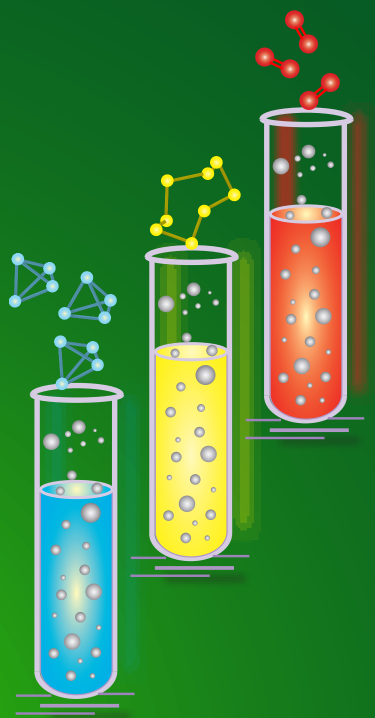
CHEMISTRY AND MATERIALS



- Iron
- Zinc
- Copper
- Alloys
- Glass
- Ceramics
- Plastics
- Rubber
- Chemical fibres

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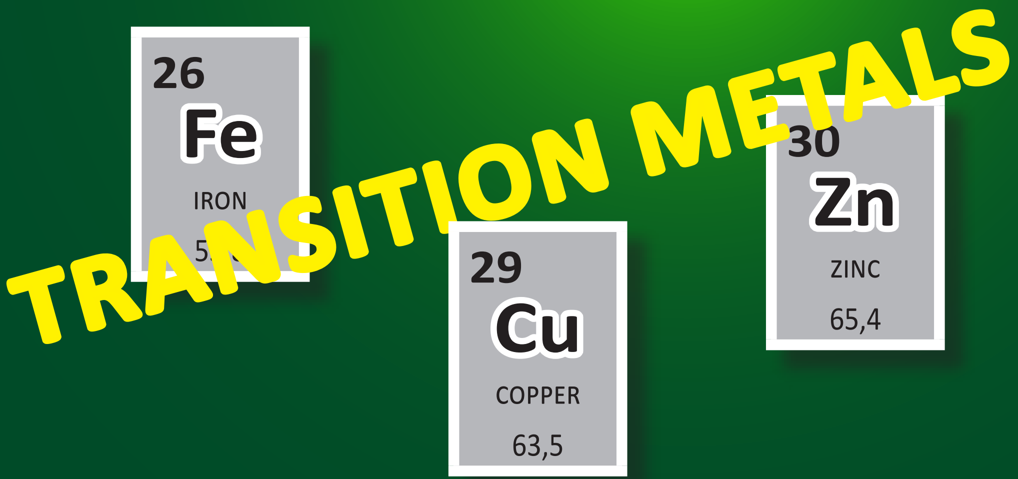
28 Metals in real-life.

Iron Fe, copper Cu, zinc Zn and their compounds

KEY TOPICS

1. What are transition metals?
2. What is the most used metal?
3. Why are copper and zinc widely used metals?



KEY WORDS

- Transition metals
- Iron
- Ferrous ion
- Ferric ion
- Copper
- Cuprous ion
- Cupric ion
- Zinc
- Zincate ion

Most of the chemical elements are metals. Alkali (1, IA group) alkaline-earth metals and magnesium (2, IIA group) are typical active metals. All elements of the secondary groups (3rd - 12th or IB - VIIIB) are also metallic elements. They are known as **transition metals**. Some of the most important metals are iron Fe, copper Cu and zinc Zn.

26
Fe
IRON
55,8

IRON Fe is a 8th (VIIIB) group silvery-gray metal. Iron is one of the most abundant elements in the universe. On Earth it is found as the minerals **hematite** Fe_2O_3, **magnetite** Fe_3O_4, **limonite** $FeO(OH).nH_2O$, **siderite** $FeCO_3$, **pyrite** FeS_2 and others. Only aluminum is a most abundant metal in the Earth crust. The human body contains about 4,5 g of iron (65 % in the form of hemoglobin).

Iron has three allotropes with different metal lattices. **δ-iron** is stable above 1 390 °C. **γ-iron** is stable between 1 390 °C and 910 °C. At a temperature lower than 910 °C iron exists as **α-iron**.

Iron is a good conductor of electricity and heat. It is soft, ductile, malleable and has tensile strength.

OXIDATION STATES

Unlike alkali and alkaline-earth metals, iron is present in chemical compounds in different oxidation states. The most common are Fe^{2+} and Fe^{3+}. The ion Fe^{2+} is named ferrous ion and the ion Fe^{3+} is named ferric ion. The aqueous solutions containing Fe^{2+} ions are pale-green in colour, while the aqueous solution containing Fe^{3+} ions are yellow in colour.

CHEMICAL PROPERTIES

Iron is an active metal. In dry air it reacts vigorously upon heating with **oxygen O_2**, **halogens**, **sulfur** and other nonmetals. In the reaction with oxygen two oxides are formed – the greenish to black ferrous oxide **FeO** and the reddish-brown to black ferric oxide **Fe_2O_3**.

$$3Fe + 2O_2 \xrightarrow{t^o} FeO.Fe_2O_3$$

The product is a mixture of the two oxides and is expressed as **Fe_3O_4** ferrous ferric oxide.

With halogens and sulfur iron forms salts – ferrous chloride $FeCl_2$, ferric chloride $FeCl_3$, ferrous sulfide FeS, etc.

$$2Fe + 3Cl_2 \xrightarrow{t^o} 2FeCl_3 \qquad Fe + S \xrightarrow{t^o} FeS$$

When iron is in contact with water it **corrodes** (it reacts with the dissolved in the water oxygen and transforms into rust $Fe_2O_3.nH_2O$).

Iron is before hydrogen in the activity series of metals. It easily reacts with dilute acids and displaces less active metals from their compounds.

$$2Fe + 2HCl \rightarrow 2FeCl_2 + H_2\uparrow \qquad Fe + CuSO_4 \rightarrow FeSO_4 + Cu$$

The reaction with strong acids that are strong oxidizing agents (e.g. HNO_3) is more complex.

$$Fe + 4HNO_3 \xrightarrow{t^o} Fe(NO_3)_3 + NO\uparrow + 2H_2O$$

USES

Iron is the most used of all metals as it is a low cost and high strength metal. The world production is over 500 million tonnes per year. In addition, the recycled iron is over 300 million tonnes.

Iron is used everywhere. Most often it is used in the form of alloys. The sulfates and chlorides of iron are also produced on a large scale. $FeSO_4$ is a fertilizer and a pesticide. It is used to treat iron deficiency. $Fe_2(SO_4)_3$ is used to purify water and in textile dyeing. $FeCl_2$ is a reducing agent and is also used in textile dyeing. Both $FeCl_2$ and $FeCl_3$ are used to treat sewage waters.

29
Cu
COPPER
63,5

Copper Cu is an 11th (IB) group reddish metal. Like iron, copper has been used since ancient times. Copper is not a reactive metal and In nature it occurs in pure form but also in many minerals as chalcopyrite $CuFeS_2$, covellite CuS, chalcocite Cu_2S, malachite $Cu_2CO_3(OH)_2$, cuprite Cu_2O, tenorite CuO and others. Copper is a corrosion resistant metal (it is after hydrogen in the activity series of metals). It is a very good electrical and thermal conductor. It is malleable and ductile.

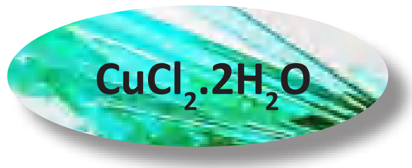
OXIDATION STATES

Copper is present in chemical compounds in oxidation states Cu^+ and Cu^{2+}. In a flame test compounds containing Cu^+ burn blue, while compounds containing Cu^{2+} burn green. The ion Cu^+ is named cuprous ion and the ion Cu^{2+} is named cupric ion. The aqueous solution containing Cu^{2+} ions are usually **blue** in colour.

CHEMICAL PROPERTIES

Under normal conditions copper is stable in air. It reacts with oxygen upon heating. The product is the reddish coloured Cu_2O (cuprous oxide) or when it reacts with excess O_2 – the black coloured CuO (cupric oxide).

$$4Cu + O_2 \xrightarrow{t^o} 2Cu_2O \qquad 2Cu + O_2 \xrightarrow{t^o} 2CuO$$



Cooper reacts with halogens forming salts with different colours, e.g. CuF_2 is a white substance, $CuBr_2$ is black in colour, dry $CuCl_2$ is a yellow-brown salt, while the crystal $CuCl_2.2H_2O$ is blue-green in colour.

