RUBBER CHEMISTRY

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Summary

Rubbers - elastomers - are polymeric materials characterised by their ability of reversible deformation due to external deforming forces. Their deformation rate depends on the structure and molar mass of the deformed rubber and on external conditions of the deformation. This characteristics, referred to as elastic and/or hyper elastic deformation, is entropic in nature and results from the ability of rubber macromolecules to form a more organised state under influence of deforming forces without deformation of chemical bonds between atoms of the polymer chain or without deformation of their valence angles. Ideally, the macromolecules can restore their initial position once the deforming forces are removed.

Rubbers usually have long and regular macromolecule chains without bulk substitutes with spatially oriented structural units. This is the reason why their segments are movable and able to rotate around simple chemical bonds even at low temperatures, as it can be seen in their low vitrification temperature $T_g$. They are tough and similar to plastomers below the vitrification temperature or crystallisation temperature (if rubber can be crystallised). When heated, rubbers change their elastic and/or hyper elastic state to a visco-elastic state; and they become plastic and flow above the softening temperature ($T_m$). It is advantageous if rubbers crystallise at normal temperature only when subjected to voltage and their $T_g$ is significantly lower that the temperature they are used at.

Natural rubber comes from a plant. In industrial applications, it is obtained primarily from Hevea Brasiliensis tree grown in orchards in South-East Asia, Western Africa and northern parts of Southern America. Synthetic rubbers are made by constructional polyreactions of chain or grade nature. In terms of their application and basic properties they can be divided into:

- general - they have properties satisfying requirements of multiple products, often with various properties; they are relatively cheap; manufactured and consumed in large volumes (butadiene-styrene, butadiene, synthetic isoprene rubbers, natural rubber);
- special - in addition to the basic elastic properties they have at least one special feature, such as resistance to aging, resistance to chemicals, resistance to budding in non-polar oils, resistance to high/low temperatures etc. They are usually manufactured and consumed in lower volumes than general rubbers and they are much more expensive (ethylene propylene, chloroprene, acrylic, silicone, urethane, epoxy, fluorine rubbers and others).

Rubbers are used most often in the form of vulcanizates - a vulcanized rubber. They can be brought to this form by vulcanization. This process is based on creation of chemical and physical transverse bonds between rubber macromolecules resulting in a spatial vulcanizate mesh, giving unique properties to the material. Various chemical - vulcanizing - agents are used to create the chemical transverse bonds between rubber macromolecules (such as sulphur, peroxides, metal oxides, resins, quinones and others), which can react with appropriate functional rubber groups in the process of vulcanization to create transverse bonds between them. The cross-linking can be induced also by radiation, however its energy must be sufficient to
generate reactive forms of rubber macromolecules - radicals in most cases. They react with each other giving rise to transverse bonds. Cross-linking can occur also due to microwave energy or ultrasound. Most rubbers require vulcanisation; though it is not inevitable for some type of thermoplastic rubbers.

Anyway, the optimum vulcanizate (rubber) properties cannot be achieved only by cross-linking rubber molecules, but other additives must be added. Besides cross-linking agents and antidegradants (used to slow down the process of aging), they include fillers that have a positive influence on some of the utilisation properties and make them cheaper, as well as additives allowing admixture of all the powdery or liquid additives, often referred to as supplementary processing additives.

Rubbers, just like any other chemical compounds, can participate in other chemical reactions (polymer-analogical reactions) under suitable conditions because they have reactive function groups in their macromolecules (double bonds, reactive α-hydrogen, other function groups). These usually include modification of undesired properties of rubbers (e.g. resistance to aging, polarity, adhesion to other materials, linkage of antidegradants), or production of rubbers with some new properties (CIIR, BIIR, carboxyl rubbers). Intermediary reactions (cyclisation, isomerisation, degradation, cross-linking and others) can occur simultaneously with the main chemical reaction.
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1. Introduction

Rubbers – elastomers - are polymer materials that are characterized by ability of reversible deformation under influence of external deformation forces. Extent of deformation depends on the structure and molecular weight of deformed rubber and also on external conditions of deformation; it can achieve some 100 up to 1000 % already at low stress. This property, marked as elastic, eventually highly elastic deformation, has entropy character. It rests in ability of the rubber macromolecules to occupy more ordered forms under stress, and on removal of stress to return to their ideal statistically random conformation, under ideal conditions without deformation of chemical bond distances or their angles (only non-combinatorial entropy is changed). The entropy reduction (∆S) at unchanged free energy of the stressed system (ΔG = ΔH – TΔS = 0) must be connected with enthalpy reduction (∆H), which becomes evident externally by heat-up of the deformed sample. In ideal case the macromolecules may return to original position after elimination of stress and the stressed samples cooled down to original temperature.

The rubbers have usually long and regular macromolecule chains without large substituents, with spatially oriented structural units. Thus their segments are movable and also at low temperatures they can freely rotate around simple chemical bonds. It is related to their low glass transition temperature Tg. Typical examples of such rubbers are poly-cis-1.4-butadiene and poly-cis-1.4-isoprene. They have Tg around –110, eventually –70 °C. With increasing of the content of irregularities in polymer chain (trans-1.4, 1.2 or 3.4 structural units) or under presence of large substituents (styrene-butadiene rubbers) their Tg is increasing. Under glass transition temperature or crystallization temperature (when rubber crystallizes) the rubbers are solid polymers similar to plastomers. During heating they changed from elastic, eventually high elastic state to viscoleastic state and above softening temperature they are plastic and they flow. It is advantageous when rubbers at normal temperature crystallize only under stress and their Tg is significantly lower than their usage temperature.

The rubbers gain optimum properties of engineering materials only in form of vulcanizates. It is possible to transfer them into this form by means of vulcanization. Basis is in creating of chemical and physical cross-links among rubber macromolecules, in consequence of that three-dimensional network is created and material obtains unique properties. In no case this can not be achieved only by cross-linking itself, but also some other additives must be added to rubbers. Except of cross-linking agents and antidegradants (they reduce ageing process) those are mainly fillers (they are making rubbers not only cheaper but they positively influence also some of their commercial properties) and also additives allowing compounding of all necessary powder or liquid ingredients to the rubbers, very often marked as auxiliary processing additives.
Presently, a lot of rubber types are on the market that can be divided into more groups in accordance with different criterion (e.g. saturated an unsaturated, natural and synthetic, polar and non-polar, crystallizing and non-crystallizing, etc.). From view of their usage and basic properties these can be also divided onto:

- **rubbers for general use** – they have properties complying with requirements of more products, often also with different properties, they are relatively cheap, produced and consumed in big volume
- **special rubbers** – except of basic elastic properties they have at least one special property, e.g. ageing resistance, resistance against chemicals, resistance against swelling in non-polar oils, resistance against high or low temperatures etc. Normally they are produced and consumed in lower volume than general rubbers and they are significantly more expensive.

In professional literature and also in practice the rubbers are named besides commercial names also with abbreviations (in accordance with ASTM-D 1418-76 or ISO-R 1629). Basis for the abbreviation creating is the rubber chemical composition. The abbreviation consists of a number of capital letters. The last letter of appropriate abbreviation characterizes typical atom or group that is present in the rubber macromolecule:

- **M** – rubbers with saturated hydrocarbon chain of methylene type
- **N** – rubbers containing nitrogen in polymer chain
- **O** – rubbers containing oxygen in polymer chain
- **Q** – rubbers containing oxygen and silicium in polymer chain
- **R** – rubbers with unsaturated hydrocarbon polymer chain (diene)
- **T** – rubbers containing sulfur in polymer chain
- **U** – rubbers containing carbon, oxygen and nitrogen in polymer chain
- **Z** – rubbers containing phosphor a nitrogen in polymer chain

Other letters of the abbreviation characterize monomers, the rubber was produced from. For example, in accordance with that the SBR abbreviation means butadiene-styrene rubber, CR is chloroprene rubber, EPM is ethylene-propylene rubber, BR is butadiene rubber etc. Also some other letter can create a part of abbreviation, and these closer characterize appropriate rubber, e.g. OE-SBR is oil extended styrene-butadiene rubber, L-SBR means styrene-butadiene rubber produced by polymerization in solution, H-NBR is hydrogenated acrylonitrile-butadiene rubber, CIIR is chlorinated isobutene-isoprene rubber etc. Natural rubber is marked with abbreviation NR. Such abbreviations are used also in this paper for marking of the rubbers.

### 2. Natural rubber

*Natural rubber* (NR) has vegetable origin. It is created by enzymatic processes in many plants, belonging mainly to families of Euphorbiacea, Compositea, Moracea and Apocynacea. It is industrially achieved mainly from the tree called Hevea Brasiliensis belonging to Euphorbiacea family. It is grown in
planted in warm (average monthly temperature 25 – 28 °C) and humid (humidity around 80%) climate of South-Eastern Asia (Malaysia, India, China, Sri Lanka, Vietnam), in Western Africa (Nigeria, Cambodia) and in North part of South America (Brazil, Guatemala). Annual production of rubber is presently varying around 3000 – 3500 kg per 1 ha and it depends on weather, soil quality, used stimulation means, age of threes and other external factors. The first source of rubber is sucrose that is created from carbon oxide and water during photosynthesis process. In the first biosynthesis stage the acetyl-coenzyme A is created from it and this is changed onto iso-pentyl-pyrophosphate through mevalone acid and the rubber in form of latex is generated by polymerization. The rubber is achieved from it by means of coagulation.

Natural rubber obtained from Hevea Brasiliensis is practically pure poly-cis-1.4 isoprene (contains more than 99.9 % of cis 1.4 structural units) from chemical view. At the ends of its macromolecules there may be bonded also non-isoprene structural units, mainly proteins, amino acids and phospholipids, in macromolecules backbone those may be also epoxide, ester, aldehyde, eventually lactone groups. Also part of non-rubber additives that are present in latex is remaining in rubber. Their content may be different but generally it is varying in range 5 – 10%. In spite of their small amount in rubber they have significant influence on its properties and they represent one reason of different properties of natural rubber and its synthetic equivalent (IR).

$$\begin{align*}
\text{CH}_2 & \quad \text{CH} = \text{C} \quad \text{H} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}$$

poly-cis-1.4-isoprene

NR achieved from fresh latex and immediately dried-out after coagulation contain small portion of gel, too. Gel-rubber has higher content of nitrogen and minerals in comparison with sol-rubber, which leads to vision that rubber chains are more branched in gel-rubber and they are mutually connected with proteins through hydrogen bridges. This assumption is approved also by discovery that content of gel-rubber in deproteinized rubber is much lower. Average amount of side branches per one rubber macromolecule is varying approximately from 1 to 6 and it is higher in macromolecules with higher molecular weight. Accompaniment of the natural rubber storing is gradual increasing of its viscosity that is externally shown by its hardening. Reason of this phenomenon is not well known, but it is accredited to cross-linking reactions of non-rubber groups present in its macromolecules.

Macromolecules of NR are long, regular, flexible and practically linear, thus it has very good elastic properties (Tg ~ -70°C) and spontaneously crystallizes (maximum crystallization rate is approximately at -25°C) also under influence of deformation forces already at relative prolongation of more than 80%. It has also excellent strength characteristics and keeps them also in form of vulcanizates. Tensile strength of NR vulcanizates filled with active fillers may be also more than 30 MPa. Its molecular weight $M_w$ varies the most often in between $10^4$ - $10^7$.
and polymolecularity $\frac{M_w}{M_n}$ approximately from 2.5 to 10. In non-vulcanized status it is reversible prolonged under high deformation rates already to 800 – 1000 %. It belongs to highly resilient rubbers. Some commercial types of NR rubbers must be *masticated* prior to compounding. NR types with regulated viscosity (CV) practically do not need mastication and they have good processing properties.

NR rubbers belong to highly non-saturated rubbers, because each their structural unit contains one double link. Also reactive $\alpha$-methylene hydrogens are related with its presence. Both types of these function groups may take part in different addition or substitution polymeranalogical reactions that can run also as parallel reactions (e.g. during hydrohalogenation). They are utilized for chemical modification of the rubber itself as well as for its vulcanization. In general, the NR rubbers are vulcanized by means of sulfur systems, but also other vulcanizing agents can be used (phenol formaldehyde resins, urethanes, peroxides and others). Ozone and oxygen react very easily with NR function groups, which cause its very low aging resistance.

### 2.1 NR latex

**NR latex** in Hevea Brasiliensis is located in latex vessels to be founded in various parts of the tree. The lowest occurring is in the wood and the highest in the secondary phloem. There are the vessels aligned to spirals in concentric circles close to cambium. It is obtained from them by *tapping* based on cutting of the tree bark by special knife under approximate angle of 30°. Latex spontaneously flows out of this slot, because it occurs in spurges under hydrostatic pressure of 1–1.9 MPa. It is collected into special bowls.

Natural rubber latex is a colloid system having the rubber particles dispersed in water. *Latex particle* size is varying approximately from 0.05 to 3µm. In fresh latex they have mainly spherical shape that is under their aggregation gradually changed to pear shape (*Section through rubber particles*). Besides these also small amounts of proteins, resinous matters (including lipids), hydrocarbons and mineral substances are present in NR latex. Part of these non-rubbery matters, mainly proteins and lipids, is surrounded by a surface of rubbery particles and gives them negative charge, which assures the latex stability.

Specific weight of fresh NR latex is 0.96 – 0.98 g x cm$^{-3}$ and its pH is varying within 6.5 – 7.0. It coagulates by standing on the air, and from this reason it must be stabilized. The most often used item for this stabilization is ammonia (HA latex – maximum 0.7 % NH$_3$) or its combinations (LA latex – 0.2 % NH$_3$) with secondary stabilizers, such as dithiocarbamates, combination of tetramethylthiuram disulfide and ZnO, lauric or boric acid. These are added to latex only in very small amounts, normally 0.01 – 0.05 %.

Some rubber products (e.g. foam rubber, gloves, condoms, glues) are produced directly from latex. The latex is modified for these reasons to have higher DRC values (minimum 60 – 65 % of rubber). It is performed by means of its concentrations, the most often by centrifugation and sedimentation, but also water evaporation thickening and electro-decantation is used. During these operations also...
eventual dirtiness and non-rubbery additives are removed from rubber besides increase of the dry rubber content in latex.
Composition of fresh NR latex

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Content, %</th>
</tr>
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<tbody>
<tr>
<td>Rubber</td>
<td>30 – 40</td>
</tr>
<tr>
<td>Proteins</td>
<td>1.0 – 1.5</td>
</tr>
<tr>
<td>Resins</td>
<td>1.5 – 3.0</td>
</tr>
<tr>
<td>Minerals</td>
<td>0.7 – 0.9</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>0.8 – 0.1</td>
</tr>
<tr>
<td>Water</td>
<td>55 – 60</td>
</tr>
</tbody>
</table>

Mastication is process during which the elastic rubber achieves plastic properties. During mastication breaking of chemical bonds in its macromolecules take place by means of high shear forces. This process results in the decreasing of molecular weight and viscosity of rubber and consequently it becomes treatable. Mastication of NR is performed either at low temperature on mills or at higher temperature in closed mixers, often in the presence of peptizers (they act as donors of electrons or hydrogen), that increase its efficiency. Besides mechanical degradation of rubbery macromolecules also their oxidation degradation occurs in this process and its rate is upgraded with mastication temperature increasing. Mastication of the NR is the most efficient at temperatures below 60 – 70°C and above 120 – 130°C, its efficiency is low in interval between these temperatures.

Mastication of synthetic rubbers is much less efficient, and thus they are either produced with the molecular weight and viscosity suitable for their processing or they are modified in final production stages by means of suitable oils (e.g. SBR extended by oil). Advantage of such modification is in possibility to keep the high molecular weights, that normally afford better physical-mechanical and dynamic properties to vulcanizates and also processing of rubbers is good.

3 Synthetic rubbers

3.1 Some fundamental of synthetic rubbers production

Synthetic rubbers, similarly to other polymers, are the most often produced by means of polyreactions of the chain or gradual character. Great part of them is achieved by the chain polyreactions, namely:

- radical
- ionic or
coordination polymerization and copolymerization, which are the most often used in:

- emulsion
- solution or
- suspension

Chain polyreactions run in more following actions, running in parallel. Primary act of the whole process is creation of the reactive particle that is able to start the monomer molecules addition process on it. Reactive particle may be radical, ion or ionic pair. According to this the whole process can run by radical or ionic (anionic, cationic, coordination) mechanism.

In free radical polymerization and copolymerization systems used during synthesis of rubbers, the primary radical is the most often generated by decomposition of suitable initiator. At temperatures around 50°C those are mostly peroxides (dibenzoyl peroxide, potassium persulfate, ammonium persulfate) and azo-compounds (azo-bis-isobutyronitrile), at temperatures around 5°C oxidation-reductive systems consisting of hydroperoxide (p-menthane hydroperoxide, pinane hydroperoxide) and metal salt of transition valence (Fe$^{2+}$), eventually activator (sodium salts of suitable acids).

Macromolecules of polymers prepared by radical polymerization or copolymerization have polydispersion character. It is mainly because of the fact that growing polymer radical terminated not only in consequence of termination reactions with other polymers radical, but also in consequence of transfer reaction to other reaction system components (polymer, monomer, initiator, and solvent). Chain transfer reactions are used also for targeted regulation of molecular weights of rubbers. Chain transfer agents (e.g. mercaptanes, halogenides, disulfides) are added into reaction systems in these cases.

Rubbers based on vinyl and diene monomers are the most often prepared by means of radical polymerization and copolymerization. Diene monomers keeps its reactive function groups also in form of structural unit mutually connected into polymer, eventually copolymer chain (α-methylene hydrogens and double bonds), thus there may take place under their presence also transfer reaction of growing polymer radical to polymer and also to its addition to double bonds. These reaction leads to branching and cross-linking of created rubber. In consequence of their rate increasing with elevated temperature, the rubbers prepared under higher temperature are more branched and they have also higher content of gel. To reduce these unwanted reactions, the polymerization and copolymerization of diene monomers is normally finished at about 60 % conversion. Polymers with randomly distributed structural units (cis-, trans, 1.4, 1.2, eventually 3.4) are created during radical polymerization of diene monomers. Rubbers with such microstructure have worse elastic properties than their stereo-regulated equivalents.

Primary radical from both co-monomers are created during copolymerization. They also react with both monomers in elementary propagation act, so the copolymer molecule is combined from structural elements of both monomers. Their structure and arrangement in macromolecules depend mainly on mutual reactivity of growing copolymer radicals against individual monomers (it is characterized by the
monomer reactivity ratios) and from their content in monomer feeds. In such case when copolymerization monomers create azeotropic mixtures, the composition of copolymers is equal to the composition of monomers mixtures.

The most of radical synthesis are performed in emulsion. Mainly rubbers of copolymer character with randomly arrangement monomer units are produced in them (SBR, NBR, ACM, FM) and also CR rubber.

In the ionic polymerization systems there are created reactive particles that are able to initiate growth of polymer chain by means of the charge transfer from initiator ion to monomer, in cationic polymerizations those are cations and in anionic anions. During cationic polymerization four elementary reactions run in similar way as in free radical reaction – initiation, propagation, termination and transfer. The most frequently acids used for initiation are Brönsted’s or Lewis’s acids (H₂SO₄, HClO₄, HCl, BF₃, AlCl₃, SnCl₄) itself or in combination with small amount of co-catalyst (water, alcohols, ethers and others). During propagation the monomer molecules enter between polycation and opposite anion of initiator. Termination of the polycation is the most often achieved by its monomolecule fragmentation or reaction with anion fragment of the initiator. In cationic polymerization systems similarly to radical system there can transfer of growing polycation onto some of the polymerization system compounds (monomer, polymer, solvent, or impurities) take places; consequently created various length macromolecules and they can be branched. Cationic polymerizations are performed under very low temperatures (around – 50 to – 100 °C). In this condition activation energy of transfer reaction is higher than the activation energy of initiation and propagation, accordingly polymers with narrower distribution and lower branching than in radical polymerization are formed. Cationic polymerizations are performed the most often in polar solvents. Typical example of rubber produced by means of cationic polymerization is IIR rubber.

Anionic polymerization and copolymerization can be performed in non-polar as well as polar solvents. In non-polar medium (aromatic and aliphatic hydrocarbons) alkyl metals (butyl lithium) are the most often used for initiation, but they only partially dissociate to ions. In polar solvents of the electron-donor character (tetrahydrofurane, naphthalene, benzophenone) total dissociation of initiator (phenyl lithium, sodium, potassium) onto ions take places, and at the same time also solvent becomes a part of stabilizing cation. Reactive anions that are able to initiate the growth of polymeric chain may be created by addition of initiator’s anion to monomer, by means of the electron transmission from initiator onto monomer or through amphions that generate reactive monomer anion by means of reaction with monomer. During propagation the present monomer is added to created anion and if no impurities are present in the system (e.g. water, oxygen, carbon oxide) the polyanion grows until all monomer is consumed (living anionic polymerization). Termination takes places only after addition of terminating agent (substances that are able to accept electrons - water, carbon oxide, alcohols, ethylene oxide and others). Living anionic polymerization can be used also for preparation of „pure“ block copolymers (thermoplastic styrene-butadiene rubbers). In this case the second monomer is added into system already after finished reaction of the first one; from this reason neither random connecting of its structural units into the first monomer block can not take place. Final structure of copolymer depends on type of used
termination agent. If termination agents with more functional groups are used, thus star-shaped copolymers may start-up.

