

Biopolymers overview



Biopolymers CHEM-E2155

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Schedule

| Day | Subject of lecture | Discussion part |
|-------------|------------------------------|--------------------------|
| 08 January | Introduction to the course | |
| 15 January | Biopolymers overview | Reading 1 |
| 22 January | Biopolymers for packaging | Reading 2 |
| 29 January | Discussion day | Reading 3 & Assignment 1 |
| 05 February | Biodegradation 1 | Reading 4 |
| 12 February | Biodegradation 2 | Reading 5 |
| 26 February | Discussion day | Reading 6 & Assignment 2 |
| 04 March | Chitin, alginates and others | Reading 7 |
| 12 March | Proteins | Reading 8 |
| 19 March | Discussion day | Reading 9 & Assignment 3 |
| 25 March | TBD | Reading 10 |

Learning Outcomes

After today's course you

- are familiar with common definitions relevant for biopolymers
- know different ways to categorize biopolymers
- Understand the challenges and opportunities of PHAs

Biopolymers

Animal based

Polysaccharides

- Chitin
- Alginates
- Xanthum gum

Proteins

- Collagen
- Gelatin
- α/β -Keratin

Plant based

Polysaccharides

- Starch
- Cellulose
- Hemicellulose
- Pectine

Proteins

- Soy protein
- Gluten

Vegetable fats
and oils

Natural rubber

Lignin

From microorganisms

- Polyhydroxyalkanoates
- Pullulan
- Bacterial cellulose

Synthetic

Bio-derived

- Polylactic acid

Oil-based

- Poly(alkylene dicarboxylate)s
- Polycaprolactone

Definitions

Potential for production of sustainable goods

- products made from natural renewable resources
- products that decompose into environmentally friendly constituents

...but they need to provide same results with products made from synthetic materials

Possible challenges:

- costs
- inferior properties

Definitions

No consensus over the exact definition of the generic terms:

- Degradable
- Biodegradable
- Bio-based
- Compostable
- Biopolymer

ISO International Organization for Standardization

EN European Norm

ASTM American Society for Testing and Materials

Degradable Polymers

broad term applied to polymers or plastics that disintegrate by a number of processes (physical disintegration, chemical degradation, and biodegradation by biological mechanisms).

A polymer may be degradable but not biodegradable.

Biodegradable Polymers

degrade under the action of microorganisms such as molds, fungi, and bacteria within a specific period of time and environment.

On its own, the term biodegradable has no clear meaning and creates confusion.

Withdrawn standard ASTM D5488-94de1: biodegradable polymers refer to polymers that are “capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the **enzymatic action of microorganisms** that can be measured by standard tests, over a specific period of time, reflecting available disposal conditions.”

ISO 17088:2012 / EN 13432:2000, EN 14995:2006 / ASTM D6400-12

Bio-based

Term focused on the raw materials basis (polymers **derived from renewable resources**).

Raw materials are **renewable if they are replenished by natural procedures** at rates comparable or faster than their rate of consumption

ASTM bio-based materials: “an organic material in which carbon is derived from a renewable resource via biological processes. Bio-based materials include all plant and animal mass derived from carbon dioxide (CO₂) *recently* fixed via photosynthesis, per definition of a renewable resource.”

A bio-based polymer is not *per-se* a **sustainable polymer**; this depends on a variety of issues, including the source material, production process, and how the material is managed at the end of its useful life.

- Not every bio-based polymer is biodegradable
(*bio-based polyethylene or polyamide 11*)
- Not every biodegradable polymer is bio-based
(*poly(ε-caprolactone) or poly(glycolic acid)*)
- Some fall into both categories
(*polyhydroxyalkanoates, PHAs*)

The **bio-based content** of a biopolymer (ASTM D6866-12, ASTM D7026-04):
Number of carbon atoms that come from the short CO₂ cycle
(from biomass as raw material).

Carbon-14 (¹⁴C), which has a half-life of about 5700 years, is found in bio-based materials but not in fossil fuels.

“Bio-based materials” refer to organic materials in which the carbon comes from non-fossil biological sources.

A bio-based PET comprises at least about 0.1 dpm/gC (disintegrations per minute per gram carbon) of ¹⁴C (decay rate).

Compostable Polymers

ASTM D6002: as “a plastic which is capable of undergoing biological decomposition in a compost site as part of an available program, such that the plastic is not visually distinguishable and breaks down to carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with known compostable materials (e.g., cellulose) and leave no toxic residue.”

This definition drew much criticism, and the standard was withdrawn.