Copper can not displace hydrogen of acids as it is after hydrogen in the activity series of metals. But copper dissolves in nitric acid HNO_3. It reacts with both diluted and concentrated HNO_3 as nitric acid is a strong oxidizing agent. Both reactions are highly exothermic.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$

$$Cu + conc.4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

Soluble salts as $CuSO_4$, $CuCl_2$, $Cu(NO_3)_2$ react with soluble bases as NaOH, $Ca(OH)_2$, etc. as a blue precipitate of $Cu(OH)_2$ is formed.

$$Cu(NO_3)_2 + 2NaOH \rightarrow Cu(OH)_2\downarrow + 2NaNO_3$$

USES

Thanks to its corrosion resistance, high electrical and thermal conductivity, ductility and malleability and its easy of joining copper is widely used for pipes, cables, cookware, etc. It is also used in constructions roofing, plumbing. Often copper roofs are coated with greenish patina – compounds (oxides, carbonates, sulfides, sulfates) that form on its surface when it is exposed to air.

Copper is also an efficient solid catalyst.

Copper sulfate $CuSO_4$ (commonly known as *blue vitriol* $CuSO_4$) is used in agriculture. A mixture of $CuSO_4$ and slaked lime $Ca(OH)_2$ is known as Bordeau mixture (solution). It is used as an insecticide.

Brass, bronze and alpaca are widely used alloys of copper.

30
Zn
ZINC
65,4

ZINC Zn is a 12th (IIB) group element. It is a lustrous bluish-grey in colour metal. As it is a reactive metal it does not occur in elemental state in nature. One of the most important minerals of zinc is sphalerite ZnS. As all metals zinc is a conductor of heat and electricity.

CHEMICAL PROPERTIES

Zinc is a strong reducing agent In its compounds Zn is present in oxidation state Zn^{2+}.

Pure Zn burns in air with a bright blueish-green flame forming zinc oxide ZnO.

$$2Zn + O_2 \xrightarrow{t^o} 2ZnO$$

ZnO is an insoluble in water amphoteric oxide. It reacts with both acids and strong bases.

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$

$$ZnO + 2NaOH \xrightarrow{melting} Na_2ZnO_2 + H_2O$$

The salt Na_2ZnO_2 is named disodium zincate.

At high temperature zinc reacts with halogens forming zinc halides (e.g. $ZnCl_2$, $ZnBr_2$). They react with bases as a precipitate of $Zn(OH)_2$ is formed.

$$ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2\downarrow + 2NaCl$$

Zinc dihydroxide $Zn(OH)_2$ is an amphoteric hydroxide. It reacts with both acids and strong bases.

$$Zn(OH)_2 + 2HNO_3 \rightarrow Zn(NO_3)_2 + 2H_2O \text{ (a reaction of neutralization)}$$

$$Zn(OH)_2 + 2KOH \rightarrow K_2Zn(OH)_4$$

USES

Zinc is a widely used metal. Iron and steel are coated with a layer of Zn to prevent them from corrosion. When exposed to moisture air, zinc reacts with carbon dioxide CO_2 forming a layer of $Zn_2CO_3(OH)_2$. It coats its surface and stops the destruction of the metal.

Zinc is used in batteries. It is an additive in rubbers, plastics, ceramics, glass. It also a component of alloys (e.g. brass).

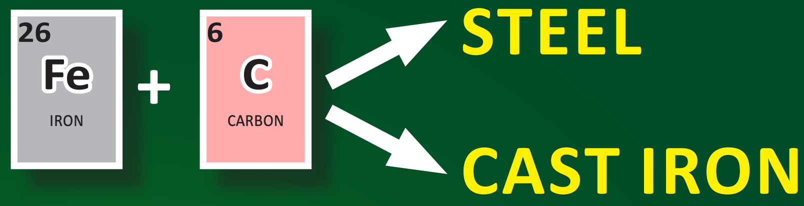
Zinc is an important microelement that is indispensable to the normal functioning of the human body.

Zinc oxide ZnO is a white pigment in paints. It is also a catalyst and a semiconductor.

CAN YOU ANSWER THESE QUESTIONS?

1. What are transition metals?
2. What is the most used metal in the industry and the everyday life?
3. Why is iron a widely used metal?
4. What are the most common oxidation states of iron Fe?
5. Why is iron an active metal?
6. What are the most common compounds of iron?
7. Why is copper widely used in electrical and plumbing industry?
8. What are the two oxides of copper?
9. Why does copper occur in elemental state in nature?
10. Why is Zn a reactive metal?
11. What character do ZnO and $Zn(OH)_2$ display?
12. Why is Zn used to protect iron and steel from corrosion?

29 Alloys

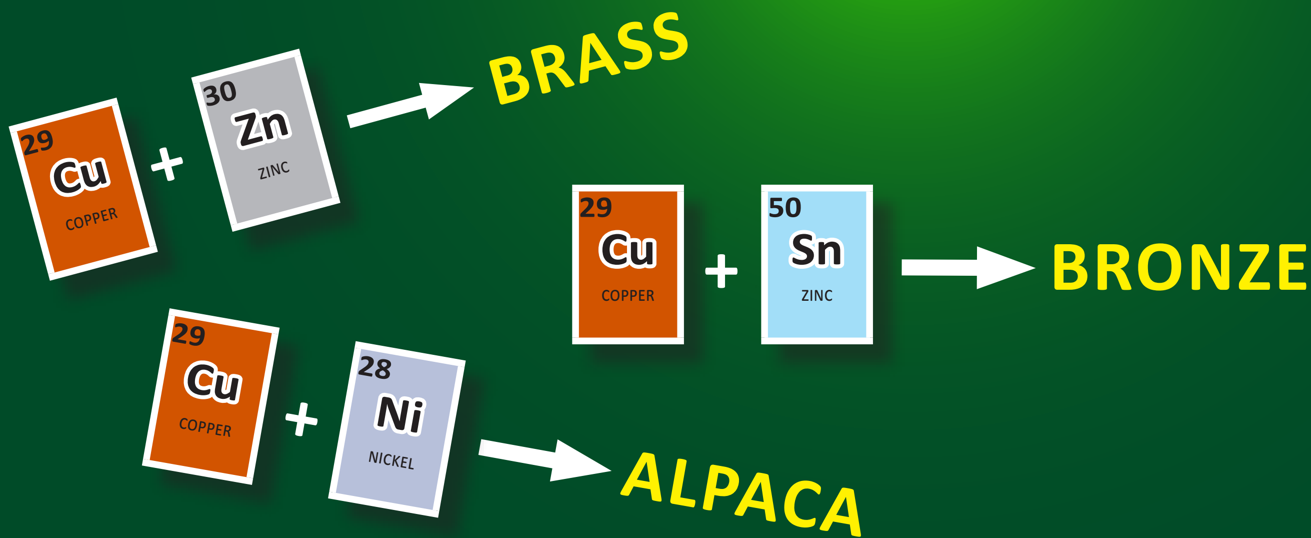


KEY TOPICS

1. What are alloys?
2. Why are alloyes widely used materials?
3. What are steel and cast iron?
4. What are bronze, brass and alpaca?

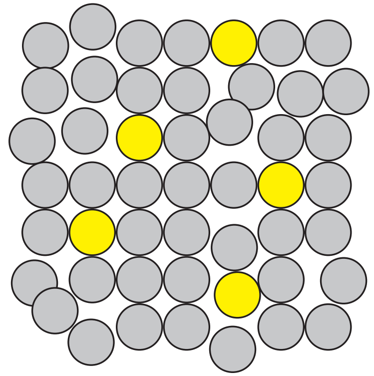
KEY WORDS

- Alloy
- Solid solution
- Mixture
- Intermetallic compounds
- Steel
- Carbon steel
- Alloy steel
- Stainless steel
- Tool steel
- Cast iron
- Bronze
- Brass
- Alpaca (nickel silver)



WHAT ARE ALLOYS?

ALLOYS are materials made of at least two elements one of which is always a metal. When heated metals melt and can be mixed with other melted metals or nonmetallic elements. Upon cooling the melt crystallises and transforms into a **solid solution**, a **mixture** or **intermetallic compounds** are formed. Solid solutions are homogeneous solid materials. Their crystalline lattices ares built up of the atoms of the alloys elements. Solid mixtures are composed of crystals of the alloy elements. Sometimes metallic elements react in molten state and form intermetallic compounds, e.g. Fe_3C (iron carbide) that makes cast iron hard and brittle, Al_2Cu is a component of duraluminum – an alloy composed of Al, Cu (about 4 %), Mn (0,5-1,5 %), Mg (0,5-1,5 %). Tis is a widely used alloy (e.g. in aircraft industry) as it is strong, lightweight and hard.



