UNIVERSITY OF ZAGREB

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

POLYMER SCIENCE AND TECHNOLOGY

Lecturer: Dr. Ljerka Kratofil Krehula, Associate Prof.

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The schedule for the lectures:

Thu 9th October 2025

Thu 16th October 2025

Thu 23rd October 2025

Thu 30th October 2025

Thu 6th November 2025

Thu 13th November 2025 *the first exam*

All lectures will be held in the lecture room Vijećnica 2, at 10:00.

The second part of the lectures: 20th November 2025

Dr. Zvonimir Katančić, Associate Prof.

Seminar task:

Ana Šaravanja, mag. ing, cheming. and Lucija Fiket, mag. ing. cheming.

- Exam

- two partial exams or

- one exam in exam terms

Total score =	1st exam	max 30 points
	2nd exam	max 30 points
	presentation	max 15 points
	presence at lectures	max 5 points
	Total	max 80 points

Positive mark: 60 % of each partial exam or

60 % of complete exam

Total score	**MARK**	
60-70%	dovoljan (2)	48-56 points
71-80%	dobar (3)	57-64 points
81-90%	vrlo dobar (4)	65-72 points
91-100%	odličan (5)	73-80 points

POLYMERS SCIENCE AND TECHNOLOGY

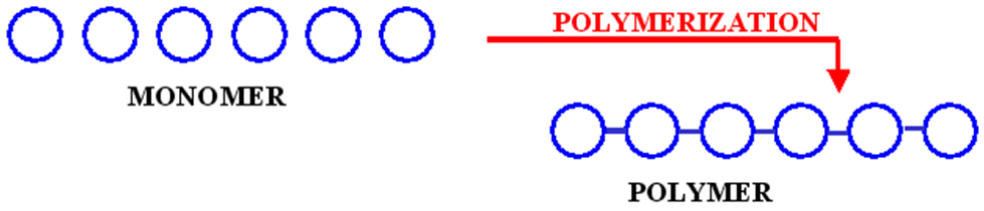
1. Introduction to polymers

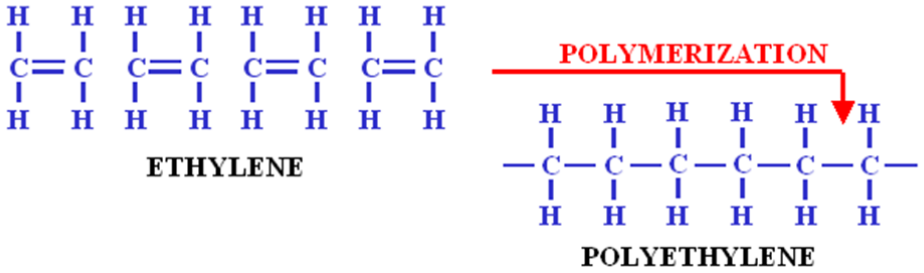
Polymers – definition?

- Types of polymers? Natural? Synthetic?
- Everyday life – examples? (just look around ☺)
  - packaging materials?
  - textile materials?
  - civil engineering?
  - farmacy, medicine?
- Advantages and disadvantages of polymer materials (comparing to metal, paper, wood)?

Polymers - definition

- Polymer - a large molecule composed of many repeated subunits (small molecules, monomers)
- Polymer - macromolecule
- Polymers are formed by polymerization reactions
- The name polymer is given in 1833. by Jöns Jacob Berzelius
- 1839. – first polymerization - Eduard Simon
- Polymers - unique properties among different types of materials





- The progress in technology is directly connected with development of new materials. In history the periods of development are named by the used materials: stone age, bronze age and iron age.

- The most important materials of modern age are: **polymer materials – 20th century „polymer age”**

DP – degree of polymerization

– number of repeating units in polymer molecule

$$M_n = DP \times M_0$$

M_n– molecular mass of polymer

M_0 – molecular mass of repeating unit

Synthetic polymers - development

- **1839.** rubber was obtained by vulcanization from natural caoutchouc – highly elastic material was gained
- **1870.** commercial celluloid (film tape) is obtained, which consists of 75 % cellulose nitrate + 25 % camphor.
- **1892.** Textile fiber – ***Rayon –*** artificial silk
- **1907.** Phenol formaldehyde resin an - it is a thermosetting phenol formaldehyde resin,
- **1920.** Staudinger - hypothesis about macromolecules
  - development of rubber industry and tire industry
- **1930.** - development of polymer industry
- **1950.** - development of synthetic polymers and their industry

NOMENCLATURE OF POLYMERS

COMMON NAMES

- Names derived from the place of origin of the material:
  - natural rubber - “rubber from Brazil” *Hevea brasilliensis*

- Polymers named after their discoverer:
  - the three-dimensional polymer produced by condensation of phenol and formaldehyde – *Bakelite (*commercialized by Leo Baekeland in 1905)