In order for a polymer to be called compostable, it should meet any of the following international standards:

- *ASTM Standard D6400 (for compostable plastics) or*
- *D6868 (for compostable packaging)*
- *CEN standard EN 14995:2006 (for compostable plastics)*
- *or EN 13432:2000 (for compostable packaging)*
- *ISO 17088:2012*

- 1. Disintegrate rapidly during the composting;**
- 2. Biodegrade quickly under the composting conditions;**
- 3. Do not reduce the value or utility of the finished compost and the compost can support plant life;**
- 4. Do not contain high amounts of regulated metals or any toxic materials.**

Biodegradable polymers and compostable polymers are determined **by the rate of biodegradation, disintegration, and toxicity.**

All compostable polymers are by default biodegradable but not vice versa.

Biopolymers

(or “bioplastic”)

Criteria:

- the source of the raw materials
- the biodegradability of the polymer.

- Biopolymers made from renewable raw materials (bio-based), and *being biodegradable***
- Biopolymers made from renewable raw materials (bio-based), and *not being biodegradable***
- Biopolymers *made from fossil carbon* and being *biodegradable*.**

A. Biopolymers made from renewable raw materials (bio-based), and *being biodegradable*

Can be produced **by biological** systems (microorganisms, plants, and animals), **or chemically synthesized from biological starting materials** (e.g., corn, sugar, starch, etc.):

1. Biopolymers produced by microorganisms, such as PHAs
2. Synthetic polymers from renewable resources such as poly(lactic acid) (PLA)
3. Natural occurring biopolymers, such as starch or proteins; **natural polymers are by definition those that are biosynthesized by various routes in the biosphere.**

B. Biopolymers made from renewable raw materials (bio-based), and not being biodegradable

Can be produced from biomass or renewable resources and are non-biodegradable:

1. Synthetic polymers from renewable resources such as specific polyamides from castor oil (polyamide 11), specific polyesters based on biopropanediol, biopolyethylene (bio-LDPE, bio-HDPE), biopolypropylene (bio-PP) or biopoly (vinylchloride) (bio-PVC) based on bio-ethanol (e.g., from sugar cane), etc.
2. Natural occurring biopolymers such as natural rubber or amber.

C. Biopolymers *made from fossil carbon* and being *biodegradable*.

Can be produced from fossil fuel, such as synthetic aliphatic polyesters made from crude oil or natural gas, and are certified biodegradable and compostable:

At least partly fossil fuel–based polymers:

1. Poly(ϵ -caprolactone) (PCL)
2. Poly(butylene succinate) (PBS)
3. Certain “aliphatic-aromatic” copolyesters

According to *European Bioplastics* a plastic material is defined as a bioplastic if it is either **bio-based**, **biodegradable**, or **features both properties**:

Biopolymers or Bioplastics:

Biodegradable polymers (e.g., polymers of type A or C)

Bio-based polymers (e.g., polymers of type A or B)

Biopolyethylene derived from sugarcane (“green polyethylene”) is nonbiodegradable, but emits less greenhouse gases when compared to fossil-based polyethylene, and is classified as biopolymer.

“Biopolymers are defined as polymers that are derived from renewable resources, as well as biological and fossil-based biodegradable polymers.”

TABLE 1.1 Biodegradable versus Bio-Based Polymers

| Origin | Biodegradable | Nonbiodegradable |
|---------------------|--|--|
| Bio-based | CA, CAB, CAP, CN, P3HB, PHBHV, PLA, starch, chitosan | PE (LDPE), PA 11, PA 12, PET, PTT |
| Partially bio-based | PBS, PBAT, PLA blends, starch blends | PBT, PET, PTT, PVC, SBR, ABS, PU, epoxy resin |
| Fossil fuel-based | PBS, PBSA, PBSL, PBST, PCL, PGA, PTMAT, PVOH | PE (LDPE, HDPE), PP, PS, PVC, ABS, PBT, PET, PS, PA 6, PA 6.6, PU, epoxy resin, synthetic rubber |

ABS, acrylonitrile-butadiene-styrene; CA, cellulose acetate; CAB, cellulose acetate butyrate; CAP, cellulose acetate propionate; CN, cellulose nitrate; HDPE, high density polyethylene; LDPE, low density polyethylene; PA 6, polyamide 6; PA 6.6, polyamide 6.6; PA 11, aminoundecanoic acid-derived polyamide; PA 12, lauractam-derived polyamide; PBAT, poly(butylene adipate-co-terephthalate); PBS, poly(butylene succinate); PBSA, poly(butylene succinate-co-adipate); PBSL, poly(butylene succinate-co-lactide); PBST, poly(butylene succinate-co-terephthalate); PBT, poly(butylene terephthalate); PCL, poly(ϵ -caprolactone); PE, polyethylene; PET, poly(ethylene terephthalate); PGA, poly(glycolic acid), polyglycolide; P3HB, poly(3-hydroxybutyrate); PHBHV, poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PLA, poly(lactic acid), polylactide; PP, polypropylene; PS, polystyrene; PTMAT, poly(methylene adipate-co-terephthalate); PTT, poly(trimethylene terephthalate); PVOH, poly(vinyl alcohol); PVC, poly(vinyl chloride); PU, polyurethane; SBR, styrene-butadiene rubber.

