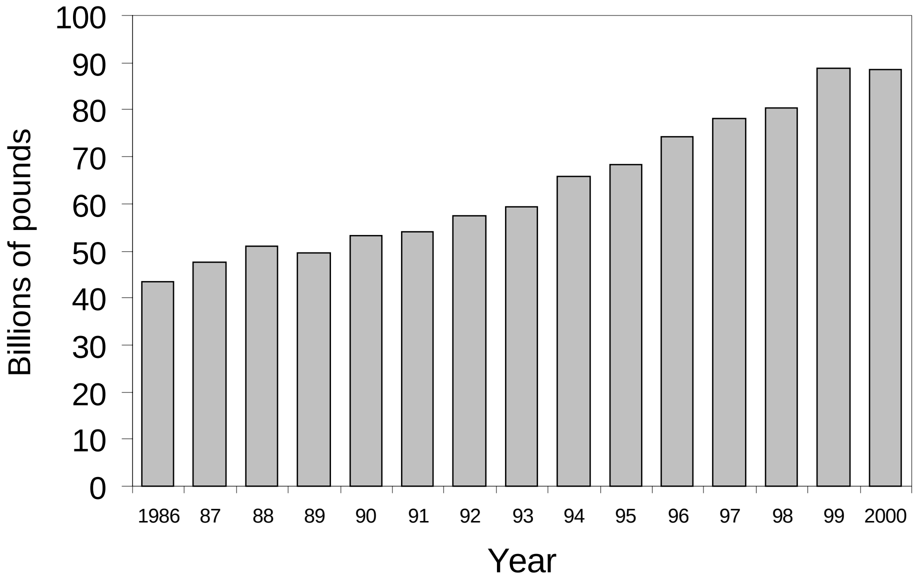
Plastics and the Environment

Plastics production has been increasing.



U. S. plastics production

Worldwide production exceeds 200 billion pounds. By volume, plastics production exceeds steel production. We are in the Age of Plastics

Increased production has lead to environmental concerns.

(1) Plastics are made from diminishing fossil resources.

Current plastics production technologies are not sustainable in the long run.

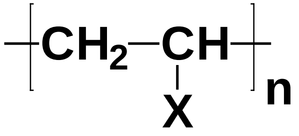
6-8% of petroleum use is for plastics, contributing to U.S. reliance on imports.

(2) Plastics Waste

Municipal solid waste (MSW) contains about 10% plastics by weight and 18% by volume. The figures are increasing.

Less than 10% of plastics waste is recycled; over 90% is incinerated or landfilled. Composting infrastructures are being developed to divert MSW from incinerators and landfills, but over 90% of current plastics are neither biodegradable nor compostable.

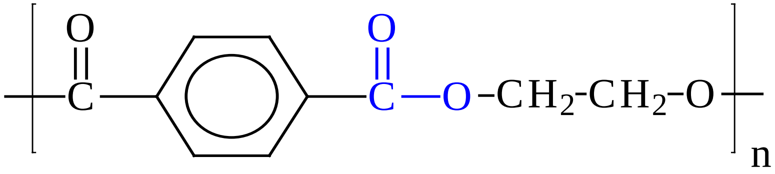
Five polymers account for 90% of all plastics. Four are polyolefins.



$$\left[CH_2 - \underset{X}{CH} \right]_n$$

Polyolefins are not biodegradable. The single most important reason for their stability is that they have carbon-carbon single bonds in their backbone.

The fifth is PET.

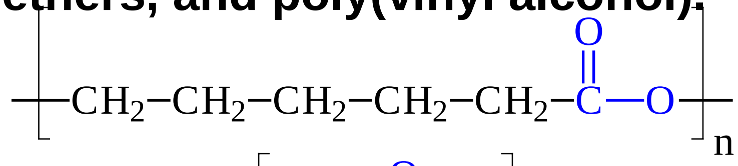


Most recycled plastic is PET. Polyesters are generally biodegradable; the oxygen heteroatom in the back-bone leads to environmental degradation by hydrolysis. PET is an exception. PET is not biodegradable. The phenyl ring stiffens the chain and increases crystallinity, which impedes access of water molecules.

Some petroleum-derived polymers are biodegradable, but they are specialty polymers, and produced in much smaller amounts.

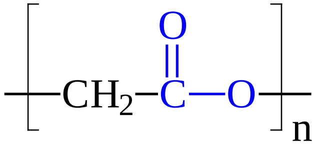
They include thermoplastic polyesters and copolyesters, polyamides (nylons), copoly(ester amides), polyethers, and poly(vinyl alcohol).

poly(ε-caprolactone) (PCL)



$$-\!\left[CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O\right]_n\!-$$

polyglycolic acid (PGA)

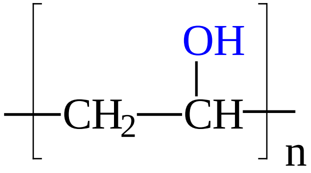


$$-\!\left[CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O\right]_n\!-$$

poly(ethylene glycol) (PEG), equivalent to poly(ethylene oxide) (PEO).

$$-\!\left[CH_2-CH_2-O\right]_n\!-$$

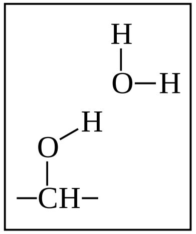
poly(vinyl alcohol) (PVA)