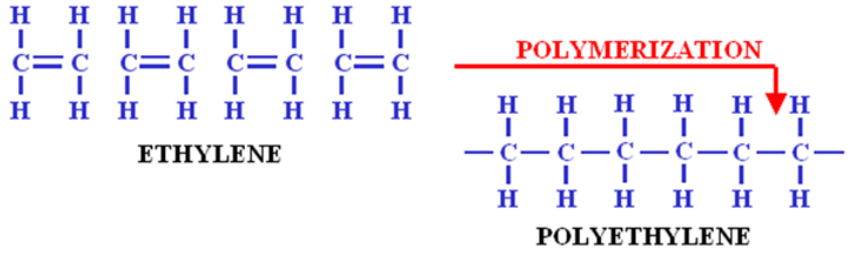
- *Nylons* were named according to the number of carbons in the reactants used in their synthesis:
  - the *nylon* produced by the condensation of 1,6-hexamethylenediamine (6 carbons) and adipic acid (6 carbons) is called *nylon 66.*

SOURCE-BASED NAMES

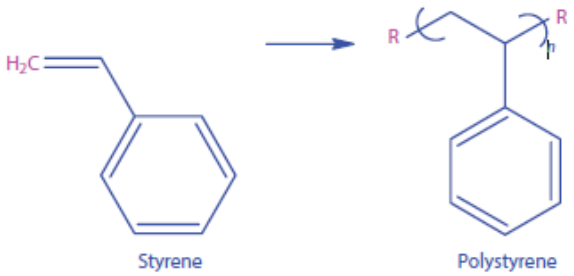
- Names consisted of:

common name of the reactant monomer, preceded by the prefix “poly”:

poly + ethylene = polyethylene, PE

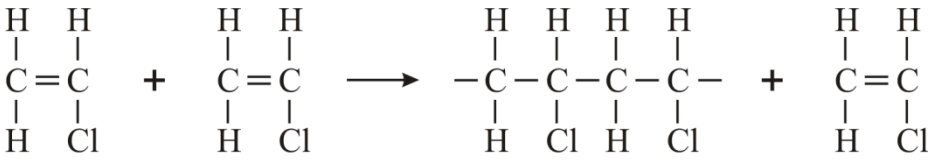


poly + styrene = polystyrene, PS

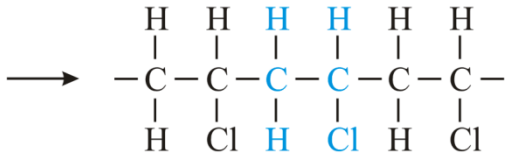


polymers based on the vinyl group H_2C-CHX

for example poly(vinyl chloride) from the monomer vinyl chloride



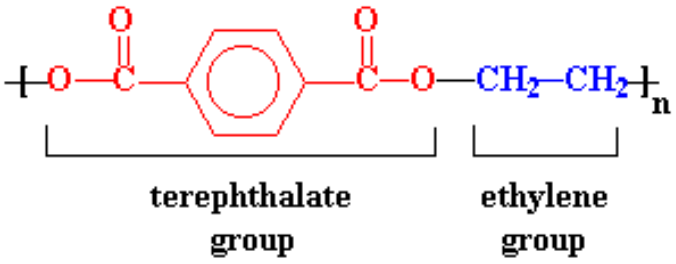
vinyl chloride monomers



poly(vinyl chloride)

poly(ethylene terephthalate), PET:

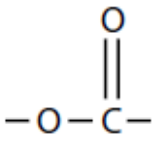
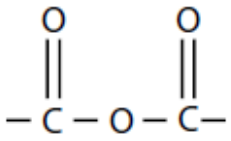
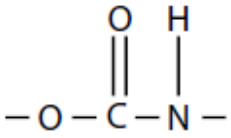
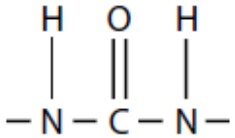
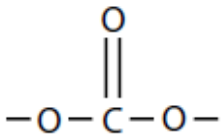
The glycol portion of the name of the monomer, ethylene glycol,
is used in constructing the polymer name together with the second reactant terephthalic acid



Source-Based Names	Structure-Based Names
Polyacrylonitrile	Poly(1-cyanoethylene)
Poly(ethylene oxide)	Polyoxyethylene
Poly(ethylene terephthalate)	Polyoxyethyleneoxyterephthaloyl
Polyisobutylene	Poly(1,1-dimethylethylene)
Poly(methyl methacrylate)	Poly[(1-methoxycarbonyl)-1-metylethylene]
Polypropylene	Poly(1methylethylene)
Polystyrene	Poly(1-phenylethylene)
Polytetrafluoroethylene	Polydifluoromethylene
Poly(vinylacetate)	Poly(1-acetoxyethylene)
Poly(vinyl alcohol)	Poly(1-hydroxyethylene)
Poly(vinyl chloride)	Poly(1-chloroethylene)
Poly(vinyl butyral)	Poly[(2-propyl-1,3-dioxane-4,6-diyl) methylene]

LINKAGE-BASED NAMES

- by the name of the particular linkage that connects the polymers

Family Name	Linkage	Family Name	Linkage
Polyester		Polyanhydride	
Polyurethane		Polyurea	
Polyether		Polycarbonate	
Polysiloxane		Polysulfide	

TRADENAMES AND ABBREVIATIONS

Trade names and abbreviations - used to describe material:

- to identify the product of a manufacturer, processor, or fabricator

  for example: *Mipolam*, *Opalon*, *Pliofex*, *Rucon* are all tradenames for poly(vinyl chloride) manufactured by different companies