TABLE 1.2 Classification of Biopolymers

| Biodegradable | | | Nonbiodegradable | |
|---|--|-----------------------------|--|--|
| Bio-Based | | Fossil-Based | | Bio-Based |
| Plants | Microorganisms | Animals | | |
| Cellulose and its derivatives ¹ (polysaccharide) | PHAs (e.g., P3HB, P4HB, PHBHV, P3HBHH _x) | Chitin (polysaccharide) | Poly(alkylene dicarboxylate)s (e.g., PBA, PBS, PBSA, PBSE, PEA, PES, PESE, PESA, PPF, PPS, PTA, PTMS, PTSE, PTT) | PE (LDPE, HDPE), PP, PVC |
| Lignin | PHF | Chitosan (polysaccharide) | PGA | PET, PPT |
| Starch and its derivatives (monosaccharide) | Bacterial cellulose | Hyaluronan (polysaccharide) | PCL | PU |
| Alginate (polysaccharide) | Hyaluronan (polysaccharide) | Casein (protein) | PVOH | PC |
| Lipids (triglycerides) | Xanthan (polysaccharide) | Whey (protein) | POE | Poly(ether-ester)s |
| Wheat, corn, pea, potato, soy, potato (protein) | Curdlan (polysaccharide) | Collagen (protein) | Polyanhydrides | Polyamides (PA 11, PA 410, PA 610, PA 1010, PA 1012) |
| Gums (e.g. <i>cis</i> -1, 4-polyisoprene) | Pullulan (polysaccharide) | Albumin (protein) | PPHOS | Polyester amides |
| Carrageenan | Silk (protein) | Keratin, PFF (protein) | | Unsaturated polyesters |
| PLA (from starch or sugar cane) | | Leather (protein) | | Epoxy |
| | | | | Phenolic resins |

HDPE, high density polyethylene; LDPE, low density polyethylene; P3HB, poly(3-hydroxybutyrate); P3HBHH_x, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); P4HB, poly(4-hydroxybutyrate); PBA, poly(butylene adipate); PBS, poly(butylene succinate); PBSA, poly(butylene succinate-co-adipate); PBSE, poly(butylene sebacate); PC, polycarbonate; PCL, poly(ϵ -caprolactone); PE, polyethylene; PEA, poly(ethylene adipate); PES, poly(ethylene succinate); PESA, poly(ethylene succinate-co-adipate); PESE, poly(ethylene sebacate); PET, poly(ethylene terephthalate); PFF, poultry feather fiber; PGA, poly(glycolic acid), polyglycolide; PHA, polyhydroxyalkanoate; PHBHV, poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PHF, polyhydroxy fatty acid; PHH, poly(3-hydroxyhexanoate); PLA, poly(lactic acid), polylactide; POE, poly(ortho ester); PP, polypropylene; PPF, poly(propylene fumarate); PPHOS, polyphosphazenes; PPS, poly(propylene succinate); PTA, poly(tetramethylene adipate); PTMS, poly(tetramethylene succinate); PTSE, poly(tetramethylene sebacate); PTT, poly(trimethylene terephthalate); PVC, poly(vinyl chloride); PVOH, poly(vinyl alcohol); PU, polyurethane.

¹Acetyl cellulose (AcC) is either biodegradable or nonbiodegradable, depending on the degree of acetylation. AcCs with a low acetylation can be degraded, while those with high substitution ratios are nonbiodegradable.



Biopolymers can also be classified based ...

on how they respond to heat:

- **Thermoplastics**
- **Thermosets**
- **Elastomers**

The volume of bio-based thermoset biopolymers exceeds the volume of bio-based thermoplastic biopolymers

on their composition:

- Blends
- Composites
- Laminates.

Biocomposites: biopolymers or synthetic polymers reinforced with natural fibers, such as sisal, flax, hemp, jute, banana, wood, and various grasses, and/or fillers and additives.

Novel biocomposites are based on a biodegradable matrix polymer reinforced with natural fibers.

Types and chemistry of biopolymers

- chemical synthesis



- PLA obtained by polymerizing lactic acid, which is produced by fermenting saccharides and starch derived from corn, potato, and sugarcane.
- Poly(butylene succinate) resins, produced from succinic acid derived from starch and 1,4-butane diol.
- Polyamide 11, produced from castor oil.