Polymers with very narrow distribution are created in anionic polymerization systems and their molecular weights depend only on concentration ratio between initiator and monomer. Blocks length in the block copolymers depends on amount of monomer that was added into system.

Specialty of the coordination polymerization is in creation of sterically regular polymers. The most frequently used initiators in these systems are Ziegler-Natta’s catalysts. These are created by transition metal salts of Group IV to VIII elements, and organometallic alkyl- or acyl-compounds of Group I to III elements of Periodic Table. As transition metal salts the most often used are halides or others compounds of titan, cobalt, nickel, vanadium and similar metals, the second part is mostly created by diethylaluminum chloride or triethylaluminum. One should expect that effective initiator is created by means of alkylation of transition metal in salt. Its initiation activity is based on the fact that transition valence metal in lower valence is able to create not only covalent bonds (alkyl – metal), but also the coordination bonds with unpaired $\pi$-electrons of double bonds and to change them mutually. If molecule of olefin or diene occurs in catalyst’s coordination field, than coordination bond is created between them, during which time the bond between alkyl carbon-metal is destabilized, monomer molecule is inserted between atoms of carbon and metal and at the same time condition for creating the new coordination bond is established. To allow the polymer chain to be created in this way, the monomer molecules must enter spatially oriented into the propagation step. From this reason stereo regular polymers are created by means of coordination polymerization. Depending on catalyst composition polymers with high content of same structural units may be prepared by this way.

With gradual polyreactions the polymer molecules grow gradually. It is done by reactions between function groups of monomers or polyreaction intermediate products. If the reacting monomers are bifunctional, thus linear polymers are created; if at least one monomer is multifunctional than the branched or cross-linked polymers results. Typical examples of the polyreactions running in gradual mechanism are polycondensation and polyaddition. During polycondensation also low molecule product is created besides polymer; normally no stand-by products are created during polyaddition. Gradual polyreactions run slower than chain reactions. Molecular weights of the creating polymers are increasing with reaction time and they use to be normally lower than molecular weights of polymers prepared by means of the chain reactions.

Gradual polyreactions are seldom used during production of rubbers. Urethane rubbers are prepared by polyaddition, and it is polyaddition of diols (very often polyesters or polyethers with lower molecular weight are used) and diisocyanates; polycondensation is used for some types of Q rubbers and TM rubbers (polycondensation of alkylene dichloride’s with sodium sulfide). They can be used also during synthesis of thermoplastic block copolymers of polyurethane and polyester type.
Initiation:

Initiator $\longrightarrow 2 \text{R}^\cdot$

decomposition of initiator to radicals

$\text{R}^\cdot + \text{M} \longrightarrow \text{RM}^\cdot (\text{P}^\cdot)$

$\text{R}^\cdot + \text{M} \longrightarrow \text{RM}^\cdot$ (P$^\cdot$)

formation of primary radicals

Propagation:

$\text{P}^\cdot + \text{n M} \longrightarrow \text{P}_{n+1}^\cdot$

formation of polymer radical

Termination:

$\text{P}_n^\cdot + \text{P}_m^\cdot \longrightarrow \text{P}_{n+m}^\cdot$

recombination

$\text{P}_n^\cdot + \text{P}_m^\cdot \longrightarrow \text{P}_n + \text{P}_m$

disproportionation

Transfer:

$\text{P}_n^\cdot + \text{T H} \longrightarrow \text{P}_n^\cdot + \text{T}^\cdot$

transfer (on chain transfer agent, initiator, solvent,..)

$\text{T}^\cdot + \text{M} \longrightarrow \text{T M}^\cdot$

addition of T$^\cdot$ on monomer

**Simplified reaction scheme of radical polymerization**

R$^\cdot$ - initiator radical, M – monomer molecule, RM$^\cdot$ - primary radical formed during addition of monomer molecule on initiator radical, P$^\cdot$, P$_{n+1}^\cdot$, P$_m^\cdot$ - polymer radical with n, n+1, m structural elements, P$_n$, P$_m$, P$_{n+m}$ - polymer with n, m, n+m structural elements, TH – chain transfer agent molecule, T$^\cdot$ - chain transfer agent radical, TM$^\cdot$ - radical formed during addition of chain transfer agent radical on monomer.
Initiation

Initiator $\rightarrow$ 2 R

$R^\cdot + M_1 \rightarrow RM_1^\cdot (P_1^\cdot)$

$R^\cdot + M_2 \rightarrow RM_2^\cdot (P_2^\cdot)$

Propagation:

$P_1^\cdot + M_1 \rightarrow P_1^\cdot$

$P_1^\cdot + M_2 \rightarrow P_2^\cdot$

$P_2^\cdot + M_2 \rightarrow P_2^\cdot$

$P_2^\cdot + M_1 \rightarrow P_1^\cdot$

Termination:

$P_1^\cdot + P_1^\cdot$

$P_1^\cdot + P_2^\cdot \rightarrow$ Copolymer

$P_2^\cdot + P_2^\cdot$

*Simplified reaction scheme of radikal copolymerization*

$R^\cdot$ - initiator radical, $M_1, M_2$ – monomer molecules, $RM_1^\cdot, RM_2^\cdot$ - primary radical formed during addition of monomer molecules on initiator radical, $P_1^\cdot, P_2^\cdot$ - polymer radical with $M_1$ structural unit end, polymer radical with $M_2$ structural unit end.
Simplified reaction scheme of branching and cross-linking during polymerization or copolymerization of butadiene 1.4
Simplified reaction scheme of anionic polymerization of butadiene

Effective Ziegler–Natta initiator
3.2 Butadiene rubbers

Butadiene rubbers (BR) are rubbers for general use. They are produced by butadiene polymerization. It may be present in polymer macromolecules in form of cis-1,4, trans-1,4 and 1,2 structural units. 1,2 units have pendant vinyl group, thus they may create isomeric forms (syndiotactic, isotactic or atactic). Content of individual forms of butadiene structural units in polymeric chain depends on the polymerization method and type of **used initiator** and it determines basic properties of BR. Trans-1,4 and also highly stereoregular 1,2-polybutadienes does not have elastic properties. But these are owned by 1,2 isomers with lower stereoregularity degree that contain around 35-50 % of 1,2 structural units and with their properties they are similar to the SBR (styrene structural units are substituted by 1,2 units of butadiene). Polybutadienes with high content of cis-1,4 structural units have the best elastic properties. Pure poly-cis-1,4-butadiene has Tg below −100 °C and pure polybutadiene 1,2 around −15 °C, Tg of commercially produced polybutadienes depends on mutual arrangement of these units in their macromolecules and it normally varies in between −100 and −80 °C. Presence of other structural units in poly-cis-1,4-butadiene significantly limits its crystallization ability, thus BR rubbers have low tensile strengths. Presently they are produced by means of coordination or anionic polymerization in solution.

![Butadiene structural units](image)

**Butadiene structural units**

The largest portion of the globally produced BR is obtained by the coordination polymerization of butadiene. It is performed in non-polar medium of benzene, toluene or other aliphatic, eventually cycloaliphatic hydrocarbons, in presence of Ziegler-Natta catalysts based on Ti, Co, Ni or Ne salts and alkyl aluminum compounds. Content of the cis-1,4 structural units is high and it normally varies between 90 and 98 %. It depends predominantly on type of used catalyst system. The BR produced in these polymerization systems have molecular weights of approximately 250 000 – 300 000 g.mol⁻¹, they are branched by long chains and have rather broad distribution of molecular weights. In comparison with Li-BR, they are easier for processing, they have lower ratio of cold flow, fillers are better distributed in them, they can be extruded in higher ratio under lower temperature, and their compounds have higher strength and lower viscosity.

The most often used initiators during anionic polymerization are alkyl lithium compounds (Li-BR). If polymerization take places under low temperatures, then linear polymers are created, with increased polymerization temperature also probability of their branching is increased. Polarity of used solvent has important influence on the Li-BR microstructure. In presence of non-polar solvents the BR is prepared with low content of 1,2 units and content of cis- and trans-1,4 units is approximately same (hexane), in BR produced in polar medium solvent
(tetrahydrofurane) there is even around 90 % of 1.2 units and it practically does not contain cis-1.4 units.

BR is non-polar, highly unsaturated rubber. Because of irregular set-up of their structural units in macromolecules they hardly crystallize, what is shown also by their low tensile strength. By temperature influence they are easily subject to cis-trans isomerization. Besides low strength also high resistance against abrasion is characteristic for them (that is increasing with increased content of 1.2 structural units in their macromolecules), high resilience and good elastic properties under low temperature. These properties are maintained also in compounds with other rubbers. BR reacts slower with oxygen and ozone than NR, but presence of antidegradants in their compounds is necessary. They are filled to the high degree with active fillers, which requires presence of suitable softeners the most often of aromatic or naphthenic character.

The most often BR is cured by sulfur systems. They react slower with sulfur than NR, thus the vulcanizing systems used during their curing contain normally less sulfur (up to 2 phr). Mainly sulfenamides or their combinations with thiurams are suggested as accelerators for them. Normally no reversion takes places during their over-vulcanization.

More than 90 % of produced BR is consumed during production of tires. Mostly they are used for their ability in reducing the tire rolling resistance and they have favorable influence on riding properties of winter tires. They are used also in shoemaking trade, during production of conveyor belts and other technical products that require good resistance against abrasion. Li-BR is not used very frequently more often only for modification of impact strength of thermoplastic polymers.

<table>
<thead>
<tr>
<th>Microstructure of some BR types</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR type</td>
</tr>
<tr>
<td>cis-1.4 content, %</td>
</tr>
<tr>
<td>trans-1.4 content, %</td>
</tr>
<tr>
<td>1.2 content, %</td>
</tr>
</tbody>
</table>

### 3.3 Styrene-butadiene rubbers

Styrene-butadiene rubbers (SBR) are copolymers of styrene and butadiene. They are of the most commonly used rubbers. Their properties are influenced not only by micro- and macrostructure of polymer chains but also by styrene content. Butadiene structural units can be arrangement as cis-1.4, trans-1.4 or 1.2 (vinyl) units. Mutual arrangement of styrene and butadiene units can have random, partially-block or block character. SBR do not crystallize even under stress, hence, influence of mutual arrangement of „cis“ and „trans“ units on their properties is lower than it is in the case of BR. Increasing content styrene and 1.2 structural units contributes to increase of glass transition temperature, Tg of SBR.
copolymers of butadiene and styrene can also have two $T_g$; their values depend on presence of individual types of structural units in the block. Butadiene and styrene may copolymerize by means of radical, ion and coordination mechanism. Today the most commonly used is free radical copolymerization in emulsion and anion copolymerization in solution.

![Structural units of styrene-butadiene rubber](image)

Free radical copolymerization of butadiene and styrene in emulsion (E-SBR) takes place at temperatures around 50°C (hot rubbers) or 5°C (cold rubbers). In both cases, the emulsion systems used are practically identical (anionic emulsifiers, mercaptans as chain transfer agents, dithiocarbamates as stopping agents of copolymerization) however; they use different types of initiators. While at temperature 50°C they are mainly peroxodisulfates, at 5°C they are reduction-oxidation initiation systems consisting of hydroperoxide (p-menthane hydroperoxide or pinane hydroperoxide) and redox component, most usually in the chelate form (sodium salt of ethylenediaminetetraacetate acid and sodium formaldehyde sulfoxylate). The monomer feed usually contains 23.5 % by weight of styrene and 76.5 % by weight of butadiene; however, the composition may be different, too.

E-SBR has high molecular weights, broad distribution, high level of branching, and usually contain gel, too. Decreasing of the polymerization temperature reduces the rate of elementary reactions leading to branching and transfer; hence, cold E-SBR are less branched, have more narrow distribution and less gel content. Gel formation and chain branching is also reduced by termination of copolymerization at 60 – 70 % conversion. Emulsion-type SBR have good processing properties, however, possible remains of emulsifiers (they may contain) impair their hysteresis properties. The special types of E-SBR are so-called oil-extended rubbers (OE-SBR) and their carbon black master batch.

Solution type butadiene styrene rubbers (L-SBR) are made either by anion copolymerization of butadiene and styrene, or by live anion polymerization, during which first one monomer is present in polymerization system and when polymerization is finished, the second monomer is added. A sequential anion polymerization produces block polymers, with the blocks containing no structural units of the other polymer. Their length is given only by monomer-initiator ratio;
depending on type of termination agent can be prepared linear, branched or star copolymers. They are typical representatives of thermoplastic rubbers.

Copolymerization of butadiene and styrene in non-polar solvents (most often in presence of alkyl-lithium initiators) also produces block-type copolymers; however, we cannot exclude possibility that in blocks of one monomer some structural units of the other monomer may be present. It is caused by higher reactivity of polybutadiene and polystyrene radicals to butadiene than to styrene (monomer reactivity ratio of butadiene \( r_{bu} \) is much higher than monomer reactivity ratio of styrene \( r_{st} \); \( r_{bu} / r_{st} \geq 50 \)); due to this, butadiene connects to copolymerization chain as first, while styrene follow later. In polar solvents or in presence of polar compounds, the ratio \( r_{bu} / r_{st} \) is considerably lower (in presence of butyl lithium at 30°C \( r_{bu}/r_{st}=1,38 \)); hence, created copolymers are mostly statistical type, however, depending on particular composition of system, they can contain more or less block-type sequences. Differences can be found also in alignment of butadiene structural units in copolymer; SBR prepared in non-polar medium have ca 10 % of structural units 1.2, those from polar medium have 40 - 70 %. Statistical L-SBR is similar to E-SBR but usually they have higher content of cis-1.4 butadiene structural units.

L-SBR have very narrow distribution of molecular weight (\( Mw/Mn \approx 1 \) for live anion polymerization; in case of copolymerization \( Mw/Mn \approx 2 \)), they are almost linear and contain no gel. Compared to E-SBR unit is more difficult to process them, however, they have better affinity against \( \text{SiO}_2 \) (at the end of their polymeric chains they may have functional groups capable to integrate with this filler). They are more expensive than E-SBR, but their share on overall SBR consumption is increasing (especially of types with higher content of 1.2 structural units of butadiene, which improve riding properties of car tires). Elastic properties of SBR worsen with increasing styrene content (elastic properties almost vanish when the content is too high). So-called styrene resins already have thermoplastic characteristics (contain more than 90 % of styrene) and they are used only as active fillers or processing additives for rubber compounds.

Variability of arrangement of structural units and content of styrene and butadiene in copolymer molecules allow production of SBR rubbers with various properties. SBR with low styrene content (3-13%, E-SBR) are suitable for low-temperature applications, L-SBR with styrene content ca 15 % are used in combination with BR rubbers for production of radial tires, SBR with high content of styrene (40-55%) are known as self-reinforcing rubbers or fillers (70 – 90 % of styrene). Considering the appropriate combination of elastic and plastic properties, the most advantageous are rubbers with styrene content from 23 to 25 %.

SBR are most usually vulcanized by sulfur systems (similar to other unsaturated rubbers). Unlike with NR, here it is common to use less sulfur and more accelerating agents; sulfur content increases when hard rubber is produces. In most cases we use safe sulfenamide accelerators, which sometimes are combined with very fast accelerators (thiurams, dithiocarbamates) or slow accelerators (guanidines) and vulcanization inhibitors.

In order to improve original low strength of SBR, reinforcement fillers are added in their compounds. Difficult SBR mastication and high level of filling of their
compounds require use of efficient softeners and processing additives. Degradation of SBR rubbers and their vulcanizates is lower than for NR, however, presence of antidegradants is necessary.

Major part of SBR is used for production of car tires and products for automotive industry, mainly owing to their high abrasive, good resistance against thermal degradation and generation of cracks (better than NR and BR), and also thanks to lower rolling resistance. Their non-vulcanized compounds have lower building tack and strength as NR-compounds. These properties may be modified by combination with NR or by adding some suitable agents increasing tack of the compounds (resins).

*Glass transition temperature Tg of some SBR. 1 – cis-SBR, 2 – E-SBR, 3 – L-SBR (19 % styrene, 8% butadiene 1.2), 4 – L-SBR (25 % styrene, 8 % butadiene 1.2), 5 – SBR 1500, 6 – L-SBR (25 % styrene, 25 % butadiene 1.2), 7 – SBR (40 % styrene)*
Microstructure and macrostructure of L-SBR

<table>
<thead>
<tr>
<th>L-SBR Type</th>
<th>Styrene, %</th>
<th>1.2 butadiene, %</th>
<th>1.4 butadiene, %</th>
<th>Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buna VSL 2525-0 (Bayer)</td>
<td>25</td>
<td>25</td>
<td>50</td>
<td>-48.2</td>
</tr>
<tr>
<td>Buna VSL 5025-1</td>
<td>25</td>
<td>50</td>
<td>25</td>
<td>-76.0</td>
</tr>
<tr>
<td>Buna VSL 5525-1</td>
<td>25</td>
<td>55</td>
<td>20</td>
<td>-27.2</td>
</tr>
<tr>
<td>Sol 5520</td>
<td>24.7</td>
<td>41.9</td>
<td>35.4</td>
<td>-44.6</td>
</tr>
<tr>
<td>SBR Duradene 715 (Firestone)</td>
<td>23.5</td>
<td>46</td>
<td>30.5</td>
<td>-35</td>
</tr>
<tr>
<td>SBR NS 116 **a (Nippon Zeon)</td>
<td>23.5</td>
<td>60</td>
<td>20</td>
<td>-21</td>
</tr>
<tr>
<td>SBR NS 114 **b</td>
<td>20</td>
<td>50</td>
<td>32</td>
<td>-43</td>
</tr>
<tr>
<td>SBR SL 574 ** (JSR)</td>
<td>18</td>
<td>57</td>
<td>28</td>
<td>-40</td>
</tr>
<tr>
<td>SBR 1500 (emulsion)</td>
<td>23.5</td>
<td>18</td>
<td>58.5</td>
<td>-48</td>
</tr>
<tr>
<td>BR Taktene 1203 (Polysar)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-100</td>
</tr>
</tbody>
</table>

3.4 Acrylonitrile-butadiene rubbers

Acrylonitrile-butadiene rubbers (NBR) are special rubbers. They are statistical copolymers of acrylonitrile and butadiene. Their specific properties are resistance to non-polar solvents, fats, oils and motor fuel. Oil resistant increases together with increasing of acrylonitrile content in rubber. They are produced by radical copolymerization in emulsion, most often at low temperatures (5-30°C), in the similar systems like SBR (oxidation-reduction initiation systems, chain transfer agent, polymerization stopper). At higher conversion it can come to branching, eventually also to cross-linking of rubber macromolecules. This is the reason why copolymerization normally leads only to 60 – 90 % of conversion. Butadiene structural units can appear in them in several forms:
The ratio of monomer reactivity ratio of butadiene $r_{bu}$ and acrylonitrile $r_a$ is at the used copolymerization temperatures lower than 1 (at $5^\circ C$ $r_{bu} = 0.28$ and $r_a = 0.02$). Butadiene and acrylonitrile content in copolymer can affect also their ability to create azeotropic blend, which composition depends on temperature (at $25^\circ C$ it contains 38% wt. of acrylonitrile and 62% wt. of butadiene). Therefore final copolymer composition depends on conversion and polymerization temperature.

The ratio of cis-1.4 and trans-1.4-butadiene content is effected by polymerization temperature (at $28^\circ C$ and acrylonitrile content 36% cis/trans $\approx 0.16$ and with increasing polymerization temperature it raises), content of 1.2 units is decreasing with acrylonitrile content increasing (at 28% acrylonitrile in monomer feed it is approximately 10%) and it is not much dependent on the copolymerization temperature.

Molecular weight of commercially produced NBR is changed in broad range from the liquid oligomers ($M_h \approx 3000 \text{ g.mol}^{-1}$) suitable for the compounds with the low plasticizers content to high molecular polymers ($M_h \approx 10^6 \text{ g.mol}^{-1}$) suitable for high-pressure applications. Copolymers can be linear to highly-branched depending on the preparation conditions. Distribution of molecular weights and the level of macromolecules branching depend on copolymerization temperature; they are increasing with increasing of temperature.

The basic characteristics of NBR rubbers depend on the acrylonitrile content. Their swell resistance in non-polar agents improves with acrylonitrile content increasing. At the same time the glass transition temperatures and brittle temperatures are increasing. This causes elastic properties and flexibility falling-off at low temperatures but also improvement of NBR compounds processing caused by increase of their thermoplasticity. The most often produced are rubbers with acrylonitrile content 18 – 51%.

For NBR vulcanization are used several types of cross-linking systems. Sulfur systems involve fast (thiurams, dithiocarbamates) or safe (sulfenamides, MBTS) accelerators, eventually their combinations. Since the sulfur is not much soluble in NBR semi-EV and EV systems are preferred; they can generate also thermal resistant vulcanizates. Thermal resistant vulcanizates are also obtained during peroxide or phenolformaldehyde resin vulcanization of NBR. The resins are used as vulcanizing agents at co vulcanization of NBR with PVC or with others suitable polar thermoplastics.