- may be associated with a particular product or with a material

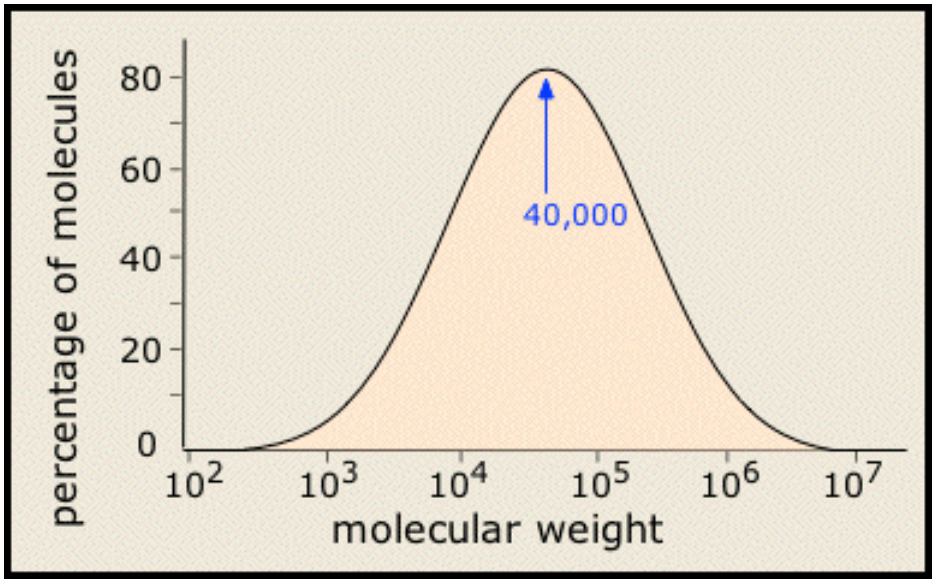
Abbreviation	Polymer	Abbreviation	Polymer
ABS	Acrylonitrile-butadiene-styrene terpolymer	CA	Cellulose acetate
EP	Epoxy	HIPS	High-impact polystyrene
MF	Melamine-formaldehyde	PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile	SBR	Butadiene-styrene copolymer
PBT	Poly(butylene terephthalate)	PC	Polycarbonate
PE	Polyethylene	PET, PETE	Poly(ethylene terephthalate)
PF	Phenyl-formaldehyde	PMMA	Poly(methyl methacrylate)
PP	Polypropylene	PPO	Poly(phenylene oxide)
PS	Polystyrene	PTFE	Polytetrafluoroethylene
PU	Polyurethane	PVA, PVAc	Poly(vinyl acetate)
PVA, PVAl	Poly(vinyl alcohol)	PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)	SAN	Styrene-acrylonitrile
UF	Urea-formaldehyde		

Polymers vs. „small molecules”

Lowmolecular substances („small molecule”) have a definite structure, molar mass and properties.

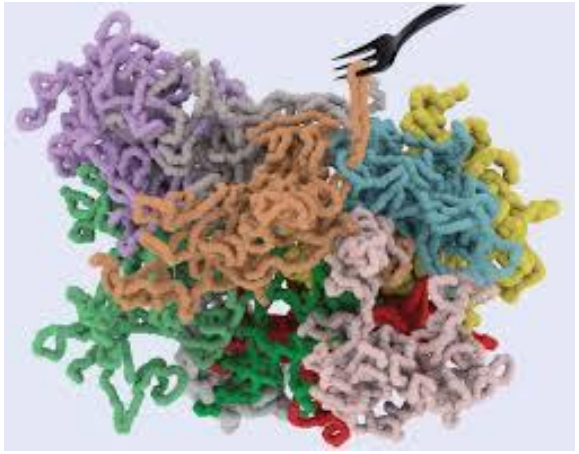
Polymeric substances are not uniform:

- their molecular weights cover a range of values,
- the most synthetic polymers are the *mixtures* rather than pure substances
- their molecular weights are typically distributed over a wide range



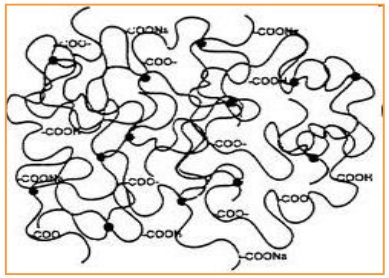
average molecular weight

Shapes of polymer molecules: "spaghetti"

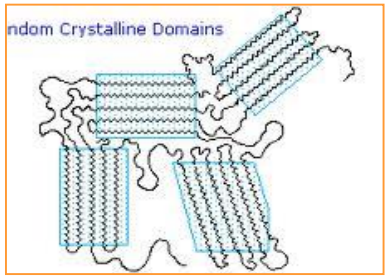


Polymers are not straight, linear chains.