- microorganism production



- poly-3-hydroxybutyrate type resins
- copolymers of 3-hydroxybutyrate and 3-hydroxyhexanoate

- natural

(derived from the biomass, i.e., from plants)



- cellulose acetate
- esterified starch
- chitosan-cellulose-starch
- starch-modified polyvinyl alcohol

Polyhydroxyalkanoates (PHA)

Koller, M.; Mukherjee, A. A New Wave of Industrialization of PHA Biopolyesters. *Bioengineering* 2022, 9, 74. <https://doi.org/10.3390/bioengineering9020074>

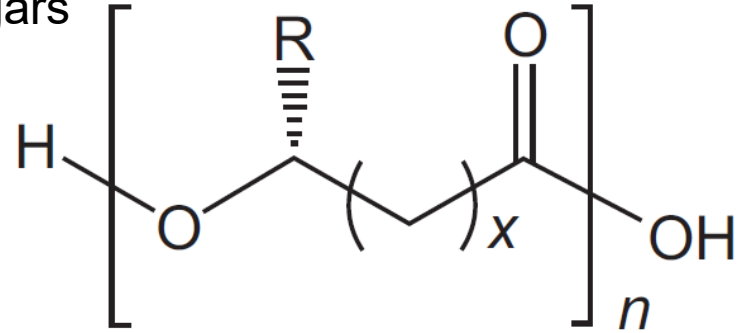
Li, Z.; Yang, J; Loh X.J. Polyhydroxyalkanoates: opening doors for a sustainable future. *NPG Asia Materials* 2016 8, e265; doi:10.1038/am.2016.48

Raza, Z.A.; Abid, S.; Banat, I.M. Polyhydroxyalkanoates: Characteristics, production, recent developments and applications. *International Biodeterioration & Biodegradation* 2018, 126, 45–56. doi: 10.1016/j.ibiod.2017.10.001



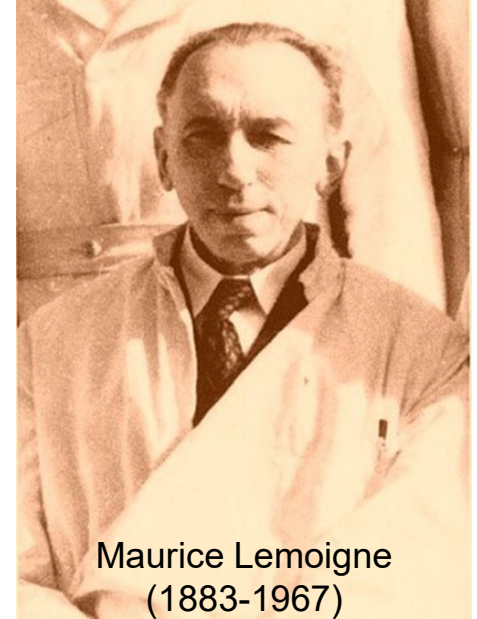
Polyhydroxyalkanoates (PHAs)

- PHAs are polyesters produced in nature by microorganisms (prokaryotic and eukaryotic), including through bacterial fermentation of sugars or lipids
- two groups of bacteria with regards to PHAs production
 - requiring limitation of a nutrient such as phosphorous, nitrogen, oxygen or magnesium to accumulate PHAs; no accumulation during growth phase
 - accumulates PHAs during the growth phase and do not require any nutrient limitation



Polyhydroxyalkanoates

- Lemoigne first discovered PHA in *Bacillus megaterium* in the form of poly (3-hydroxybutyrate) (PHB) in 1925/6
- PHAs serves intracellular carbon and energy storage purposes
- despite the discovery of more than 150 different hydroxyalkanoate (HA) building blocks that constitute the PHA biopolyester family, only a limited number of PHA copolymer types have reached industrial maturity