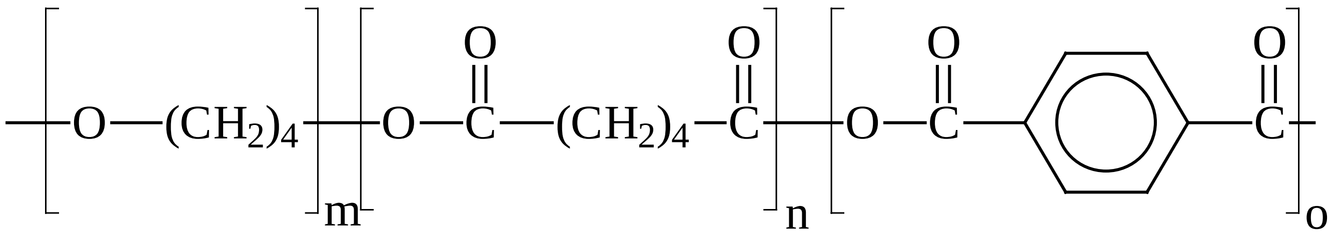
$$-\!\left[CH_2-\overset{\overset{\displaystyle OH}{|}}{C}H\right]_n\!-$$

Polyesters, polyethers, and polyamides have heteroatoms in the main backbone chain; they are biodegradable.

PVA also degrades by hydrolysis, in spite of its –C–C– backbone, because the hydroxyl group on alternate carbon atoms leads to strong interactions with water.



copolyesters and poly(ester amides)



A generic copolyester.

Synthesis often involves diols (e.g., ethylene glycol, 1,4-butanediol, 1,6-hexanediol) and dicarboxylic acids (e.g., adipic, succinic, sebacic). Terephthalic acid is sometimes a component; the aromatic diacid increases chain rigidity.

An example is Eastar Bio™ copolyester, manufactured by Eastman Chemical. It is a random poly(butylene adipate-*co*-terephthalate) containing 50% terephthalate. Film is prepared by solvent casting.

A compostable garbage bag made from EastarBio™ copolyester.

Tensile properties of EastarBio, Grade GP.

Tensile strength (MPa)	22
Elongation at break (%)	700
Modulus (MPa)	107

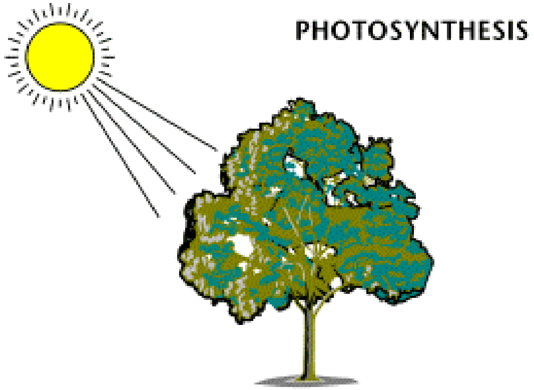
In response to environmental (and other) concerns:

Plastics manufacturers (some old companies and some new companies) are aiming to produce new plastics that are made from renewable feedstocks and biodegradable.

- **Both commodity plastics and specialty biomedical plastics are being developed.**
- **Thermal processing is preferred over film casting because of the ease and speed of processing with current thermal processing equipment.**
- **Two requirements of new materials are adequate properties and favorable cost-performance ratios.**
- **Governments are providing incentives and academics are active in research.**
- **The technologies have not yet been optimized, in contrast to petroleum-based technologies. Costs can be reduced.**

The new materials are coming to be called biomaterials or bioproducts.

Biomaterials are made from biomass.



- Biomass is the total mass of matter generated by the growth of living organisms, including plants, animals, and microorganisms.

- 100 to 200 billion tons of new biomass are produced each year.

- Most biomass now simply returns to the ecosystem through natural processes of decay, without being exploited for practical use.

- Some biopolymers are already available for biomaterials; they are being extracted for commercial, non-food purposes on large scales.

Multiple strategies have been adopted in producing new biopolymeric materials.

1. **Natural polymers are extracted and used as is. [starch]**
2. **Natural polymers [starch] are broken down into monomers [sugars]. The monomers are converted to other monomers by *fermentation* [lactic acid] which are then polymerized by conventional methods [poly(lactic acid)].**
3. **Natural polymers [starch] are broken down into monomers [sugars]. The monomers are then converted directly to polymers by microorganisms through *fermentation* [microbial polyesters].**
4. **Small biomolecules [vegetable oils] are extracted and then cross-linked by conventional methods to produce strong thermosetting plastics [vegetable oil thermosets].**

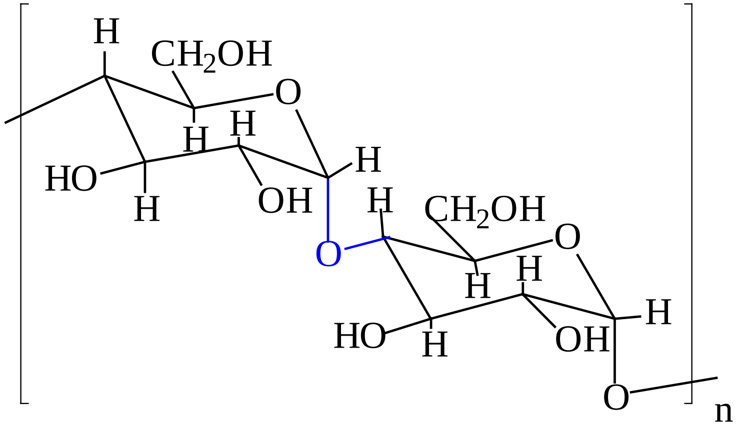
Approach 1. Natural polymers are extracted and used as is.

