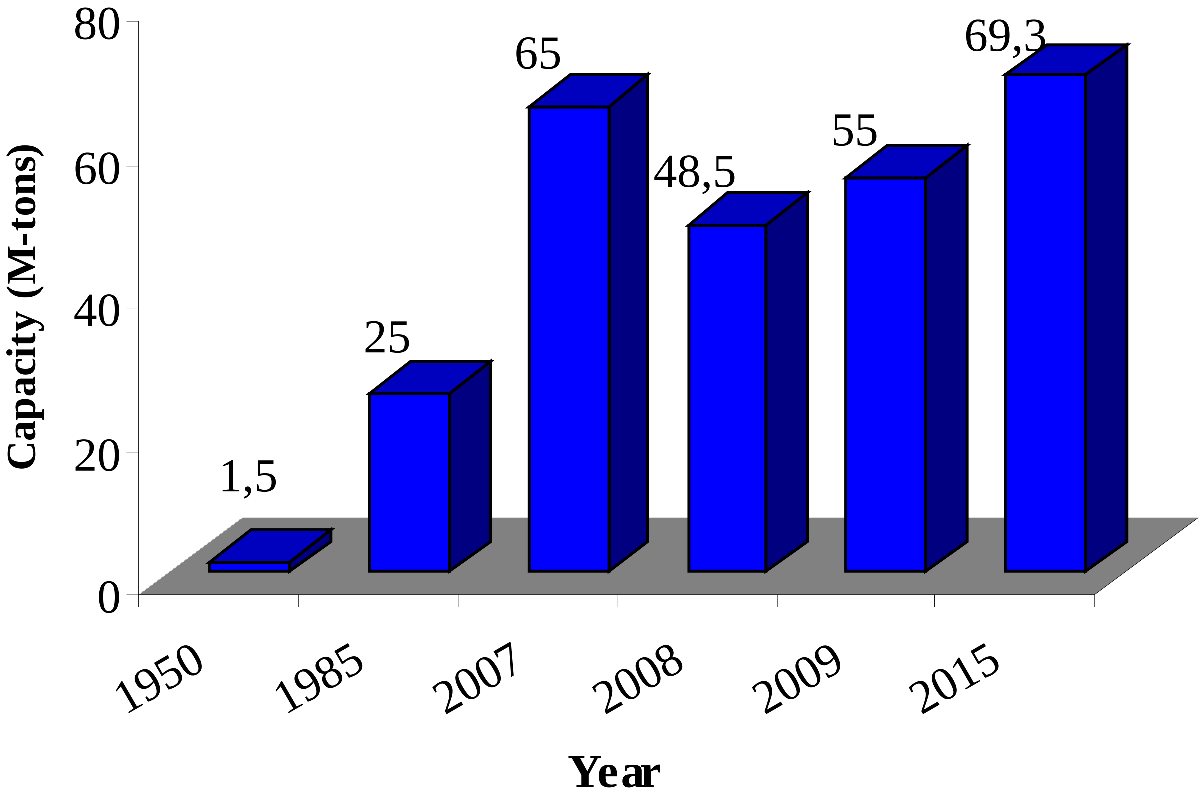
Source: press@european-bioplastics.org, *"Bioplastics- Statistic on Plastic Production"*.

Global Biobased Polymer Production Capacity by Type: 2015



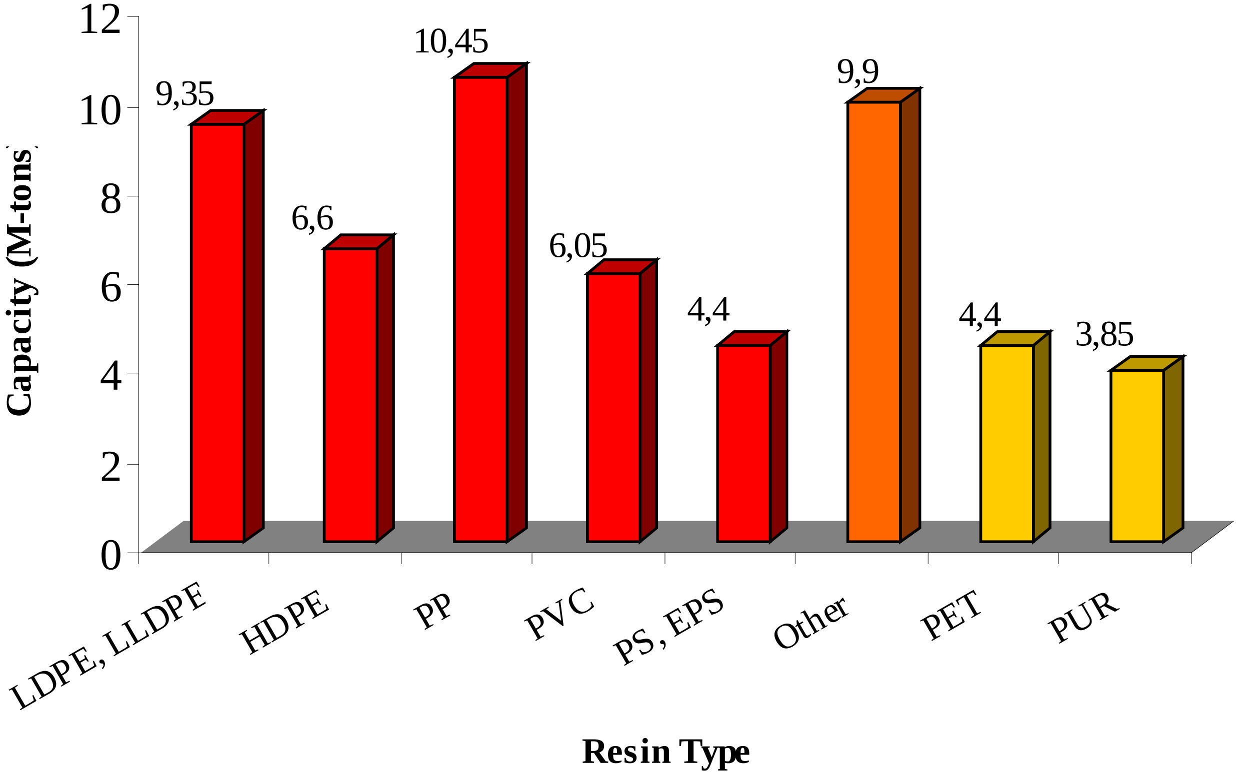
Source: press@european-bioplastics.org, *"Bioplastics- Statistic on Plastic Production"*.

