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# **Classification and Comparison of Thermal and Mechanical Properties of Commercialised Biodegradable Polymers.**

**Matter Selection way for industrial applications**

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# Biodegradable Production Capacity

Company	Products	Production Capacity (t/y)	Scaling up Forecast (t/y)
Dow Cargill	Ecopla	8000	140 000
PVAXX	PVAXX	15000	100 000
Rodenburg	Solanyl	7000	15 000
Novamont	Master-Bi	8 000	
Bayer	BAK	4 000	
BASF	Ecoflex	8 000	
Eastman	EASTAR BIO	15 000	

Regarding Plastics produced for packaging :



Matter	T/Y
LDPE/HDPE (Films)	4 600 000
PP (Films)	840 000
HDPE (Bottles & containers)	1 200 000
PVC (Bottles)	480 000
PS (Sheets for thermoforming)	720 000
PET (Bottles)	600 000
OthersAutres	3 600 000



## Market Distribution

In 1999 :

Starch Based Plastics :	75 - 80 %
PLA	10 - 15 %
Synthetic	10 %

### World Distribution in 1998

	<u>Capacity</u>	<u>Production</u>	<u>Consumption</u>
<u>USA</u>	11 kT	10 kT	8 kT
<u>W Europe</u>	29 kT	8 kT	7 kT
<u>Japan</u>	6 kT	1.5 kT	2 kT



# Materials

- Starch

- Cereal or Potato Flour

- Starch + Petrochemical additives

- Polymers Produced in micro-organism

  - PHB (Polyhydroxybutarates)

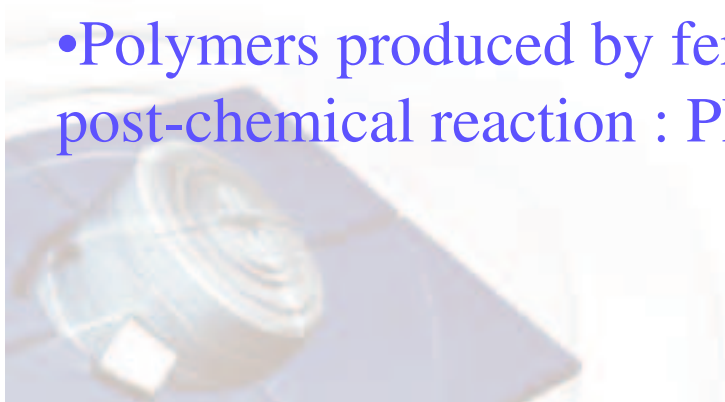
  - PHB-PHV (Polyhydroxybutyrate and polyhydroxyvalerates)

  - PHA (polyhydroxyalcanoate)

  - Blends

- Polymers produced by fermentation of sugar and post-chemical reaction : PLA

• First generation  $\supset$  10-80% of non  
By-products of wheat, rice or corn flour  
biodegradable polyesters  $\rightarrow$  Faise  
Cheaper but sensitive to humidity  
High T<sub>g</sub> T<sub>m</sub>  
Small injected parts, dishes, packaging chips  
Bio-compatible  $\rightarrow$  Medical applications  
Ex. of additives : caprolactone  
resistance





# Materials (continued)

## Polymers produced inside plants

## Polymers derived from polypeptides

## Natural polymers and by-products

- Cellulose by-products
- Chitin derivative
- Wood and lignin by-products
- Biodegradable reinforcements

## Chemically Synthetised Polymers

## Polyolefins (Catalyst)



Cellulose diacetate is produced inside plants  
 PHB is produced inside genetic modified plants  
 PP Plant PCLs  
 CO<sub>2</sub> barrier, sensitive to humidity  
 Chitin derivative: Edible, Films ⇒  
 Ex: Watercress, rape, maize  
 Food-packaging application  
 Aspartic ac. and Lysine plastics :  
 high yield, R&D Trends  
 Wood and lignin by-product : ±  
 composite material containing  
 plasticizer  
 Soya Proteins plastics : Films and  
 1) Obtained by co-polymerisation  
 composite material → medical  
 Region of films within fragile plastic,  
 important Biodegradable family :  
 sensible groups Biodegradable  
 Mainly based on polyester  
 thermoplastics or Thermosets.  
 2) Introduction of a photosensible  
 catalyst application for Car  
 DuPont, BASF, Eastman Chemical  
 Industries.  
 3) introduction of a thermosensible  
 catalyst, in the compound, in order  
 to increase the degradability during  
 composting process.



