The scientific basis of standards

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Why do we need standards?

- **Protection of the environment**
- **To provide a ‘level playing field’ for business**
- **To clarify competing claims for the benefit of the consumer**

***The ‘Green Report’*, Attorneys General of the USA, 1990**

“Level Playing field”

- **Industry cannot be allowed to set its own test methods**
- **“Environmental claims must be uniform and supported by competent and reliable scientific evidence”**

***The “Green Report”*, Attorneys General of the USA, 1990**

“Environmentally friendly”?

“Product life-cycle assessment involves consideration of environmental effects at every stage in the product’s lifecycle, including the natural resources and energy consumed and the waste created in the manufacture, distribution and disposal of a product and its packaging……Such assessments will only provide useful comparative information about how to reduce environmental problems associated with products if they are conducted using uniform and consistent assumptions”

***The “Green Report”*, The Attorneys General of the USA (1990), p.21-22**

Biology or chemistry?
Natural or synthetic?

•Hydro-biodegradable polymers

Formation of bioassimilable sugars, carboxylic acids and alcohols from hetero-chain polymers by biotic or abiotic hydrolysis

Examples: cellulose, starch, PHA, PLA, PCL etc.

•Oxo-biodegradable polymers

Formation of bioassimilable aldehydes, carboxylic acids, alcohols from carbon-chain polymers by biotic or abiotic oxidation

Examples: lignin, tannin, humus, rubbers, polyolefins, etc.

G.Scott, *Polymers and the Environment*, Royal Society of Chemistry, 1999, Chapter 5

Natural carbon-chain polymers

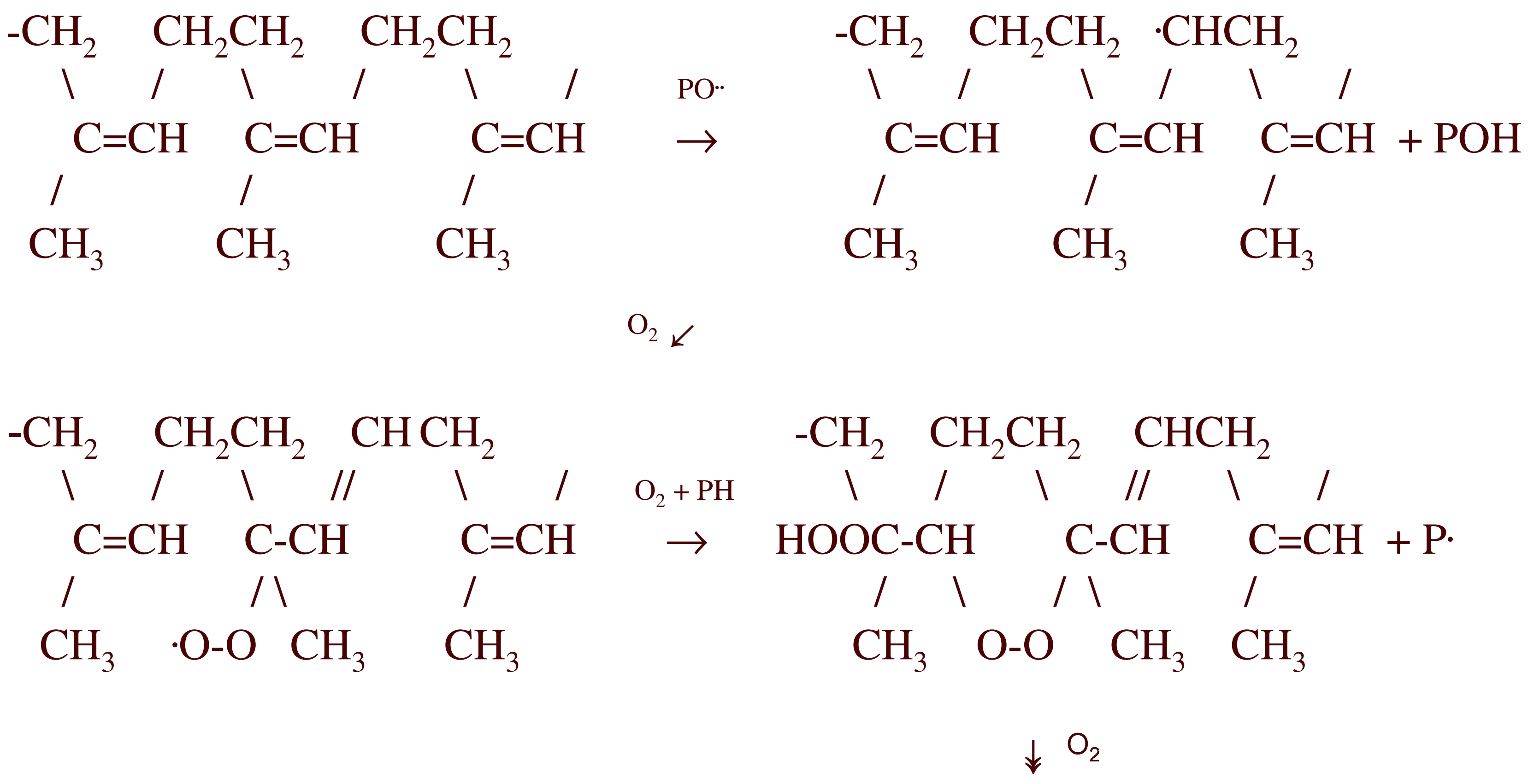
Natural rubber (*cis*-polyisoprene)