European Plastics Production: 1950-2015



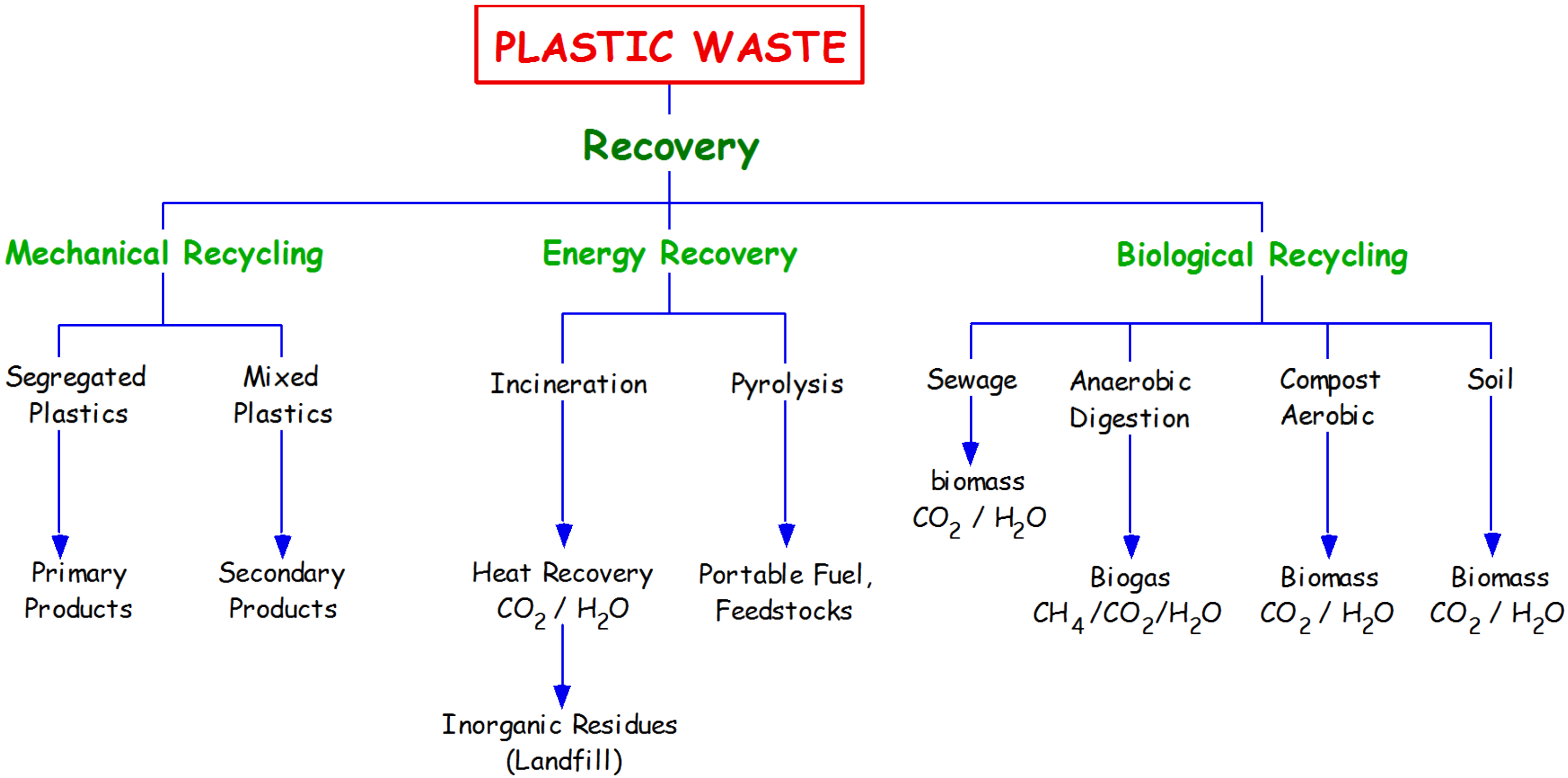
Source: www.plasticseurope.com: [1] *"I "Compelling Facts"*- Statistic on 2008 Production; [2] *"Plastics-The Facts 2010"*- Statistic on 2009 Production; [3] www.gtai.com: Trade & Invest, *"The Plastic Industry in Germany"*, Issue 2010/2011.

