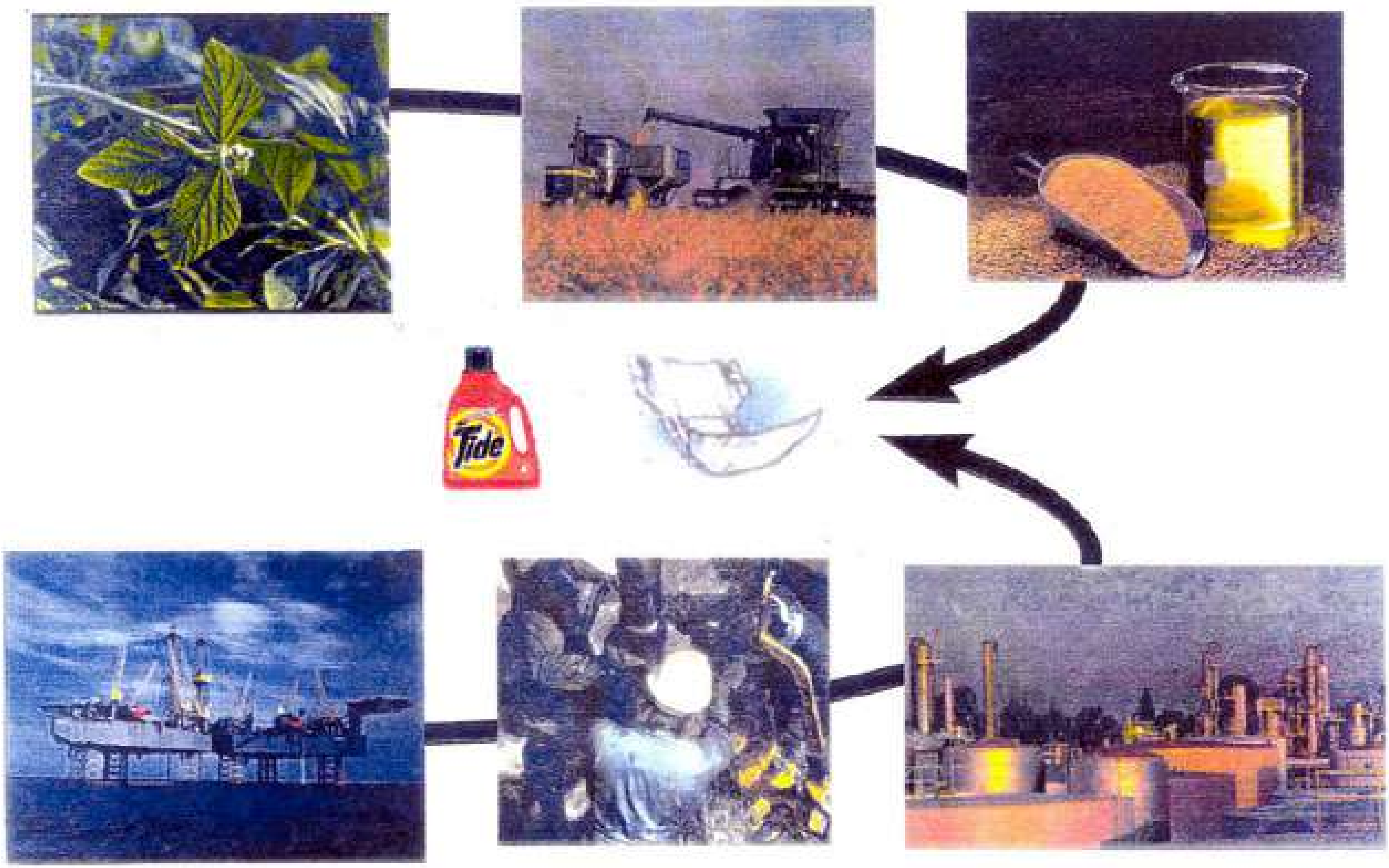
NODAX

Combines the performance of plastics with environmental sustainability.

P&G's Nodax™

Biodegradable thermoplastics from renewable resources



Nodax^{TM} Project

Overall Objective

Produce a novel and functional polymer from a renewable resource that is competitive with conventional petroleum-based polymers in price, and offers improved end-use properties.

Approach

Thermoplastic aliphatic polyester (*Nodax^{TM})* production in microorganisms or agricultural crops to achieve price and volume objectives.

Commercialization

- **Broadly license and transfer R&D for production of neat polymer, resins and forms.**
- **Create demand by internal use and broad licensing of other end users.**
- **Cooperate and collaborate with other companies to capitalize on synergies with other bioplastics to grow entire market.**

Nodax^{TM} - P&G Bioplastics

Materials Properties

- Comparable to high-grade polyethylene
  - Strength, flexibility, toughness
- Additional beneficial characteristics of polyesters
  - Dyeability, printability, compatibility, etc.
- Gas Barrier properties combined with heat sealability
- Hard springy elasticity upon stretching
- Chemically digestibility in hot alkaline solutions

Additional Features

- Produced from renewable resources
- Fully biodegradable and compostable
- Novel and proprietary materials

Estimated Cost

- $ 1.00 - $ 2.50/kg. (Target)
- Competitive with high-end commodity plastics

Historical Background

Issues

- P&G's detergent phosphate experience1970 ~
- Increasing solid Waste concerns1980 ~
  - Are we running out of landfills?
  - Plastic packages, diapers and other disposable products

Technical Approach

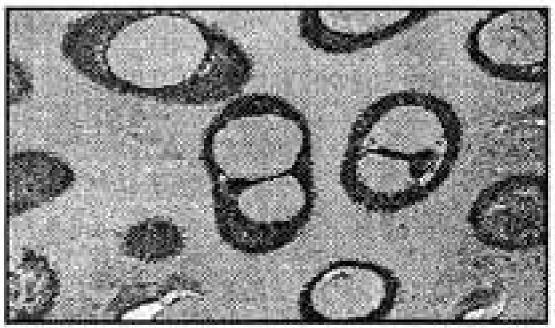
- Biodegradable/compostable plastics1990 ~
  - Disintegration to pieces
  - Mineralization to CO_2, CH_4, and H_2O

Specific Actions

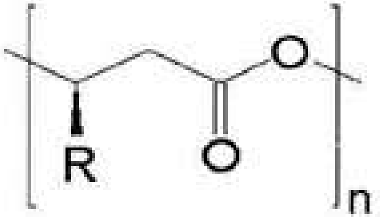
- Quick fix with available materials
  - Starch-based resins
  - Cellulose derivatives
- Long-term solution
  - Next generation degradable polymers
  - Major technical discontinuity

Polyhydroxyalkanoates (PHAs)

- Semicrystalline, biodegradable, thermoplastic polyester
- Produced *(up to now)* by microorganisms

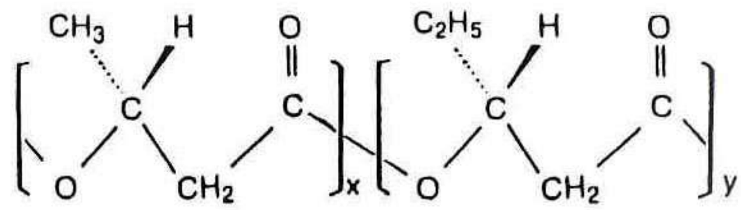


Schematic representation of *Ralstonia eutropha* containing PHB granules (white fractions)



	PHA	R
	PHB	$-CH_3$
	PHV	$-CH_2CH_3$
	PHBV (Biopol™)	$-CH_3$ and $-CH_2CH_3$
Nodax™ family {	PHBHx (Kaneka)	$-CH_3$ and $-CH_2CH_2CH_3$
	PHBO	$-CH_3$ and $-(CH_2)_4CH_3$
	PHBOd	$-CH_3$ and $-(CH_2)_{14}CH_3$
	etc.	

