

POLYMER SCIENCE AND TECHNOLOGY

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Vulcanization

Chemistry and technology of vulcanization

- Charles Goodyear was first who vulcanized rubber just unexpectedly, in 1839 he heated natural caoutchouc cis-1,4-polyisoprene with small quantity of sulphur.

Vulcanization – a process by which uncrosslinked material (caoutchouc) becomes crosslinked (rubber).

Crosslinked material (rubber) can not be dissolved or melted.

For reaction of vulcanization the components are:

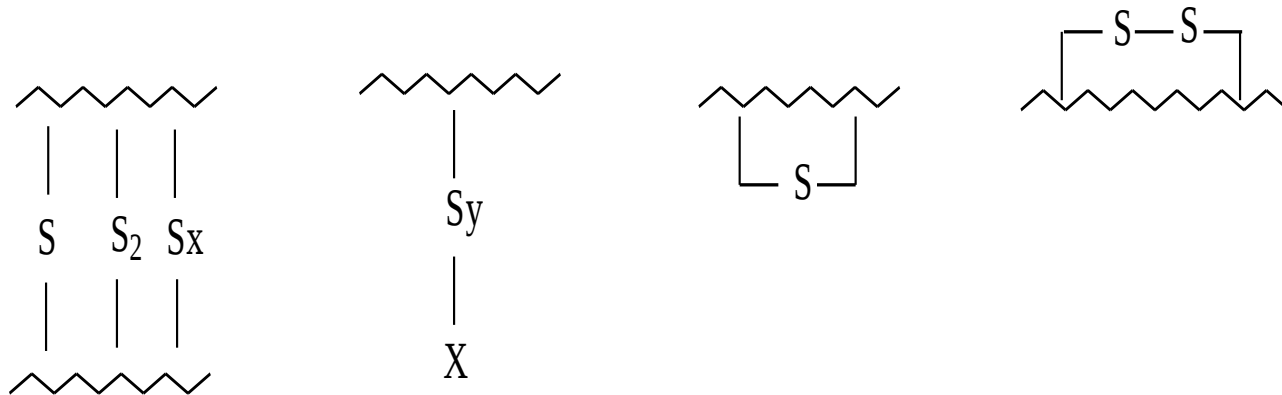
1. uncrosslinked material (caoutchouc)
2. agents for vulcanization (sulphur or other)
3. accelerators (merkaptanes)
4. ZnO – activator of accelerator
5. stearic acid

and different types of additives

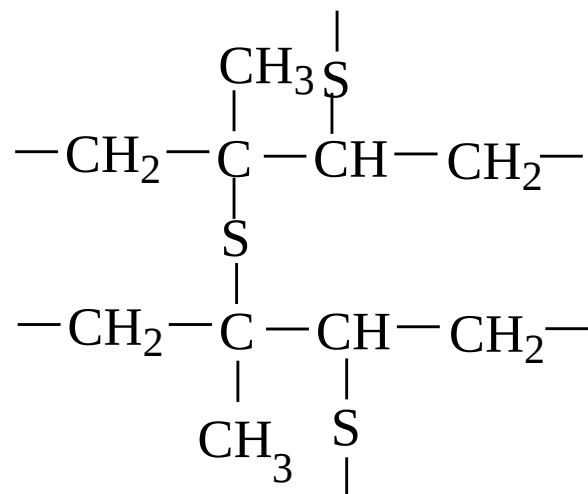
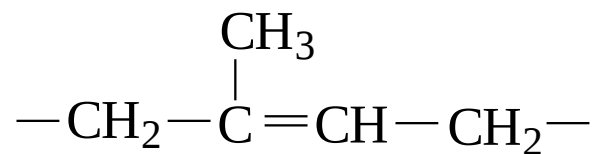
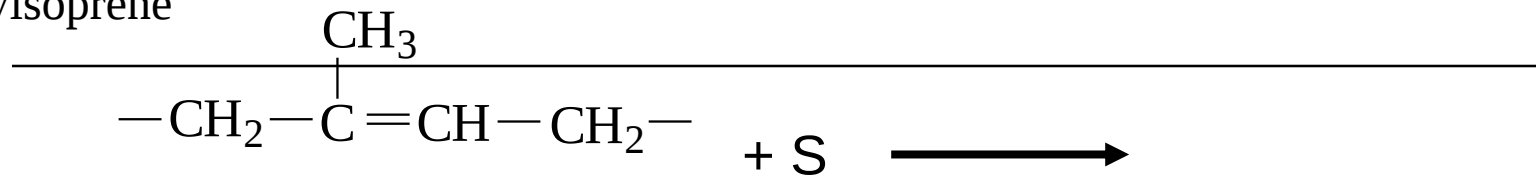
A. Sulphur vulcanization