European Plastic Demand by Resin Type: 2009

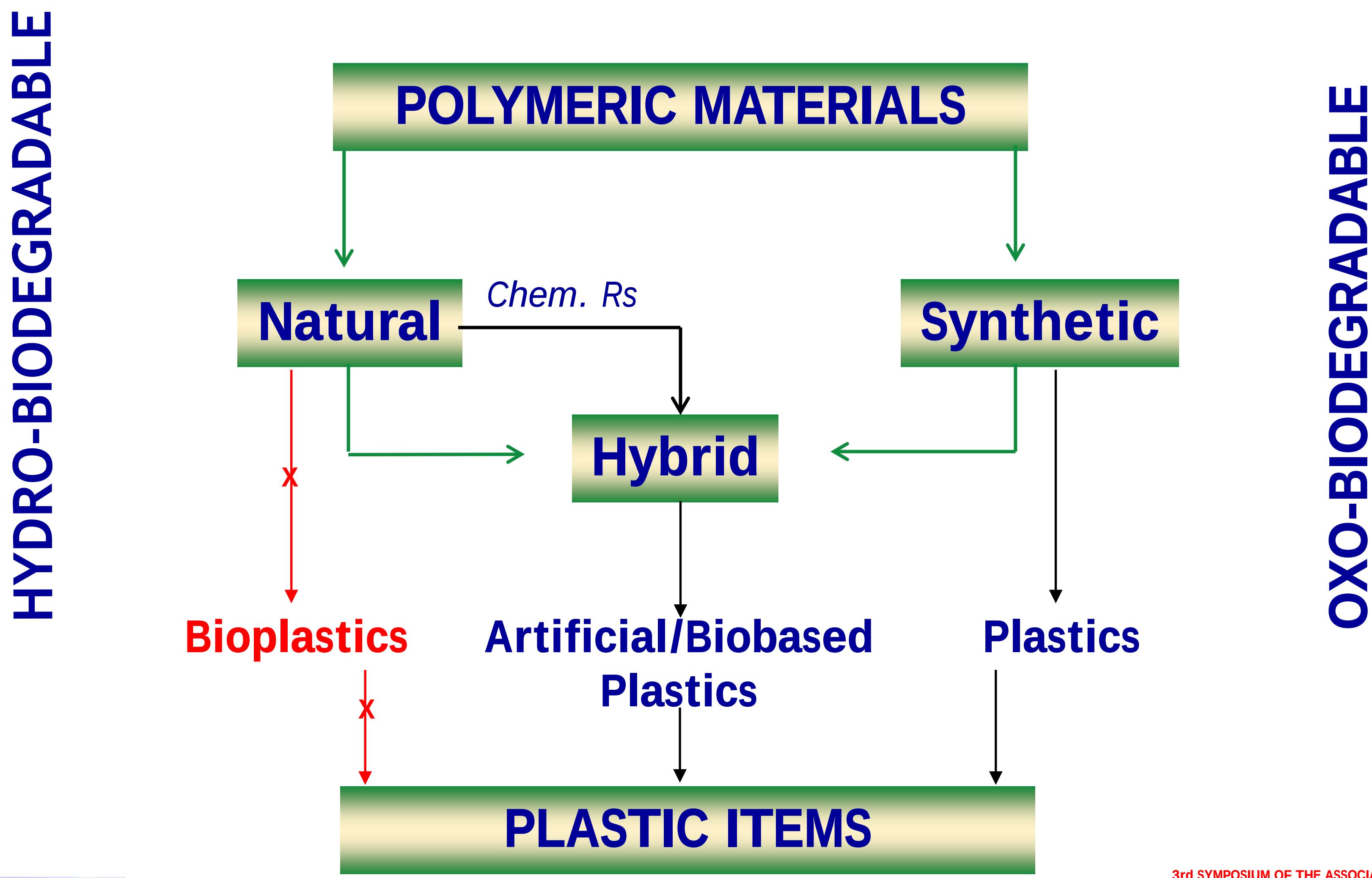


Source: www.plasticseurope.com, *"Plastics-The Facts 2010"*- Statistic on 2009 Production.

Plastic Waste Management Options



Biodegradable Polymeric Materials & Plastics Nomenclature



Environmentally Degradable Polymers & Plastics

Hydro-Biodegradable	Oxo-Biodegradable
↓ H_2O - Uptake, Enzyme mediated or not	↓ O_2 - Uptake, Catalyst
Functional Fragments	**Oxidized Fragments**
↓ Exo-Endo Enzymes	↓ Exo-Endo Enzymes
CO_2, H_2O, Cell biomass	**CO_2, H_2O, Cell biomass**
• Polyesters • Polyamides • Polysaccharides	• Polyolefins • Polyvinylalcohol • Lignin, Rubber

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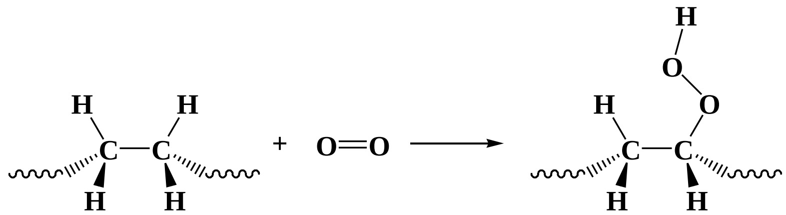
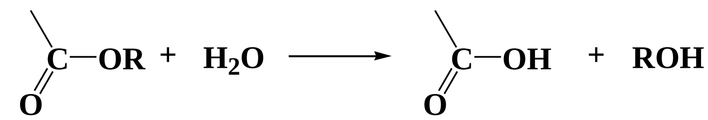
Oxo-Biodegradables



$$E_{att} = (E_{O\text{-}H} + E_{O\text{-}O} + E_{C\text{-}O}) - (E_{C\text{-}H} + E_{O=O})$$

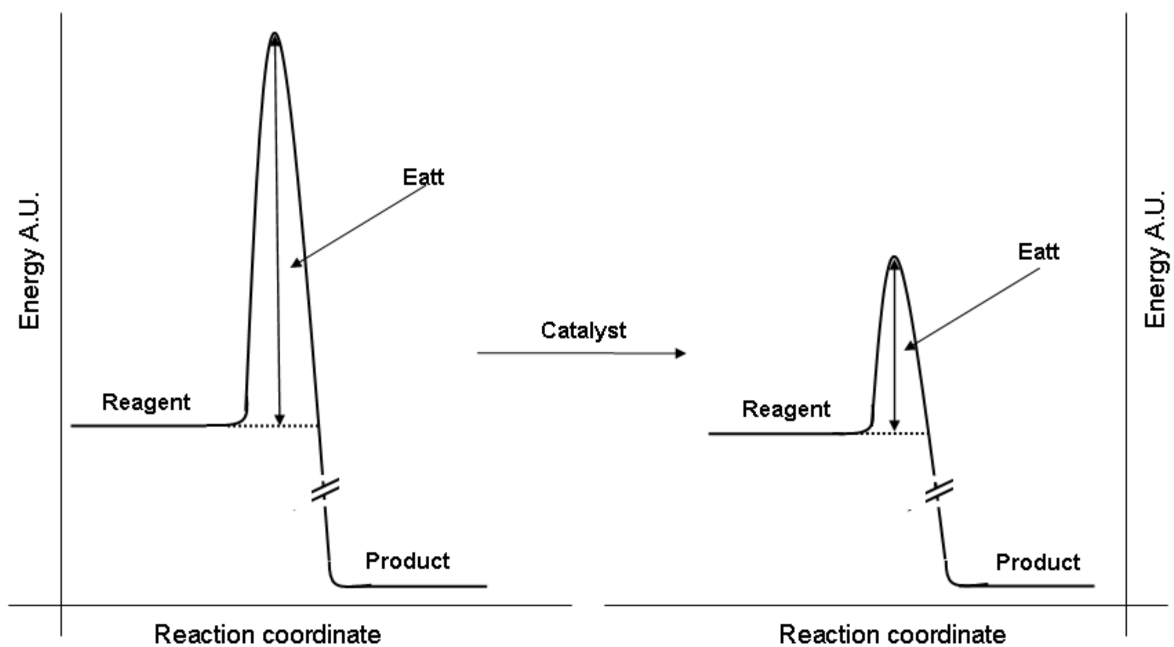
E_{att} = +50.6 Kcal/mole ΔH = - 204 Kcal/mole

Hydro-Biodegradables



$$E_{att} = (E_{C\text{-}OH} + E_{O\text{-}H}) - (E_{C\text{-}OR} + E_{O\text{-}H})$$

E_{att} = + 3.3 Kcal/mole ΔH = - 1.9 Kcal/mole



Full Carbon Backbone Synthetic Polymers

- Polyethylene - TDPA
- Polypropylene - TDPA
- Polystyrene - TDPA
- Polyisobutene
- Polybutadiene
- Polyisoprene
- Poly(vinyl chloride)
- Poly(vinylalcohol) PVA
- Poly(cyanoacrylates)
- Poly(alkyl acrylates)
- Poly(alkyl metacrylates)
- Poly(acrylonitrile)
- Poly(acrylamide)
- Poly(vinyl amine)

Oxo-Biodegradable Polyethylene-PE*

Oxo-Biodegradation of Alkanes

- Terminal oxidation (*Pseudomonas*)

$$RCH_3 \rightarrow RCH_2OH \rightarrow RCHO \rightarrow RCOOH$$

- Diterminal oxidation (*Candida*)

$$H_3CRCH_3 \rightarrow \rightarrow \rightarrow H_3CRCOOH \rightarrow HOCH_2RCOOH \rightarrow OCHRCOOH \rightarrow HOOCRCOOH$$

- Subterminal oxidation (*Nocardia*)

$$RCH_2CH_2CH_3 \rightarrow RCH_2CH(OH)CH_3 \rightarrow RCH_2COCH_3 \rightarrow RCH_2OC(O)CH_3 \rightarrow RCH_2OH + CH_3COOH$$