Resins (e.g. rosin, polycyclic condensation product of terpenes)

Lignin, humus, tannin (oxidation condensation products of polyphenols)

Natural carbon-chain polymers (unlike cellulose) do not hydro-biodegrade

Biodegradable oxidation products from *cis*-polyisoprene



Biodegradable oxidation products .

$CH_3COCH_2CH_2COOH$

$+\ CH_3COOH\ +\ HCOOH$

$(+\ CO\ +H\ O\ )$

Relative rates of biodegradation of carbon-chain polymers

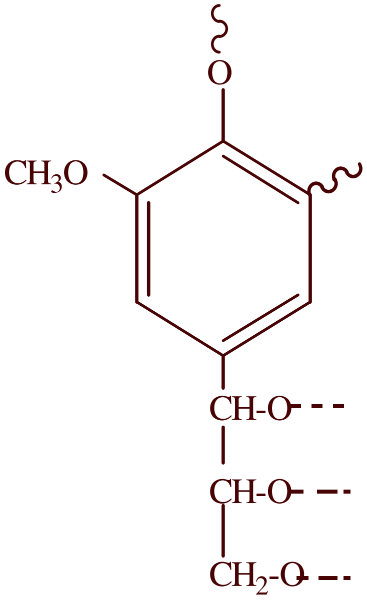
- **Steinbüchel et al. (2000) *Pseudomonas aeruginosa*/6 weeks, *cis*-PI (NR 26% mineralised; *cis*-PI (IR) 21% mineralised**
- **David et.al. (1995) Thermally peroxidised PE (Co catalysed at 40-70°C) 30% mineralised at plateau.**
- **Kawai et al. (1999) Environmentally exposed PE incubated with microbial consortia from field soils 30-50% mass loss**
- **Ikram et al (2000) in soil/48 weeks *cis*-PI (NR) 94% mass loss >> PVC (plasticiser only) > Nitrile-butadiene (NBR) 10% > Polychloroprene (PCR) negligible**
- **Singh et al. (in press). In compost/6 months PP 40% mass loss > EPR > LDPE 10% mass loss**

Effect of rubber extraction on its biodegradability

“Extraction of NR latex gloves by organic solvents resulted in an enhancement of growth for three of the selected strains….growth of Gordonia sp. (strain Kb2 and Kd2), *Mycobacterium fortuitum* NF4 and *Micromonospora aurantiaca* W2b on synthetic cis-1,4-polyisoprene did only occur after removal of the antioxidants, that are usually added during manufacture to prevent aging of the materials.”

M M. Berekaaa, A. Linosa, R. Reicheltb, U. Kellerb and A. Steinbüchel, (2000) *FEMS Microbiology Letters*, 184, 199-206

Lignin general structure

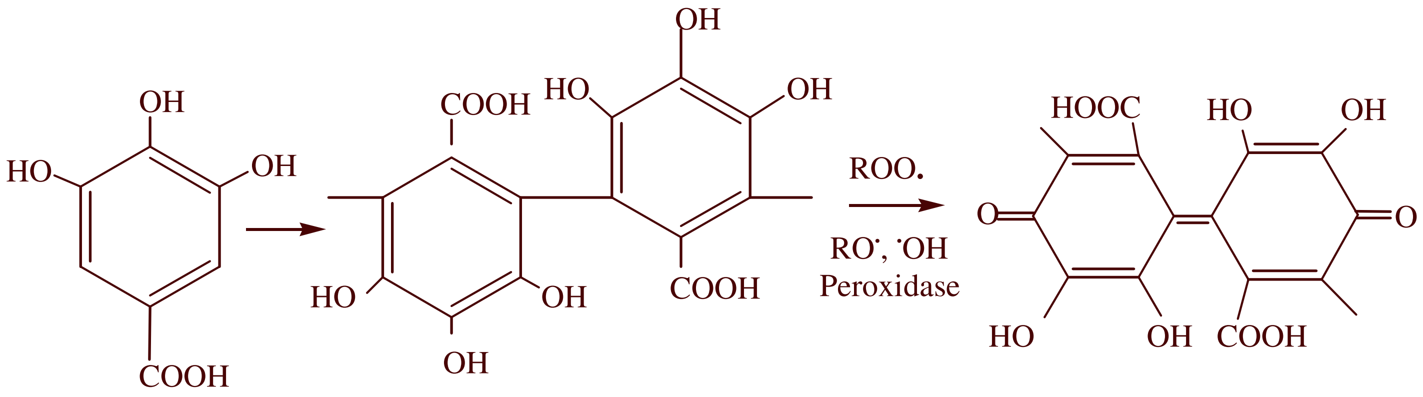


Lignin monomeric unit

〰 indicates potential sites through which dehydropolymerisation and cross-linking may occur.