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# Nowadays Applications

## Horticultural :

Mulching Films

Greenhouse Films

Plant pots

Soluble bags for plant-care products

**Medical**  $\Leftrightarrow$  Resorption, Compatibility

Capsules

Resorbable Implants

Suture threads, clips

Orthopaedic fixations : screw, pin, ...

Anastomosis ring

Ligature Clips, ...



## Objects often left on the ground

Firearms ammunition wads or shells

Disposable dishes, Golf Tees

Cemetery decoration

## Packaging :

Packaging bags and films

Bags for selective organic dustbin

Food-sector :

container (for micro-wave)

Hollow parts : pots, bottle, ...



## Comestible :

Toys for pets

« Plasticine® » thermosettable

Casing

## Eco marketing / Aesthetic :

Hydro-soluble bags for baits

Bank card

Watch case

Ballpoint pen, toys, gadgets

## Others :

Funeral cover

...

# Processing Machine



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## Blown Films

PHB/V (Biopol)  
Starch (BIOPLAST)  
Co polyester (Ecoflex)  
Co polyester (Eastar BIO)  
Corn Starch- polyacétal (Mater-Bi)  
Polycaprolactone (CAPA)

## Thermoforming

PLA  
PHB/V (Biopol)  
PET mod. (Biomax)  
PVA (Orex)  
Corn Starch- polyacetal (Mater-Bi)  
Polycaprolactone (CAPA)

## Extruded Films

PLA  
PHB/V (Biopol)  
Starch (BIOPLAST)  
Starch (BIOFlex)  
Co polyester (Ecoflex)  
PET mod. (Biomax)  
PVA/PVOH (EPG Polymers)  
Co polyester (Eastar BIO)  
PVA (Orex)  
PVA/PVOH (Hydrolene)  
Corn Starch- polyacetal (Mater-Bi)  
Cellulose di-acetate (Bioceta)  
Polymers, additives, Starch, catalyst (Ecostar)  
Polycaprolactone (CAPA)



# Processing Machine



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## Extruded Fibers

PLA  
PHB/V (Biopol)  
Co-polyester (Estar BIO)  
PVA (Orex)  
PLA-Corn (Lactron)  
Polymers, additives, starch catalyst  
(Ecostar)  
Polycaprolactone (CAPA)

## Injection-Moulding

PLA  
PHB/V (Biopol)  
Starch (BIOPLAST)  
PET mod. (Biomax)  
PVA (Orex)  
Cellulose di-acetate (Bioceta)  
Polymers, starch, additives (Ecostar)  
Polycaprolactone (CAPA)

## Blow-moulding extrusion

PLA  
PHB/V (Biopol)  
Cellulose di-acetate (Bioceta)  
Polymers, additives, starch  
catalyst (Ecostar)  
Polycaprolactone (CAPA)

