

# BASIC KNOWLEDGE OF RUBBER

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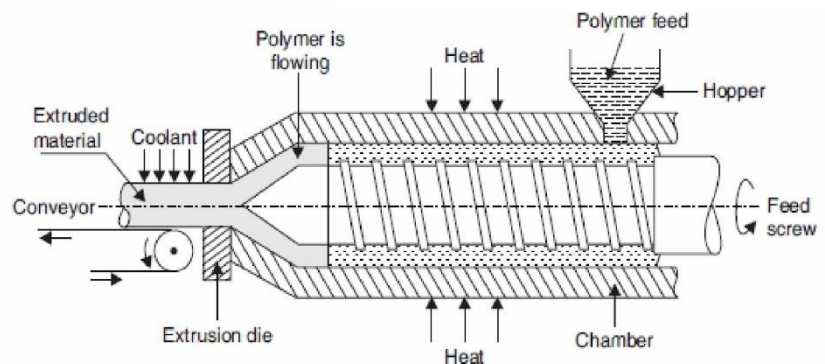


Fig. 4.2 Extrusion of plastics

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# I - Introduction

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## 1. General properties of rubber or elastomer

Elasticity, strain of 500% under stress with an initial elastic return after releasing the stress over a wide range of temperatures and the properties stay the same as initial state.

Solvent, oil and chemical resistance, good resilience and damping, gas impermeability, abrasion resistance, resistance to aging (necessary when one needs elasticity and sealing)

The raw material is not black but 80% of the products are. The black color is due to the addition of Carbon Black (CB) in the recipe which improve the mechanical properties of the elastomer.

## 2. Applications of the rubber

Rubber industry represents 28.5 million tons produced whose 59% of synthetic rubber and 41% of natural rubber.

Rubber industry: 161 companies in France for 63M€ sales per company and a total of 10B€ sales

Plastic industry: 1372 companies in France for 17M€ sales per company and a total of 23B€ sales

General applications: sealing, damping, filtration, insulation and waterproofness.

Specific applications:

- Automotive industry (15%) and pneumatics (70%):
  - 1<sup>st</sup> industry to consume rubber (85%). Elastomer parts represent 70kg in a vehicle, being 7-10% of the vehicle weight (sealing, gasket, foams, tubes, engine parts, damping, fuels and brakes,...)
  - Pneumatics: This industry has continuously improved since the 20 century with a lifetime of 3 000km to more than 50 000km, flat tires frequency of 5 000km to 30 000km
- Industry and aeronautic (5,1%) (tubes, pipes, electrical cables, glass gasket, sealing,...)
- General public (4,5%)
  - Daily life (washing machine, rubbers, gloves, tubes, cooking utensils,...)
  - Clothing (boots, waterproof jacket,...)
  - Sport (tennis balls, golf, diving equipment, tennis court,...)
  - Hygiene (condoms, prosthesis, surgeon gloves, syringe cap, bottle teat, band-aid,...)
  - Interface assembly materials (glue, adhesives, paint,...)
- Construction industry (3%) (specials gaskets, tap coating, asphalt, snow caterpillars,...)

# II - History

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## 1. Discovery of the natural rubber

Late 15 century, Europeans observe the American natives which were using latex/natural rubber from the *Hevea Brasiliensis*.

Native Americans used the latex to make a plenty of daily life object, boots, torch, hessians, containers. The explorers brought back those object to study the latex and they conclude the following : latex is sticking when exposed to sun, at very high temperature it disintegrate, very brittle at low temperature, and become brown when exposed to air.

It began a lot of scientific travels to study the latex culture, applications, properties to understand this new material.

## 2. Development of heveaculture and industrialization

1736-1744: Charles Marie de LA CONDAMINE(Fr) and François FRESNEAU de La Gataudière (Fr) presented to the Académie Royale des Sciences, France, the 1<sup>st</sup> scientific paper on rubber which described many of its properties.

The native word *caotchu*, in Quechua, means *cao* – wood and *tchu* – crying. They introduced a new French word to this new material: *le caoutchouc*.

1770 : Joseph PRIESTLEY (UK) used the rubber to wipe from paper the mark of pencils. This is the first use of an eraser, also called a rubber in Canada, the UK, Ireland, India, Australia, New Zealand, and South Africa.

1791 : Samuel PEAL (UK) developed the 1st rubber patent by manufacturing a method of waterproofing cloth by treating it with a mixture of chemical products and natural rubber.

1819: Thomas HANCOCK (UK) invented the masticator, a machine that shredded rubber scraps and which allowed rubber to be recycled after being formed into blocks or sheets.

1823: Charles MACINTOSH (UK) invented the waterproof fabric obtained by dissolving the rubber in naphtha.

1834: RATTIER (FR) and GUIBAL(FR) invented suspenders and garters rubber-based.

Charles DIETZ(GE) invented a rubber-layer between the wood rim and steel wheel to protect the wheel and cushion. This is the ancestor of the pneumatic.

1839: Charles GOODYEAR (US) developed the vulcanized rubber after 5 years of research for more stable rubber which led to an accidental discovery. Thomas Hancock is acknowledged that he discovered the vulcanization process 8 weeks before C. Goodyear but without pending a patent.

1853: Hiram HUTCHINSON (UK) bought the vulcanization patent from C. Goodyear and founded the 1<sup>st</sup> rubber company in France.

1870: C. MACINTOSH industrialize the 1<sup>st</sup> condoms latex-based.

1876-1877: Henry WICKAM exported 70K Hevea Brasiliensis' seeds from Brazil to Oriental English colonializations, in order to develop the rubber exploitation and to decrease the price.

1888: John DUNLOP (UK) invented the 1<sup>st</sup> pneumatic tire

1892: MICHELIN's brothers (FR) invented the 1<sup>st</sup> removable pneumatic tire which permits the start of the pneumatic industry.

### **3. 20 century: Synthetic rubber**

1909: Fritz HOFMANN (GE) patented and synthesized for the 1st time the rubber by polymerization.

1938: 100K tons of synthetic rubber to 1.4M tons of natural rubber per year

1942: Japan is blocking the provision of natural rubber due to WWII. The shortage speed up the development of synthetic rubber.

1960: 2M tons of synthetic rubber and 2M tons of natural rubber per year.

More specialized rubber are invented, better resistance to aging/oils/fuels/solvents

1975: 1<sup>st</sup> elastomer thermoplastic (TPE)

2000: 11.5M tons/year of natural rubber, 93% of the plantation in Asia, 2% in South America.

17M tons/year of synthetic rubber, it becomes an irreplaceable raw material (elasticity and waterproof)

# III - Rubber DNA

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## 1. Brief introduction

### 1.1 Introduction of the rubber/elastomer

The base product is often called the rubber whereas the finished product is rather called elastomer. It belongs to one of the big family of polymers in the same way as the Thermoplastics, Thermosets or Thermoplastic Elastomers.

A polymer is a group of macromolecular chains defined by its chemical nature, called microstructure and the chains length, called macrostructure.

### 1.2 Families of polymers

**Thermoplastic:** Reversible polymer during the process. Above a particular temperature, they soften to be implemented. Under this temperature, they harden with keeping the same initial properties. Recyclability is the main advantage of this polymer.

**Thermoset:** Irreversible polymer during the process. When the polymer is melt and transformed, you cannot go back to the initial state. It could offer better properties but impossible to recycle.

**Elastomers:** Irreversible polymer during the process. Elastic properties is the main advantage. The recycling is nearly impossible but a lot of research try to reverse this problem (powder, regenerate rubber...) Flexibility, elasticity, resilience in a large range of temperature, good chemical resistance, high deformability, absorption (vibration, impact) are one of the main properties of elastomers.

**Thermoplastic elastomer:** New family of polymer which ally thermoplastic properties (recyclable) and elastomer properties (elastic).

### 1.3 Chemical structure

**Micromolecule:** can be composed by 1 type of link (homopolymer), 2 types of link (copolymer) or 3 types of links (tripolymer). The links are mostly formed by Carbon and Hydrogen, they can also contain Oxygen, Nitrogen and Chlorine.

A link is the repetition of a chemical pattern, infinitely, to form a macromolecular chain.

**Macromolecule:** a chain composed of atoms linked by covalent bounds, repeating themselves to form a chain

The repartition of those links is random, no organization, no sequences. This is the reason why the entire majority of elastomers are amorphous. One could represent them by a spaghetti meal.

At a rest state, an elastomer is a group of macromolecular chains, curled up, tangled, linked by chemical affinity (Van der Waals bounds, Hydrogen bounds)

The chemical nature of the links composing the macromolecular chain of the rubber will influence the service properties of the finished product, the chemical/thermal resistances.

The length of chains will influence the aptitude of transformation and the mechanical properties.

The rubber alone has no mechanical properties, no dimensional stability and no aging resistance. This is the reason why the rubber need to be formulated with other ingredients.

## 2. Latex

### 2.1 Chemical composition

It is produced by the tension of the tree bark, the phloem, this is the living contents of a cell. The sap of the tree ensuring the distribution of water, mineral salts or sugars while the latex is more involved in the natural mechanisms of the tree defense.

The proteins in the latex of natural rubber are the cause of latex allergies.

Rubber is located in small particles in the latex, accounting for over 90% of the dry weight. These particles consist of 97% oil, Isoprene (or 2-methyl-1,3-butadiene ( $C_5H_8$ )), the membrane that surrounds contains proteins, lipids and carbohydrates.

The natural rubber latex is a colloidal dispersion of a polymer, the molecules are not only dissolved but dispersed in an aqueous medium at pH between 7.0 and 7.2, produced by Hevea Brasiliensis tree whose composition is as follows:

Water	45 – 60 %
Natural rubber	30 – 45 %
Diverse	5 – 6 %
Proteins	0.5 – 1%
Lipids	1.6%
Carbohydrates $C_m(H_2O)_n$	1.3 %
Inorganics ions ( $Mg^{2+}$ , $Ca^{2+}$ , ... )	0.5 %

### 2.2 Harvesting

In order to harvest latex, we tap the Hevea until the cambium without harming the tree. This operation is called bleeding process.

The cut lets flow very quickly latex drops (30g/day) because the internal pressure is very strong (10-15 atm.).

The harvest stops during the rain season, it is called the Wintering. The tree is put in sleep.

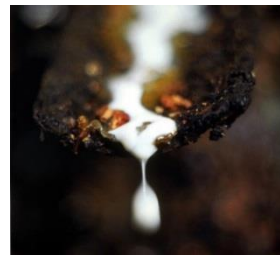
The tree starts producing latex when is diameter is more than 50cm, which is corresponding to a 7 years tree.

### 2.3 Heveacultur

A well exploited Hevea is producing 5kg of dried rubber per year during 25 to 30 years.

With an average of 550 trees by hectare, we get 1 ton of dried rubber per year.

1 tree is producing annually the quantity of natural rubber necessary to produce 4 truck tires.