Starch is a polysaccharide.

•Carbohydrates include monosaccharides, disaccharides, and polysaccharides. Polysaccharides are the most abundant type of carbohydrate; they make up approximately *75 percent of all organic matter*.

•Starch is by far the most inexpensive commercial biopolymer. It is the only biopolymer that is competitive with polyethylene in price.

•The major polymer components of starch are amylose and amylopectin.

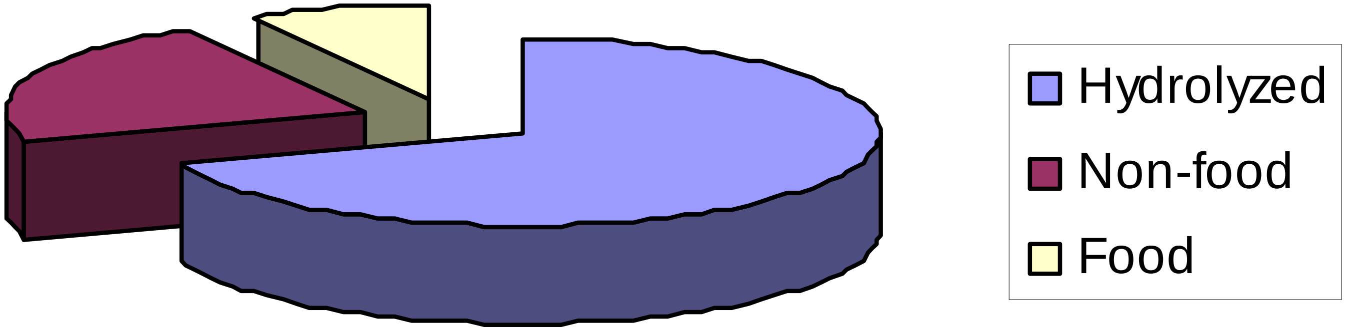


Amylose

Amylose is a linear polymer.

Amylopectin is branched amylose.

Starch is found in agricultural crops, including corn (maize), potatoes, wheat, and many others. Annual world production of starch is over 70 billion pounds, half of which is produced in the United States.

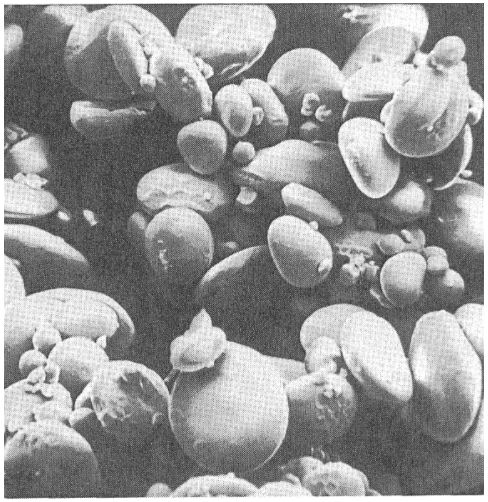


Commercial uses of starch

Three forms of starch are granular, gelatinized, and thermoplastic.

Granular Starch

Natural starch occurs in the cell in the form of granules.



Scanning electron microscope image of wheat starch.

The first use of starch in plastics was polyethylene film filled with granular starch. The film was marketed as "biodegradable", but the PE residue does not biodegrade. The film is not a biomaterial.

Gelatinized Starch

Starch granules are gelatinized upon heating in the presence of water; the granules are disrupted and the starch molecules become more disordered. The gelatinization temperature ranges from about 70 °C in excess water to above 200 °C at low moisture content.

Films can be cast from gelatinized starch if it is plasticized. Common plasticizers are glycerol, sorbitol, and other polyols.

$CH_2OH–CHOH–CH_2OH$

glycerol

Thermoplastic Starch (TPS)

Under proper conditions of temperature, pressure, water content, and shear (as in an extruder), the crystalline structure of the starch granules is destroyed, and the starch becomes thermoplastic. TPS can be processed with standard plastics equipment.

A Brabender extruder

If a burst of steam is generated as the starch leaves the extruder die, the starch expands to form extruded starch foam. The foam has a *cellular* structure, made up of numerous cells distributed throughout the material.

Starch-based packaging "peanuts" now make up 20% of the loose-fill packaging market.

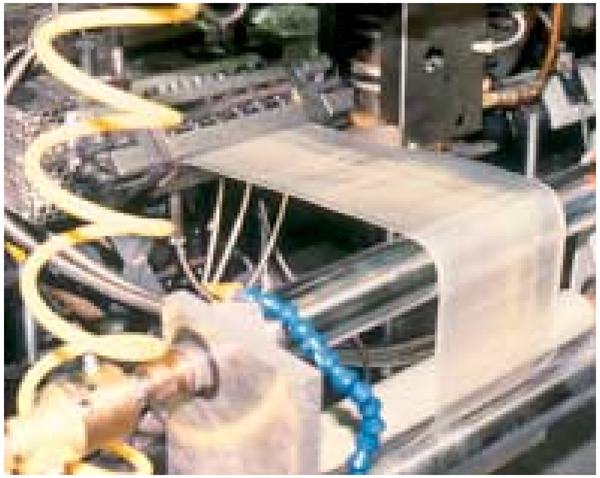
The major limitation of starch as a material is its hydrophilicity. Its physical properties are water sensitive.