- - - - - indicates sites through which attachment to cellulose may occur.

Bio-oxidation of polyhydroxy phenols to tannin and humus

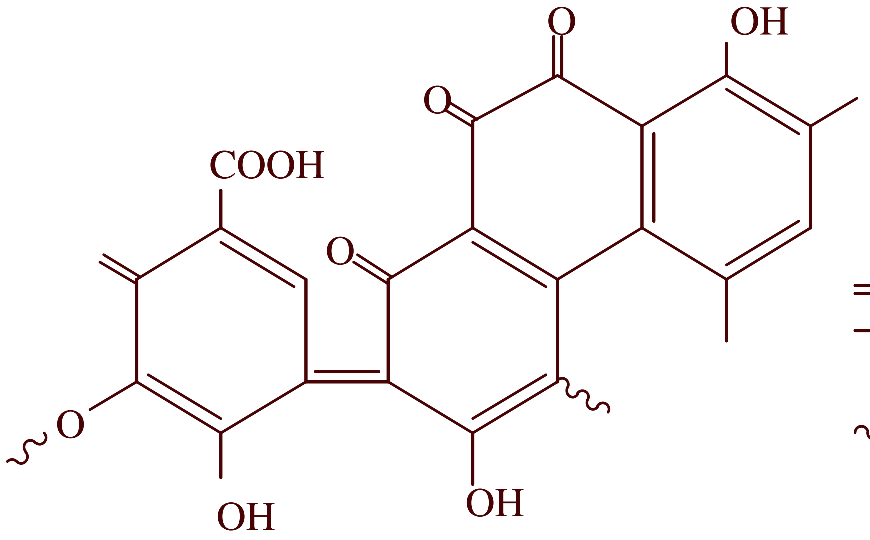


Gallic acid

Polyphenolic dehydrodimers
(Tannic acids)

Polyhydroxy polyquinones
(Humus precursors)

Humus



═ — Indicate the extension of the macromolecular structure

∿ Indicates the attachment of other groups through either C-C bonds ot C-O bonds

Lignolytic Microorganisms

Peroxidase enzymes oxidise lignin to improve the quality of Kraft papers. Many fungi produce these enzymes, which oxidise the deeply coloured quinonoid structures without affecting the cellulose content of paper pulp. They are the active constituents of ‘white-rot’ fungi.

Pleurotis pulmonarius excretes a peroxidase that effectively and selectively oxidises lignin in wheat straw, leaving cellulose unaffected .
I.D.Reid and M.G.Paice, *Appl. Environ. Microbiol.,* **64**, 2273 -2274 (1998) (and references therein).

***Panaeolus sphinctrinus, Panaeolus papilonaceous* and *Coprinus friesii*,** formed in Wood-rotting fungi are produce lignolytic extra-cellular peroxidases.
T.Anke et al. *Appl. Environ. Microbiol.,* **64**, 1601-1606 (1998)

Peroxidase mechanism
Dehydrodimerisation of phenols

Peroxidase + ROOH → Compound I + ROH (1)

Compound I + PhOH → Compound II + PhO· (2)

Compound II + PhOH → Peroxidase + PhO· (3)

$$2\mathrm{PhO}^{\cdot} \rightarrow \mathrm{HO\text{-}Ph\text{-}Ph\text{-}OH} \xrightarrow{\text{repeat}} \text{Polymeric phenols} \qquad (4)$$

D.Metodiewa and H.B.Dunford, *Atmospheric Oxidation and Antioxidants*, Ed. G.Scott, Elsevier, 1993, Chapter 11.

Transition metal catalysed peroxidation (accumulation of hydroperoxides)

$$\mathrm{POOH} + \mathrm{M}^{+} \rightarrow \mathrm{RO}^{\cdot} + \mathrm{OH}^{-} + \mathrm{M}^{2+} \qquad (1)$$