- Finnerty's pathway (*Acinetobacter*)

$$RCH_3 \rightarrow RCH_2OOH \rightarrow \rightarrow RCHO \rightarrow RCOOH$$

$$RCHO \searrow RCH_2OH \text{ — } RCOOCR$$

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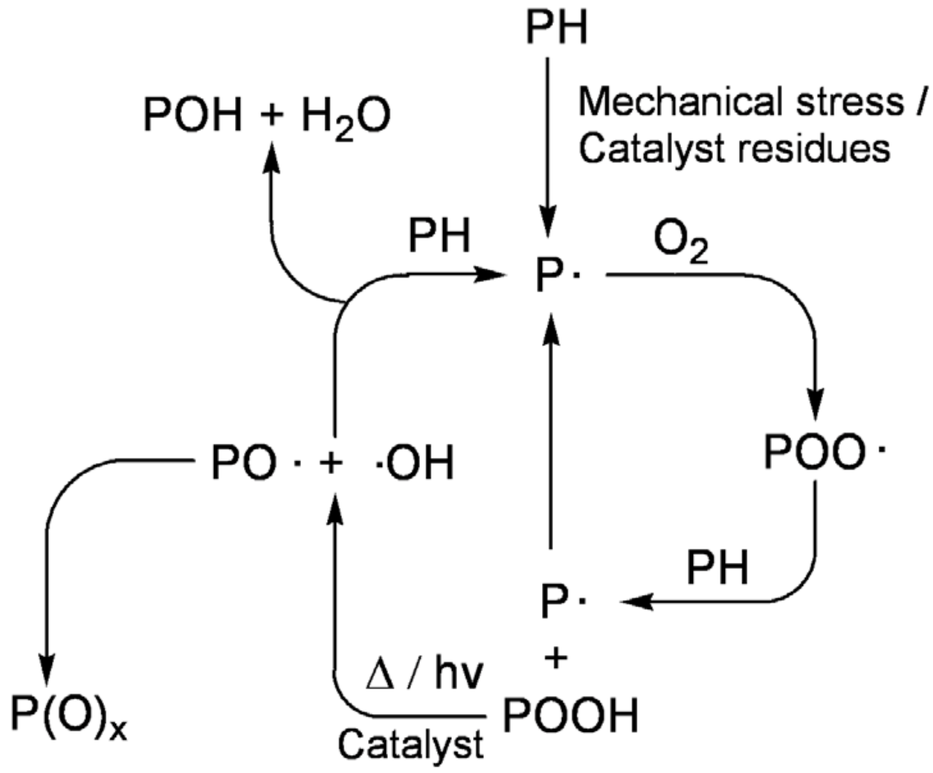
Microorganisms Capable to Oxidize Hydrocarbons [a)]

Genera of Bacteria and Yeasts that reportedly contain aliphatic hydrocarbon-oxidizing species

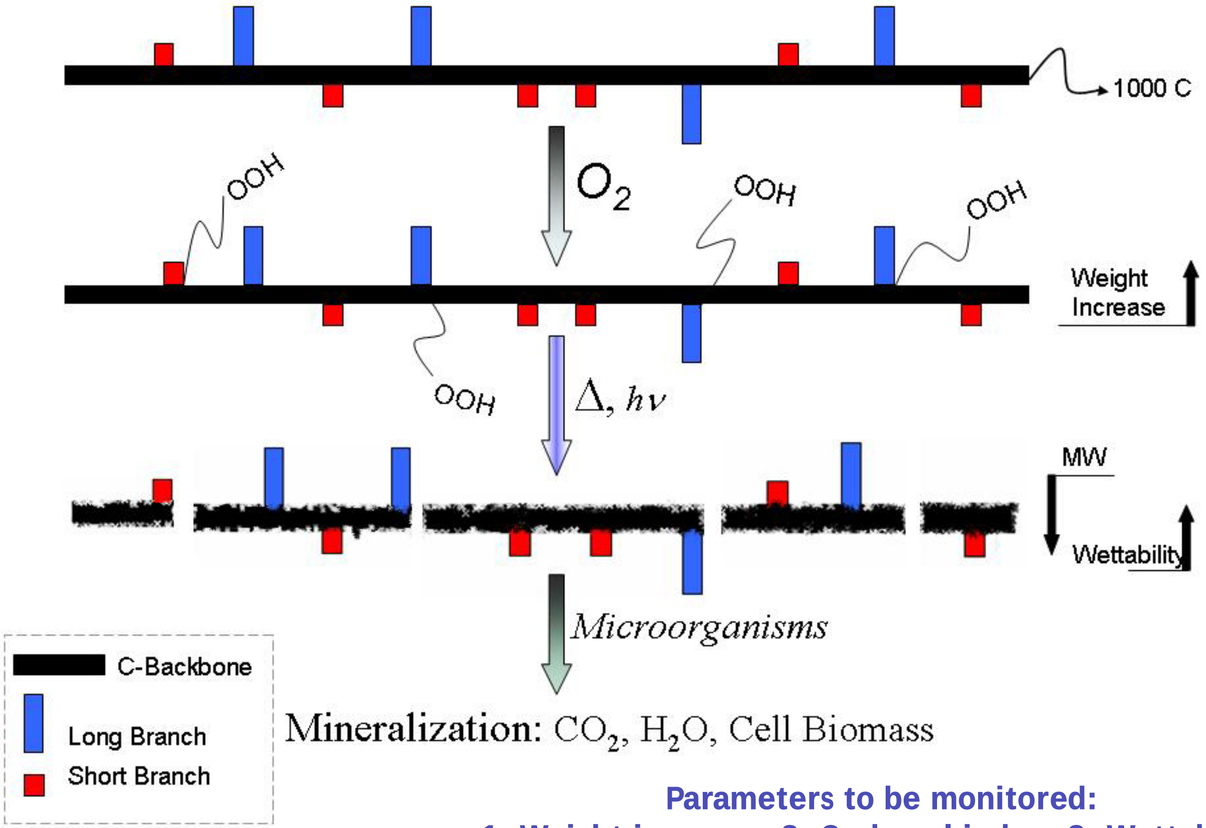
Bacteria	Yeasts
Achromobacter	*Candida*
Acinetobacter	*Cryptococcus*
Actinomyces	*Debaryomyces*
Aeromonas	*Endomyces*
Alcaligenes	*Hansenula*
Arthrobacter	*Mycotorula*
Bacillus	*Pichia*
Beneckea	*Rhodotorula*
Brevibacterium	*Saccharomyces*
Corynebacterium	*Selenotila*
Flavobacterium	*Sporidiobolus*
Micromonospora	*Sporobolomyces*
Mycobacterium	*Torulopsis*
Nocardia	*Trichosporon*
Pseudomonas	
Spirillum	
Vibrio	

[a)] "Microbial Degradation of Organic Compounds" edited by David T. Gibson, Marcel Dekker Inc. New York and Basel, 1984.

