UNIVERSITY OF ZAGREB

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

Polymer science and technology

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Course Schedule

LECTURES

10:00 – 11:45 h

21.11.2024.	1st lecture
28.11.2024.	2nd lecture
5.12.2024.	3rd lecture
12.12.2024.	4th lecture
19.12.2024.	5th lecture
January 2025.	seminar
23.1.2025.	2nd partial exam

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Different classification of polymers

1. Properties

- Plastics
  - Thermoplastics
  - Thermosets
- Elastomers
- Fibers

2. Structure

- Linear
- Branched
- Cross-linked

3. Number of monomer

- Homopolymer
- Copolymer
  - Random
  - Alternating
  - Block
  - Graft

4. Configuration

- Isotactic
- Syndiotactic
- Atactic

5. Origin

- Natural
- Synthetic

Source of hydrocarbons

Synthetic polymers (petrochemical)

- Non-renewable carbon
- Produced from oil (but can be made from methane and coal)
- 4% of the world's fossil resources are used in plastics production

- Not environment friendly due to CO_2 emission
- **Mostly** not biodegradable (there are exceptions, PCL, PVA)

Biopolymers

- From renewable carbon sources
- Produced from biomass (plant and animals)

- More environment friendly, carbon neutral
- **Mostly** biodegradable

Biopolymers definition

- **Biopolymers are natural polymers produced by the cells of living organisms (IUPAC definition)**

*International Union Of Pure And Applied Chemistry

Natural polymers

- Produced by the cells of living organisms (plants and animals)
- Natural rubber, cellulose, silk, wool, natural resins, chitin

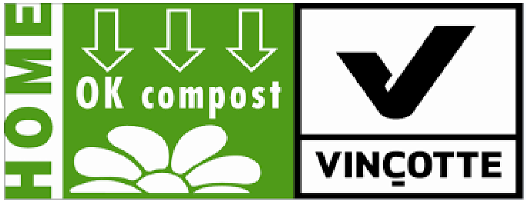
- Sometimes biobased polymers are also called biopolymers

Biobased polymers

- Monomers obtained from plants
- Polymers are then chemically synthesized
- Polylactic acid (PLA), biopolyethylene from plants (sugar cane, sugar beet)
- Also called bioplastic

Biodegradability

- **Some** biopolymers are **biodegradable**: they are **broken down into CO_2 and water by microorganisms**
- **Some of these biodegradable biopolymers are compostable**: they can be put into an industrial composting process and will break down by 90% within 6 months
- Biopolymers that do this can be marked with a 'compostable' symbol, under European Standard EN 13432. Packaging marked with this symbol can be put into composting processes and will break down within 6 months (or less)



- Compostable polymer is PLA film under 20 µm thick: films which are thicker than that do not qualify as compostable, even though they are biodegradable

Biodegradability

Biopolymers – biodegradable

- cellulose, starch

Biopolymers – NOT biodegradable

- wool (1–5 years), leather (25–40 years), natural rubber (>100 years)

Biobased polymers – biodegradable

- polylactide (PLA)

Biobased polymers – NOT biodegradable

- biopolyethylene

Petrochemical polymers – biodegradable

- polycaprolactone (PCL), poly(vinyl alcohol) (PVA)

Biosourced vs. synthetic polymes

- Today, there is a **bioplastic alternative for almost any ordinary plastic** material for the corresponding application
  - **PLA** is an excellent **replacement for PS, PP and ABS**
  - A new polymer PEF (polyethylene furanoate) is expected to appear on the market in the upcoming years. **PEF is comparable to PET**, but consists of biological raw materials and has excellent barrier and thermal properties, which makes it an ideal material for packaging for drinks, food and non-food products
- Bioplastics have the similar properties as conventional plastics and offer advantages, such as a reduced carbon footprint or additional waste management options, such as industrial composting
- **World annual production of plastics (2022) 391 million tons**
- **~1% is bioplastics**

Biosourced vs. synthetic polymes

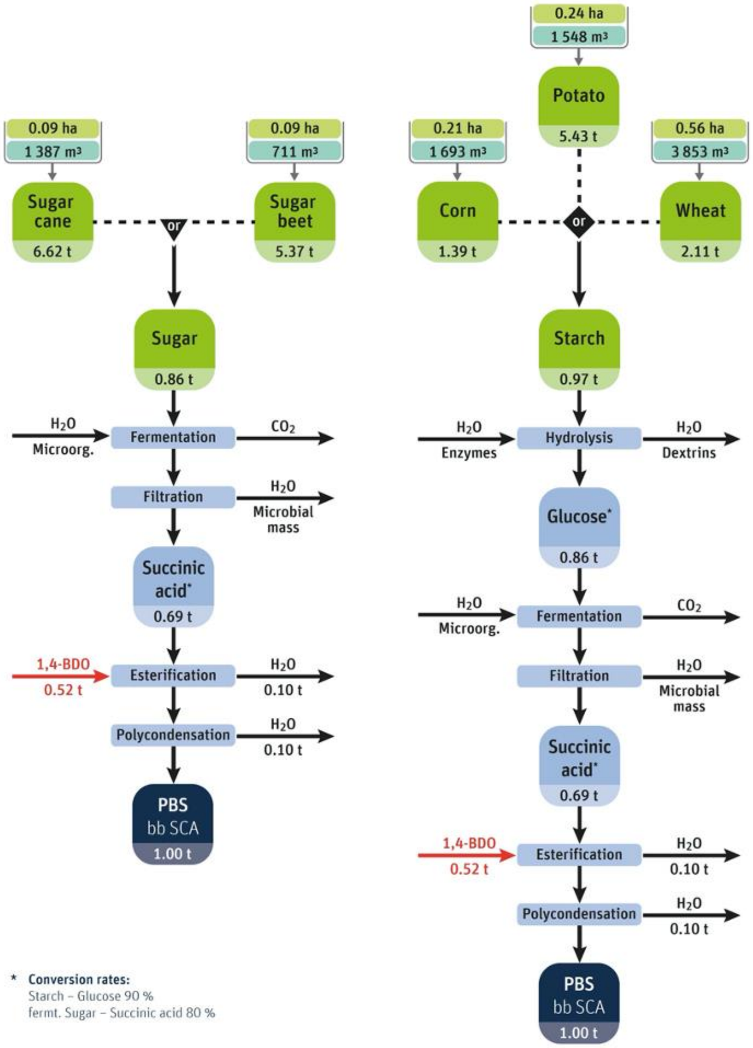
- **Biodegradable bags cannot be recycled**, they will ruin ordinary plastic

- For biodegradation of a PLA-based polymer, certain conditions are necessary: temperature and oxygen

- **Biotechnological production** from renewable raw materials (e.g. sugar fermentation - synthesis of thermoplastic polyesters, polyhydroxybutyrate, polyhydroxyalkanoates (PHA)) **is usually expensive** from the point of view of profitability **for industrial production**

- **Food is used to synthesize plastic** (PLA is obtained from corn, sugarcane, sugar beets), while millions of people in the world suffer from hunger

Biosourced vs. synthetic polymes



* **Conversion rates:**
Starch – Glucose 90 %
fermt. Sugar – Succinic acid 80 %

For the production of **1 tonne of PBS**:

- 6.62 tonnes of sugar cane
  or
- 5.37 tonnes of sugar beet
  or
- 5.43 tonnes of potato
  or
- 1.39 tonnes of corn
  or
- 2.11 tonnes of wheat

Biobased/natural polymers application

Biomedical

- Due to their biocompatible properties, biopolymers are used for **tissue engineering**, regenerative medicine, medical devices and drug delivery
- Biopolymers are normally better with bodily integration as they possess complex structures similar to the human body (synthetic polymers can cause immunogenic rejection and toxicity after degradation)

Industrial

- Used in the food industry for **packaging**, edible encapsulation films
- Biopolymers used in packaging are polyhydroxyalkanoate (PHA), polylactic acid (PLA), and starch
- **Chitosan** has been used for water purification as **flocculant** that degrades in a few weeks or months rather than years

Biopolymers

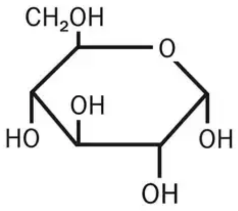
- Based on monomeric units and the molecular structure

1. **Polysaccharides** – **linear or branched** polymeric carbohydrate structures joined with **glycosidic bonds** (starch, cellulose, glycogen)
2. **Polypeptides** – longer, continuous, unbranched peptide chain composed of **amino acids**, **more than 50 amino acids** form **proteins** (wool, silk)
3. **Natural rubber** – linear polymer obtained from latex of some plants
4. **Polyhydroxyalkanoates (PHA)s** – polyesters produced in nature by numerous microorganisms

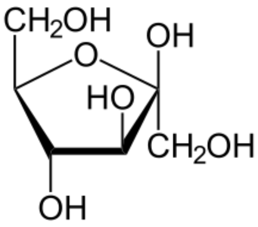
POLYSACCHARIDES

- Polymer composed of **long chains** of **monosaccharide**, where units are bound together by **glycosidic linkages**

- Monosaccharides are simple carbohydrates with general formula $(CH_2O)_n$, $n \geq 3$ or more



glucose



fructose

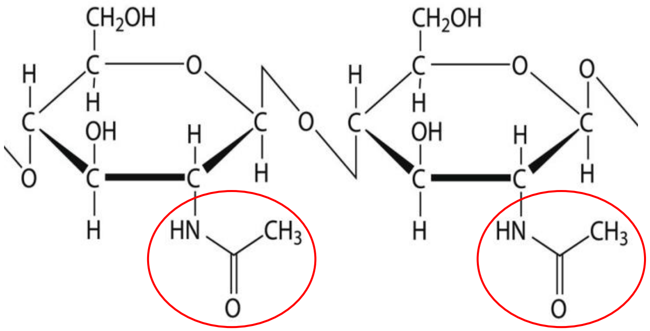
- Polysaccharides have a general formula $C_x(H_2O)_y$, $x = 200$ to 2500