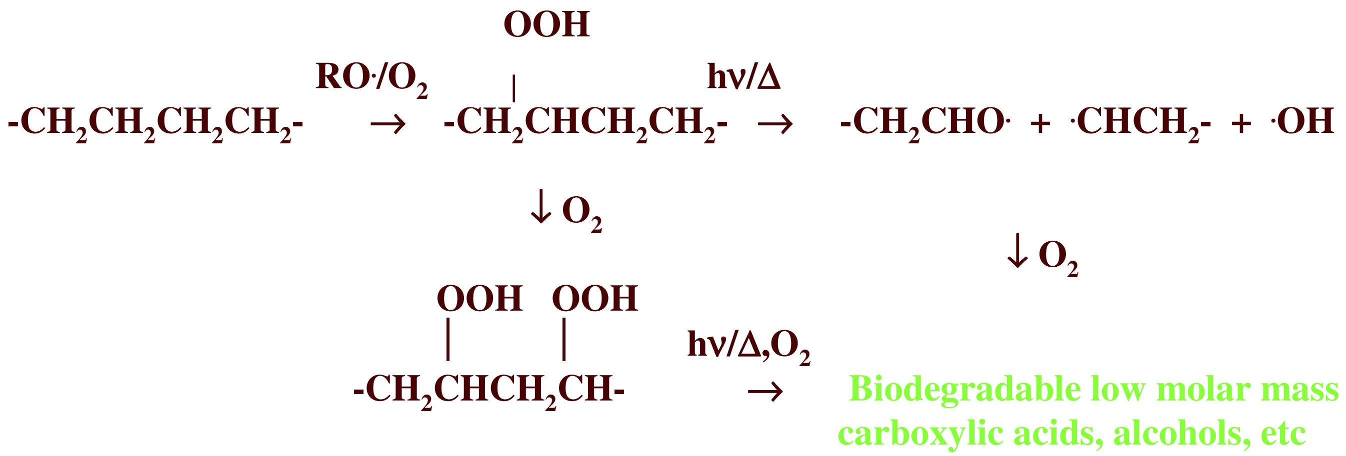
$$\mathrm{POOH} + \mathrm{M}^{2+} \rightarrow \mathrm{ROO}^{\cdot} + \mathrm{H}^{+} + \mathrm{M}^{+} \qquad (2)$$

$$\mathrm{PO}^{\cdot} + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R}^{\cdot} \xrightarrow{\mathrm{O_2+RH}} \mathrm{ROOH} + \mathrm{R}^{\cdot} \rightarrow 2\mathrm{ROOH} \qquad (3)$$

$$\mathrm{POO}^{\cdot} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}^{\cdot} \xrightarrow{\mathrm{O_2+\ RH}} \mathrm{R}^{\cdot} + 2\mathrm{ROOH} \qquad (4)$$

PH = Hydrocarbon polymer,
POOH = Polymer hydroperoxide

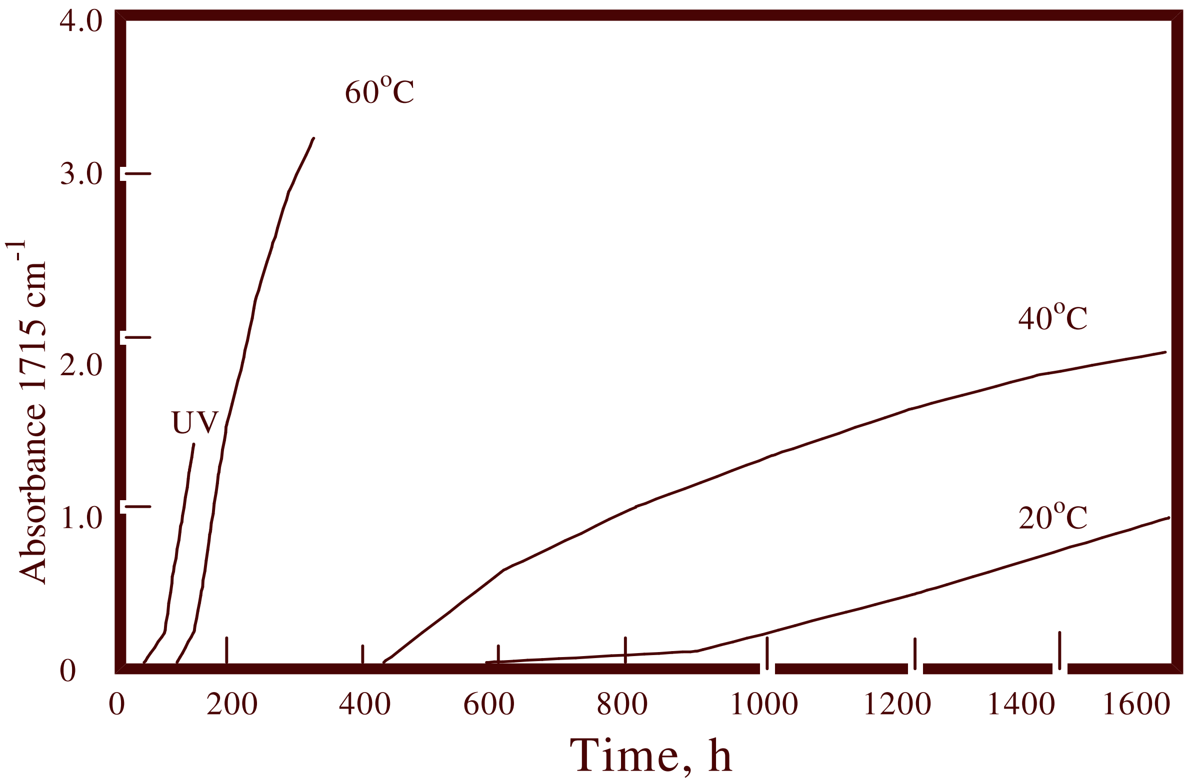
Biodegradable products from polyethylene



