Seminar No. 11
Topic "Polymeric materials. Concept, classification application. Rubbers and rubbers. Technological process of production of rubber products. Plastics. Types, advantages, disadvantages. Thermoplastic and thermoset materials. Methods for the manufacture of plastic products"

The main questions to be discussed at the seminar:

1. Polymeric materials. Concept, classification, application. Requirements for polymers used in medicine.
2. Elastomers. Rubber (natural and synthetic) and rubber.
3. Stages of technological production of rubber products. Rubber test.
4. Latexes and products from them. Consumer properties of latexes. The process of obtaining products from latex.
5. Silicone rubbers. Properties, application in medicine.
6. Plastic masses. Kinds. Advantages and disadvantages.
7. Thermoplastic masses. thermosetting materials.
8. Methods for the manufacture of plastic products.

Polymeric materials by origin can be:

natural (proteins, polysaccharides, cellulose, starch, natural rubber, mica, asbestos, natural graphite)

synthetic (synthesized macromolecular substances obtained by polymerization or polycondensation (synthetic resins, fibers, rubbers, etc.).

The leading group of polymers used are synthetic polymers.

Because macromolecules form chains consisting of individual links and extending in length over distances thousands of times greater than their transverse dimensions; macromolecules are characterized by flexibility (which is limited by the size of segments - rigid sections consisting of several links).

The flexibility of macromolecules is one of the distinguishing features of polymers.

Classification of polymers (according to various criteria based on the relationship composition - structure - properties), according to:

- composition
- the shape of macromolecules
- phase state
- polarity
- in relation to heating

and etc.

According to their composition, polymers are divided into:

- organic
- organoelement
- inorganic

Inorganic polymers:

Inorganic polymers include silicate ceramics, mica, asbestos . These compounds lack a carbon skeleton.

The basis of inorganic materials is oxides of silicon, aluminum, magnesium, calcium, etc.

In silicates, there are two types of bonds: the atoms in the chain are connected by covalent bonds (Si–O), and the chains are connected by ionic bonds.

Inorganic polymers are characterized by high density and high long-term heat resistance. However, glasses and ceramics are brittle materials and do not withstand dynamic loads well. Inorganic polymers include graphite, which is a carbon chain polymer.

The main characteristics that play a decisive role in assessing the possibility of using polymers for medical devices:

- the presence of the necessary complex of physical, chemical and mechanical properties; high purity and homogeneity of the material;
- the possibility of processing into products without decomposition and isolation of low molecular weight products;
- the absence of irritating, toxic, carcinogenic effects on living organisms, both the polymers themselves and the products present in the material or formed during its storage and operation;
- the ability to withstand sterilizing treatment by various methods and means.

Of particular importance is the toxicological evaluation of polymeric materials used in medicine in conditions of direct contact with a living organism. The products of thermal and thermal-oxidative degradation can be present in the material in adsorbed form and have a toxic effect on the body, which is not directly related to the chemical nature and structure of the original polymer.

The blastomatous effect (the occurrence of malignant tumors) of polyvinyl chloride, fluoroplastic, polyacrylates, polyamides, organosilicon rubber was observed only on small animals (rats, mice, hamsters, guinea pigs), in a similar way manifested themselves under these conditions such inert materials as glass, precious metals. It has also been established that the implantation of polymers in the form of powder or perforated plates does not cause tumors and has a weak blastomatous effect.

The blastomogenic effect of bioinert polymers is due not to their chemical nature, but to mechanical long-term irritation of the walls of the connective tissue capsule that occurs around the implanted material, and disruption of normal metabolism in it.

The polymeric material should be easily processed into products in simple and relatively cheap ways.

Of great importance is the availability of the used polymeric materials and their cost, which affects the economic efficiency of the use of polymers in comparison with traditional materials.

The possibility of processing in order to comply with the rules of sanitation and hygiene without changing the properties and shape creates additional restrictions in the choice of materials.

Many plastics cannot be used to make syringes because they deform during high-temperature sterilization.

Plastics - materials based on polymers that are in a viscous or highly elastic state, and during operation - in a glassy or highly crystalline state. In other words, plastics are formed from natural or synthetic macromolecular substances that, under the influence of heat and pressure, are able to take a given shape and retain it after cooling. In most cases, they are complex multicomponent compositions. The composition of the composition, in addition to the high-molecular base , includes fillers, plasticizers, stabilizers, dyes, hardeners and other special additives (Iigredients).