Poly(hydrocarbon)s Oxidation



Schematic Representation of PE* Oxo-Degradation

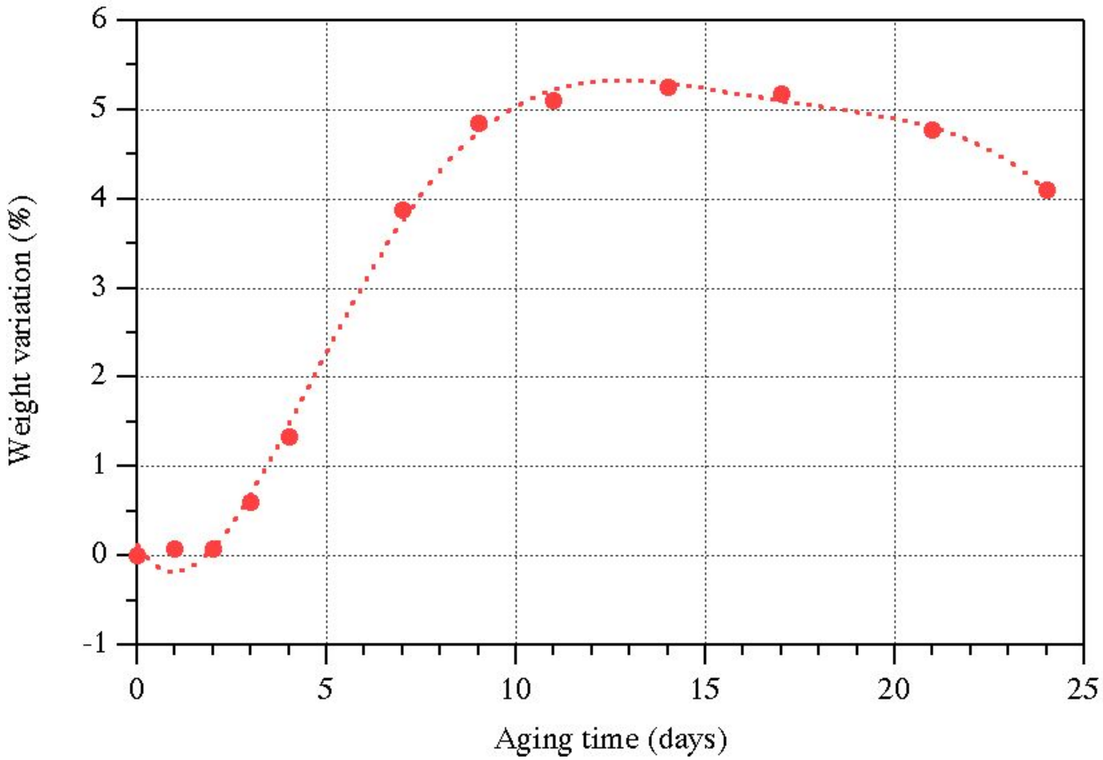


Mineralization: CO_2, H_2O, Cell Biomass

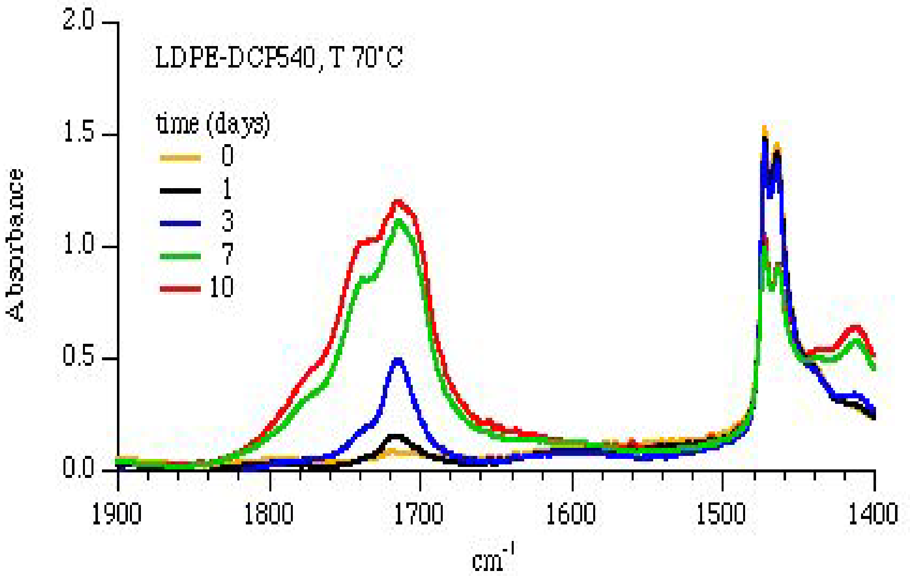
Parameters to be monitored:
1. Weight increase; 2. Carbonyl index; 3. Wettability;
4. Molecular weight; 5. Solvent extraction

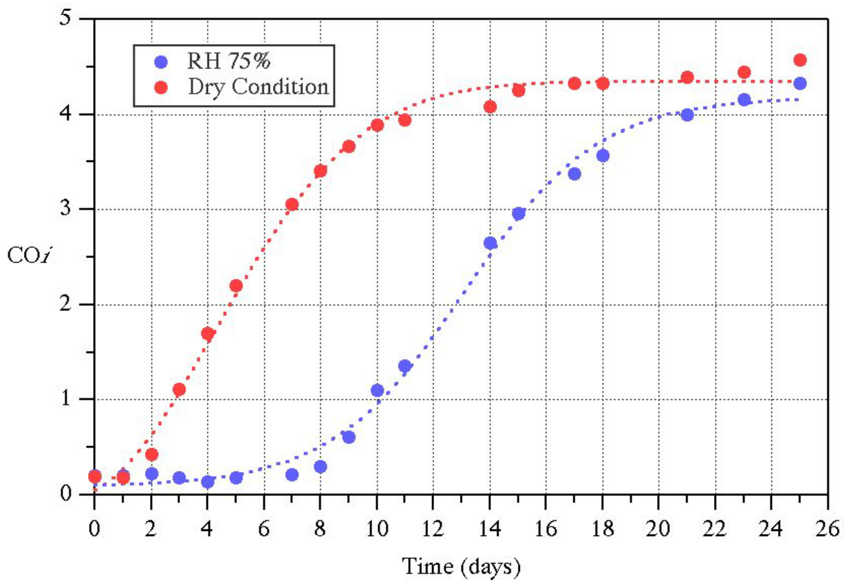
BIOLAB

Weight Variation Profile of LDPE Sample Containing Pro-Degradant Upon Aging in Oven at 70°C