Properties of Conventional PHAs



Biopol™

- Commercial PHA from Metabolix
- Bacterial fermentation of sugar

Advantages

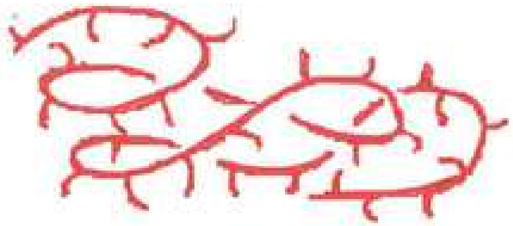
- Produced from renewable resources
- Biodegradable (compostable)
- Thermoplastic
- Moisture resistant

Limitations

- Cost$5 ~ $8/lb?
- SupplyLimited production scale
- PollutionBiomass disposal
- End-use propertiesHard, brittle, weak, unstable
- ProcessabilityHigh Tm, poor thermal stability
  Low extensional viscosity
  Slow crystallization rate

Branched PHAs (Nodax™)

Linear PHB



Branched PHB (Nodax™)

Molecular design analogous to soft polyethylene

- Disruption of crystals by chain defects
- Enhanced molecular entanglement

Benefits

- Processability

Lower T_m	Process temperature, degradation
Higher melt viscosity	Extrusion blowing

- End-use properties

Lower crystallinity	Flexible, tough, ductile
Lower T_g	Soft, drapable

- Proprietary structure

NMR Spectrum of Nodax™ Produced by Pseudomonas sp. 61-3

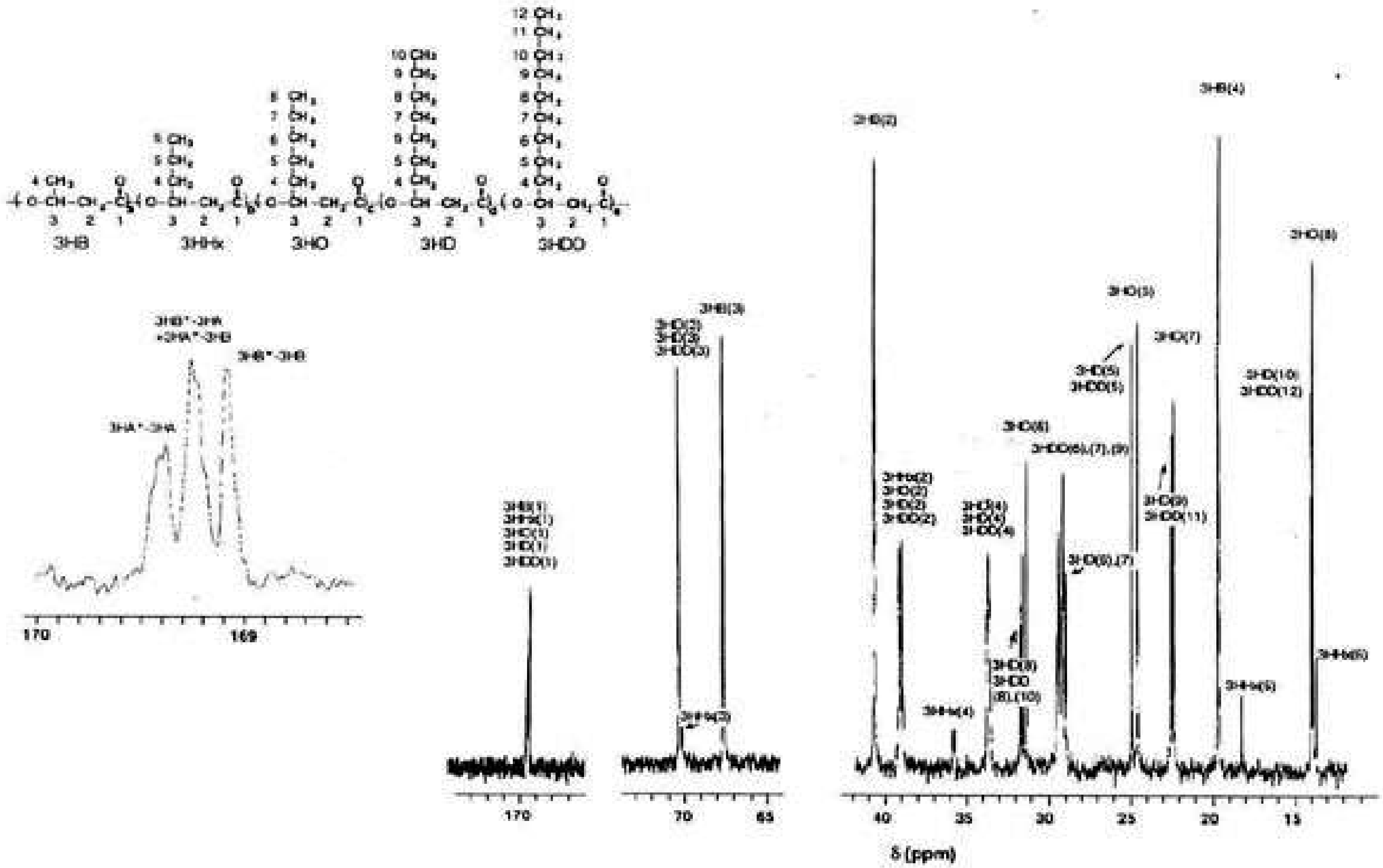


Fig. 2 125-MHz ^{13}C-NMR spectrum of P(51% 3HB-co-3HA) produced by recombinant *R. eutropha* PHB^{-}4 harboring pJKSc46-*pha* from tetradecanoate. 3HB, 3-hydroxybutyrate; 3HHx, 3-hydroxyhexanoate; 3HO, 3-hydroxyoctanoate; 3HD, 3-hydroxydecanoate; 3HDD, 3-hydroxydodecanoate. 3HA denotes 3-hydroxyalkanoates from C6 to C12

H. Matsusaki, H. Abe, K. Taguchi, T. Fukui, and Y. Doi
Appl. Microbiol. Biotechnol. **53**, 401-409 (2000).

PHA Copolymer Compositions

	C_4	C_5	C_6	$C_{>=7}$	$C_{>7}$
Literature	1				
Metabolix		1			
Literature			1		
Literature				1	
Metabolix	2	2			
Kaneka	2		2		
P&G	2			2	
P&G	3	3	3		
P&G	3	3		3	
P&G	3		3	3	
P&G	4	4	4	4	
P&G		4	4	4	4

1 Homopolymers
2 Di-copolymers
3 Tri-copolymers
4 Tetra-copolymers

P&G claimed the use of C4C6 in films, fibers, nonwovens, hygiene products, etc.

C4's level is at least 50%

P&G also claimed all PHA opolymers with 5 components and above

Properties of Nodax™

Biological Properties

- To be made from renewable resources
- Biodegradable - aerobic, anaerobic

Thermo-mechanical Properties

- Similar to polyethylene, polypropylene
- Versatility - films, fiber, elastomers, etc.
- Exhibit hard (springy) elasticity

Physico-chemical Properties

- Affinity/compatibility with certain materials
- Higher surface energy - printing, adhesion
- Hot alkali digestibility
- Barrier properties
- UV resistance, high density, etc.