$$\begin{tikzcd}
\mathrm{-CH_2CH_2CH_2CH_2-} \arrow[r, "\mathrm{RO\cdot/O_2}"] & \mathrm{-CH_2\overset{\overset{OOH}{|}}{C}HCH_2CH_2-} \arrow[r, "h\nu/\Delta"] \arrow[d, "\mathrm{O_2}"] & \mathrm{-CH_2CHO\cdot + \cdot CHCH_2- + \cdot OH} \arrow[d, "\mathrm{O_2}"] \\
 & \mathrm{-CH_2\overset{\overset{OOH}{|}}{C}HCH_2\overset{\overset{OOH}{|}}{C}H-} \arrow[r, "h\nu/\Delta\mathrm{,O_2}"] & \text{Biodegradable low molar mass carboxylic acids, alcohols, etc}
\end{tikzcd}$$

G.Scott in *Macromolecular Symposia; Degradability,Renewability and Recycling*, eds. A-C.Albertsson, E.Chiellini, J.Feijen, G.Scott and M.Vert, Wiley-VCH, 1999, p.117

Abiotic peroxidation of degradable polyethylene EPI TDPA™



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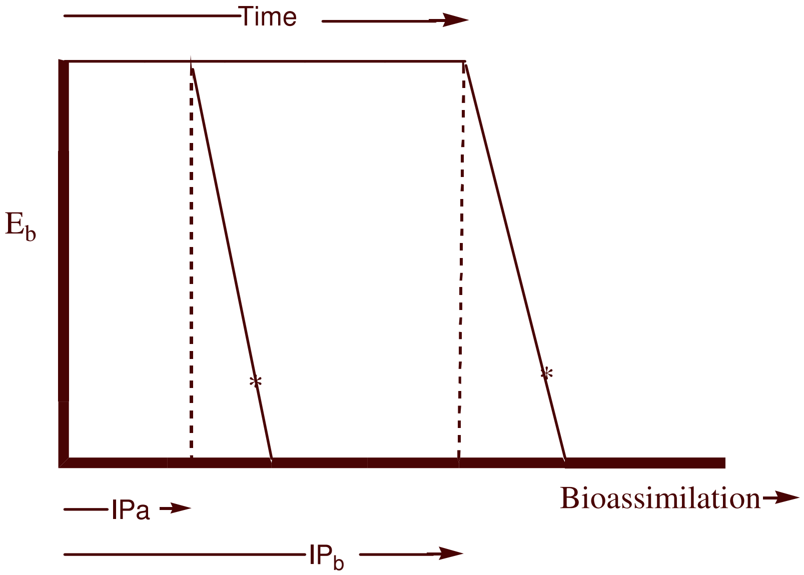
Properties of the ideal biodegradable plastic



$IP_{a,,b}$	Induction periods during which no change in mechanical or chemical properties occur
E_b	Elongation at break
*	Fragmentation (embrittlement)

G. Scott, *Polymers and the Environment*, Royal Society of of Chemistry, 1999, Chapter 5

Antioxidants

Chain-breaking (CB-D)

$$\mathrm{POO\cdot} + \mathrm{AH} \rightarrow \mathrm{POOH} + \mathrm{A\cdot}$$

Typical CB-Ds are hindered phenols and aromatic amines

Peroxide decomposing (PD)

$$\mathrm{POOH} \xrightarrow{\textbf{Catalyst}} \text{Non-radical products}$$

Typical catalytic PDs are aliphatic sulphides, RS_nR' and metal dithiocarbamates, $(R_2NCS_2)_n$ M