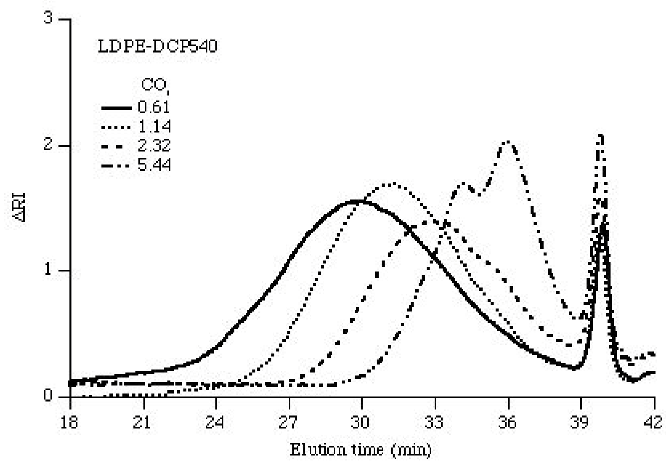


Carbonyl Index (CO*i*) Variation of LDPE Film Sample Aged in Oven at 70ºC

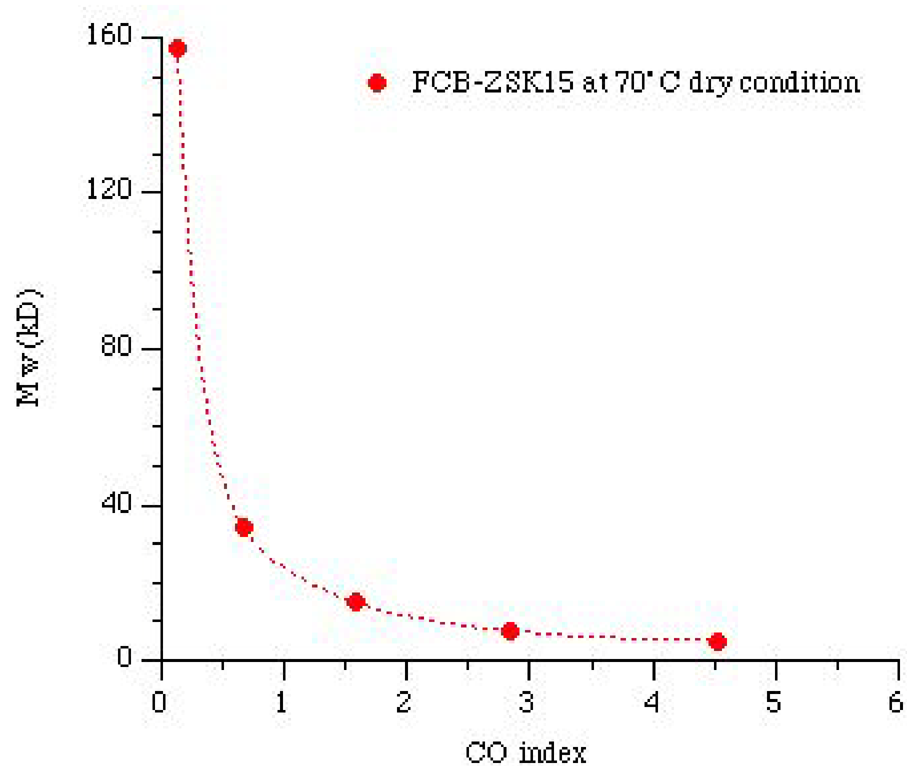




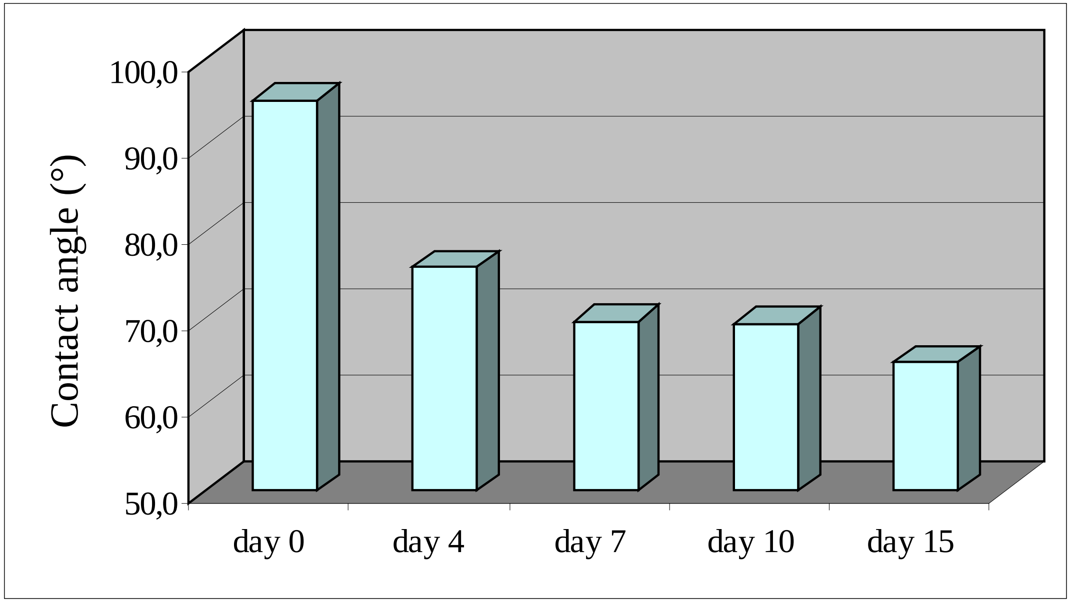
PE*-Degradation at 70° C under Dry Conditions



Time	CO index	Mw	I_D
(days)		(kD)	
0	0.61	39.4	4.24
1	1.14	19.5	2.96
2	2.32	9.7	2.59
9	5.44	4.5	1.27



Contact angle and density change of LDPE Samples at Increasing Level of Oxidation



Water Contact Angles on Heat-Aged LDPE-TDPA

Sample density increase upon oxygen uptake

BIOLAB

Fragmentation of PE in Landfill Burial Test

PE films with (right) and without (left) TDPA® before (top) and after (bottom) 10 months burial in a UK landfill

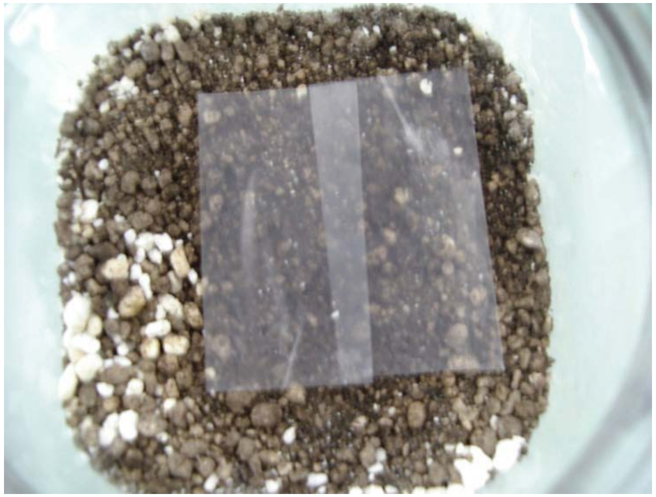
Fragmentation in Outdoor Exposure of PE Bags