SOLID SOLUTION

Metallic atoms of the main component of the alloy

Atoms of the dissolved metal

The physical properties of alloys are not a „sum“ of the physical properties of the elements composing them. They are quite different as the alloys structure is completely different. As an idea, solder (made of tin Sn and lead Pb) melts at 180 °C, while both metals melts at a significantly higher temperature. Pure gold is soft and in jewelry most often is used an alloy containing about 50 % gold. Its colour depends on the identity of the other components of the alloy (most often silver, copper, zinc).

Some of the most widely used alloys are **steel**, **cast iron**, **bronze**, **brass**, **alpaca**.

STEEL and CAST IRON

Steel and **cast iron** are carbon-containing alloys of iron. Pure iron is a soft metal and it is not useful as a material for constructions, tools, pipes, etc. – objects containing mainly (but not only) iron and widely used in industry and the everyday life. The addition of small amounts of carbon strengthen iron, makes it harder and lowers the temperature of solidification.

Mechanical properties of the carbon-containing alloys of iron strongly depend on the amount of the added carbon. Steel contains up to 2 % of carbon, while the amount of carbon in cast iron ranges from 2 % to 4 %.

STEELS. Today are known thousands of steel grades but depending on their chemical composition steels are classified as **carbon steels**, **alloy steels**, **stainless steels**, **tool steels**.

- **Carbon steels** are composed of iron and carbon only. Their properties depend on the amount of carbon and on the heat-treating. With the increase of the amount of carbon the steel strengthens and become more brittle. The most used grades of steels contain 0,1 % - 0,25 % carbon. Almost 90 % of the steels produced in the world are carbon steels
- **Alloy steels** contain small amounts of other metals (Mg, Si, Ni, Ti, Cu, Cr, Al) to improve their mechanical properties. They depend on the amount and the identity of the added elements. For example, Mg makes steels harder and stronger and improve their resistance to shocks, strains and hammering. Cr makes steels also harder. Ni improves the steels corrosion-resistance and their strength and make them plastic. As a whole, alloy steels are with improved mechanical properties as compared to the most commonly used carbon steels – they are harder, their strength, corrosion-resistance, ductility, weldability are improved.

- **Stainless steels** contain 10 % - 20 % chromium Cr. Their corrosion-resistance is greatly improved as an invisible layer of chromium oxide coats their surface. These alloys may contain also niobium Nb, molybdenum Mo, titanium Ti.
- **Tool steels** contain tungsten W, molybdenum Mo, vanadium V, cobalt Co. They are durable and heat resistant. Molybdenum improves the steels resistance to shocks and heat, while cobalt improves the hot hardness of steels.

Steels are the most widely used material for engineering purposes because of their good mechanical properties, the low cost of their production and processing and the abundance of the raw material (iron ores and scraps). Annually, in the world are produced billions of tonnes of steels.

CAST IRON. This alloy of iron and carbon (2 % - 4 %) contains also silicon Si and manganese Mn and small amounts of impurities of sulfur S and phosphorous P). Cast iron is brittle and with a relatively low melting point. It is low cost, resistant to corrosion and deformation, neither malleable nor ductile and can not be harden.

Cast iron is used to make cookware, stoves, pipes, engine blocks and others.

BRASS. BRONZE. ALPACA

Brass, bronze and **alpaca** are alloys containing copper Cu.

BRASS. These alloys are bright-yellow in colour and contain mainly **copper Cu** and **zinc Zn**. They are produced mainly from copper scrap.

Brasses are strong, machinable, tough, corrosion-resistant (the first commercial brass was used on naval ships), conductive and with a nice appearance. Brasses containing less than 45 % Zn are malleable. Similarly to steels, the mechanical properties of brasses are improved by adding other elements (Pb, Zn, Al and others) – brasses become easy machinable, with improved corrosion resistance, strengthened.

Brasses are widely used alloys. Today are known about 60 types of brasses that are specified by EN (European norms) standards. Brasses are used to make pins, bolts, screws, faucets handles, clocks and watches components (as they ares nonmagnetic) and many other objects.

BRONZE. These alloys are composed mainly of **copper Cu** and **tin Sn**. They are hard and brittle. They are corrosion-resistant as a layer of copper oxide coats the surface of objects made of bronze when they ar exposed to air. But if by some raison coppers chlorides form on the bronze surface, the objects are destroyed as copper chlorides are soluble. This phenomenon is commonly known as „bronze disease“.

Bronzes are used in doors, windows, mail boxes, furniture, etc. Due to their low friction bronzes are also used to make pistons, rotor liners, springs. As these alloys do not cause sparks when struck, tools (e.g. hammers) designed for flammable and explosive environment are also made of bronze. Since ancient times bronze has been used to make sculptures.

ALPACA. These alloys contain **copper Cu** and **nickel Ni**, sometimes also zinc Zn, tin Sn, lead Pb cadmium Cd and other elements to improve their properties. The most widely used alloy is composed of 62 % Cu, 18 % Ni and 20 % Zn. Alpaca is commonly known also as nickel silver, nickel brass, German silver.

Alpaca alloys are white to pale-yellow (with low content of Ni) in colour. They are ductile, with good mechanical properties, malleable, hard and can be shaped. Alpaca alloys are corrosion-resistant materials. They are used in boats, plumbing, heating coils, also to make food and chemical equipment, etc. It is interesting to know that alpaca alloys are also used in musical instruments (oboes, clarinets and other wind instruments have components made of alpaca). There is no need to coat their surfaces with lacquer as alpaca is a shiny material.

Alpaca looks like silver (for this reason it is named also nickel silver) and is used in jewelry. It is less expensive than pure silver and is easy to clean.

CAN YOU ANSWER THESE QUESTIONS?

1. What are alloys?
2. Do all alloys contain metallic elements?
3. Why is it necessary to melt the metals to produce alloys?
4. Why are steel and cast iron different materials?
5. What are the most widely used steels?
6. Why are alloy steels very important materials for many engineering purposes?
7. What is stainless steel?
8. What are the most common alloys containing copper?
9. Why are brasses widely used alloys?
10. Why is bronze used to make sculptures?
11. Why is alpaca commonly known as nickel silver?

30 Glass and ceramics

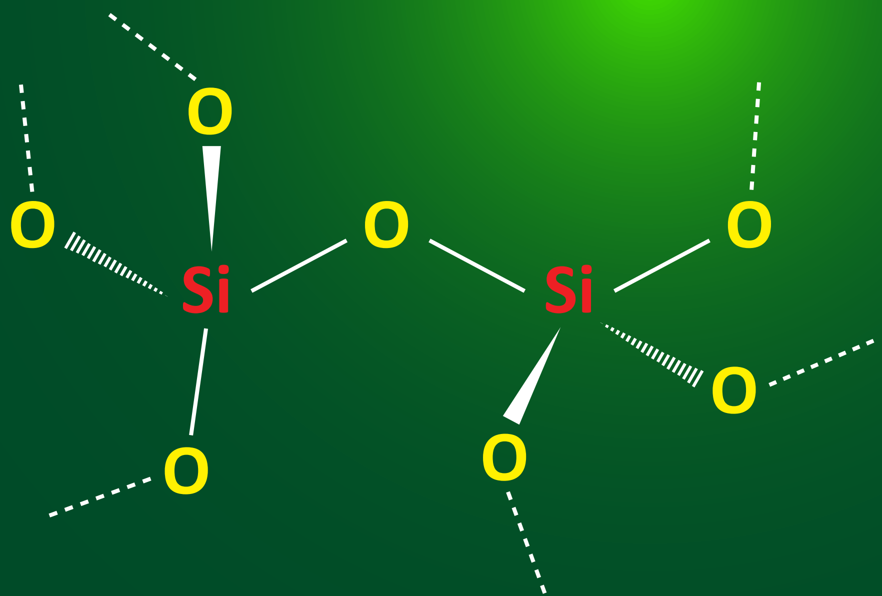
KEY TOPICS

1. What is the main component of glass?
2. Why are there many types of glasses?
3. What is ceramics?

SiO_2

KEY WORDS

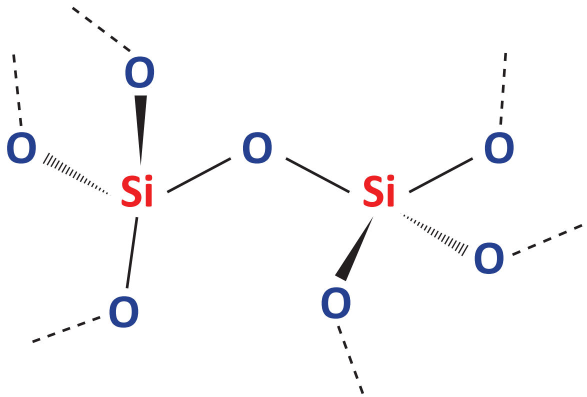
- Silica (SiO_2)
- Quartz
- Glass
- Ceramics
- Clay
- Pottery
- Porcelain



SiO_2 crystal is a giant covalent structure

SILICON Si and SILICA SiO_2

Silicon Si is an element with amazing properties. It is a 14th (IVA) group element. In the periodic table it is situated on the border line linking boron B and astatine At that separates metals and nonmetals. Silicon is a crystalline blue-grey in colour and with metallic lustre solid substance but amorphous silicon is also known. Silicon is a metalloid. It is hard and it is a poor conductor of electricity. Its oxide **silica SiO_2** is one of the most abundant compounds in the Earth crust. It is insoluble in water and other solvents (HF dissolves silica).



