POLYMERS AND THEIR ENVIRONMENTAL DEGRADATION

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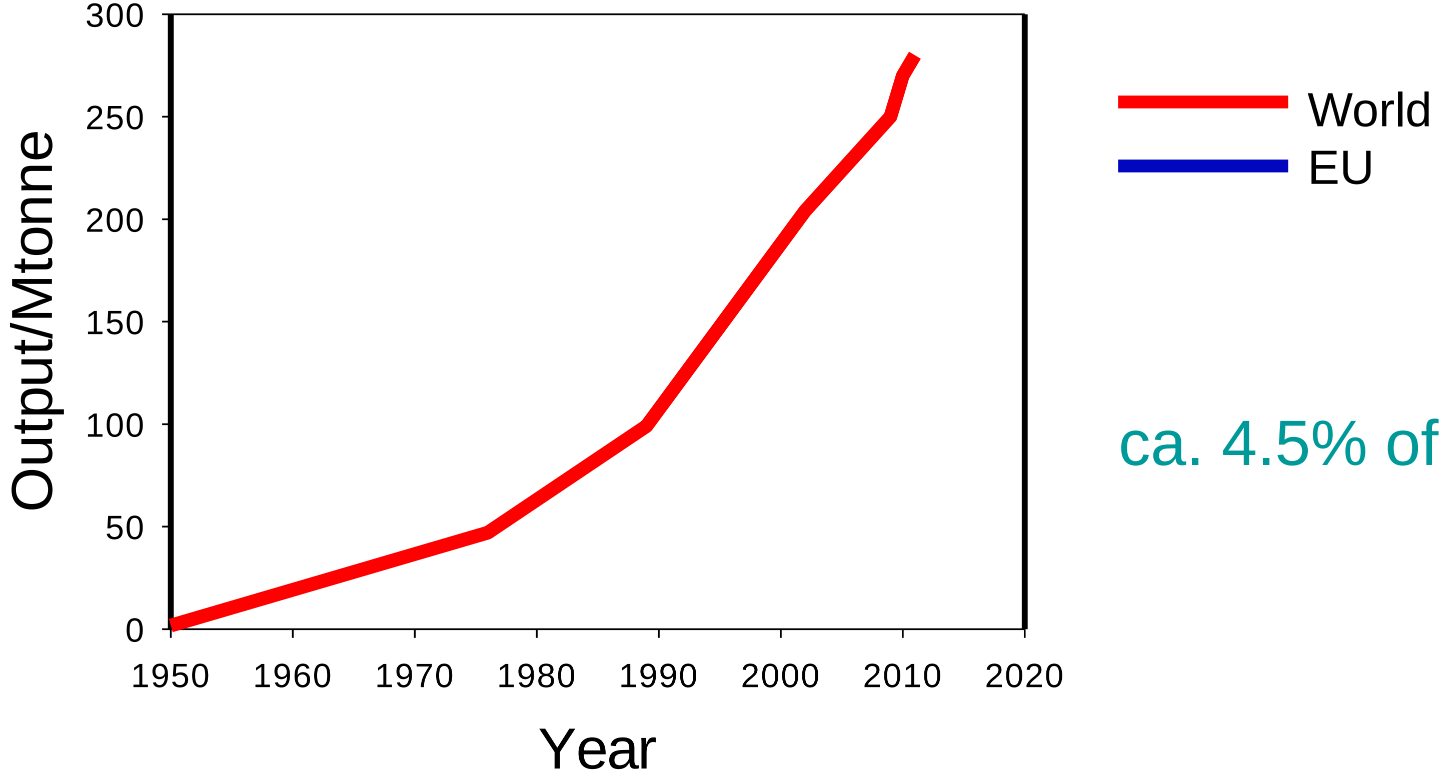
Polymers

“I am inclined to think that the development of polymerization is, perhaps, the biggest thing chemistry has done, where it has had the biggest effect in everyday life. The world would be a totally different place without artificial fibres, plastics, elastomers, etc. Even in the field of electronics, what would you do without insulation? And there you come back to polymers again.”

Lord Todd, president of the Royal Society, in reply to the question What do you think has been chemistry's biggest contribution to science, to society?

Chem. Eng. News 58(40), 29 (1980).

WORLD PLASTICS PRODUCTION



ca. 4.5% of all oil

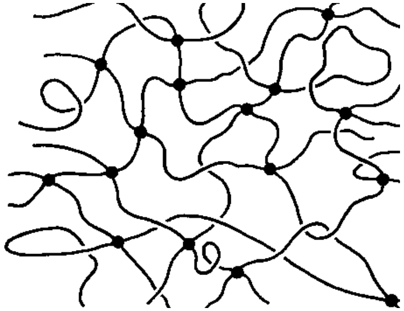
Includes thermoplastics, polyurethanes, thermosets, elastomers, adhesives, coatings and sealants and PP-fibres. Not included PET-, PA- and acrylic fibres.

Source: Plastics Europe Market Research Group (PEMRG)

ONE CLASSIFICATION

- Thermoplastics
  - Typically linear chains
  - Soften on heating and can flow
  - Often soluble in appropriate solvents
  - Poor durability

- Thermosetting
  - Typically cross-linked chains
  - Insoluble (but may swell)
  - Bakelite, epoxy, rubbers etc.
  - Extremely durable

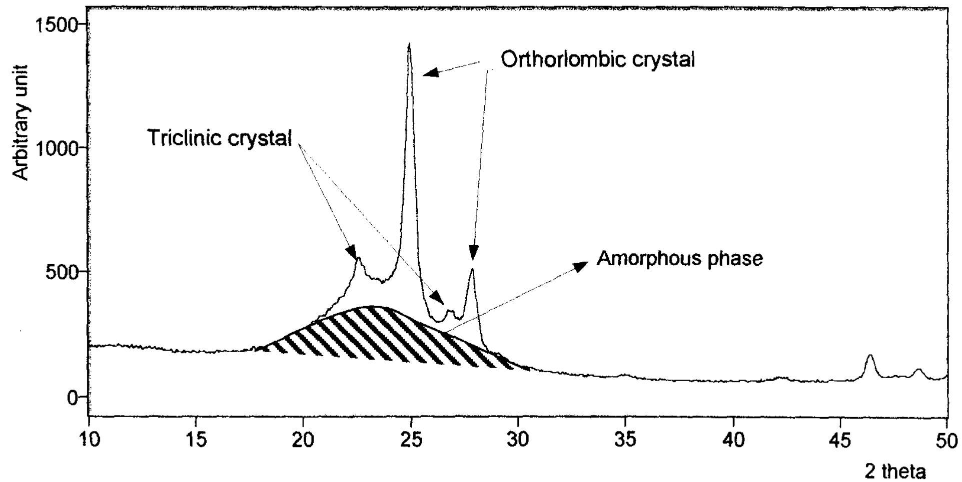


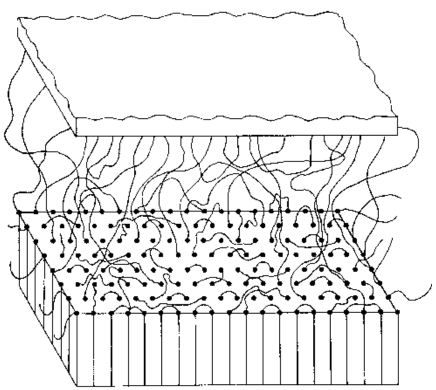
ANOTHER CLASSIFICATION

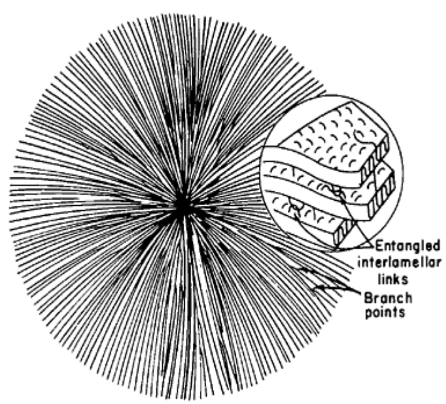
- Amorphous:
  - polymer chains cannot crystallise
  - pack randomly with no long-range order
  - Most vinyl polymers and crosslinked polymers
  - Glass transition temperature
- Semi-crystalline:
  - Chains are regular and intermolecular forces allow local packing into crystal lattice
  - polyamides, polyesters, polyethylene, stereoregular polyolefins, cellulose
  - Glass transition and melting temperatures