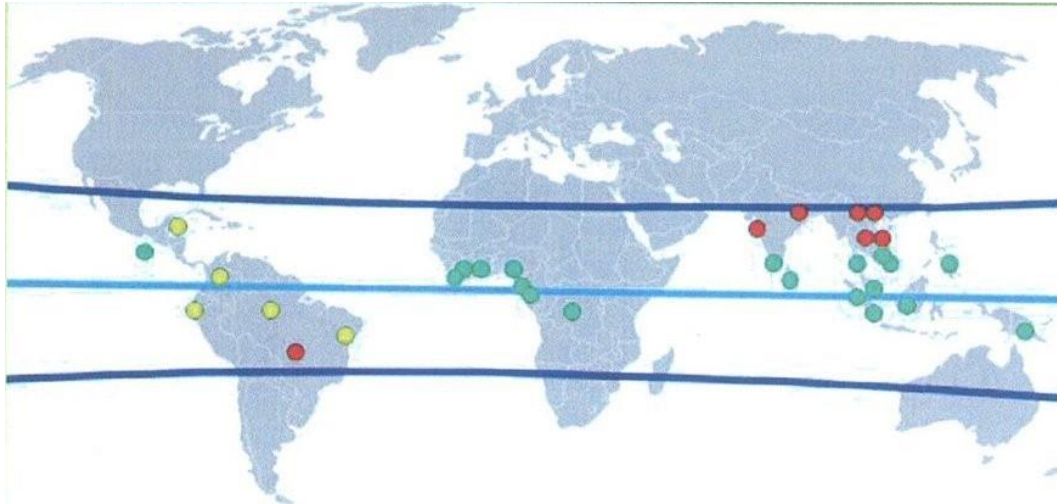


## 2.4 Plantation area

In 2015, there are, on an average, 10 millions of hectares of *Hevea Brasiliensis* which are planted in subtropical regions. The tree needs a hot and humid climate.

The « *Rhizoctonia solani* Kühn » illness or usually called « Target leaf spot » is a parasite on young trees which lead to a growth-retardant et death of the tree.

South-East Asia countries are the main producers of natural rubber. They are producing 94% of the natural rubber in the world. Thailand and Indonesia produces 58% of the natural rubber.



Difficult areas - Illness areas - Favorable areas

## 3. Transformation of natural rubber into liquid latex or solid rubber



### 3.1 Liquid latex

To avoid the latex to coagulate, ammonium drops are added before putting in centrifuges which eliminate a little of water and increase the concentration of rubber between 61% and 63%. Chemical stabilizers are then added to assure the conservation.

After formulation the latex of natural rubber will be used for gloves, condoms, balloons,...



### 3.2 Solid rubber

The harvested latex from the *Hevea Brasiliensis* is put in long steel tanks and filtered to remove impurities. Indeed, without filtration, the liquid will be contaminated by the air exposition of impurities which can lead to a moisty and perishable mix with the temperature.

The next step is to coagulate the latex of the natural rubber by:  
Natural way by evaporating the water; we obtain coagulum which are then washed, dried and compacted in 33kg ball.  
Adding an acetic acid; we obtain rubber natural “bread” which will be cut, crushed, washed, dried and compacted in 33kg ball.

The ocre coloration of the solid natural rubber is directly linked to the oxidation.  
It will be determined by its impurities rate, its color and its viscosity.  
The NR has properties that the synthetic rubber cannot reach. This is the reason why it is still many used around the world.

Its main domain of application is the dynamical applications : pneumatics, engine supports, hydraulic circuit, building engineering, transportation, mechanical/electrical/chemical/nuclear industries, bridges, road, hobbies



Photo :  
Société Mondo America

## 4. Synthetic rubber

In an historical point of view, the transition between natural rubber and synthetic rubber has increased significantly with the nearly full-stop of production and exportation of natural rubber from Japan during the WWII.

The synthetic rubber (or artificial) is made from fossil energy. They are produced by polymerization or polymer synthesis which can lead to different reaction in different conditions.

The polymerization is the chemical reaction or process where small molecules (monomers) react between themselves to create molecules of higher molecular weight (polymers).  
In general, macromolecular chains are made with reactives, catalysts, heat and pressure.

The main process used is the chain-growth polymerization which follows 3 steps:

- 1<sup>st</sup> step, chain initiation: linking of many molecules between themselves by activating covalent bounds
- 2<sup>nd</sup> step, chain propagation: a chain of molecules is made and the size grows. This step is  $10^5$  faster than the 1<sup>st</sup> step
- 3<sup>rd</sup> step, chain termination: the free radicals combine and the growth of the chain is stopped. This is the end of the polymerization process.

The global production of synthetic rubber is the following: 52% Asia, 48% rest of the world for 15.5 million tons per year.

The main producers are: Lanxess, Petrochina, Exxon, Sibur, Versalys and Zeon.

The main consumers are: China(35%), UE(15%), US(15%) and Japan(6%).

## 5. The chemistry of elastomers

Elastomers are composed in 3 families: general elastomers, special elastomers and very special elastomers. It exists more than 20 elastomers, which are differentiated by their chemical nature and their performances in different environment. This will determined which elastomers to use. Each grade has different behavior during the transformation and has singular intrinsic properties.

Family	Elastomers	Properties and main applications
General rubber 82 % of the world consumption 1-2 €/kg	NR – Natural Rubber (45% tonnage)	Good mechanical properties, tacky uncured, elasticity, strong aging sensitivity Gloves, pneumatics, engine supports, condoms,...
	IR – Isoprene Rubber (1.5% tonnage)	Close properties to NR
	SBR – Styrene Butadiene Rubber (25% tonnage)	Good fatigue resistance by flexion and good wear resistance Tread tire,...
	BR – Butadiene Rubber (12.5% tonnage)	Excellent resistance to abrasion and low temperatures
Special rubber 12% of the world consumption 2-3 €/kg	CR – Chloroprene Rubber	Good resistance to oils and sea water, good mechanical properties, specific resistance to fire Pipes, cables, belts, palms, diving suit,...
	NBR - Nitrile Butadiene Rubber copolymer	Very good resistance to oils, fuels and hydro-carbonated solvents Pipes and gaskets for fuels, roll coating, petrol industry...
	EPM and EPDM – Ethylene Propylene (Diene) Monomer (saturated)	Excellent resistance to aging, ozone and water, easy to use for extrusion, bad resistance to oils Gaskets, profiled, brakes parts, cables,...
	IIR - Isobutylene Isoprene Rubber (saturated)	Very good impermeability to gas and chemical resistance, excellent resistance to aging and damping properties, bad resistance to oils Internal skin of pneumatics, civil gas pipes, tubes...
Very special rubber 6% of the world consumption 4.5-45 €/kg and to 3000 €/kg for very special grades	VMQ, PVMQ, FVMQ: Silicon rubber or Fluoroelastomer	Excellent resistance to cold and hot temperatures, biocompatibility, excellent resistance chemical for FVMQ Cables, aeronautics parts, prosthesis,...
	FKM: Fluorinated rubber	High inertia chemical and thermal Automotive parts (gaskets,...)
	ACM and AEM – Acrylic rubber	God resistance to oils and heat Automotive parts
	CM and CSM : Chlorinated polyethylene rubber	Good resistance to heat, ozone and fuels Cables
	HNBR - Hydrogenated Nitrile Butadiene Rubber	Good resistance to oils, ozone and heat Automotive parts
	ECO - Epichlorohydrin Copolymer Rubber	Good resistance to oils, fuels and ozone Automotive parts

## 5.1 General elastomers:

They are principally used in pneumatics and dynamical applications.

General elastomers have excellent mechanical properties (failure resistance, bending, abrasion, resilience) and good resistance to cold temperature (solidifying at -60 to -90°C).

They are sensitive to aging, heat, environment (oxygen, UV, rain, ozone). To protect them, chemical products need to be added and the service temperature must not exceed 80°C.

Because of the chemical structure, their chemical, oils and hydro-carbonated solvents resistances are low. Those products can penetrate easily inside the material; it is called the swelling process. All those elastomers have unsaturated chains (double bounded C=C).

One of the main property of the NR-Natural Rubber is the tack uncured which could justify its use in pneumatics parts.

General elastomers			
Properties	SBR	NR	BR
Uncured properties			
Processing	Very good	Very good	Average
	Plasticizing decreasing	Need to plasticize	
	Few scorch	Reversion	
Tack	Average	Excellent	Low
Cured/Vulcanized properties			
Failure resistance (MPa)	Very good (charged mixing)	Excellent	Average
Tearing resistance (kN/m)	Average	Excellent	Low
Resilience – Elasticity (%)	Good	Very good	Excellent
Repetitive bending resistance	Good	Average	Very good
Service temperatures (°C)	-50 to 80	-50 to 70	-90 to 80

## 5.2 Special elastomers:

The main applications are in the automotive industry (gaskets, sealings,...), petrol & gas industry and diving industry.

They have better resistance to temperature and to aging than general elastomers.

They could reach high temperatures on service, 100-150°C, with significant properties at cold temperatures.

Special elastomers				
Properties	NBR	EPDM	CR	IIR
Uncured properties				
Processing	Dispersion of Sulfur difficult Heating during the mixing	Important dilution Excellent extrudability	Scorch sensitive	Dispersion of ingredients difficult High trend to creep Slow vulcanization with Sulfur
Tack	Average	Very low	Very good	Low
Cured/Vulcanized properties				
Aging resistance	Good heat resistance Low ozone and UV resistance	Excellent (Except on the UV)	Good flame-retardant	Excellent
Oils and fuels resistance	Excellent to good	Acceptable	Good to acceptable	Acceptable
Resilience – Elasticity (%)	Good to low	Good to low	Average	Very low
Impermeability to gas	Excellent to low	Average to low	Average	Excellent
Service temperatures (°C)	-45/-10 to 100	-60/-40 to 150	-40 to 100	-50 to 150

## 5.3 Very special elastomers:

It contains 10 elastomers families with specific chemical groups, used in extreme conditions and with excellent properties such as: excellent resistance to chemical products (oils, fuels...), excellent resistance to heat (260°C and more).

The process and transformation are more difficult and more expensive, this is the reason of the specific applications: aeronautic, spatial, military, chemical and high-technological automotive.

Silicon rubbers are particularly appreciated thanks to the possibility of coloration and the flexibility property.

# IV - Design

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In contrary to metals and alloys, polymers and in particularly elastomers have a completely different behavior model.

To understand the model for an elastomer given, laboratories tests are required. This tests will lead to understand the influence of parameters (time, T°C, strain,...) and it will lead to a mathematical model representative to the intrinsic behavior of the material.

We proceed like this because simulation on computer is easy, economic and fast compared to real scale test on production lines.

# V - Materials in an elastomer

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## 1. Polymer

All the properties of the basis of the mixing and so on the finished product. We need to have in mind the service T°C (high and low), dynamical properties, fluids contact etc... before selecting the polymer.

To select the right polymer, one needs to study its chemical nature (=microstructure), know if it is easy to shape, determined by macrostructure (chain length).

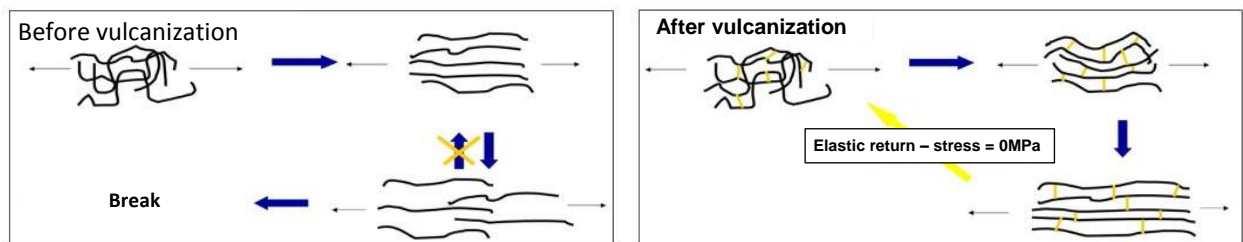
## 2. Vulcanizing agents

This material is used to create strong and irreversible links between the macromolecular chains. Those links will work like a spring and it will give the elastic behavior to the elastomer.

The most used agent is the Sulfur but it exists others like peroxides, metallic oxides and phenol-formaldehyde resins. The more chemical links, the harder the elastomer. The chemical nature of the links will have a strong impact on the mechanicals properties and thermal resistance of the mix.

### 2.1 The vulcanization

This is a chemical reaction which forms link between macromolecular chains and it changes the plastic behavior of an elastomer to an elastic behavior. As seen before, it was discovered by Charles Goodyear in 1839.