Covalent bonds in SiO_2 crystals

Silica SiO_2 exists as an amorphous substance or as a variety of crystalline substances – **quartz**, **sand**, **flint** and other minerals. SiO_2 crystals are giant molecular structures. Silicon is tetravalent and it bonds to four oxygen atoms forming tetrahedral structures. One of the crystal structures is similar to that of diamond.

One of the most important uses of silica is the manufacture of glass and ceramics.

GLASS

Glass is an amorphous inorganic material. it is hard and brittle. It is known since ancient times. The earliest glass objects (Egyptian glass beads) date back to about 4500 years ago. It is believed that glass blowing was developed about 2000 years ago in Syria.

Glass is made by cooling molten silica sand (quartz broken down into small granules) and other ingredients. Quartz melts at about 1600 °C. Many covalent bonds disrupt and the crystalline silica transforms into an amorphous substance.

The glass properties depend on its composition. The most common is the **soda-lime-silica** glass. It is made mainly from silica sand SiO_2, lime $CaCO_3$ and sodium bicarbonate (soda) Na_2CO_3. Soda lowers the melting point of pure silica and lime makes the silica-soda mixture insoluble in water. Upon heating both lime and soda decompose and transform into the corresponding oxides liberating carbon dioxide CO_2.

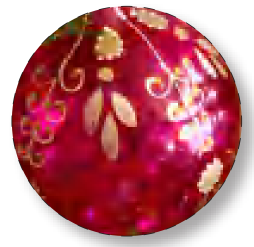
$$\mathbf{CaCO_3}(s) \xrightarrow{t^o} \mathbf{CaO}(s) + \mathbf{CO_2}(g) \qquad \mathbf{Na_2CO_3}(s) \xrightarrow{t^o} \mathbf{Na_2O}(s) + \mathbf{CO_2}(g)$$

The optimum composition is 76 % SiO_2, 12 % CaO and 12 % Na_2O. Other ingredients are often added to improve the quality of glasses.

- The addition of lead oxide **PbO** (instead of CaO) increases the glass density and its refractive index.
- The use of **K_2O** (instead of Na_2O) makes the glass harder and increases its melting point.
- The addition of **B_2O_3** increases the glass melting point and improve the glass resistance to thermal expansion.

Glass is coloured by adding oxides of transition metals, e.g. FeO (green colour), Fe_2O_3 (yellow colour), CuO (green-blue colour), CoO (blue colour), Mn_2O_3 (purple colour), etc.

Decorative coloured glass



Depending on their composition (i.e. on their properties) glasses have various applications. Glass is a part of our life almost everywhere – in constructions, cookware, laboratory glassware, medicine, astronomy, bottles, cups, decorative art, etc. Optical fibres used in telecommunications to transmit light signals at a very high speed over long distances are made of fused pure SiO_2. They are flexible, transparent and very thin – about the thickness of a human hair. In optical cables bundles of many (hundreds, thousands) optical fibres are covered with a protective material.

Glass objects can be recycled.

Learn more about the glass properties and uses and fill the table in your study book!

CERAMICS

Ceramics are all objects made of clay and hardened upon heating – pottery, porcelain, bricks, etc. **Clay** is a natural material made of soil particles of diameter less than 0,005 mm. Most clays have been formed as a result of the weathering (the breaking down into small particles) of rocks owing to natural physical, chemical or biochemical processes.

CERAMICS

To manufacture ceramic objects the clay is first wet with water to become soft and easy to shape. After that the object is shaped, dried and then heated at high temperature (about 1 000 ^{o}C). The surface of ceramic objects is usually coated with a thin glassy layer to make them coloured, shiny or waterproof.

Porcelain is a type of pottery made of kaolin (known also as china clay) and petuntse or other clays. Kaolin is a white to yellowish or greyish powder containing mainly $(Al_2O_3)(SiO_2)_2(H_2O)_2$. Petuntse is a rock that is powdered and mixed with kaolin. Porcelain was first made in China.

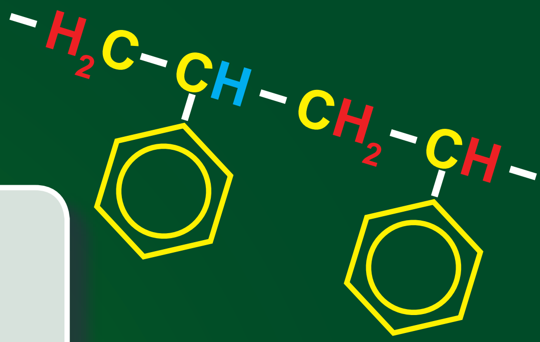
Ceramics objects are used in constructions (bricks, roof tiles), as decorative articles (pottery, porcelain cups, plates, vases, small sculptures, etc.), in the electrical industry (insulators), in medicine (orthopaedic and dental purposes), in the production of new composite materials and many others.

Unlike glass, ceramics objects can not be recycled. They can not be melted and reshaped.

CAN YOU ANSWER THESE QUESTIONS?

1. What is silica?
2. What is the structure of silica?
3. What is glass?
4. Why are there many types of glasses?
5. Do glass properties depend on the glass composition?
6. What are optical fibres?
7. What is clay?
8. How are ceramic objects manufactured?
9. What are the main components of porcelain?
10. What are the most important uses of glass and ceramics?

31 Plastics

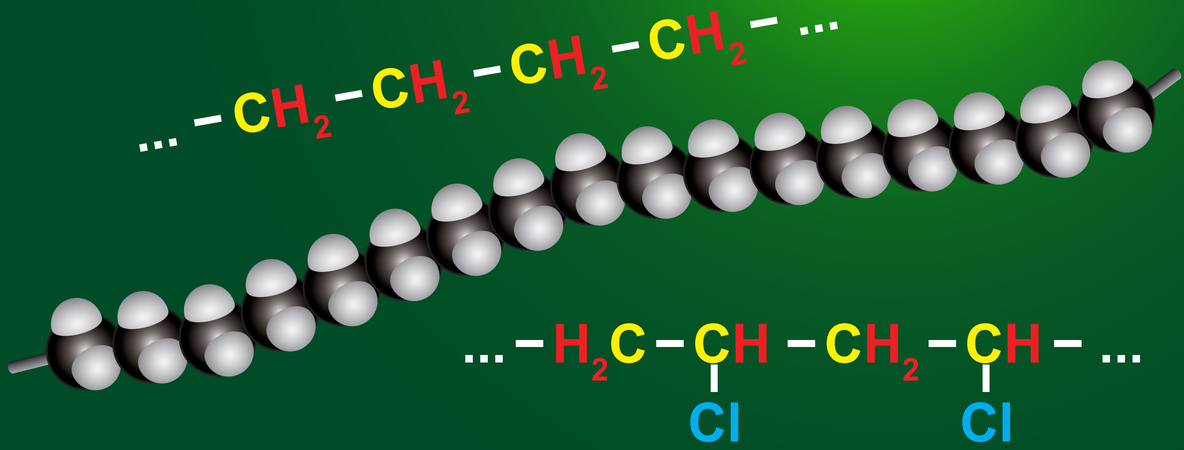


KEY TOPICS

1. What are plastics?
2. What are the most widely used plastics?
3. Are all plastics recyclable?
4. Why is the development of green technologies and bioplastics essential for safeguarding the environment?

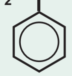
KEY WORDS

- Polymers
- Monomers
- Polymerization
- Polycondensation
- Plastics
- Additives
- Fillers
- Plasticizers
- Pigments
- Anti-aging additives
- Thermoplastic plastics
- Termoset plastics
- Elastomers
- Bioplastics



PLASTICS are widely used material with various properties and applications. They are man-made materials and are part of our contemporary world. The basic component of these synthetic materials are different organic **polymers** (in Greek language means *composed of many parts*). Polymers are high molecular weight (more than 5 000) compounds. One polymer molecule may be made up of millions of atoms.