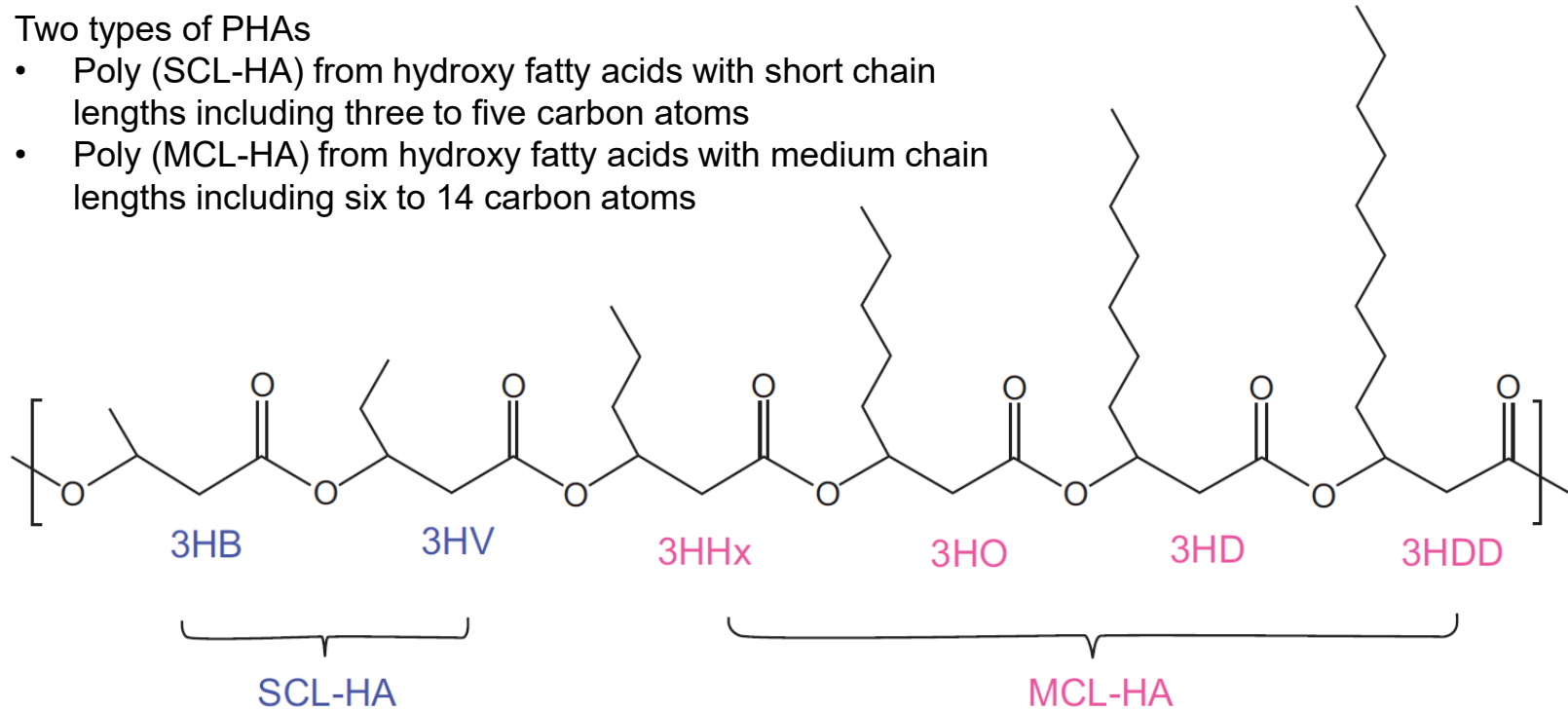


Maurice Lemoigne
(1883-1967)

Polyhydroxyalkanoates

Two types of PHAs

- Poly (SCL-HA) from hydroxy fatty acids with short chain lengths including three to five carbon atoms
- Poly (MCL-HA) from hydroxy fatty acids with medium chain lengths including six to 14 carbon atoms



Some commonly synthesized short-chain-length

PHA monomers (SCL-HA) and middle-chain-length PHA monomers (MCL-HA). 3HB: 3-hydroxybutyrate, 3HV: 3-hydroxyvalerate, 3HHx: 3-hydroxyhexanoate, 3HO: 3-hydroxyoctanoate, 3HD: 3-hydroxydecanoate, 3HDD: 3-hydroxydodecanoate.

PHA development

- ecological concerns of fossil plastics and limitations of fossil resources motivated research towards the industrial use of PHA biopolymers
- skyrocketing crude oil prices in the 1970s prompted the first commercialization efforts
- however, much of that effort slowed down after the recovery of crude oil prices
- Price and availability still primary obstacles towards commercialization of PHAs



Sources: Federal Reserve; Energy Information Administration; Bloomberg Financial Markets

PHA development

- calculations based on several life cycle studies estimate that replacement of 1 kg fossil plastic by PHA could salvage on average CO₂ emissions by 2 kg and around 30 MJ of fossil resources on an energy basis
- material properties of PHAs depend on the type and distribution of various monomeric building blocks
- versatile group of biomaterials, with characteristics that range from elastomeric to semicrystalline thermoplastic-like polymers
- The material properties of PHAs do not exactly match those of the fossil-based competitors
- → PHAs were not drop-ins for fossil plastics



PHA production

- main drawback is the high cost associated with fermentative production
- major factors affecting the cost of production include the type of carbon source, running cost of fermentation, and process productivity
- PHAs contents in the cell biomass are very important for economical extraction process
- also, the selection of a hyper productive microorganism is equally important
- average cost of PHB production (100,000 ton/year scale) were reported to be between 2.6 and 6.69 USD/kg

What is the price of common synthetic polymers?