Biodegradable Summary

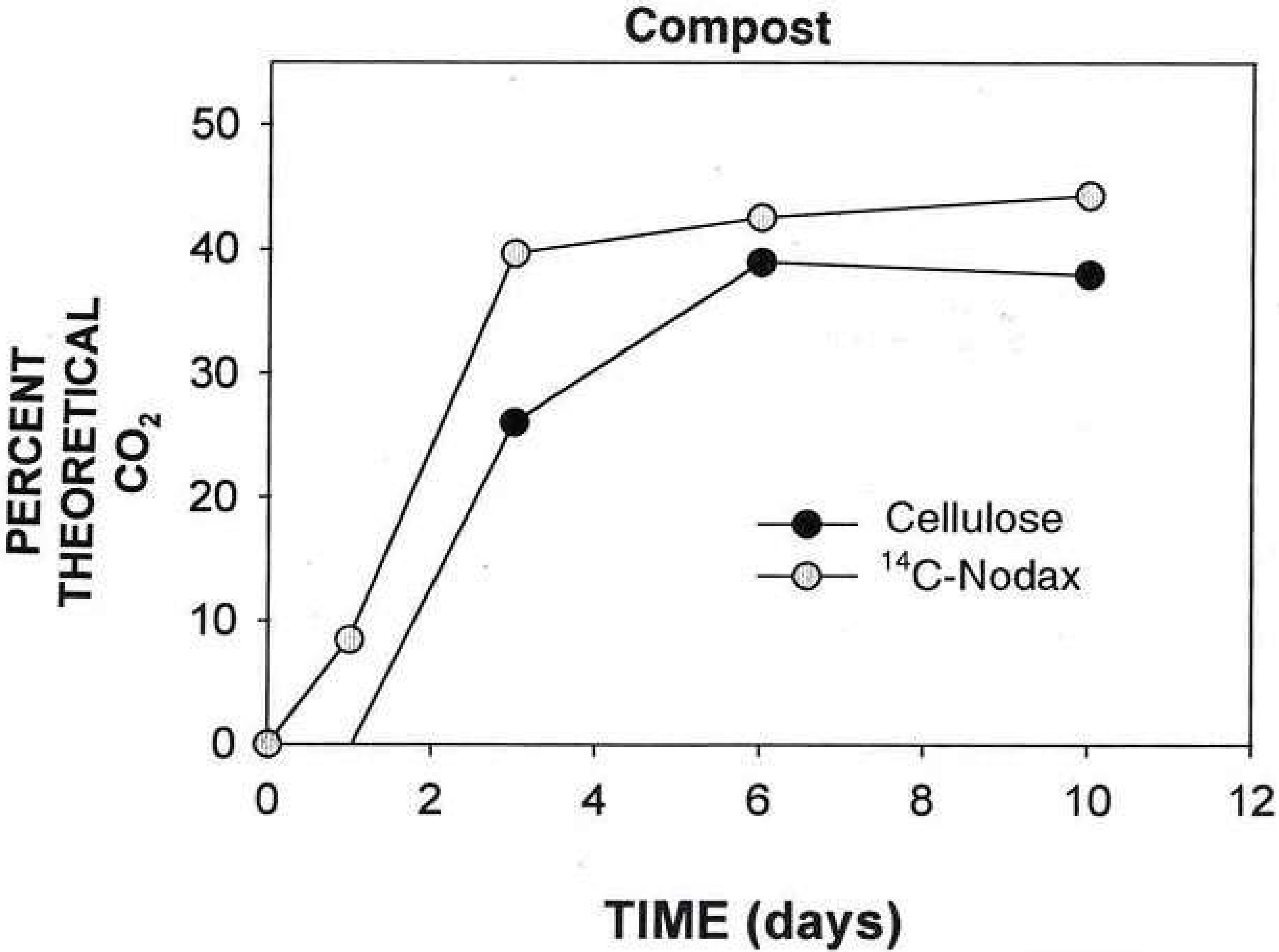
<u>Aerobically Degradable:</u> Compost, surface exposure

- 78% / 45 days via intensive aerobic compost simulation.

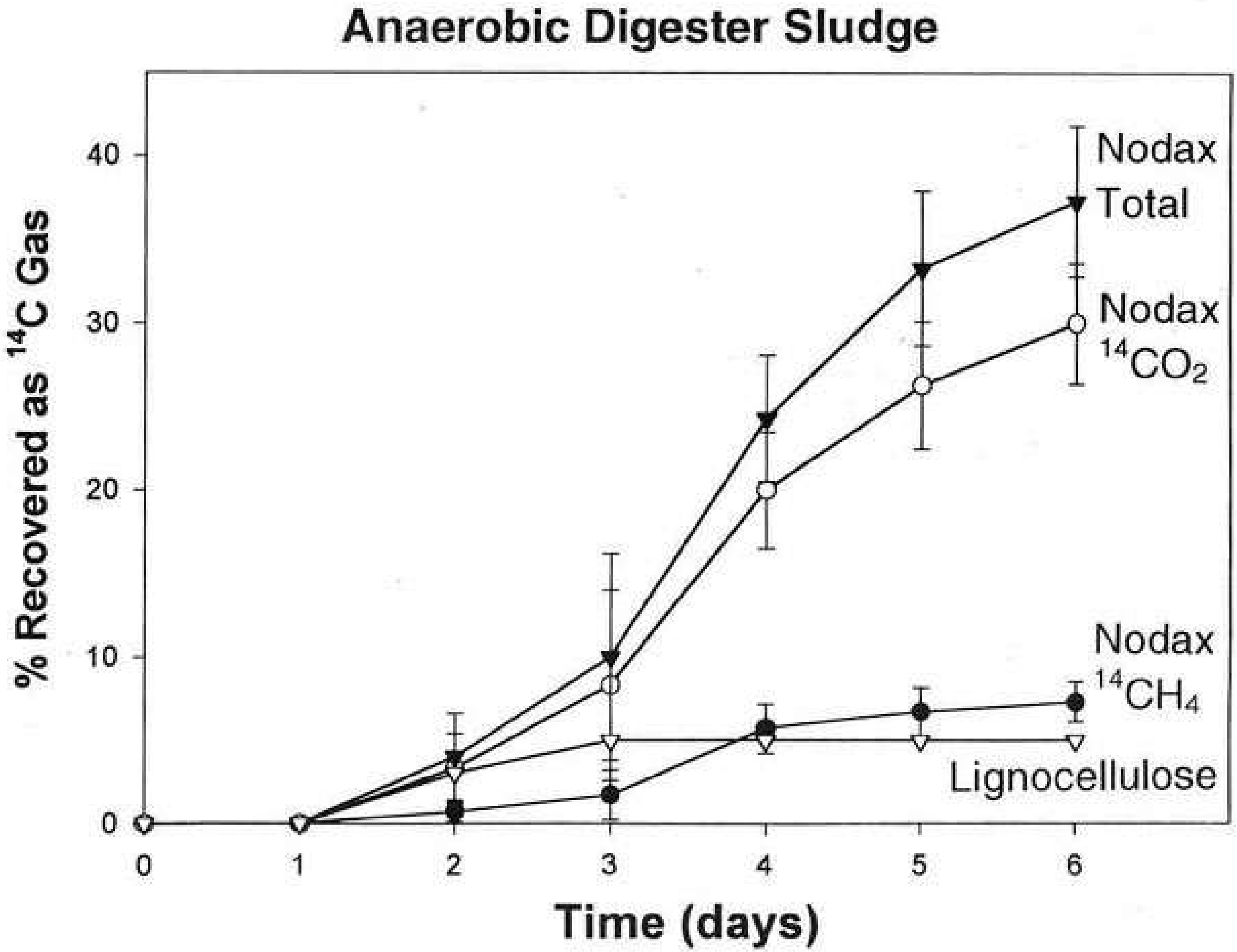
<u>Anaerobically Degradable:</u> Septic, sediment, marine

- Good in simulated landfill conditions. Same rate or better than reference materials like yard waste, various papers.
- Good in septic systems. Disintegration in 7 days in model system.
- Slower in marine conditions. 40% / 40 days. Reference material was 55% / 15 days.