G.Scott, *Antioxidants*, Albion, 1997, Chapters 3 and 4

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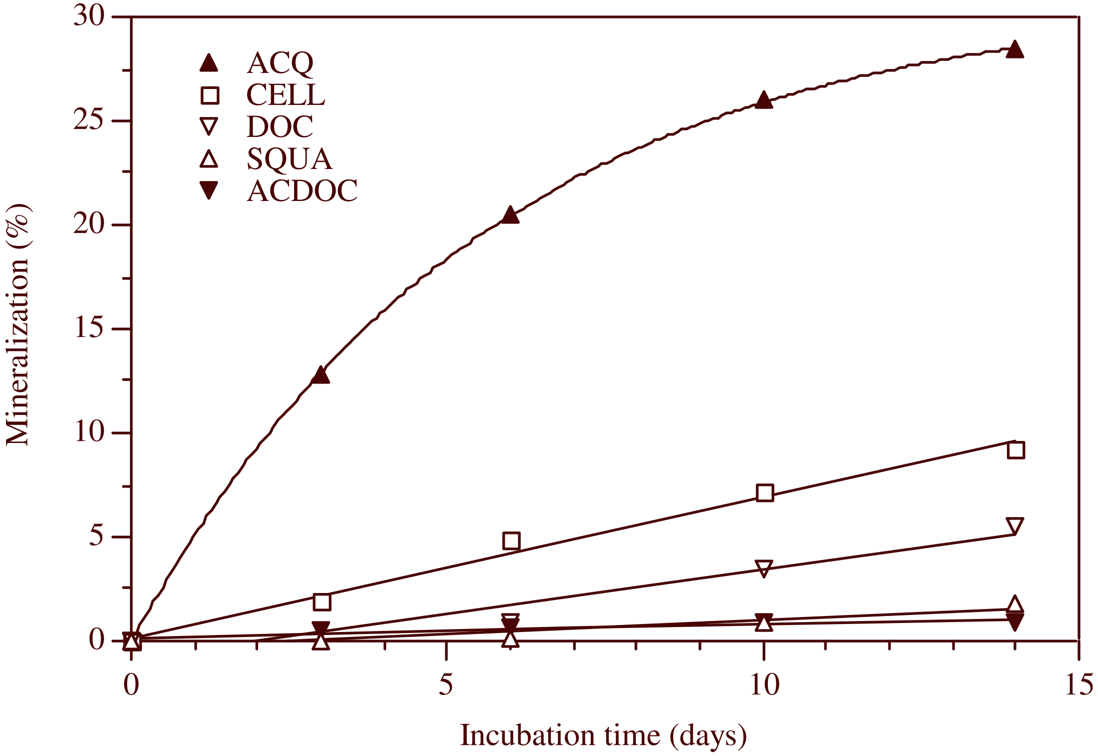
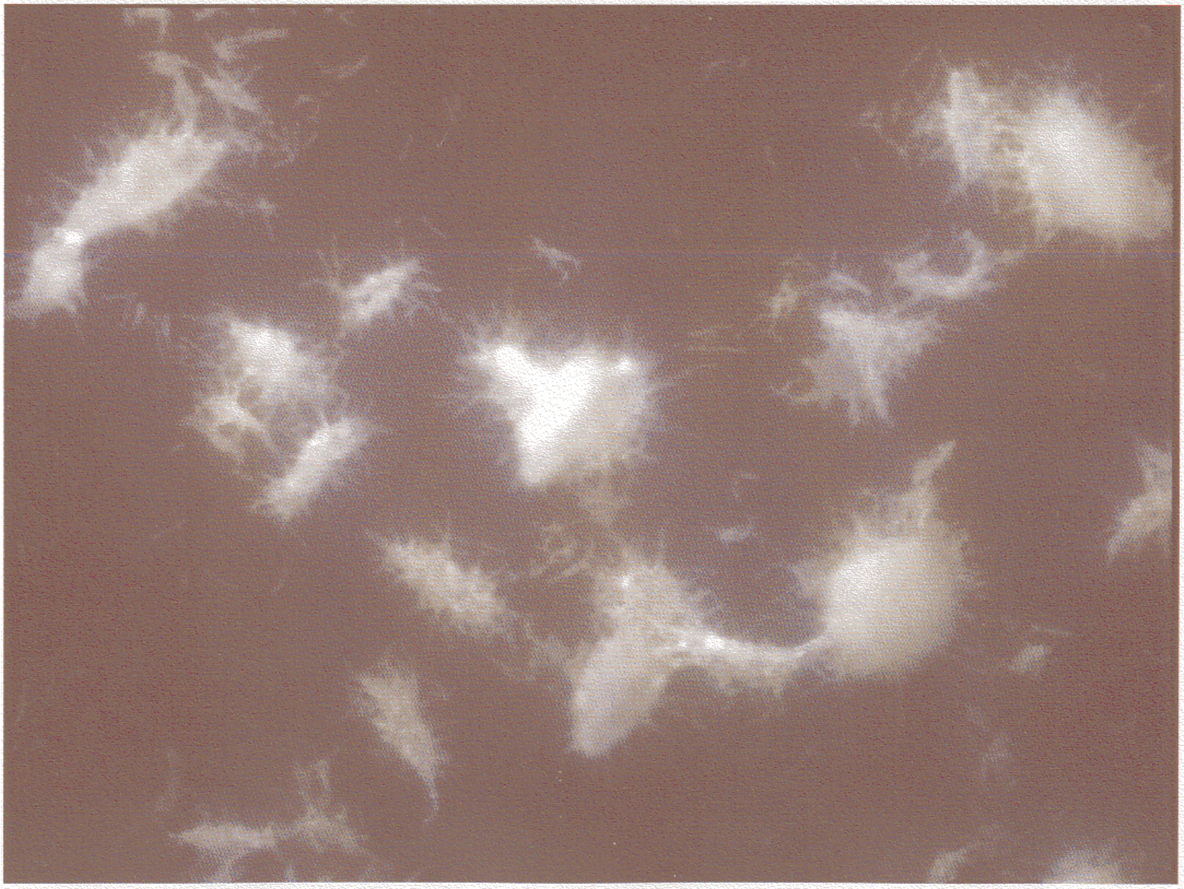
Mineralization of oxidation products of polyethylene incubated in forest soil