NBR rubbers contain double bonds and have limited resistance to oxidation and ozonization. They are often used at higher temperatures (e.g. as sealing in hot
oils) there have to be volatile antidegradants added to the compounds. Occasionally antidegradants able to bond to network of vulcanizates. Problems with volatility are solved also with the combination of NBR with saturate rubbers (EPDM) or thermoplastics (PVC).

NBR do not crystallize under stress and they have low tensile strength. For the required properties of vulcanizates they have to be filled up with reinforcement fillers. Plasticizers and process aids added to NBR compounds must have polar character because of tolerance with rubber matrix. For this purpose ester and ether based plasticizers or their oligomere derivatives are used. From the processing aids these are mainly different resinous materials of synthetic and natural character. NBR vulcanizates which are filled with reinforcement fillers have higher abrasion resistance than equivalent materials from NR and SBR.

The essential part of produced NBR is used for production of sealings, tubes and different supports for auto industry, for oil and engine fuel transport equipment, for machinery and pumps; they are used at coating of printing machinery surfaces, at production of oil-proof conveyor belts and others products requesting resistance to oils.

Special NBR are also known; mainly hydrogenated acrylonitrile-butadiene rubber (HNBR), which is known for its increased temperature resistance and terpolymer of acrylonitrile, butadiene and small amount of acrylic or methacrylic acid (X-NBR), which has higher affinity against light fillers.

The influence of the copolymerization conversion on the butadiene content in NBR; 1 – NBR with 50% acrylonitrile, 2 – NBR with 28% acrylonitrile, 3 – NBR with 5% acrylonitrile.
The influence of the acrylonitrile content on glass transition temperature of NBR.

### NBR classification

<table>
<thead>
<tr>
<th>Classification</th>
<th>Acrylonitrile content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low nitrile</td>
<td>&lt; 24</td>
</tr>
<tr>
<td>Medium nitrile</td>
<td>25 – 30</td>
</tr>
<tr>
<td>Medium–high nitrile</td>
<td>31 – 35</td>
</tr>
<tr>
<td>High nitrile</td>
<td>36 – 42</td>
</tr>
<tr>
<td>Ultra-high nitrile</td>
<td>&gt; 43</td>
</tr>
</tbody>
</table>

**Hydrogenated acrylonitrile-butadiene** rubber (HNBR) is produced by partial or complete hydrogenation of NBR in solution, under presence of catalysts typical for hydrogenation reactions (cobalt, rhodium, ruthenium, iridium, and palladium complex salts). During complete hydrogenation all unsaturated C = C links are saturated, but polar C ≡ N links remain chemically unchanged. Saturated polar polymer is developed, and it distinguishes with high oxygen and ozone resistance and after peroxide vulcanization or other non-sulfur systems also with high resistance against hot air and hot oils. It offers also resistance against oils containing sulfur, hydrogen sulfide, different sulfur and nitrogen substances and also different technical chemicals. It possesses excellent tensile strength, good elastic properties under low temperatures and very good abrasion resistance. It keeps these properties also during ageing; the extent of some properties (e.g. tensile strength, resilience, and ageing resistance in ATF oil) retention is higher than in the case of FKM.

**X-NBR** rubbers are terpolymers of butadiene, acrylonitrile and acrylic acid or methacrylic acid. Carboxyl groups are linked on copolymer chain as side groups and they are used in particular for cross-linking. They react easily with metal oxides.
(ZnO), and from this reason during cross-linking of X-NBR by sulfur systems, mainly under presence of surface modified ZnO, there are created not only cross-links but also coordination bonds between oxide and carboxyl group. Such cross-linked vulcanizates have significantly higher swelling resistance in oils, higher abrasion resistance, but also higher strength and limited ageing resistance. Because of polarity the X-NBR rubbers have better affinity against light fillers than NBR.

Terpolymers of butadiene, isoprene and acrylonitrile (they have higher tensile strength than NBR, and they are suitable for production of color products) and terpolymers of butadiene, acrylonitrile and divinylbenzene or ethylene glycol dimethacrylate (better dimensional stability during extrusion) are also known as special NBR rubbers.

3.5 Isoprene rubbers

Isoprene rubbers (IR) belong to general rubbers. Their molecules are created by isoprene structural units that may be arrangement in polymer chain in position cis-1.4, trans-1.4, and eventually also as 1.2 or 3.4 units:

\[
\begin{align*}
\text{cis} - 1.4 & \quad \text{trans} - 1.4 & \quad 3,4 & \quad 1,2 \\
\text{Isoprene structural units in IR rubbers}
\end{align*}
\]

The best elastic properties are possessed by polyisoprene with high content of cis-1.4 units; trans-1.4 polyisoprene is thermoplastic material. IR is produced by anionic or coordination polymerization in solution of non-polar aliphatic hydrocarbons. The most often used initiator during anionic polymerization is n-butyl lithium. The rubber created during this synthesis (Li-IR) has high molecular weight (1.5 x10^6 - 2.0 x10^6 g x mol\(^{-1}\)), very narrow molecular weight distribution and its macromolecules are almost linear. Because of irregular arrangement of the structural units (90 – 92 % cis-1.4, 2 – 3 % trans-1.4 and 6 – 7 % of 3.4) it crystallizes only in restricted way. This is demonstrated mostly on its low tensile strength in non-vulcanized and also in vulcanized state. Processing of the Li-IR is quite difficult.

Coordination polymerization of isoprene is usually done under presence of combination of Ti(Cl)\(_4\) and alkyl aluminum compounds modified by aromatic or aliphatic ethers in molar ratio 1:1 (Ti-IR). Unused initiator is removed from the system after finished polymerization to avoid reduction in molecular weight and Ti-IR stability. Polymer molecules of Ti-IR are branched, they have relatively broad distribution and their molecular weights are usually ranging 1x10^5-1.5x10^6 gxmol\(^{-1}\). Usually they contain around 15-20 % of micro-gel. Their microstructure is similar
to NR; they contain around 98% of cis-1.4 and approximately 2% 3.4- structural units. But also low content of such other structural units as cis-1.4 causes much lower rate of their crystallization (Ti-IR crystallization half-time is 5 hours at –25°C, NR has 2 hours). It becomes evident by lower strengths in non-vulcanized and also vulcanized status. Their processing is easier than Li-IR.

The IR are non-polar, resilient, highly unsaturated rubbers. They contain a double bond in each structural unit. They have low oxygen and ozone resistance, but them aging more slowly than NR. They are cross-linked almost exclusively by means of sulfur systems. The IR in contrary with NR does not contain non-rubber substances that could increase curing rate, thus they react slower with sulfur and their compounds have higher scorch time. They are also characteristic by low building tack and green strength. To make properties of their vulcanizates comparable with properties of the NR vulcanizates, one must use Ti-IR and reinforcement fillers. Li-IR and their vulcanizates look more like BR and SBR by their properties.

In general, the Ti-IR rubbers may be used for the same purposes as NR, but Li-IR are more suitable for applications in combination with BR or SBR. The main field of the IR utilization is in production of tires, conveyer belts and technical rubber, but also protective and medical gloves, sucking-bag nipples and other sanitary goods are produced from them, because unlike NR they do not contain allergenetic ingredients.

### 3.5 Isoprene-isobutylene rubbers

Isoprene-isobutylene rubbers (IIR) are special rubbers. Their characteristic properties are small gas and steam permeability and also very good resistance to oxidation, ozonization and thermal degradation and against various chemicals.

They are produced by cationic copolymerization of isobutylene and isoprene in chloromethane solution in the presence of AlCl₃ as catalyst and water or HCl as co-catalyst at temperature under –90°C. The copolymerization proceeds also at this temperature with very high rates. The produced copolymer has high molecular weight and it precipitates from the reaction environment (precipitation copolymerization) in the form of hard non-agglomerated particles (temperature of polymerization is lower than IIR Tg). Isobutylene and isoprene copolymerization in hexane and in the presence of Al(alkyl)₂Cl as catalyst is homogeneous and can be performed at temperatures -40 to -50°C.

![Structural units of IIR rubbers](image)
Molecular weights of IIR rubbers are between 150 000 – 450 000 g/mol and they have quite broad distribution, Mw/Mn ≈ 2.5-5. Isobutylene structure units are arrangement in copolymer chains mainly by the way head-to tail. Content of isoprene is low (0.5 - 6 % mol) and his structural units are statistically arrangement in copolymer macromolecules in form of trans-1.4 units. In commercial types IIR to one isoprene structural unit appears approximately 40 structural units of isobutylene. Isoprene does not affect the IIR properties, double bonds in his structural units are used mainly for cross-linking.

IIR rubbers have very low content of unsaturated bonds which during the vulcanization expire. That is why they and their vulcanizates are resistant to ageing. Low rate of sulfur vulcanization is proportional to low content of unsaturated bonds. IIR hardly co-vulcanize with other unsaturated rubbers (NR, BR, SBR), the rate of cross-linking is increasing by increasing of double bond content, however at the same time the properties of vulcanizates are deteriorated. In the sulfur cross-linking systems fast (thiurams) or very fast accelerators (dithiocarbamates) and also in combinations with thiazoles (MBT) or systems based on sulfur donors are preferred. For vulcanization of IIR the quinone dioxime in combination with oxidizing agent are used (lead oxides, MBTS) and phenolformaldehyde resins in combination with chlorine containing substances (SnCl₄, FeCl₃, chlorinated polymers) or their halogenated derivates. In the presence of these cross-linking systems can be obtained vulcanizates resistant to thermal degradation. The use of peroxides is not suitable for cross-linking because they can cause degradation of the rubbers’ macromolecules.

**Halogenated** IIR is more suitable for co-vulcanization with diene rubbers. Its properties are very similar to IIR rubbers but their sulfur cross-linking is faster and vulcanizates with higher level of cross-links are achieved. They can be vulcanized by multifunctional amines, too.

Developmental types of rubbers which are isobutylene based are **star-branched** IIR which can be processed easier and also brominates copolymers of isobutylene and p-methyl styrene which are resistant to ozone and high temperatures and they are reactive at co-vulcanization with rubbers for general use.

![IIR degradation in presence of peroxides](attachment:image.png)
Halogenated IIR is produced by means of post polymerization modification of the IIR. It is done by chloration (CIIR) or bromation (BIIR) in solution of suitable alkane (pentane or hexane), the most often in dark, under temperatures 40 – 60 °C. Reactions proceed as electrophilic substitution reactions (chloration is approximately 5-times faster than bromation) and only one atom of halogen is substituted during them to one isoprene structural unit, the most often in allylic position. Approximately 80 – 90 % of halogenated units of isoprene have form (I) and 10 – 20 % form (II), other forms of halogenated units is occur only sporadically (<2 %):

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH} = \text{CH} \quad \text{CH}_2 \\
\text{C} & \quad \text{CH} \quad \text{CH}_2 \\
\text{Cl} & \quad \text{C} = \text{CH} \quad \text{CH}_2 \\
\end{align*}
\]

\(X = \text{Cl, Br}\)

The content of halogen in them is low (commercially the most frequently used CIIR with unsaturation 1.9 – 2.0 % mol contain approximately from 1.1 to 1.3 % wt. of chlorine and BIIR with unsaturation 1.6 – 1.7 % mol contain from 1.8 to 2.2 % wt. of brome), but it significantly increases the rate ratio of their co-vulcanization with diene rubbers.

Properties of halogenated IIR and conditions of their processing and utilization are practically the same as with IIR, but their compounding is usually performed at temperatures below 100°C (presence of reactive halogen in allylic form). Significant increase of the sulfur curing rate is accredited to ability of ZnO to participate on curing (similar to CR).

During cationic copolymerization of isobutylene and isoprene under presence of the „branching“ agents of the type of block styrene-butadiene copolymers grafted copolymers are created. Their backbone is created by SBS copolymer and branches are created by isobutyl-isoprene copolymer:

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_3 \\
\text{C} & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH} = \text{CH} \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{C} = \text{CH} \quad \text{CH}_2 \\
\end{align*}
\]

\(\text{cationic kopolymerization}\)

\[
\begin{align*}
\text{SSSSBBBBSSSS} & \quad \text{SSSSBBBBSSSS} \\
\end{align*}
\]

isobutylene isoprene styrene block kopolymere

\[
\begin{align*}
\text{IIR} & \quad \text{SSSSBBBBSSSS} \\
\end{align*}
\]

stars

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Its differential distribution curve has got a bimodal character. Approximately 87% of the product is IIR and about 13% has star-branched structure. It is easier for processing because of this bimodality.

### 3.6 Chloroprene rubbers

Chloroprene rubbers (CR) belong to the oldest types of synthetic rubbers. They are produced by radical emulsion polymerization of chloroprene (2-chlorobutadiene 1,3). Potassium or ammonium peroxodisulphate is the most frequently used for initiation and sulfur (G-CR) or mercaptanes (W-CR) are used for regulation of molecular weights. Sulfur behaves during polymerization of chloroprene as co-monomer and it creates sulfur bridges in polymer chains with 2 – 6 sulfur atoms that improve their flexibility, but reduce their temperature resistance. The W – CR does not contain sulfur bridges but their macromolecules can be terminated with the rest of transfer agent molecule (in presence of n-dodecyl mercaptane – SR ≡ – S (CH₂)₁₁ CH₃). They are more resistive against temperature, but less flexible. CR used for rubber industry purposes is normally produced at temperature around 30 – 40 °C.

\[
\begin{align*}
G - CR & : \quad \text{Cl} \quad \left[ \begin{array}{c}
\text{CH₂} - \text{C} = \text{CH} - \text{CH₂} \\
\text{n}
\end{array} \right] \quad \text{Cl} \quad \left[ \begin{array}{c}
\text{CH₂} - \text{C} = \text{CH} - \text{CH₂} \\
\text{m}
\end{array} \right] \\
W - CR & : \quad \text{Cl} \quad \left[ \begin{array}{c}
\text{CH₂} - \text{C} = \text{CH} - \text{CH₃} \\
\text{Cl}
\end{array} \right] \quad \text{Cl} \quad \left[ \begin{array}{c}
\text{CH₂} - \text{C} = \text{CH} - \text{CH₂} - \text{SR} \\
\text{Cl}
\end{array} \right]
\end{align*}
\]

Structural units of chloroprene are bonded in polymer chain mostly in form of 1.4-trans structural units. Content of other types of structural units (1.4 – cis, 3.4 and 1.2) is low.

\[
\begin{align*}
\text{chloroprene trans -1,4} & : \quad \text{Cl} \quad \left[ \begin{array}{c}
\text{CH₂} - \text{C} = \text{C} - \text{H} \\
\text{Cl}
\end{array} \right] \\
\text{chloroprene 1,2} & : \quad \text{Cl} \quad \left[ \begin{array}{c}
\text{CH₂} - \text{C} = \text{CH} - \text{CH₂} \\
\text{CH} = \text{CH₂}
\end{array} \right] \quad \leftrightarrow \quad \text{Cl} \quad \left[ \begin{array}{c}
\text{CH₂} - \text{CH} - \text{Cl} \\
\text{CH} = \text{CH_-Cl}
\end{array} \right]
\end{align*}
\]

**Structural units of CR rubbers**
Normally is increased with increasing of polymerization temperature. The presence of 1.2 structural units is very important. Chlorine atom may be bonded in them in allylic position and it can easily take part in electrophilic substitution reactions, what is used during CR cross-linking.

Rate and degree of its crystallization have close relation with content of 1.4-trans structural units of chloroprene. The higher it is thus the higher are these parameters. High-crystalline types of CR (A types of CR) have very good adhesion properties to other materials and they serve mostly as basic materials for production of adhesives. High crystallization ability has close interrelation with high CR strength their non-filled vulcanizates (more than 20 MPa) and also their relatively low permeability of gases and vapors. Non-crystalline CR types may be prepared only by copolymerization of chloroprene with other monomers, e.g. with styrene, isoprene or acrylonitrile. Crystallization half-time of individual CR types is different and it is as shorter as more regular the polychloroprene chain is.

Presence of the chlorine atoms in each of its structural unit has influence also on basic CR properties:
- they are high-polar, resistant to paraffinic and also to naphthenic oils, but they are partially swelling in aromatic solvents and they degrade during contact with engine fuels
- they have very low flammability (they are self extinguishing)
- they can eliminate HCl at higher temperatures (self-vulcanization), thus metallic oxides are added to them, because these affects as acceptors
- they have worse dielectric properties than non-polar rubbers
- polar substituents in their structural units definitely increase their resistance to oxidation and ozonization, mostly in consequence of reduced reactivity of double bond against these agents. This fact has negative effect on reactivity of CR in sulfur curing. From this reason other vulcanization systems are preferred during their curing.

In practice the CR are the most frequently vulcanized by means of metallic oxides (combination of ZnO and MgO in weight ratio 5:3), but also other curing agents can be used, as diamines, diphenols, thio ketones or diazines.

<table>
<thead>
<tr>
<th>CR type</th>
<th>Crystallization ability</th>
<th>Crystallization half-time $\tau_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A – CR</td>
<td>high</td>
<td>minutes – hours</td>
</tr>
<tr>
<td>W – CR</td>
<td>middle</td>
<td>months – years</td>
</tr>
<tr>
<td>G – CR</td>
<td>low</td>
<td>months – years</td>
</tr>
<tr>
<td>Chloroprene copolymers</td>
<td>they do not crystallize</td>
<td>-</td>
</tr>
</tbody>
</table>
3.8 Ethylene-propylene rubbers

The important special rubbers are ethylene and propylene copolymers (EPM) and terpolymers of ethylene, propylene and suitable diene monomer (EPDM), the most often ethylidene norbonene, eventually 1,4-hexadiene or dicyclopentadiene:

\[
\begin{align*}
\text{ethylene} & : \quad \text{CH}_2=\text{CH}_2 \\
\text{propylene} & : \quad \text{CH}_2=\text{CH}\left(\text{CH}_3\right) \\
1,4\text{-hexadiene} & : \quad \text{CH}_2=\text{CH} \quad \text{CH}-\text{CH}_2 \quad \text{CH}_3 \\
\text{dicyclopentadiene} & : \quad \text{CH}_3 \quad \text{C} \quad \text{CH}_3 \\
\text{ethylidene norbornene} & : \quad \text{C} \quad \text{CH}_3 \
\end{align*}
\]

Their typical properties are related mainly to absence of unsaturated bonds in their polymer backbones. EPM rubbers do not have any unsaturated bonds and those are resistant to oxygen, ozone and to several types of chemicals. EPDM have unsaturated bonds only in the side groups. Their content is low (up to 10 % wt.) in commercial EPDM rubbers and they expire by vulcanization. This is the reason why they do not appear the scission of polymer backbones during their potential oxidation or ozonization. The important properties of ethylene rubbers are also their excellent resistant to heat, electrical insulating and dielectric properties (also at raised temperatures and in the humid environment), resistance to chemicals (also to diluted acids and alkalis). Their importance is still increasing because they have wide exploitation in the auto industry, too.

Both rubber types are produced by coordination polymerization in aliphatic hydrocarbon solution (pentane, hexane) in the presence of catalysts based on vanadium salts (VCl₄, VOCl₃) and ethyl chloride aluminum. Exception is synthesis of high molecular EPDM, which is normally done without solvents in excess of fluid propylene. Advantage of this synthesis is that incipient rubber is precipitated from the reaction environment in the form of coagulum, which facilitates its insulation.

EPM rubbers with approximately same content of ethylene and propylene (45-60 %wt. ethylene) are randomly copolymers. Although they can contain short segments of individual monomers they are amorphous and they have low mechanical strengths. By increasing of ethylene content (to 70-80 %wt.) probability of segmental arrangement of ethylene units is increasing. It can leads to formation of thermal irreversible and partly crystalline domains and by this to increasing of their strengths.

Macrostructure of EPDM rubbers and some of their properties can be affected by the type and the quantity of termonomer used in the production. The most suitable for this purpose are non-conjugated dienes with different reactivity of double bonds;
one of them can take part in terpolymerization (suitable are mainly the monomers with the similar monomer reactivity ratios like ethylene and propylene have) and the other can take part in vulcanization. These requirements are nowadays best fulfilled with ethylidene norbonene, which take part in copolymerization by double bond in bicyclic formation and in vulcanization with double bond in ethylidene group. Reactivity difference of double bonds in dicyclopentadiene is relatively small and both can enter the terpolymerization process. That is why branched, eventually partly cross-linked macromolecules (containing gel) arise in his presence. Residual double bonds are less active during the vulcanization than double bonds in ethylidene norbonene terpolymers. Disadvantage of 1,4-hexadiene is lower activity of his double bond (between carbon 1 and 2) in the terpolymerization process.

EPM are the most often vulcanized by peroxide systems. For the vulcanization EPDM the typical vulcanization systems for unsaturated rubbers are preferred, mainly sulfur in the combination with fast and ultra accelerators, resins and quinones. Sulfur vulcanization rate of EPDM is increasing with the increasing of double bond content in its macromolecules. Both rubber types can be cross-linked also with high energy radiation (for cable insulations), in the optimal cases in the presence of suitable co-activators.