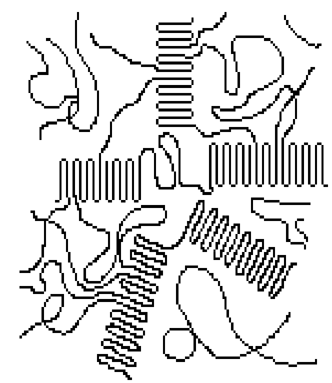
Crystallinity in polyethylene

- X-ray diffraction shows mixture of crystals and amorphous material

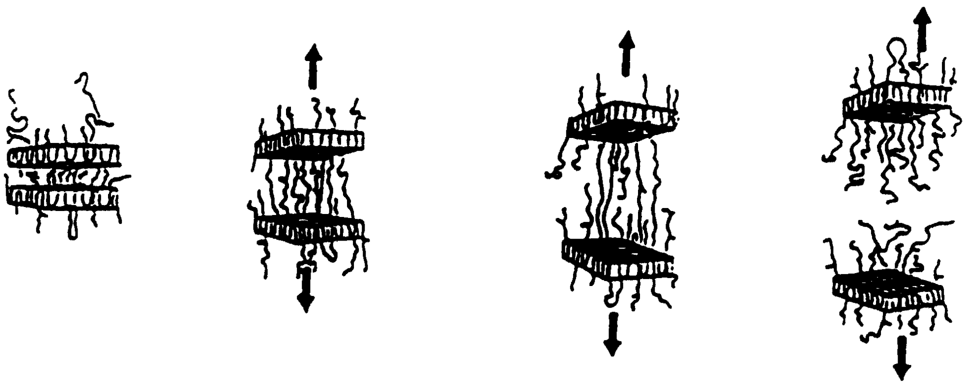








Toughness in semi-crystalline polymers



- Crystallites act as “cross-links” and “fillers”
- Increase stiffness and toughness
- Polymer responds to load by chains pulling through crystals
- Critically dependent on “tie molecules”

Synthetic plastics are environmentally friendly

- Convert low-value oil fractions (otherwise flared) into high value polymers.

In typical applications, e.g. Packaging:

- They reduce energy costs by up to 40%.
- They reduce waste by 75 - 80%.
- They reduce emissions by 70%.
- They reduce water pollution by up to 90%.

POLYSTYRENE v PAPER CUPS

	Polystyrene	Paper
Weight	1.5 g	10 g
Materials		
Tree	0	33 g
Oil	3.2 g	4.1 g
Other Chemicals	0.05 g	1.8 g
Utilities/tonne		
Steam	5000 kg	10000 kg
Power	150 kWh	980 kWh
Cooling Water	150 m^3	50 m^3
Pollution/tonne		
Effluent water	1 m^3	100 m^3
solids	trace	50 kg
BOD	0.07 kg	40 kg

Source: M B Hocking, Science, 251, 504 (1991)