- When the repeating units in the polymer backbone are six-carbon monosaccharides (glucose), the general formula is $(C_6H_{10}O_5)_n$, $40 \leq n \leq 3000$

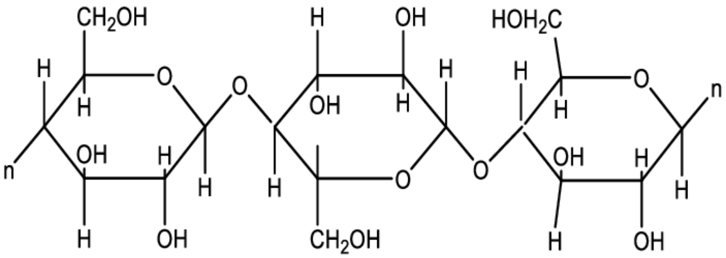
POLYSACCHARIDES

- Depending on **which monosaccharides** are connected, and **which carbons** in the monosaccharides **connects**, they take on a variety of forms: **linear** or **highly branched** polysaccharide
- Depending on their structure can have a wide variety of functions (they have different properties) like **storing energy** or **providing support to cells** and tissues
- Examples: **starch** (plants) and **glycogen** (animals) – **storage energy**
  cellulose (plants) and **chitin** (animals) – **support to cells**

Chitin ($C_8H_{13}O_5N$)



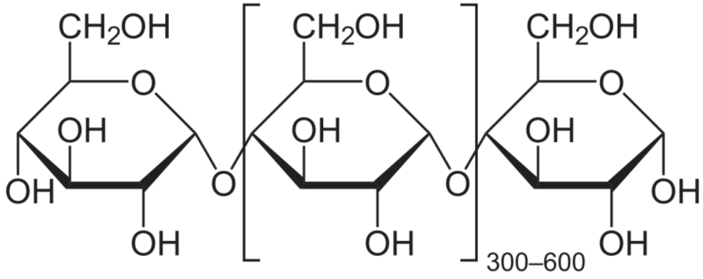
Cellulose ($(C_6H_{10}O_5)_n$)



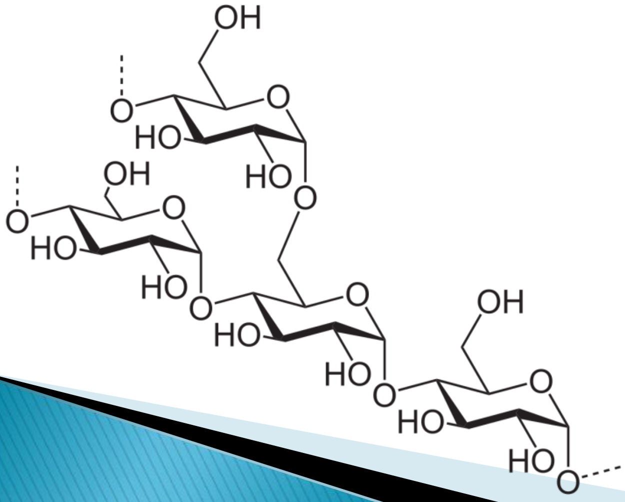
POLYSACCHARIDES

Starch $(C_6H_{10}O_5)_n$

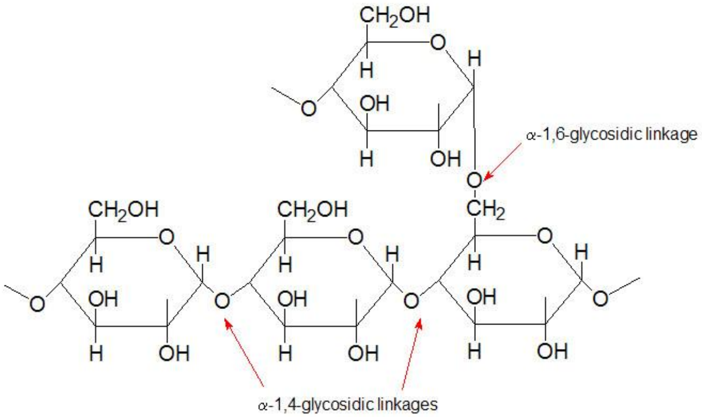
20 to 25% amylose
(linear polymer of glucose)

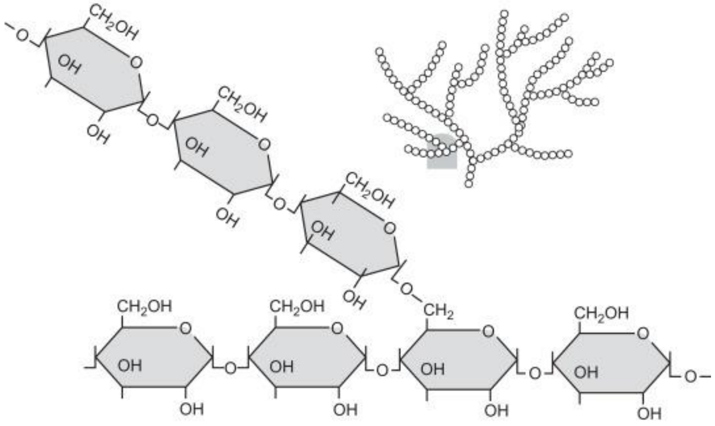


75 to 80% amylopectin
(branched polymer of glucose)



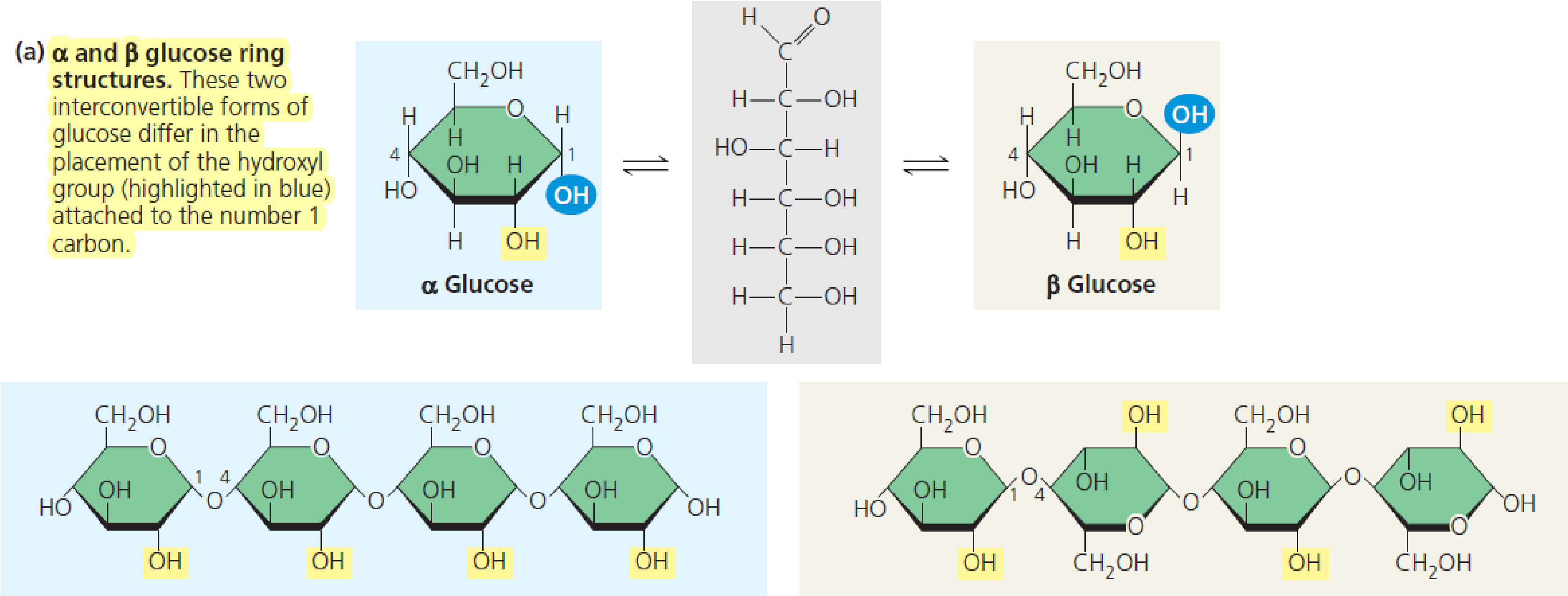
Glycogen $(C_6H_{10}O_5)_n$





POLYSACCHARIDES

Starch and cellulose difference

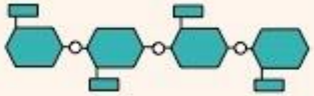
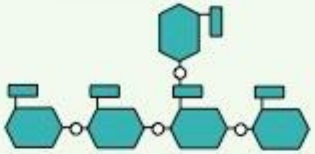
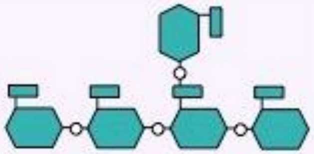
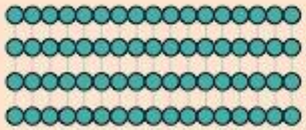
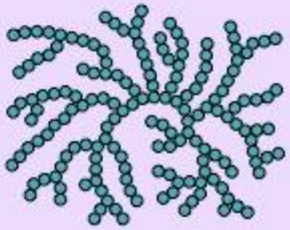


(a) α and β glucose ring structures. These two interconvertible forms of glucose differ in the placement of the hydroxyl group (highlighted in blue) attached to the number 1 carbon.

(b) Starch: 1–4 linkage of α glucose monomers. All monomers are in the same orientation. Compare the positions of the —OH groups highlighted in yellow with those in cellulose (c).

(c) Cellulose: 1–4 linkage of β glucose monomers. In cellulose, every β glucose monomer is upside down with respect to its neighbors. (See the highlighted —OH groups.)