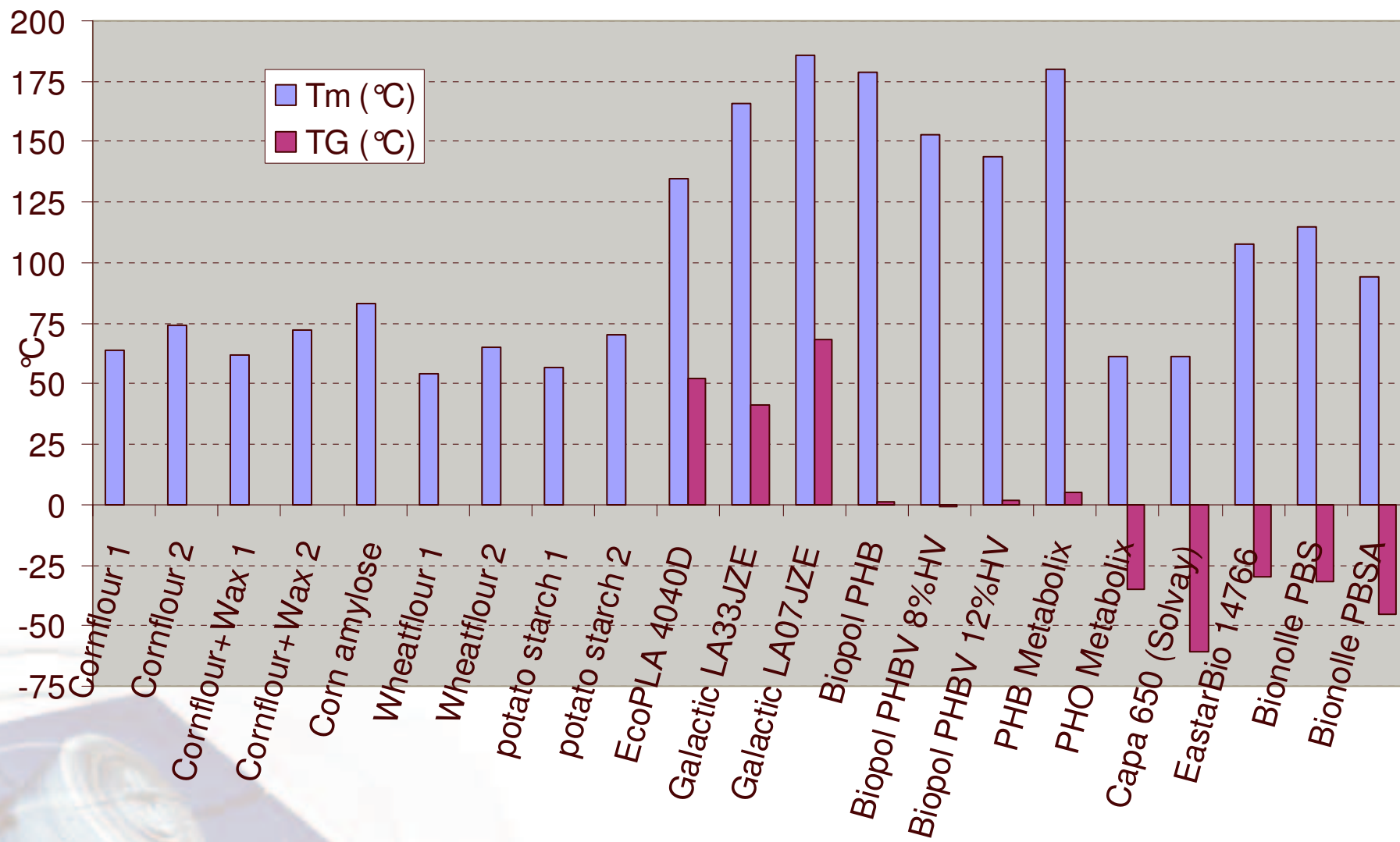
## Extrusion-coating and lamination

PHB/V (Biopol)  
Co-polyester (Ecoflex)  
PET mod. (Biomax)  
Co-polyester (Estar BIO)  
PVA (Orex)  
Corn Starch - polyacetal (Mater-Bi)  
Polymers, additives, starch (Ecostar)





# Melting and Glass Transition Temperature





## •Mechanical properties :

•Important differences inside biodegradable classes (cf. Conventional plastics)

•f (fabricant, grade, processing)

Ex. : PLA

Elongation at the break :