Mineralization of Nodax™



Mineralization of Nodax™



Thermal Properties

Melting

- C_2 branches (PHBV) do not affect T_m much
- $C_{\geq 3}$ branches (Nodax^{TM}) depresses T_m
- Branch size above $C_{\geq 3}$ has less effect on T_m lowering efficacy

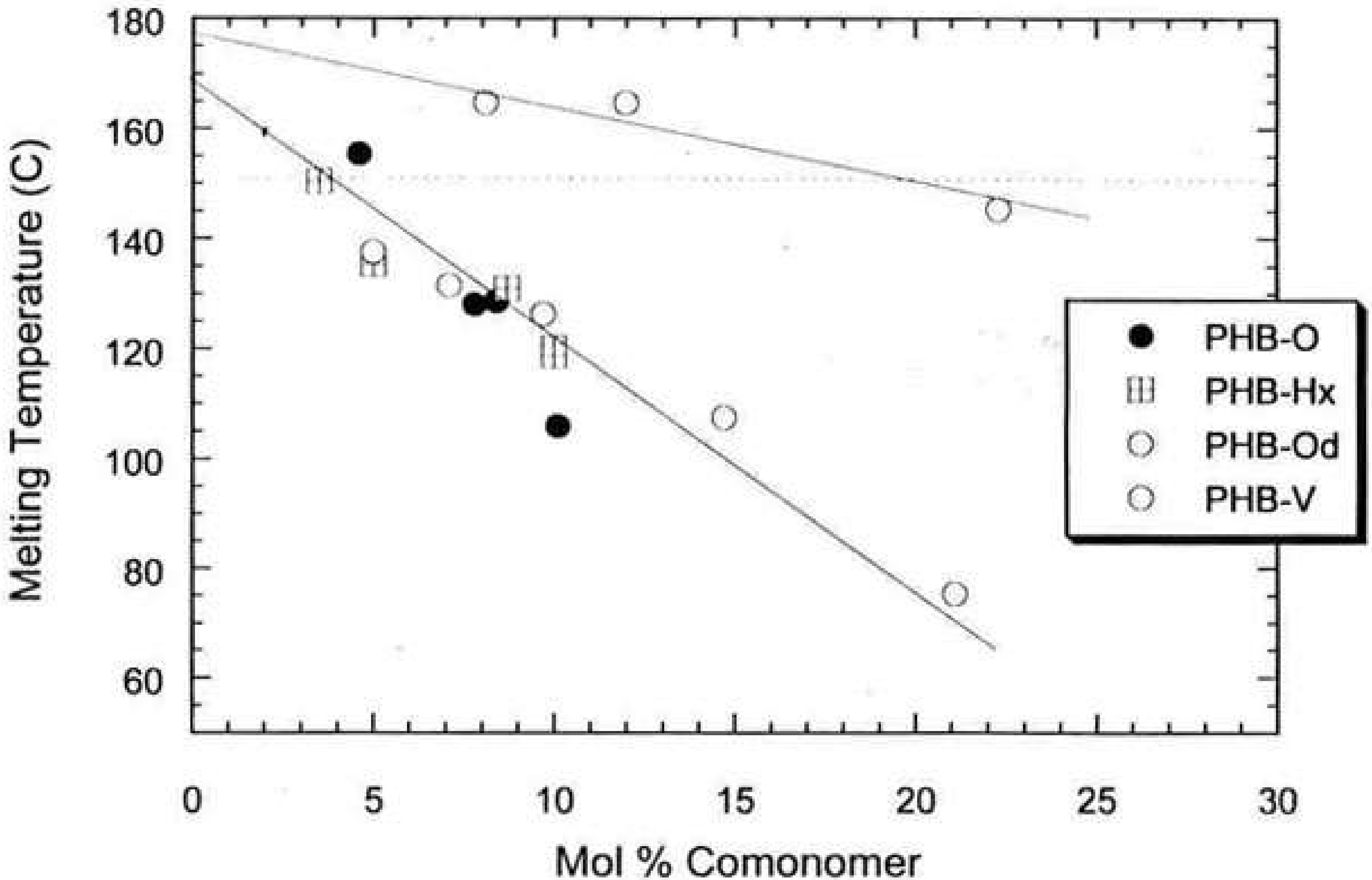
Crystallinity

- C_2 branches has little effect on total crystallinity
- Nodax^{TM} has the same crystal structure as PHB
- $C_{\geq 3}$ branches depresses crystallinity
- Larger branches depresses crystallinity
- Higher branch content slows down crystallization rate