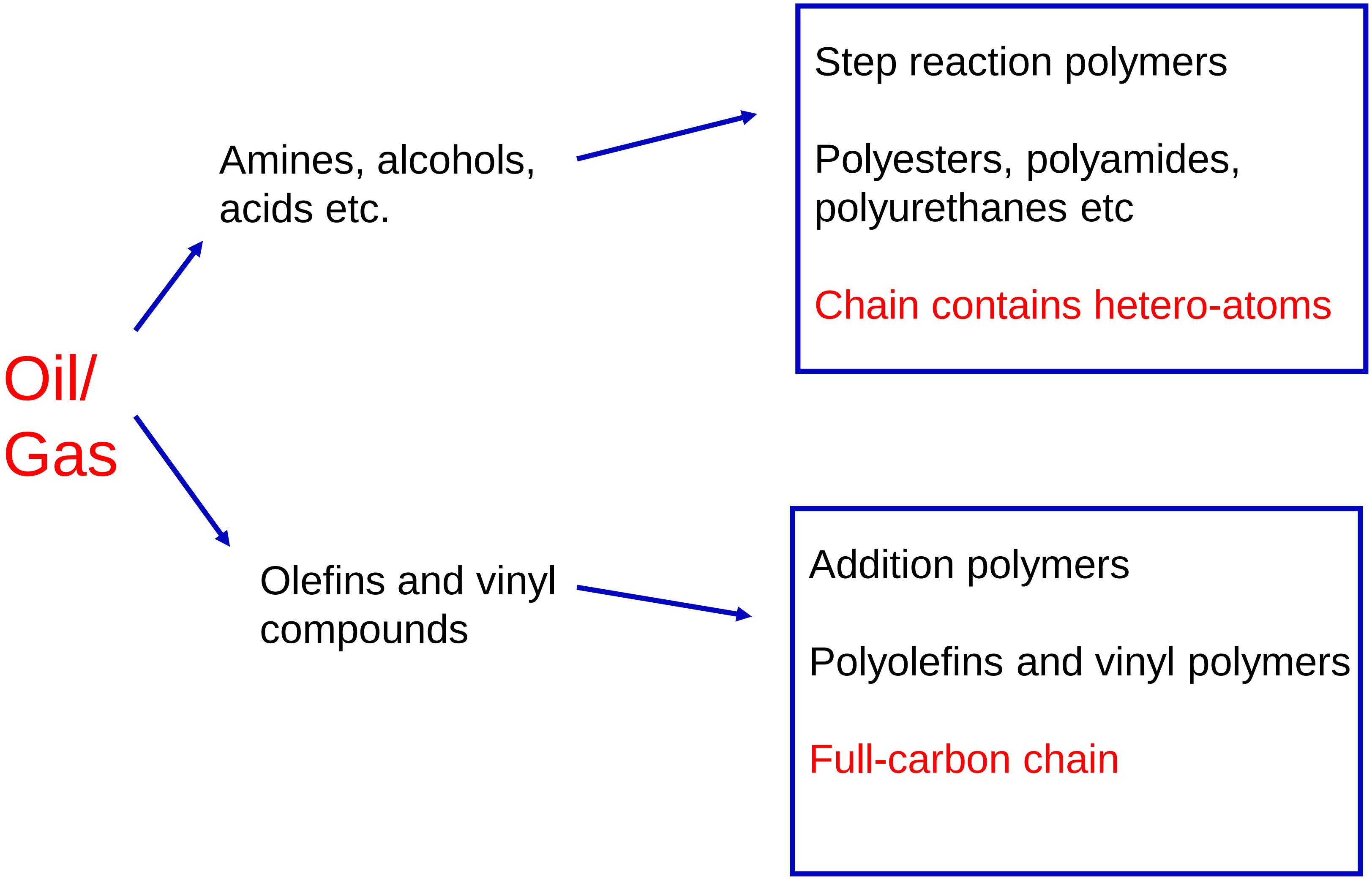
POLYMERS FROM NATURE

- Proteins
- Lipids
- **Natural rubber**

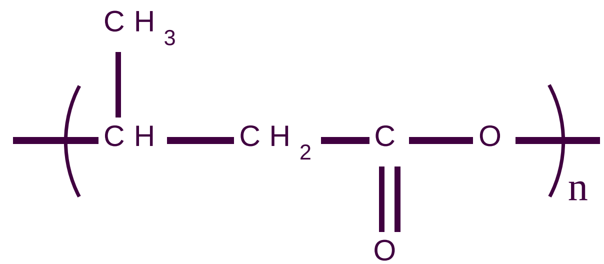
Usually chemically modified

- **Polysaccharides**
  - Starches – derived from corn/potato
  - Cellulose – derived from wood pulp
  - Chitosan/Chitin – derived from shellfish residues

PLASTICS FROM FOSSIL RESOURCES



Polymers from biosynthesis in organisms



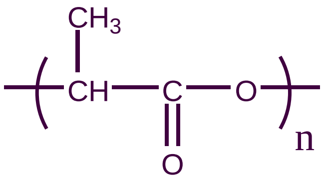
polyhydroxybutyrate

- Originally from bacteria
- More recently genetically-modified plants
- 40 year history of survival but has never thrived

Polymers from bio-derived monomers

Classical polymers from bio-derived monomers

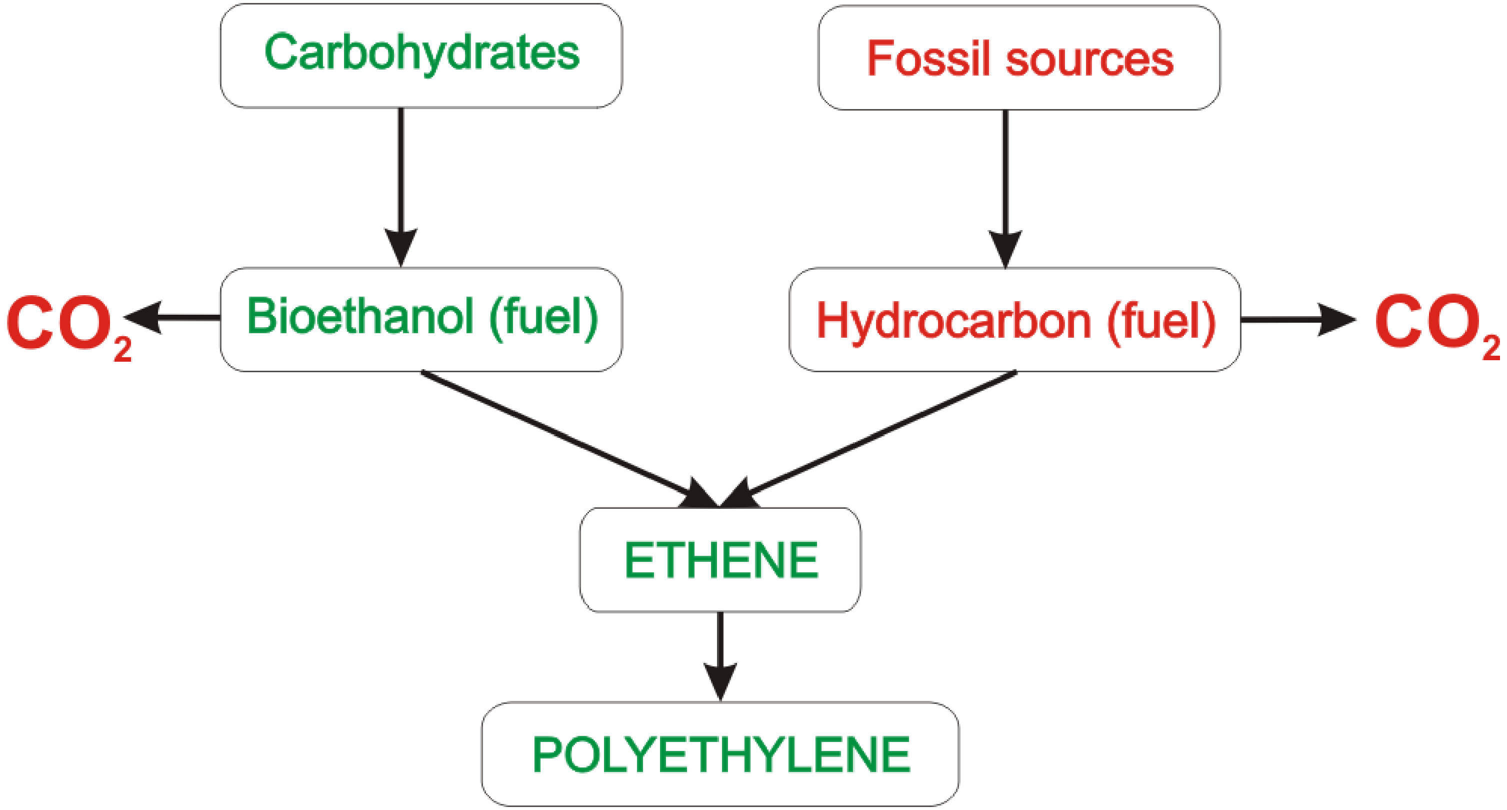
- **Polylactide** – monomer from corn fermentation



polylactide poly(lactic acid)

- Good film forming properties
- Very rapid recent growth
- Catalyst developments?
- Corn subsidies and competition from biofuels?