Polymers giant molecules are composed of many repeating units called **monomers units**. These are residues of molecules of low molecular weight compounds (called **monomers**), covalently bonded to each other and forming long chains. Monomers always contain double or triple bonded atoms.

SYNTHETIC POLYMER	MONOMER	MONOMER UNIT
Polyethylene	$H_2C=CH_2$ Ethene	$-CH_2-CH_2-$
Polyvinyl chloride PVC	$H_2C=CH-Cl$ Vinyl chloride (chloroethene)	$-CH_2-CH(Cl)-$
Polypropylene	$H_2C=CH-CH_3$ Propene	$-CH_2-CH(CH_3)-$
Polystyrene	$H_2C=CH-$  Styrene (ethenylbenzene)	$-CH_2-CH-$ 
Teflon	$F_2C=CF_2$ Tetrafluoroethene	$-CF_2-CF_2-$

POLYMERS are high molecular weight compounds made up of covalently bonded repetitive atomic groups (monomers units).

Starch, cellulose, proteins are **natural** biopolymers. They may be processed to produce polymers with specific properties (e.g. nitrates and acetates of cellulose, vulcanized rubber). These polymers are considered as **semi-synthetic**. **Synthetic polymers**, products of chemical reactions, are polyvinyl chloride (PVC), polyethylene, polypropylene, polystyrene, teflon, synthetic rubbers, synthetic fibres, etc.

THE DEVELOPMENT OF NEW POLYMERS WITH NOVEL CHARACTERISTICS IS A MAJOR ACHIEVEMENT OF THE CONTEMPORARY CIVILIZATION.

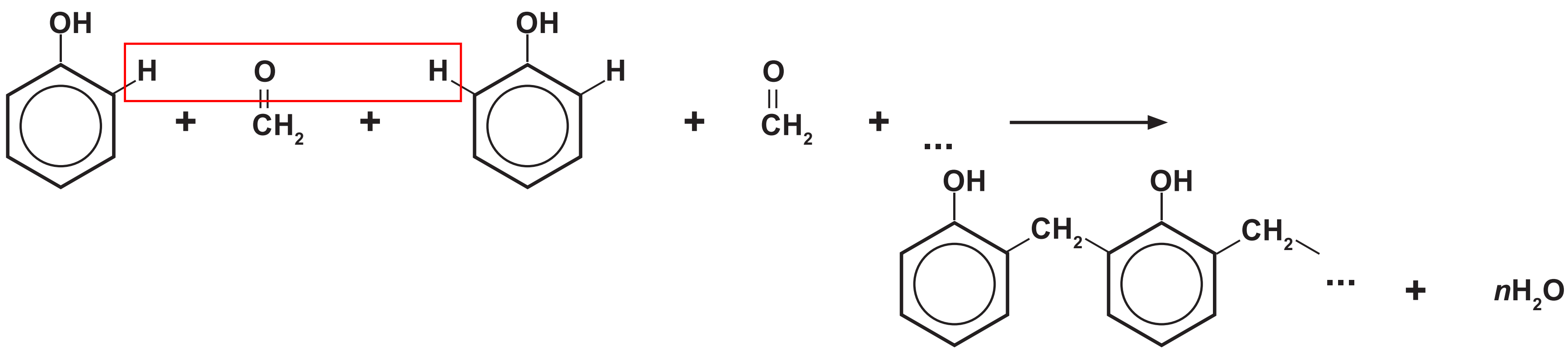
Synthetic polymers are produced in chemical reactions called **polymerization** and **polycondensation**.

- **Polymerization** is a type of addition reaction. Many monomer molecules are covalently bonded to each other in long chains owing to the disruption of multiple (double or triple) bonds. Generally, polymerization is a catalytic process and undergoes at high temperature and pressure. The only product is a polymer. For example, the production of polyethylene may be expressed as:

$$n(H_2C = CH_2) \longrightarrow -CH_2-CH_2-CH_2- \ldots\ldots\ldots\ldots - CH_2-CH_2-CH_2-$$

Polymerization products are PVC, polyethylene, polypropylene, teflon, polystyrene, polyacrylonitrile $\left(\underset{\displaystyle C\equiv N}{\underset{|}{HC}} - CH_2 \right)_n$, rubber $\left(H_2C - \underset{\displaystyle H_3C}{\underset{|}{C}} = CH - CH_2 \right)_n$ and many others.

- **Polycondensation** is a process that always involves monomers with at least two functional groups or two different monomers. In addition to the polymer a low molecular weight compound is formed. The long polypetide chains are products of the polycondensation of α-amino aids. Phenol formaldehyde resin (main component of bakelite) is produced in a polycondensation reaction of phenol and methanal (formaldehyde):



Polyamide and polyester synthetic fibres are polycondensation products (see lesson 33).

PLASTICS are synthetic polymeric materials that can be shaped when soft in different forms to manufacture products of different uses.

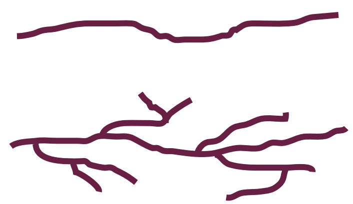
PLASTIC are made up mainly from polymers and many **additives** as **fillers**, **plasticizers** and **softeners**, **pigments**, **anti aging agents** and others (antimicrobial, antistatic, biodegradable, heat and light stabilisers, fragrance and many others).

- **Fillers** – improve plastics performance characteristics and reduce manufacturing costs. As fillers are used calcium carbonate (limestone), kaolin, talc, potters beads, milled glass fibres, sawdust, synthetic silicon dioxide, fibre fillers, etc.
- **Plasticizers** – low volatile organic solvents. They make materials more flexible and resilient. Plasticizers are essential for PVC plastics as the polymer PVC is rigid at room temperature. PVC plastics containing plasticizers are flexible. Some oils, used to facilitate rubber processing, are called **softeners**.
- **Pigments** – organic as well as inorganic substances used for colouring plastics. They are known by their brand names and may add shining or other visual effects and emphasize the products uses.
- **Anti-aging additives** – antioxidants, antiozonants, ultraviolet absorbers, stabilizer against dehydrochlorination (for chlorine-containing polymers), etc. They prevent the change in the plastic properties (as a result of structural changes) with time.

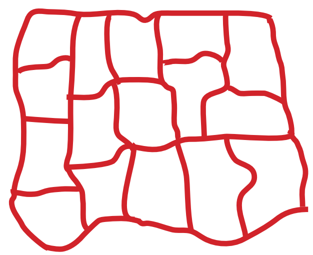
Also **lubricant** and **flow promoters** are additives indispensable to the processing processes.

Historically, scientists first had modified natural polymers to produce plastics. For instance, cellulose was the raw material for the production of celluloid. The first patent for a synthetic plastic (called bakelite, see p. 26) had been granted to Leo Baekeland in 1906. Today many plastics are known. They are classified into two major groups – **thermoplastics** and **thermosets**. **Elastomers** are considered as a third main group of plastics. This classification is based on the properties and structure of plastics.

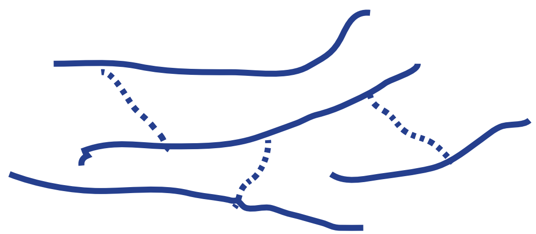
- **THERMOPLASTICS** when heated, they soften and if cooled, they solidify (they are *melt-processable* plastics). They can be heated and reshaped many times. The polymers building these plastics are with long branched or unbranched chains. Typical thermoplastics are polyethylene, polypropylene, polyvinyl chloride, polystyrene.



- **THERMOSTES** when heated, they remain rigid until they decompose. They can be heated and shaped only once. Their molecules are cross-linked and these materials are harder than thermoplastics. Thermosets are phenol-formaldehyde resins (bakelite and others), epoxy resins, etc.



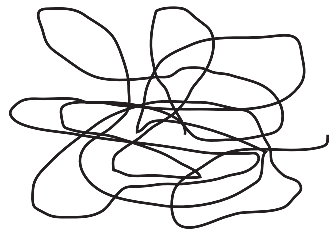
- **ELASTOMERS** (as suggests their name) are „elastic" polymers. They recover their shape after being stretched without permanent deformation. They do not melt as they decompose at low temperature. The long winded and entangled chains form a loose net. When stretched they try to line up and if released they recover their initial state. They are soft even at room temperature. Elastomers are natural rubber, polyisoprene, polybutadiene, neoprene, polyurethane, etc.