POLYSACCHARIDES

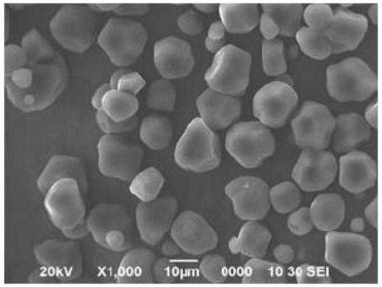
	Cellulose	**Starch**		**Glycogen**
		Amylose	**Amylopectin**	
Source	Plant	Plant	Plant	Animal
Subunit	β-glucose	α-glucose	α-glucose	α-glucose
Bonds	1-4	1-4	1-4 *and* 1-6	1-4 *and* 1-6
Branches	No	No	Yes (~per 20 subunits)	Yes (~per 10 subunits)
Diagram				
Shape				

POLYSACCHARIDES

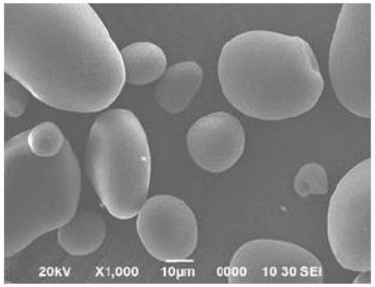
Name of the Polysaccharide	Composition	Function
1. Starch	Polymer of glucose containing a straight chain molecules (amylose) and a branched chain of molecules (amylopectin)	Storage of reserve food in plants
2. Cellulose	Polymer of glucose	Cellwall matrix in plants
3. Chitin	Polymer of glucose	Exoskeleton of arthropods, fungi and crabs
4. Glycogen	Polymer of glucose	Storage of reserve food in animals
5. Pectin	Polymer of galactose and its derivatives	Cellwall matrix in plants
6. Lignin	Polymer of glucose	Cellwall matrix in plants

Starch

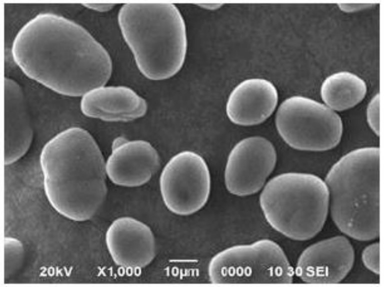
- The most common carbohydrate in human diets, and is contained in large amounts in foods like wheat, potatoes, maize (corn), rice
- White, tasteless and odorless powder, insoluble in cold water or alcohol
- In industry is converted into sugars and fermented to **produce ethanol in the manufacture of beer, whisky and biofuel**
- The starch industry **extracts and refines starches from seeds**, roots and tubers, by wet grinding, washing, sieving and drying
- The main commercial refined starches are cornstarch, tapioca, wheat, rice, and potato starches
- In 2020, production was 93 million ton



corn



potato



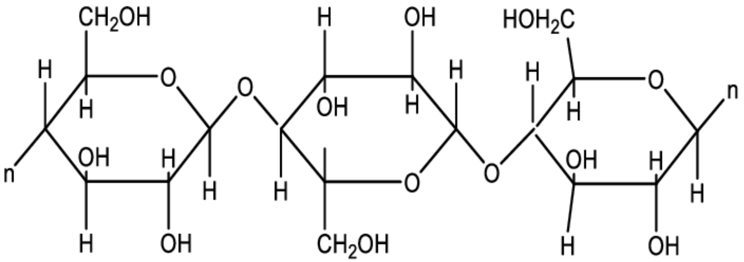
pea

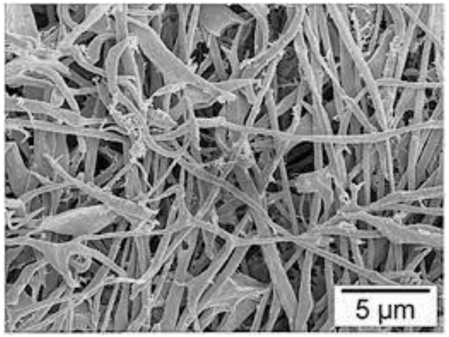
Starch application

- **Food additive** – used as **thickeners and stabilizers** in foods such as processed meats, puddings, soups, sauces, gravies
- **Pharmaceutical industry** – excipient, as tablet disintegrant, and as binder
- **Papermaking**
  - It gives the **strength** to the final **paper sheet**
  - Used in paper coatings as one of the **binders for the coating formulations** (mixture of pigments, binders and thickeners). Coated paper has improved smoothness, hardness, whiteness and gloss for improved printing characteristics
- **Construction industry** – **gypsum wall board** manufacturing process, **glue for the cured gypsum** rock with the paper covering, and provide rigidity to the board
- **Adhesives (glue)** – book-binding, wallpaper adhesives, envelope adhesives and school glues
- **Bioplastics** – with water and plasticisers such as glycerol, starch can be processed into "**thermoplastic starch**" using conventional polymer processing techniques such as extrusion and injection molding

Cellulose

- Linear chain of several hundred to many thousands of **β(1→4) linked D-glucose units**

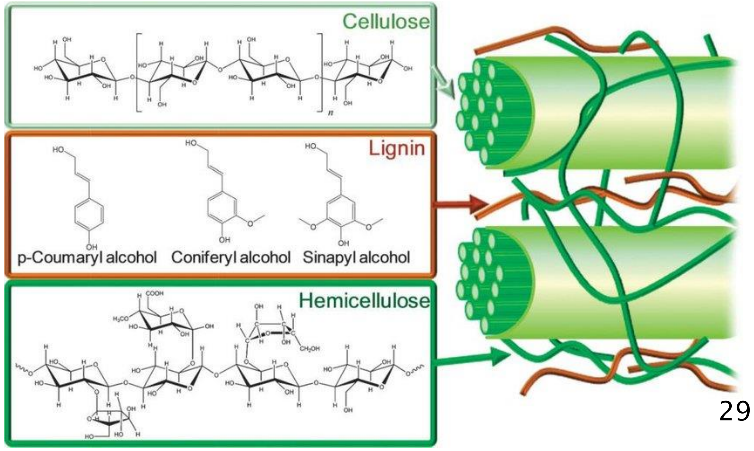




- Glucose units in cellulose are combined in a way that results in the formation of very **linear, flat molecules (no branching)**
- Multiple hydroxyl groups on the glucose from one chain form **hydrogen bonds** with oxygen atoms on the same or on a neighbor chain, holding the chains firmly together and forming **microfibrils with high tensile strength**
- As a result of these bonds, sheets of cellulose are **particularly strong** — a property critical to the function of plant cell walls

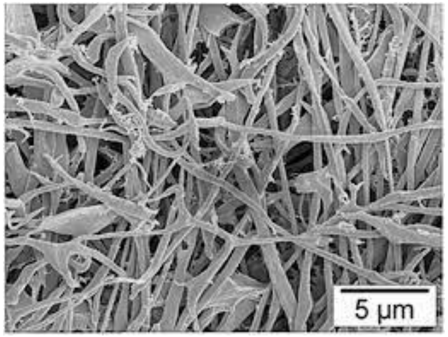
Cellulose

- Tasteless, odorless, hydrophilic, insoluble in water and most organic solvents and biodegradable
- Obtained from **wood (40-50 mass%)**, **cotton (90 mass%)**, and **bacteria**
- The **most common organic polymer**, representing about 1.5×10^{12} tons of the total annual biomass production
- **Properties depend on chain length**, ie. degree of polymerization (DP), which is the number of glucose units that make up one polymer molecule
  - **wood** cellulose DP = 300-1700
  - **cotton** or **bacterial** cellulose DP = 800-10000
- **Wood cellulose** is a **mixture** of cellulose, hemicellulose and lignin
  - hemicellulose is derived from several sugars in addition to glucose (especially xylose but also including mannose, galactose)
  - lignins are polymers made by cross-linking phenolic precursors

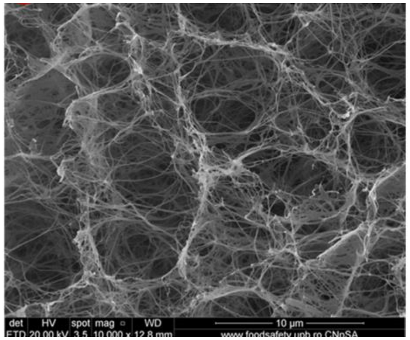


Bacterial cellulose

- Produced by certain types of bacteria, genera *Acetobacter*, *Sarcina ventriculi* and *Agrobacterium*
- **Plant cellulose**, is a tough, mesh-like formation in which cellulose fibrils are the primary architectural elements
- **Bacterial cellulose** is more chemically **pure**, containes no hemicellulose or lignin, has a **higher water holding capacity** and hydrophilicity, greater tensile strength resulting from a larger amount of polymerization, **ultrafine network architecture**
- It has a more crystalline structure compared to plant cellulose and forms characteristic ribbon-like microfibrils significantly smaller than those in plant cellulose, making **bacterial cellulose much more porous**