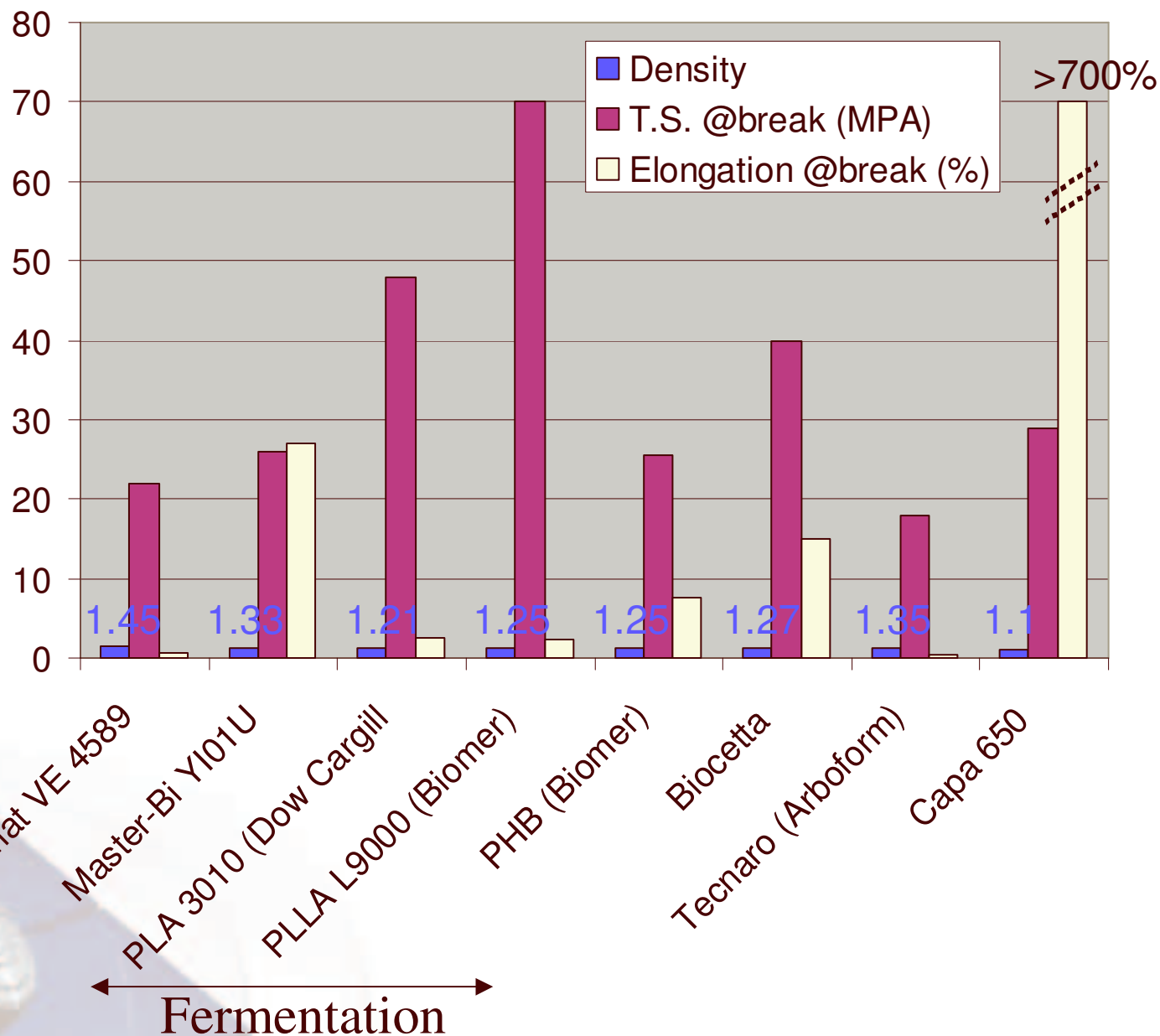
	4040D Cargill Dow	2000D Cargill Dow	H100 Mitsui Toatsu	S100 Mitsui Toatsu	Lacty Shimadzu Corp
%	160 - 100	6	5	110	3