| Sr.No. | Carbon source | Bacterial strain | Fermentation mode | Type of polymer | Limiting factor | CDW (g/l) | Accumulation of PHA of CDW | Extraction method | Yield (g/l) | Ref. |
|--------|--|--|-------------------|-------------------------------------|-----------------|-----------|---|---------------------------------------|--|---------------------------|
| 1 | Triglycerides | <i>Pseudomonas resinovorans</i> NRRLB-2649 | Fed-batch | mcl | NA | 3.3 | 45% | Solvent | 1.1–2.1 | (Ashby and Foglia, 1998) |
| 2 | Hexadecane | <i>P. aeruginosa</i> ATCC 10145 | Continuous | mcl | Nitrogen | 1 | 7.5% | NA | NA | (Chayabutra and Ju, 2001) |
| 3 | Glucose | <i>Bacillus cereus</i> | Batch | scl | NA | 3.4 | 47.9% | Solvent | 1.19 | (Devi et al., 2015) |
| 4 | Octanoate | <i>P. oleovorans</i> ATCC 29347 | Continuous | mcl | Carbon Nitrogen | NA | 10.1% 56.1% | NA | NA | (Durner et al., 2000) |
| 5 | Technical oleic acid Waste free fatty acids from soybean oil Waste frying oils Glucose | <i>P. aeruginosa</i> 42A2 NCIB 40045 | Batch | mcl/lcl | Nitrogen | 3.2 | 54.6% 66.1% | Solvent | NA | (Fernandez et al., 2005) |
| 6 | Fatty acids | <i>P. putida</i> Bet001 | Batch | md | Nitrogen | NA | 29.4% 16.8% 49.7–68.9% | Solvent | 10.12–15.45 | (Gumel et al., 2014) |
| 7 | Glucose Soybean oil | <i>P. stutzeri</i> 1317 | Batch | mcl | NA | 2.3 | 52% 63% | Chloroform-sodium hypochlorite method | NA | (He et al., 1998) |
| 8 | Decanoate | <i>P. aeruginosa</i> IFO 3924 <i>P. aeruginosa</i> PAO 1 <i>P. aeruginosa</i> IFO 3755 <i>P. aeruginosa</i> IFO 14164 | Batch | md | Nitrogen | 2.2 | 23% 2 10% 3.1 22% 2.8 21% | Solvent | NA | (Hori et al., 2002) |
| 9 | Terephthalic acid | <i>P. putida</i> GO16 <i>P. putida</i> GO19 <i>P. frederiksbergensis</i> GO23 <i>P. putida</i> KCTC 2407 | Batch | md | Nitrogen | 1 | 27% 23% 24% | NA | 0.25 0.25 0.27 | (Kenny et al., 2008) |
| 10 | 10-undecenoic acid and 10-undecynoic acid | <i>P. oleovorans</i> ATCC 29347 | Batch | md | NA | 0.40–0.94 | 1.8–37.4% | Solvent | 0.01–0.32 | (Kim et al., 2000) |
| 11 | n-alkanes and 1-alkenes | <i>P. aeruginosa</i> IFO3924 | Batch | mcl | Nitrogen | 2 | 25% | Solvent | NA | (Lageveen et al., 1988) |
| 12 | Palm oil | <i>P. aeruginosa</i> IFO3924 | Batch | mcl | Nitrogen | 1.8–2.7 | 16–39% | Solvent | 0.28–1.06 | (Marsudi et al., 2008) |
| 13 | Glucose | <i>Lysinibacillus sphaericus</i> GBS1 <i>L. sphaericus</i> GBS2 <i>L. sphaericus</i> GBS3 <i>L. sphaericus</i> GBS4 <i>L. sphaericus</i> GBS5 <i>L. sphaericus</i> GBS6 | Batch | scl | NA | NA | 60% 50% 33% 14% 66% 70% | Chemical Digestion | 1.2 0.9 1.3 0.2 0.12 1.3 | (Biradar et al., 2015) |
| 14 | Commercial glycerol Waste glycerol | <i>Cupriavidus necator</i> DSM 545 | Fed-batch | scl | Nitrogen | NA | 62% 52% | Solvent | 51.2 38.1 | (Cavalheiro et al., 2009) |
| 15 | n-octane | <i>P. oleovorans</i> GPo1 | Fed-batch | N.A | Nitrogen | 37.1 | 33% | NA | 12.1 | (Preusting et al., 1993) |
| 16 | Sugarcane liquor | <i>P. fluorescens</i> A2a5 | Batch | scl | Nitrogen | 32 | 70% | Solvent | 22 | (Jiang et al., 2008) |
| 17 | Waste cooking oil | <i>Pseudomonas</i> sp. PS1 <i>Pseudomonas</i> sp. | Batch | N.A | Nitrogen | NA | NA | Solvent | 2.3 2.7 | (Prasad and Sethi, 2013) |
| 18 | Crude palm oil kernel oil Crude palm oil Palm kernel oil Palm olein Cooking oil Olive oil Coconut oil Sunflower oil | <i>C. necator</i> H16 | Fed-Batch | scl co-polymer (P3HB & P3HB-co-3HV) | Nitrogen | 5.0 | 67% 4.6 75% 5.6 77% 5.2 70% 5.4 78% 4.9 80% 4.7 72% 4.4 76% | Solvent | 3.4 3.5 4.3 3.6 4.2 3.9 3.3 3.4 | (Lee et al., 2008) |
| 19 | Pigeon pea waste Paddy waste Waste frying oil Sugarcane bagasse Rice bran | <i>P. aeruginosa</i> | Batch | N.A | NA | NA | 39% 41% 42% 60% 48% | NA | NA | (Khandpur et al., 2012) |