Sulphur is usually present in quantities of 2,5-3,0 phr (phr – parts per hundred)

Sulphur in vulcanization process may be present as: monosulphide, disulphide, polysulphide or cyclic monosulphide and cyclic disulphide:



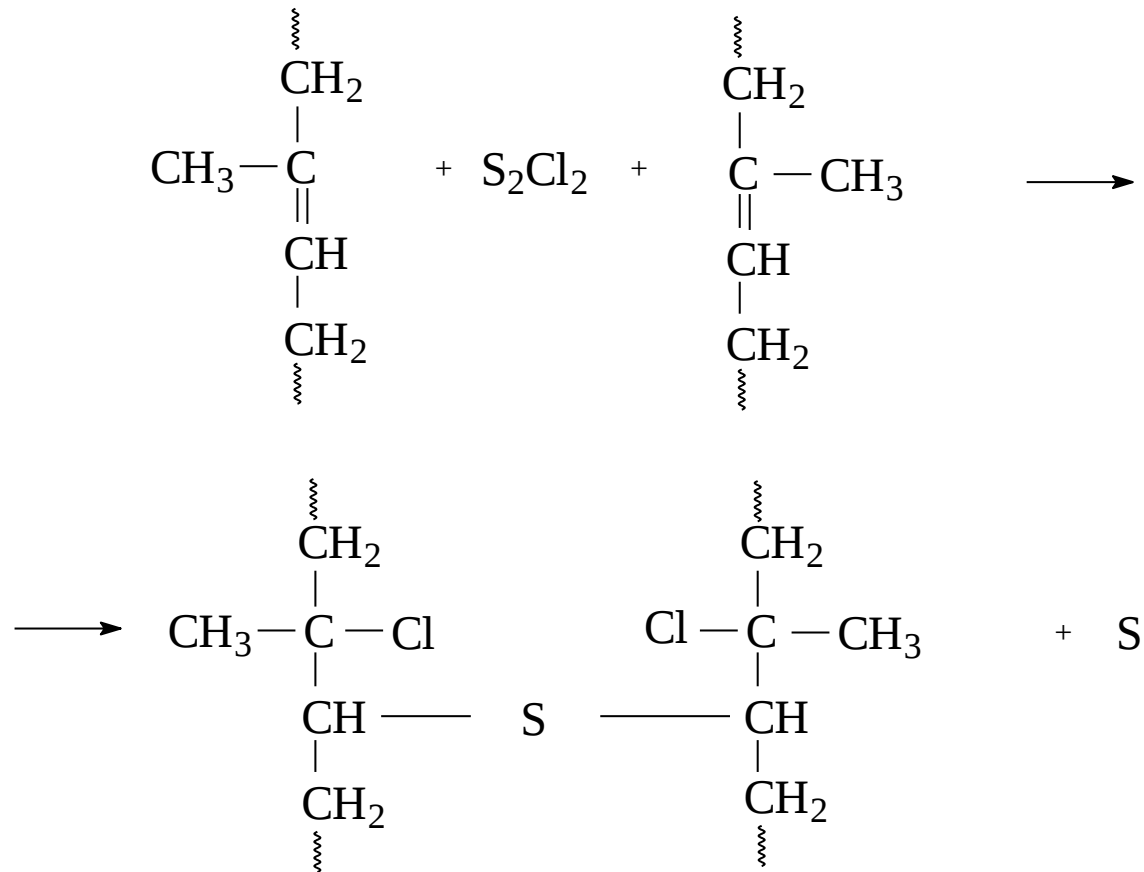
polyisoprene



crosslinked
polyisoprene

B. Nonsulphur vulcanization systems for olefinic rubber

1. Example of vulcanization of rubber with disulfur dichloride (S_2Cl_2)



- For vulcanization of olefinic rubber with accelerator SnCl_2 , usually halogen resin is used:



Technological processes of vulcanization

- Vulcanization takes place in a large plants and factories for production of tires and other products.
 1. Vulcanization in autoclaves
 2. Continuous vulcanization
 3. Vulcanization by pressing

1. Vulcanization in autoclaves

- the type of vulcanization with water vapour, which is carried out in cylindrical autoclaves, which can be vertical or horizontal, it is possible to use hot air vulcanization.
- *advantage: uniform heating because there are no parts of cold surfaces.*
- *disadvantage: rubber is easily oxidized in the air, therefore, vulcanization is often carried out in autoclaves with steam.*

Vulcanization in autoclaves



2. Continuous vulcanization

This process is usually connected to the extrusion or calendering (production of pipes, profiles, rubber insulated wires and cables).

- a) Vulcanization in a tunnel with hot air – it is rarely performed because of low heat transfer and the possible deformation of extruded profiles and the product.
- b) Vulcanization in the tunnels of hot steam – continuous vulcanization of cables and wires for insulation
- c) Vulcanization in a bath of ethylene glycol - a simple procedure but with disadvantage because of the evaporation of the ethylene glycol from the bath and a product after vulcanization must be washed.

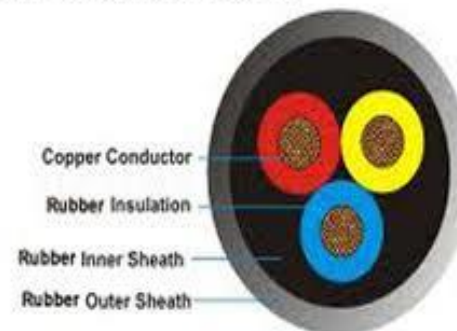
d) Vulcanization in the bath with the molten metal - not a suitable procedure for vulcanizing - the frequent deformation of products and harmful phenomena which metals cause to the surface of the product.

e) Fluid bed vulcanization - procedures in which the products pass through a heated bath stuffed with small glass pearls of diameter of ~ 0.2 mm; from the bottom of the bath the air, nitrogen or steam blows and the beads (pearls) behave as a liquid media.

- *advantage: fast vulcanization $\rightarrow$ heat transfer in a media is higher than in gas and deformations are minimized.*



v.r.i electric cable



3. Vulcanization by pressing

-molding product is molded by pressing while warming up, the procedure is carried out in strong hydraulic presses

-moulds in presses are heated with steam or by electricity for vulcanizing at higher temperatures



DEGRADATION OF POLYMERS



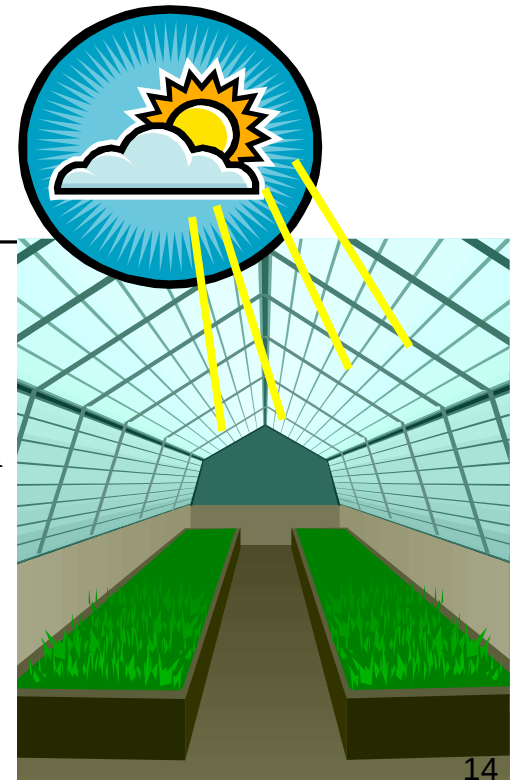
DEGRADATION OF POLYMERS

Degradation of polymers is each process where polymers lose their properties.