Also some other ethylene copolymers and as well chlorinated and chlorosulphonated polyethylene have got elastic properties.

Copolymers of ethylene and vinyl acetate (EVM) have elastic properties only with vinyl acetate content of 30 – 75 % wt. They are produced by radical copolymerization of these monomers (the most often with content of 40 – 50 % wt. of vinyl acetate) in solution of solvents with low transfer activity (e.g. tert.-butanol), at middle pressures.

\[
\begin{align*}
CH_2 = CH CH = CH & \quad \text{ethylene} \\
CH_2 = CH C(O)OCH_3 & \quad \text{vinylacetate}
\end{align*}
\]

Peroxides or azo-compounds are generally used for initiation of the copolymerization. Created copolymer is high molecular, less branched and practically without gel. They are vulcanized by means of peroxide systems.

EVM are saturated polar rubbers with very good resistance to degradation in hot air and very good weather and ozone resistance. Other advantageous properties are swelling resistance to mineral, plant and animal oil; their resistance against them is increasing with increasing of vinyl acetate content in their macromolecules. They contain oxygen, thus they are less resistent against burning than hydrocarbon rubbers.

Random terpolymers of ethylene, methylacrylate and small amount (1-5 %) of acrylic acid (carboxyl groups are used for curing) are produced by radical terpolymerization.
They are characterized by very good ageing and heat resistance, and also swelling resistance to non-polar solvents. Their elastic properties depend on the ethylene content.

Commercial types of chlorinated polyethylene (CM) are produced by chlorination of high-density polyethylene in suspension. Reaction takes place in radical mechanism and for its initiation UV radiation or organic peroxides are often used. CM macromolecules can contain three structural unit types - ethylene (a), vinyl chloride (b) and 1-dichleretylene (vinylidene chloride) (c):

\[
\begin{align*}
&\text{Cl} & \text{Cl} \\
&\text{a} & \text{b} & \text{c}
&\text{CH}_2\text{CH}_2 & \text{CHCH}_2 & \text{CH}_2\text{Cl}
&\text{CH}_2 & \text{CH}_2 & \text{Cl} & \text{CH}_2
\end{align*}
\]

Chlorine atoms disturb the regularity of polyethylene chain. Accordingly its crystallization ability is essentially decreased and CM has the elastic properties at the suitable content of chlorine. Ethylene structural units have tendency to create longer ethylene sequences at the low chlorine content and to form hard crystalline domains partly.

CM characteristic properties depend mainly on the chlorine content in its macromolecules; with chlorine content raising also the CM polarity increases and also its burning and to swelling resistant in non-polar oils resistance. It becomes brittle and loses its elastic properties. It has optimal properties when the content of chlorine is around 35 % (brittle temperature \(\approx -40 \, ^\circ\text{C}\)). CM is saturated polymer like polyethylene and therefore it is resistant to oxygen and ozone. It cleavages of HCl at higher temperatures (over 160°C), so it has to be protected by adding of the suitable acceptors (MgO, lead oxides, not ZnO) to its compounds. It has good processing characteristics. Organic peroxides are most often used for its vulcanization. The reactive chlorine atoms can be also used for cross-linking.

Chlorosulfonated polyethylene (CSM) is obtained by chlorosulfonation of polyethylene (in solution of chlorinated hydrocarbons in the presence of chlorine and sulfur oxide). In its macromolecules are present not only of chlorine but also sulfonyl chloride \(\text{SO}_2\text{Cl}\) functional groups. Their content in CSM is low (sulfur content is \(\approx 0.8 - 1.5 \, \%\)) and they are used for its vulcanization. Practically, CSM properties correspond with CM but it is more easily cross-linked (with some of metal oxides, poly-functional alcohols, multifunctional amines, and peroxides).
3.9 Acrylic rubbers

Acrylic rubbers (ACM) are unsaturated polar rubbers that are characterized with very good swelling resistance in non-polar oils and also in oils containing sulfur substances. Because of the fact they do not have unsaturated bonds in polymer backbone, thus they have good heat, oxygen and ozone resistance. From chemical point of view they are copolymers, eventually terpolymers of different types of acrylic monomers or acrylic monomers and other monomers containing functional groups suitable for curing. The most frequently those are vinyl monomers with reactive atoms of chlorine, epoxy or carboxylic groups. Content of these monomers is low (1-3 % wt.) and has no significant influence on their properties.

ACM are produced by emulsion (exceptionally by suspension) radical polymerization. For its initiation peroxides, azo-compounds or oxidation-reduction initiation systems are used. Because of the fact, that acrylic monomers have ester groups in their molecules, thus pH of reaction medium must be > 7, to avoid their hydrolysis. The same negative influence may have also fillers or other additives of acidic character in their compounds.

ACM properties under low temperatures are influenced mainly by structure of alkyl substituents in their ester groups; generally they are improved with increasing of carbon number in alkyl groups (brittle temperature of poly-n-alkylacrylate is reduced for substituents with carbon number C = 1-8 from temperature +3 °C down to temperature – 65 °C). Simultaneously, their polarity is decreasing, and thus their non-polar oil and ageing resistance is decreasing, too. ACM based on polyethyl acrylate are high-polar and very well resistant to oils and increased temperatures, but they have relatively high Tg (approximately -15°C) and their vulcanizates are less flexible under low temperatures. Replacement of ethyl groups by butyl one will reduce Tg to approximately –50 °C, their vulcanizates are significantly more flexible under low temperatures, but their swelling resistance in non-polar oils is lower. Polyoctyl acrylate is practically not resistant against non-polar oils. Properties of ACM under low temperatures may be modified by copolymerization of acryl monomers (ethyl acrylate, butyl acrylate, eventually by octyl acrylate or acryl monomer with alkoxy groups) and they can be partially modified also by adding of suitable, less volatile softeners; the best one is of ester type.

The most industrially produced acrylic rubbers are based on ethyl-, butyl- and metoxy ethyl acrylate and monomers containing chlorine or carboxyl groups. Their suitable combination usually compromise between ACM oil resistance, appropriate properties under low temperatures, heat resistance and acceptable curing rate can be achieved.

For cross-linking of ACM rubbers mainly function groups of non-acrylate monomers, despite the fact that under presence of metallic oxides of alkaline character one cannot exclude even self-curing of polyacrylate chains caused by reactions of their ester groups and active hydrogen in α-position against them (Claisen’s condensation) are used. Older types of ACM were cured mostly by diamines or polyamines, present types of rubbers are cured also by combination of polyamines, higher fatty acids or their esters and sulfur, eventually by sulfur donor.
Their efficiency is increased by addition of very fast or ultra accelerators. The most often used systems for curing of ACM with epoxy and carboxyl groups is based on quaternary ammonium salts.

Acrylic rubbers are used mainly for production of materials resistant to oils applicable in automotive motors and other mechanical equipments, in form of latexes for impregnation of textile and paper and in form of solutions as adhesive agents and coating compositions.

**Examples of the acrylic monomers used during production of ACM**

- Ethyl acrylate
- Butyl acrylate
- Octyl acrylate
- Ethylethoxy ethyl acrylate
- Chloromethyl acrylate
- Allyl glycidyl ether
- N-methylol acrylamide

**Examples of functional co-monomers used during production of ACM**

- 2-Chloroethyl vinyl ether
- Chloromethyl acrylate
- Methacrylic acid
3.10 Fluorocarbon rubbers

The special properties of fluorocarbon rubbers (FKM) are determined by their chemical structure. Polymer chains of these rubbers are saturated and they are created by structural units of different fluorohydrocarbons of ethylene and propylene type. For their properties are important not only C - C bonds and small number of C - H bonds but firstly C - F bonds. These have higher bond energy (442 kJxmol⁻¹) and low chemical activity comparing to remainder bonds. That is why FKM have incomparable resistance to chemicals including oxygen and ozone and also to high temperatures. These rubbers are highly polar, very good resistant to oils, to motor fuels with hydroperoxides (sour gas) to aliphatic, aromatic and also to chlorinated hydrocarbons and concentrated acids, but they are not resistant to esters or ketones. The level of resistance is increasing with increasing of fluorine content in their macromolecules. The presence of chlorine in their macromolecules provides them excellent flame resistance.

FKM are produced during the radical copolymerization or terpolymerization of fluorinated hydrocarbons mainly vinylidene fluoride, hexafluoro propylene and tetrafluoro propylene. They are usually combined with small amounts of monomers with reactive groups (e.g. bromine, iodine, perfluorated aromatic rings, and nitrile groups) which are able take part in cross-linking. Polymers are performed at increased temperature and increased pressure because polymerized monomers are in gaseous state at reaction temperature. Water soluble peroxide catalysts are used for initiation (ammonium peroxodisulfate or potassium) and chlorinated hydrocarbons, alkyl mercaptans or alkyl esters are used as transfer agents. Final properties of FKM can be affected also with the monomer feed composition or by usage of other types of monomers. Copolymers containing perfluormethylvinyl ether have for example essentially lower glass transition temperature Tg and brittle temperature than conventional fluorine rubbers.

The oldest type of vulcanizing agents for FKM are diamines (at vulcanization temperature they are usually volatile therefore they are used in form of salts). FKM with higher fluorine content are normally cross-linked by peroxides. In the function of cross-linking agents are also used bisphenol A, bisphenol F or organotin compounds. During the cross-linking as a by-products HF can be produced; therefore its acceptors are added to rubber compounds. These are often alkali metal oxides such as MgO, CaO or lead oxides. Final properties of FKM vulcanizates depend on the structure and stability of its network, too. When the cross-links are predominantly created by hydrogen-containing bonds (in the case of some peroxide cross-linking), heat and oxygen resistance of FKM is poorer than in the presence of C-C bonds (in the case of bisphenols or organotin vulcanizing agents) in their network.

FKM are too expensive rubbers. They are used mainly as sealing components in car engines, aircraft engines and rockets. More developmental types of FKM are attached to rocketry. These are fluorotriazine, nitroso or fluoralkoxyphosphazene rubbers.
Examples of monomers used during FKM production

3.11 Epichlorhydrin rubbers

Epichlorhydrin rubbers (O) are special rubbers with saturated polymer backbone, in which the ether C–O–C bonds and in form of pendant groups also chloromethyl substituents are present. They are produced through ring-opening polymerization of epichlorhydrin (CO rubbers) and by its copolymerization with ethylene oxide (ECO rubbers), eventually by the terpolymerization epichlorhydrin, ethylene oxide and monomer with unsaturated bond (allyl glycidyl ether - ETER rubbers):

ETER rubbers have unsaturated residues in pendant groups and saturated backbones. Similar type of rubbers may be produced also by polymerization of polypropylene oxide or its copolymerization with allyl glycidyl ether (PO, GPO rubbers). Opening of epoxide ring in present monomers is primary act of polymerization process. Combination of trialkyl aluminum Al(R)₃ and water in molar rate 0.5:1 is the most often used initiator. Its equivalent modified by means of the acetyl acetone in form of chelate is used during copolymerization. Polymerization may be performed in aliphatic, aromatic or chlorinated hydrocarbons and also in ethers. It proceeds with high rate already at laboratory temperature.
Polyepichlorhydrin CO is a polar polymer with relatively high glass transition temperature \( T_g \) and small flexibility of polymer chains at low temperatures. It has the highest heat and swelling resistance, very good flame resistance and low permeability, also against fuels from among all O rubbers. Its copolymer with ethylene oxide ECO has better elastic properties, but at the same time it is less resistive against heat and burning. Terpolymers have double bonds only in pendant groups, thus it has similar ageing resistance as CO and ECO. Unsaturated bonds in pendant group are used for their cross-linking. Their properties are similar to ECO rubbers. All O rubbers are resistant against oxygen and ozone. Compounds of CO and ECO or ETER rubbers are often used in practice. Rubber material with optimum properties may be achieved by means of their combination (the most often in ratio 40:60). GPO rubbers have better elastic properties, but they have lower oil and fuel resistance.

Mostly reactive chloromethyl groups that are able to react with different curing agents are used for cross-linking of CO. The most often used for this reason is ethylene thiourea in combination with HCl acceptors (oxides of lead and magnesium, but also phosphites, phthalates, or lead silicates, alkali metal stearates), created during cross-linking as side product. ETER rubbers may be cross-linking also with peroxides under presence of the ethylene thiourea or sulfur. Characteristic field of the O rubbers usage are oil resistant products, resistant to ageing and higher temperatures. Those are mostly different sealing, hoses and membranes, used in the automotive industry and also materials used as coatings for paper, polygraphic or copying rollers use to be formulated on their basis.

### 3.12 Silicone rubbers

Polymer backbones of silicone rubbers (Q) don’t have hydrocarbon character. Oxygen and silicon atoms to which the hydrocarbon substituents, the most often methyl (MQ) or combination of methyl and vinyl (VMQ) or phenyl substituents (PMQ) are joined create them:
They are produced by multilevel hydrolysis and by subsequent condensation of dimethyldichlorosilane in acid medium or by ring opening polymerization of cyclotetrasiloxane, catalyzed by strong acids or bases.

Si – O – Si bond angles in rubbers Q are bigger than bond angles of C – C or C – H bonds therefore their polymer chains are elastic and flexible also at low temperatures. In consequence of spiral organization of polymer chains (polar backbone is covered by non-polar substituents) cohesive energy density between macromolecules of Q rubbers is very low. This is proved in low viscosity and its small temperature change, low tensile strength and high steam and gas permeability. High resistance to temperature is given mainly by presence of polar bonds Si-O in polymer backbone. Their bond energy is determined by the side groups type; phenyl groups being electron acceptor, weaken the siloxane bonds and it also contribute to chain flexibility (Tg of polysiloxanes with phenyl substituents is around –120°C), electron-donor methyl groups reinforce Si-O bonds.

Q rubbers with methyl and vinyl substituents are cured at higher temperature (usually low as 100 °C) by peroxide, the most often by dibenzoyl peroxide or its chlorinated derivate (2,4-dichlorobenzoyl peroxide). Polyhydroxy siloxanes are cured at ambient temperature, and it is performed in the presence of multifunctional alkoxy silanes or alkoxy silanes and organotin salt of higher fatty acids combinations.

Q rubbers and its vulcanizates are extremely resistant to high temperature, in the long time they resist to 200 °C. They intermittently suffer temperatures 300 – 400 °C. However in hot steam (120-140°C) they underlie to hydrolysis and they degrade. They are resistant to oxygen and ozone ageing and they are actually used for production of tubes transporting ozone. The Q are highly adhesive, hydrophobic and physiological compatible materials; therefore they are used not only as separation agents but also as implantation and other materials which are acceptable by human organisms.

3.13 Polyurethane rubbers

Polyurethane rubbers (U) are produced by polyaddition of diisocyanates and diols. Possible usage of different types of monomers and also combination of diisocyanate monomers and pre-polymer diols, their mutual ratio content and selection of reaction conditions allow creating polyurethanes with different chemical structure and various properties. Accordingly the polyurethane polymers may be conventional or thermoplastic rubbers, hard and tough thermoplasts, reactive solutions or foams, too. Common function group of polyurethanes are urethane structural units:

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{NH}
\end{array} \\
\text{O}
\]

Polyurethane elastomers are usually prepared in excess of diols. Those are polyurethane-polyester (AU) or polyurethane-polyether (EU) copolymers. The AU rubbers are the most often vulcanized by diisocyanates (toluene diisocyanate or its
combination with hydroquinone dioxyethyl ether) or peroxides in combination with co-catalysts (triallyl cyanurate); very small importance in polyurethane technology plays their sulfur curing.

\[
\begin{align*}
\text{CH}_3 & \quad \text{OCN} \\
\text{OCN} & \quad \text{OCN}
\end{align*}
\]

Toluene diisocyanate

\[
\text{OCN} - (\text{CH}_2)_6 - \text{NCO}
\]

Hexamethylene diisocyanate

\[
\begin{align*}
\text{HO} & - (\text{CH}_2)_2 - \left[ \text{OCO(CH}_2)_4\text{COO(} \text{CH}_2)_2 \right]_n \text{OH} \\
\text{HO} & - (\text{CH}_2)_4 - \text{OH}
\end{align*}
\]

Polyethylene adipate

\[
\begin{align*}
\text{HO} & \left[ \text{CH}_2 - \text{CH} \quad \text{O} \right]_{\text{n}} \text{CH}_2 - \text{CH} - \text{OH} \\
\text{HO} & \left[ (\text{CH}_2)_4 \text{O} \right]_{\text{n}} \text{H}
\end{align*}
\]

Poly(propylene)glycol

\[
\begin{align*}
\text{OCN} - \text{CH}_2 - \text{CH}_2 - \text{NCO}
\end{align*}
\]

Diphenylmethane 4,4' diisocyanate

\[
\text{OCN} - \text{NCO}
\]

Naphtalene 1,5-diisocyanate

Some monomers used by polyurethane rubber production

To characteristic properties of the AU and their vulcanizates belong mainly their high strengths, ageing resistance (they practically does not react with oxygen not even with ozone), heat resistance, excellent abrasion resistance and relatively good elastic properties at each their hardness, small permeability of gases and vapors and also relatively good swelling resistance in non-polar oils. Their disadvantage is in possible hydrolysis, mainly in medium of hot water, steam, acids and alkalis, and finally also under influence of lubricants, heat and long-term influence of tropical climatic conditions. Thus effective hydrolysis inhibitors are added into their compounds, e.g. polycarbon diimides. In urethane rubbers the associates may be created in consequence of physical attractive forces among their macromolecules (polar forces, hydrogen bridges), which affect as particles of the reinforcement.
fillers. From this reason AU rubbers are normally processed without fillers and hardness of their vulcanizates is regulated by content of curing agent. But usage of reinforcement and also non-reinforcement fillers is not excluded; the problem is usually with mixing temperature that must be adapted to their volatility during application of isocyanates as curing agents.

The polyurethane rubbers are used mainly for products in automotive industry and machine engineering, as different elements of dampers, flexible connections, and electric lines and also in such cases, when simultaneous high abrasion resistance of the product is required.

### 3.14 Polysulfide rubbers

Polysulfide rubbers (TM) are special rubbers. Their vulcanizates are characterized by extraordinary swelling resistance in ketones, aromatic and halogenated hydrocarbons. Besides this they are very well resistant to oxygen, ozone and UV radiation and they have low permeability of gases and vapors.

They are produced by polycondensation of aliphatic dihalides \( X – R – X \) and sodium polysulfide \( \text{Na}_2\text{S}_x \) \((x \geq 2)\) in water phase:

\[
n \ X – R – X + n \ \text{Na}_2\text{S}_x \rightarrow [– R \text{S}_x ]_n + 2n \ \text{NaCl},
\]

Created polymer is insoluble in reaction medium and under presence of suitable dispersion agents it precipitated. It has mostly -OH end groups (these are created by hydrolysis of halogen groups). The oldest type of polysulfide rubbers is Thiokol A produced by polycondensation of 1.2-dichloro-ethane and sodium polysulfide. Liquid polysulfide rubber with end -SH groups may be prepared from it by reduction splitting of the -S-S- bonds in its polymer chain under influence of NaHS, \( \text{Na}_2\text{SO}_3 \) or other suitable agents.

Presently, also other types of dihalides are used for production of polysulfide rubbers, mainly di-2-chlorethylformal and its combination with 1.2-dichlorethane (Thiokol FA, sulfur content 49%) and also with 1.2.3-chloro-propane (Thiokol ST, sulfur content 37%), when branched polymer is created. The sulfur content determines their elastic properties and partially also swell resistance.

Selection of curing agents depends on the type of end groups. TM with end –SH groups are cross-linking by means of oxidation agents, e.g. p-quinone dioxime, oxygen, cobalt salts, or peroxides; TM with –OH or halogen end groups by \( \text{ZnO} \). TM compounds are formulated and processed in similar way as compounds of other rubbers.

Usage of the TM is closely connected with their specific properties – they are used mostly for products swelling resistant in solvents and oils and at the same time resistant to ageing, mainly hose coatings for polygraph rollers and different sealing products.
3.15 Thermoplastic rubbers

Thermoplastic rubbers (TPE, eventually TPR) are polymer materials characterized by elastic properties of vulcanizates and processing properties of thermoplastic materials. These properties have connection not only with their chemical but also with morphological structure. They may be:

- block copolymers consisting of elastic and non-elastic blocks
- mixtures of elastomers and non-elastomers
- ionomere polymers.

All TPE consist of soft (elastomeric) and hard (non-elastomeric), thermodynamically non-compatible segments or macromolecules, that penetrate mutually only on level of interfacial layer. Elastomer normally creates a continuous phase – matrix – in them. Its chemical structure influences mostly elastic properties of given thermoplastic rubber. Non-elastomer in elastomeric matrix is dispersed in form of hard domains. It defines mainly its strength and processing characteristics. The content of soft and hard components in rubber determines their hardness and modules and other properties corresponding to them.