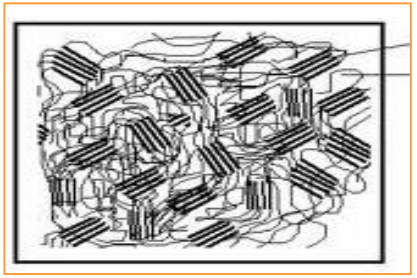
- long polymer molecules tend to curl up – it is allowed by a free rotation around C—C bonds
- polymers tangle like spaghetti.
- for that reason polymers generally form *amorphous* solids.
- certain polymers can be partially oriented



Amorphous



Crystalline



Semicrystalline

POLYMERS - classification

- **Polymers can be classified according to:**
  - **Origin**

    natural & synthetic polymers
  - **Physical-mechanical properties**

    plastic & rubber
  - **Chemical composition**

    olefines, polyesters, polyurethanes…
  - **Application**
    - Coatings
    - Fibers
    - Packaging
    - Special use: medicine, pharmacy, electronics…

Chemical structure:

- nature of the monomeric units
- method of polymerization
- average chain length and molecular weight
- *homopolymers* (one type of monomeric unit) or *copolymers* (two or more types of monomeric unit)
- with or without branching and/or crosslinking

Properties:

- density PE, PP lower than 1 g cm^{-3}
  PET, PVC higher than 1 g cm^{-3}
- Degree of crystallinity
- thermal properties - are they melted when heated?
- physical properties: hardness, strength, toughness
- permeability to gases
- solubility,

Applications:

- sheets, films, foils
- elastomers
- adhesives
- fibres and yarns
- coatings
- paints
- inks

Polymers by their origin

Natural polymers

Synthetic polymers

- with addition of additives (fillers, dyes, stabilizers)
  – polymers are converted to polymer materials

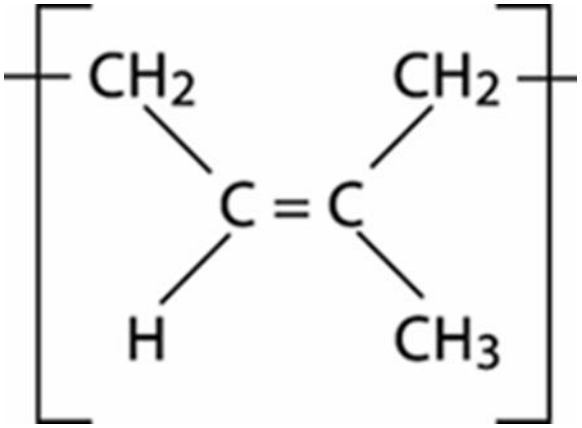
Natural polymers – biosynthesis in nature

- Some natural polymers are not used as polymer materials like: polysaccharides, enzymes and proteins, but they are macromolecules by their structure - polymers.

- Materials from natural polymers:
  natural leather, silk, cellulose, cellulose derivates,
  natural rubber.

***Natural rubber* -** the only one of natural materials which is by its structure completely equal to synthetic polymer (repeating structural unit – isoprene)

Natural rubber comes from latex (natural caoutchouc), a milky substance produced by plant *Hevea Brasiliensis.*



polyisoprene

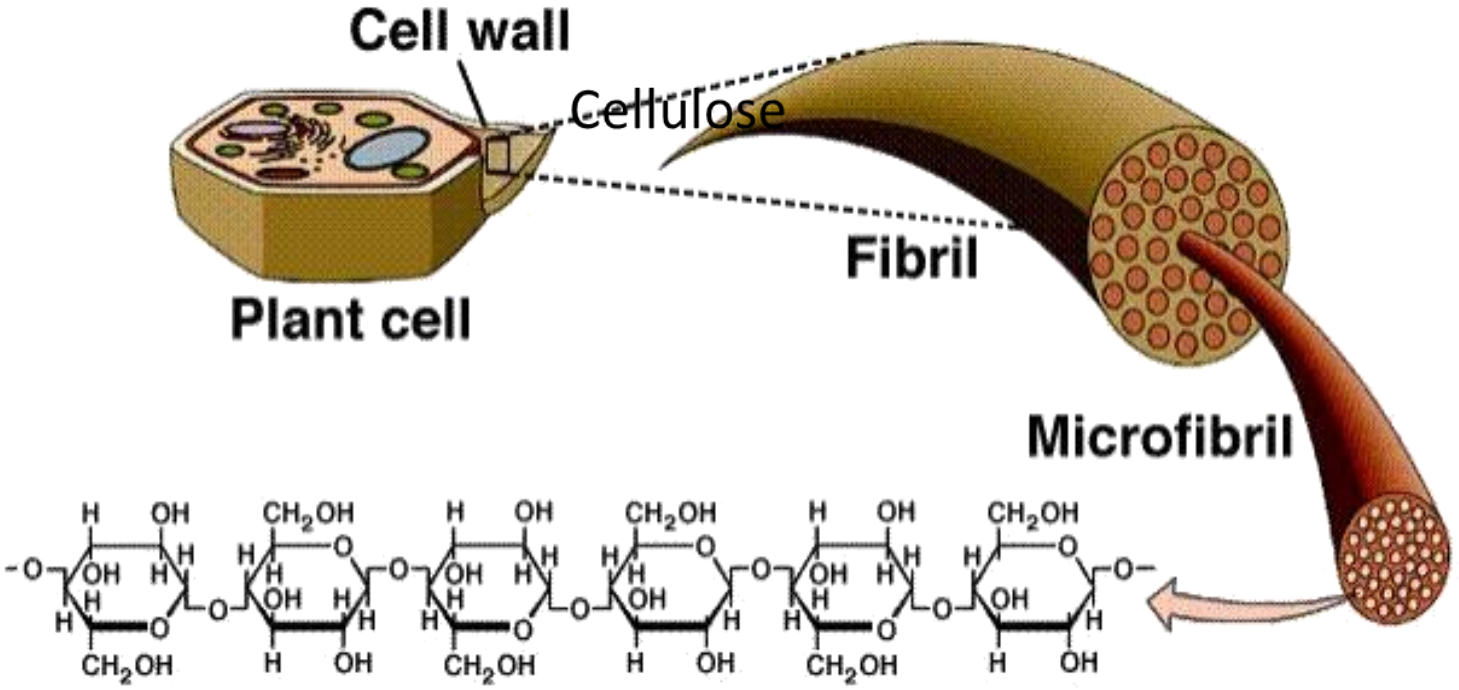
Charles Goodyear – the first vulcanization of **caoutchouc**
1839. - heating of natural caoutchouc with sulphur – **rubber is produced**