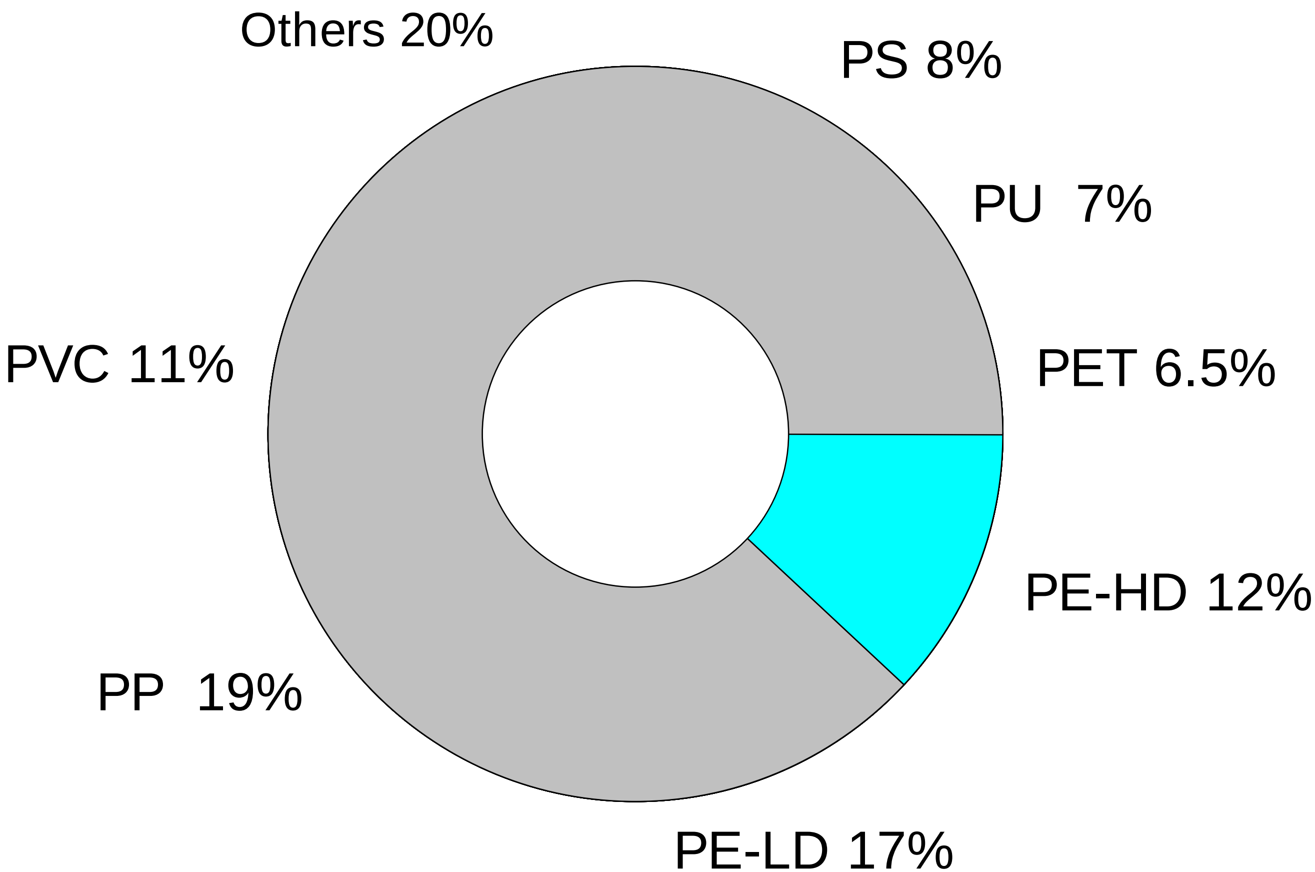
Polyethylene sources



Biomass polymers

- High energy inputs – plant growth and polymer recovery
- High pollution associated with recovery – e.g. delignification of wood pulp
- Price depends heavily in some cases (e.g. cornstarch) on farming subsidies
- Competition from bio-fuel use in future? (e.g. bio-ethanol from cornstarch?)
- Often poor properties – gas and moisture permeability