Sometimes the filler is in the polymer matrix in the gas or condensed phases. In the latter case, its modulus of elasticity may be lower (low modulus fillers) or higher (high modulus fillers) than the elastic modulus of the binder.

In medicine, gas-filled plastics (styrofoams) are used to make splints instead of heavy plaster casts. These are the lightest materials of all polymers; their apparent density is usually between 0.02 and 0.8 g/cm3.

Plastics are polymer -based organic materials that can soften when heated and take on a certain stable shape under pressure.

Polymer (from the Greek words poly - many and meros - share, part) - a compound with a high molecular weight, the macromolecules of which consist of a very large number of simple, identical, repeating units (monomers) or repeating groups.

The molecular weight of the polymer may be from 5,000 to 1,000,000 atomic mass unit. With such large sizes of macromolecules, the properties of substances are determined not only by the chemical composition of these molecules, but also by their mutual arrangement and structure.

According to the method **of processing into products, plastics are divided into:**

- casting
- pressing.

Castings are processed into products **by methods injection molding** and are thermoplastic materials are processed into products **by hot pressing methods** and are thermosetting.

Methods for obtaining products from plastics. The processing of plastics into products is carried out by one of the following methods: extrusion, injection molding, molding in molds, molding in dies, vacuum and pneumatic molding, welding, gluing, machining.

By purpose, plastics are divided into:

- structural,
- chemically resistant,
- gaskets and seals,
- friction and anti-friction,
- heat-insulating and heat-shielding,
- electrical insulating,
- optically transparent,
- facing and decorative and finishing .

According to the phase state, polymers are divided into:

- amorphous
- crystalline .

Amorphous polymers are single-phase.

The structures in these polymers are fluctuating, thermodynamically unstable, and characterized by a relatively short lifetime . The amorphous phase reduces the rigidity of the system and makes it elastic. This property is used in some technological processes to increase the elasticity of products by rapidly cooling (quenching) the polymer melt.

All polymers, according to the state during heating and after cooling, are divided into thermoplastic and thermosetting .

Thermoplastic polymers (thermoplastics) are polymers that soften when heated, even melt, and harden when cooled, without undergoing any chemical transformations (this process is reversible). This behavior of polymers is explained by the fact that weak intermolecular bonds are destroyed during heating, while covalent bonds are preserved. This circumstance makes it possible to repeatedly process thermoplastics. Thermoplastics have increased plasticity, but low heat resistance, and are soluble in solvents.

Thermoset polymers (thermosets) are polymers that, when heated, undergo irreversible chemical transformations, as a result of which they harden, losing solubility and the ability to change shape. These polymers do not soften with increasing temperature, but break down when a sufficiently high temperature is reached. Thermoplastics are insoluble and can only swell in solvents.

Fiberglass - structural materials based on polymers on a fiberglass or fiberglass basis.

Depending on the type of binder and filler, technological regimes, properties and methods of processing the material into products, glass-reinforced plastics are divided into two groups:

- fiberglass based on phenol-formaldehyde, organosilicon, urea and other resins, requiring high temperatures (180 °C and above) and pressure (250 ... 1,000 MPa (25 ... 100 kg / cm2) for processing into products).

- fiberglass based on unsaturated polyester and epoxy resins is obtained by "cold" curing at normal temperatures by contact method without pressure.

Rubber is a product of special treatment (vulcanization) of a mixture of rubber and sulfur with various additives.

Rubbers are polymers with a linear structure and, during vulcanization, are converted into highly elastic rare-mesh materials - rubbers.

Vulcanization *is* the transformation of rubber into rubber, carried out with the participation of so-called vulcanizing agents and under the influence of ionizing radiation.

Rubber materials are classified according to:

- type of raw material
- type of filler
- degree of ordering of macromolecules and porosity
- ecological methods of processing
- types of thermal aging and volume change after exposure to petroleum fluid.

Among **the technological methods of processing** for rubber materials are used:

- extrusion
- pressing
- casting.

By purpose, the main groups of rubber are distinguished:

- ✓ ***general purpose***
- ✓ ***special purpose***

For general purpose rubbers, the main components are non-polar rubbers .

General purpose rubber materials are used for the production of products operating in water, in air, in weak solutions of acids and alkalis at operating temperatures of -35–+ 130°C.