Some of the most widely used plastics are **polyethylene** (polyethene), **polyvinyl chloride** (PVC), **polypropylene** (polypropene), **polystyrene** (or polystyrol), **teflon** and many others.

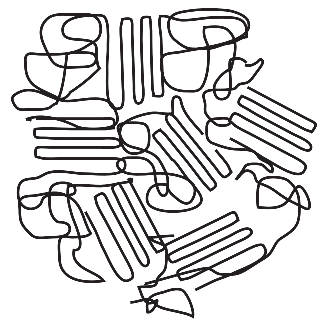
POLYETHYLENE PE $-\!\left(CH_2 - CH_2 \right)\!-_n$

Polyethylene is the most commonly used plastic. It is based on the simplest polymer (polyethene). It is thermoplastic and have a good chemical resistance. Its mechanical properties depend on its structure. If the carbon chains are linear, the plastic is called **HDPE** (High Density PolyEthylene). If the chains are branched, it is called **LDPE** (Low Density PolyEthylene). The linear plastic is semi-crystalline and very strong. The branched one is cheaper and is easily processed as it is amorphous.



AMORPHOUS POLYMER

The relative molecular weight of HDPE is usually in the range 200 000 – 500 000 but may be much greater. Polyethylene with a relative molecular weight of a few millions is called **UHMWPE** (Ultra High Molecular Weight PolyEthylene). It is used to make very strong fibres (used, for example, in the bullet proof vests) and sheets (may replace the ice rinks). It is also used to make gear wheels, gaskets, bearings. Also polyethylene of very low density is known (metallocene polyethylene). It is very tough and is used to reinforce other plastics.



SEMI-CRYSTALLINE POLYMER

PE

- PACKAGING
- MACHINERY
- HOUSEHOLD
- ANTICOROSIVE COATING
- HEAT INSULATION
- ELECTRICAL INSULATION

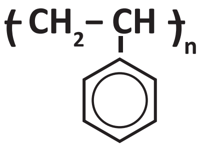
Annually tens of millions of tones of PE are produced in the world. This is a plastic of unlimited uses which makes it a part of our everyday life.

POLYVINYL CHLORIDE PVC $\left(CH_2 - \underset{Cl}{CH} \right)_n$. PVC is also a widely used amorphous water and chemically resistant thermoplastic. It is the most commonly used plastic for the production of pipes and windows frames. The ignition temperature of PVC is high compared to PE and PP (polypropylene) which are hydrocarbon plastics. The risk of fire incidents is lower (PVC materials also release less heat in burning). Furthermore, generally, PVC is more durable than PE and PP as it is more resistant to oxidation processes. PVC products are everywhere around us.

PVC

- PACKAGING
- CONSTRUCTIONS
- SYNTHETIC LEATHERS
- PIPES AND HOSES
- WIRE INSULATIONS
- TABLECLOTH
- WALL PAPERS

POLYPROPYLENE PP $\left(CH_2 - \underset{CH_3}{CH} \right)_n$. PP is a chemically resistant, elastic, tough, thermoplastic polymer. It is opaque in colour but can be made transparent. It is an insulator. It retains its shape after torsion, bending and flexing (the reason to use it to make hinges). It is mainly used in the packaging industry, in the electrical and equipment manufacturing, to make household appliances, in the automotive industry.

POLYSTYRENE PS  . PS is a thermoplastic or a thermoset material produced in the form of a solid plastic, a rigid foam or a film. Solid PS is used to make medical devices, objects used in the everyday life (food-containers, cups, etc.). The foam is used mainly as a packing material.

TEFLON PTFE $\left(CF_2 - CF_2 \right)_n$

Teflon is the trade name for pol ytetrafluoroethylene (the polymer monomer is tetrafluoroethene). It is a slippery, non-stick material with a smooth surface commonly known for its uses as coating inside cookware. It is resistant at high temperature, chemically stable and corrosion-resistant plastic. It is used also to make windshield wiper blades, hair styling tools, hoses, nail polish.

ENVIRONMENTAL ISSUES

Plastics are known for about a century and our contemporary life-style is unthinkable without these materials. But plastics usages also trash. The development of highly efficient recycling technologies is an urgent need as the quantity of plastics produced in the first decade of the XXIst century is almost as the quantity produced in the entire XXth century.

Today every plastic bottle or container has a recyclable symbol – a number (from 1 to 7) in a triangle. Number 1 is assigned to the easiest and most common plastic to recycle – polyethylene therephthalate (PETE) (see p.44). Number 7 is for products made up of combination of different plastics or specific formulations and are difficult to recycle.

1. PETE – polyethylene terephthalate
2. HDPE – high density polyethylene
3. V – polyvinyl chloride
4. LDPE – low density polyethylene
5. PP—polypropylene
6. PS – polystyrene
7. Other

Today plastics sustain the quality of the modern life. But „sustainable development“ means new needs and new high quality materials which means new challenges for polymer production and polymer processing industries. Modern trends are searching for new materials and special compounds, **bioplastics** (biodegradable plastics made from renewable resources), recycled materials, development of renewable energy technologies, green technologies (technologies that are environmental friendly i.e. they are not harmful for the environment and conserve natural resources).

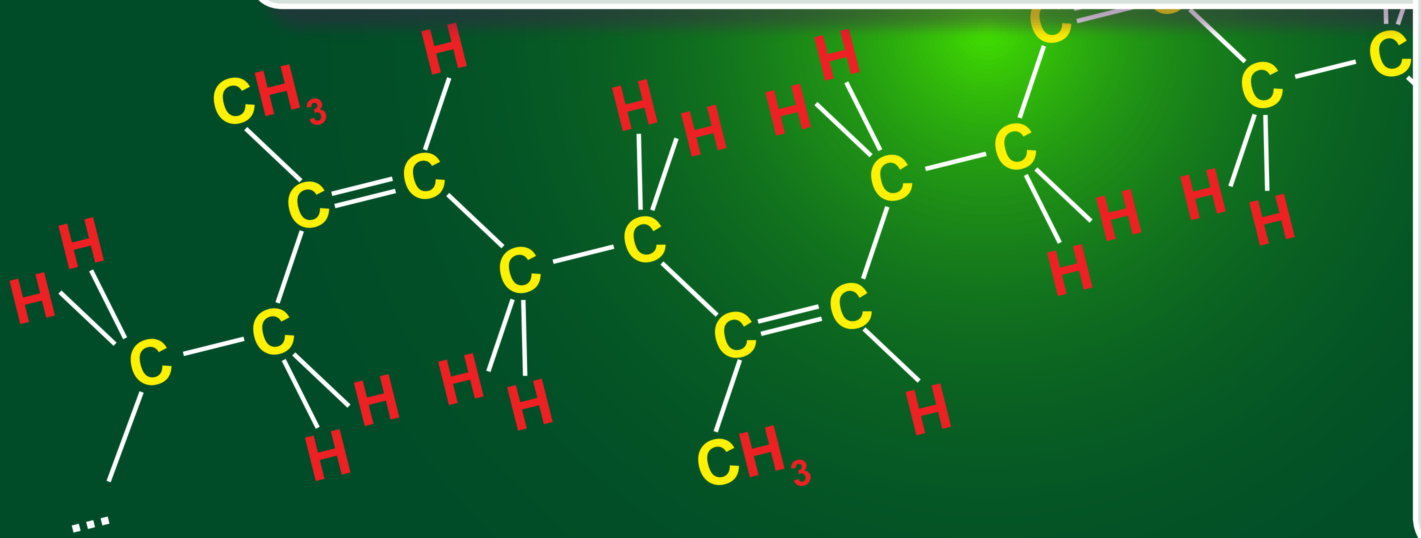
CAN YOU ANSWER THESE QUESTIONS?

1. What is the difference between polymers and plastics?
2. What are the main components of plastics?
3. What is the difference between thermoplastic and thermoset plastics?
4. What are polyethylene and polyvinyl chloride widely used plastics?
5. Why should plastics not been burned outdoor or in a wood stove?
6. Why is recycling of plastics a key point for safeguarding the environment?

32 Rubber (caoutchouc)

KEY TOPICS

1. Why is natural rubber a polymer?
2. Why is nature rubber a widely used raw material?
3. Why are dozens of synthetic rubbers known today?



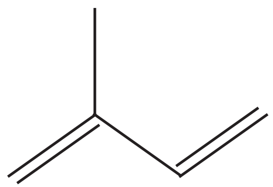
KEY WORDS

- Natural rubber
- Caoutchouc
- Izoprene
- Vulcanization
- Vulcanized rubber
- Ebonite
- Buna

Natural rubber is a natural polymer obtained from latex (a milky secretion) of the rubber tree *Hevea Brasiliensis* and other tropical plants. Latex is treated with lactic acid – rubber macromolecules coagulate and can be removed.