Non-elastomeric domains are created in amorphous systems by aggregation of the blocks or particles of non-elastomers in consequence of their insolubility in elastomeric matrix. In case when dispersed polymer crystallizes or creates associates (hydrogen bridges, polar forces), the domains create crystallites or associates. The shape of domains depends on composition of TPE, but it is determined also by their thermal and shearing pre-history. Frequently they are spherical, but they may have also cylindrical or lamellar character. Regardless of their generation reason they represent thermal labile formations and under their decomposition temperature they have in thermoplastic rubbers similar function as cross-links in vulcanizates. As consequence of their mutual interaction between phases they limit movement of rubber chains and avoid their flowing. In block copolymers this interaction is given by presence of chemical bonds between individual copolymer blocks, in polymer mixtures this take place in consequence of the intermolecular forces between mixed polymers in interfacial layer.

Thermoplastic rubbers keep their morphologic structure also under influence of deformation forces. They are solid and brittle below glass transition temperature of the elastomeric matrix and elastic above this temperature and below glass transition temperature of polymer that creates domains, eventually below crystallites melting temperature or decomposition of associates, respectively. Mutual movement of macromolecules and polymer system flowing occurs after decomposition of domains. But these processes have reversible character. Elastomeric part is sometimes slightly cross-linked in case of elastomer and non-elastomer compounds (dynamic vulcanization).

Block styrene-diene (butadiene, isoprene) copolymers belong to the oldest and the most important thermoplastic rubbers. Pure block copolymers (styrene block does not contain any diene structural units and vice-versa) are produced the most often by living anion polymerization. Depending on type of active polyanion and functionality of used termination agent, double and triple
block copolymers of type SB and SBS (S – styrene, B – diene), eventually radial copolymers of type (S – B)xC (where x = 3 or 4, C – copulation group) are created at the same time. The SEBS copolymer is produced by hydrogenation of triple block styrene-butadiene copolymer. Its elastomeric blocks consist of ethylene (it is created by means of hydrogenation of 1.4-butadiene units) and butylene (it is created by hydrogenation of 1.2-butadiene units) and it features with extraordinary resistance against degradation. Styrene-butadiene TPE may be produced also by copolymerization of butadiene and styrene, but blocks of both monomers contain also small amounts of the other monomer structural units.

Continuous phase is created in styrene-diene TPE by diene blocks and domains by styrene blocks. In light of their elastic and processing properties the most suitable copolymers are those with molecular weights of styrene blocks varying between 10 000 – 20 000 and butadiene blocks between 40 000 – 80 000 g/mol. With increasing of styrene content in copolymer their mechanic and processing properties are improving, but at the same time also elastic properties are getting worse. Copolymers containing styrene higher than ~ 75 % have thermoplastic properties. In the most cases of commercially produced styrene TPE, the styrene content ranges around 20 - 30 %. Domains of the polystyrene blocks are very small and thanks to narrow molecular weight distribution and presence of chemical bonds between blocks located in the interfacial layer those are equally distributed in the whole TPE volume, thus the anisotropy of their properties is small. At the same time the domains act as active filler particles, thus they have very good strength characteristics. Normally they are used in form of compounds where content of styrene TPE is only 25-50 %. Also other polymers create constituent part of polymer basis, e.g. polyolefins or polystyrene. Besides them also naphthenic or paraffinic oils are added as softeners and antidegradants, in case of butadiene or isoprene copolymers. Styrene TPE is used for different purposes, the most often as materials for sport and other footwear and also as electro-insulating and noise-insulating materials.

Polyester, polyurethane and also polyamide types of TPE are the most often multi-block copolymers of type (AB)n, where also soft (elastic) and hard (non-elastic) blocks alternate. In polyester types the amorphous polyethers or also polyesters based on alcohols with longer aliphatic chain are used as soft blocks. Hard polyester blocks are longer and able to create lamellar crystals acting as physical cross-links below their melting temperature. Continuous phase has amorphous character and also amorphous parts of hard block participate on it. Typical example of polyester TPE is poly(tetramethyleneglycol terephtalate – b – tetramethylene terephtalate):

\[
\left[ \text{C} - \text{C} - \text{O} - \left( \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} \right)_x \right]_{y} \times \left[ \text{C} - \text{C} - \text{O} - \left( \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} \right)_x \right]_y
\]

Glass transition temperature Tg of polyether blocks is normally varying around – 50°C. Melting temperature of hard segments is growing with increasing of their content in copolymer and the most often it ranges in between 170 – 250 oC. From this reason the polyester TPE have very good elastic properties and flexibility under low temperatures and at the same time also high softening point. They are characterized by high strengths and very good resistance against oils and other non-
polar agents. Their disadvantage is in possible hydrolysis of ester groups, thus if used in humid medium above 70°C, they must be stabilized (e.g. by means of carbon diimide). They are relatively expensive, so they are used only in cases when high strength is required in parallel with resistance to oils or high temperature in dry medium, e.g. in automotive industry.

Polyurethane TPE are similar to polyester TPE with its properties. They are extremely **strength**, have excellent abrasion resistance and at the same time they resists to oils. Those are linear multi-block copolymers of the (AB)n type. Hard segments in them are created by segments achieved by polyaddition of diisocyanate and diol with short chain. Soft segments are either polyurethane segments achieved by polyaddition of diisocyanate (4,4'-diphenylmethane diisocyanate) or diol with long linear chain (1,4-butanediol). Also polyesters or polyethers with end OH groups are often used in function of diols, and their molecular weights are usually varying in range 600 – 4000 g.mol⁻¹:

![Chemical structure of polyurethane TPE](image)

They are normally produced by polyaddition of diisocyanates and diols with short chains under presence of polyester or polyether. In polyurethane TPE in consequence of strong hydrogen bonds in polar polyurethane blocks the highly oriented pseudo-crystalline and crystalline fields are created, and these are separated from fields containing polyester or polyether blocks. Polyurethane segments with short diol chain then create domains and polyurethanes with long diol chain, eventually polyester or polyether segments create a matrix. **Morphological structure** of these TPE is practically the same as in polyester TPE and the same is also temperature interval, in which they keep double phase structure (~ from –50 to 170 – 230°C) and their utilization areas.

Polyethers or polyesters create soft segments also in polyamide TPE. Typical hard blocks are normallynylons (Nylon 6, 11 or 12). The most often they are produced by copulation reactions of polyester or polyether with end OH groups and polyamide with end COOH groups:

![Chemical structure of polyamide TPE](image)

They are produced in broad hardness interval (approximately from Shore A 60 to Shore D 75) and they keep double phase structure in approximate range from – 40 to 170 – 220 °C. Their small disadvantage is in possible sorption of the atmospheric humidity, thus they are dried just before processing. They have similar **strength**
characteristics as other TPE. They have also good dynamic properties, low hysteresis, high resiliency and good fatigue resistance.

From polymer mixtures of elastomeric and non-elastomeric character practically the most often used as thermoplastic rubbers are compounds based on polyolefins. Elastomeric phase in them is created by EPDM and non-elastomeric component use to be polypropylene (PP), polyethylene (PE) or their mixture. Sometimes also fillers, antidegradants and other additives normally added into rubber compounds are used. Good ratios of processing and elastic properties have systems where non-elastomeric component creates continuous phase and rubbery phase is dispersed in form of small (diameter of particles ≤ 10µm) partially vulcanized domains. Peroxides, resins or sulfur systems are used as curing agents. More factors affect resulting properties of the thermoplastic polyolefins, mainly size of elastomeric particles and degree of their cross-linking and also ratio of elastomeric and plastomeric component content.

Oil resistant thermoplastic materials may be prepared by mixing of the NBR and polyolefins. The main problem of these mixtures is significant incompatibility between their phases. This problem is solved either by usage of suitable compatibilisation agent, e.g. phenolic resins, or the part of both polymers is chemically modified in appropriate way (e.g. PP maleinization and NBR aminization) and joined function groups in mixing process in situ will mutually react and create chemical bonds between phases. Significant improvement of the compounds properties is achieved already at low content of modified polymers, usually lower than 10 %.

Also thermoplastic elastomers based on NR and polyolefins are known. These have, similarly to compounds with EPDM, optimal properties when prepared by dynamic vulcanization and NR particles are slightly cross-linked simultaneously. Continuous phase in mixtures at low content of NR is polyolefin and cross-linked NR particles create discontinuous phase. With increasing of NR content their morphological structure is changed, it moves to mutually penetrating continuous phases under the same content of both components. NR-polypropylene mixtures may be used approximately from –50 to 100°C.

Thermoplastic elastomeric materials characterized by low permeability of gases like oxygen, nitrogen, water steam and also noise, are prepared by combination of polyolefins and IIR. Continuous phase is created in them also by polyolefins and dispersed phase by cross-linked IIR particles. Their service temperature is from –50 to 120°C.

Main application field of the polyolefin thermoplastic elastomers is automotive industry. Many exterior and interior parts of cars are produced on their basis; they are used also as insulating and coating materials of electrical and telephone lines, mainly if environment and heat resistance is required.

The third group of the polymeric materials with elastic-plastic properties is ionomere elastomers. This term is normally used for marking of elastomers, that contain small amount (<15 %) of polar function groups in form of pendants on polymer backbone. In scientific literature you can very often find stated zincous salts of sulfonated and maleinized EPDM with high content of ethylene
(ZnSEPDM, ZnMEPDM) as examples of such polymers. Under normal temperature two types of thermo labile domains are present in morphological structure of EPDM modified in such way, one of them are ethylene crystalline domains (EPDM with high ethylene content contains long ethylene sequences that may crystallize) and the second are ion associates created by polar sulfo-zincous groups joined on EPDM polymer backbone. Both types of domains act as particles of active filler and contribute to increasing of the EPDM strength characteristics to the level of equivalent properties of its vulcanizates filled with reinforcement fillers. Elastomeric phase glass transition temperature of these systems is around –35 °C and top service temperature is varying around 50 °C, it is usually lower in filled compounds. Similar effect in NBR mixtures has presence of carboxylated NBR in combination with oxide or zinc stearate and one can assume its presence also in other rubber systems containing carboxylated rubbers and oxide or zinc stearate.

Schematic termoplastic elastomers phase structure
Simplified reaction scheme of anionic living butadiene and styrene polymerization

Styrene-butadiene block copolymer morphology
Properties of uncompounded styrene-diene TPE

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Styrene content, %</th>
<th>Hardness, Shore A</th>
<th>$M_{300}$, MPa</th>
<th>Tensile strength, MPa</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear SBS</td>
<td>31</td>
<td>71</td>
<td>2.76</td>
<td>31.7</td>
<td>880</td>
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<tr>
<td>Linear SBS</td>
<td>17</td>
<td>53</td>
<td>0.93</td>
<td>4.8</td>
<td>1100</td>
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<tr>
<td>Linear SIS</td>
<td>14</td>
<td>37</td>
<td>0.69</td>
<td>21.4</td>
<td>1300</td>
</tr>
<tr>
<td>Linear SIS</td>
<td>21</td>
<td>52</td>
<td>1.38</td>
<td>20.0</td>
<td>120</td>
</tr>
<tr>
<td>Branched (SB)$_n$</td>
<td>21</td>
<td>65</td>
<td>2.42</td>
<td>31.7</td>
<td>900</td>
</tr>
<tr>
<td>Branched (SB)$_n$</td>
<td>30</td>
<td>75</td>
<td>5.52</td>
<td>27.6</td>
<td>820</td>
</tr>
<tr>
<td>Branched (SI)$_n$</td>
<td>10</td>
<td>32</td>
<td>0.69</td>
<td>8.6</td>
<td>1300</td>
</tr>
</tbody>
</table>

SBS, SB – styrene-butadiene copolymer; SI, SIS styrene- isoprene copolymer

Properties of polyurethanes TPE (Desmopan™)

<table>
<thead>
<tr>
<th></th>
<th>Hardness, Shore D</th>
<th>Tensile strength, MPa</th>
<th>Elongation, %</th>
<th>$M_{100}$, MPa</th>
<th>Rebound resilience, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>32</td>
<td>40</td>
<td>55</td>
<td>59</td>
<td></td>
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<tr>
<td></td>
<td>40</td>
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</tr>
<tr>
<td></td>
<td>450</td>
<td>450</td>
<td>400</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>9.0</td>
<td>15.0</td>
<td>20.0</td>
<td></td>
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<tr>
<td></td>
<td>42</td>
<td>33</td>
<td>32</td>
<td>33</td>
<td></td>
</tr>
</tbody>
</table>

Morphological structure of semi-crystalline polyester TPE
### Properties of polyether aramides (Pebax™)

<table>
<thead>
<tr>
<th>Property</th>
<th>25</th>
<th>35</th>
<th>40</th>
<th>55</th>
<th>63</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness, Shore D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>29</td>
<td>34</td>
<td>36</td>
<td>44</td>
<td>51</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>715</td>
<td>710</td>
<td>485</td>
<td>455</td>
<td>380</td>
</tr>
<tr>
<td>Tensile modulus, MPa</td>
<td>10.4</td>
<td>14.6</td>
<td>50</td>
<td>145</td>
<td>260</td>
</tr>
<tr>
<td>Tear strength, kN.m⁻¹</td>
<td>38</td>
<td>45</td>
<td>70</td>
<td>115</td>
<td>150</td>
</tr>
</tbody>
</table>

### Some properties of ionic elastomer ZnSEPDM* at 25 °C

<table>
<thead>
<tr>
<th>Property</th>
<th>EPDM</th>
<th>ZnSEPDM</th>
<th>ZnSEPDM + 20 phr HAF carbon black</th>
<th>ZnSEPDM + 20 phr silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness, Shore A</td>
<td>56</td>
<td>69</td>
<td>75</td>
<td>77</td>
</tr>
<tr>
<td>M₁₀₀, MPa</td>
<td>2.7</td>
<td>7.1</td>
<td>12.9</td>
<td>11.8</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>11.0</td>
<td>21.0</td>
<td>22.5</td>
<td>21.7</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>1036</td>
<td>691</td>
<td>494</td>
<td>520</td>
</tr>
<tr>
<td>Tear strength, kN.m⁻¹</td>
<td>63</td>
<td>115</td>
<td>144</td>
<td>177</td>
</tr>
</tbody>
</table>

*Zinc salt of sulfonated EPDM with 75 % ethylene content
1. Introduction

Rubbers similarly to other chemical compounds may take part under suitable conditions in different types of chemical reactions. As they have polymeric character they can participate mainly on polymer-analogical reactions (1). Basic assumption of their participation in these processes is presence of suitable reactive function groups in their macromolecules. Unique and especially important polymer-analogical reaction of all rubbers is their vulcanization (cross-linking, curing). From chemical point of view is vulcanization complicated chemical process. During its the reactive fragments are created normally by interaction of used vulcanization systems components that are able to react with functional groups of vulcanized rubber in such way that they create assumptions for their cross-linking. Plastic rubber compounds achieve properties of final rubber product with elastic properties with it. Chemical transformation of some functional groups of rubbers occurs also during their mastication or ageing.

The polymer-analogical reactions of rubbers are used also for other purposes similar to other polymers. Here belongs mostly modification of inconvenient properties (e.g. ageing resistance, polarity, adhesion to other materials, bonding of antidegradants), implementation of new functional groups or production of rubbers with some new properties (CIIR, BIIR, carboxylated rubbers). If conversion of the original functional groups is low, the characteristic rubber properties are changing only in very little, but rubber obtains also a new special property. With increasing of its conversion (20 – 30, eventually also more %) the change of original rubber properties is increasing. For instance, if NBR is selectively hydrogenated, it will keep its swelling resistance in non-polar oils, but with increasing of the hydrogenation extent also its ageing resistance is improving and NBR hydrogenated up to 100 % conversion has practically the same ageing resistance as some FM rubbers.

Characteristic functional group in the most often used general rubbers is double bonds. Their typical representatives are unsaturated rubbers of polymer (e.g. NR, IR, BR, and CR) as well as copolymer (e.g. SBR, NBR) character based on diene monomers. Concentration of double bonds in these rubbers is high, because each diene structural unit contains one of such bonds. Past of them indeed terminates in cross-linking process of appropriate rubber, but also their vulcanizates have unsaturated character. Also some special rubbers have double bonds (e.g. EPDM, IIR). These rubbers generally contain them only in such amount, that will not influence their properties and they are implemented into the polymer chain only to simplify cross-linking. Practically all double bonds in these rubbers vanish during cross-linking and obtained vulcanizates have saturated character.
Reactivity of the polydiene double bonds depends in chemical reactions on their position in macromolecule of appropriate rubber and also on the type of substituents situated in their surroundings. Normal polydienes have basically two types of double bonds:

1. double bonds that are situated in their cis- and trans-1.4 structural units (in the polymer backbone). They are more reactive during polymer-analogical reactions with halogens, with oxygen, sulfur, and peracids;
2. double bonds situated in structural units 1.2 (in pendant vinyl groups) that are more reactive mainly during radical reactions.

Also substituents present in structural units of rubber backbone have an influence on reactivity of double bonds. Their reactivity in nucleophilic reactions is increased by nucleophilic and reduced by electrophilic substituents. Good example of this influence is significantly slower oxidation of CR rubber than NR or IR rubber, that differ only by type of substituent on the second carbon of each structural unit. The IR and NR has CH$_3$- group in this position and CR has Cl atom there. These rubbers behave similarly also during cross-linking reactions with sulfur and also in reactions with peracids (2). Reactivity of double bonds in trans-1.4 structural units is normally lower than in cis-1.4 units. Nucleophilic structural units similarly influence also reactivity of double bonds in 1.2 and 3.4 structural polydiene units. While double bond in 3.4 structural units is more reactive during epoxidation, oppositely double bond in 1.2 structural units is more reactive during hydrosilanization.

Existence of reactive hydrogens in $\alpha$ – position has close connection also with presence of double bond in polydiene macromolecules. Polyisoprene has even 3 hydrogens in each structural unit in $\alpha$-position against double bond on the first, fourth and fifth carbon. In general in substitution reactions the most reactive hydrogen is treated on carbon 4, and activity of other hydrogens follows this pattern $C_4 \geq C_1 > C_5$:

$$\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2=\text{C} & \quad \text{CH}_2=\text{C} \\
\text{CH}_2 & \quad \text{CH}_2 \\
1 & \quad 2 \quad 3 \quad 4 \\
\end{align*}$$

Reactivity of hydrogen on carbon 3 is very low ($C_3 \ll C_5$). Also hydrogens in structural units of poly-cis-butadiene-1.4 have similar reactivity. The $\alpha$-hydrogens of these polymers are more reactive than their double bond, mainly during radical reactions, e.g. during their oxidation or curing.

Reactive place in polydiene chains is also bond 4.1 connecting individual structural units. This bond is weakening because of high mesomeric energy, and from this reason it easily decomposes onto radicals. Its activity is shown mainly in degradation reactions, specifically during mechanical stress of appropriate rubbers.
The most often it takes places during their potential mastication and mainly during preparation and processing of rubber compounds.

Some unsaturated rubbers have also other functional groups that are able to participate on creation of cross-links. Those are mainly polymers containing chlorine atoms, like for instance CR rubbers. Mainly reactive chlorine in 1.2 structural chloroprene units is often used for their curing, and that is effectively reacting for example with metal oxides (MgO, ZnO, PbO and others). Similarly also –COOH groups in carboxylated diene rubbers may participate on cross-linking reactions (these create coordinating bonds with more compounds, e.g. metal oxides, epoxide compounds, polyols, polyamines) or halogen in chlorinated or brominated types of the IIR.

Saturated rubbers are normally less reactive against low-molecular reagents, but some of them contain besides functional groups suitable for cross-linking also such functional groups, which chemical transformation may be undesirable and it is normally connected with deterioration of their properties. Typical example is hydrolysis of ester groups in acrylic rubbers, in some types of polyurethanes, eventually also thermoplastic rubbers based on polyesters.

Besides chemical reactions of polymers also more types of side reactions may take place together with the main polymer-analogical reaction. Those are mostly reactions in which these polymers may participate regardless of the fact, which functional groups they contain. In case of polydienes it is mostly cyclization and cis-trans isomerization, eventually degradation or cross-linking.

The cis-trans isomerization (3) of diene rubbers occurs in presence of suitable catalysts (organic bromides and mercaptanes, NO₂, SO₂) or by influence of radiation (UV radiation, γ radiation) in polydiene solution or in its solid status. From practical view it is necessary to calculate with cis-trans isomerization also in sulfur curing conditions. During BR curing under presence of 4 phr of sulfur at temperature 140 - 160 °C the content of cis-1.4- structural units is reduced from original 97 to 92 %, what causes significant reduction of tensile strength of created vulcanizates. Cis-trans isomerization may be used also aimed at increasing of the trans- structural units content in polybutadiene with mixed structural units, which leads to increase of the crystalline phase content. In case of NR the cis-trans isomerization may be used also for reduction of the crystalline phase content. In this case its macromolecules segments moving ability is increased and it has good long-term elastic properties also under low temperatures, but its strengths are reduced proportionally.