# Mechanical Properties of Commercial grades for injection moulding



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	V E4589 - Végémat	2000D Dow Cargill	PVAXX	CAPA 650 Solvay	Arboform Technaro
Specificity	Starch + Maize Plant	PLA	Polyvinyl alcohol	Caprolactone	Wood Plastic
Density	1.45	1.25	1.28	1.1	1.3 – 1.4
TS@Yield (MPa)		60	11.5	17.5	-
TS@break (MPa)	22	53	28.7	29	10-22
Elong.@break (%)	0.67	6	-	>700	0.3-0.7
Modulus (GPa)	3.3	3.5	0.383	0.470	1-5





# Properties

• **Optical properties**, ex. :Transparency of PLA → Optical application

• **Chemical properties**

• Water and oil resistance (PCL, PLA);

• Solvent resistance (PCL, PLA);

• or not (mainly starch based plastics);

• Chlorine resistance (PCL);

• Odour, O<sub>2</sub> barrier (PLA);

• Heat resistance (PHB- 120°C);

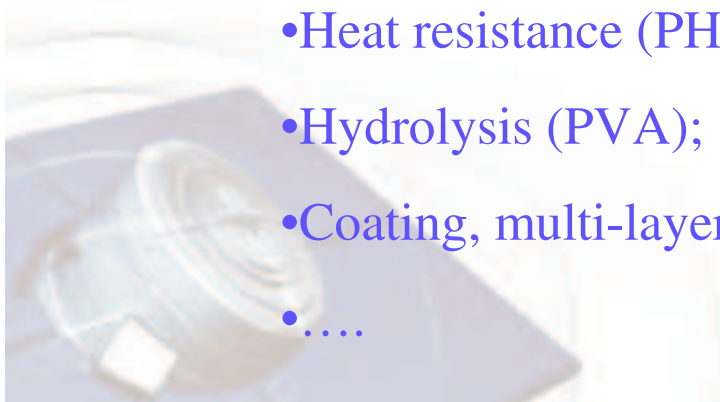
• Hydrolysis (PVA);

• Coating, multi-layers product;

•.....

Food Packaging

Regulation





## Food contact, Safety and Legislation

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Directive	Field
89/109/EEC	Framework
93/10/EEC amended by 93/111/CEE	Cellulose, ceramics and plastics
82/711/CEE amended by 93/8/CEE and 97/48/CEE	Tests conditions
85/572/CEE	Food simulants
90/128/CEE amended by 92/39/CEE, 93/9/CEE, 95/3/CEE, 96/11/CEE and 99/91/CEE	Overall and specific migration limits
Other areas are in progress or not yet covered	

### Positive list of authorised substances :

Starting substances :

Glucose, sucrose, lactic acid, albumin

Cellulose, lignocellulose

Starch

Additives :

Gelatin, dextrin, pectin, casein, ...