ACQ = acetone extracted TDPA film after oxidation and evaporation of acetone, CELL = cellulose, DOC = docosane ($C_{22}H_{46}$), SQUA = 2,6,10,15,19,23-hexamethyl tetracosane, ADOC = docosanoic acid ($C_{22}H_{44}O_2$)

Unpublished work by E.Chiellini et al. with permission

PLASTOR, hν, 0_2, 60°C
Epifluorescence Microscopy
Nocardia asteroides



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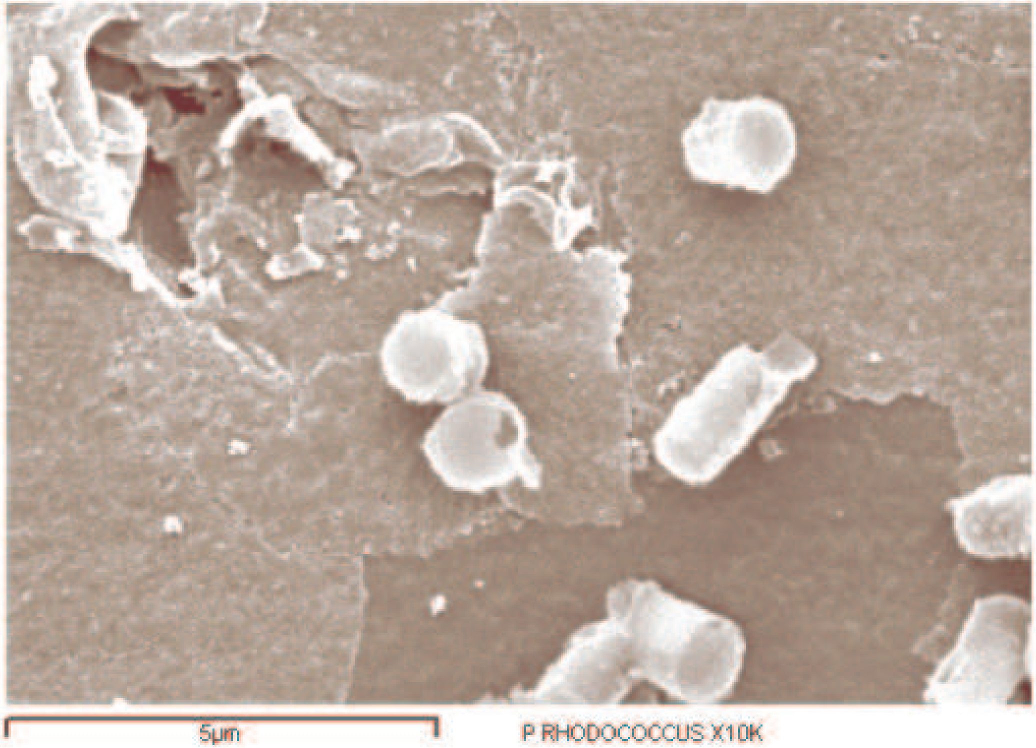
14th of june 2001

Sample: P RHODOCOCCUS

ID: P RHODOCOCCUS 1 MOIS +µ



Oxo-biodegradable polyethylene bioassimilation time-scale

Photooxidation (SEPAP, 60^{o}C)	**100 h**
or	
Thermooxidation (60^{o}C)	**300 h**
Biofilm formation	**0.25 h**
Surface disintegration (*R.rhodocrous)*	**1 month**
Mass loss (6 months)	**15-20%**

Note: in compost and in soil, thermooxidation and biooxidation occur synergistically

Weight loss of polyolefins* in compost

Polyolefin	Treatment		Weight loss
	abiotic	compost	%
Polyethylene (PE)	none	6 months	10
	UV (100h)	6 months	20
Polypropylene (PP)	none	5 months	40
	UV (100h)	5 months	85

* All films were made from solvent-extracted polymers.

J.K.Pandey and R.P.Singh, *Biomacromolecules*, 2, 880-885 (2001)

Criteria for biodegradation of packaging materials in compost (EN 13432)

1. **Characterisation: identification of packaging constituents, dry solid content, ignition residues, hazardous metal residues.**

2. **Biodegradability: 90% of the total theoretical CO_2 evolution in compost or simulated compost in 6 months.**

3. **Disintegration: Not more than 10% shall fail to pass through a >2mm fraction sieve.**

4. **Compost quality: No negative effects on density, total dry solids, volatile solids, salt content, pH, total nitrogen, ammonium nitrogen, phosphorus, magnesium and potassium. Eco-toxicity effects on 2 crop plants.**

5. **Recognisability: “must be recognisable as compostable or biodegradable by the end user by appropriate means”**