The plastic behavior, before vulcanization, is due to the fact that large macromolecular chains folded in on themselves but free with each other will stretch irreversibly under the effect of a stress and slide between each other until the break in the elastomer.

This phenomenon, known as creep, translate the plasticity of crude elastomers, ie the ability to an irreversibly modification of their shape.

The role of vulcanization is therefore essential. It consists in creating links between the chains and bringing the elastic behavior of the material. Those chemical bonds sulfur / carbon (mono or polysulfide) between the macromolecular chains, called "crosslinking bridges", can only take place under the effect of heat.

The heat activates a chemical reaction which allows the sulfur (vulcanizing agent) to cause irreversible bonds between individual polymer chains.

This reaction is now irreversible but many studies are being conducted to find a way to remove this irreversibility and enable recycling of vulcanized rubber.

## 2.2 How to realize this operation?

For the vulcanization operation, we need:

- A vulcanizing agent to pass from the plastic state to the elastic state.
- Active sites, ie areas on the macromolecular chain where bridges can be anchored
- Thermal energy, the vulcanization is a chemical reaction generally occurring at elevated temperatures (140 -200 ° C).

The oldest vulcanizer and the most commonly used is sulfur. It could be found in yellow powder or in predispersed (80%) inert matrix.



The sulfur may be used only in the presence of unsaturated diene elastomers (carbon = carbon double bonds). These double bonds are the active sites for the sulfur. The unsaturation rate conditions the cure rate.

The reaction between sulfur and diene elastomer is very slow, it cannot be used as such in the industry.

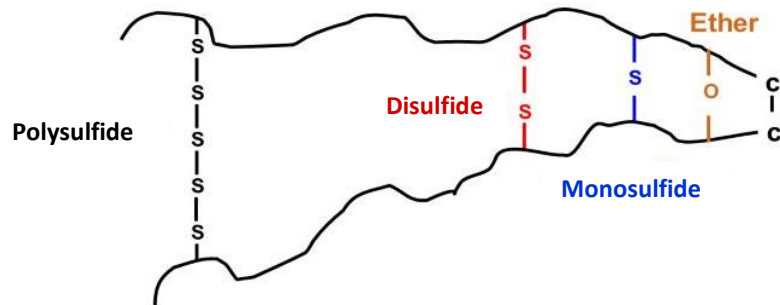
This is the reason why Sulfur is always used with:

- Activators, stearic acid and zinc oxide, are activating the vulcanization reaction and thus promote the reaction of the sulfur.
- Accelerators that will act on the vulcanization reaction to:
  - Increase or limit the vulcanization rate. We talk about superfast, fast or slow accelerators.
  - Permit the triggering more or less faster or slower of the curing reaction.
  - Allow the formation of more or less bridges. We talk about high or low modules accelerators.

The accelerators are used in small amounts.

There are other curatives:

- Peroxide: for (almost) all rubbers
- Metal oxides: specially for CR (polychloroprene)
- Formophenolic resins: specially for butyls and EPDM



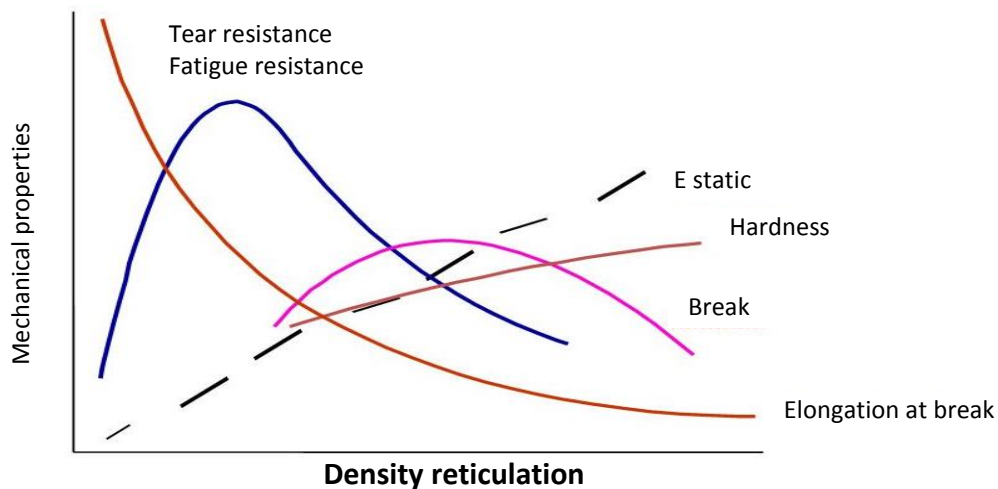
Peroxide systems (peroxide + co-agent) are almost universal vulcanization systems for saturated elastomers (Silicon, FPM, EPM ...) and unsaturated (EPDM, BR, IR, NR, SBR, NBR), leading to the formation of bridges (C-C-), more thermally stable than the sulfur bridges.

The nature of bridges formed and the mechanical properties differs according to the vulcanizing agent used. The energy to break a covalent C-C bond is 343 kJ/mol, while the energy to break a C-S bond is 276 kJ/mol and a S-S bond is 205 kJ/mol.

Also, the polysulfide bridges will be less resistant to heat than the disulfide bridges and the vulcanization with peroxides leading to the bridging C-C are more resistant to thermal aging.

The polysulfide bridges lead to better mechanical properties (breaking strength, tear and fatigue).

The evolution of the main mechanical properties depending on the density of reticulation can be represented by the following diagram:

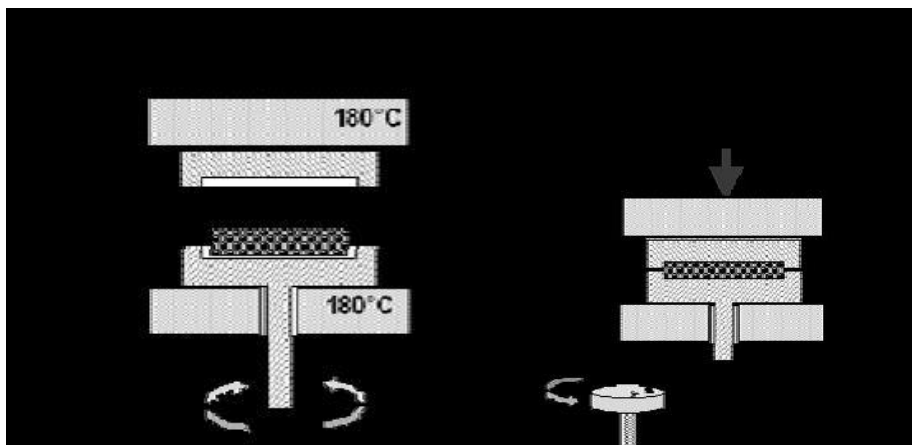


Depending on the bridging density, some properties will be improved and other altered. One has to find the best compromise to achieve the optimum characteristics with respect to the expected product function and the requirements of process for its industrial implementation.

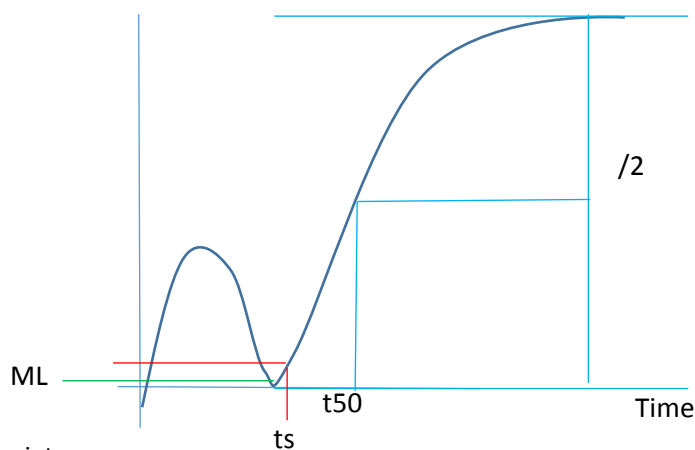
The proceeding and the speed of the chemical reaction can be followed with a rheometer. We measured continuously the opposition of the rubber to a sinusoidal oscillation for a given time and temperature.



If a thick vulcanized piece is made, one uses slow cure speed and low vulcanization temperature (130-140°C). The goal is to vulcanize evenly the part. Remember that the rubber is a good thermal insulator. A too high temperature would cause an outside vulcanization and an under vulcanization at the core.



Torque



ML = minimum viscosity point

ts = ML + 5 points, maximum time at constant T°C before vulcanization

t50 = time at 50% of vulcanization process. The lower, the faster the vulcanization process.

T90 = time needed to finish the vulcanization (180°C)

The ideal compound is represented by a ts high, a t50 and t90 very fast. After the vulcanization, the compounds are filtered to eliminate pollutions. Otherwise, we could have a scorching problem, ie non dispersed particles into the matrix.

In order to see more details and to go deeper in the rubber behavior and vulcanization, one could look at the "rubber\_technology.pptx" presentation.

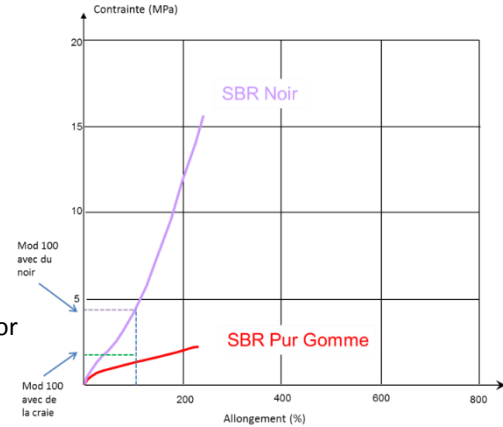
## 3. Fillers

### 3.1 General properties

Fillers can be described by the increase of the stress for a given elongation

Fillers incorporated in an elastomer are used in order to:

- Increase the mechanical properties:
  - break strength,
  - modulus,
  - tear strength,
  - abrasion resistance,...
- Improve specific properties:
  - gas waterproofness with talc,
  - fire resistance with aluminum hydroxide,
  - electrical properties with carbonized kaolin or conductive blacks,
  - the touch with talc,...
- Optimize the cost, the price of fillers is, mostly always, below the price of elastomers. The optimal rate with fillers will be evaluated to decrease the final price in the formulation.



It exists 3 category of fillers:

- Reinforcing fillers (enhance the mechanical properties)

Silica coupling agent, Carbon black

- Semi-reinforcing fillers

Silica without coupling agent, Carbon black, hard kaolin, chalk ( $\text{CaCO}_3$ ) precipitate

- Inert fillers

Natural chalk, soft kaolin, talc

### 3.2 Characterization

The characterization of the fillers is determined by the:

- Chemical activity with the surface (= chemical affinity with elastomer)
- Size of the elementary particles or specific surface
- Structure
- Shape

The surface chemistry determine the compatibility of the filler with the rubber:

- Carbon black are compatible with carbonated rubbers,
- Silica/kaolin which are made in surface with an  $-\text{OH}$  group are incompatible with carbonated rubbers; the addition of compatibilizing agents is required

The specific surface is inversely proportional to the size of particles. It is defined as the total surface area of a material per unit of mass.

Carbon blacks are defined by the size of particles (from 10 to 500 nanometers), silica's are generally fine particles while kaolin's and chalks are bigger particles.

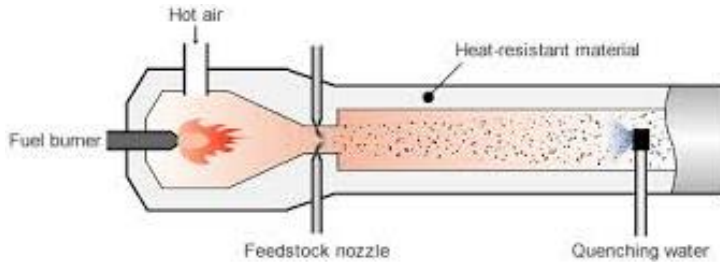
The sizes of particles have a direct influence on the properties of rubbers.