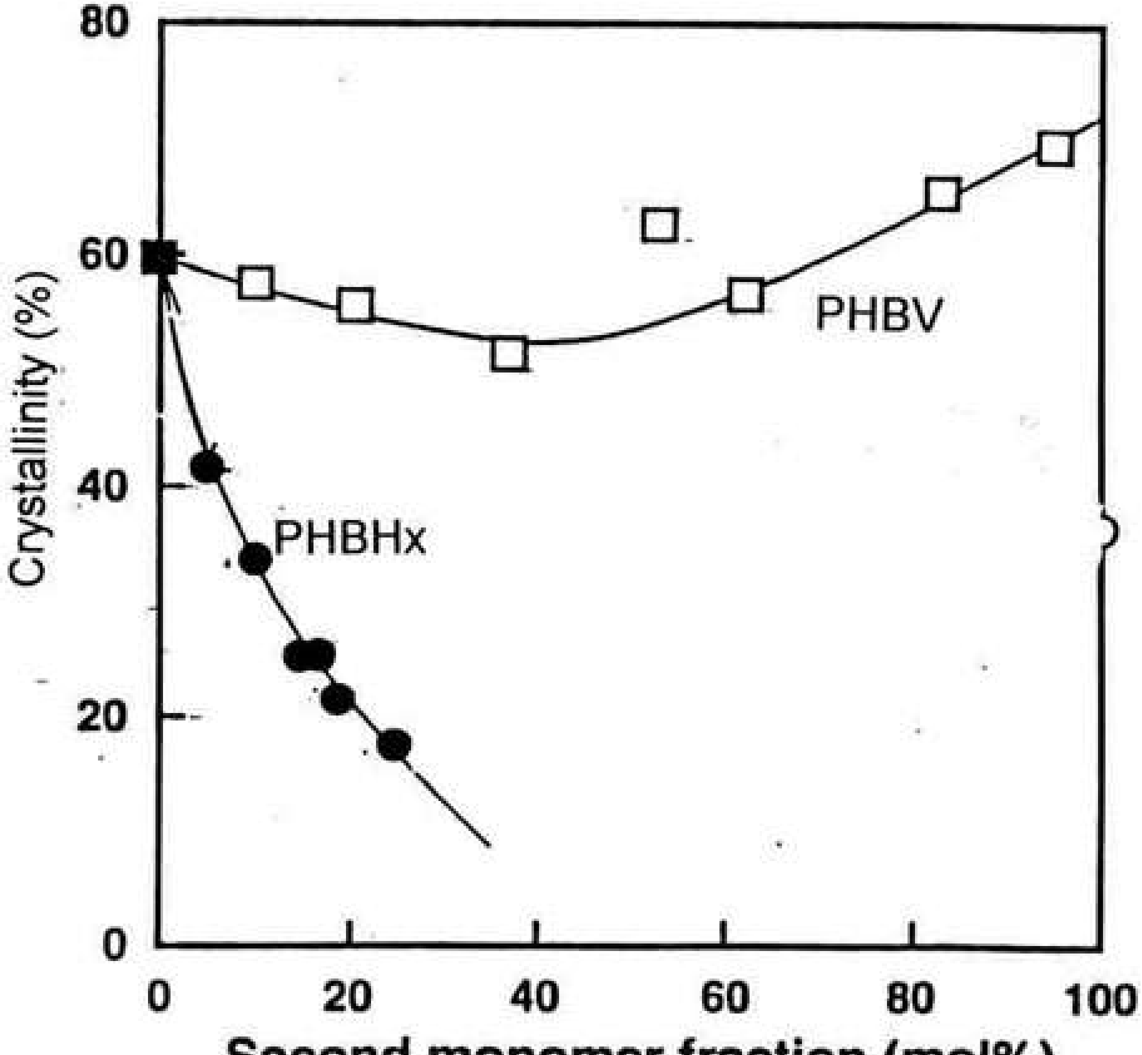
Glass Transition

- Higher branch content depresses T_g
- Larger branches depresses T_g

Melt Temperature



Crystallinity



Mechanical Properties

Young's Modulus (Stiffness)

- Content and size of branches reduce modulus
- Between HDPE and LDPE
- Molecular weight has little effect
- Aging slightly increases modulus

Yield Stress

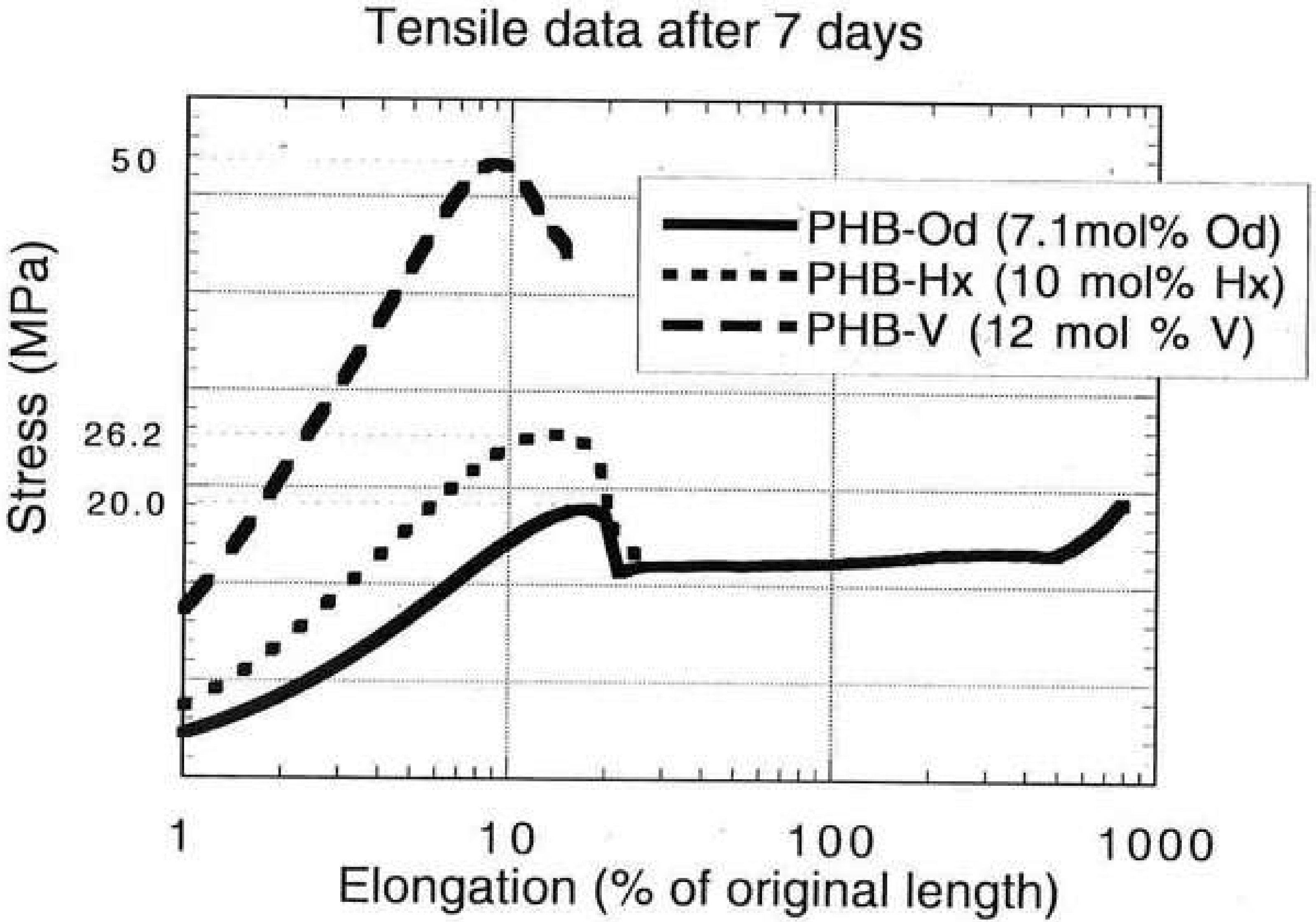
- Content and size of branches reduce yield stress
- Between HDPE and LDPE
- Molecular weight has little effect

Toughness and Ultimate Elongation

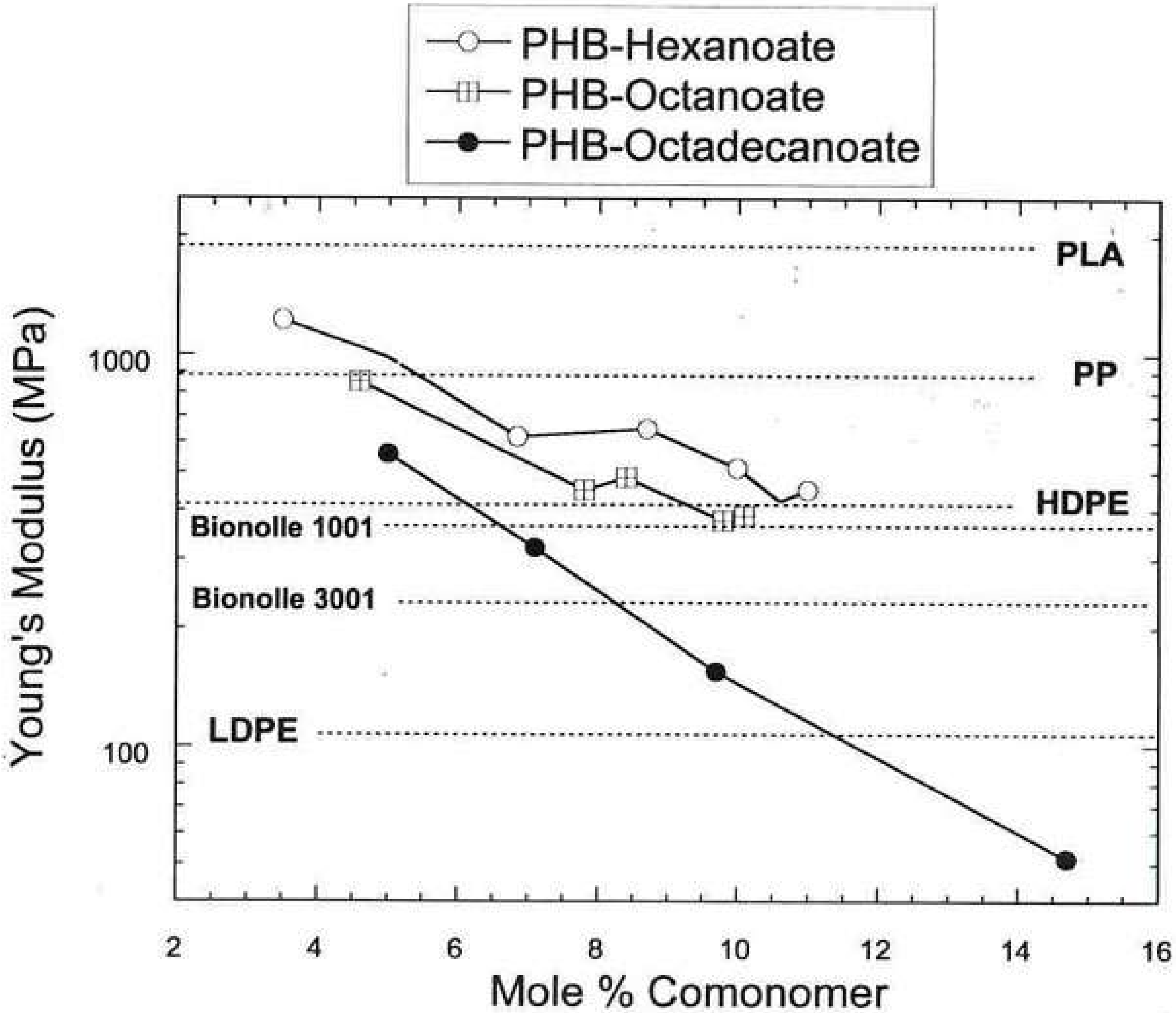
- Molecular weight has profound effect (preferably > 600K)
- Size of branches improves both