Plastics by type, EU 2011

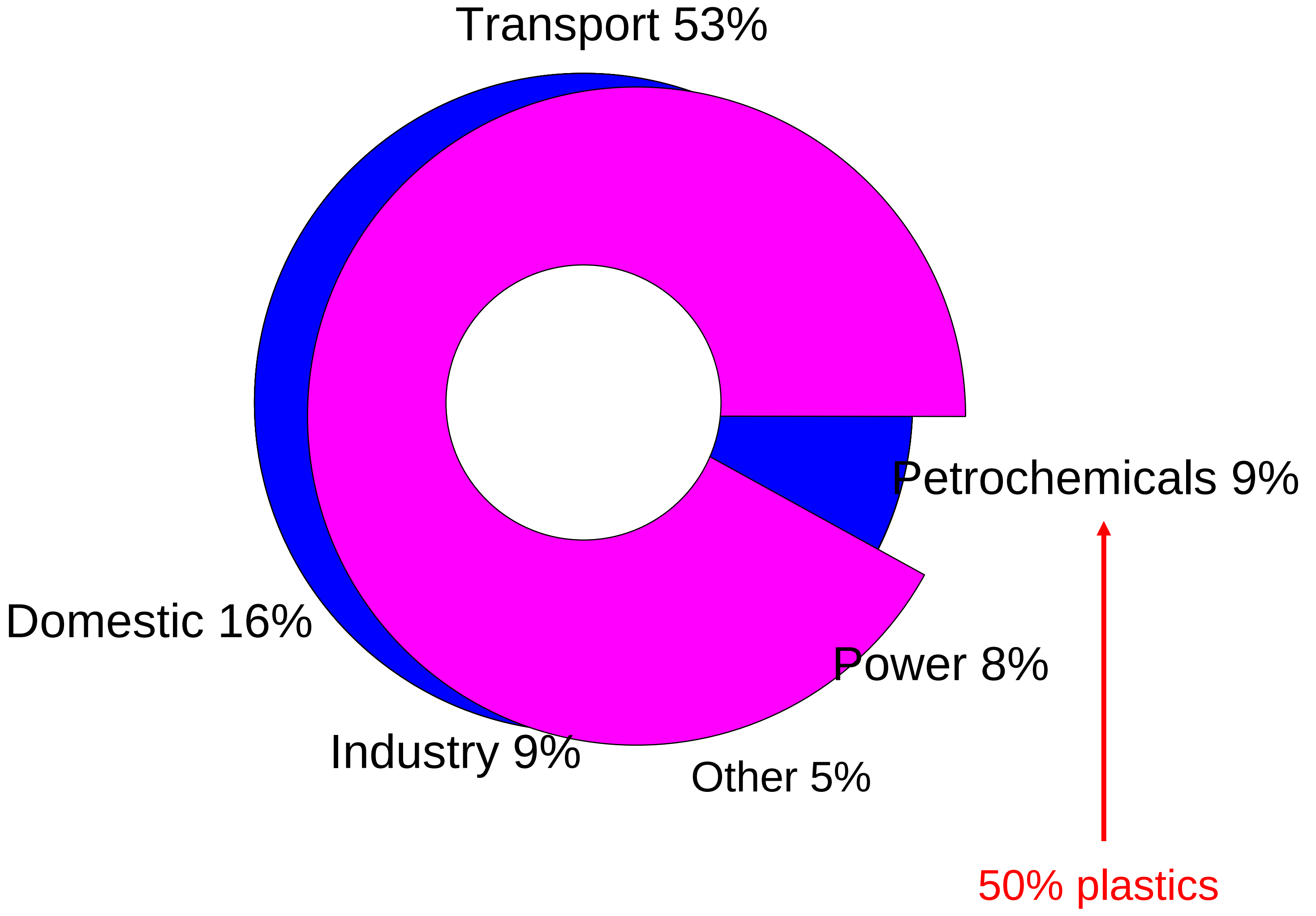


Total 47Mt

Total PE + PP
48% = 22.6 Mt

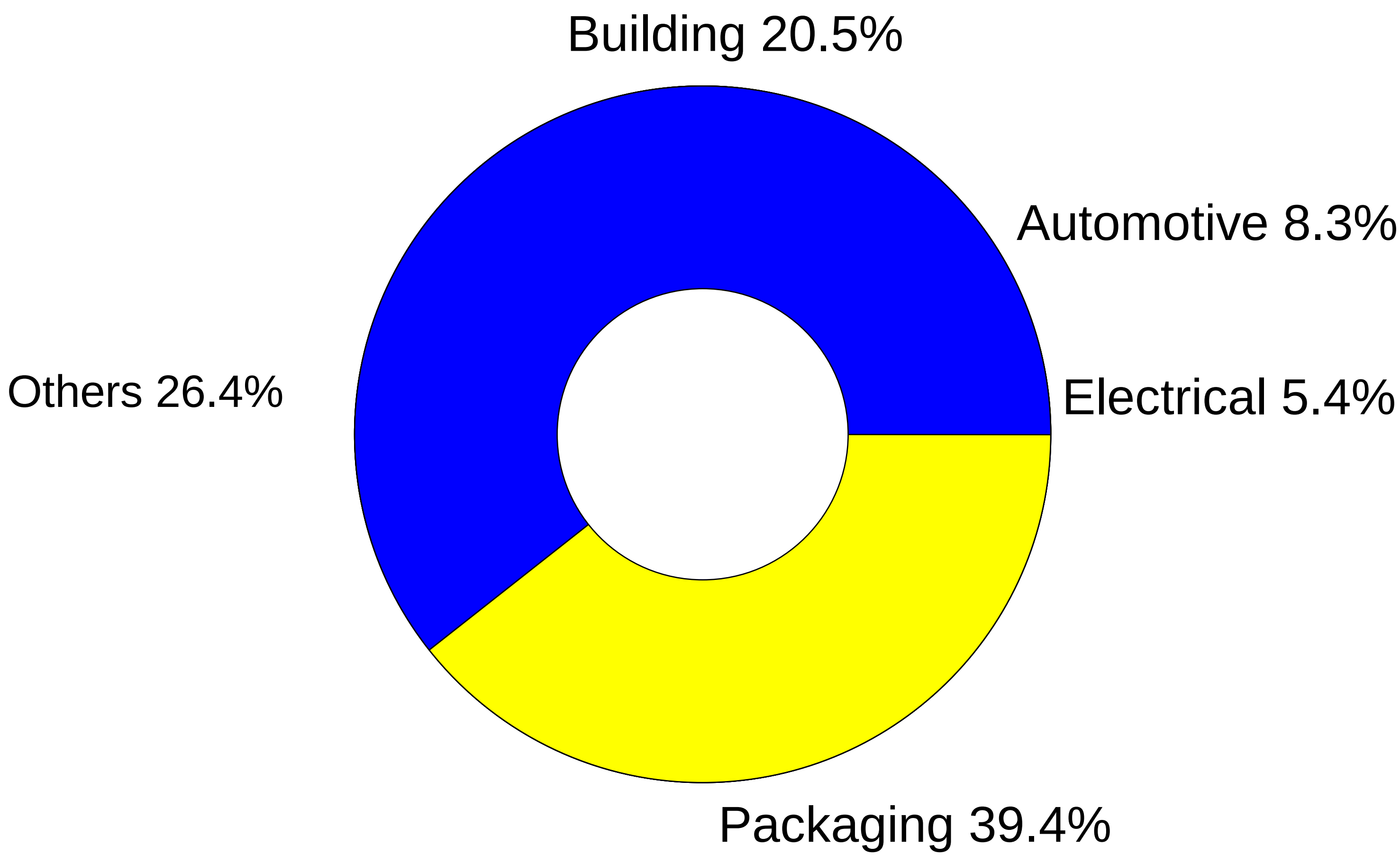
Source: Plastics Europe Market Research Group 2012

Oil use – Western World



Source: Shell Europe

Plastic by application, EU, 2011



Source: Plastics Europe Market Research Group 2012

Polymers can be very sensitive to degradation

Filled HDPE pot after 24 months indoor exposure (W-facing window)

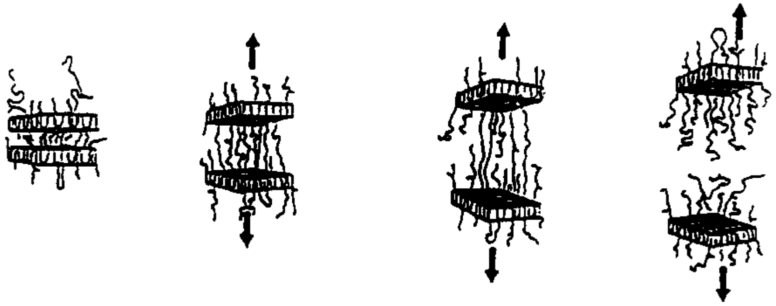
- Since the properties derive from the long molecular chains, anything which breaks those chains can have a very profound effect on properties

Degradative influences

- Heat
- Oxygen
- Light, especially solar radiation (>300 nm)
- High-energy radiation
- Mechanical stress
- Biological attack - hydrolysis
- Contacting liquids
    - » Removal of additives
    - » Stress cracking

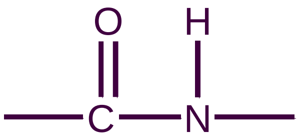
Sensitivity to degradation

- Increased density and crystallinity leads to surface cracking
- Cleavage of tie molecules stops load transfer via crystals
- Overall – loss of toughness

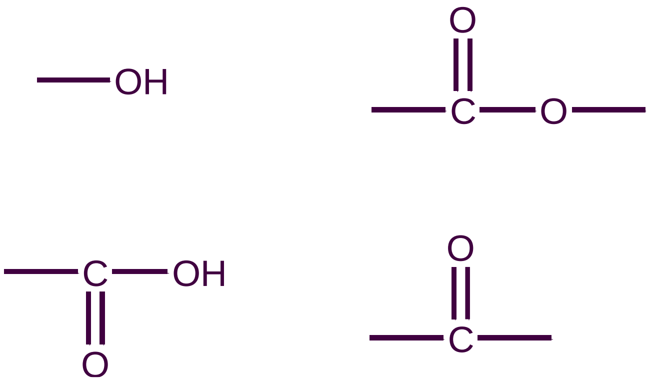


POLYMER BIOASSIMILATION

- Loss of mechanical properties needs very little scission
- Complete conversion to CO_2 and H_2O is much slower
- Needs hydrophilic surface – allows water to spread
- Needs functional groups susceptible to attack