caoutchouc – unvulcanized
rubber – vulcanized
Caoutchouc is by vulcanization transferred to rubber.

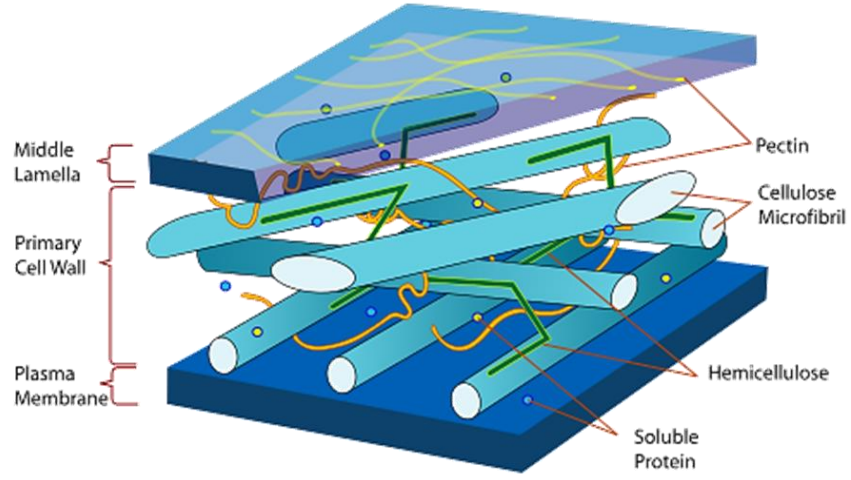
Cellulose

Cellulose is a long-chain polysaccharide carbohydrate. It is a polymer made of repeating beta-glucose molecules attached end to end. A cellulose molecule may be from several 100 to over 10,000 glucose units long.

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



- Cellulose - discovered in 1838 by the French chemist Anselme Payen, who isolated it from plant and determined its chemical formula
- Cellulose is the most abundant naturally occurring organic substance
- Cellulose can be found in almost pure form in cotton fibre – 98 % in combination with lignin and hemicellulose, pectin and other substances



Synthetic polymers

Plastic materials

Rubber materials

Synthetic polymers – *plastic materials*

Thermoplastics – a definite softening point that is observed
This defines the glass transition temperature Tg .

At a higher temperature, the melting point Tm - the crystalline regions come apart and the material is a viscous liquid.

- polymer can be easily injected into the molds to manufacture objects of different shapes
- polymer can be extruded into sheets or fibers.

- Thermoplastics - about 80 % of the commercially produced polymers

Thermosets – polymers which do not melt at all
The polymerization reaction must take place within the molds if they are to be made into molded objects

- thermosets - about 20 % of the commercially produced polymers

Synthetic polymers – *plastic materials*

Thermoplastic

- **Thermoplastic polymers**
  - Polyethylene (PE)
    - low density polyethylene (LDPE)
    - high density polyethylene (HDPE)
  - Polypropylene (PP)
  - Polystyrene (PS)
  - Poly(vinyl-chloride) (PVC)
  - Polycarbonate (PC)
  - Polyamide
  - Poly(methyl-methacrylate)(PMMA)
  - Poly(ethylene-terephthalate) (PET)

- **Used as:**
  - Plastics in everyday use
  - Fibers
  - Packaging materials
  - Bottles

  Synthesized by polymerization process and then processed into different products.

- **Processing Technology:**

  - extrusion,
  - injection molding
  - yarn, coatings

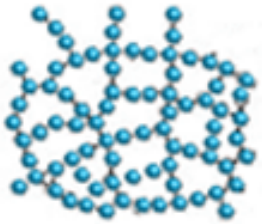
- **Thermosets** (resin)
  - Polyesters
  - Polyurethanes
  - Epoxy resins
  - Polyacrylates

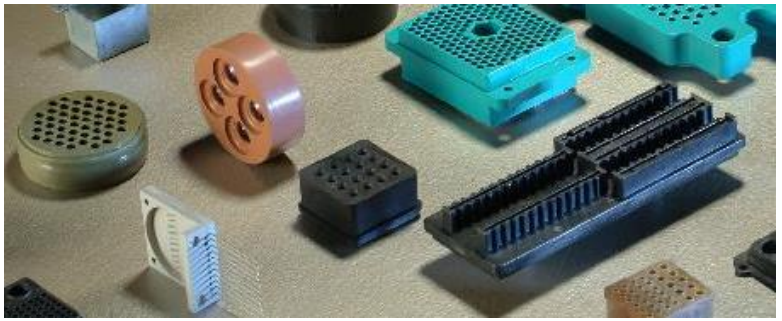
Synthesized by condensation polym. and process at the same time.