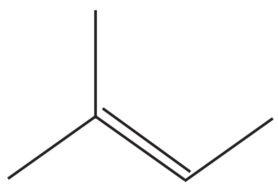
STRUCTURE AND PROPERTIES OF NATURAL RUBBER

$$H_2C = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH = CH_2$$



2-methylbuta-1,3-diene
(Izoprene)

$$- H_2C - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 -$$

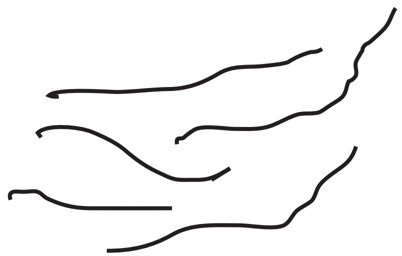


MONOMER UNIT
OF NATURAL RUBBER

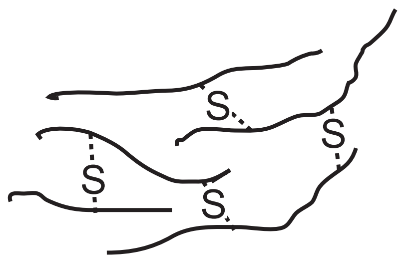
Macromolecules of the natural rubber are linear and very long. It is an amorphous substance as the polymer chains are folded and highly entangled. Its relative molecular mass ranges between 150 000 and 200 000. Natural rubber is a pale-yellow and insoluble in water polymer.

Natural rubber macromolecules are made up of hydrogen and carbon atoms – the monomer is a hydrocarbon with 5 C atoms and two double carbon-carbon bonds (2-methylbuta-1,3-diene), commonly known as **isoprene**. The units, composing the polymer chains of natural rubber, contain only one double carbon-carbon bond (between the second and the third C atom). 1 000 – 5 000 isoprene units are linked to form the natural rubber polymer chains.

The intermolecular forces, holding together the long polymer chains of the natural rubber, are not so strong. Natural rubber is a sticky elastomer. Exposed to air it becomes brittle. But if heated in the presence of sulfur, its structure changes – sulfur bridges hold together the long chains and a cross-linked 3-dimensional „net“ is formed. The process is known as **vulcanisation** of natural rubber and was discovered by Charkes Godyear in the first half of XIXth century. The vulcanised rubber is stronger and more elastic. Depending on the amount of sulfur, materials with specific properties can be produced. If the content of sulfur is low, the product is a soft rubber. If more sulfur bridges are formed, the product is harder and is called **ebonite.**



NATURAL RUBBER

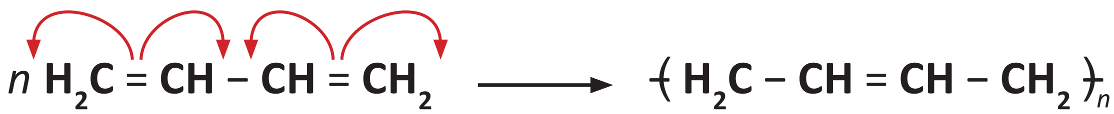


VULCANISED RUBBER

Natural rubber is used since over 1 000 years. Its a raw material for the production mainly of tires and related products but also for latex products, footwear, non-automotive engineerings, belting and hoses, etc. Its quantity is not enough to satisfy all industrial needs. So about century ago started the development of technologies for the production of synthetic substituents of the natural rubber.

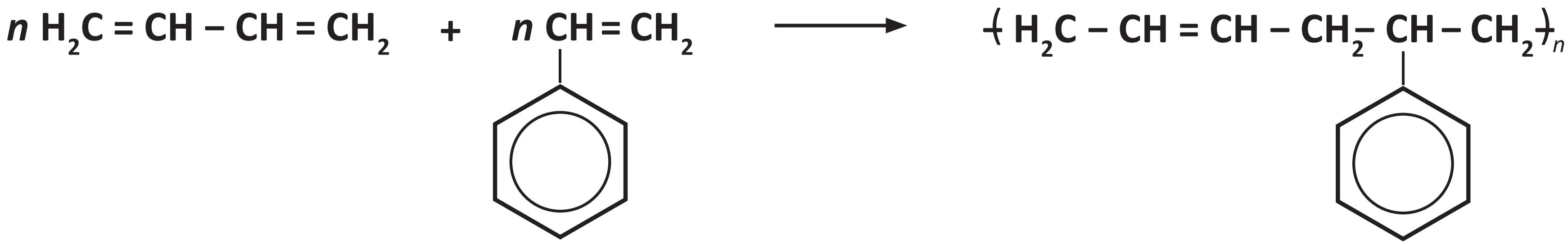
SYNTHETIC RUBBERS

The increasing demands of the industry forced scientist to develop technologies to produce synthetic rubbers. The first synthetic rubber was synthesized in the early XXth century by Fritz Hofmann and his team from 2,3-dimethylbuta-1,3-diene. The first factory for the production of synthetic rubber was built near Petersbourg in the 30s of the XXth century. Synthetic rubber, commonly known as „Buna“ (BU for butadiene and NA for sodium Na (the polymerization catalyst)) was produced from buta-1,3-diene by the Lebedev’s method:



Buta-1,3-diene „Buna“ – rubber

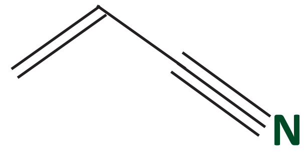
Another synthetic rubber is the so called „Buna-S“ (S for styrene). It is produced from buta-1,3-diene and ethenylbenzene (styrene) in a reaction of copolymerization (two different monomers polymerise).



Ethenylbenzene (styrene) „Buna-S“ – rubber

„Buna-N“ is another synthetic rubber – a copolymerization product of buta-1,3-diene and acrylonitrile „Buna-S“ and „Buna-N“ are oil-resistant materials. „Buna-N“ is also resistant to heat aging.

$$H_2C = CH - C \equiv N$$



Acrylonitrile

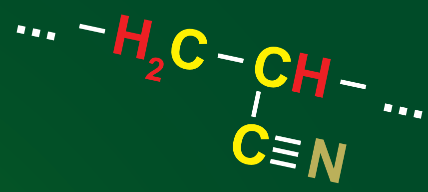
Synthetic rubber produced from isoprene is also widely used. The monomer is the same as in the natural rubber. It is a substitute for natural rubber but, generally, is not so strong and sticky.

Today are known dozens of synthetic rubbers. Some of them are superior to the natural rubber for special uses.

CAN YOU ANSWER THESE QUESTIONS?

1. What is rubber (caoutchouc)?
2. Why is natural rubber elastic?
3. Why is natural rubber both a hydrocarbon and a polymer?
4. What process is known as vulcanisation of natural rubber?
5. What is the difference between natural and synthetic rubbers?
6. Why do some synthetic rubbers display advantageous properties that are not typical for natural rubber?

33 Chemical fibres

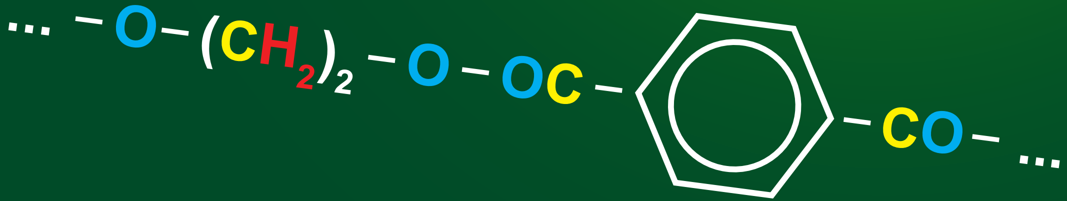


KEY TOPICS

1. What are chemical fibres?
2. What are the differences between natural and synthetic fibres?
3. What are biofabrics?

KEY WORDS

- Natural fibres
- Chemical fibres
- Semi-synthetic fibres
- Synthetic fibres
- Viscose rayon (Rayon)
- Acetate cellulose fibres
- Polyamide fibres
- Nylon
- Polyester fibres
- Polyethylene terephthalate
- Polyacrylic fibres
- Polyacrylonitittrile
- Biofabrics



FIBRES have been known for many centuries as the cotton, linen, wool fibres were spun by hand. With the development of science (chemistry, engineering) the production of synthetic polymers, which can be spun into threads, became prevailing. The long polymer chains are hold together by strong intermolecular forces to form bundles which depending on the used raw materials (mainly petrochemical products) and processing technologies form fibres with various characteristics.

FIBRES are polymers with linear or slightly branched chains, which can be spun into threads.