Rubbers for special purposes:

heat resistant,
frost-resistant,
oil and petrol resistant,
resistant to chemically aggressive environments,
dielectric,
conductive,
magnetic,
fire resistant,
radiation resistant,
vacuum,

friction (wear-resistant),
food and medical purposes,
for tropical and other climate conditions

MECHANICAL PROPERTIES OF RUBBERS AND RUBBERS

The peculiarities of the mechanical properties of rubbers and rubbers include:
- highly elastic character of deformation of rubbers;
- dependence of deformations on their speed and duration of the deforming force, which manifests itself in relaxation processes and hysteresis phenomena;
- dependence of the mechanical properties of rubbers on their pre-treatment, temperature and the impact of various non-mechanical factors (light, ozone, heat, etc.).

The main deformation-strength properties of rubbers and rubbers include:
- plastic and elastic properties,
- tensile strength,
- relative elongation at break,
- residual elongation after rupture,
- conditional stresses at a given elongation,
- conditionally equilibrium modulus, modulus of elasticity, hysteresis loss, tear resistance, hardness.

The technological process of manufacturing medical rubber products consists of the following operations:

1) obtaining a rubber mixture;
2) production of a semi-finished product;
3) shaping or obtaining rubber products;
4) vulcanization;
5) post-form processing, installation, sorting;
6) quality control, labeling, packaging.

Receiving a rubber compound includes four main stages:

1. Plasticization of rubber is carried out in rubber mixers at a temperature of 100–110 ◦ C and a pressure of 8–10 atm. Previously, the rubber is cut into pieces and hung.
2. Preparation of the ingredients of the rubber compound and their introduction in a certain sequence. In cases where the ingredients come in substandard form, preliminary preparation is necessary. Light ingredients (for example, chalk, kaolin) are subjected to jet-air drying and air separation (screening).
3. Mixing is carried out in rubber mixers for 20–40 minutes.
4. Cooling the rubber compound using various cooling devices: shower systems, scalloped cooling devices, conventional baths, etc. The temperature of the cooling water should be 8–10 ˚ C. The quality of the resulting homogeneous rubber compound is checked in the control laboratory of the preparatory workshop. Several samples are taken from each gas station and an express control is carried out; while determining the plasticity of the mixture, hardness, density. Production of a semi-finished product or blank. This operation is carried out in the manufacture of rubber heating pads, ice packs, bedpans, catheters, tubes. Typically, rubber blanks for tubular products are made by extrusion (syringing) on worm presses. Blanks are extruded in the form of cords and strips of rectangular sections. After exiting the worm machine, the workpieces pass through emulsion baths, then they are placed on trays. Sheeting of the rubber mixture is carried out by calendering on 4–7 rolls, the last roll has a corrugated pattern. Blanks are obtained by cutting calendered rubber. Cutting methods are distinguished depending on the direction of the cut, the required shape of the part and the type of material. Use disk, wedge, circular and punching knives, punching presses.

Vulcanization is carried out in various ways. Distinguish between cold and hot vulcanization. Hot vulcanization is carried out by a periodic method in boilers, presses or autoclaves or by a continuous method in special devices. This is one of the easiest ways to reduce curing time. Thus, with an increase in the commonly accepted temperature of vulcanization in molds from 140–160°C to 170 – 190 °C, the vulcanization time of products decreases from 10–90 to 1–5 min. Cold vulcanization is carried out by immersing the product in a solution or vapor of sulfur semichloride, followed by drying the product with hot air. This method is more expensive, less efficient, and the harmful gases that are released complicate the process. Therefore, it is used relatively rarely, only for the production of medical gloves and sanitary and hygiene items. If the vulcanization process is disturbed, then defects may appear:

- under-vulcanization leads to increased stickiness, adhesion of surfaces and accelerated aging of the product.

- overvulcanization leads to excessive rigidity and a decrease in the strength of the product.

Post-form processing, installation, sorting of products. The process of manufacturing molded products after the stage of vulcanization ends with mechanical processing. Its main types are: removal of extrusion (flash), trimming the working surfaces of rubber products. In practice, processing is used on various spindle machines, rotating emery stones, on machines for trimming burrs and manually. At present, a method for removing flash in tumbling drums by freezing parts with a refrigerant (solid carbon dioxide, liquid nitrogen, etc.) is widespread. When the drum rotates, frozen burrs break off easily and cleanly. The best results are given by installations for processing pre-frozen parts with shot. For tubular products, after vulcanization, uneven ends are cut off, profile blanks of a certain length are cut. Then the assembly of products from individual vulcanized parts or the assembly of vulcanized semi-finished products with non-rubber parts is carried out.

in heating pads, ice packs, circles and vessels and checked for tightness.