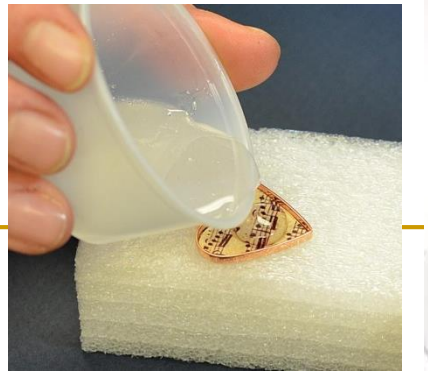
- **Processing Technology:**

by irreversible curing process in mould - transforming the resin into a plastic or rubber by a cross-linking process.

Used as: adhesive, coatings, products of various shapes, elastomers







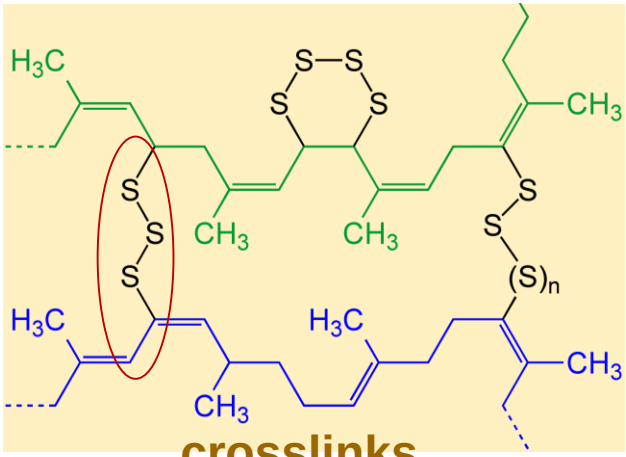
Synthetic polymers – *rubber materials* (elastomers)

Natural(NR) & Synthetic rubber

- Polybutadiene
- Polychloroprene
- Polyisoprene also NR
- Polyurethane
- Styrene Butadiene
- Polysiloxane

Vulcanization

- Modification of unvulcanized polymer by forming crosslinks (bridges) between individual polymer chains: rubber is obtained.



crosslinks

Unvulcanized rubber – obtained by polymerization

Processing Technology

- **Rubber is always first compounded with additives:**

sulphur or peroxide – for vulcanization,

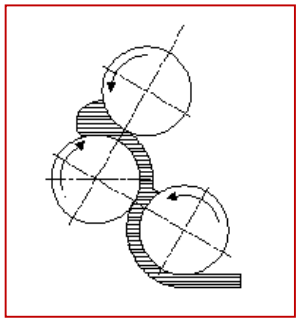
fillers antioxidants, plasticizers

to achieve uniform dispersion of ingredients in rubber.

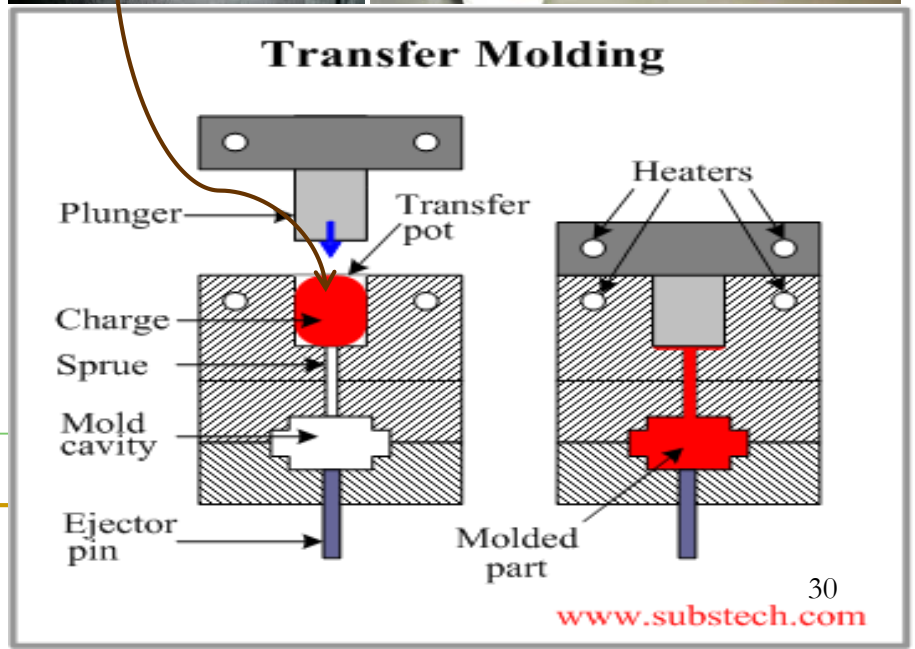
Formed compounds are shaped during processing by