Plant cellulose



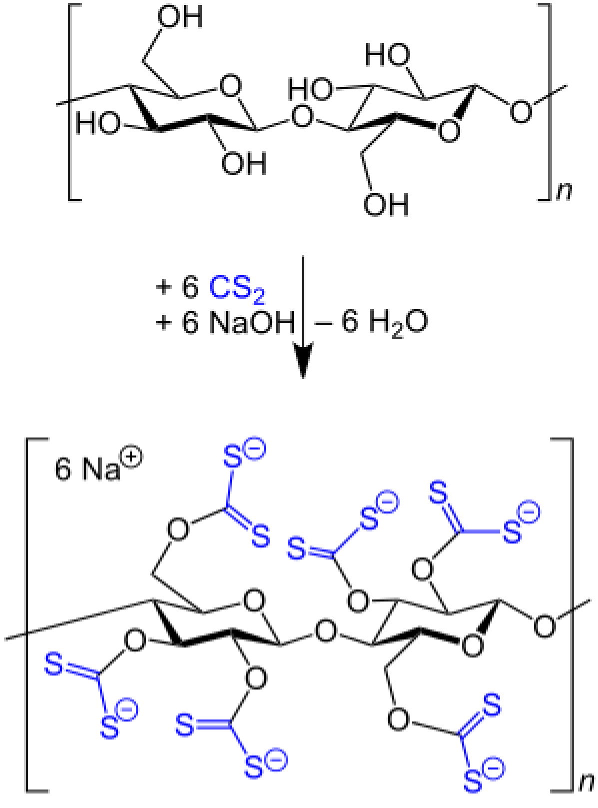
Bacterial cellulose

Cellulose application

- Cellulose for industrial use is **mainly obtained from wood pulp and from cotton**, price of bacterial cellulose is too high to make it commercially viable on a large scale
- **Cellulose**
  - major **constituent of paper** and **paperboard, electrical insulation paper** in transformers, cables, and other electrical equipment
  - Cellulose fibers are the **ingredient of textiles**
  - Inactive fillers in drug tablets, soluble cellulose derivatives are used as emulsifiers, thickeners and stabilizers in processed foods (different E numbers)
- **Bacterial cellulose**
  - **ultra-strength paper**, acoustic or filter membrane in hi-fidelity loudspeakers (Sony Corporation), additive in the cosmetic industry
  - **In medical sector** – wound dressing, especially in burn cases, bone grafts and other tissue engineering and regeneration

Cellulose modification

- Chemically modified is used in the manufacture of viscose (rayon) – **textile fibre**
- Viscose is the **third most used textile fibre** in the world, it imitates the feel and texture of natural fibers such as silk, wool, cotton
- Cellophane is identical in chemical composition to viscose but it is spun into sheets
- Other cellulose derivatives are used as plastics, photographic films, **adhesives, explosives, thickening agents for foods**, and in moisture-proof coatings



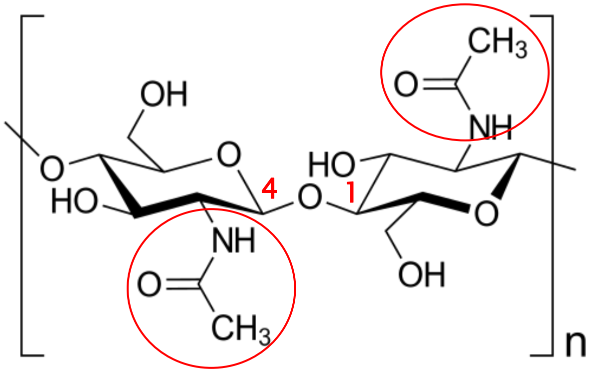
Cellulose is dissolved in NaOH and treated with CS_2 to convert it to VISCOSE (rayon)

Chitin

- From the Greek word *khiton*, meaning **covering**
- Structural polysaccharide made from modified **glucose**

Acetyl-amine group

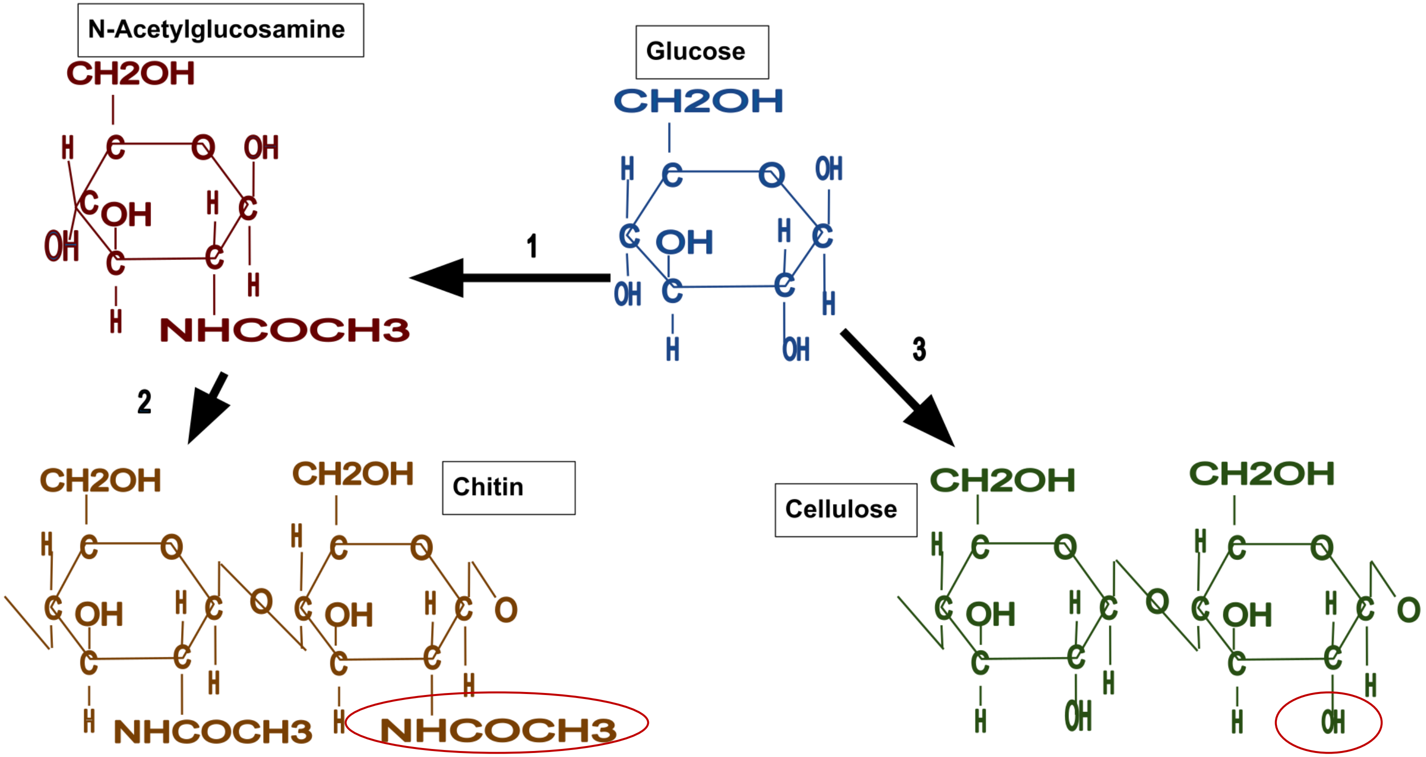
N-acetylglucosamine units linked **β-(1→4)**-bonds



- Found in the **exoskeletons of insects** (wings), the **cell walls of fungi**, and in **hard structures of crabs (shell)**
- In terms of **abundance**, chitin is **second** after cellulose
- **Over 1 billion tons of chitin** is obtained by biosynthesis each year **in organisms**
- In exoskeletons is always associated **with some proteins,** it does not exist alone
- In crabs form composite material: **chitin** (about 20-40%), **protein** (about 20-30%) and **calcium carbonate** (about 30%), harder and stiffer material than pure chitin

Chitin

- Cellulose/chitin difference – hydroxyl group on each monomer is replaced with an acetyl amine group



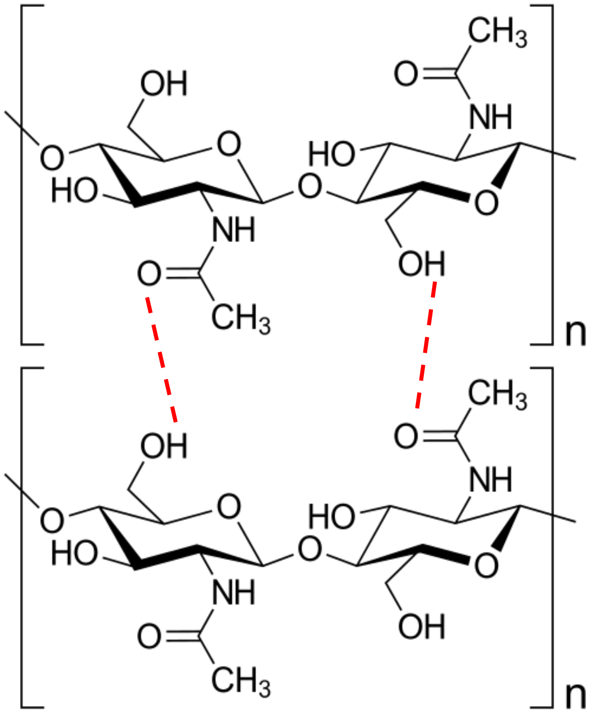
in **crustaceans and insects** cell walls

in **plant** cell walls

Chitin

- Molecules of chitin are structural due to formation of fibers and their secondary interactions form the **crystal form**

- Formation **of hydrogen bonds** between chitin molecules (similar to cellulose)