International Biodeterioration & Biodegradation 2018, 126, 45–56. doi: 10.1016/j.ibiod.2017.10.001

PHA production

Extraction of PHAs from bacterial cells:

- solvent extraction
- flotation method
- chemical or enzymatic digestion of cell components
- supercritical fluid extraction
- aqueous two-phase extraction

Further downstream and purification processes



https://youtu.be/YWs_VVLNWC0

PHA production

- to lower the price different materials and side-products can be used as carbon sources: whey, wheat, rice bran, starch, sugar-cane molasses, vegetable oils
- current annual production <10 kt
- however, capacity expansions of over 1.5 million t have already been announced for the next 5–10 years (an additional 1 million t are in the planning stages)
- (estimated global plastic production: roughly 400 Mt per year)



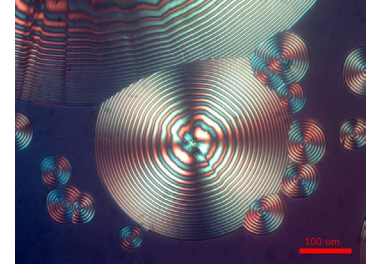
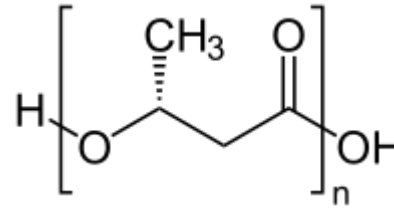
most prominent PHAs

- homopolymer poly(3-hydroxybutyrate) (P(3HB))
- the copolymers poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3HB-co-3HV)), poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P(3HB-co-4HB)), and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (P(3HB-co-3HHx))
- to a minor extent, the homopolymer poly(4-hydroxybutyrate) (P(4HB)) and some medium-chain-length PHA (mcl-PHA) copolymers



P(3HB) or PHB

poly(3-hydroxybutyrate) (homopolyester)



constitutes the by far best-studied representative of the PHA family; produced by the largest number of microbes

Cons:

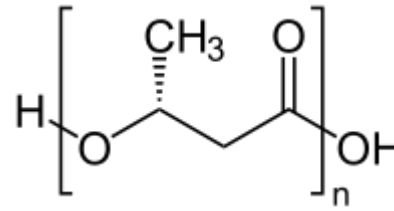
- very narrow melt processing window since its melting temperature is close to its degradation temperature
- highly crystalline; therefore, it has a low elongation at break and is brittle
- lower biodegradability rates compared to other types of PHA

Pros:

- production of hard, creep-resistant items, which do not change their properties over a broad temperature range even when stored for several years
- outperforms many competing petrochemical plastics in UV resistance and mechanical stability



P(3HB) or PHB

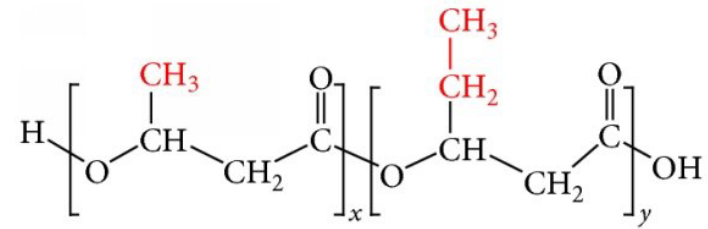


Applications:

- films, coatings, injection molded products
- 3D-printed objects
- biomedical application (implants, artificial esophagus)
- replacement for LD-PE in electronics



P(3HB-co-3HV)



poly(3-hydroxybutyrate-co-3-hydroxyvalerate) copolyester

- can be produced by feeding appropriate 3HV precursors
- with increasing 3HV content, melting point T_m decreased: 170 °C for P(3HB) and 140 and 130 °C for the two P(3HB-co-3HV) grades, degree of crystallinity (80, 60, and 35%), tensile strength (40, 25, and 20 MPa), flexural modulus (3.5, 1.2, and 0.8 GPa), elongation at break (8, 20, and 50%), and impact strength (60, 110, and 350 J/m))
- lower T_m broadens processing windows, making them suitable especially for extrusion, injection, and blow molding, which enabled more applications of injection-molded parts, bottles, extruded sheets, films, fibers, and coated paper

Summary questions

- What is the difference between degradable and biodegradable?
- Name a fossil-based biodegradable polymer.
- Name a biobased non-degradable polymer.
- What are PHAs?
- Which PHAs are used industrially already?