Comparable to high-grade PE

Tensile Properties



Tensile Properties



Interactions with Other Materials

Bulk Phase Properties

- Solubility – “green” non-CFC solvents (acetone, ethyl acetate, etc.)
- Compatibility – plasticizers, antioxidants, processing aids
- Blendability, miscibility
- Dyeability

- Moisture and grease resistance
- Barrier – O_2, CO_2, odor

Surface Properties

- Adhesion
- Dispersibility
- Wettability
- Printability

PLA vs. PHA (Nodax^{TM})

Polylactic acid

Physical Properties

- Often amorphous
- Transparent
- Brittle, hard, and stiff
- Use temperature < 60° C

Degradation Mechanisms

- Hydrolytic attack
- Not directly biodegradable
- Temperature, pH, and moisture effect
- Spontaneous degradation

Processability

- Quick quench
- Fiber spinning

Polyhydroxyalkanoates

- Semicrystalline
- Tough, ductile and drapable
- Usually opaque
- Use temperature < 120º C

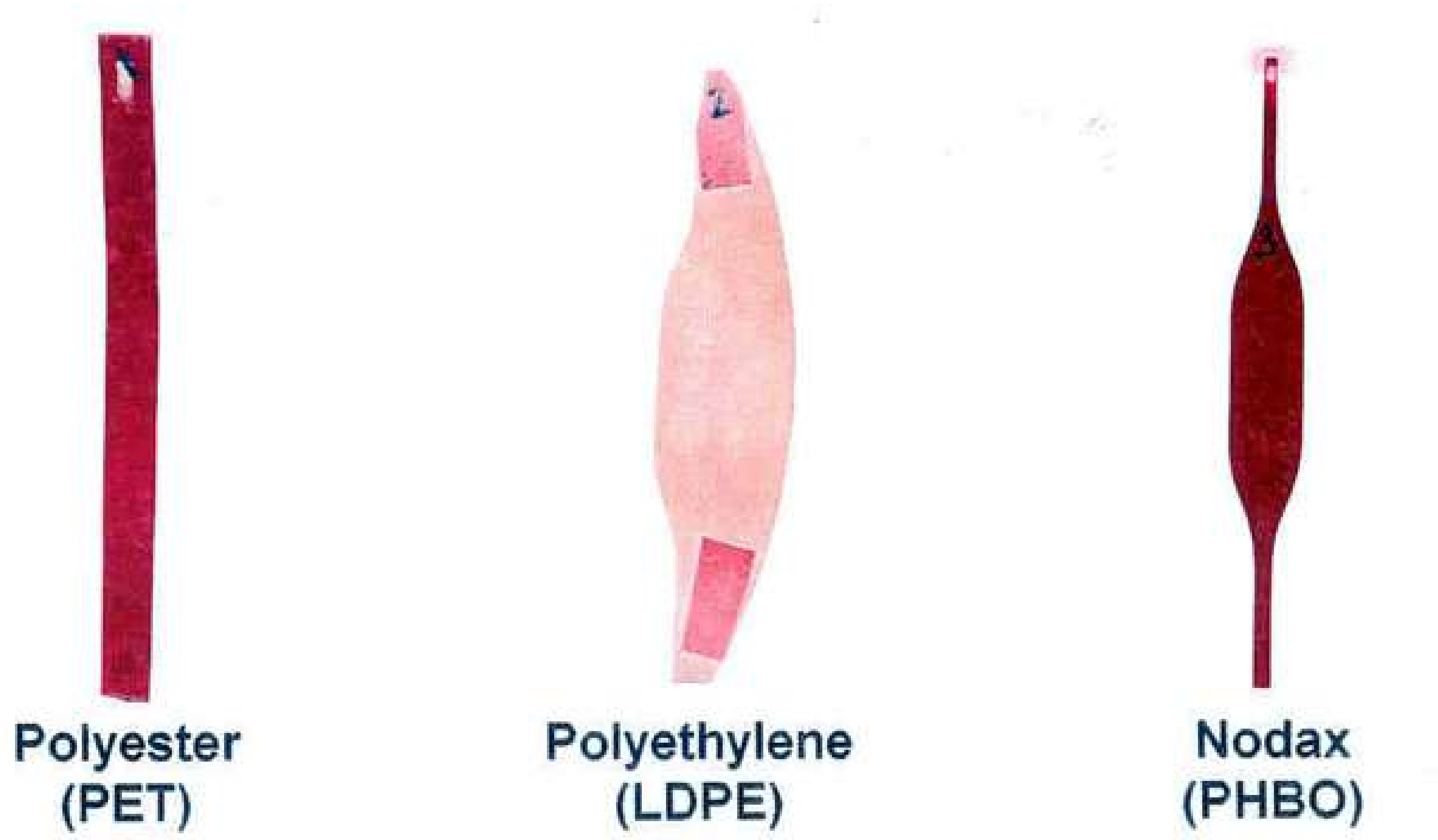
- Enzymatic digestion
- Rapid biotic degradation
- Aerobic or anaerobic conditions
- Relatively stable in ambient