0 days

33 days

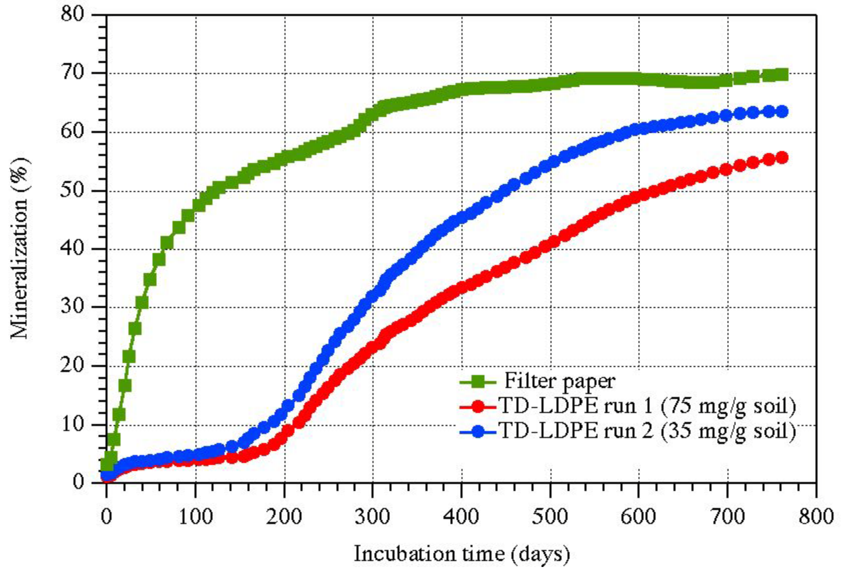
55 days

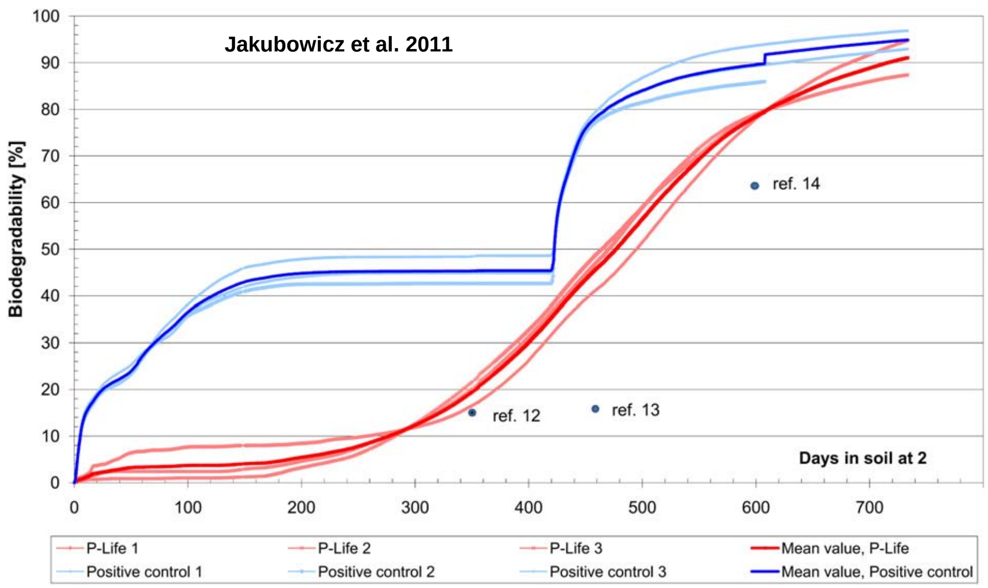
Mature Compost Respirometric Tests



Biodegradation in Soil Burial Respirometric Tests of Oxidized LDPE-TDPA Samples

Two-step mineralization kinetic of thermally fragmented LDPE-TDPA samples in soil