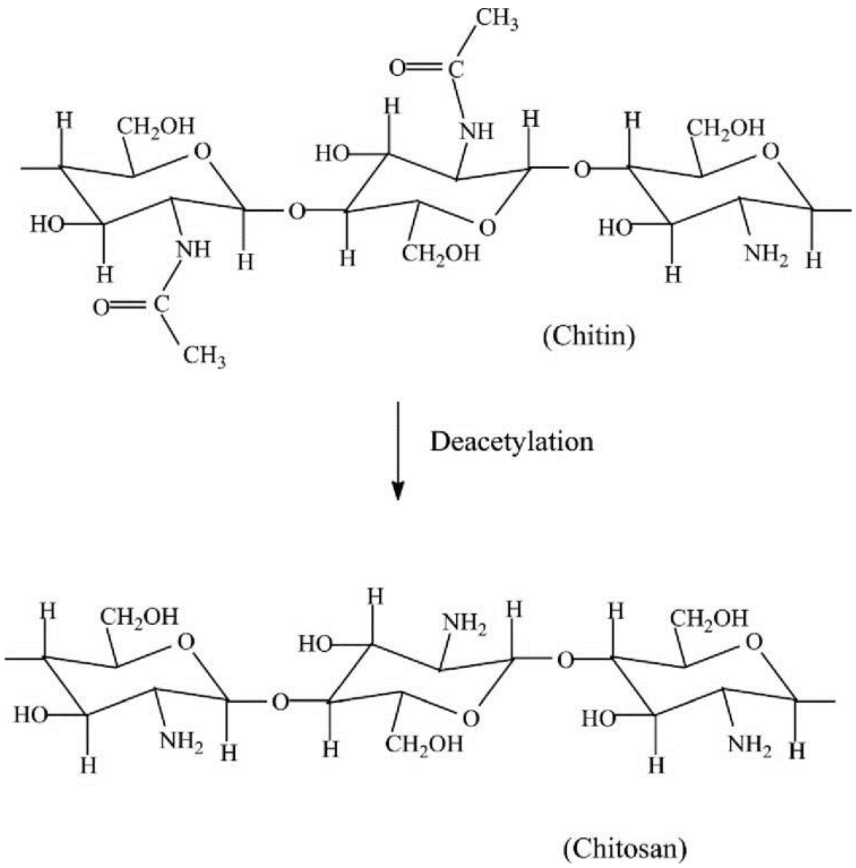


Properties

- Biodegradable and biocompatible
- **Low solubility** (difficult for the application)

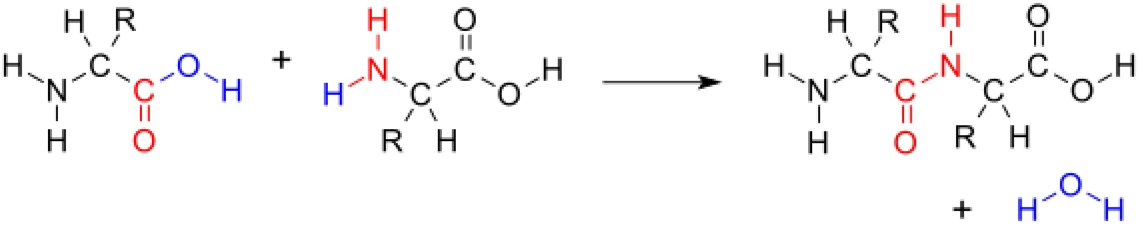
Chitin/chitosan

- Usually chitin is modified in **chitosan** **soluble** in water and has **vast applications** in various fields
- **Agricultural and horticultural** uses – for plant defense and yield increase
- To **strengthen paper**
- **Medicine** – wound dressings to decrease bleeding, improved drug delivery systems
- As an **additive in water filtration** (flocculant)
- **Biodegradable antimicrobial food packaging**

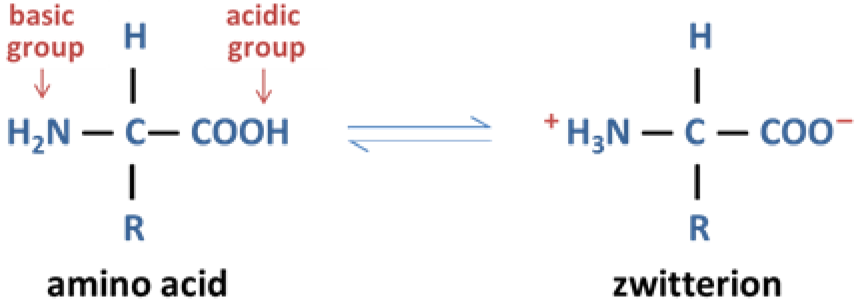


POLYPEPTIDES

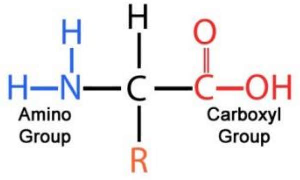
- **Peptides** – biomaterials composed of repeating amino acid units linked by a peptide bond
- Peptide formation by condensation reaction



- **Usually** in ions form – named **zwitterions**
- They contain an amine group (basic) and a carboxylic group (acidic). The $-NH_2$ group is the stronger base, and so it picks up H^+ from the $-COOH$ group to leave a zwitterion (i.e. the amine group de-protonates the carboxylic acid)



The **20 common amino acids** are shown with their R groups highlighted



- **Every amino acid** has **another atom or group** of atoms bonded to the central atom, known as the **R group**, which determines the identity of the amino acid
- E.g. If the R group is a **H atom**, then the amino acid is **glycine,** if **methyl** (CH_3) the amino acid is **alanine**
- The properties of the **side chain** determine an amino acid's **chemical behavior**
- **Divided:**
  - ☐ Nonpolar and hydrophobic
  - ☐ Polar and hydrophilic
  - ☐ Electrically charged (acidic and basic)

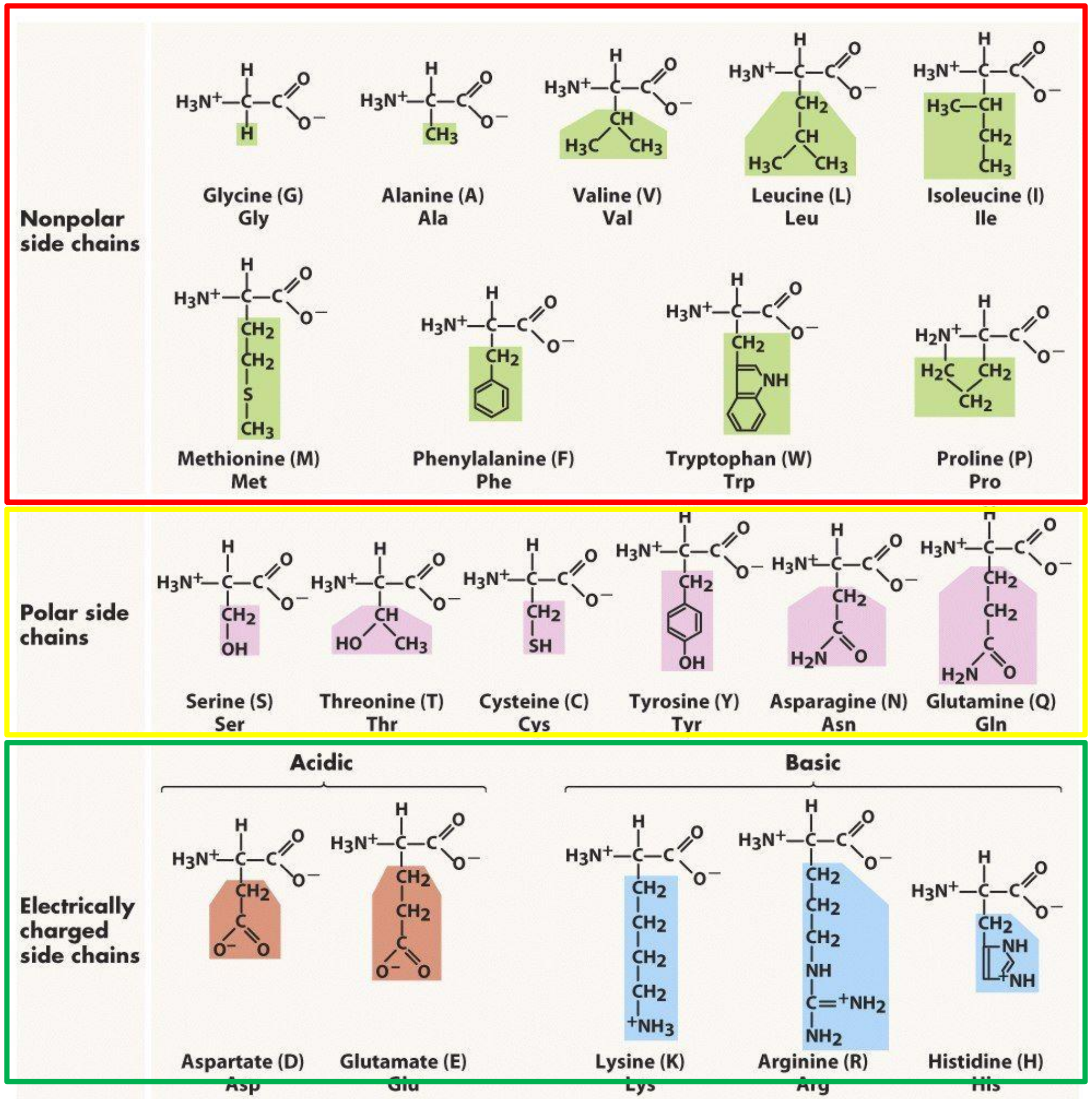
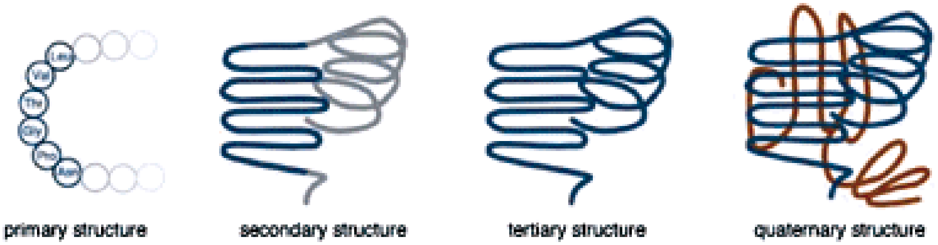


Figure 3-5 Biological Science, 2/e

- Chains of **fewer than ten or fifteen** amino acids are called **oligopeptides**, a polypeptide is a longer, continuous, and unbranched peptide
- A polypeptide that contains **more than approximately fifty amino acids are called proteins**, size boundaries which distinguish peptides, polypeptides, and proteins are arbitrary not strictly defined
- Single chain **proteins generally range from 50 to 1000 amino acids** in length
- In protein structure we distinguish primary, secondary, tertiary, and quaternary levels of structure