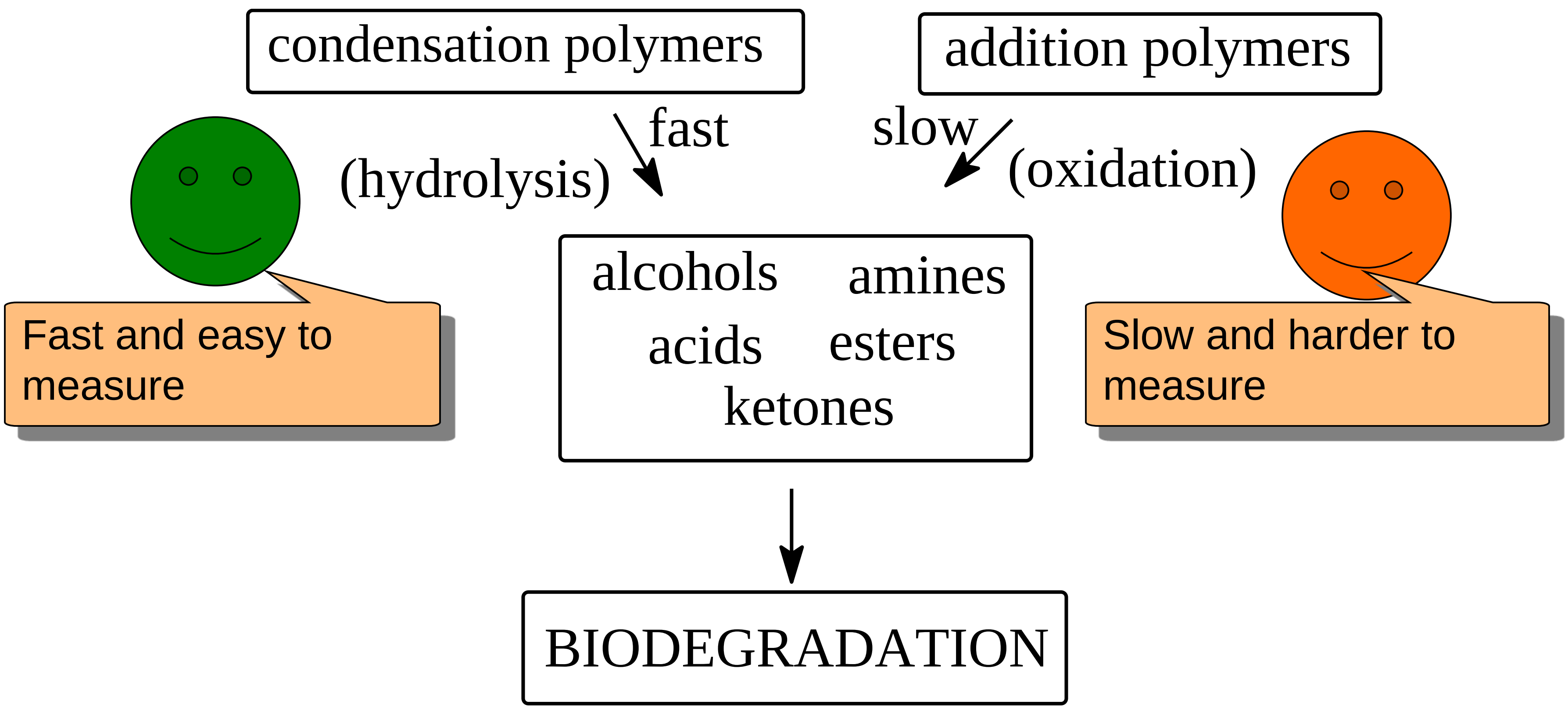


α-amino acid
(protein)



Oxygen-containing groups
Alcohol, acid, ester etc

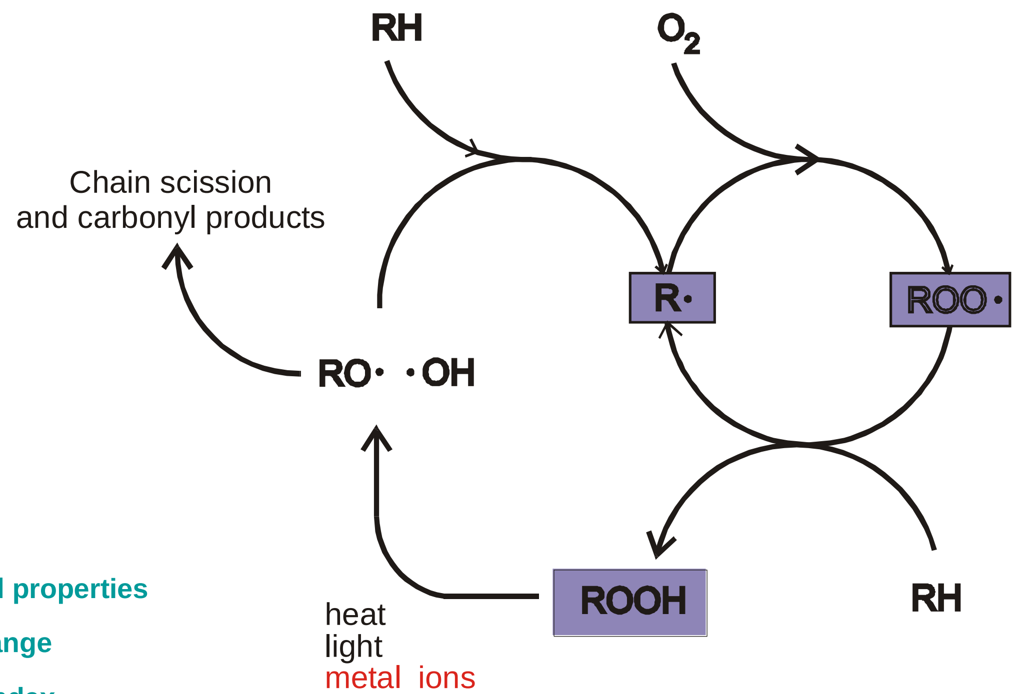
PLASTICS AT THE END OF THEIR LIFE



Hydro-biodegradation

- Hydrolysis of ester groups
- May be natural or enzyme mediated
- Rate controlled by polymer type
- Amide and urethane much slower
- Restricted by hydrophobicity and by $T < T_g$
- Degradation according to EN13432 – high mineralisation rates only in industrial composting ($T > 50\ ^oC$)
- Very few polymers will compost in home composting conditions
- Common polyesters (PET) and polyamides (Nylons) are highly resistant to biodegradation