### 3.3 Carbon black

#### 1.1.1. Industrial process

This is a material produced by the incomplete combustion of heavy petroleum by the furnace method. Heavy petroleum are burned in an oven and quenching water is applied to block the combustion reaction. Depending on the oven control parameters (temperature, gas ratio or heavy oil / hot air, quenching water), we get different black grades.

The closer quenching water is to the flame, the smaller blacks will be.

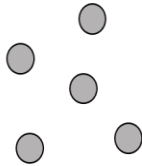


*Industrial furnace to produce carbon black*

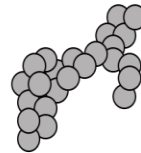
#### 1.1.2. Structure

The carbon black particles produced are spherical, called elementary particles. These particles don't exist in this state because they bind to form an aggregate. These aggregates are indestructible. The aggregate is the smallest dispersible component in a rubber matrix. These aggregates are also called primary structure.

##### Elementary particles



##### Primary structure



**INDESTRUCTIBLE**



These aggregates will congregate to form agglomerates or secondary structure under the influence of weak physical forces, non-covalent (Van der Waals, hydrogen). These agglomerates are destroyed during mixing.

The elementary particle size is important in the reinforcing/strengthening concept. For the same weight of carbon black, the smaller the particles are, the larger the surface area (or surface area available to be in contact with the polymer) will be and therefore the more important will be the reinforcement as more bounds will be formed between the elastomer and the aggregate.

The shape of the aggregate is also involved in the reinforcement because some carbon blacks are said low structure (= several tens of elementary particles), while others are high structure (= few hundreds of elementary particles).

We can observe in this case the occluded rubber or trapped rubber in the structure therefore unavailable, to participate in the deformation.

#### 1.1.3. Classification and designation

The designation of the carbon blacks allows us to have information on these notions of reinforcement/strengthening.

Carbon blacks are noted: N XYZ.

- N refers to NORMAL = no influence on the vulcanization kinetics
- X is a number that is related to the average diameter of the elementary particles (1 to 9). The higher the number, the more reinforcing
- Y is linked to the structure. If  $Y > X$ , we are in the case of an high structure
- Z is specific to each manufacturer

\* OAN (Oil Adsorption Number) structure index blacks by measuring the amount of oil absorbed by 100g of black, see Laboratories Characterization file.

The amount of carbon black introduced into a rubber matrix will directly impact properties such as the:

- Breaking strength
- Elongation at break
- Constraints for a given elongation (what is called in the rubber industry, the modulus)
- Hardness
- Tear resistance

Example of evolution of mechanical properties depending on the amount of SBR N330 introduced into a matrix

Example of evolution of mechanical properties depending on the grade of carbon black introduced in equal amounts (50 phr) in a SBR matrix

Example of corresponding mechanical properties between different grades and different amount of carbon blacks

### 3.4 White fillers

These fillers are from chemical nature:

- Silica =  $\text{SiO}_2$
- Talc =  $4 \text{ SiO}_2, \text{MgO}_3, \text{H}_2\text{O}$
- Kaolinite = Silicates aluminum hydrated:  $2\text{SiO}_2-2\text{H}_2\text{O Al}_2\text{O}_3$  (39.5% - 46.5% -14%)
- Chalk

White fillers are not based on carbon chemistry. That is why in the carbonaceous elastomers, white fillers do not provide any reinforcement in the majority of cases.

Their chemistry surface is incompatible: one cannot have a bond between the filler and the elastomer.

#### 1.1.4. Silica

To make the silica reinforcing the elastomer, we must introduce a bifunctional chemical in the rubber matrix. These products, silanes, will be able to hang on one hand the polymer and on the other the silica; they are called coupling agents.

#### 1.1.5. Talc

The use of talc is to improve the impermeability of the rubber with its lamellar structure (photo at the right). The orientation of the lamellas within the elastomer will create a labyrinth which will artificially increase the transit time of a fluid through the rubber.

#### 1.1.6. Kaolinite

This is a clay mineral which could allow a material to be more plasticized and to decrease the melting point.

#### 1.1.7. Chalk

Chalk is an inert filler which is mainly used to lower the price of rubber formula.

## 4. Plasticizers

### 4.1 Main plasticizers

Three families of plasticizers can be found:

- Mineral oils derived from petroleum refining: esters and ethers
- Synthetic plasticizers from petrochemical: aromatic oils, eradication, naphthenic oils and paraffinic oils.
- Vegetal plasticizers: for food applications, they are often more expensive (soybean oil, peanut oil, rosin ...)

### 4.2 Purpose of plasticizers

The plasticizers which are incorporated in the rubber matrix have the following functions:

- Facilitating the implementation in the mixing phase and in the final processing stage: introducing a liquid body in a very viscous matrix
- Providing the flexibility: The insertion of fillers may be possible if only there is mobility between molecular chains. The fillers will be inserted more easily during the mixing operation
- Adjusting the mechanical properties (elongation, hardness ...): introducing a liquid body in a rigid matrix
- Providing specific properties (resistance to cold, self-lubricating, decreasing hardness, increasing elongation at break, ...)

Thus, the image of the preparation of a cake, the introduction of an oil/fat is essential for the consistency of a homogeneous mixture and soft after cooking.

### 4.3 Choice of plasticizers

The choice of a plasticizer will depend on the:

- Chemical compatibility with the rubber: if the plasticizer selected is not compatible with the elastomer (chemistry too different...), an exudation of grease/oil on the surface will be seen quickly after the vulcanization
- Permanence of the plasticizing effect:
  - All plasticizers do not have the same boiling points. One must choose a compatible plasticizer having a boiling point farthest from the service temperature at the risk of seen a premature evaporation of the plasticizer and therefore variations of mechanical properties of the rubber during service
  - All plasticizers do not have the same solubility parameter. One must choose a compatible plasticizer with the elastomer and incompatible with the fluid in contact. If the choice is wrong, we risk seeing the plasticizer migrating to the fluid and therefore variations in mechanical properties of the rubber during service.
- Migration of aromatics: some plasticizers can migrate to the surface in contact with the part and leave halos
- Required properties (mechanical resistance to cold, heat, UV, implementation, price ...)

### 4.4 Properties of plasticizers

**Molecular weight and chemistry:** the choice of plasticizer is a function of the chemistry of the elastomer to allow its solubility and hence its compatibility.

For example, aromatic oils are particularly compatible with the SBR (Styrene Butadiene Rubber), natural and butadiene rubber (BR), esters with more polar elastomers such as nitrile rubber (NBR) and paraffinic commonly used oils in EPDM.

It will also depend on fluid in contact with the finished product.

**Viscosity:** the higher the viscosity, the higher its implementation will be difficult but it will be more permanent in mixtures and vulcanized rubbers.

**Flash point:** Ignition temperature of the oil vapor. The higher the temperature, the lower the oil will volatilize during the implementation or the vulcanization or service.

**Freezing temperature:** the lower the temperature, the better the cold behavior of the vulcanized rubber.

## 4.5 Effect on the properties

Properties	Effect of the addition of plasticizers
Viscosity	↓
Hardness	↓
Modulus for a given elongation	↓
Elongation/Break	↑
Resistance/Break	Equivalent or ↓
Compression set	↑
Cold resistance	↑
Swelling in a solvent	↓

## 5. Protective agents

### 5.1 Introduction

Elastomers are organic materials which are sensitive to the environment. To protect them we add some chemical compounds.

Some deterioration could appear.

### 5.2 Explanation of the degradation in the material

It is due to the breaks inside the elastomeric chain and/or on sulfur links. Reticulation process carbon-carbon and/or new sulfur links could have been created which lead to a hardening. Unsaturated elastomers (double bounded carbon, NR, NBR, BR) and a Sulfur cure system are the most sensitive to those deterioration.

### 5.3 Factors

Temperature, oxygen, ozone, UV, mechanical stress. They also can combine with each other's: thermo-oxidative aging, fatigue thermo-oxidative aging and photo-oxidation aging (Black mix are less sensitive to this phenomenon).

### 5.4 Determination of the factor

Thermo-oxidation is seen in the thickness of the part with more marks on surface, hardness is higher. Fatigue thermos-oxidation is located in a stress concentration. Apparition of cracks and the material become brittle. Ozone does parallel cracks and perpendicular to the stress. Those cracks could be very located. Photo-oxidation is seen only in surface, we could observe an increase of hardness.

## 5.5 Solutions

First, make sure that the elastomer has been well chosen to be used in defined service properties (T°C, environment, ozone,...) and the cure system is optimized.

Second, is it possible to decrease the thermal stress or mechanical stress?

Third, add protectives agents:

- Anti-oxidants: chemical protection. We use one primary agent which will trap the radicals (= molecules very actives at the origin of the degradation) and a secondary anti-oxidant which will limit the formation of the radicals.
- Anti-ozonants: Chemical barrier, anti-ozonants will migrate into the surface to react faster with ozone than elastomer with ozone
- Physical barrier: anti-ozonants will migrate into the surface to form a film to protect the part. This kind of system cannot work in dynamic parts because the film cannot strain as the part, it will break and let the ozone pass through.
- Anti-UV: stabilizer agent (or UV absorbers), antioxidants which will capture free radicals and limit the degradation process or minerals pigments (black fillers protect with transforming solar energy on thermal energy).

## 5.6 Limits

All those products need a migration into the surface. We can then have exudation or evaporation, washing, chemical consumption etc...

There are no perfect solution at the moment to protect the rubber.

See below a list of general families of protectives agents used for elastomers:

Class Antioxidant	Antioxidant Activity	Flex-Cracking Activity	Antiozonant Activity	Discolouration	Staining	Volatility	Solubility	Chemical Stability	Cost Ratio
Monohydric hindered phenols	Good to poor	Mod. to poor	none	Slight to mod.	Slight to mod.	Low to mod.	No bloom	Stable	0.70-1.00
Bis-phenols	V good to Mod.	Mod. to poor	negligible	Moderate	Moderate	V low to low	No bloom	Slight oxidation	0.65-2.50
Polyphenols	V good to Mod.	Mod. to poor	negligible	Slight to mod.	Slight	Very low	No bloom	Slight oxidation	1.50-5.50
Phenolic sulphides	Good to Mod.	Mod. to poor	negligible	Moderate	Moderate	V low to low	No bloom	Slight oxidation	2.00-2.50
Phosphites	Good to Mod.	Mod. to poor	none	Slight	Slight	V low to low	No bloom	Hydrolysis	0.60-0.70
Alkylated Diphenylamines	Good to Mod.	Moderate	negligible	Mod. to considerable	Moderate	V low to low	No bloom	Slight oxidation	0.95-1.05
Aryl naphthylamines	Good	Good	negligible	Considerable	Moderate to considerable	V low to low	No bloom	Oxidation	1.75
Polymerised dihydroquinolines	Moderate	Moderate	Moderate	Moderate	Slight	Low	No bloom	Slight oxidation	1.05-1.25
Acetone-diphenyl-amine products	Good	V good to good	Moderate	Considerable	Considerable	Moderate	No bloom	Oxidation	1.05
Dialkyl-p-phenylene diamines	Good	Good to mod.	V good to good	Severe	Severe	V low to low	No bloom	Considerable oxidation	1.60-1.75
Aryl-alkyl-phenylenediamines	Very Good	Very good	V good to good	Severe	Considerable to severe	V low to mod.	No bloom	Oxidation	1.25-2.00
Diaryl-phenylenediamines	Very Good	Very good	Good to mod.	Severe	Considerable	V low to low	Possible bloom	Oxidation	1.35-2.25

V = very, Mod. = moderate

# VI - Mixing

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This process consists in incorporating raw materials according to a defined order and to disperse them evenly in the matrix.