Strategies for decreasing sensitivity to water include:

(a) derivitization (chemical modification), such as acetylation, whereby some of the hydroxyl (–OH) groups are converted into acetyl (–$OCOCH_3$) groups (e.g. packaging peanuts).

(b) coatings and laminates (using other materials)

Starch foam coated with a microbial polyester (PHBV) to provide resistance to hot and cold water.



Starch-poly(ε-caprolactone) laminate for packaging.

(c) blending with other polymers

Blends. **A blend is a homogeneous mixture of two of more polymers.**

By varying the composition and processing of blends, it is possible to manipulate properties.

The aim with starch is to combine the low-cost of starch with higher-cost polymers having better physical properties.

******The leading commercial starch-containing plastic is a blend of starch and poly(ε-caprolactone).******

It is a hybrid material, part biopolymer and part petroleum based polymer; but it is biodegradable. The blends are thermoplastic. PCL increases water resistance and adds strength.

Starch-poly(ε-caprolactone)

Its strength and water resistance depend on composition. Film properties can be varied from those resembling LDPE to HDPE.

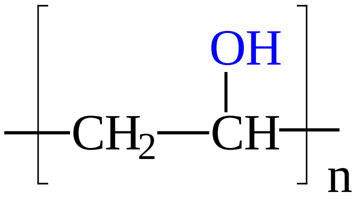
Applications include agricultural mulching film (12-15 μm), clips, plant pots, yard waste bags, shopping bags, packaging film, cutlery and food service ware, and others..

Agricultural products made from MaterBi™, manufactured by Novamont S.P.A., Italy. Two fabricators that use MaterBi are Biocorp North America and Polargruppen A/S.

Properties of MaterBi,

	grade AF05H	Z class
Tensile strength (MPa)	20	20-30
Elongation at break (%)	409	780-890
Tensile modulus (MPa)	107	180-185

Starch-poly(vinyl alcohol) blends (a hybrid) have also been commercialized. They are thermoplastic.



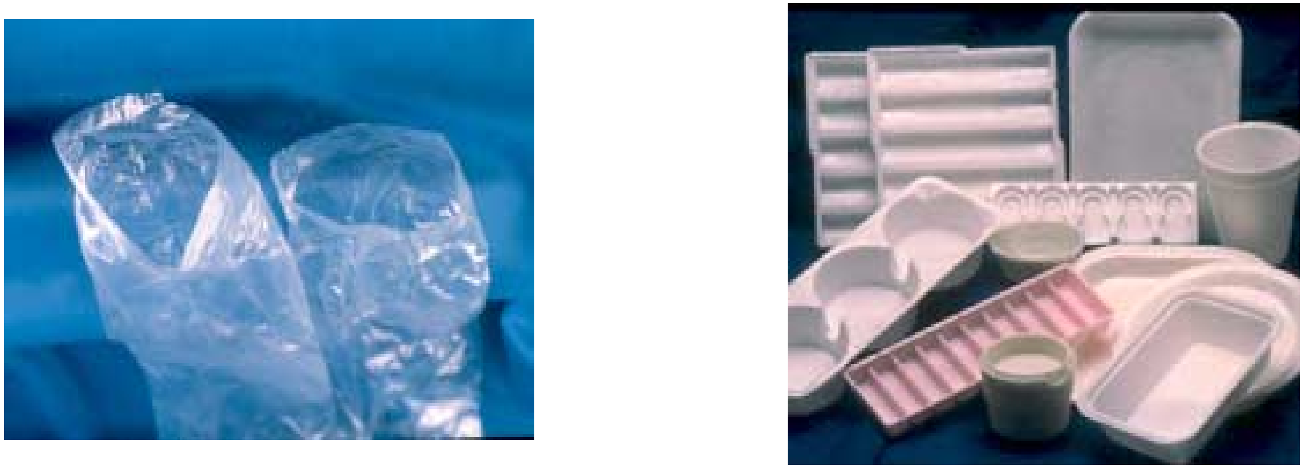
$$\left[-CH_2-\overset{\overset{OH}{|}}{CH}- \right]_n$$

PVA is produced by alcoholysis of poly(vinyl acetate). The amount of residual acetate groups can be controlled.

That affects the degree of crystallinity of the PVA.

A wide range of blends can be produced by varying the amount of PVA, its molecular weight, and its crystallinity.

With one formulation, the mechanical properties at 55 percent relative humidity are similar to those of polyethylene.



Examples: (a) starch-PVA blown film (e.g., for water-soluble laundry bags used in hospitals); (b) starch-PVA extruded foam (e.g., for food service items).

(d) composites (consisting of two or more phases). Minerals, like silicates(clay) or carbonates, increase stiffness and toughness.

Example. A starch-calcium carbonate-fiber composite.

Potato starch and limestone make up about 80% of the composite.

They are mixed with water and fiber (e.g., cellulose from recycled paper) to form a batter.

Thickeners and release agents are added and the batter is placed between two heated mold plates.

The water is converted to steam, expanding the batter. The product is finished with protective and water-proofing coatings.