Cotton, wool, linen, silk, hemp fibres are called **natural fibres**. The fibres produced in chemical reactions are known as **chemical fibres**. Depending on the used raw material they are classified as **semi-synthetic** and **synthetic**.

NATURAL FIBRES

Raw material for natural fibres are fibres plants (cotton, flax, hemp, ramie, jute) and animal wool (from sheeps, goats, rabbits, camels, llamas) or silkworms. Natural fibres from fibres plants are made of polysaccharides $(C_6H_{10}O_5)_n$. Wool and silk fibres are made up of long polypeptide chains – they are proteins.

Natural fibres are high quality materials. It is easy to identify them by burning a bit of the fibre – cotton burns rapidly and smells like burning paper, while wool and silk burn slowly, even outside the flame, smell like burning hair and form a coal-black fragile ball. (For more details see your study book.)

The increasing demands for textiles with specific properties and the restricted resources of natural fibres forced the development of the chemical fibres industry.

CHEMICAL FIBRES

Chemical fibres are products of chemical reactions. Different raw materials are used to manufacture different types of fibres but, generally, chemical fibres are **semi-synthetic** or **synthetic**.

SEMI-SYNTHETIC FIBRES

Semi-synthetic fibres are produced from chemically treated natural polymers. They are mainly derivatives of cellulose (from wood pulp). The production of cellulose started in the late XIXth century. Almost by that time dated also the production of semi-synthetic silk-like fibres – **viscose rayon** or simply **viscose**. Cellulose and viscose polymers are made up of the same macromolecules but their structure and consequently their physical properties are different. Viscose polymer molecules are aligned and bound to form strong threads. Technically, a spinning solution of cellulose passes through a spinneret (a device that looks like a shower) thus forming fibres of aligned polymer molecules, structure similar to the natural fibres.

Rayon textiles and yarns are not expensive. They can be easily dyed, are soft and comfortable to the skin but are not as strong as natural fibres.

Cellulose may be treated to produce cellulose acetates. Semi-synthetic fibres (textiles and yarns) produced from cellulose acetates are expensive as compared to rayon, but are stronger. Acetate cellulose textiles are with a silk-like appearance. They are shiny, soft, dry quickly but they wrinkle easily and melt if the iron is too hot.

Rayon and acetate cellulose fabrics burn in different ways – rayon burns quickly with a slight smell of burning paper and turns to ashes. Acetate cellulose burns also quickly but only inside the flame, smelling like vinegar and turns to a white powder or to a brown-like ball. (See your exercise book.)

SYNTHETIC FIBRES

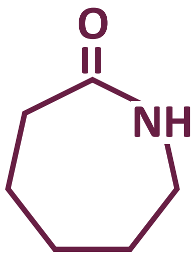
Synthetic fibres are produced from synthetic (man-made) polymers. Depending on the type of the monomers synthetic fibres are classified as **polyamide**, **polyester**, **polyacrylic fibres**.

Polyamide fibres. Their monomers (dicarboxylic acids and diamines) link to each other to form long polypeptide chains (the peptide bond $-\overset{\overset{\textstyle H}{|}}{N}-\overset{\overset{\textstyle O}{\|}}{C}-$ is also known as **amide bond**) in polycondensation reactions. Nylons are commonly used polyamide fibres. **Nylon 66** is produced from hexane-1,6-dioic acid (commonly known as adipic acid) and hexane-1,6-diamine.

amide (peptide) bond

$$nH_2N-(CH_2)_6-NH_2 + nHOOC-(CH_2)_4-COOH \rightarrow \left(NH-(CH_2)_6-NH-CO-(CH_2)_4-CO\right)_n + n\,H_2O$$

Hexane-1,6-diamine Hexane-1,6-dioic acid Nylon 66



Caprolactam

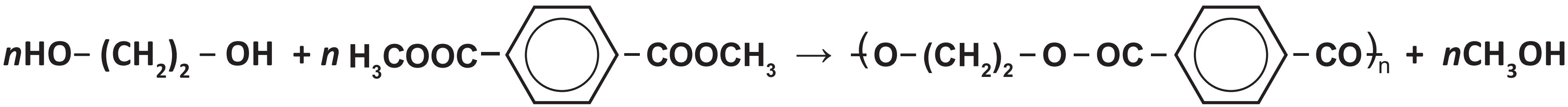
Nylon 6 (**polycaprolactam**) is synthesized from caprolactam. Polymer chains are made up of residues of 6-aminohexanoic acid (caproic acid). They look like the nylon 66 units, but there is a difference in the spacial orientation of the NH and C = O groups. The mechanism of the polymerization process is complex.

Monomer unit of polycaprolactam (residue of caproic acids $H_2N-(CH_2)_5-COOH$)

Nylon does not burn. It melts evolving an unpleasant smell of plastic and forms a hard shiny ball.

Polyamide fibres are durable, elastic, light and fine. Fabrics are easy to wash and dry. They are resistant to the action of abrasives and chemicals (alkali). Nylon is exceptionally strong and is used for tires cords, hoses, conveyer belts, racket strings, ropes and nets, fishing lines, etc. From nylon are also made raincoats and windbreakers as its absorption of moisture is low.

Polyester fibres. These polymers are products of polycondensation processes – esterification of dicarboxylic acids (or their esters) and polyhydric alcohols. One of the most commonly used polyesters is **polyethylene terephthalate** (**PETE** or **PET**). Its monomers are ethane-1,2-diol (glycol) and dimethylterephthalate – an ester of benzene-1,4-dicarboxylic acid (terephthalic acid) and methanol (you might try to express the reaction of the formation of dimethylterephthalate as you are already familiar with the basis of organic chemistry). Besides the long polymer chains of *polyethylene terephthalate* another low molecular weight product is obtained – methanol.



Ethane-1,2-diol Dimethylterephtalate Polyethylene terephtalate Methanol

Polyesters burn only inside the flame which is yellow and smoky. The smell is not unpleasant and a hard shiny ball is formed.

Polyesters fibres are strong, resistant to stretching and shrinking, resilient, resistant to chemicals and abrasion, easy to wash and dry.

Polyesters are used to manufacture clothes and home furnishings upholstery, curtains, carpets, sheets and pillows, hoses and many others.

Polyacrylic fibres. They are polymerization products of acrylonitrile $H_2C = CH - C \equiv N$.

$$n\,H_2C=\underset{\substack{|\\ C\equiv N}}{CH} \longrightarrow \left(H_2C-\underset{\substack{|\\ C\equiv N}}{CH} \right)_n$$

Acrylonitrile Polyacrylonitrile (PAN)

Polyacrylic fibres burn rapidly with an unpleasant fishy smell and form a dark, hard, shiny ball.

When processed polyacrylic fibres may become crimped (with high bulk) and feel like wool. They are soft, resilient, retain heat and are easy to care and dry. They are used in the knitwear industry as wool-like materials.

USES

Materials made of synthetic fibres are widely used. New textiles, threads and other products with improved quality are coming to the market. In 1994 man-made fibres consisted 51 % of the world fibre production (cotton, wool and synthetic fibres). In 2014 man-made fibres share had jumped to 71 %. But synthetic fibres are mainly made from petrochemicals and their environment impact becomes more and more significant. Efficiency in the use of resources, reduction of waste and emissions are key factors to reduce the unfavourable impact of synthetic fibres industry on the environment.

Man-made fibres are not biodegradable and recyclable. That is why one of the modern trends in man-made fibre industry is the production of the so called **biofabrics**. These fibres are based on polymers derived from plants rather than petrochemicals.

CAN YOU ANSWER THESE QUESTIONS?

1. Why do woollen clothes keep us warm in winter, while we wear cotton clothes in summer?
2. Why do woollen and cotton clothes shrink if washed with hot water?
3. How can you check if your sweater is really made of wool?
4. Why can't synthetic silk be a substituent of natural silk?
5. Which are the major types of synthetic fibres?
6. Why do synthetic fibres dominate the market?

PROJECTS

1. SPECIAL TYPES OF GLASSES

Search information about the properties and applications of some special types of glasses (photochromic glass, conductive glass, optical fibres).

2. ALLOY STEELS

Learn more about the different type of alloy steels and their uses. Pay attention to the identity of alloying agents and how they alter the mechanical properties of alloys.

3. POLYMERS OF THE FUTURE

Imagine that you are a scientist and your task is to invent a new polymer with properties unknown until now. What will be the special properties of this polymer? What will it be used for? What trade name would you propose for this polymer?

4. CHEMICAL FIBRES IN YOUR HOME

Fabrics made of synthetic or natural fibres are used in our everyday life – clothes, carpets, curtains, upholstery, etc. What are they made of? Do their uses depend on their properties?. Present your observations and conclusions in a table.