- changes in molecular and supramolecular structure due to the chemical and physical influences
- chemical process which changes the configuration of molecule

Table 1. Types of degradation

Reason	Degradation
Heat	Thermal degradation
Oxygene	Oxidative degradation
Ozone	Ozone degradation
Electromagnetic radiation	Photochemical degradation
Radioactive radiation	Ionization degradation
Chemical effects	Chemical degradation
Mechanical strains	Mechanical degradation
Atmosphere activity	Ageing
Biological activity	Biodegradation



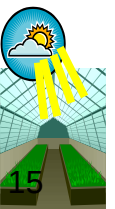
The harmful influences on polymers

Polymer materials and products are during their life always in interaction with environment and may progressively degrade.

The processes of degradation proceed during **production, manufacturing, use, recycling and disposal** of polymer materials - degradation is specific for every polymer and the conditions of its usage

During the manufacturing polymers are exposed to:
temperature, oxygene and mechanical strains

During their use in nature they are exposed to
light, oxygene, moisture, ozone, mechanical strains



The consequences of degradation

- hardening, increase of brittleness and fading of colour
- diminishing of mechanical, electrical, reological and other properties.
(e.g the white colour of plastic boxes exposed to the light during a few years becomes yellow; cracking of a plastic vessel left in garden for a few years)

The most serious and expensive examples of degradation of polymers: some crashes of aeroplanes are caused by the degradation of polymer electric insulations.



Stabilizers

Stabilizers are added to the polymer materials to prolong their useful life:

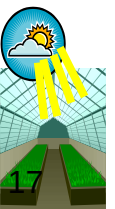
thermal stabilizers

antioxidants

antiozonants

ultraviolet stabilizers

The choice of stabilizer depends on polymer type and the conditions during the use of polymer material.



Favourable degradation

Some polymers can be converted to monomers using chemical degradation - the starting chemicals for synthesis of new polymers
(chemical recycling)

With burning of polymers at the end of their life we can get energy
(energy recycling)

Favourable mechanical degradation – mastication of unvulcanized rubber – drop of molecular masses – the process of vulcanization becomes easier



Mechanism of degradation

Degradation is occurring **by breaking of** primary or secondary bonds and the result is:

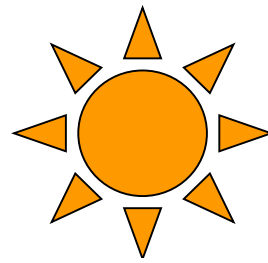
- *lower molecular weight*
- *crosslinking*
- *cyclization of degradation products*

This kind of degradation is irreversible and the basic mechanisms are :

1. breaking of the main chain
2. breaking of the side chains connected to the main polymer chain



Thermal degradation



For most polymers this process occurs at 200-300 °C and it is enough to break the bonds in polymer chains.

Thermal breaking of polymer molecules can proceed with different reaction mechanisms and the results are low molecular products, chains with unsaturated groups or even branched and crosslinked structures.

At pyrolysis, e.g. temperature over 400 °C, the rate of degradation of most polymers is very strong and proceeds during a few minutes.

The process of thermal decomposition at lower temperatures, typically below 200 °C, can be prevented by the addition of thermal stabilizers.

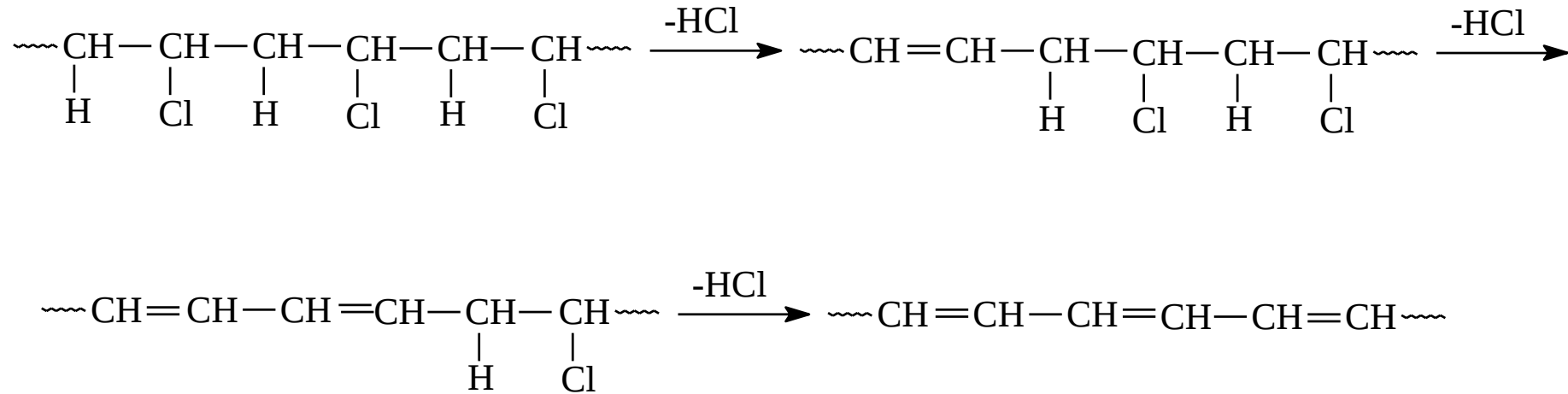
It is especially important to prevent degradation during processing of polymers (because the resulting degradation products accelerate the degradation of polymer during use under normal outdoor conditions).