Cyclization (4) as side reaction take places easier in IR than in BR. It occurs under influence of heat, light, ultraviolet or nuclear radiation or also in presence of cation-donor catalysts (mineral, organic, Lewis’s acids). Two neighboring polymer structural units participate in primary act of the 1.4-IR catalyzed cyclization; these will create monocyclic structure, whilst one double bond will vanish. Mostly bi- or tri-cyclic structures are created in later process stages. In general, isolated cyclic structures are created by cyclization of 3.4 structural units of IR along the polymer chain, in which also other polymer chains may be engaged. Gradually their unsaturation and elasticity is reduced as result of successive cyclization of IR and NR, and their toughness is increasing. At high cyclization degree these are changing.
onto thermoplastic powdery products having excellent adhesive properties, mainly to metallic materials. They do not crystallize not even under deformation and they are characterized by high strengths. Cyclized natural rubber was probably the first meaningful modification of natural rubber. The cyclization takes places either during its mixing with suitable initiator on rollers or in mixers and also in latex. Butadiene rubbers have lower tendency to cyclization than polyisoprene rubbers.

Degradation and cross-linking as side reactions of polymer-analogical reactions are exercised mainly during reactions performed at higher temperatures, during mechanical-chemical modifications or under influence of the high-energetic radiation.

1.1 polymer-analogical reactions

The polymer-analogical reactions are normally defined as chemical reactions between function groups of polymer and low-molecule reagents that lead to change of function groups and afterwards also to modification of original polymer properties. These belong to the oldest practically performed chemical reactions. Typical example is cellulose nitration or cross-linking of the natural rubber by means of sulfur, that were known and used already in middle of the 19th century, when no one even know about polymer character of these natural materials.

In ideal case no other changes of reaction system take places during polymer-analogical reactions, but in reality the polymer presence have often influence mainly on the reaction rate, on transformation extent of the polymer function groups and in some cases also on mechanism of major reaction. Changes may occur under influence of such factors, as changes in local concentration of reacting groups, conformation and configuration setting of the polymer macro-molecules in reaction environment, electrostatic impact of ionized molecules, aggregation and association of reagents, supra-molecular structure of the polymers or their eventual change during reaction.
1.2 peracids

Relative reactivity of some polydienes during their reactions with perbenzoic acid

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>Structural units</th>
<th>Relative reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polychloroprene</td>
<td>$\sim \text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 \sim$  (\text{Cl})</td>
<td>1</td>
</tr>
<tr>
<td>Polybutadiene 1,2</td>
<td>$\sim \text{CH}_2 - \text{CH} \sim$  (\text{CH} = \text{CH}_2)</td>
<td>25</td>
</tr>
<tr>
<td>Poly-cis-1.4-isoprene</td>
<td>$\sim \text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 \sim$  (\text{CH}_3)</td>
<td>5000 – 6000</td>
</tr>
<tr>
<td>Poly-2,3-dimethylisoprene</td>
<td>$\sim \text{CH}_2 - \text{C} = \text{C} - \text{CH}_2 \sim$  (\text{CH}_3)</td>
<td>above 10000</td>
</tr>
</tbody>
</table>

1.3 cis-trans isomerization

"On-off “mechanism of cis-trans isomerisation of diene elastomers"
1.4 Cyclization

Cationic cyclization of 1.4-IR. A – mono, B – bi, C – tri-ring structure

Cationic cyclization of 3.4 structural units - IR
2. Some polymer-analogical reaction of conventional unsaturated rubbers

2.1 Hydrogenation, halogenation, hydrohalogenation

Together with reactions of unsaturated polymers with halogens, hydrohalogens and hydrogen also addition and substitution reactions take place at the same time and also side reactions like isomerization, cyclization and cross-linking, eventually some other reactions, e.g. separation of the hydrohalogene. Thus the resulting products may have different composition and also different properties depending on reaction conditions.

Hydrogenation of polyisoprene and polybutadiene rubbers belongs to the polymer-analogical reactions studied in details, but it does not have big practical importance. Normally it is performed under high temperatures, and thus also considerable degradation of polydiene chain may occur during it. Catalysts which are able to react with double bonds of polydiene are also used during hydrogenation, which is the reason of their deactivation and they must be added in rather big amounts. Furthermore, if their rests remain in hydrogenated product, they accelerated its degradation.

The main hydrogenation product 1.4 BR is crystalline polyethylene, if BR has middle content of 1.2 structural units, thus elastic poly(ethylene-co-butylene) is created:

\[
\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \xrightarrow{\text{H}_2} \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2
\]

Isotactic 1.4-poly(2-methyl pentadiene) is created by hydrogenation of 1.4-IR, syndiotactic 1.2-polybutadiene is hydrogenated to poly(ethylene-alt-propylene), hemitactic polypropylene, eventually syndiotactic poly (1-butene). Hydrogenated copolymers of butadiene have bigger practical importance, mainly hydrogenated acrylonitrile-butadiene rubber (HNBR) (1) and also hydrogenated thermoplastic styrene-butadiene block-copolymers with middle content of the 1.2 butadiene structural units and also similar copolymers with isoprene. In both cases their ageing resistance is significantly improved, whilst they keep their special properties.

Hydrogenation of polydienes and their copolymers is the most often performed under participation of catalysts that are soluble or insoluble in reaction medium (Pt or Pd on suitable carrier) and they have different catalyst activity. It occurs also as non-catalyzed reaction under presence of hydroboranes or diimides. Polybutadienes are much faster hydrogenated in homogenous catalysis conditions than polyisoprenes; 1.2- units are the most reactive ones among butadiene structural units.
Some catalysts act selectively and under conditions of homogenous catalysis the hydrogenation of 1.2 polymers has randomly, and hydrogenation of 1.4 polymers has more block character. In general, hydrogenation of unsaturated polymers reduces their reactivity, increases their resistance against their degradation and cross-linking. It increases also their propensity to crystallization.

Chlorine is in practice the most often used for halogenations of polydienes. The chlorination occurs in optimum rate with most of unsaturated polymers and also ratio of destructive reactions is lower under presence of this halogen than in presence of more reactive fluorine. Chlorination of natural rubber can be performed in mass, solution or latex. Resultant product has thermoplastic properties; it can be obtained in form of fragile and non-elastic foil or in form of white powder. Chlorination is significantly increasing its polarity and adhesion to other materials. From this reason the solutions of such rubber are used for binding of rubbery and metallic, eventually rubbery and wooden materials. In combination with resins it creates also basis of coating materials for protection of metals against corrosion.

Halogenation belongs to important commercial processes also in case of synthetic rubbers; specifically it is used during production of halogenated IIR rubbers (CIIR, BIIR). By their halogenation these rubbers achieve mainly higher curing activity, better compatibility with other rubbers and at the same time they keep special properties of IIR, it means low permeability of gases and vapors, high ageing resistance and resistance against chemicals and good hysteresis properties. Chlorination of IIR runs almost selectively on allylic carbon of isoprene structural units:

\[
\begin{align*}
\text{CH}_3 & \quad \text{Cl}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 \\
\end{align*}
\]

Bromination of IIR runs less selectively.

By hydrohalogenation of unsaturated rubbers their polarity is increasing and their unsaturation is reduced. NR may react on one hand with arbitrary hydrogenhalogen, but only its hydrochloration has practical sense. In this case HCl addition occurs according to the reaction:

\[
\begin{align*}
\text{CH}_3 & \quad \text{HCl} & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{C} & \quad \text{CH}_2 \\
\end{align*}
\]

Hydrochlorination of NR may be performed in solution, in latex or also in solid status. Hydrochloride of NR is highly crystalline material, which is melting at temperature around 115 °C. It is not compatible with original rubber, it well resists to some chemicals, has excellent adhesion properties and it is compatible also with polar materials. It does not allow humidity to go through and in fifties of the previous century almost 3500 tons of foils were produced from it for food industry purposes, later it was replaced by plastic foils.
2.1.1 HNBR

Profile of some properties of NBR, HNBR and FKM
2.2 Epoxidation

The double bonds of diene rubbers are well known to react with peracids to yield epoxide groups:

\[
\begin{align*}
\text{CH} = \text{CH} & \quad \text{RCOOH} \\
\text{CH} & \quad \text{CH} \quad \text{O}
\end{align*}
\]

The epoxide groups bonded to rubber polymer chains influence not only rubber properties (they increase polarity, improve resistance to swelling in oils, modify adhesion properties to other materials, improve their resistance against penetration of gases and vapors), but they can be used also for other modification reactions. Disadvantage is that during epoxidation also reactions connected with opening of the epoxide ring may proceed at the same time, which makes resulting product to be non-homogeneous. During NR epoxidation the conversion of epoxide groups onto furan groups depends mainly on concentration of present peracid. Epoxidized NR is created at low concentrations, the level of furan groups in modified rubber is upgrading with its concentration increase and also with the epoxidation temperature increase.

With increasing of the level of furan groups in rubber also its Tg is increased and resiliency gets worse. Epoxidized NR with 50 % mole of epoxide groups under influence of deformation forces crystallizes, thus it has still very good strength characteristics. Totally furanized product does not have elastic properties, its Tg is varying around 100°C and its properties are similar to tough polystyrene. Epoxidized NR (ENR) with 25 (ENR-25) or 50 (ENR-50) % mole of epoxide groups is produced also industrially.

Considerable caution is given to natural rubber epoxidation also in connection with possible usage of siliceous fillers (mainly SiO₂) in tire and improvement of their driving properties (4) mainly adhesion on wet road and tire rolling-resistance.
2.2.1 Rubber properties

Oil resistance of ENR-25 and ENR-50 compared to NR, CR, and NBR after 70 hours in ASTM No. 1, 2, and 3 oils

Comparative air permeability of rubbers at 30 °

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Air permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
</tr>
<tr>
<td>ENR-25</td>
<td>32</td>
</tr>
<tr>
<td>ENR-50</td>
<td>8</td>
</tr>
<tr>
<td>SBR 500</td>
<td>48</td>
</tr>
<tr>
<td>IIR</td>
<td>6</td>
</tr>
<tr>
<td>NBR (34% acrylonitrile)</td>
<td>4</td>
</tr>
</tbody>
</table>
2.2.2 Modification reactions

Some transformation of epoxide groups on macromolecules of unsaturated rubbers

2.2.3 Furan groups

Epoxidation of NR and furan formation
2.2.4 Driving properties

![Graph showing wet grip rating versus rolling resistance for steel radial tires retreated with various ENR-25 blends.](image)

*Wet grip rating versus rolling resistance for steel radial tires retreated with various ENR-25 blends*

2.3 Ene-reactions

Reactive function group of unsaturated rubbers in cycloaddition reactions is their hydrogen in $\alpha$-position against double bond (ene). This hydrogen is able to react with double bond of the low-molecular reagent (enophile), during which time its bonding to rubbery chain and replacement of double bond will take place:

\[
\begin{array}{c}
\text{H} & \text{X} & \text{Y} \\
\text{CH}_2 & \text{X} & \text{Y} \\
\text{HX} & \text{Y} \\
\text{CH}_2 & \text{X} & \text{Y}
\end{array}
\]

\[X \rightleftharpoons Y \equiv O = N, -N=N-, \quad C = S, \quad C = O, \quad C = C\]

Ene-reactions often run by radical mechanism, mainly if the low-molecular enophile is less reactive and initiator of radical type is present in reaction system. They are used for implementation of polar substituents (maleic anhydride, fumaric acid, acrylonitrile) to non-polar rubbers. By this their polarity is increasing, solubility is changing, also oil and aging resistance and possibility of vulcanization by sulfur-free systems is enable. Typical example of such reactions is the reaction
of natural poly-cis-isoprene with maleic anhydride that may run either under its cold mechanical loading on mills or in presence of the radical character initiators \( (1) \).

Also different azo-compounds may be bonded to unsaturated rubber chain through reactive \( \alpha \)-hydrogens. If these are bonded to \( BR \ (2) \) with different structural units (cis and trans-1.4 and 1.2) in polymer chain than the position of bonded-on substituents will be different. Substituent will be bonded to 1.4 structural units on allylic carbon in polymer backbone, and to 1.2 structural units on the end carbon of the vinyl group. Reactivity of cis- and trans-1.4 units to azo-esters is approximately the same and higher than reactivity of the 1.2 units.

One of the possibilities how to avoid migration of antioxidants onto the surface of rubber products is their chemical bonding to rubber macromolecules, that should create a continuous phase in rubber compounds. That will not only avoid their migration, but also their efficiency will increase. During these reactions the bonding normally occurs in position of rubber double bond.

### 2.3.1 Initiators

The primary act in presence of initiators is decomposition of the initiator \( \text{I} \) onto radicals \( \text{R} \cdot \), that react with rubber \( \text{KaH} \) under of the rubber radical \( \text{Ka} \cdot \). The radical that is able to react with present maleic anhydride \( \text{MA} \) is created in positions of reactive \( \alpha \)-hydrogens, and thus the \( \text{MA} \) may be bonded along the present rubber macromolecule. The process may be repeated:

\[
\text{I} \rightarrow 2 \text{R} \cdot
\]

\[
\text{R} \cdot + \text{KaH} \rightarrow \text{RH} + \text{Ka} \cdot
\]

\[
\text{Ka} \cdot + \text{CH} = \text{CH} \rightarrow \text{Ka} \cdot \text{CH} = \text{CH}
\]

\[
\text{Ka} \cdot \text{CH} = \text{CH} + \text{KaH} \rightarrow \text{Ka} \cdot \text{CH} = \text{CH}_2 + \text{Ka} \cdot
\]

Bonding of \( \text{MA} \) runs in similar way also under mechanical loading conditions of rubber at low temperatures and absence of oxygen. In this case the rubber radical \( \text{Ka} \cdot \) accrues in consequence of the shear forces effecting on rubber between rollers of used double roller, under which the 4.1 bond is breaking. It is the radical at the end of polymer chain, and thus the present \( \text{MA} \) is bonding under such conditions to the ends of its macromolecules. But it is not possible to exclude also bonding of \( \text{MA} \) molecule into rubber backbone, as de-activation of „maleinized“ radical may take place either as result of its transfer to rubber or also as result of its termination with rubber radical.

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2.3.2 BR

Bonding of the azo-ester onto 1.4 structural unit of BR

\[ \text{Bonding of the azo-ester onto 1.2 structural unit of BR} \]

2.4 Grafting

Also grafting of the natural rubber by means of suitable monomer may be regarded as polymer-analogical reaction. It is basically its transformation to thermoplastic rubber, because bonded-on polymer chains have normally plastomeric character and they create a separate phase in NR matrix. This method is industrially used for production of special NR – **Hevea MG (1)** (Hevea MG30, Hevea MG49, with MMA content of 30, eventually 49 %), that represents the natural rubber grafted by methyl methacrylate. It contains polar and also non-polar chains in its macromolecule, thus it can be used also as compatibilizer of polymer blends based on polar and non-polar polymers. In rubber compounds it sometimes combined with non-modified NR and it appears in vulcanizates as active filler. It has also excellent adhesion properties and in solution form it is used at connecting of NR and PVC.

Grafting of natural rubber by other monomers is not in practice applicable

2.4.1 Hevea MG

Special type of natural rubber (Hevea MG) is produced by grafting of natural rubber with methyl methacrylate (MMA), and it is by polymerization of MMA under presence of its latex. Dibenzoyl peroxide or tert.butyl hydroperoxide is used as polymerization initiator. Graft copolymer is practically not created under presence of AIBN, because its radicals as result of their low reactivity are not efficient to perform neither transfer nor addition to present rubber macromolecules and so they
do not create on them the radical centers that could be able to participate on reactions leading to copolymer development. In simplified way this process may be described by means of following reactions:

1. DBP $\rightarrow$ 2 RO
2. RO$^+$ + MMA $\rightarrow$ RO - MMA$^*$ $\rightarrow$ PMMA$^*$
3. RO$^+$ + KaH $\rightarrow$ RO - KaH$^*$ (addition to double bond)
4. RO$^+$ + KaH $\rightarrow$ ROH + Ka$^+$ (transfer of initiator’s primary radical to rubber)
5. Ka$^+$ + MMA $\rightarrow$ Ka - MMA$^*$ $\rightarrow$ Ka - PMMA$^*$
6. RO - KaH$^+$ + MMA $\rightarrow$ RO - KaH - MMA$^*$ $\rightarrow$ RO - KaH - PMMA$^*$
7. Ka$^+$ + PMMA$^*$ $\rightarrow$ Ka - PMMA
8. RO - KaH$^+$ + PMMA$^*$ $\rightarrow$ RO - KaH – PMMA
9. PMMA$^*$ + PMMA$^*$ $\rightarrow$ PMMA

Because of the fact that reactive centers on rubber macromolecules were created by means of transfer (reaction 3) or addition to their double bonds (reaction 4), they occur along their whole length and so grafted copolymer is created during polymerization (termination reactions 7 and 8). Their backbone is created by rubber macromolecules and grafted-on blocks are polymethyl methacrylate. Besides grafted copolymer also homopolymer PMMA is created during polymerization and that is in consequence of the present MMA initiation by radical of initiator (reactions 3 and 9). Also block copolymer is created during polymerization under usage of the plasticized rubber, that contains also at the ends of its macromolecules the hydroperoxide groups (Ka-OOH), that are able to dissociate under development of polymer rubber radicals and low-molecule radicals $^\bullet$OH (Ka-OOH $\rightarrow$ KaO$^+$ + HO$^+$).

Modified natural rubber MMA may be prepared also by mechanical-chemical synthesis. Polymerization process is initiated in this case by rubber radicals that are created in consequence of its mechanical loading in presence of MMA. They are sufficiently reactive to initiate MMA polymerization. It was discovered by selective fractionation that achieved product contains two different block copolymers: free rubber and small amount of free PMMA.

It is supposed that the free rubber remains in the product due to incomplete degradation of rubber molecules being present, while the free polymethylmetacrylate is a result of the shear degradation of the originating block copolymer. The creation of block copolymer I is connected with the preferred tearing of long rubber molecules and with the polymerization of methylmetacrylate practically not influenced by the jelly effect. Block copolymer II originates as late as when the termination rate decreases due to the jelly effect, thus extending the growing polymeric radicals. Consequently, this leads to the increase of the mole weight of PMMA blocks and also to the considerable increase of the rate of polymerization.
3. Vulcanization of rubbers

3.1 Introduction

Vulcanization (curing, cross-linking) is one of the most important processes for most of rubber technologies. During vulcanization the rubber compound is changing to elastic final product – vulcanizate (rubber). This is done by consecutive and parallel changes of chemical and physical nature. Vulcanization essence is the creation of cross-links between rubber macromolecules at which three dimensional network \((1)\) of rubber matrix is formed. The part of vulcanizate network are also physical bonds like hydrogen bond, polar or dispersed powers between individual macromolecules or their snarls, which were created at preparation or processing of relevant rubber compound. The rest of ingredients participating in rubber compound are in original or changed form chemically connected, dispersed or soluble.

For the formation of chemical cross-links between rubber macromolecules are most often used different chemical – vulcanization agents (sulfur, peroxides, metal oxides, resins, quinones and others), which are in vulcanization process able to react with suitable functional rubber groups and to create cross-links between them. Curing can be caused also by the different types radiation influence, which energy is satisfactory for generation of rubber macromolecules reactive forms most often radicals. With each other these interactive while there are cross-links formed. Also microwave energy or ultrasound can cause curing creation. Vulcanization is required from most of rubbers but it is not necessary for some types of thermoplastic rubbers.

Vulcanization is in the presence of vulcanization agents formally divided into three stages. In the first one – induction period – gets to reciprocal elements interaction of used vulcanization system and the cross-links are even not created or only a little. Its length depends on the type of vulcanization system and vulcanization temperature. In the case of sulfur vulcanization it is affected by present accelerators, eventually vulcanization retarders or pre-cure inhibitors. In the main second vulcanization stage gets to the important vulcanization part which is fast curing of rubber macromolecules and the formation of ones' own vulcanizate. That is why the vulcanization rate can be considered as the rate of this stage. After the vulcanization optimum in the third stage can be applied restructuring of created cross-links and modification of rubbers chains. This stage can be also connected with number of cross-links decreasing (reverse), which can be shown at the property change of final vulcanizate. Vulcanization course and its basic characteristics (scorch time, optimal vulcanization time, difference between maximum and minimum torsion moment, cure rate index, and eventually reverse rate) is most often evaluated on the basis of so called vulcanization curves \((2)\) measured on different types of rheometers.

The number of created cross-links between rubber macromolecules (characterized by crosslink density)\((3)\) and their chemical structure depend mainly on the content and activity of vulcanization agent, temperature and vulcanization time. A temperature influence at which the vulcanization is performed is shown mainly at its cure rate and it may be considered in the same matter like chemical reactions on the basis of Arhenius equation. With the vulcanization time the cross-links content
is at first non-linear increased and after the vulcanizing optimum achievement can be decreases (reverse). At the same time the vulcanizing compound properties are changing but their dependence on the vulcanization time is different. Some of vulcanizates properties reach optimum values even before vulcanization optimum achievement.

Modulus and the tensile strength at breaking are at low elongation proportional to their crosslink density $\nu$, eventually reciprocal value of average molecular weight of rubber macromolecules segments between two cross-links $M_c$. Their relative connection is described by the relation:

$$\sigma = \frac{\rho}{M_c} R T A^* (\lambda - \lambda^{-2})$$

($\sigma$ is stress, $\lambda$ is relative extension, $R$ is gas constant, $T$ is absolute temperature, $A^*$ is the cross sectional area of the test specimen in non-deformable status).