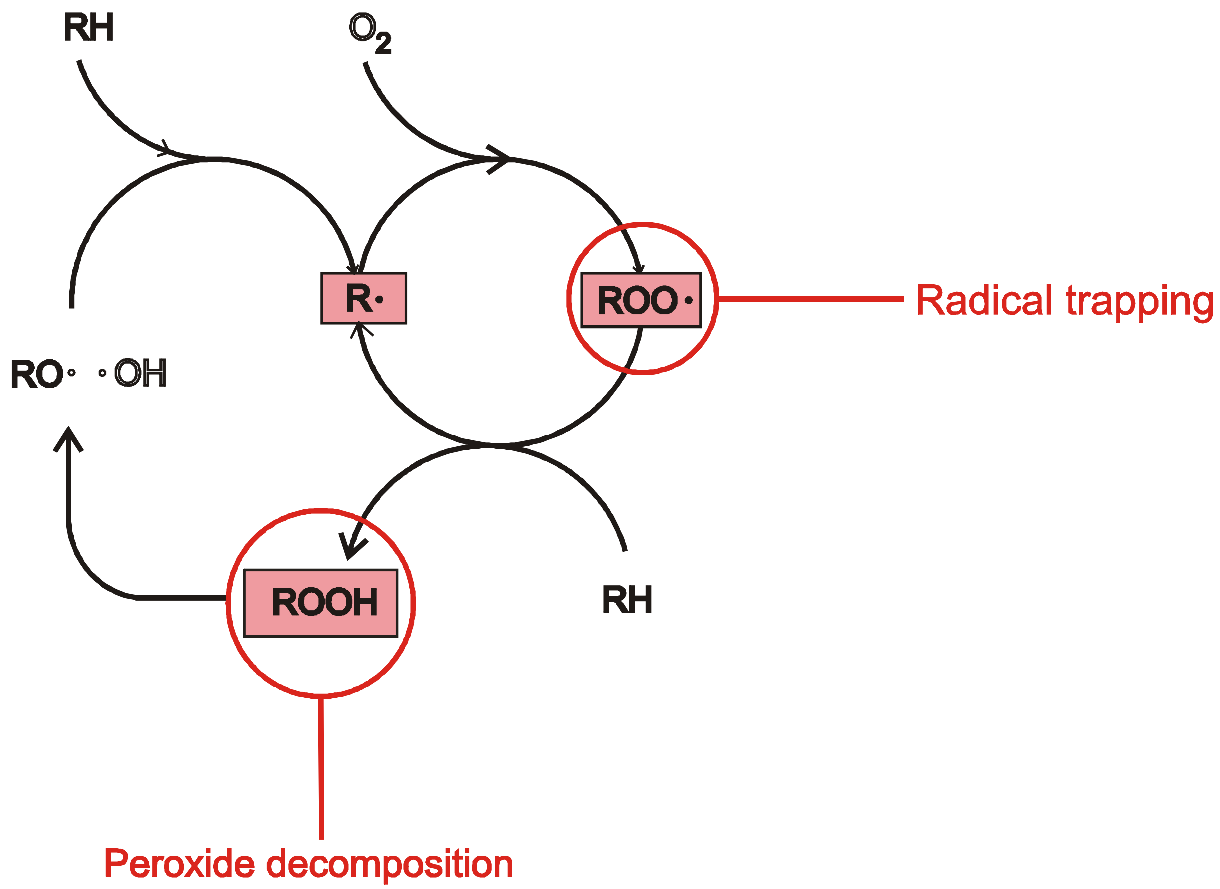
The oxidation cycle



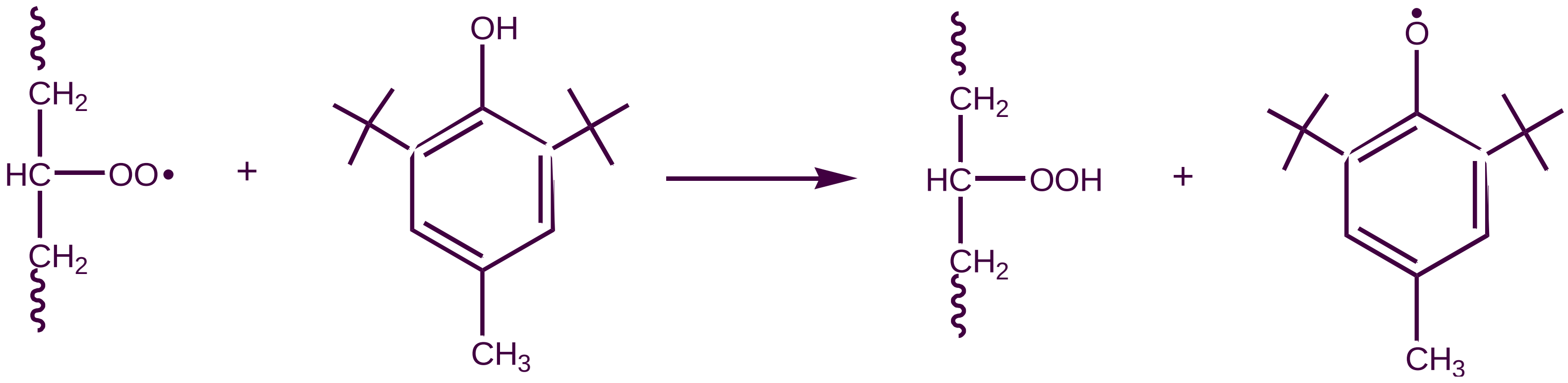
Monitored by

- Mechanical properties
- Weight change
- Carbonyl index
- Wettability
- Molecular weight

Opportunities for stabilisation

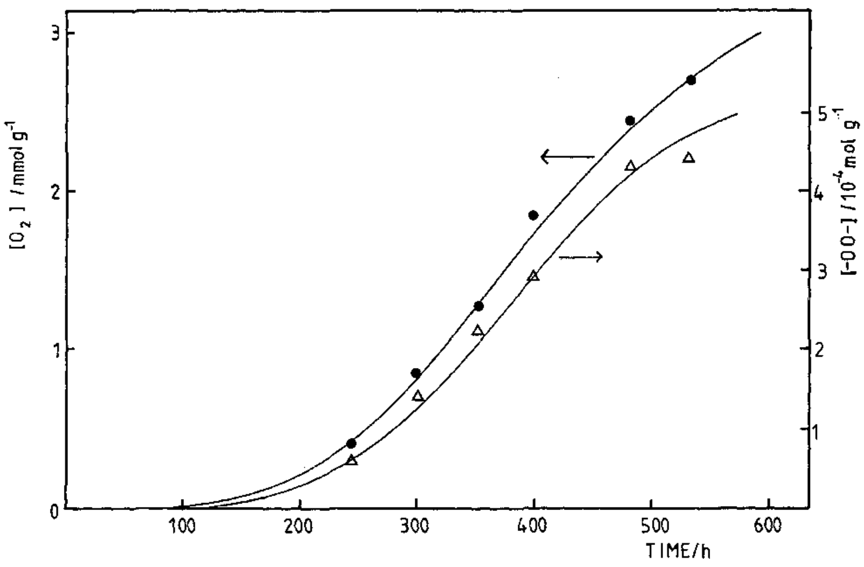


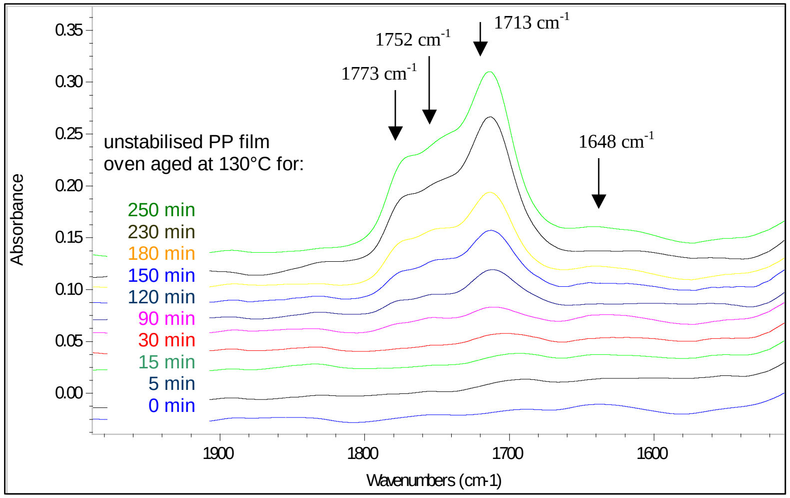
Simple phenolic antioxidant - BHT



- Able to trap peroxy radical
- Producing new radical too stable to reinitiate

Autoaccelerating oxidation in PP



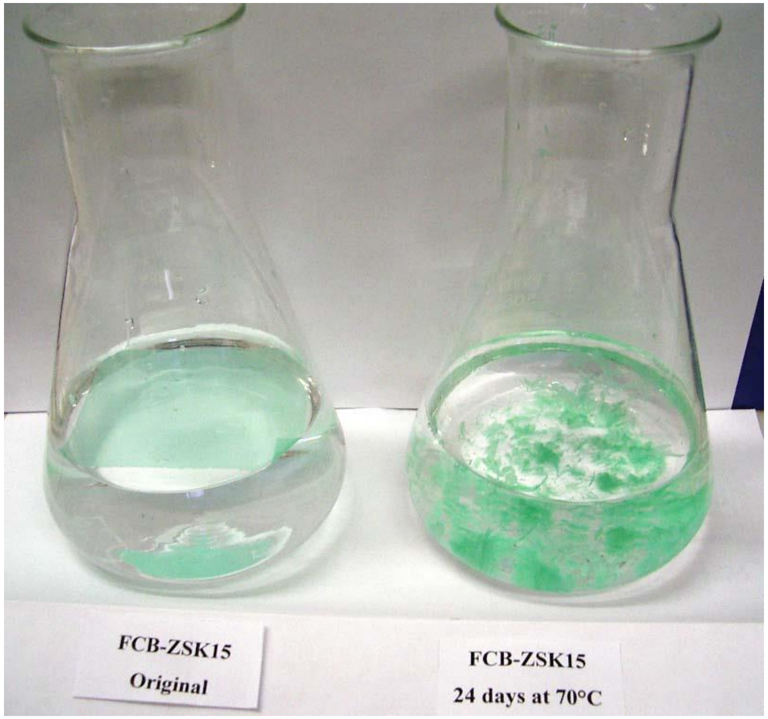


- Development of bands in region 1700 – 1750 cm^{-1} is characteristic of carbonyl-containing products of oxidation (ketones, acids and esters.