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- One of the most thermally unstable polymers is **poly(vinyl-chloride) PVC**

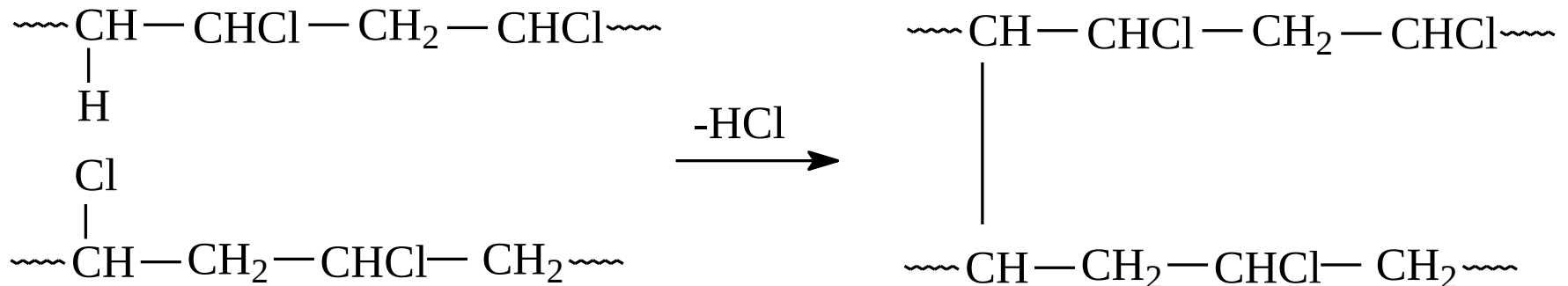
Its decomposition takes place with successive elimination of gaseous hydrogen chloride (HCl) through the ***intra-and inter-molecular dehydrochlorination*** without cleavage of the basic chain.

- Formed HCl has the function of an autocatalyst.
- Rapid reaction is almost complete at a temperature of 250 °C.
- Dehydrochlorinated chains can continue to interact with the formation of crosslinked and cyclic structures.

Intramolecular dehydrochlorination of PVC macromolecules



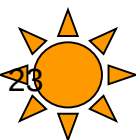
Intermolecular dehydrochlorination of PVC macromolecules



Thermally initiated process of degradation proceeds **in the presence of oxygen** with very fast oxygen degradation:

process is called **thermooxidative degradation** and occurs at the temperatures lower than for thermal degradation.

Example: polypropylene is thermally rather stable polymer but in the presence of oxygen it is susceptible to thermodegradation.

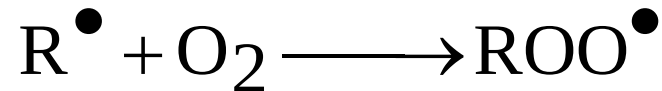


Oxidative degradation

Oxidative degradation of polymers occurs by the mechanism of free radicals, as autooxidative process.

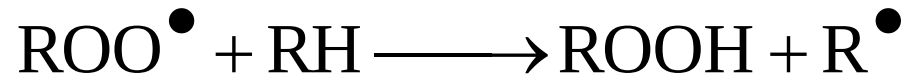
- Initiation occurs through the formation of free radicals and can be caused by heat, UV light.