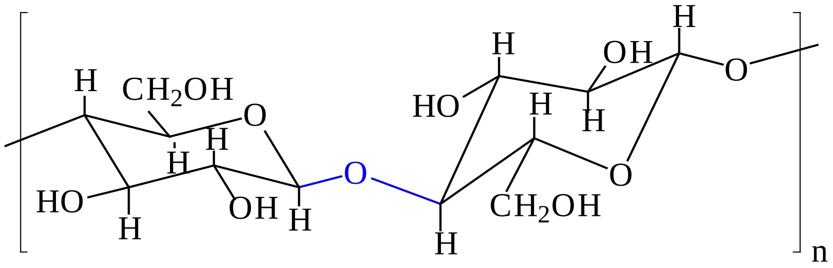
Earthshell® Packaging disposable food service ware, including the hinged-lid “clamshell” sandwich containers used in the fast-food industry.

Summary on starch-based plastics:

- **Starch is inexpensive and can be made thermoplastic.**
- **The water-sensitive nature of starch has to be controlled.**

Other commercial polysaccharides

Cellulose is the most plentiful polysaccharide. It is the most abundant organic compound on earth and alone accounts for *40 percent of all organic matter.* Oven-dried cotton contains about 90 % cellulose. An average wood has about 50% cellulose.



Cellulose

Well over 150 billion pounds of cellulose are produced commercially each year, mainly from wood but also from cotton.

Cellulose is not thermoplastic, which limits plastics applications.
Upon heating, it thermally degrades before softening.

Some materials can be film cast even when they are not thermoplastic; cellophane is regenerated cellulose formed by film casting.

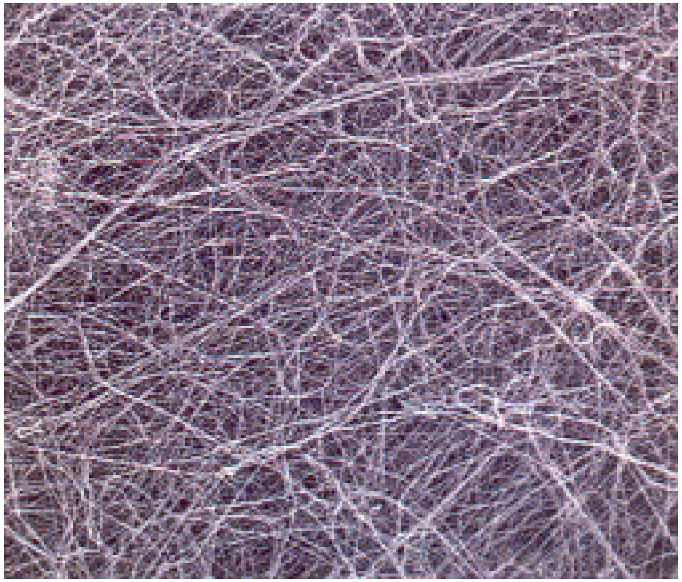
A recent development:
C&E News, April 26, 2004

Bacterial cellulose

Acetobacter xylinum cells make cellulose and spin it out in thin fibrils. The fibrils organize into flat ribbons. [In contrast, plant cellulose forms fibril bundles that are less uniform, not as crystalline, and 200 times thicker.] Bacterial cellulose has a porous structure that can hold water.

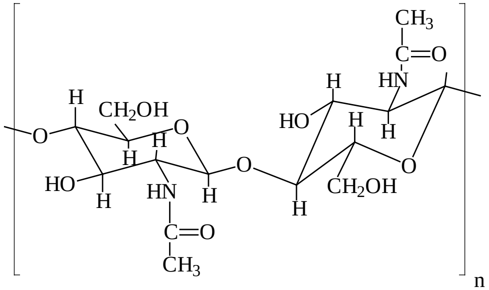
Properties: regular homogeneous nanostructure, capacity to hold water, stable, mechanically strong, flexible, biocompatible.

Application. Wound dressing for chronic wounds, ulcers, and burns.

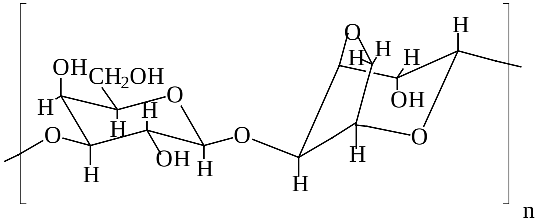


Chitin and chitosan

Chitin, another abundant polysaccharide, is found in shellfish and insects and some fungi. It is not thermoplastic. Films can be cast.



chitin



agarose, the main component of agar

Seaweed Polysaccharides: agar, carrageenan, alginate

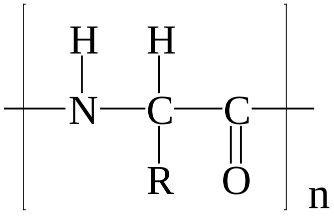
Seaweed polysaccharides are thermoplastic. They also are gelling polysaccharides, and form good cast films. They have been used to form encapsulating gel beads for drug delivery systems. They are also used as thickeners, emulsifiers, or stabilizers in food products, toothpastes, and other products.

Bacterial polysaccharides: xanthan, dextran, welan,and others.

Bacterial polysaccharides are prepared through large-scale fermentation. Xanthan is produced in the largest amounts, currently 20-40 million pounds a year. Molasses or corn syrup is the feedstock, and *Xanthamonas campestris* is the biological agent. Bacterial polysaccharides are used as thickeners and stabilizers in food applications, and in miscellaneous industrial applications.