- **primary** – is the actual size and composition of one molecule
- **secondary** – refers to **local bonds**, along the chains
- **tertiary** – refers to the **shape** of the entire polypeptide chain
- **quaternary** – describe proteins that consist of **more than one polypeptide** chain

- **Collagens, silks and keratins** are some of the more common structural proteins considered for protein-based biomaterials

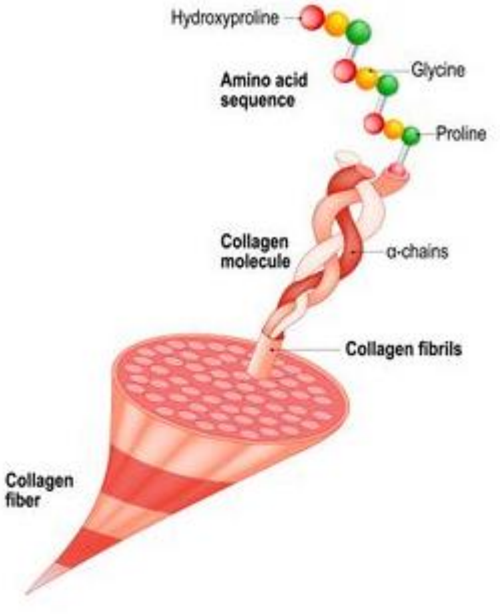
- Collagen – human skin consists of collagen, 25% of all proteins in the human body are from collagen, it is found in connective tissue (cartilage, bones, ligaments)

- It consists of three polypeptide chains, which are spirally connected in a triple helix

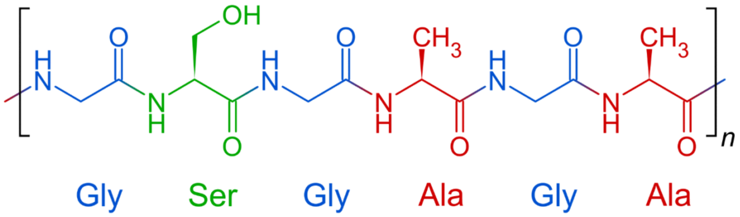
- A repeating sequence of 3 amino acids, **approximately every 3rd is glycine**, the rest are proline and hydroxyproline

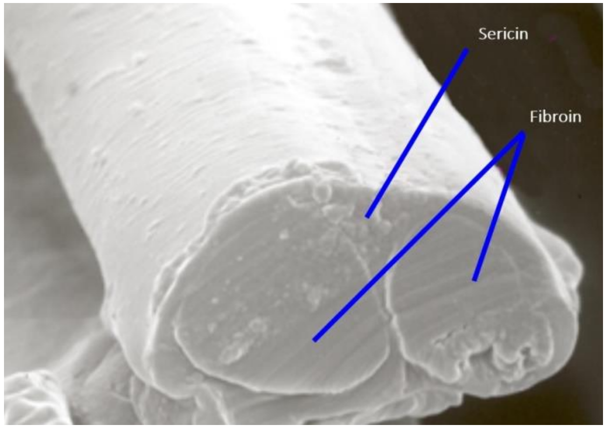
- Hydroxyproline is formed with the presence of vitamin C; deficiency slows down the process of collagen formation → scurvy

- **Application**: clothing (leather), tissue regeneration (artificial skin – burns), wound dressings, 3D bioprinting of artificial tissue



- Silk – natural protein fiber, main use as a **textile fiber**
- It is obtained from cocoons of mulberry silkworm and some species of spiders
- It consists of proteins **fibroin** and **sericin**, where sericin acts as an adhesive layer between two fibroin filaments
- **Fibroin** is a polypeptide where amino acids (mostly **alanine** and **glycine**) are connected by peptide bonds, and its parallel chains are connected by hydrogen bonds, which cause the formation of a crystalline structure that gives silk its unique flexibility and shine

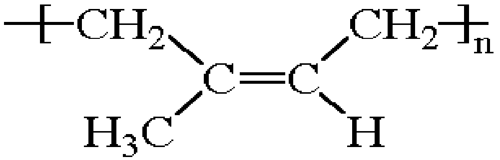




- **Obtaining silk** – from the cocoon of mulberry silkworm (Bombyx mori)
- The silkworm secretes fibroin from the gland, which hardens in the air, and sericin, which connects two fibroin fibers and thereby creates a cocoon
- During the construction, of the cocoon, it turns about 300,000 times and produces about 1 km of filament
- As hatching from the cocoon destroys the fiber, the cocoons are placed in hot water or exposed to hot air, which softens the sericin and allows the fiber to be extracted
- As the larva is killed by this procedure, an attempt was made to pull out the fiber as the insect creates it, but in that case it would tear it off and it was not possible to obtain a fiber longer than 6 m
- Each cocoon creates one fiber with an average length of about 350 m fiber
- 2500-3000 cocoons are needed to produce 1 m of finished silk fiber

NATURAL RUBBER (NR)

- Macromolecule, **formed by biosynthesis in the plant** with the repeating unit ***cis*–1,4 –isoprene (caoutchouc)**
- Repeated unit of the same chemical structure was **used as template to prepare synthetic polymers**
- **Pure hydrocarbons**, with only **one repeated unit**
- Obtained from **rubber tree** (e.g. *Havea brasiliensis*) by **collecting latex**
- Used in 15th century by **Mayan** and **Aztec** peoples, for producing **water resistant footwear**
- Around 25 million tonnes of rubber are produced each year, 30% is natural



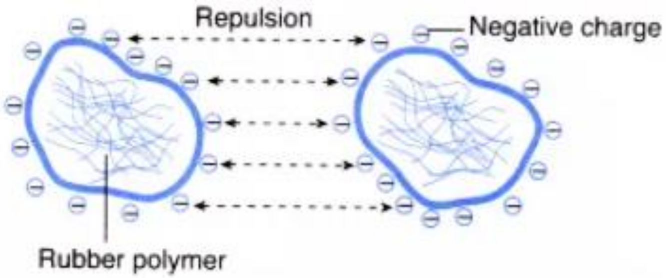
***cis*–1,4–polyisoprene**

the **bark is cut** and collected in **cans**

Natural rubber

- **Natural latex** obtained from **rubber tree** is water serum consists of:
  - **60% water**
  - **35-40% rubber particles**
  - other substances: protein, sugar, inorganic salts, and resins

- Each rubber particle is made of rubber polymers covered by a layer of proteine membrane
- Negative charges are found on the surface of the membrane, making **each rubber particle negatively charged.** The negatively-charged particles repel each other preventing them from coagulating (**at pH 6.5-7.0 latex is stable**)



Natural rubber

- Acids such as formic or acetic acid are added to make **latex coagulate at pH 4.8**
- Hydrogen ions from the acid neutralize the negative charges on the surface of the membrane and a neutral particle is formed
- When these neutral particles collide with each other, their outer protein membrane break up
- The **rubber polymers start to coagulate** by combining to form large lumps of rubber polymers which then precipitate out of the latex solution

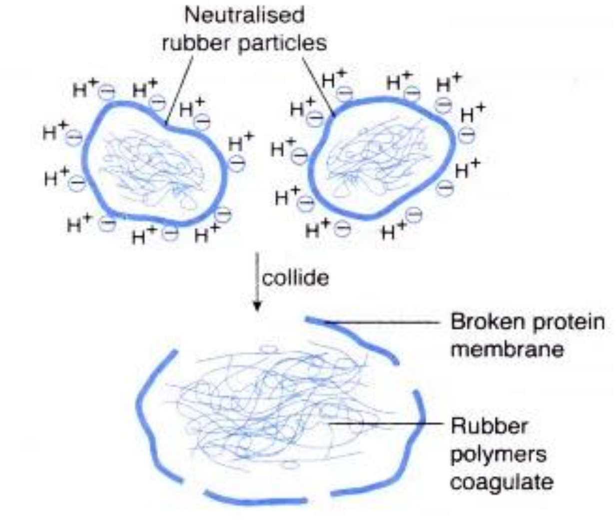


Figure *Coagulation process of latex*

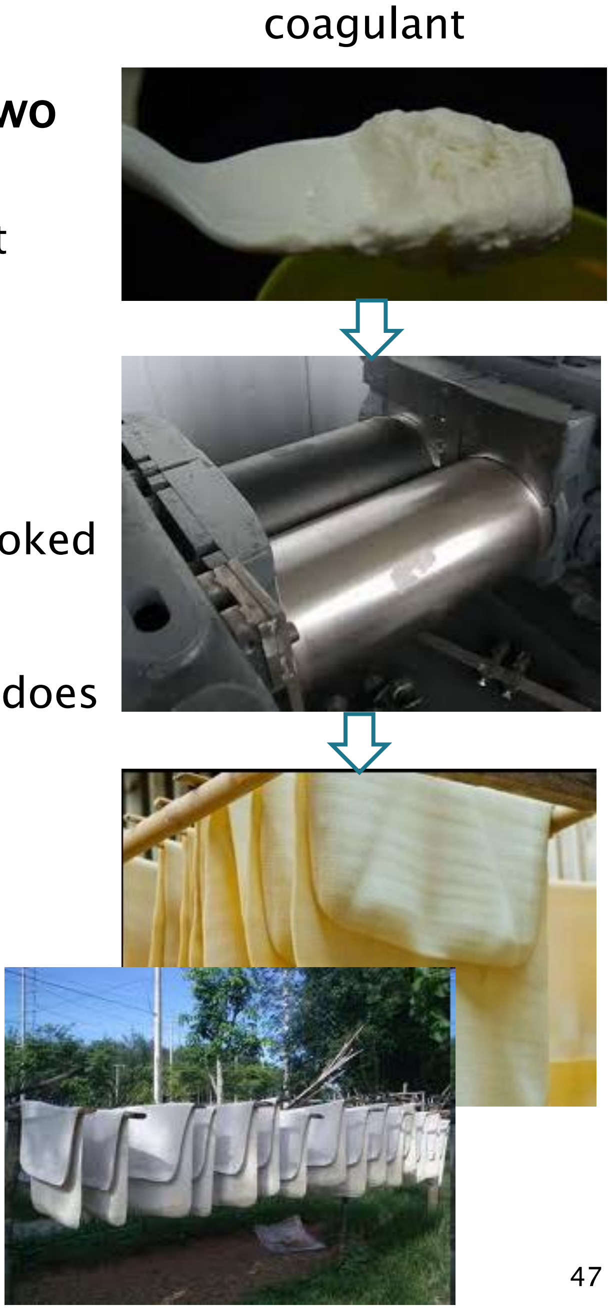
Rubber coagulate separated from the water and further produced