- Slow crystallization
- Films, fibers

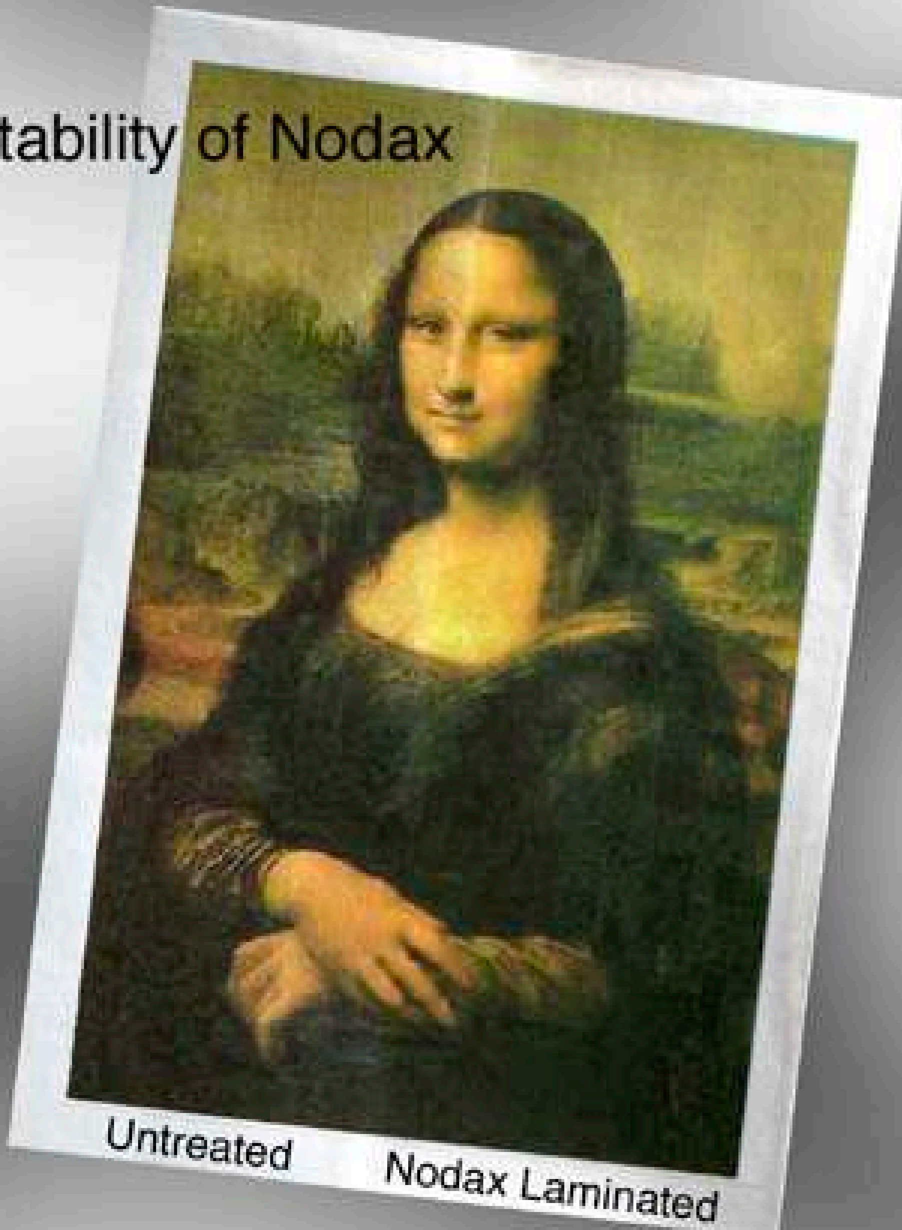
Dyeability

Dyeability test

– Immersion of films in aqueous dispersion of nonionic dye



Printability of Nodax



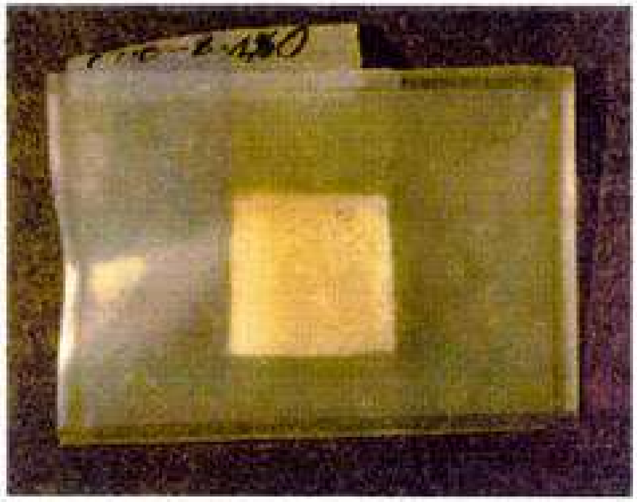
Ink-jet Printability of Nodax Paper

100% Nodax pulp

Mixed furnish (90% Nodax : 10% NSK)

Heat Sealability

- PHB-A (neat) are slow to crystallize. Typically order of minutes.
- Nucleation package needed for processing. Typically reduces time to crystallize to order of few seconds.



- Still heat sealable under appropriate conditions even without nucleation package.
- Can be sealed via *dielectric heating*.

Gas Permeability of Films

Transmission Rate

<u>PolymerMoistureO_2</u>

Saran 110

Nodax™ 9040

PET 5060

Polypropylene 10 2300

Polyethylene 20 7000

Bionolle 300

Natural rubber 1000 24000

Cellulose acetate 3000 1000

Margin of error 0.5x - 2x

For most polymers, CO_2 permeability is ~ 5x O_2 permeability

Chemical Digestibility

Alkaline DIgestion

- Hot alkaline solutions attack bioplastics
  - Caustic solution, *e.g.,* Cascade
- Rapid disintegration to particulate
- Degradation to water-solubles (monomer, oligomer)
- Full biodegradation of digested products

Implications

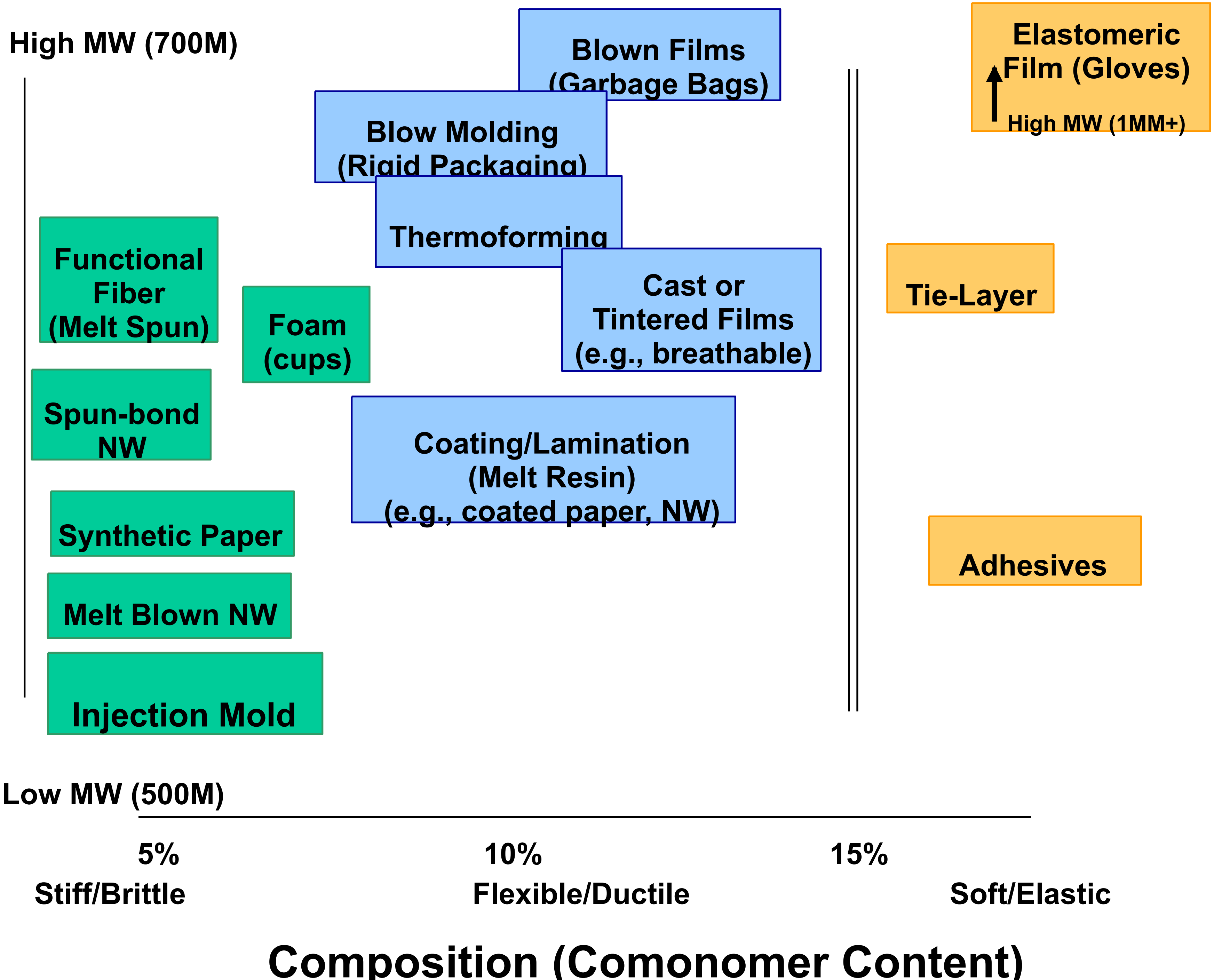
- Flushable after digestion
- Household digestion possible
- Institutional uses:
  - Fast-food restaurants, hospitals, marine transportation, military use
- Specialty uses:
  - Electronic circuit board, mold release, etc.