Commercial Proteins

A generic protein monomeric unit; the R in the structure represents the side chain of an amino acid.



Animal proteins: Collagen (gelatin), casein, silk, keratin, whey protein

Collagen is the most abundant protein found in mammals. It is an insoluble fibrous protein found in connective tissues, animal skins and hides, blood vessels, tendons, and ligaments.

Gelatin is denatured collagen in which the triple helices of collagen are disrupted and partially hydrolyzed, leaving polymer chains that are largely disordered and unorganized. Gelatin is soluble in water. It has both food and non-food uses, including drug encapsulation.

Casein, from cow's milk, has food and non-food uses, including as an adhesive.

Silks are externally spun fibrous protein secretions. Silkworm silk is as strong as nylon; spider silk is stronger than nylon. On a strength-to-weight basis both outperform steel.

In **fibroin**, silk's major component, ordered helical regions pack together in bundles to give silk its strength. Amorphous connecting segments provide reduced crystallinity and increased flexibility.

Plant proteins: soy protein, zein from corn (maize), wheat gluten, potato proteins, and pea proteins

Soy protein is thermoplastic. Soybeans consist of approximately 30 to 45 percent protein and 20 percent oil. Soy protein is currently used for making plywood adhesive and coatings for paper and paperboard.

A historical note

Henry Ford experimented with soy meal in the manufacture of automobiles. [Soy meal is what is left after the soy oil is extracted from soybeans.] In 1941 he produced an entire prototype "soybean plastic automobile," including a plastic body. World War II interrupted Ford's development of soybean plastics.

Ford's "soybean plastic" automobile.

Zein, from corn, is thermoplastic. It is water insoluble (hydrophobic). Zein forms fibers and films that are strong, tough, glossy, washable, dyeable, and grease resistant. Zein fabrics were at one time commercialized.

Summary on Approach 1.

Apart from starch, biopolymers extracted directly from biomass are currently too expensive for commodity plastics.

Some may find use as components in starch-based plastics.

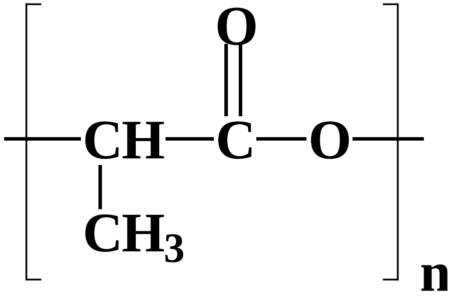
Some are already being used in biomedical applications, where cost is less of a factor.

Approach 2. Natural polymers [starch] are broken down into monomers [sugars]. The monomers are converted to other monomers by *fermentation* [lactic acid] which are then polymerized by conventional methods [poly(lactic acid)].

Hydrolyzed corn starch (dextrose, or "corn sugar") is fed to microorganisms in large "bioreactors". The microorganisms produce lactic acid, ($CH_3CHOHCOOH$) through fermentation.

Yields of lactic acid are greater than 90%. The lactic acid is recovered from the fermentation broth and purified in a multi-step process that represents a major part of production costs.

Poly(L-lactic acid) (PLA) is then synthesized from lactic acid. PLA is a polyester and is biodegradable.



$$\left[-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O- \right]_n$$

Properties

PLA is thermoplastic and can be processed by extrusion, injection molding, blow molding, and thermoforming.

It is insoluble in water and has good moisture and grease resistance. Other features include favorable flavor barrier properties and aroma barrier properties, low temperature heat-sealing, and good printability.

PLA degrades by hydrolysis, even in the absence of enzymes.

Its mechanical properties depend on molecular weight and crystallinity. Properties can be varied, through processing, so as to display, for example, the stiffness and tensile strength of poly(ethylene terephthalate).

Tensile properties of Natureworks 4042D (biaxially oriented film).

Tensile strength (MPa)	110/145
Elongation at break (%)	160/100
Tensile modulus(MPa)	3310/3860

Applications of PLA include (a) clear thermoformed articles for disposable food service items and other containers, and (b) fibers for bedding products, clothing, carpets, sheets and towels, and wall coverings.

Sealed packaging tray, and bedding products made from Natureworks PLA. (Cargill Dow Company). The major distributor of the PLA resin in the United States is Biocorp North America.

Poly(lactic acid-*co*-glycolic acid) has been used for several types of biomedical application, including microcapsules for drug delivery systems and orthopedic bone regeneration-repair materials.

Commercialization of a new plastic. Once a promising material is found in the laboratory, the next step is its commercialization. Commercialization includes the scale-up of production processes and the marketing of products. This can take investment capital of tens or hundreds of millions of dollars.

The joint-venture company, Cargill-Dow LLC, has taken the lead in the commercialization of PLA resins. It was formed in 1998.

- Cargill is a strong, private company in the agricultural, food, and commodity business. It has annual revenues of $60 billion and 100,000 employees. If it were a public company it would rank #12 in the Fortune 500. Cargill has the experience and patents to produce lactic acid by fermentation on large scales.

- Dow is a large chemical company. It has annual revenues of $33 billion and 46,000 employees. It ranks #44 in the Fortune 500. Dow has the experience, and the patents, for polymerizing PLA.