At higher crosslink density tensile strength does not proportionally increase with the crosslink density increasing but after achievement of optimal value decreases. Concrete values of strength characteristics of vulcanizate depend on the other factors mainly on rubber structure and crosslink structure. Most of synthetic rubber vulcanizates have lower strength than NR vulcanizates, because they can not crystallize in their macromolecules by different types of structural units (cis, trans, 1.4, 1.2,) or more co-monomer units (e.g. butadiene, styrene, acrylonitrile and others). Also the vulcanizates with polysulfide cross-links have higher tensile strength than vulcanizates with monosulfide, eventually carbon-carbon cross-links. Elongation at break is with the increasing of crosslink density lowered at first and then is asymptotically approached to minimum value. Vulcanizates hardness is by the vulcanization time increased like their crosslink density. The highest structural strength has soft under-vulcanized vulcanizate. After vulcanization optimum achievement this characteristic together with the time decreased. Elasticity change is similar to change of modulus. It is proportional to crosslink density and to relative elongation in all three coordinates. After vulcanization optimum achievement or at high content of cross-links between rubbers macromolecules can be with the vulcanization time decreased.

3.1.1 Network

![General scheme of vulcanizate network](image)
3.1.2 Vulcanization curves

![Rheometer curve for vulcanization](image)

3.1.3 Crosslink density

For characterization of network, the most often used is network density and average molecular weight of rubber segments situated between two cross-links. Both these characteristics may be determined in the same way, because dependence:

\[ \nu = \frac{\rho}{M_c} \]

is valid. (\(\nu\) is crosslink density, \(\rho\) is rubber density, \(M_c\) is molecular weight of rubber segments between two cross-links).

Sometimes the network of vulcanizates is characterized also with number of cross-links created in the vulcanizate volume unit. It can be calculated also from network density under assumption that cross-links are created between two rubber segments:

\[ n = \frac{\nu}{2} \]

(n is number of cross-links in the vulcanizate volume unit, \(\nu\) is its cross-link density)

Several types of methods are used for determination of these characteristics of the vulcanizate network. Chemical methods may be used only in that case, when exact curing mechanism of using cross-linking system is known and either change of the curing agent or definable products of the low molecule character may be sufficiently determined in quantitative way. Number of the cross-links \(n\) can be calculated in this case on the basis of material balance of appropriate chemical equation related to curing.
Physical methods are based on evaluation of deformation properties of appropriate vulcanizates. In case, that these evaluations are performed under low deformations (<100 %), thus $M_c$ may be calculated from experimentally determined modulus $E$ (for tensile strain):

$$E = \frac{3 \rho R T}{2 M_c}$$

or $G$ (for shearing strain):

$$E = 3G$$

($E$ is Young’s modulus; $G$ is shearing modulus; $\rho$ is rubber density, $R$ is gas constant; $T$ is absolute temperature; $M_c$ is molecular weight of rubber segments between two cross-links).

Mooney-Rivlin equation:

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + C_2 \lambda^{-1}$$

($\sigma$ is stress, $\lambda$ is relative elongation and $C_1$, $C_2$ are constants)

is used much more often for determination of $\nu$, eventually $M_c$ because this allows performing measurements also under higher deformations. Values $\nu$, eventually $M_c$ may be in this case determined by means of constant $C_1$ ($C_1 = \frac{1}{2} \nu R T = \frac{\rho R T}{2 M_c}$) that is determined graphically from linearized form of Mooney-Rivlin equation.

Crosslink density of unfilled vulcanizates $\nu$, eventually molecular weight of rubber segments between two cross-inks $M_c$ may be determined also from kinetics of vulcanizates swelling in suitable solvent. For the $\nu$ calculation Flory-Rehner equation is used:

$$\nu = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s \left(V_r^{1/3} - 0.5 V_r\right)}$$

($\nu$ is crosslink density, $V_r$ is volume fraction of rubber in equilibrium swolled vulcanizate sample, $V_s$ is mole volume of used solvent, $\chi$ is Huggins’ parameter)

Presently also other latter methods are used for characterizing the network of vulcanizates, e.g. sol–gel analysis, differential scanning calorimetry, ultrasonic, small angular neutrons scattering (SANS) in swelled cross-linked gels and also methods based on the $^1$H NMR and $^{13}$C NMR spectroscopy of swollen and non-swollen vulcanizates.
3.1.4 Vulcanizates properties

Change of some properties of rubbers compounds during vulcanization.
1 – tensile strength, 2 – elongation at break, 3 – hardness, 4 - elasticity

3.2 Sulfur vulcanization

Sulfur(1) is the oldest vulcanization agent for unsaturated rubbers used in rubber practice. Its effective and fast link in form of cross-links to rubber macromolecules occurs only in the presence of accelerators (2) and activators(3). If these are missing sulfur reacts with rubbers very slowly and it bonds to rubbers in a form of side cyclic structures not in a form of sulfur cross-links. These ingredients both affect also the kinetic parameters of vulcanization – temperature and time – and they effects scorch time of vulcanized compounds and sulfur content necessary for creation of optimal network of vulcanizates. Type and the content of present accelerators and also the accelerator: sulfur ratio in rubber compounds affect final properties of vulcanizates mainly their thermo-oxidative stability and some of their tensile and dynamic properties. The term “sulfur curing” is often used for sulfur vulcanization.

From the chemical point of view is sulfur curing of unsaturated elastomers complicated. A lot of parallel and consequential chemical reactions take place in it. These reactions can have substitute, addition or also elimination character. The part on these reactions can take not only original elements of rubber compounds but also the products of their chemical transformation. In addition unsaturated polymers normally contain several types of reactive functional groups (reactive hydrogen, double bonds), which can react with components of sulfur curing system at different rate and also by different mechanism and during the creation of different intermediate products or final products take part. In this process take important part also additional reaction such as isomerization and cyclization of single elastomers and also the creation of diene and triene structures in their macromolecules. Course of individual reactions can affect also the specific composition of vulcanization.
systems mainly the type and content of accelerator or activator, the presence of retarder or pre-cure inhibitor\(^{(4)}\) and the rest ingredients normally presence in rubber compounds. The study of detailed curing mechanism is obstructed also by the fact that the final cross-linking product – vulcanizate – is complicated system and at his analysis can not be used analytical methods which require the work in solution or in homogeneous environs.

On the present opinion sulfur vulcanization\(^{(4)}\) of unsaturated rubbers in three stages is preceded. In the first stage the transitional complex is created by element interaction of vulcanization system. This complex together with rubber creates active curing agent. In the second stage the primary network of vulcanizate is created with mainly polysulfide cross-links. During the third stage it is restructured by modification of cross-links (sulfidity decrease) and rubber macromolecules (isomerization, dehydrogenation, and cyclization). The final network of vulcanizate is created. From the point of chemism the first stage prefers the concept about ion character of reactions leading to the creation of reactive curing agent. During the next curing stages also the reaction with radical character are allowed. These reactions lead to the formation of reactive cross-linking fragments and also to the single creation of cross-links between macromolecules of present rubber eventually to their changes in the third stage of vulcanization. Formation of complexes\(^{(5)}\) created between accelerator, sulfur and activator and also the creation of cross-links between rubber macromolecules is in literature described in several ways.

Some of tetraalkylthiuram sulfides and sulfenamides are able to cured unsaturated rubbers also without sulfur. These are mainly thiuram sulfides with higher number of sulfur atoms in sulfur bridge (tetramethylthiuram disulfide, dipentamethylenethiuram tetra-, eventually hexa- sulfide) and morpholine (or other amine) derivatives 2-mercaptobenzothiazole or dithiodimorpholine. These substances are generally called sulfur donors\(^{(6)}\) and in the vulcanization process they generate active sulfur fragments. They are able to react with present rubber macromolecules and induce its curing. On the present there is not united opinion that like in a case of vulcanization with the presence of sulfur regarding mechanism of their effect in the curing process. On one hand there is the expectation that in the consequence of spontaneous and induced decomposition of thiuram sulfides (except monosulfides) generate sulfur radicals with one or more sulfur atoms, which are able to start rubber macromolecules curing. Other authors state that in the inception stages the vulcanization is ionic process. This process is significantly influenced by vulcanization activator ZnO. It inducts heterolysis of C-S bond in thiuram disulfides\(^{(7)}\) and consequently heterolysis of other bonds can be take place. It is proposed that curing of rubber macromolecules in second stage of vulcanization proceeded by radical mechanism. Higher thiuram sulfides with higher number of atoms in sulfur bridge (dipentamethylenetetra- and hexa- sulfide) are decomposed at vulcanization and they generate active sulfur that is taking part in curing. The creation of sulfur fragments is assumed also in the presence of morpholine of others sulfur donors, which have multi sulfur bridges in its molecules.

Real sulfur vulcanizate\(^{(8)}\) is complicated system. Its basis is network created by rubber macromolecules which are together connected with chemical cross-links mainly sulfur-sulfur (eventually carbon-carbon) character. The part of network can be also different types of physical bonds. These are not only bonds created between individual macromolecules or segments of sulfur macromolecules following their
chemical structure (e.g. hydrogen bridges; polar forces) but also their intra-
molecular and inter-molecular snarls. In consequence of complicated curing course,
possibilities of cross-links restructuralization in the third vulcanization stage,
creation of cross and others bonds by reactions of rubber macromolecules with
other elements of rubber compound mainly with accelerators and fillers, as well as
in consequence of possibility of incomplete homogenous ingredients mixing to the
whole volume of rubber matrix the three dimensional network of sulfur vulcanizate
is not ideal. Except of final, elastic ineffective chains there are also the places with
different crosslink density. In the network there are also present the others
ingredients attending in vulcanized rubber compounds in chemical transformed as
well as in original form.

**Structure of rubber cross-links** in sulfur vulcanizates influences several useful
properties of final gummy products. It is affected by several technological
parameters of vulcanization process, but it depends mainly on the accelerator type
and its content in cured rubber compounds. In the presence of slow accelerators are
created mainly polysulfide cross-links (number of sulfur atoms in cross-links is
most often 3 - 6) between rubber macromolecules while in the presence of very fast
accelerators the content of these cross-links is lower.

One of the important factors, which affect cross-link structure, is the ratio of
accelerator and sulfur content in used curing system. In the presence of
*conventional sulfur system* (9) in rubber compounds (ratio of S: accelerator > 1) are
created in the real time of vulcanization mainly polysulfide cross-links and
vulcanizates generally have good physical-mechanical and dynamical properties
and good fatigue resistance. They are not very good resistant to thermal degradation
mainly because of low bonding energy of rubber cross-links with higher number of
sulfur atoms (C-S<sub>n</sub>-C < 250 kJmol<sup>-1</sup>).

If the used sulfur system contains less sulfur and the accelerator content is high (*EV
systems* (10)), eventually sulfur is totally replaced by sulfur donor the number of
sulfur atoms in cross-links is essentially lower. The content of polysulfide cross-
links is practically negligible in comparison with monosulfide and disulfide cross-
links. It is not possible to exclude the creation of carbon-carbon cross-links in these
cases. That is why these vulcanizates are resistant to temperature. Simultaneously
they have lower initial strength characteristics and some of dynamic properties in
comparison with vulcanizates with mostly polysulfide bonds. Their advantage is
slower ageing which can bring them longer useful life. In the presence of semi EV
vulcanization systems (S: accelerator ≈ 1 – 2) are created vulcanizates with all types
of cross-links and also their properties are situated between the conventional and
EV vulcanizates properties.

### 3.2.1 Sulfur

Sulfur is a natural material. The most commonly used is its α modification,
which is stability at normal temperature. It creates clear yellow crystals of
orthorhombic system in form of octahedrons. By warming it changed to monoclinic
β modification. This melts at temperature app.115°C and creates bright yellow
liquid of \( \lambda \) modification. The insoluble plastic sulfur with polymeric nature is formed at fast fall of temperature. It melts at 80 – 90°C temperatures and the melt interval depends on its polymerization degree, molecular weight distribution, and degree of crystalline and also on the content of present impurities. For vulcanization is the most often used oil-extended sulfur. Its purity is usually lest 95%. The sulfur solubility in rubbers is relatively low (in NR at laboratory temperature it is app. 1.5% and at 100°C it is 7%). If it is insoluble in rubber, it tends to bloom to the surface of final products. The problems with blooming are often avoided by using of plastic sulfur. Plastic sulfur is insoluble in rubber and it does not bloom out (it has polymeric nature). It melts and has tendency to palletize at processing temperatures. Rubber compounds with plastic sulfur are compounded at lower temperatures; generally the suggested temperatures are those under 110°C. It is frequently used as rubber dispersions or as a paste.

Elementary sulfur has cyclic eight atoms molecules at normal temperature. Average energy of the S-S bond in these molecules is ca 252 kJ.mol\(^{-1}\). In the presence of accelerators and activators it generates sulfur fragments. These under the conditions of unsaturated rubbers vulcanization that react with reactive groups of rubbers and create cross-links such as:

\[
S_8 \xrightarrow{\cdot S_x^*} \cdot S_x^* + \cdot CH=CH=CH_2 \xrightarrow{\cdot CH=CH=CH_2} \cdot S_x^* + \cdot CH=CH=CH_2
\]

\[
\cdot CH=CH=CH_2 \xrightarrow{S_x^*} \cdot S_x^* + \cdot CH=CH=CH_2
\]

\[
\cdot S_x^* \xrightarrow{\cdot CH=CH=CH_2} \cdot S_x^* + \cdot CH=CH=CH_2
\]

\[
\cdot S_x^* \xrightarrow{\cdot CH=CH=CH_2} \cdot S_x^* + \cdot CH=CH=CH_2
\]

Sulfur is suitable not only for vulcanization of highly unsaturated diene rubber but also for rubbers with lower content of double bonds e.g. EPDM rubbers. Its quantization to compounds depends on the curing degree we want to achieve (for soft products it is app. 0.5 – 4 phr, for ebonite it is 35 – 50 phr). It also depends on the type of vulcanized rubber (for soft rubber from NR it is generally 2.2 – 2.5 phr, from SBR it is 1.5 – 2.2 phr).
3.2.2 accelerators

Accelerators are necessary ingredients of all sulfur curing systems. They increase curing ratio and efficiency of the sulfur bonding to rubber macromolecules in form of cross-links. From technological point of view their presence in rubber compounds is very important. They significantly reduce time needed for vulcanization; they allow reducing the vulcanization temperature and sulfur content in rubber compounds. They favorably affect also properties of vulcanizates, mainly their ageing resistance. Simultaneously they reduce possibility of pre-vulcanization and reversion and also probability of sulfur blooming on surface of rubber products.

The first used accelerators were at the end of 19th century inorganic compounds (the most often oxides and hydroxides) of lead, zinc, calcium and magnesium. Much greater importance for expansion of sulfur curing had organic compounds of nitrogen, mostly aniline and its derivates (1906, Oenslanger) and later also piperidine, dimethylamine, trimethylamine and their different alkaline derivates. Also accelerating effect of xanthates and dithiocarbamates was known in this period, but their usage was limited by small scorch time of vulcanized compounds. Important progress in possibility to influence process of sulfur curing meant appearance of accelerating effect of thiazoles compounds (around 1920) and their amine derivates – sulfenamides. Triazine and phosphoric accelerators (1960-1970) may be included among latter types of accelerators.

Presently exclusively organic compounds (2.1) are used in function of accelerators. Most of them contain sulfur and nitrogen atoms in their molecules. According to their chemical composition they are divided into:

- aldehydamines
- guanidines
- thiazoles
- sulfenamides
- thiurams
- dithiocarbamates
- xanthates
- other accelerators.

In technical practice the accelerators are often evaluated according to their activity in vulcanization process. According to this criterion they can be divided to:

- slow (guanidines, some aldehydamines)
- fast (thiazoles)
- very fast (thiurams)
- ultra fast accelerators (dithiocarbamates, xanthates).

Activity of accelerators in vulcanization process depends also on type of vulcanized rubber, concrete rubber compound composition and vulcanization conditions. Exactly the same accelerator can have different effect in different rubber compounds. Thiazoles are for instance fast accelerators for the most rubbers, but in compounds of chloroprene rubber they act as weak retarders; similarly also hexamethylenetetramine is very fast accelerator for chloroprene rubber compounds, but in compounds of other rubbers it seems like slow accelerator or even as non-coloring antioxidant.
Dosage of the accelerators into compounds is different. It depends not only on the vulcanized rubber type, concrete composition of rubber compounds and vulcanization conditions, but also on required functional properties of the rubber product. Usually it is valid, that as the accelerator is more effective, thus its smaller amount is added into compound, and thus smaller amount of sulfur is needed for achieving the optimal vulcanizate properties.

Aldehydeamines are condensation products of aldehydes and amines, the most often aniline, ammoniac or their derivates and also butyraldehyde, crotonylaldehyde or formaldehyde. Their accelerating effect depends mainly on aldehyde type and mole ratio of aldehyde and amine in reaction mixture used for their preparation. Whilst butyraldehydeaniline is very fast accelerator and high network density of vulcanizates is achieved by its presence in rubber compound, trcrotonylidenetetramine acts very slowly and hexamethylenetetramine is slower than guanidines. Aldehydeamines belong to less used accelerators, more often they are used as secondary accelerators in combination with thiazoles and sulfenamides. 

Guanidines are slow accelerators with short induction period and broad vulcanization plateau. In practice the most often used is diphenylguanidine and di-o-tolylguanidine, eventually o-tolyl-biguousanidine. They have alkaline character. They are suitable also into compounds containing additives of strongly acidic character and into compounds filled with SiO₂. Vulcanizates prepared under their presence have relatively high crosslink density and good physical-mechanical properties; they are less resistant to thermo-oxidative ageing, because polysulfide cross-links dominate in their network. Guanidines are used as primary accelerators in particular during production of hard rubber. But they are usually combined with fast (thiazoles) and very fast accelerators (thiurams), eventually also ultra accelerators (dithiocarbamates).

Thiazoles belong to fast accelerators frequently used in practice. They are suitable for vulcanization of high (NR, BR, SBR) and low (IIR, EPDM) unsaturated rubbers. Their main representatives are 2-mercaptobenzothiazole and bis-(2-benzothiazol) disulphide, eventually zinc salt of 2-mercaptobenzothiazole. From view of vulcanization rate 2-mercaptobenzothiazole is more effective and rubber compounds with bis-(2-benzothiazol) disulphide have higher scorch time. They have broad vulcanization plateau but relatively low crosslink density. From this reason the vulcanizates that are vulcanized under presence of solitary thiazoles does not have optimal strength and elastic properties. Also from this reason they are very often combined with other accelerators. In combination with guanidines they create synergistic systems and these lead not only to increased vulcanization rate, but also to improved crosslink density of vulcanizates and thus also to improved their final properties. Combinations with thiurams and dithiocarbamates are used mostly during curing of rubbers with low unsaturation. Generally, during application of thiazoles with fast and ultra fast accelerators combinations, the ageing resistance of vulcanizates is improving. Sometimes also 2-mercaptobenzothiazole amine derivates are integrated into thiazoles group, but these are more often marked as sulfenamides. This group of accelerators is characterized by very good scorch time and fast curing in the main vulcanization phase (thus they belong to fast accelerators). Their activity in vulcanization process depends mainly on type of amine used during production of
appropriate sulfenamide. Normally, increasing of amine alkalinity shorten vulcanization induction period and increase curing rate. Among the most frequently used sulfenamides belong presently N-cylohexyl-2-benzothiazolsulfenamide, tertbutyl-2-benzothiazolsulfenamide (TBBS) and dicyclohexyl-2-benzothiazolsulfenamide (DCBS), whilst for scorch time of compounds CBS < TBBS < DCBS is valid and for curing rate in the main vulcanization phase DCBS < TBBS < CBS. Sulfenamide accelerators are suitable also for EV and semi-EV systems. In combination with thiurams and dithiocarbamates they create very effective accelerating systems giving good scorch time, fast curing and reduced reversion. The vulcanizates have good ageing resistance. Presently also some other types of sulfenamides are known, it means bis-sulfenamides, sulfenamide derivatives of pyrimidine and dialkyldithiocarbamylsulfenamides. Under their presence the rubber compounds have not only very good scorch time, but also high curing rate and high crosslink density. Some sulfenamides (e.g. N-morfolyl-2-benzothiazolsulfenamide) are source of N-nitrosamines that are dangerous to health.

Thiurams are very fast accelerators suitable also for vulcanization of low unsaturated rubbers and into semi-EV and EV vulcanization systems. Mutually they differ by character of the substituents in amine groups (e.g. methyl-, ethyl-, pentamethylene-) and number of sulfur atoms in sulfur bridges (1, 2, 4, 6). With increasing number of sulfur atoms their stability decreases and they are easily decomposed with sulfur creation. Their main representatives are tetramethylthiuram disulfide and tetraethylthiuram disulfide. They are used very often in combination with other accelerators, mostly with sulfenamides and thiazoles. They are used also as sulfur donors. Their disadvantage is generation of secondary amines in vulcanization process; these are potential source of dangerous to health N-nitrosamines. These unwanted effects are not obtained by thiurams with hindered substituents in amine groups (e.g. benzyl-, piperidyl-). They are used also as sulfur donors.