## 1. Mixing process

### 1.1 Dry mixing

It is a continued process by mechanical grinding, without solvent, which generates the heating of raw materials, promoting the absorption of products between them. This heat can be harmful because the mixture can vulcanized before the shape of the products.

Therefore, those mixers are equipped with a cooling device and the T°C of the mixture is one of the critical feature of the process.

### 1.2 Wet mixing

It is a discontinued process with non-chlorinated solvents. The applications with this mixer are for dissolution products such as adhesives rubber-based.

## 2. Mixers

### 2.1 Open mixer/mill or cylindrical mixer

This machine is simple and solid with two parallel and horizontal cylinders rotating in opposite directions at different speeds (10-25 RPM.) The friction ratio (=shearing of materials) and incorporation of the products depend of the speed difference between those two cylinders.

### 2.2 Closed mixer/mill or internal mixer

The internal mixer contains one chamber, two rotors (reverse) to work the materials and to incorporate them, a hopper, a ram to prevent materials to go up and to maintain a compacting pressure to improve the efficiency of mixing and then a discharge door to evacuate the product.

The walls are cooled or heated by fluid circulation. Capacity 1-400L. Rotor speed 20-80RPM.

## 3. Dosage and mixing steps

Units in phr: per hundred rubber. For a base of 100 type of elastomer, other products are proportional to this base (see weigh-in sheet example below).

### 3.1 Weigh-in scale or recipe

#### 1.1.1 Open mill:

If we want to make 1kg of this formulation on an open mill, we have to determine the proportion of each materials compared to the elastomer base.



Mult. coeff. = quantity to product / total products = 1000g/136g = 7.353

Formulation	phr	Weight (g)
Elastomer	100	735
Carbon black	30	220
Plasticizer	5	36.8
Vulcanization agent	1	7.35
Total	136	999.15

### 1.1.2 Closed mixer:

If we want to make 20L of this formulation in a closed mixer, we have to determine the proportion of each materials compared to the elastomer base. Density is calculated regarding suppliers information. Considering the phr as a mass (kg), we could say that:

Volume (L) = phr (kg) of product / density (kg/L), theoretical density of total compound = 136/131.3 = 1.04

Formulation	phr	Density	Volume (L)
Elastomer	100	0.92	108.7
Carbon black	30	1.80	16.7
Plasticizer	5	0.92	5.4
Vulcanization agent	1	2.07	0.54
Total	136	1.04	131.3

Mult. coeff. = quantity to product / total products = 20L/131.3L = 0.152

Formulation	phr	Weight (kg)
Elastomer	100	15.2
Carbon black	30	4.6
Plasticizer	5	0.8
Vulcanization agent	1	0.2
Total	136	20.8

To verify the data, one could check if the density of the mixing is good by: *total mass of product / Volume of the mixer* = 20.8kg / 20L = 1.04 kg/L which is the same than the total density calculated before.

## 3.2 Mixing steps

- Plasticization of the raw elastomer to soften him and facilitate the incorporation of other products
- Addition of vulcanization agents
- Addition of fillers and various products
- Follower mixer to cool, homogenization, incorporation of cure system (accelerators, dies,...)
- Blending
- Cooling and packaging by making a batch-off, depositing an anti-tack agent (anti-sticking), drying and packaging

NB: in an open mill, the addition of the vulcanization system comes after otherwise there is a scorch risk of the product.

## 4. Laboratory control

In order to control the product, several tests in laboratory are made such as the viscosity (Mooney, knowing the consistence of the mixture, avoid self-heating...), rheometry (determine torque settings, scorch time...), hardness, aging tests (ozone, oxygen, T°C...), tensile strength, abrasion resistance, DSC, DMA, DRC etc...

To see in more details those tests, please refer to the file [Laboratory\\_characterizations.docx](#).

# Process

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## 5. Extrusion

This process is used to obtain long products with small section, called profiles (pipes, seals or windshield, electric cables,...) which will be then vulcanized. EPDM seals are generally produced on an extrusion line.

It represents only 10% of finished products processing techniques against 85% by molding and 5% for calendering. It is also the most used technique for the manufacture of semi-products, blanks, intended either as direct molding (O-rings large) or vulcanization on shape (elbows), or in making more elaborate pieces (bands bearings, high pressure sleeves ...).

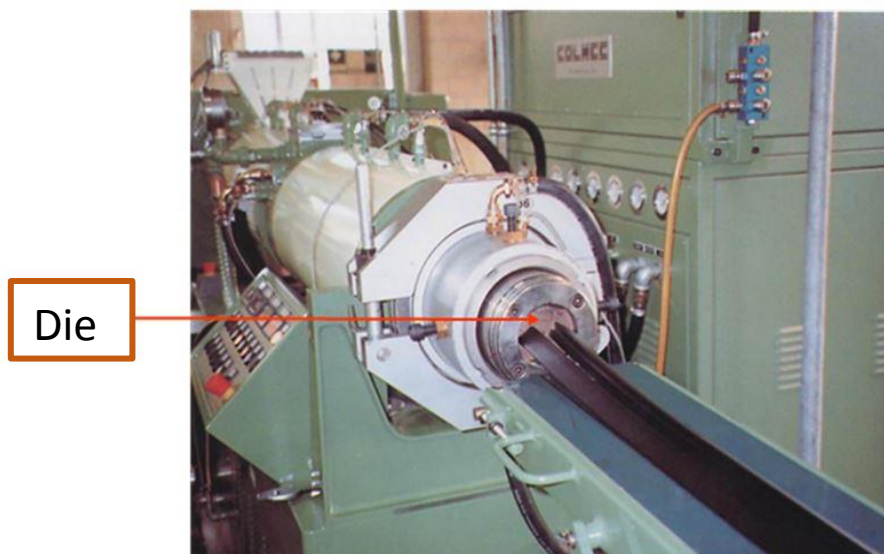
Extrusion has emerged in the rubber industry for several reasons:

- The complexity of the section of certain profiles prohibits molding processing because the preparation of such molds would make the cost prohibitive of the manufacturing parts
- Extrusion is the only method to obtain products of large length over the section
- Due to changes of devices and vulcanization techniques, extrusion allows continuous manufacturing of complex products at a lower cost.

### 5.1 Principle

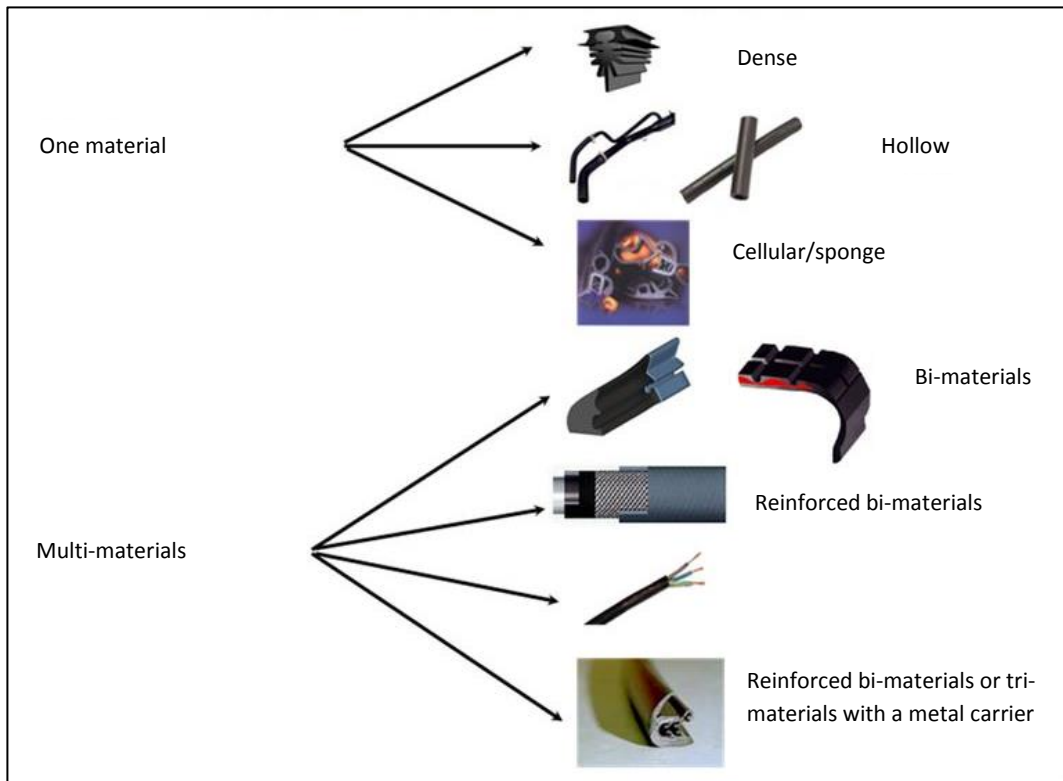
The extrusion is a thermomechanical process by which the compressed mixture is forced through a die (a metal block with a shaped orifice through which material is extruded) having the section of the piece to be obtained. Inside each extruder, different areas, called bodies, are presents. These bodies are not systematically at the same temperature, it depends on the mixture used. Then, air can be blown inside the tubing.

The resulting profiles are then cured discontinuously or continuously.



## 5.2 Different kind of profiles

The die is the main element of the extruder and which can be complex depending on the profiles, in particular polycomponents profiles, metal rubber or textile rubber for example.



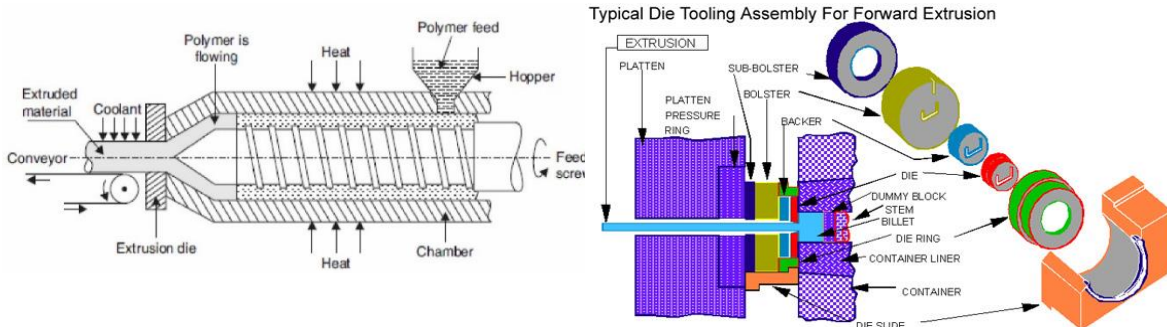
The dies are very important parts because the openings practiced there determine the shape and dimensions of the profiles.

This opening (or profile) generally has neither the form nor the dimensions of the profile to obtain because the walls of the die slow the mixture and causes lower flow velocities at the edge than at the center.

The excess material accumulated at the center resulting in swelling which depend in particular on the viscosity of the mixture.