Key Attributes of Nodax™

- Excellent barrier for odor, oxygen, CO2, and moisture
- Impervious to grease, water, and other liquids
- Heat-sealable, thermally processable
- Good PE-like mechanical properties
- Alkali digestible (*e.g.,* with Cascade solution)
- Dyeable and printable
- Compatible with various additives and fillers
- Made into laminated paper, layered plastic sheets, nonwovens, etc.
- Blendable with many other polymers
- Low cost, when made by crop plants
- Available from renewable resources
- Biodegradable, compostable

Conversion to Formed Articles

- **Films and sheets**
- **Molded articles**
- **Fibers**
- **Elastics**
- **Laminates and coated articles**
- **Nonwoven fabrics**
- **Synthetic paper products**
- **Foams**


High MW (700M)
Blown Films (Garbage Bags)
Elastomeric Film (Gloves)
High MW (1MM+)
Blow Molding (Rigid Packaging)
Thermoforming
Functional Fiber (Melt Spun)
Foam (cups)
Cast or Tintered Films (e.g., breathable)
Tie-Layer
Spun-bond NW
Coating/Lamination (Melt Resin) (e.g., coated paper, NW)
Synthetic Paper
Adhesives
Melt Blown NW
Injection Mold
Low MW (500M)
5%
10%
15%
Stiff/Brittle
Flexible/Ductile
Soft/Elastic
Composition (Comonomer Content)

Protoypes of Nodax™ Products

Compression molded container

Micro-extrusion molded cylinders

Syringe machined from two molded cylinders

Self-sealing thermoform pac

Thermoformed disposable pill cup

Thermoformed disposable container

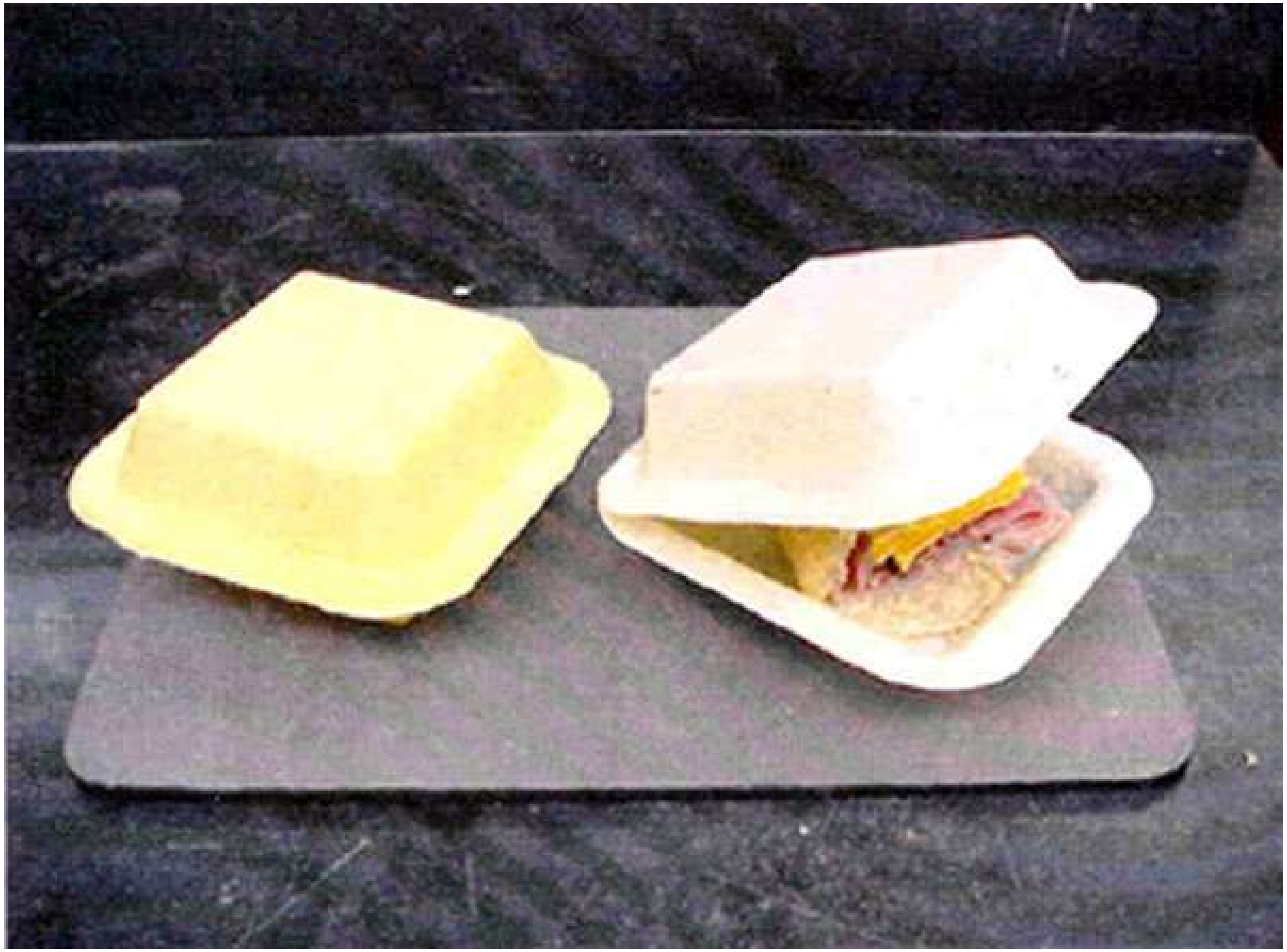
Paper Laminates/Coatings

- Shows good adhesion to paper, cellulosics
- Water/grease barrier
- Heat sealable
- More flexible and crack resistant than PHB/PHBV
- Repulpable
- <u>Navy Drinking Cup Application:</u>

Heat sealing rate sufficient for drinking cups to be processed at production speeds

- Extrusion coating rheology is acceptable
- Crystallization rate of neat material needs to be adjusted

Nodax^{TM} Foam



Clam-shell containers made of Nodax^{TM} foam

Nodax™ Fiber

Nodax bicomponent fiber

Combines the performance of plastics with environmental sustainability.