**Biopol, Master-bi.**

**Dow Cargill?**





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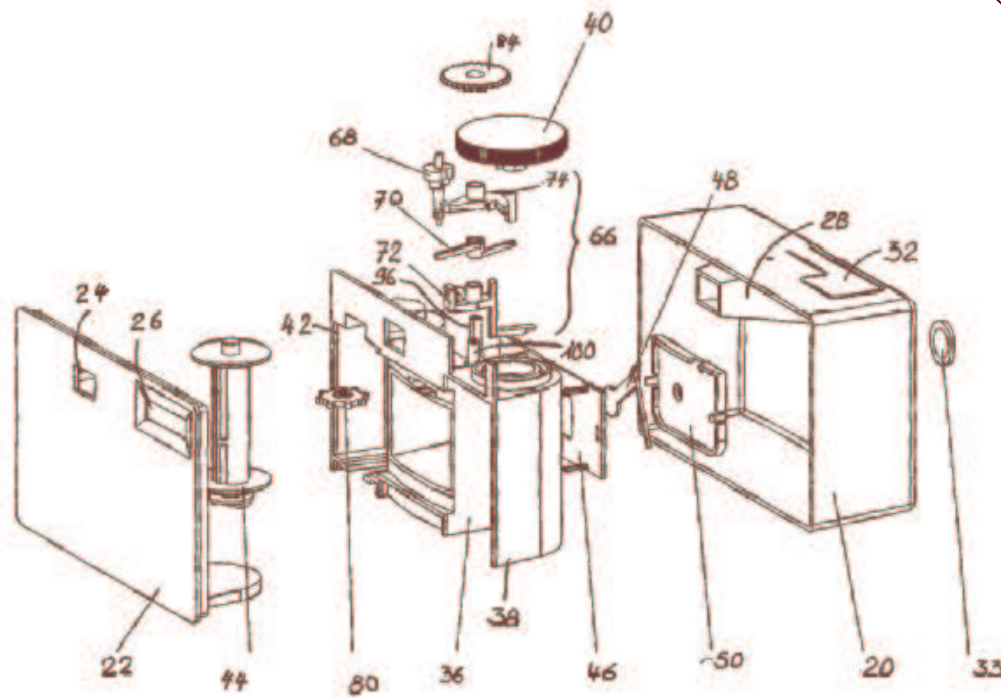
# Optical application

Biodegradable disposable Camera.

Patent Number : EP 1074881

*Competition*

Disassembling  
factory

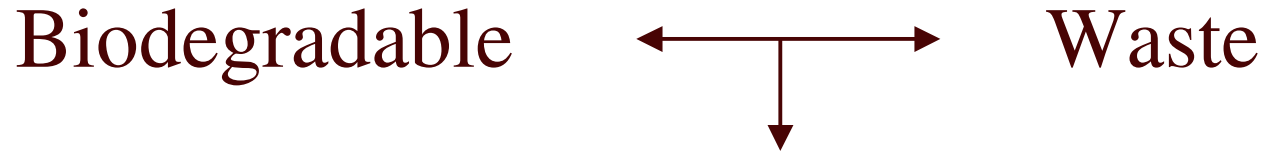


Waste regulation





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### European Legislation

- **75/442/EEC** → 91/156/EEC (Framework directive)
- 94/62/EC (packaging and waste packaging)
  - EN 13432 ? Future Directive « Compostable »
- Agricultural legislation ÷ soil enrichment
- ...

### Biocompatible

#### European Legislation

- Active Medical (implant) Device :
- directive 90/385/EEC;
- directive 93/42/EEC
- directive 93/68/EEC





## Competitive Prices ?

Traditional Polymers (€/kg)		Biodegradable Polymers (€/kg)	
HDPE	0.92	PLA	3.00-4.00
PELDPE	0.85	Starch (blends) polymers	2.00-4.00
LLDPE	0.85	Biodegradable Polyesters	3.50-5.0
PP	0.82-0.89	Lignin or other vegetal matter	4.55-10.22
PS	1.17-1.22	Cellulose Acetate	6.2
PVC	0.81	Végémat (maize plant)	<b>1,00</b>





## Differences between US and European Market

### Application share in 1998

	<b>US</b>	<b>Europe</b>
<b>Loose-fill</b>	72 %	25 %
<b>Compost bags</b>	15 %	50 %
<b>Food packaging</b>	-	8 %
<b>Paper coating</b>	-	12 %
<b>Other</b>	13 %	5 %

### Growing Sectors :

Food Packaging (food contact agreement pending)

Compost bags (increasing in Europe)

Paper Coatings

Dishes & Cutlery

Hygiene Disposables → Human Excrements ↔~~X~~→ Compost

→ Pathogenes





## Conclusions

- **High Diversity of Polymers**
  - Chemistry
  - Production process
  - Application possibilities
    - packaging
    - agricultural
    - medical
    - .....
- **Mechanical and physical Properties  $\Leftrightarrow$  Application**
- **Processable on conventional machine**
- **Open and promising market But very sensitive to the legislation and to consumer psychology.**
- **Competitive Prices :  $\pm$**