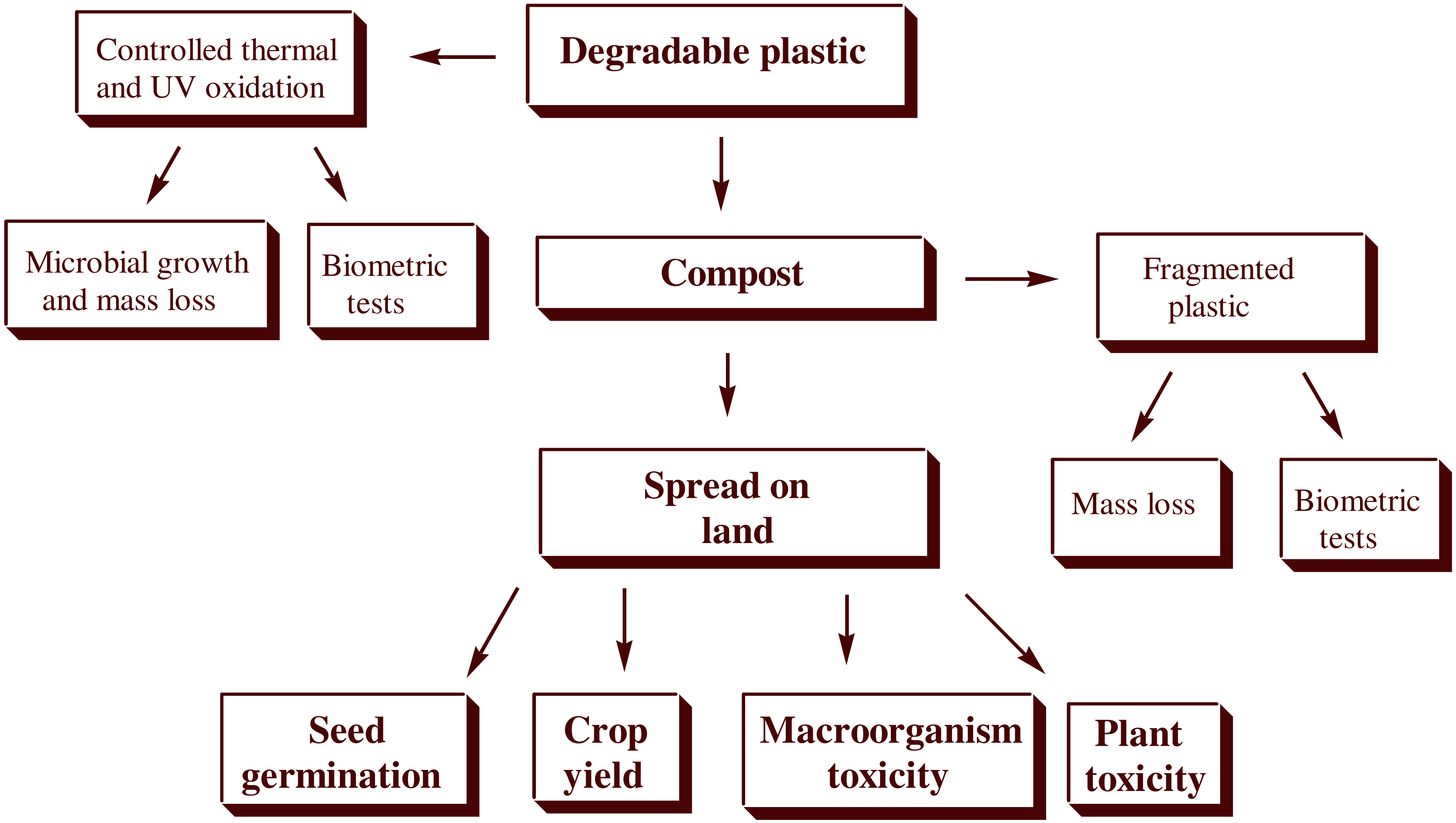
Composting of carbon-chain polymers

- **Full scale composting trials**
  - Particle size reduction (<10 mm)
  - Visual impact

- **Ecotoxicity tests on soil**
  - Plant germination and growth rate
  - Accumulation of metals in stems, leaves and fruit
  - Effect on soil macroorganisms

- **Background scientific studies**
  - Rate of abiotic peroxidation
  - Rate of biomass formation and polymer weight loss
  - Biometric measurements on peroxidised polymer
  - Correlation of bioerosion with extent of peroxidation

Oxo-biodegradation - Draft Protocol



Degradable plastic

Controlled thermal and UV oxidation

Microbial growth and mass loss

Biometric tests

Compost

Fragmented plastic

Mass loss

Biometric tests

Spread on land

Seed germination

Crop yield

Macroorganism toxicity

Plant toxicity

Nature’s way

- Abiotic and biotic chemistry are used synergistically in the bioassimilation of both natural and synthetic waste products
- Carbon is preferentially biocycled in the soil as a plant nutrient rather than in the atmosphere as CO_2
- Biometric tests have little relevance to the biocycling of nature’s lignocellulosic wastes
- The model for the biodegradation of carbon-chain polymers wastes should be lignocellulose rather than pure cellulose
- Standards for the biocycling of synthetic materials should be designed to harmonise with natural processes