Natural rubber processing

- After coagulation dry rubber is processed with **two roll mill into** sheets
    - roll mill rotate in different directions at different speeds (to achieve higher friction)
    - rubber sheets of 4-5 mm are obtained

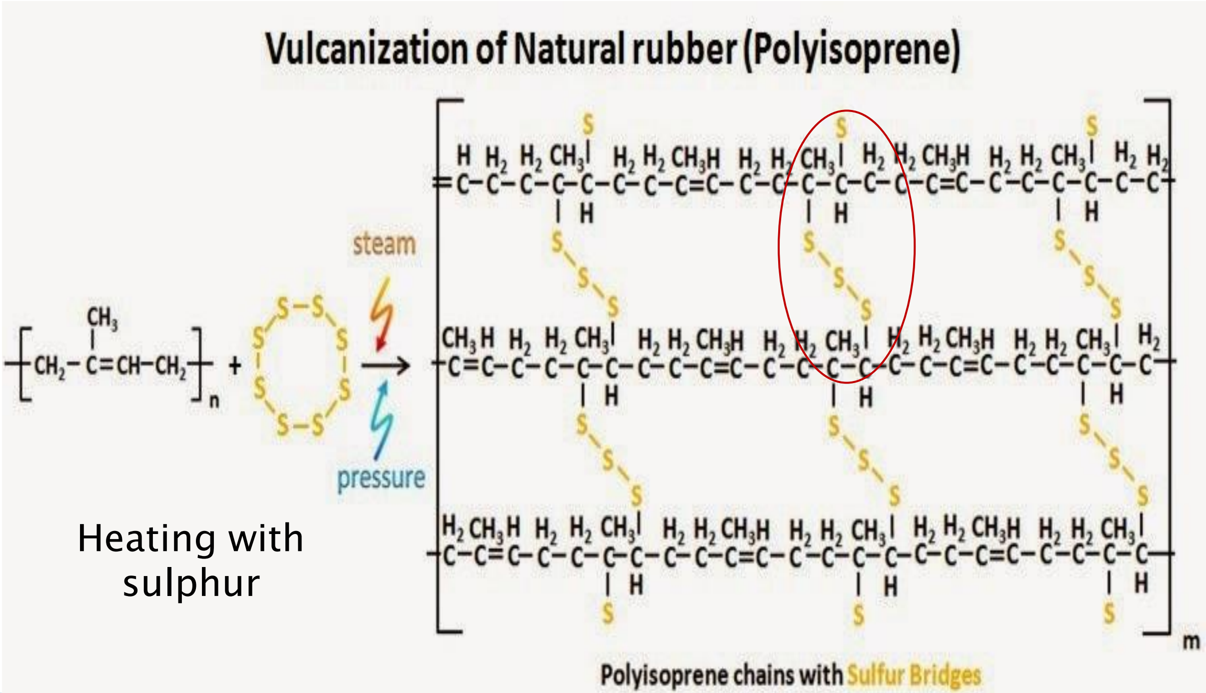
- **Ribbed smoked sheets** grade
    - **dried** for 4 – 7 days in large dryer where are smoked (oven on wood or oil)
    - the smoke acts as a fungicide, at temp. of 55 ˚C (stabilizes and preserve the rubber, lower temp does not harm the fungi

- **Pale crepe** grade
    - yellow carotenoid pigments is removed by bleaching before coagulation
    - obtained sheets are **dried** in **oven** instead of smoked
    - **white sheets** are obtained – superior grade

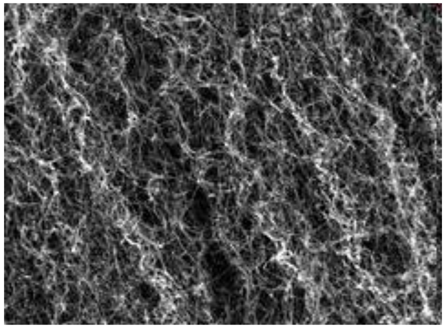


Vulcanization

- Process of **crosslinking** where polymer **chains become chemically bonded** usually by **sulphur (S_8), peroxide**, or others, resulting in 3D network formation
- **Carbon black is often used as an additive** to rubber to improve its strength, especially in vehicle tires, which account for about 70% (~9 million tons) of carbon black production



Heating with sulphur



Vulcanization

- **Crosslinked rubber**
  - **Plastic properties** turn to highly **elastic**
  - Can **not be dissolved** in organic solvent
  - Can **not be melt** by heating

- **The vulcanization process** is taking place **parallel** with the **processing** in press machine during forming the final product

VULCANIZATION PROCESS
- at higher temp. *(160 –180 °C)*
- time *(5 – 20 min)*

Natural rubber application

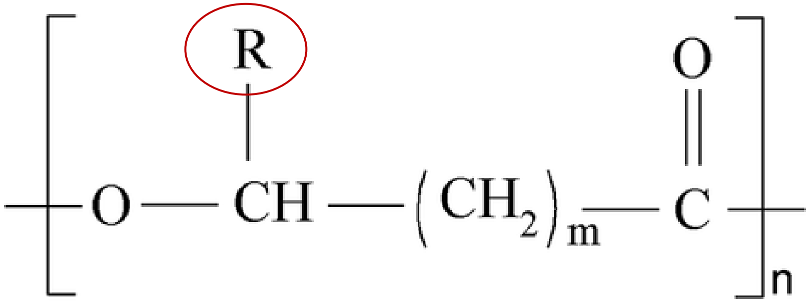
- **Uncured** rubber is used for **adhesive, insulating**, friction tapes and footwear
- Vulcanized rubber has many more applications
- Due to abrasion resistance **softer** kinds of rubber are used for the **treads of vehicle tires and conveyor belts**, while **hard rubber** is used for **pump housings** and **piping**
- Flexibility and elasticity – for shock absorbers and for mountings designed to reduce vibration
- Low gas permeability – useful in the manufacture of air hoses, balloons and balls
- Resistance of rubber to water and most fluid chemicals – use in **rainwear, diving gear**, and chemical and **medicinal tubing, lining for storage tanks**, processing equipment and railroad tank cars

POLYHYDROXYALKANOATES (PHA)s

- Linear polyesters produced in nature by **microbial/bacterial fermentation** of glucose from corn starch, sugar or lipids
- When produced by bacteria PHAs are biopolyesters that are **stored within cells as energy** storage material of living organisms
- For the first time, PHA was discovered in *Bacillus megaterium* in the form of **poly(3-hydroxybutyrate)** (PHB) in 1925
- More than **150** different monomers can be combined within this family to give materials **with extremely different properties**
- They can be either **thermoplastic** or **elastomeric materials,** melting point **40-180 °C**

Polyhydroxyalkanoates (PHA)s

- General molecular formula of PHAs



$$\left[-O-\overset{\displaystyle R}{\overset{|}{CH}}-\left(CH_2\right)_m-\overset{\displaystyle O}{\overset{\|}{C}}- \right]_n$$

$-CH_3$	methyl	poly(-3-hydroxybutyrate) (P3HB)
$-CH_2-CH_3$	ethyl	poly(-3-hydroxyvalerate) (PHV)
$-(CH_2)_2-CH_3$	propyl	poly(-3-hydroxyhexanoate) (PHH)
$-(CH_2)_4-CH_3$	pentyl	poly(-3-hydroxyoctanoate) (PHO)
$-(CH_2)_6-CH_3$	nonyl	poly(-3-hydroxydecanoate) (PHD)

Polyhydroxyalkanoates (PHA)s

- Properties
  - Vary according to composition of monomeric unit and final polymer structure
  - T_g from −50 °C to 4 °C, T_m from 40 °C to 180 °C
  - Can be processed on conventional processing equipment
  - UV stable, in contrast to other bioplastics such as polylactic acid
  - The crystallinity in the range 5 to 70%
  - **biodegradable** and **biocompatible** (not toxic and compatible with human tissue)

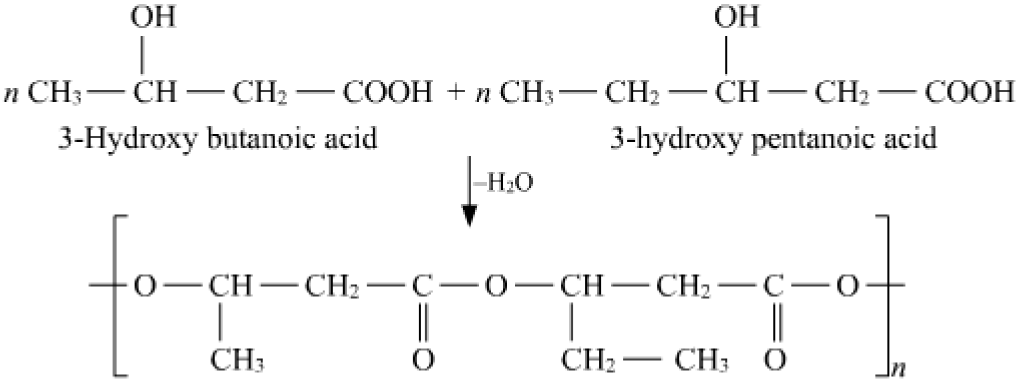
- Application
  - **biomedical** sector
  - tissue engineering
  - bioimplant patches
  - drug delivery
  - surgery and wound dressing