## 5.3 Extruder

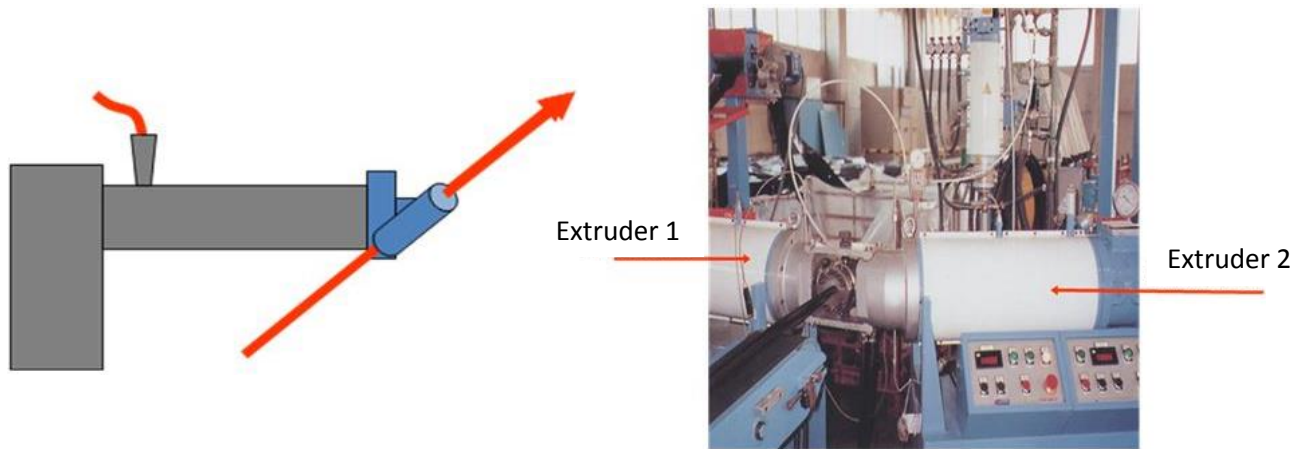
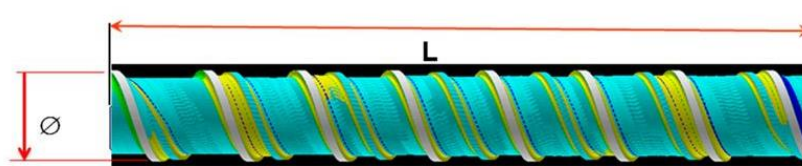
The extruder consists of a cylindrical body, thermally regulated, wherein rotates a lead screw driven by a geared motor unit. At the rear is a feed hopper into which is introduced the mixture in the form of plates or granules. The mixture is then driven by the screw to the head of the extruder where is put the die to which the shape of the profile depends.



To achieve multi-component profiles will be used extruders with "head angle" or "crosshead" or for making bi-material profiles, one can use several extruders. Extruder designation.

## 5.4 Extruder designation

The screw is the main body of the extruder and it gives its name. For example, an extruder 60-12D contains a 60 mm diameter screw and a length of  $60 \times 12D = 720$  mm.



Examples of designation of extruders:

- ANDOUART: 40-5D  $\rightarrow L = 200$ mm
- LESCUYER: 45-20D  $\rightarrow L = 2000$ mm
- BERSTORFF: 60-17D  $\rightarrow L = 1020$ mm
- RHEOMEX: 19-10D  $\rightarrow L = 190$ mm

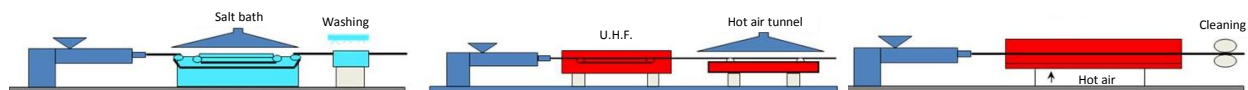
## 5.5 Principle of vulcanization

After extrusion of the raw profile there are two principles of the vulcanization.

### 5.5.1 Discontinued vulcanization

In this type of curing, raw profiles, are introduced in autoclaves (curing under air pressure or steam) or in hot air ovens without pressure.

### 5.5.2 Continued vulcanization



Several techniques are used:

- Bath salt

For the vulcanization in a salt bath, the profiles are immersed in a stainless steel tray and filled of salts of a mixture of potassium nitrate and sodium electrically heated. The solution is very fluid and

perfectly penetrates the interstices of the profiles. It is therefore a direct heating characterized by a heat transfer 50 times faster than in a hot air oven.

- **Oven UHF (Ultra High Frequency) + Hot air**  
The profile is driven into a tunnel then subjected to electromagnetic waves High Frequency. The temperature rise is homogeneously at any point in the profile. However microwaves gradually losing their effectiveness, there is a significant risk of under vulcanization profiles. To avoid it, a UHF tunnel is always followed by a hot air oven.
- **Hot air tunnel**  
The hot air vulcanization comprises passing the profiles through a tunnel furnace in which circulates the air heated by a heat exchanger, electric heaters or infra-red radiation tubes.
- **Ballotini oven**  
The profile passes through a fluidized bed of glass beads called "Ballotinis". The ovens are divided into 12 areas in which the temperature can vary from one to another. In general, the temperatures are about 180-210°C at the head and about 240-260 °C at the end. Because of agitation, hot air bubbles appear, which will give the tubing shape. According to the agitation, we will have different shapes. The glass beads are here to convey the heat. At the end of the oven, the vulcanization is finished.

The steps after are:

- **Cleaning and washing** all the residues made during the process (beads,...)
- **Tubing perforating:** This step permits to degas the seal. Some gas remains captive inside (gas resulting from vulcanization, blown air). These vent holes are also here to allow the swift and balanced release of air upon door closure.
- **Post-forming:** to finish forming the seal, in particular the carrier is closed; and then, with a cutting head, a cut is made on the seal at the correct length. The seal arrives at low speed at the cutting head and some sensors measure the seal position before cutting it.

In general, mixtures for extrusion must be specifically formulated for:

- Providing smooth profiles
- Allowing a cure without significant deformation (compromise between the sag profile and mesh)
- Do not over inflate the die exit (compromise between plasticity and elastic recovery)
- Replying to the corresponding specification

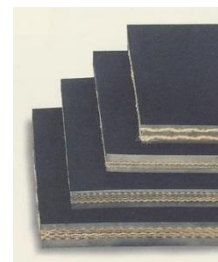
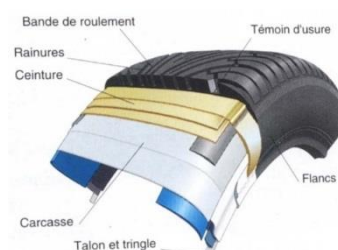
## 6. Calendering (=roller leveling)

These techniques produce objects of great length, large width and small thickness: 0.1mm to 2mm for calendering and 0.01mm to 0.1mm for coating.

This process only represents 5% of finished products in rubber processing techniques.

They are used particularly for the manufacturing of raincoats, carpets, inflatable boats or diving clothing (in cellular rubber).

It is also a technique for preparing flat semi-finished products for the manufacture of tires or compression molded parts, conveyor belts or belts, carpets, coating and printing cylinders.



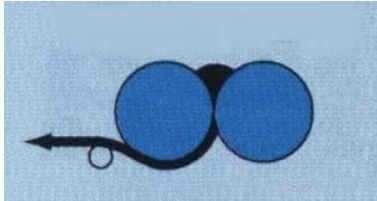


It consists in obtaining, from a “dry” raw rubber mixture, a homogeneous sheet, smooth and even by passing between the cylinders of a calender.

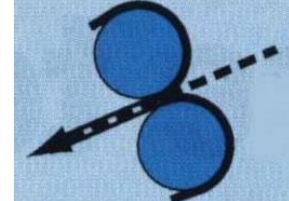
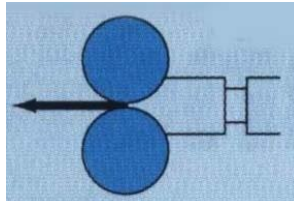
Mixtures for calendering should include:

- Few fillers to prevent the sheet from breaking and obtain thicknesses less than 0.5mm
- A very good plasticity: ML (1 + 4) at 100 ° C of 40 to 70 Mooney points to obtain minimum 0.09mm thickness and less than 25 points Mooney to obtain sheets lower than 0.25mm
- Vulcanization systems without reversion and not grilling

Calendering process can be done in two cylinders:

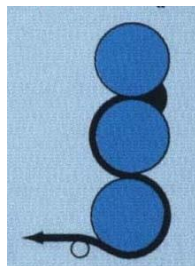


For the draw of all rubber sheets, for calibrating a sheet already prepared,

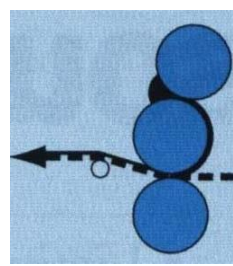


for cold lamination

Calendering can also be done in three cylinders:

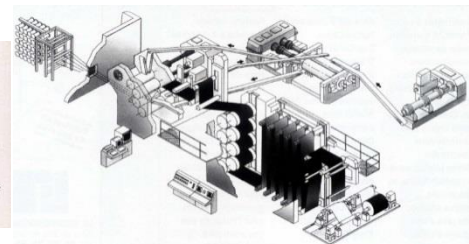
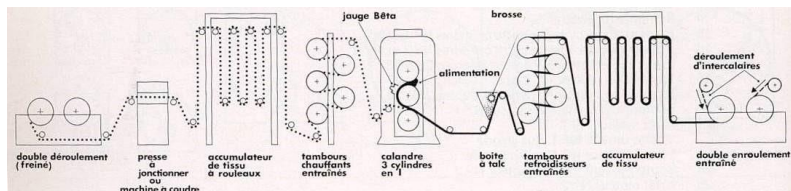


For the draw of all rubber sheets,

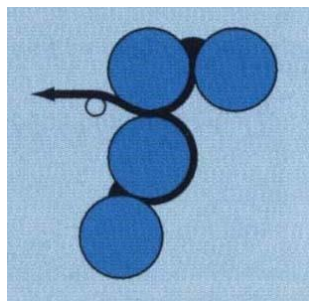


for covering the rubber with a fabric

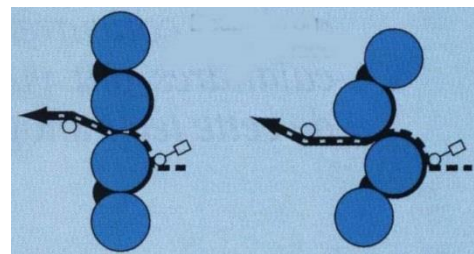
The calendering line 3-cylinders consists of several devices for the unwinding and winding the coated fabric to obtain continuous large lengths in rolls.



Calendering can also be with four cylinders or calendering "two sides": which is used especially for the manufacture of tire carcass:



For the draw of rubber sheets (bi material),



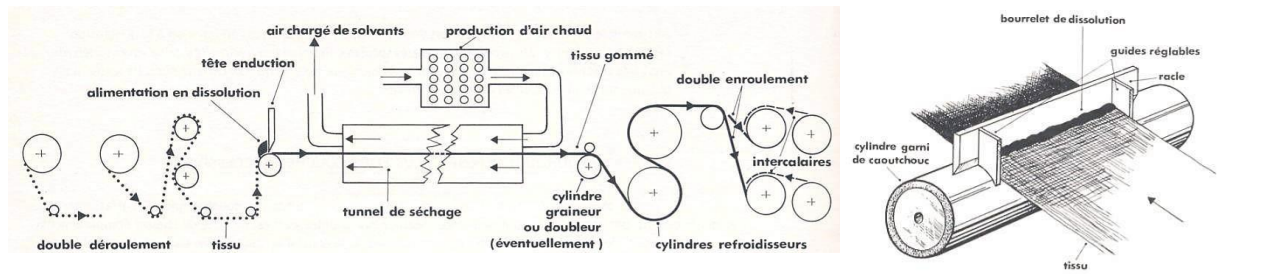
for covering 2 sides of a fabric simultaneously

## 7. Coating

It consists in obtaining from a liquid raw rubber mixture, a film on a homogeneous fabric, smooth and even by passing between the cylinders of a coater.