Quality control, marking and packaging are carried out in accordance with the requirements of the state standard for the product. At the same time, special attention is paid to the following defects in the technological process, detected by external inspection:

- bubbles, dents, foreign inclusions;
– surface roughness;
- inconsistency in size;
– displacement of contours;
– tears, cracks, porosity, delamination;
- swelling at the ends of products;
- underpressing;
– under-vulcanization (stickiness) or over-vulcanization.

<u>Latexes</u> are colloidal systems, the dispersed phase of which consists of particles (globules) of a spherical shape.

The colloid-chemical characteristics of latex - the size of globules, viscosity, concentration, or the amount of dry residue, aggregation stability - significantly affect the technological behavior of latexes during their processing.

The stability of latexes is due to the protective layer adsorbed on the surface of the globules, which prevents spontaneous coagulation. This layer contains anionic, cationic or non-ionic surfactants (emulsifiers).

Types of latex:

1. Natural latex - milky juice of rubber plants. Synthetic latexes are aqueous dispersions of synthetic rubbers resulting from emulsion polymerization.

2. Artificial latexes (artificial dispersions) - products that are formed when "finished" polymers are dispersed in water.

The use of latexes makes it possible to obtain products that cannot be made from solid rubbers at all, for example, thin-walled seamless medical gloves. Natural latex is mainly used for medical products.

The use of latexes makes it possible to obtain such products that cannot be made from solid rubbers at all, for example, thin-walled seamless medical gloves. Generally, natural latex is used for medical products.

The technological process for obtaining medical products from latex includes the following main stages:

1) preparation of the latex mixture;
2) obtaining a semi-finished latex product;
3) gel seal;
4) drying of the finished product;
5) vulcanization of the finished product;
6) quality control, packaging and labeling.

Preparation of the latex mixture. As a rule, the composition of the latex mixture, in addition to the usual ingredients of the rubber mixture, includes surfactants, thickeners, antiseptics, defoamers, etc.

Obtaining a semi-finished latex product by the dipping method.

To do this, a mold simulating the product, heated to 60–100 ◦C, is lowered into a bath with a latex mixture. The thin layer of gel formed on the surface is dried in air and dipped again. Repeat several times until you get the product of the required thickness (no more than 2 mm).

Gel seal. The form with the product obtained on it is lowered into a bath of water and kept at room temperature. This causes the gel to thicken.

Drying of the finished product in an air chamber at a temperature of 40–80 ◦C for 10–15 hours.

Vulcanization of the finished product is carried out in special chambers with hot air at a temperature of 100–140 °C. To do this, the mold with the product is placed in the chamber and kept at a given temperature for the required amount of time in accordance with the technological regulations for a particular product.

Quality control, packaging and labeling is carried out in accordance with the requirements of the state standard or the technical specifications of the enterprise for the product.

Silicone rubbers - *organosilicon polymers with rubber-like properties,* are a transparent, colorless, jelly-like mass, tasteless and odorless.

Silicone rubbers are characterized by high thermal-oxidative stability to ultraviolet radiation.

The physiological inertness of silicone rubbers allows them to be widely used in medicine, for example, in the production of tubes for blood transfusion, artificial heart valves, and implants in maxillofacial surgery.

Two types of silicone elastomers are most widely used:

1) rubbers vulcanizing at elevated temperature (hot curing);
2) rubbers vulcanizing at room temperature (cold curing).

Rubbers are used in medical practice:

hot and cold curing .

For endoprosthetics, silicone rubber compounds are used, which vulcanize when heated. Hot curing silicone rubber is non-toxic, it is characterized by the absence of pathological reactions from the contact tissues and the organism as a whole.

Silicone mixtures for medical purposes that vulcanize when heated have also found application in orthopedic and traumatological practice for the manufacture of endoprostheses for interphalangeal and cystophalangeal joints, carpal bones (navicular, lunate, trapezius), articular end of the big toe, heads of the ulna and radius bones, etc.