Poly-3-hydroxybutyrate (P3HB)

- Properties similar to those of polypropylene (PP)
  - Good oxygen permeability and UV resistance
  - Biocompatible and suitable for medical applications
  - Poor resistance to acids and bases
  - **Water insoluble** and relatively resistant to hydrolytic degradation (other biodegradable plastics are water-soluble or moisture-sensitive)

- Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) **copolymer PHBV**

- PHBV is used in speciality packaging, orthopedic devices and in controlled release of drugs



$$n\,CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-COOH + n\,CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-COOH \xrightarrow{-H_2O} \left[-O-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{CH_2-CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O-\right]_n$$

PHBV

BIOBASED POLYMERS

- **Biopolyesters**
  - Polylactic acid polymer or polylactide (PLA)

- **Polyamide 11** – derived from natural oil (castor beans)

- **Biopolyethylene** – derived from sugar cane and corn

- The **raw material** for their **synthesis are biomonomers derived** from the various type of **plants**

- Today are intensively studied to **replace synthetic polymers** which are not **biodegradable**

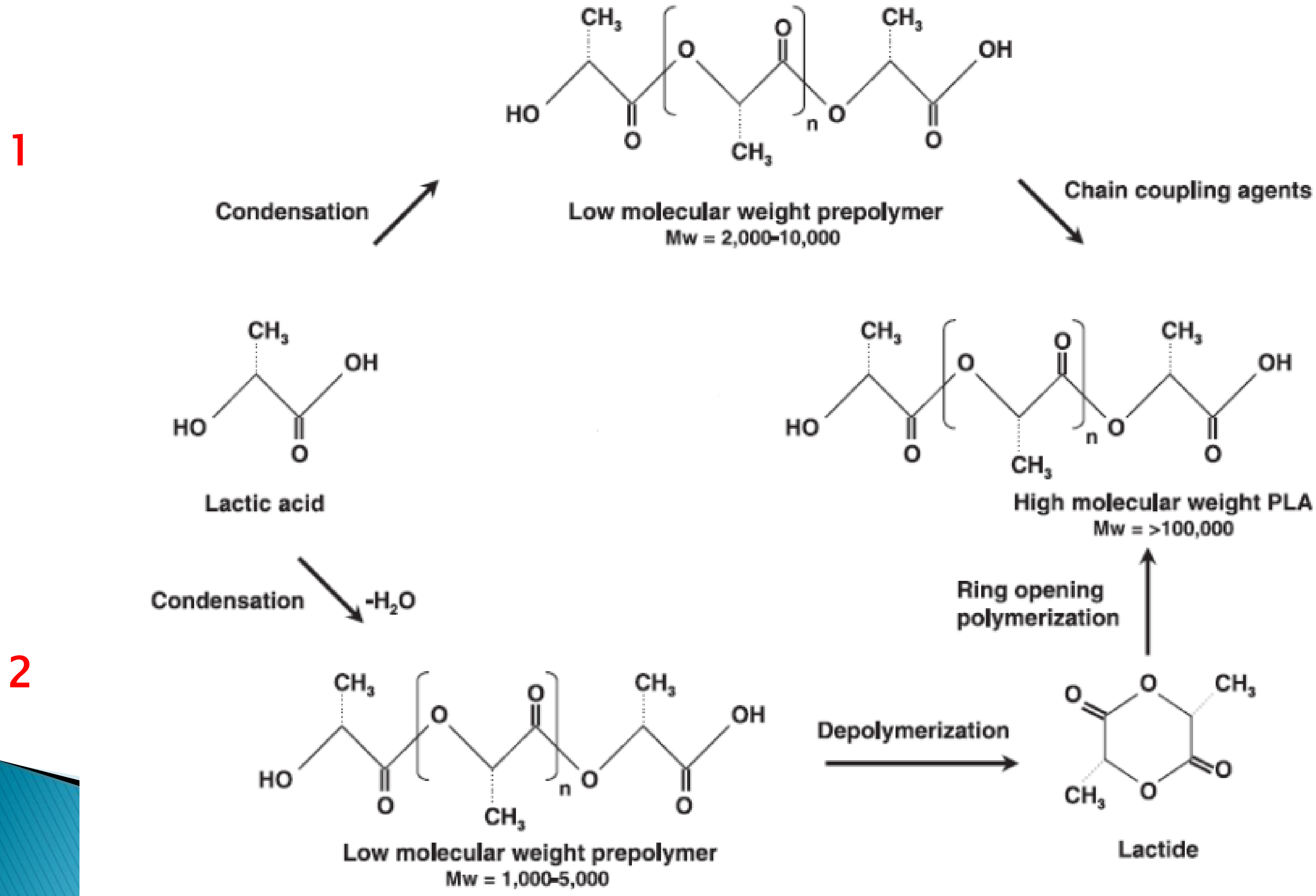
Polylactid acid (PLA)

- Poly(lactic acid) by IUPAC nomenclature
- Obtained from **biomonomer lactic acid** or cyclic dimer **lactide**
- Made from fermented plant **starch from corn, cassava, sugarcane or sugar beet**
- Biodegradable **thermoplastic** – linear polyester
- **Biodegradable under industrial composting conditions** – chemical hydrolysis followed by microbial digestion
- Under industrial composting conditions (60 °C), PLA about **half decomposes into H_2O and CO_2 in 60 days**, the remainder decomposes much more slowly, rate depends on the degree of crystallinity
- Without necessary conditions very slow decomposition similar to non-bioplastics, not fully decomposing for hundreds or thousands of years

Polylactid acid (PLA)

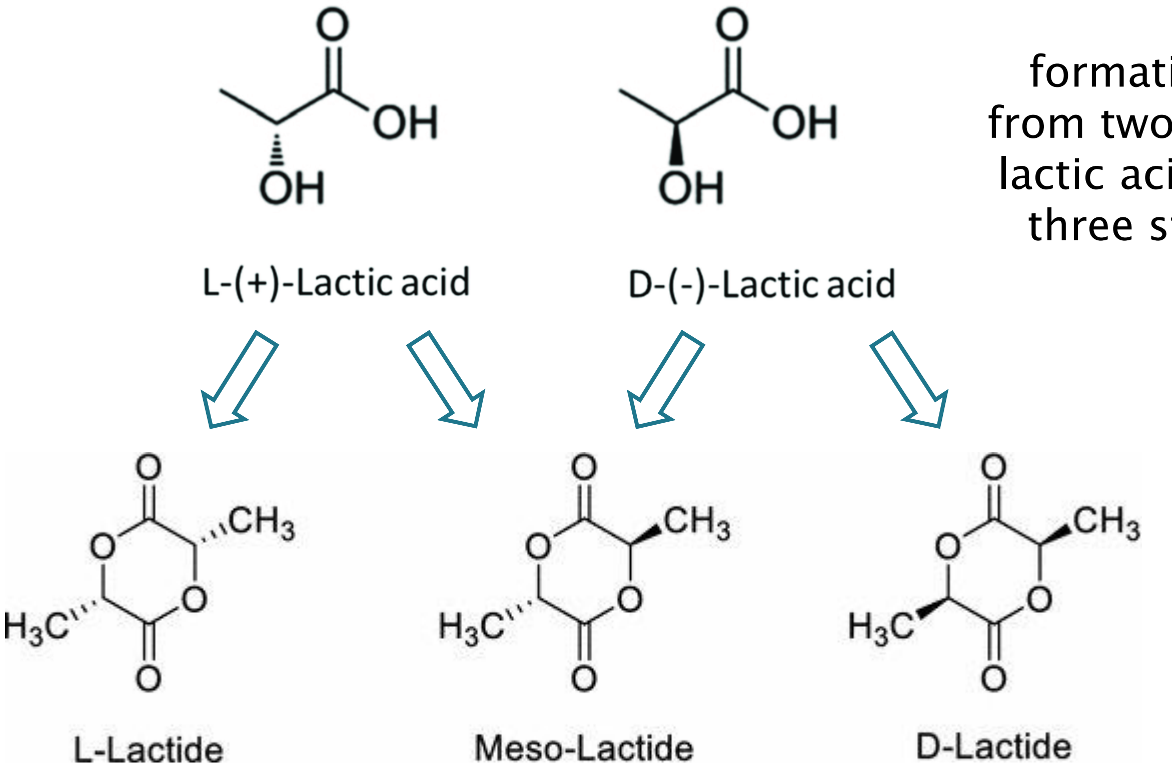
- Two important methods for PLA synthesis:

1) **direct polycondensation** of **lactic acid**
2) **ring opening polymerization** of lactic acid cyclic dimer **lactide**



Polylactid acid (PLA)

- Lactic acid gives **3 type of lactide monomers** for the synthesis of PLA



formation of lactide from two equivalents of lactic acid gives rise to three stereoisomers

- Because of that, **various structure** and properties of PLA are obtained

Polylactid acid (PLA)

- Several **different types** of PLA:
  - PLLA (Poly-L-lactic acid), product resulting from **polymerization of L-lactide**
  - PDLA (Poly-D-lactic acid), product resulting from **polymerization of D-lactide**
  - PDLLA (Poly-D,L-lactic acid), **racemic mixture**=equal amounts of left- and right- handed enantiomers of a chiral molecule

- **Amorphous** glassy polymer to **semi-crystalline** and **highly crystalline**, depending on the type of PLA (PDLA is highly crystalline)
  - Tm (melting point) = 130-180 °C
  - Tg (glass transition temperature) = 60-65 °C
  - Mechanical properties of PLA are between those of PS and PET

- **Application**
- **Consumer products** - disposable tableware, cutlery, housings for kitchen appliances and electronics, compost bags, food packaging

- **Automotive parts** - floor mats, panels, and covers

- **Medical biodegradable implants** - anchors, screws, plates, pins, rods, and mesh

- **PLA is the most widely used plastic filament material in 3D printing!**