The coating is a complementary process to the calendering which includes all techniques for depositing thin layers of liquid rubber (latex or dissolution) on a textile backing.

The coater consists in a cylinder surmounted by a scraper blade and two adjustable guides forming a reservoir for receiving the liquid mixture.

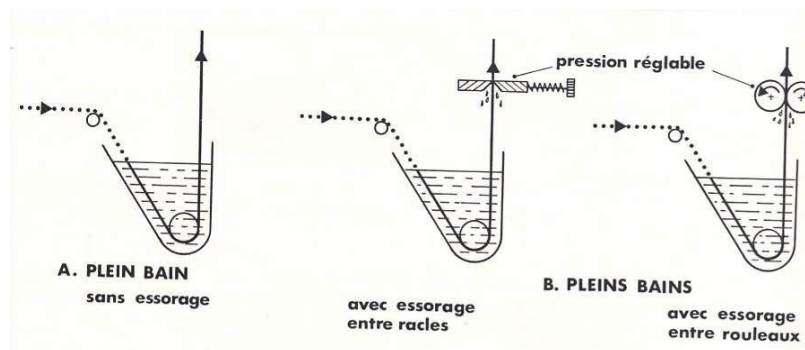


The coating line as the calendering line, fitted with accessories to:

- allow the progress of the fabric
- ensure drying of the water or solvent
- realize the winding with an anti-sticking interlayer

The impregnation is complementary to the coater, it:

- Uses the technique of immersion or "full bath"
- Is used for coating "double-sided"
- Imposes a low viscosity and high wettability liquid



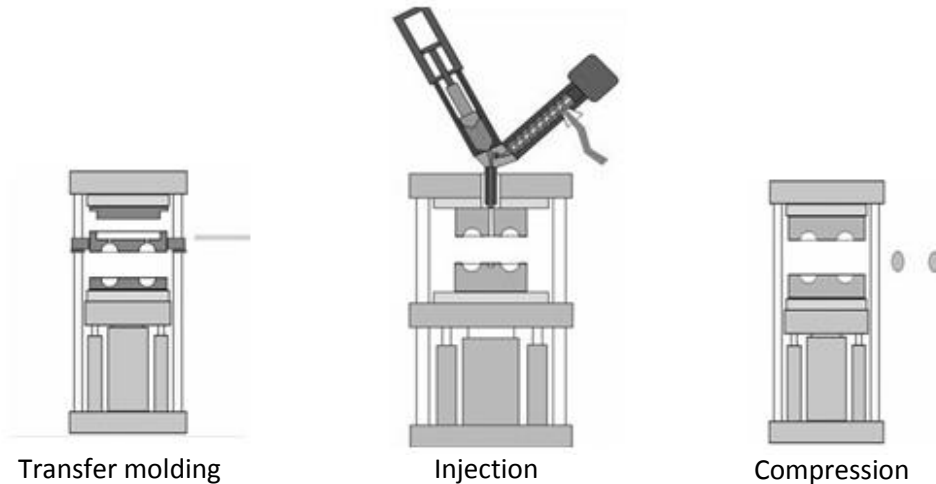
The sheets obtained by these techniques are:

- Either used as semi products and then make complex parts (tires, belts, boats ...)
- Or vulcanized to obtain a finished product.



## 8. Molding

This process represents 85% of used processing techniques. Three techniques are used by molding. The part is vulcanized by putting it into a mold with a press (140-210°C). Easy parameters settings, big parts, small series.



- Transfer molding: Put preforms in a transfer cabin, located above the cavities. The material is transferred to the cavity by the transfer nozzles.  
Small parts, large series, simple sketches, loading faster, curing time divided by 3 because the mixture is heated in the passage in the nozzles, uniformity is better, fill in the cavity is simultaneous, more complex molds.
- Injection molding: Recent process, plasticize and heat the mixture in a metering extruder then injected into a closed mold.  
Introduction of the mixture into the mold at a temperature close to the vulcanization, very short cycle time (divided by 10), large molding series, high investment, large parameter settings.
- Compression molding: more used process, represents 80% of the tonnage of molded parts, less evolved, less expensive, principle of the waffle device, drop off preforms then curing under pressure.  
Number decisive footprint, complex sketches and a volume greater than the footprint to mold filling, vulcanizing heterogeneous and difficult to reproduce  
Manual release, and compulsory finishing to remove burrs

## 9. Adhesion

Industries are increasingly using assemblies associating elastomers with different materials. These assemblies, often referred to as "composites", cover a wide range of applications and meet various requirements. The final use of the "Composite", the nature of the materials to be assembled, the economic requirements determine the best of the process to be used.

## 9.1 Elastomeric assemblies - flexible supports

Elastomer-textiles, first intended for the waterproofing of fabrics in order to obtain a good protection against the weather, then for the tire industry, inflatable boats, inflatable structures, flexible tanks, floor and wall covering, belts and conveyor belts.

Several processes are commonly used, necessitating in all cases a preparation of the textiles (degreasing, to remove impurities from the textile and / or Coating or impregnation with latex or mixing solutions by spraying, blade or single contact for the lowest technical characteristics bleaching and drying according to the fibers):

- Pretreatment of textiles and adhesive baths type RFL (Resorcin, Formaldehyde and Latex) for more technical applications
- Self-adhesive mixes
- Or mixed techniques for the most severe applications

## 9.2 Rigid elastomer-rigid assemblies

Mainly rubber-metal or elastomer-rigid plastics (steel, stainless steel, aluminum, zinc, polyamide, PTFE, glass).

Originally, the vulcanized elastomers were assembled to their rigid supports by the usual mechanical means: screws, bolts, nuts,... Besides their weight, these assemblies were cumbersome and long to realize.

The appearance of the adhesives allowed to limit the weight, the bulk and the assembly time, but the characteristics of the bonds in time and temperature remained poor.

The appearance of chemical adhesives called "bonding agents" made it possible to adhere almost all the elastomers to most rigid supports of good quality and high reliability in solving problems of temperature resistance and longevity.

This method of adhesion is widely used for the production of technical parts such as tank lining, armored profiles, electric cables, safety shoes, tire cables, cylinder lining, engine supports, supports Bridges or anti-seismic devices,... for industries of:

- Automotive
- Aerospace
- The SNCF (French high speed train)
- Household appliances
- Printing / stationery
- Marine
- Bridges and highways
- Energy (electricity, wind ...)
- The chemical industry

### Glue adhesion

Assembly at ambient temperature and contact pressure only

Dissolutions

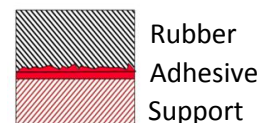
Cyanoacrylates glues, epoxy glues, polyurethanes glues



### Adhesive adhesion

Assembly impossible without the elevation of temperature and a higher pressure to the contact pressure

Ebonite, chemical adhesives, brass



## 9.3 Principle

Good adhesion is conditioned to a great extent by the prior treatment of the surfaces to be adhered. These surfaces must be perfectly clean, chemically active and of an appropriate relief.

The preparation of the supports is classified into two groups:

- Mechanical processing
- Chemical treatment particularly recommended for non-ferrous metals including stainless steels

The nature of the substrate will therefore determine the surface treatment.

Mechanical	Processing	Chemical
<b>Solvent</b>	Degreasing Removing grease and oxyde	Acide agent Neutral agent Alkalines wash
<b>Blasting (only ferrous metals)</b> <b>Sandblasting</b> <b>Abrasion</b> <b>Rectification or machining</b>	Pickling Create a mechanical or chemical hook	Specific bath according to alloy
<b>Degreasing (removing dusts)</b> <b>Drying</b>	Finishing	Passivation (protection against oxidation) Drying

### 9.3.1 Adhesion with chemical bonding agents

A good adhesion agent must be the most versatile (or universal) possible, ie to offer the maximum possibilities of combinations of rubber with materials of very varied nature.

The basic elastomer of the mixture determines the family of adhesives (polyvalent or specific)  
The hardness of the mixture and / or vulcanization mode (molding or autoclave), temperature and vulcanization time determine the best type of adhesive in a family.

For vulcanization temperatures below 130 ° C or above 170 ° C, it is necessary to select a more specific adhesive.

Also for very short vulcanization times, it is necessary to choose a very reactive adhesive and for very long times, adhesives resistant to aging in temperature.

The operating conditions of the finished product direct the choice to an adhesive system: monolayer or bilayer (especially for easily oxidizable substrates or severe applications).

The thickness of the film obtained is essential for the reaction to be optimal. Failure to comply with the recommended mini / maxi thicknesses may cause excessive separation or adhesive defects.

The formulation of the mixture will also play an essential role in achieving a quality assembly (eg low and high hardness are more difficult to adhere).

The bonding agents react under the influence of pressure and temperature. The reaction develops at the same time as the vulcanization of the mixture and follows the rheometric curve of the mixture.

The adhesion increases with the crosslinking of the agent.

### 9.3.2 Injection molding, compression, compression-transfer or extrusion

All vulcanization methods are suitable for adhesion when they combine heat and pressure. Nevertheless, precautions are necessary in the case of the molds with large number of impressions when the loading is manual: the first insert deposited in the mold undergoes a preheating which can bake the adhesive. A semi-automated loading is then recommended.

Likewise, in the case of a thick rigid support, preheating is recommended at low temperature in order to avoid baking the film while insuring a temperature heating of the inserts. Finally, the use of release agent (especially based on silicone) should be avoided as it is particularly harmful to the adhesion. In any case, the vulcanized part must cool before being checked.

The adhesion of the elastomers to various supports now appears easy. If it implements methods that are simple in theory, they are complex in practice, requiring great care and almost permanent control of the three main operations in order to obtain a quality adhesion: Preparation of supports, coating the substrates with the bonding agent and vulcanization of mixtures.

# VII - Cellular rubber

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## 1. Applications

The alveolar materials result of the desire to introduce in a controlled manner a certain proportion of gas-filled cavities in a polymer matrix skeleton in order to:

- increase flexibility: *raw latex foams for furniture*
- improve the insulating nature, thermal or sound: *foams for the building*
- make a damping material: *packaging foams*
- lighten the material by preserving structural properties



Only for insulation, the global market worth billions of dollars. The good compressibility and elasticity, absorbency and surface adhesion make even today's the foam rubber unique.

Here are some areas in which foam rubbers are used:

- Automotive industry such as puncture-proof tire or door seals, Aerospace navigation such as insulating sleeve, Shipbuilding such as portholes of sealing profiles,...
- Electrical industry, Equipment construction and steel construction, Technical household appliances and sanitary, Ventilation and air conditioning technique for drain cleaning,...
- Building machinery tools such as parts for the extraction of parts or as a buffer on the labeling or as paint application roller
- Paramedic such as orthotics

## 2. Structure

The alveolar rubber is a rubber having many cells (either open or closed, or both) distributed throughout its mass.

There are 3 types of structures:

- Sponge rubber provided with a skin and inside consists of adjoining cells, also known as semi-closed structure
- Cellular rubber, completely closed cell material and without skin, generally
- The microporous or micro cellular rubber, to the extent that the cells are invisible to the naked eye.

Alveolar rubbers can be both flexible and rigid (as porous ebonite for example).

To obtain this honeycomb structure, we add to the mixing a product capable of decomposing under the action of heat by releasing a gas, called blowing agents, which by diffusion in the material lead to the formation of cells that are "fixed" during vulcanization.

The blowing agents commonly used (Azodicarbonamide or Dinitrosopentamethylene Tetramine) release usually nitrogen or carbon dioxide from a certain temperature.

The art of the rubberman is to allow gas evolution before the rubber part is completely cured.