- Extrusion
- Calandering
- Coating
- Molding and casting and

- Vulcanization during processing



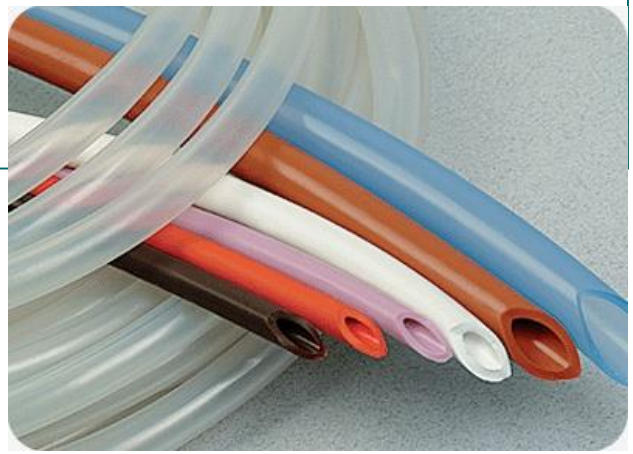
Elastomer



Elastomer

- **Rubber Latex products**
  (contain cca 35 mass% of rubber)
  products with thin walls:
  gloves, balloons...

- **Major Rubber products**
  - **tires,**
  - **pipes,**
  - **hoses**



POLYMERS

POLYMERS PROPERTIES DEPEND ON: Structure of polymer

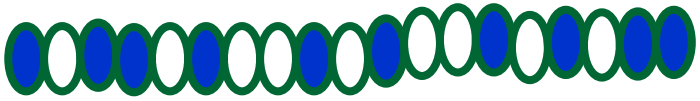
Homopolymers

Polymer chain is consisted of **one** type of monomer

Copolymers

Polymer chain is consisted of **two or more** types of monomers

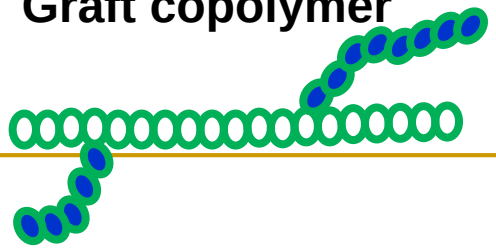
Random copolymer



Block copolymer

Alternating copolymer

Graft copolymer

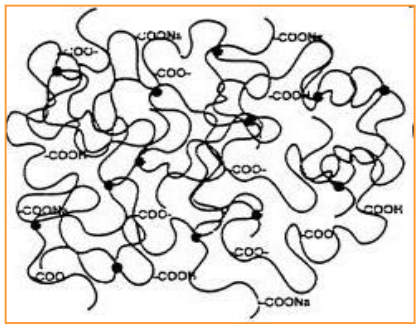


POLYMERS

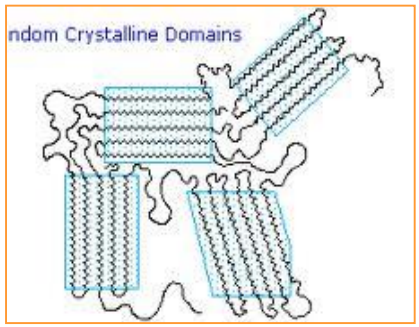
POLYMERS PROPERTIES DEPEND ON: Structure of polymer

Linear polymer chain

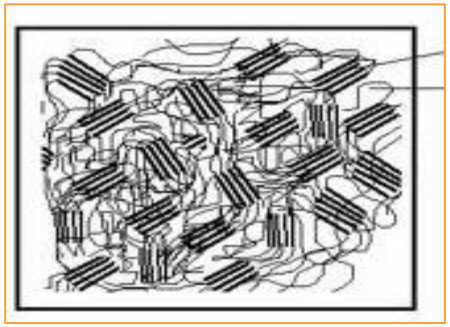
Branched polymer chain



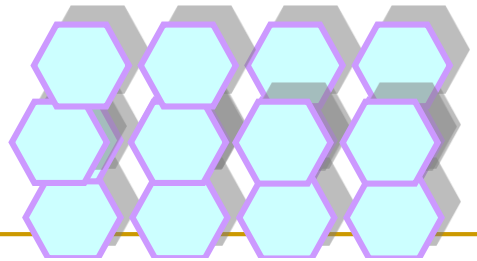
Amorphous



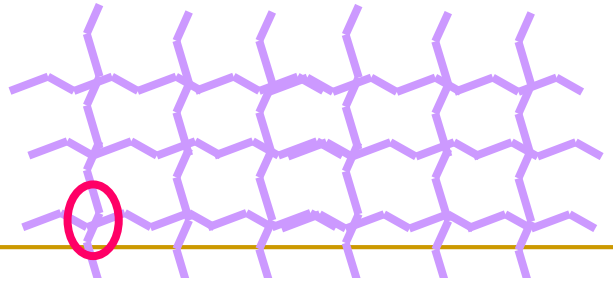
Crystalline



Semicrystalline



Cross-linked thermosets



Cross-linked rubber

PROPERTIES of POLYMER MATERIALS

- **Chemical properties**
  - Degradation
  - Solubility
  - Flammability
  - Barrier Properties
- **Mechanical properties**
  - Tensile strength
  - Elongation
  - Hardness