Reading 2

Title: Biopolymer-Based Sustainable Food Packaging Materials: Challenges, Solutions, and Applications

Authors: Perera *et al.*

Foods **2023**, 12, 2422

Read before lecture on January 22:

- Chapters 1-5
- Chapters 6.1.1 and 6.1.2
- Browse through tables 1 & 2

Reading discussion peer grading

Legend:
present: no = 0; yes = 1
camera on: no = 0; yes = 1
active participation in discussion: little to none = 0; ok = 1; very good = 2
active participation in preparing Padlet content: little to none = 0; ok = 1; very good = 2

| points | grade |
|--------|-------|
| 50-45 | 5 |
| 40-44 | 4 |
| 35-39 | 3 |
| 30-34 | 2 |
| 25-29 | 1 |
| 0-24 | 0 |

| Group 1 | | Discussion of Reading 1 | | | | score |
|---------|--|-------------------------|-----------|------------------------------------|--|-------|
| | | present | camera on | active participation in discussion | active participation in preparing Padlet content | |
| Name1 | | | | | 0 | |
| Name2 | | | | | 0 | |
| Name3 | | | | | 0 | |
| Name4 | | | | | 0 | |
| Name5 | | | | | 0 | |

Reading 1 discussion

Title: Biopolymers: overview of several properties and consequences on their applications

Authors: K. Van de Velde & P. Kiekens

Polymer Testing **2002**, 21, 433–442

Discussion items:

- Which (main) polymers are discussed in this article and how are they similar or how do they differ chemically from each other?
- Which material properties are discussed? How do they correlate with each other?
- How are those properties important for composite materials?

Instructions:

Write your names, summary and updated figures in e.g. PowerPoint. Save the text as image file (.jpg) and upload it to the Padlet page:

https://padlet.com/michaelhummel/CHEME2155_2024

| Group 1 | |
|----------------|----------|
| Babak | Abdi |
| Sagar | Gurung |
| Carl-Alfons | Antson |
| Anupama | Bhandari |
| Jianhui | Feng |

| Group 2 | |
|----------------|------------|
| Giorgia | Donatoni |
| Andrea | Bonvini |
| Christian | Zimmermann |
| Jan | Kantelinen |
| Azad | Karis |

| Group 3 | |
|----------------|------------------|
| Helmi | Hanninen |
| Eva | González Carmona |
| Sara | Hautojärvi |
| Laura | Ahvenjärvi |
| Nikita | Jamkin |

| Group 4 | |
|----------------|----------------|
| Laura | Ferrer Pascual |
| Trung | Luong |
| Rasmus | Huttunen |
| Patrick | Hyvärinen |
| Parham | Koochak |

| Group 5 | |
|----------------|----------|
| Muhammad | Umer |
| Asfar | Khan |
| Sardar | Hayat |
| Kaisla | Lehtipuu |
| Anneli | Lepo |

| Group 6 | |
|----------------|----------|
| Daniel | Schröfl |
| Clemens | Hellmig |
| Emilia | Ikävalko |
| Asle | Berget |
| Lukas | Fliri |

| Group 7 | |
|----------------|------------|
| Henna | Koponen |
| Sampsa | Mäenpää |
| Mikael | Nortes |
| Veera | Ollikainen |
| Tiina | Pasanen |

| Group 8 | |
|----------------|----------|
| Johannes | Peace |
| Ilari | Peltonen |
| Sayoojya | Prasad |
| Tiinamari | Seppänen |
| Nissa | Solihat |

| Group 9 | |
|----------------|----------|
| Eveliina | Palo |
| Oona | Hanska |
| Joona | Pystynen |
| Luka | Louhi |
| Eetu | Varttila |

| Group 10 | |
|-----------------|-----------|
| Jere | Pätsikkä |
| Krisnadewi | Suciati |
| Possathornwalee | Prasomsri |
| Öykü | Sahintas |
| Yuxuan | Sun |

| Group 11 | |
|-----------------|-----------|
| Anni | Raulahti |
| Anniina | Tamminen |
| Elsa | Vuorenmaa |
| Mimi | Tran |
| Mariel | Mylly |

| Group 12 | |
|-----------------|---------------------|
| Chamodya | Ranawaka Arachchige |
| Elizaveta | Tapaila |
| Moa | Vesterlund |
| Anitha | Venkatramani |
| Konsta | Vainikainen |

| Group 13 | |
|-----------------|---------------------|
| Anastasia | Tervo |
| Timo | Tuoresjärvi |
| Julia | Turunen |
| Fatemeh | Yahyaieian Balouchi |
| Can | Yücel |