In the **stage of propagation** oxygen in contact with macromolecular radical $R^\bullet$ gives peroxiradical ($ROO^\bullet$) in a very fast reaction





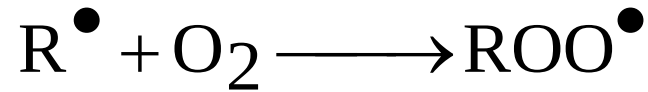
which is reactive for attack of any C-H bonds in the macromolecule:



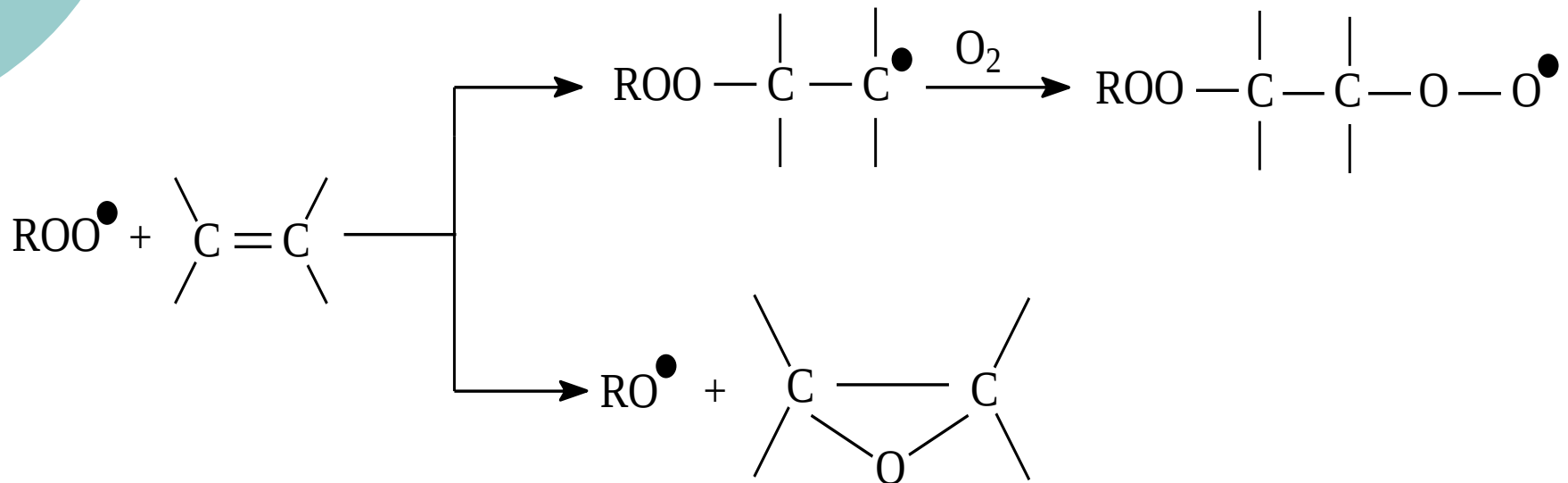
Oxygen prefers to attack the **tertiary C-atom**.

This is the reason why the rate of oxidation depends on degree of branching and the presence of **double bonds** in polymer („weak” points in polymer structure).

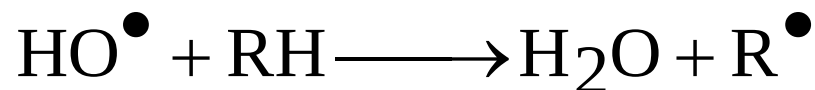
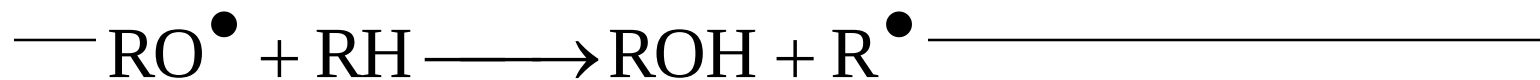
The new macromolecule radical reacts very fast with O_2 and new peroxyradical is formed:



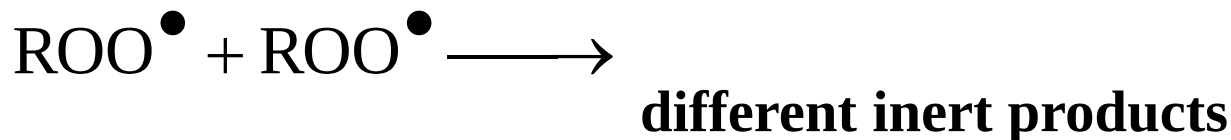
which attacks the C-H bond. If macromolecular chain contains double bond, peroxyradical will be added just on this bond:



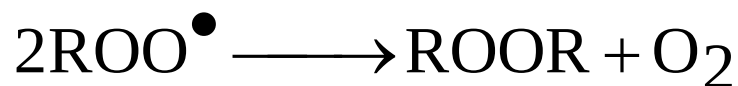
Oxy-radical $\text{RO}^\bullet$ and hydroxy-radical $\text{HO}^\bullet$ react with new macromolecules or with hydroperoxide:



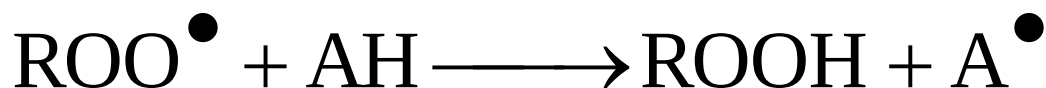
The step of propagation, i.e. activity of radicals, proceeds till the reaction of **termination** occurs: the reaction of two radicals and formation of inert products:



The most important is the reaction of **termination which gives** peroxides:



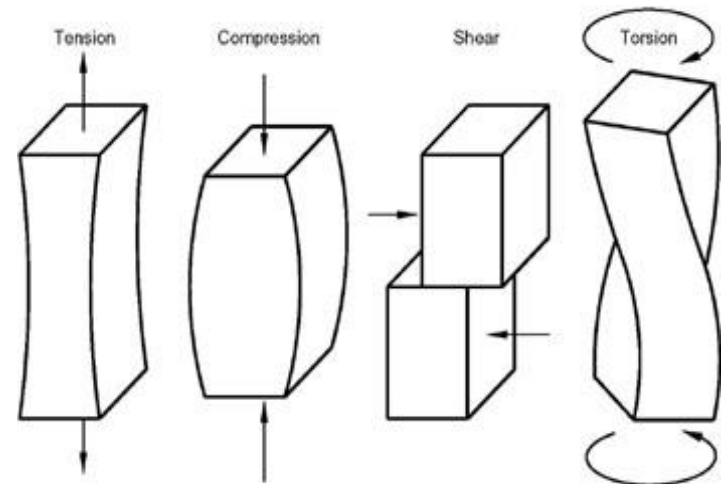
The mechanism of antioxidant (AH) is given bellow:



Antioxidant in very fast reaction with peroxy or oxyradical gives reactive H-atom and it is transfered to radical $\text{A}^\bullet$ which is stable e.g. inactive – **prevention of oxidative degradation.**

MECHANICAL DEGRADATION

- Mechanical breakdown caused by mechanical stress during processing or use of polymers.
- The consequences of mechanical degradation are:
 - lower crystallinity
 - solubility changes
 - viscosity changes
 - poor mechanical properties



AGEING

- Atmospheric ageing (weathering) is a degradation of the natural environment (solar radiation, heat, oxygen, ozone) in conditions that are simultaneously occurring: thermooxidation and photooxidation.

Also: influence of water (humidity, rain), abrasion (wind) and atmospheric pollution

The intensity of atmospheric ageing, expressed as flexural strength, depends on the temperature for the region and duration of ageing.

BIODEGRADATION

- Polymer susceptibility to degradation caused by microorganisms (bacteria, fungi) or other biological agents.

Biodegradable polymers are a group of polymers made from petrochemicals, which, under certain environmental conditions (UV radiation, oxygen, heat, moisture) decompose into small particles.

Biodegradable polymers are those polymers which degrade in the biological environment: soil, water, rivers, lakes, the human or animal body by enzymatic or nonenzymatic hydrolysis.

Natural polymers: starch, cellulose...

Synthetic polymers: polycaprolactone (PCL), poly(lactic acid) (PLA)