Fragmentation in landfill burial

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

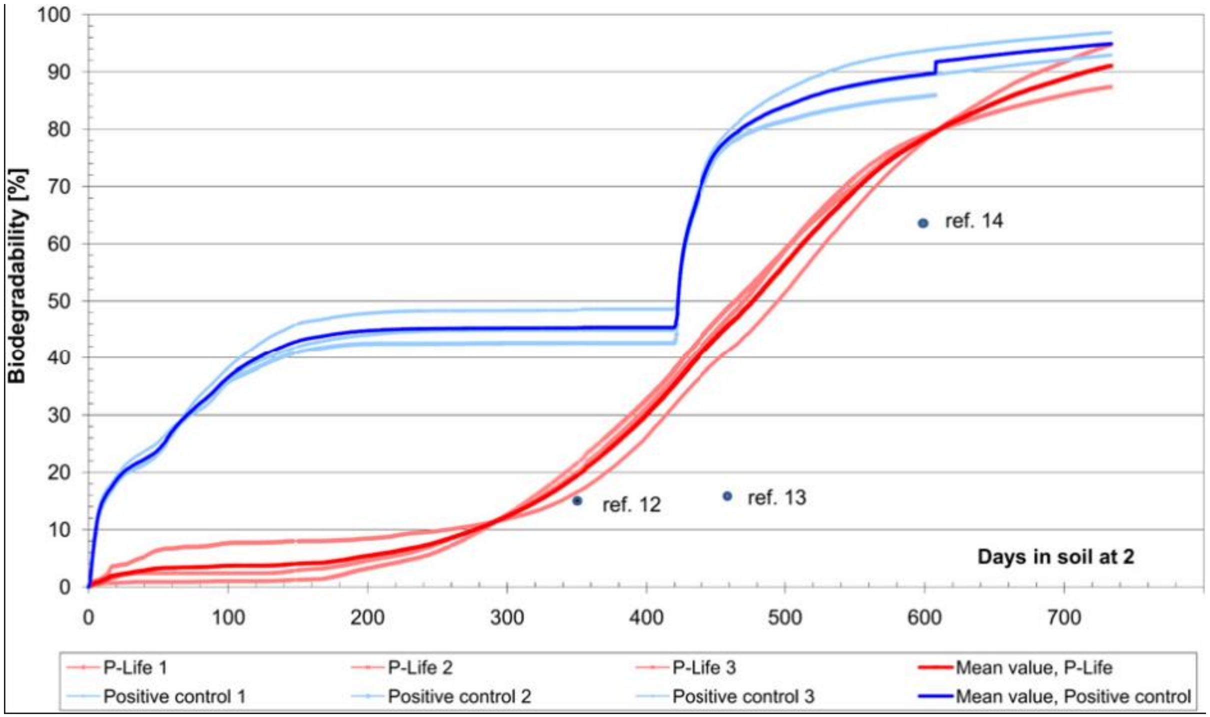
Oxidized PE sinks in water



A: FCB-ZSK15 untreated sample
B: FCBZSK15 sample after 24 days at 70°C (dry)

E Chiellini and A Corti, University of Pisa

Mineralisation of oxidised material in soil



T = 23°C

Jakubowicz et al. Polymer Deg. Stab. 96 (2011) 919

Acceleration by light

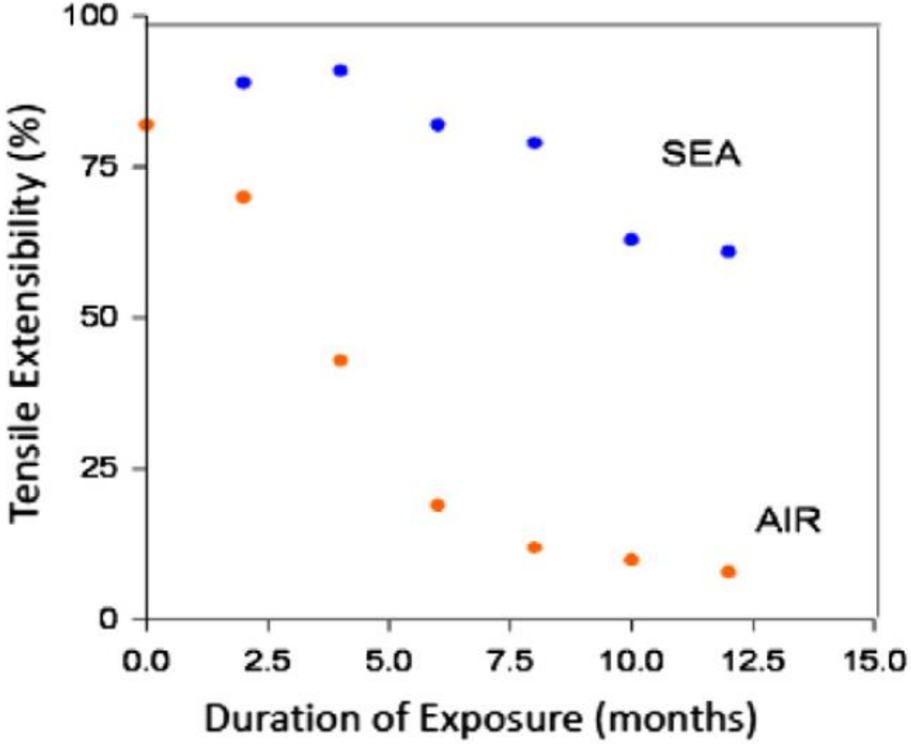
$$R = R_0 \, I^{\alpha} \, \exp\left(-\frac{E_a}{RT}\right)$$

where $0 < \alpha < 1$

Rate depends linearly on *I* but exponentially on *T.*

So the accelerating effect of IR components of radiation may be very important and *T* is much more important than *I*

Water effect on PE photo-oxidation



Natural sunlight exposure of PE film Florida

Andrady AL. Plastics and the Environment. Hoboken: Wiley Interscience, 2003. p. 392; Andrady AL. Microplastics in the marine environment, Mar Pollut Bull 2011;62(8):1596-1605.

Conclusions

- Polymers generally offer major environmental benefits as compared to any alternative
- Linear thermoplastic polymers are not indefinitely stable - learning to stabilise against degradation by using additives has been a major achievement
- The first stage of degradation of most polymers is loss of molecular weight and toughness - embrittlement

Conclusions II

- Degradation may occur by hydrolysis but most commonly is by oxidation

- Both oxidation and hydrolysis ultimately lead to bio-assimilation but oxidation is usually much slower, especially in stabilised polymers

- Low temperature is a major problem for both histolysis and oxidation in sea conditions

THANK YOU

for your attention