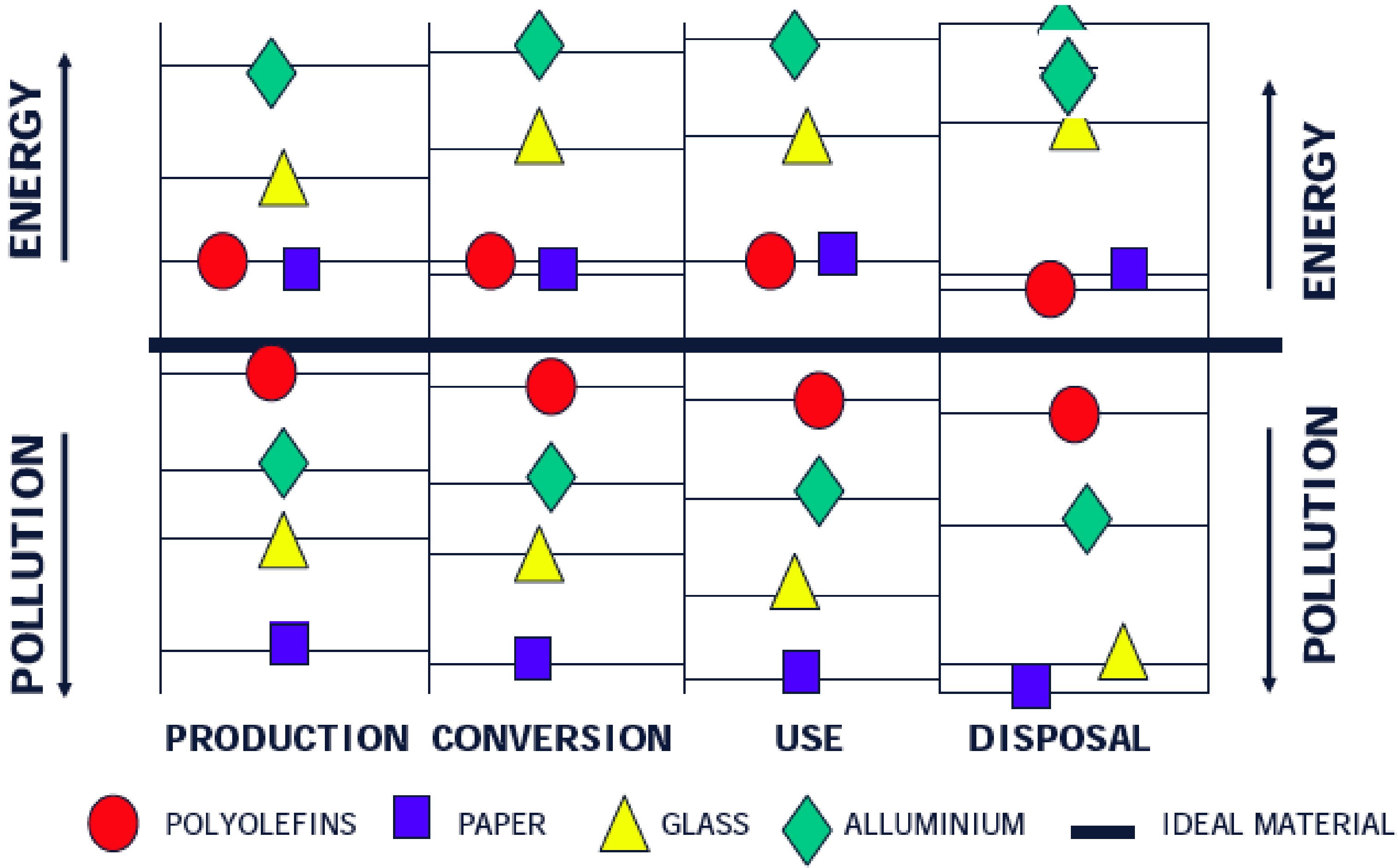




Cress Seeds Germination Test
(EPI additives submitted to a biodegradation process)

The Eco-Balance of Polyolefins

Comparison with other materials over their entire life span (excluding recycling) based on a meaningful interpretation of information from independent sources on packaging materials



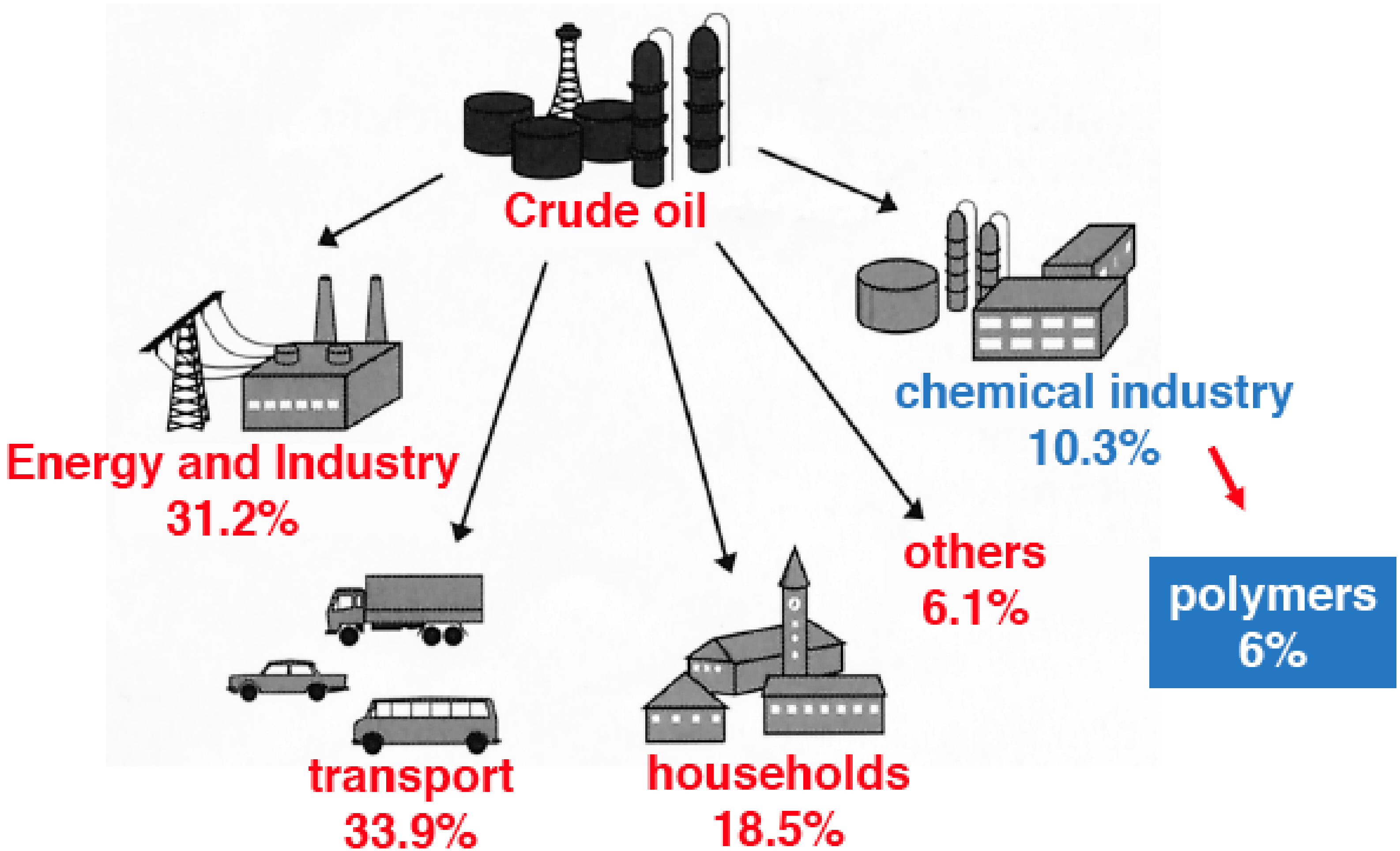
Standards in Place for Oxo-Biodegradable Polymers & Plastics

- **ASTM D6954-04 Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation**

- **ASTM D7475-11 Standard Test Method for Determining the Aerobic Degradation and Anaerobic Biodegradation of Plastic Materials under Accelerated Bioreactor Landfill Conditions**

- **BS 8472-11 Methods for the Assessment of the Oxo-Biodegradation of Plastics and of the Phyto-Toxicity of the Residues in Controlled Laboratory Conditions**

From Feedstocks to Polymers Consumption of Mineral Oil (typical pattern of developed countries)



Energy Resources Alternative to Crude Oil

- Solar [600 sq. Km of solar panels in the Sahara desert]
- Biomass & 2nd Generation Biofuel
- Hydroelectric
- Aeolian
- Hydrogen
- Nuclear

Conclusions & Recommendations

- Polymers are versatile materials ease to be converted to various useful plastic items formerly meant to be durable.
- Consumption of plastics is increasing with increasing population and hence needs of commodities.
- Nowadays plastic items are demanded as “born to last as long they serve”
- Harmonized plastics waste management within MSW management has to be enforced.
- Incineration of plastics waste with energy recovery, mechanical recycling and biorecycling with preservation criteria should all coexist.
- Polymers from renewable resources have to be revisited. Second/third generation from sources have to be used as raw material.
- Better cost/performance balance desirable for Biobased Plastics.
- Reengineering of synthetic full carbon backbone petropolymers as an effective route to Environmentally Degradable Polymeric Materials & Plastics has to be pursued.
- Seeking for energy sources alternative to fossil fuel has to be stimulated.
- From the present armed partnership, oxo- and hydro- biodegradable plastics, a front of a mutual benefit, have to get to a durable and prosperous marriage

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