Cargill-Dow has the financial resources needed to launch a new commodity polymer. It recently built a new dedicated lactic acid manufacturing plant in Blair, Nebraska, with a capacity of 280 million pounds of lactic acid a year. Cargill-Dow has now invested over $350 million in the PLA venture, and is planning expansions.

Starch-PLA eating utensils (not yet commercialized).

Courtesy of U.S.D.A.

The utensils on the left are made of 55% cornstarch and 45% poly(lactic acid). They are biodegradable and compostable.

Non-degradable polystyrene utensils are shown on the right.

Summary on Approach 2.

So far, PLA is the only example, but a very successful one. The approach is general and other examples may appear.

Approach 3. Natural polymers [starch] are broken down into monomers [sugars]. The monomers are then converted by micro-organisms, through *fermentation,* directly to polymers [microbial polyesters].

Microbial polyesters

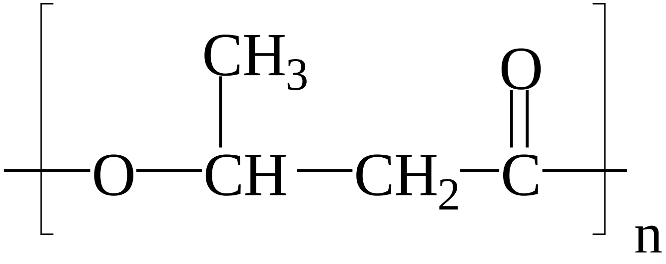
Some microorganisms produce polyesters naturally. For example, bacteria produce polyhydroxyalkanoates (PHAs), which occur as inclusion bodies deposited in granules in the cytoplasm.

PHAs serve as energy and carbon storage materials in bacteria. PHAs accumulate when carbon is in excess but some other nutrient limits growth. They are consumed when no external carbon source is available.

Large scale commercial production uses fermentation technologies. Starch is hydrolyzed and fed to microorganisms in bioreactors. (Cane sugar or beet sugar can also be used as substrates.) Cell growth is followed by polymer accumulation, which proceeds to as much as 80 to 95% of the cell's dry weight.

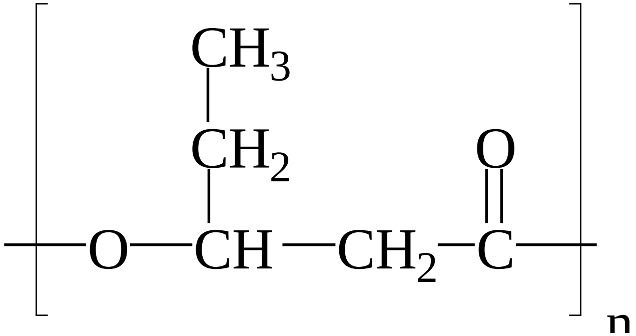
The microorganisms make the PHA, the cells are lysed, the cell debris is separated, and the PHA is extracted with a solvent, precipitated from water as a white powder, purified, and converted to pellets.

The most abundant PHA in nature, and the first to be discovered, is poly-3-hydroxybutyrate (PHB). Other PHAs have since been discovered, including those containing hydroxyvalerate units, as in poly-3-hydroxyvalerate (PHV).



$$\left[-O-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-\right]_n$$

PHB



$$\left[-O-\overset{CH_3}{\overset{|}{\overset{CH_2}{\overset{|}{CH}}}}-CH_2-\overset{O}{\overset{\|}{C}}-\right]_n$$

PHV

Microorganisms (e.g., *Ralstonia eutropha*) are fed carbon source substrates [glucose or sucrose for PHB, propionic acid for PHV; propionic acid can be produced by the fermentation of wood pulp waste.]

PHB is brittle but as the number of carbon atoms in the side chains of PHAs increases, e.g., as in PHV, the properties tend from polypropylene-like to elastomeric.

Copolymers

Copolymers, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), have a range of properties depending on composition.

The composition of the copolymer is controlled through the ratio of feedstocks used: glucose or sucrose for butyrate; propionic acid for valerate.

PHBV is thermoplastic and can be processed by injection molding, extrusion, blow molding, film and fiber forming, and lamination techniques.

It is stable in humid air and its barrier properties are not humidity-dependent.

Biodegradation begins with bacterial or fungal surface colonization. An extracellular depolymerase degrades and solubilizes the polymer into fragments. The fragments are then absorbed by the cell, resulting in complete biodegradation.

Applications

PHBV can be processed into packaging materials (bottles, jars, and film), food service products (eating utensils, cups, and plates), and consumer products (toiletry articles, credit cards, golf tees)..

An example of commercial PHBV is Biopol™ (and other PHAs) manufactured by Metabolix.

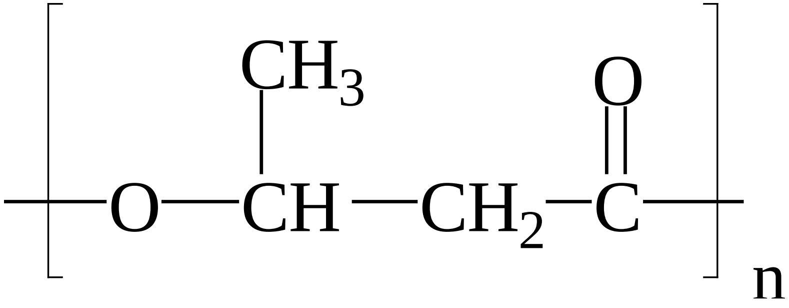
Tensile properties of Biopol PHBV*.		LDPE	PP
Tensile strength (MPa)	18-43	10	35
Elongation at break (%)	10-1000	620	--
Tensile modulus (MPa)	100-3600	165	1380

***PHBV properties depend on the relative amounts of butyrate and valerate. [PHB is strong, brittle, and stiff.]**

For each property, which value within the range of values corresponds to pure PHB?