- **Physical properties**
  - Melting Temperature
  - Density
  - Viscosity
- **Optical**
  - Transparence
- **Electrical**
  - Electrical Conductivity

POLYMER MATERIALS

Structure - properties relationship:

CHARACTERIZATION of POLYMERS

- **Properties are an outcome of composition and structure!**

By determination of properties we describe the inner structure of material

a) chemical composition
b) chain structure
c) size and distribution of molecular mass
d) amorphous / crystalline structure
e) morphology - the shape & size structure

Structure- properties

PROPERTIES

WHY

TO DETERMINE THE FIELD OF APPLICATION
TO DETERMINE THE QUALITY OF PRODUCTS

POLYMER MATERIALS

Structure - properties relationship: Molecular masses

Polymeric molecules are very large (on the molecular scale), and their unique and useful properties are mainly a result of their size.

the number average molecular mass (Mn)
the weight average molecular mass (Mw)

Every change in molecular masses of polymer like:

- size of main chain
- size of side chains
- type of side groups

can be detected and affect the properties.

Gel permeation chromatography (GPC) is often used to determine the **relative molecular mass** of polymers as well as the **distribution of molecular masses -** polydispersity index (PDI)

POLYMER MATERIALS

Structure - properties relationship!

An example:

Chain structure: **linear**

- **HDPE - high-density polyethylene**
- **Ziegler-Natta-polymerization** (catalysts)
- **Properties are:**
- **Average molecular masses**
  - **200.000-500.000**
- **The density is in the range from 0.96 to 0.97 g/cm³.**
- **Its melting point is** 125 to 135 °C and withstands temperatures of 100 °C.
- **Moleculs have only a few branches, giving it stronger intermolecular forces and higher tensile strength**

Products

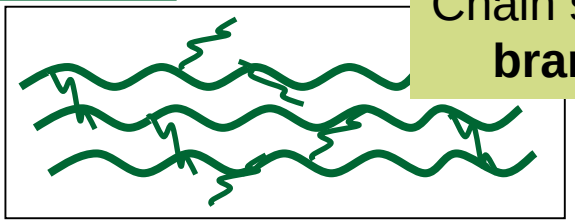
- **Bottles**
- **Gasoline tanks**
- **Milk bottles**
- **Children's toys**

Processing

- **Plastic moulding**
- **Plastic injection moulding**
- **Extrusion**
- **Film blowing**
- **Blow molding**

Structure - properties relationship!

Chain structure: **branched**



- **For example:**
- **LDPE – low-density polyethylene**
- **Free radical polymeriz.** (peroxide catalysts)
- **Average molecular masses**
  - **30.000- 300.000**
- **Density - from 0.91 to 0.94 g/cm³**
- **Its melting point is** 105 to 115 °C and withstand temperatures of 80 °C
- **Moleculs have more branches** (on about 2% of the carbon atoms**) than HDPE**
- **Branching is giving weaker intermolecular forces and tensile strength is lower but elasticity is higher**

Products

- **films & foils for packaging,**
- **trays and plastic bags (food and non-food purposes)**
- **protective coating on paper, textiles or other materials (for examp. in milk cartons)**
- **Plastic bags**
- **Garbage bags**

Processing

- **Plastic moulding**
- **Plastic injection moulding**
- **Extrusion**
- **Film blowing**

Structure - properties relationship!

Chain structure:
high mol. masses

- **For example:**
- **UHMWPE – Ultra-high-molecular-weight polyethylene**
- **Metallocene catalysts polymerization**
- **Average molecular masses**
  - **usually between 2 and 6 million**
- **Density - from 0.93 to 0.935 g/cm³.**
- **Its melting point is around 144 to 152 °C and** withstands temperatures of 80 °C
- **Longer chain serves to strengthen intermolecular interactions**
- **This results in a very tough material, being *15 times* more resistant to abrasion than carbon steel**

Products

- **Cans and bottles**
- **Handling machine parts, moving parts on machines; ice surface for skating**
- **bulletproof vests,**
- **used for implants**

artificial bones: hip and knee replacements

Processing

- **compression molding**
- **extrusion**
- **spinning**

Literature:

1. H. Mark, N. Bikales, C. Overberger, G. Menges, Encyclopedia of Polymer Science and Engineering, John Wiley & Sons, New York, Vol. 1-17, 1985-1989.

2. Joel R. Fried, Polymer Science and Technology, Prentice Hall Professional, USA, 2003.

3. L.A. Utracki: Polymer Alloys and Blends, Hanser Publishers, New York, 1989.

4. A. L. Andrady, «Plastics and the Environment», J. Wiley & Sons, Hoboken, New Jersey, 2003.

5. A. Azapagic, A. Emsley, I. Hamerton "Polymers, the Environmental and Sustainable Development" J. Wiley & Sons, N.Y. 2003.

6. C. E. Carraher, Introduction to Polymer Chemistry, Taylor & Francis, 2017.