The differences in properties between a compact rubber and a cellular rubber are mainly physical introduced by the presence of these cells:

- The density of the foamed rubber is less than 1 as compared with the density of a compact one generally near 1.2, allowing relief of the end products;

- The cellular rubber parts are much more flexible than compact rubber, hardness between 20-90 Shore A, whereas we will measure rather light foam materials, which is its resistance to crushing
- The compressive stresses are much lower for cellular rubber while maintaining a good residual compression set (return to initial state after crushing). This feature is used for example in the hood seals, and car door to reduce the closure forces while ensuring a good seal to the air and water in the time.
- The swelling in water of cell mixtures is less than 5%
- Alveolar rubber parts can be produced by molding and continuous extrusion.

### 3. Process

#### 3.1 Molding

##### 3.1.1 Open cells

Sponge rubber has open cells, communicating between each other's.



- The preform's volume has to be slightly smaller than the mould's volume.
- The blowing agent is decomposing into gas and the totality of the volume is filled
- The mixture expands freely during the vulcanization
- The closure pressure has to be very weak to allow the imprisoned air in the mold to escape

##### 3.1.2 Close cells

Cellular rubber has close cells, non-communicants between each other's.



- The preform fills completely the mold
- The blowing agent is decomposing during the vulcanization into a compressed gas
- The expansion is made during the opening of the mold, after vulcanization
- The closure pressure has to be very high

In the case of a sponge, the operator unmold the part.

In the case of a cellular, at the opening of the mold, the part will eject alone of the mold cavity.

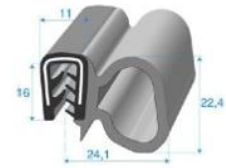
This phenomenon is taken into account when designing a cellular mold mitigating right angles to avoid the tearing of the part.

To do this, the viscosity of the mixture should be very low, the weight and positioning of preforms have to be precise as the nature and amount of blowing agent.

The decomposition temperature is the main selection criterion.

### 3.2 Extrusion

This process is made with UHF (Ultra-High Frequency) followed by a hot air tunnel to obtain cellular part in continue (sealings,...). With the use of several extruders and dies, the sealings have the possibilities to be mono-component, bi-component or tri-components ( hard plastic carrier recovered by a hard rubber where a tubular cellular part will be fixed.



# VIII - The sectors of revalorization of rubbers

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Since the clarification of vulcanization in 1839 by Charles Goodyear, the scientists are looking for techniques to develop the matters contained in scrap rubber. This scrap rubber can be generated during the cycle of production (technical waste like injection carrots or rejected products...) or to correspond to products at the end of their lifetime like worn tires.

The need for developing scrap rubber was particularly marked during the periods of raw material shortage (WWII). For more than 15 years, the pressures from the society have been increasingly strong to avoid waste. Taking into account the rarefaction in the long term of the resources, it is important to adopt good practices on the matter.

## 1. Technical challenge

For some materials, in particular the metallic materials, recycling is easy and is very largely practiced. Gold for example is melted and remelted ad infinitum. The recycling of polymeric materials, and more particularly those of vulcanized rubbers is more complex, in particular, due to the irreversibility of the process of vulcanization. Techniques, detailed after, exist nevertheless and make it possible to obtain by mechanical or chemical way secondary raw materials which will be used only or more frequently in cutting with virgin raw materials.

## 2. Regulation

The European and French regulation clearly defines the hierarchy of the different modes of processing waste: Upstream, to prolong the lifetime of the products while supporting, by maintenance/repair, the re-use (Retreading of pneumatic tire for example).

For waste, to implement the hierarchy of the following modes of valorization:

- Re-use (second-hand tires for example)
- Recycling (granulation...)
- Energy valorization

## 3. Sector of the pneumatic use

In France and in most European countries, the collection and the valorization of the worn pneumatic tires are the object of the responsibility of the producer.

The texts stipulate the assumption of responsibility by the setters on the market (manufacturers of pneumatic tires, importers...) waste collection and processing of pneumatic tires within the limit of tonnages which they put on the market the previous year.

Since now more than 10 years, the holders of worn pneumatic tires (mechanics for example) must obligatorily give the pneumatic tires dismounted to collectors approved by an green-organization (Aliapur, FRP,...). After sorting, these pneumatic tires will be re-used for the market of second-hand or directed towards platforms of valorization.

## 4. Retreading and circular economy

Retreading consists in replacing the worn tread of a pneumatic tire after being assured the quality of the carcass. This technology aims main objective to exploit all the potential of the carcass.



A healthy carcass can know a second, even a third life. The life of the pneumatic tire of trucks is thus multiplied by 2.5 on average, compared to a non-retreaded pneumatic tire, and can frequently traverse 600 000 km on a driving axle, even 1 million km in certain cases.

The increase in product life which results from this contributes to decrease the kilometeric cost price, a criterion under high surveillance in the world of road transport.

This choice, which fits completely in a circular logic of economy, presents two major advantages on the ecological level:

- On one hand, it undervalues in a substantial way consumption of raw materials and energy compared to the solution consisting in entirely manufacturing a new pneumatic tire
- On the other hand, this phase of maintenance/repair which retreading constitutes supports the lengthening of the product life and thus delays the appearance of waste. In France, for only the pneumatic trucks, that corresponds to a decrease of more than 40 000 tons of the pneumatic tires at the end of the lifetime to treat.

## 5. Material

Up to date, three principal processes of material valorization are used:

- Crushing/Granulation/Micronization
- Regeneration
- Pyrolysis

### 5.1 Crushing/Granulation/Micronization

Scraps rubber go through various mechanical operations (shredding, crushing...) aiming the reduction of their size and at separating rubber from the possible inserts (textile and metal in particular). According to the granulometry obtained, one will speak about aggregates, of fine micronized powder, the finest particles.

The fine powders are frequently used with a binder (polyurethane resin for example) for the manufacturing of playgrounds, of part of tram, tracks of athletics, synthetic grass...

They can also be in asphalt in order to obtain road mix with weak sound emission or in a thermoplastic matrix to manufacture molded pieces.

The micronization is a technique of processing waste of production used for the proper needs for the company. The formulation of waste is known and makes it possible to reintroduce the products resulting from the micronization in the same formulations.

If one introduces 20% of product resulting from the micronization, the forfeiture of the mechanical properties is about 5%. This degradation is acceptable for certain applications, but not for others (ex: treads of the tires).

<http://www.aliapur.fr/fr/les-applications/voies-de-valorisation/la-valorisation-matiere> (French link)

### 5.2 Regeneration

The reclaim rubber (chemical regeneration) was carried out during many years with a rubber waste processing in solvent medium. It was abandoned (except in India) a few years ago for economic reasons (low costs of the raw materials).

Today this process would not be authorized any more within sight of the toxicity of the products used. Thermomechanical Regeneration constitutes a close technique. It is based on a double screw which makes it possible to have a continuous rubber band which can be directly reintroduced in the product.

### 5.3 Pyrolysis

Pyrolysis is defined as the decomposition of a carbonaceous product under the effect of heat and in the absence of oxygen. In this manner, one obtains, from scrap rubber and more particularly worn tires, black product, oil and gas:

- Black products: the blacks obtained currently by pyrolysis are relatively close to the carbon black.
- Oil: If the process is well controlled, one obtains a hydrocarbon product which the composition is close to the kerosene (C8-C10-C12)
- Gas: One obtains "syngas"  $\text{CO} + \text{H}_2$ .

## 6. Energy valorization

Energy valorization is the use of scrap rubber (waste of worn production or product) crushed or not (whole tire for example) like fuel of substitution for the energy production. This energy is used to provide heat and/or electricity.

It is thus the calorific value of the rubber which is required when this one is flaring. By way of an example, on a volume of approximately 300 000 tons of worn tires collected each year by the Aliapur sector, 29% are intended for an energy valorization.

Applications concerned with energy valorization: [District heating Cement factories](#) (French links)

# IX - Industry of the rubber

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## 1. Global production

In 2013, global production has exceeded 27 million tons (12 million tons of natural rubber, 15 million tons for synthetic rubbers). 28 million tons should be achieved in 2014.

### 1.1 Chinese domination over the rubber industry

China has become the last ten years a major player in the market for rubber. In terms of consumption, the country ensures the transformation of 37% of global natural rubber and 35% synthetic rubber. China, sixteenth supplier of tire in France in 2000, advanced to fifth place in the first half of 2014. In industrial Rubber, China went from the fifteenth place in 2000 to the seventh in 2014.

### 1.2 European business world premieres seats

In 2014, there are 3 European companies in the top 5 tire manufacturers (Michelin, Continental, and Pirelli) and in the top 5 technical rubber parts manufacturers (Continental, Hutchinson, Freudenberg). The world's leading manufacturer of synthetic rubbers Lanxess and the world's largest rubber manufacturer Arburg Freudenberger.

Europe develops efficient research centers for the rubber sector including Michelin Ladoux Research Center, Hutchinson Montargis Research Center, Hamburg Continental Research Center, Goodyear-Dunlop Research Center in Luxembourg and has a representation structure of rubber industry based in Brussels ETRMA (European Tire and Rubber Manufacturers' Association).

In 2014, several European laboratories, ERLABB, consist of three European laboratories: French LRCCP, DIK German and Italian CERISIE. Strengthening partnerships with CETIM Technical Centre for Mechanical Industries and Carnot Institutes, public research organizations which allows companies including LRCCP to provide innovative solutions, integrating multidisciplinary interfaces essential to the progress of the sector companies.

### 1.3 Rubber in France: large companies and successful SMEs

In France, the major processors represent less than 5% of the total number of rubber companies, but account for over 80% of sales or employment in the sector. France has more than a hundred SMEs in positioning products highly diversified markets. Some of these companies have managed to acquire some very specific expertise in niche markets and have become hyper-specialists recognized at European or even global level.

## **2. World production of tires in 2014**

Estimated worldwide sales of tires in 2014 = \$ 180 billion / -3% compared to 2013

## **3. Rubber industry in France**

### **3.1 France key figures in 2014**

Production: 0.74 million tons

- Tires: 400 000 tonnes
- Industrial Rubber: 340 000 tonnes

Sales for the business sector (2211Z and 2219Z): 12 billion €

- Pneumatic: 7.2 billion €
- Industrial Rubber: 4.6 billion €

Employees: 47 200 people

- Tires: 25 400 people
- Industrial Rubber: 21 800 people

### **3.2 The main producers of synthetic rubber in France**

- Exxon Chemical France
- Lanxess Emulsion Rubber and Elastomers
- Michelin

### **3.3 Exports performance in France**

Exports: 4.7 billion €

- Tires: 2.7 billion €
- Industrial Rubber: 2 billion €

Export rate = 61%

### **3.4 Industrial rubber transformers in France**

250 companies in 2014, including 130 companies of 20 employees or more.

National Champions:

- World No. 2 Michelin in tires (2014)
- Hutchinson, No. 2 worldwide in Industrial Rubber (2014)

Large groups:

- Continental, Trelleborg, Freudenberg, Cooper Standard France, Goodyear / Dunlop, Bridgestone, Avon, West Pharmaceutical, Sacred, Sealynx ...

SMEs:

- Independent or related to groups

### 3.5 Industrial rubber transformers in 2013

Rank	Companies	Sales – in Millions €	Group
1	HUTCHINSON	1 400	TOTAL SA
2	COOPER STANDARD FRANCE	260	COOPER
3	TRELLEBORG INDUSTRIE	130	TRELLEBORG
4	FREUDENBERG SAS	120	FREUDENBERG
5	WEST PHARMACEUTICAL	120	WEST PHARMA
6	STELMI	100	APTAR
7	SCAPA	60	SCAPA
8	TRELLEBORG MODYN	50	TRELLEBORG
9	ANVIS France DECIZE	50	TRI
10	CARBODY	50	BAVARIA