Dithiocarbamates are metallic (the most often salts of Zn and Na, but also Se, Te, Pb, Cd, Bi) or ammonium salts of dithiocarbamoic acids. Except the cation type they can differ also by type of alkyl substituents (methyl-, ethyl-, butyl-, pentamethylene-) in dithiocarbamate group. Dithiocarbamates are polar compounds with low solubility in non-polar rubbers, thus they bloom at higher concentrations. Their solubility in rubbers is usually increased with increasing of carbons number in alkyl substituents. They belong to ultra fast accelerators; some of them operate already under laboratory temperature. Vulcanization runs very fast under their presence; practically without induction period, thus they are much more often used in combination with slower accelerators. Some of them are soluble in water. They are used not only during vulcanization of rubber and latex compounds, but also rubber solutions. Secondary amines able of nitrosation may be created in their presence.

Xanthates are metallic, predominantly zincous salts of the xanthic acids. They belong to ultra fast accelerators. They are used mainly during vulcanization of latex systems (e.g. during foam-rubber production) and rubber solutions. Some of them are soluble in water. As they cause very fast vulcanization they are suggested for lower vulcanization temperatures application, the most often from 80 to 110 °C.
Other accelerators include mainly such new types of accelerators as different triazines and sulfides or metallic and amine salts of dialkyldithiophosphoric acids. The 3-mercapto-triazine belongs to the simplest triazines, but also their disulfide and sulfenamide derivates are known. Dithiophosphates are fast accelerators. The best known from them are zinc salts of dialkyltiophosphate acids and bis- (disopropyl) tiophosphoryl disulfide (DIPDIS). They are suggested mainly for EPDM vulcanization, but they accelerate also sulfur vulcanization of diene rubbers. Sometimes also thioureas are placed among the other accelerators; they are used during vulcanization of chloroprene rubbers.

### 3.2.2.1 Organic compounds

**Chemical structure of the most used accelerators and sulfur donors**

<table>
<thead>
<tr>
<th>Name and usual abbreviation</th>
<th>Chemical structure</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aldehydamines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyraldehydeaniline (BAA)</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>very fast accelerator, leads to high crosslink density</td>
</tr>
<tr>
<td>Hexamethylene-tetramine (HEXA)</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>very slow accelerator, used only as secondary accelerator</td>
</tr>
<tr>
<td>Tricrotonylidene-tetramine (TCT)</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>very slow accelerator for hard rubber, used as secondary accelerator</td>
</tr>
<tr>
<td><strong>Guanidines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diphenylguanidine (DPG)</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>slow accelerator, used predominantly as secondary accelerator</td>
</tr>
<tr>
<td>Compound</td>
<td>Structure</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>-------------</td>
</tr>
<tr>
<td>Di-o-tolylguanidine (DOTG)</td>
<td><img src="" alt="DOTG Structure" /></td>
<td>slow accelerator, used predominantly as secondary accelerator</td>
</tr>
<tr>
<td><strong>Thiazoles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-mercaptobenzothiazole (MBT)</td>
<td><img src="" alt="MBT Structure" /></td>
<td>fast, frequently used accelerator; it is used preferably in combination with other accelerators</td>
</tr>
<tr>
<td>Dibenzothiazyl disulfide (MBTS)</td>
<td><img src="" alt="MBTS Structure" /></td>
<td>fast accelerator with slightly delayed start</td>
</tr>
<tr>
<td><strong>Sulfenamides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-cyclohexyl-2-benzthiazol sulfenamide (CBS)</td>
<td><img src="" alt="CBS Structure" /></td>
<td>fast accelerator with scorch delay, used also in semi EV and EV systems</td>
</tr>
<tr>
<td>Dicyclohexyl-2-benzthiazol sulfenamide (DCBS)</td>
<td><img src="" alt="DCBS Structure" /></td>
<td>accelerator with longer scorch delay and lower cure ratio than CBS</td>
</tr>
<tr>
<td>N-tert.butyl-2-benzthiazol sulfenamide (TBBS)</td>
<td><img src="" alt="TBBS Structure" /></td>
<td>accelerator with shorter scorch delay and lower cure ratio than CBS</td>
</tr>
<tr>
<td>N-oxydiethylenedithiocarbamyl-N'-oxydiethylene sulfenamide (OTOS)</td>
<td><img src="" alt="OTOS Structure" /></td>
<td>accelerator with scorch delay and high cure rate, used also in combinations with other accelerators</td>
</tr>
<tr>
<td>N-oxydiethylenedithiocarbamyl-N'-tert.butyl sulfenamide</td>
<td><img src="" alt="OTOS Structure" /></td>
<td>accelerator with scorch delay and high cure rate, used also in combinations with other accelerators</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-------------</td>
<td>--------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>(OTTBS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Thiurams</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetramethylthiuram disulfide (TMTD)</td>
<td><img src="structure1.png" alt="Chemical Structure" /></td>
<td>very fast accelerators, used also in semi EV and EV systems; sulfur donors</td>
</tr>
<tr>
<td>Tetraethylthiuram disulfide (TETD)</td>
<td><img src="structure2.png" alt="Chemical Structure" /></td>
<td>R = methyl, ethyl, benzyl.</td>
</tr>
<tr>
<td>Tetrabenzylthiuram disulfide (TBzTD)</td>
<td><img src="structure3.png" alt="Chemical Structure" /></td>
<td>very fast accelerators, used also in semi EV and EV systems</td>
</tr>
<tr>
<td>Tetramethylthiuram monosulfide (TMTM)</td>
<td><img src="structure4.png" alt="Chemical Structure" /></td>
<td>very fast accelerators, used also in semi EV and EV systems</td>
</tr>
<tr>
<td><strong>Dithiocarbamates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc dimethylthiocarbamate (ZDMC)</td>
<td><img src="structure5.png" alt="Chemical Structure" /></td>
<td>Me = ultra accelerators, used also at low (room) temperatures and for vulcanization of latex compounds</td>
</tr>
<tr>
<td>Zinc diethylthiocarbamate (ZDEC)</td>
<td><img src="structure6.png" alt="Chemical Structure" /></td>
<td>methyl, ethyl.</td>
</tr>
<tr>
<td><strong>Xanthates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc isopropylxanthate (ZIX)</td>
<td><img src="structure7.png" alt="Chemical Structure" /></td>
<td>the fastest ultra accelerators, used predominantly for vulcanization of latex compounds</td>
</tr>
<tr>
<td>Sodium isopropylxanthate (NaIX)</td>
<td><img src="structure8.png" alt="Chemical Structure" /></td>
<td></td>
</tr>
<tr>
<td><strong>Other accelerators</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triazines</td>
<td><img src="structure9.png" alt="Chemical Structure" /></td>
<td>base compound, used only occasionally, in small amounts, during vulcanization of the large-scale products;</td>
</tr>
</tbody>
</table>

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Dithiophosphates

\[
\begin{align*}
R_{1} & = R_{2} = \text{alkyl} \\
R_{1} + R_{2} & = \text{alkyl} \\
R_{1} \cdot R_{2} & = \text{izopropyl} \\
& \text{n-butyl} \\
& \text{terc.butyl} \\
& \text{2-etylhexyl}
\end{align*}
\]

\[
\text{Me}^{+x}
\]

They have optimum accelerating effect in combination with thiazoles.

\[
\text{Me} = \text{most frequently Zn}
\]

Bis-disopropylthiophosphoryl disulfide

\[
\text{H}_{2}\text{C}_{3}\text{O} \quad \text{P} - \text{S} - \text{S} - \text{P} - \text{O} - \text{C}_{3}\text{H}_{7}
\]

\[
\text{H}_{2}\text{C}_{3}\text{O} \quad \text{||} \\
\text{S} \quad \text{||} \\
\text{S} \\
\text{O} - \text{C}_{3}\text{H}_{7}
\]

Other sulfur donors

<table>
<thead>
<tr>
<th>Sulfur Donor</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentamethylenetriamidimorpholine</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>Dipentamethylenetriamidimorpholine</td>
<td>(x = 4 \text{ or } 6)</td>
</tr>
<tr>
<td>Dithiodimorfoline (DTDM)</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>2-morfolinodithiobenzothiazole MBSS</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>Caprolactamdisulfide (CLD)</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
<tr>
<td>Bis(diethyl-thiocarbamoyl-disulfido)</td>
<td><img src="image5.png" alt="Structure" /></td>
</tr>
<tr>
<td>hexane</td>
<td></td>
</tr>
</tbody>
</table>

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3.2.3 Activators

Optimum influence of sulphur vulcanization systems is achieved under participation of activators. For this purpose inorganic as well as organic compounds are used in practice. From the inorganic compounds these are mostly metal oxides and from organic compounds higher fatty acids and their salts, some amines or their derivates. In general it is assumed that matters increasing pH of the vulcanization compositions have activation effect.

The most widely known activator of the sulfur vulcanization is ZnO. Practically, it is always used in combination with suitable fatty acid, the most frequently stearic or lauric acid. Sometimes zinc salts or combinations of acids and their zinc salts replace these acids. Activation effect of ZnO is ascribed mostly to its ability to create complexes generating curing sulfuric fragments with sulfur and accelerators. Participating acids increase solubility of these complexes in rubbers; they improve dispersive capacity of powder additives in compounds and sometimes they also prolong induction period of the vulcanization. ZnO may act as filler or white coloring agent in rubber compositions, too. In addition to this metal oxide also MgO is used as ingredient in rubber compounds and mostly as component of curing systems of CR rubbers or also during vulcanization of some special rubbers, e.g. ACM, CSM, CO. Also PbO and PbO₄ have activation effect in the sulfur vulcanization systems but these are used only exceptionally.

3.2.4 Sulfur vulcanization

Retarders reduce the curing rate in the main phase of the vulcanization, they slightly increase processing safety of the compounds, but their presence in rubber compounds may cause also reduction of crosslink density of vulcanizates. Such effect on sulfur vulcanization have substances of acidic character, as slightly organic acids, mostly phthalic acid and phthalic anhydride, benzoic acid, salicylic acid, maleic acid and others. Similar effect has also colophony and some types of natural bitumen. Most of them may be used also into compounds for color products, because it does not change or changes only very little their color.

From practical point of view, so-called pre-cure inhibitors are more important. Those are additives prolonging induction period of vulcanization, but they do not have significant influence on the curing rate in the main vulcanization phase. Under their presence the processing safety of compounds is improved without prolongation of the optimum vulcanization time and crosslink density of vulcanizates was reduced. Such acting additives contain for instance N-nitrosodiphenylamine (it is used only very little, because it has detrimental consequences on health), dithiodichloromethane, N-thiosulphonic amides and N-thioimides. Presently, the most often used pre-cure inhibitors of vulcanization is N-cyclohexylthiophtalimide.
It is the most efficient in compounds with sulfenamide accelerators. It is added only in small amounts into rubber compounds, approximately 0.1 – 0.5 phr. Its efficiency is small when combined with other accelerators.

### 3.2.5 Formation of complexes

- Sulfur, accelerator, activator
- Sulfur donor, activator

- Active sulfurating complex
  - $X - Sy - H,X$

- Rubber RH

- Cross-linking precursor
  - $R - Sy - X$

- Initial polysulfide cross-links
  - $R - Sx - R$

- Shortening of cross-links
- Main-chain modification (dehydrogenation, cyclization, isomerization)
- Degradation of cross-links
- S-S bond interchange

- Vulcanizate network

Creation of initial polysulfidic crosslinks in the presence of 2-mercaptobenzothiazole and ZnO

3.2.6 Sulfur donors

Sulfur donors are compounds that are able to create cross-links of sulfuric or carbon character between macromolecules of vulcanized rubber also under very low sulfur content (less than 0.5 phr), eventually also without sulfur presence. In practice, two types of compounds are used for this purpose. On the one hand those are some fast and very fast accelerators having besides accelerating also curing effect. There belong mostly accelerators with at least two sulfur atoms in the sulfur bridges, as thiurams and also some sulfenamides (2.1 – 2.3.2). These sulfur donors are used mostly in EV sulfur systems with low sulfur content. Vulcanization in their presence runs in similar way as under presence of higher sulfur content; only some of its kinetic parameters and also crosslink density of vulcanizates and number of sulfur atoms in created cross-links are changed. The other type of donors may integrate compounds having only curing effect. Those are for instance dithiodimorpholine (presently it is practically no longer used because it generates nitrosable morpholine at curing), dicaprolactamsulfides, and dithioalkanes. Under presence of such sulfur donors the vulcanization runs in accordance with its own kinetic principle.
3.2.7 Thiuram disulfides

Possible reactions of tetramethylthiuram disulfide in initial stage of sulfur curing

3.2.8 Sulfur vulcanizate

General scheme of sulfur vulcanizate network

- monosulfide cross-links, b – disulfide cross-links, c – polysulfide cross-links (x = 3-6), d – polysulfide cross-links across more than two rubber macromolecules, e – vicinal cross-links, f – carbon - carbon cross-links, g, j – cyclic sulfide, h, i – conjugate fragments of rubber macromolecules, l – accelerator fragment, k – chemical unbounded additives or products of their chemical changes.
3.2.9 Conventional sulfur system

Influence of curing time at 140° on network structure of NR vulcanizates 
(S = 2.5 phr, N-cyclohexyl-2-benzthiazole sulfenamide = 0.6 phr). Mc – molecular weight of rubber segments between two cross-links, -S- monosulfide cross-links, -S-S- disulfide cross-links, -Sn- polysulfide cross-links, Total – total cross-links.

3.2.10 EV systems

Influence of curing time at 140° on network structure of NR vulcanizates 
(S = 0.4 phr, N-cyclohexyl-2-benzthiazole sulfenamide = 6.0 phr). Mc – molecular weight of rubber segments between two cross-links, -S- monosulfide cross-links, -S-S- disulfide cross-links, -Sn- polysulfide cross-links, Total – total cross-links.

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3.3 Peroxide vulcanization

By organic peroxides can be vulcanized saturated (e.g. EPM, EVM, CM, Q, some of FKM) and also unsaturated (e.g. EPDM, SBR, NBR, NR) rubbers. They were first used – specifically dibenzoyl peroxide - for NR cross-linking in 1915 by Ostromyslenskij. However, wider practical application for them was found later mainly at saturated EPM and Q cross-linking. On the present they are used as vulcanization agents of unsaturated rubbers most often if it is necessary to produce gum resistant to temperature or at vulcanization of compounds consist of combination of saturated and unsaturated rubbers.

Organic peroxides (1) used in function of vulcanization agents belong according to their chemical composition to aliphatic, aromatic but also to mixed peroxides and some of them have even more than one peroxide group. Most of them generates at thermal decomposition and possible following fragmentation of primary peroxide cumyloxy-, terc. butyloxy-, phenyl-, benzoyl- or methyl- radicals:

The basic assumption for the selection of suitable peroxide except of its ability to cross-linking of rubber compounds is the fact that it is stable at preparation and processing of and it extend fast at vulcanization temperature. These requirements are fulfilled mainly by peroxides where the peroxide group is fixed to tertiary carbon. Peroxides with peroxide group fixed to primary or secondary carbon are less stable. Less stable are also peroxides with carboxyl group in molecules. The rate of its decomposition is quickening by oxygen but they are less sensitive to presence of the acidic nature substances. That is why dibenzoylperoxide is suitable only for vulcanization at temperatures lower than 130°C where at temperature around 50°C can give out to decreasing of processing safety of rubber compounds. In the case of dicumylperoxide are these temperatures higher and they are around 170 or 120°C.

Generally it suggests that cross-linking of rubber macromolecules by peroxides has radical character. Its primary act is homolytic dissociation of peroxide to radicals, their possible fragmentation and consequential reactions with present rubber molecules. At cross-linking of diene polymers are reactive α-methylene hydrogen’s attended at these reactions. The incipient rubber radicals are recombinated at the creation of intermolecular C–C links. At the same time also addition reactions of rubber radicals to unsaturated bonds of rubber macromolecules can run over. In the case of EPDM rubbers (2) the creation of chemical cross-links by addition to double bonds in its unsaturated structural units (mostly norbornene type) practically equal to recombination of rubber macroradicals. At polydiene cross-linking, mainly of polyisoprene type, is the contribution of these reaction relatively small. They are applying more remarkable only at cross-linking of polybutadiene with higher content of 1.2 butadiene units or its copolymers. At EPM cross-linking or others
saturated rubbers (e.g. Q) cross-links between macromolecules are created only by mutual recombination of polymer radicals.

Efficiency of peroxide cross-linking increases in the presence of coactivators (3). The most often these are bi- or multifunctional substances with olefinic double bonds like allylic (triallyl-izo-cyanurate, diallylphthalate, diallylitaconate, triallylphosphate) and vinyl substances (ethylene glycol dimethacrylate and others di-, tri-, tetra- and penta-methacrylates) or different derivates of maleic acid (m-phenylenediamine-bis-maleimide). Following its polarity are these substances slightly soluble in non-polar rubbers and create there aggregates. It is assumed that during the vulcanization they are able to rapidly react with rubber macroradicals and take part in creation of small thermostic particles (4) which can be part of vulcanizate network.

However, organic peroxides at rubber cross-linking do not take place in the reactions leading to the formation of cross-links between rubber macromolecules alone. In the case that rubber radicals terminates by disproportional reactions the cross-link is not created between them. Reactive peroxide radicals can also react with rubber macromolecules so that the fragmentation appears in same cases (e.g. at IIR rubber (5)) and also their degradation is given out.

Vulcanization by peroxide systems is normally done at temperatures of 140–180°C. At the suitable selection of peroxide and vulcanization temperature does appear neither pre-cure nor reversion. Vulcanizates have good resistance to temperature and they have good electrical characteristics. In comparison with sulfur vulcanizates they are less elastic and have worse dynamic characteristics, worse tensile strength, structural resistance and also the resistance to wearing. Peroxide vulcanization systems do not generally cause the vulcanizate color change. However they are relatively expensive. Their disadvantage is also the possibility of their reactions with the other ingredients in rubber compounds (e.g. antidegradants). Following abovementioned their effective content in rubber compounds decreases and in the case of some non-reacted participation in the vulcanizates they can become potential source of oxidation-degradation reactions. That is why vulcanization time is approximately longer than half-time of used peroxide decomposition at vulcanization temperature.
3.3.1 Organic peroxides

*Examples of the peroxides used for vulcanization*

<table>
<thead>
<tr>
<th>Peroxide</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibenzoylperoxide</td>
<td><img src="image" alt="Dibenzoylperoxide" /></td>
</tr>
<tr>
<td>Bis (2,4-dichloro)benzoylperoxide</td>
<td><img src="image" alt="Bis (2,4-dichloro)benzoylperoxide" /></td>
</tr>
<tr>
<td>Di-terc.butylperoxide</td>
<td><img src="image" alt="Di-terc.butylperoxide" /></td>
</tr>
<tr>
<td>Dicumylperoxide</td>
<td><img src="image" alt="Dicumylperoxide" /></td>
</tr>
<tr>
<td>Terc.butylcumylperoxide</td>
<td><img src="image" alt="Terc.butylcumylperoxide" /></td>
</tr>
<tr>
<td>1,4-bis(terc.butylperoxyisopropyl) benzene</td>
<td><img src="image" alt="1,4-bis(terc.butylperoxyisopropyl) benzene" /></td>
</tr>
<tr>
<td>2,5-bis-(terc.butylperoxy)-2,5-dimethylhexane</td>
<td><img src="image" alt="2,5-bis-(terc.butylperoxy)-2,5-dimethylhexane" /></td>
</tr>
<tr>
<td>4,4 di-terc.butylperoxy-n-butylvalerate</td>
<td><img src="image" alt="4,4 di-terc.butylperoxy-n-butylvalerate" /></td>
</tr>
</tbody>
</table>
3.3.2 EPDM rubbers

Simplified reaction scheme of peroxide cross-linking of EPDM
### 3.3.3 Coactivators

*Examples of co-vulcanization agents used during peroxide vulcanization*

<table>
<thead>
<tr>
<th>Coactivator</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triallylisocyanurate</td>
<td><img src="image" alt="Triallylisocyanurate" /></td>
</tr>
<tr>
<td>Triallylphosphate</td>
<td><img src="image" alt="Triallylphosphate" /></td>
</tr>
<tr>
<td>Ethyleneglycol dimethacrylate</td>
<td><img src="image" alt="Ethyleneglycol dimethacrylate" /></td>
</tr>
<tr>
<td>M-phenylenediamine-bis-maleimide</td>
<td><img src="image" alt="M-phenylenediamine-bis-maleimide" /></td>
</tr>
</tbody>
</table>

### 3.3.4 Thermosetic particles

*Probable creation of the thermosetic particles of co-vulcanization agents in EPM vulcanize*

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3.3.4 IIR rubber

\[
\text{RO'} + \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \rightarrow \text{ROH} + \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2
\]

\[
\text{IIR degradation in presence of peroxide radicals}
\]