Proctor and Gamble's Nodax PHAs

Nodax™ is a family of copolymers of 3-hydroxybutyrate and one or more 3-hydroxyalkanoates having a longer side chain, where the side chain has anywhere from 3 to 20 carbon atoms.



$$\left[-O-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}- \right]_n$$

PHB

The structures thereby resemble linear LDPE, with the 3-hydroxybutyrate units providing a basis for crystallinity, and the other units introducing structural irregularity and reduced crystallinity.

The main focus now is on Nodax H (hexanoate)

poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) PHB-HH

Nodax H (cont.)

The carbon feedstocks are molasses and fatty acids.

The bacteria are genetically modified organisms (GMO), modified either through classical mutagenesis or genetic engineering.

Recent development

P&G has announced a joint agreement with Kaneka Corporation, of Osaka, Japan, for the completion of research and development leading to the commercialization of NODAX H.

P&G holds processing patents and applications patents. Kaneka holds composition of matter patents and some processing patents. They plan a scale-up in 2004 and commercialization by 2006.

Properties

% C6(hexanoate)	T_m, °C		Applications
0 (PHB)	180	hard, brittle, crystalline	
4	150	hard, some elasticitiy	molded articles
6	145	hard, elastic, flexible	fibers
10	125	soft, elastic, flexible	films
18	95	soft, rubbery	coatings

Nodax H combines the thermo-mechanical properties of PE with the physical-chemical properties (compatibility) of polyesters.

It forms blends with PLA and also with thermoplastic starch. 10% Nodax H in PLA increases the toughness four-fold.

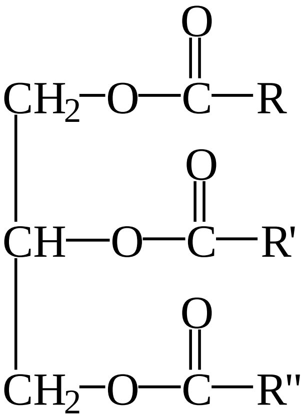
Summary on Approach 3.

With variation in microorganisms and in substrates, a wide range of polymer properties can be achieved.

Optimization in the fermentation, isolation, and purification technologies can be expected to lower costs.

Approach 4. Small biomolecules [vegetable oils] are extracted and then polymerized by conventional methods to produce strong thermosetting plastics [vegetable oil thermosets].

Plastics based on vegetable oils



Vegetable oils contain triglycerides (triacylglycerides), shown schematically on the left.

R stands for the hydrocarbon chain of the fatty acid at each of the three positions.

Commercially important oils are produced from the seeds of soybeans, corn (maize), cotton, sunflowers, flax (linseed), rape, castor beans, canola, and others.

Over 16 billion pounds of vegetable oils are produced in the United States each year, mainly from soybean, flax, and rape seed. Soy oil alone accounts for 80% of the seed oils produced in the United States and 30% of the world’s supply of vegetable oil.

Plant (and animal) triglycerides have become the basis for a new family of sturdy, durable composites that have long useful lifetimes.

The Process

- **The oils are chemically modified to make more chemically reactive (e.g., by epoxidation at the double bonds).**
- **The monomers are then chemically cross-linked to form high molecular weight macromolecules.**
- **The initial cross-linked liquid resin is a low-molecular-weight polymer that is then combined with catalysts and accelerators to facilitate the cross-linking reaction.**
- **The resin is then injected into a mold containing a reinforcing fiber.**
- **Heat-curing in the mold forms a sturdy, durable, rigid, long-lasting thermoset.**

Applications

Reinforced with glass fiber, the material serves as an alternative to sheet-metal for side panels in agricultural equipment, replacing the conventional petroleum-based options. Other applications are in the areas of the automotive and construction industries.

Example

John Deere combines now have panels made from the material. The vegetable-oil composite is strong and weighs 25% less than steel—and less than the petroleum-based products typically used to make panels.

Panel (8’ x 3’, 25 lb) made with a vegetable oil composite reinforced with glass fiber. A foam core is enclosed on both sides with the composite.

Summary on Approach 4.

This approach is the only approach that leads to strong, durable thermosetting plastics that are made from renewable resources and optionally biodegradable.

New bioproducts, from renewable resources and biodegradable, are beginning to appear. (These are not hybrids.)

Starch acetate foam packaging

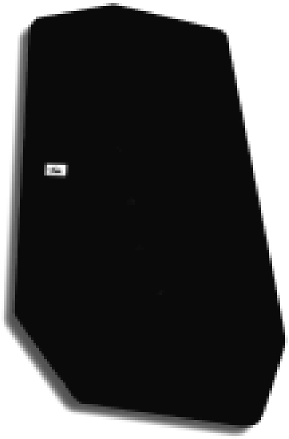
Coated starch foam for food packaging

Starch composite for food service

PS

Starch-PLA for food service

PLA packaging tray



Hay baler panel made of a soybean oil composite

plus
Nodax H
and
other
PHAs