RAW MATERIALS AND COMPUNDS IN RUBBER INDUSTRY

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SUMMARY

Within this module, the different types of compounding ingredients are discussed. The chapters focus on the following ingredients:

- Polymers
- Fillers
- Curing systems
- Plasticizers
- Anti-degradants

For all these ingredients, the most relevant details concerning production processes and structure are given, and their properties and application fields are discussed. Interactions between different ingredients are explained, and preferred combinations are mentioned. Elastomers are always used in functional applications, like tires, hoses, bearings, sealings etc., where energy savings, safety, and the specific properties like rubber elasticity play a crucial role.

The first sub-chapter focuses on the different types of **polymers**. The most important one is natural rubber (NR): Still 45% of the worldwide rubber consumption consists of natural rubber, which is a durable resource. Besides this ecologic aspect, natural rubber plays an important socio-economic role in the Far East where a significant part of the economy benefits from natural rubber production. As a natural product it's properties are influenced by environmental and seasonal variations. Natural rubber has one unique property: it shows strain crystallization, making the material exceptionally strong. Isoprene rubber (IR) is the synthetic counterpart of NR, but the properties of IR are significantly different from the properties of NR. It is mainly used in combination with other general purpose rubbers. Styrene-Butadiene rubber (SBR) is by far the most important synthetic rubber and widely used in tire applications. It is sulfur-vulcanizable and gives rubber-elastic properties; the styrene accounts for the damping, needed for the skid resistance of tires.

Ethylene-propylene-diene rubber (EPDM) and its saturated counterpart EPM are very durable rubbers. EPM can only be vulcanized with peroxides as it is fully saturated. EPDM has an unsaturation in the side chain giving it a very good aging resistance. Butyl rubber (IIR) is a specialty rubber that is used in inner tubes because of its low gas permeability.

Butadiene-acrylonitrile rubber (NBR) distinguishes itself from NR and SBR in its good resistance against non-polar substances like gasoline, diesel fuel, oils and fats, good ageing resistance and good resistance to chemicals. Chloroprene rubber (CR) distinguishes itself by good flame-resistance properties due to the chlorine atom. Contrary to the other diene rubbers, CR is vulcanized with metal oxides like MgO and ZnO, not with sulfur. Fluororubbers (FKM) allow the highest use temperatures, up to 240°C. These products have a very good oil resistance. Silicone rubbers (Q) distinguish

themselves by a good high temperature, ozone and UV resistance, good cold flexibility, little temperature dependence of the mechanical properties.

The second sub-chapter is focused on **fillers**, active or reinforcing fillers and non-active or non-reinforcing fillers. With activity or reinforcement, commonly all kinds of rubber/filler interactions are described which express themselves in physical properties. The processes occurring during mixing of polymers with fillers are described. The general properties the fillers and their effects on the structure of the material and the properties of the rubber are discussed. Carbon black and silica are discussed more in detail and compared in terms of filler and properties and reinforcing effect.

The following sub-chapter deals with **plasticizers**: They are added to the compound in order to improve the processability and to reduce the material costs. Mineral oils, or oils directly obtained from crude oil refining, as well as synthetic oils are used. The choice for a mineral oil is made based on the VGC index, a measure of the polarity of the oil. The synthetic oils are all highly polar and mainly used for polar elastomers.

Another important sub-chapter is **vulcanization**. The basics of sulfur vulcanization are given, and the most important accelerators, activators and retarders are described. This crosslinking process can be used for unsaturated polymers. In contrast to this, peroxide curing can be applied to all polymers which do not tend to decompose under the influence of radicals. Typical peroxide/coagent combinations are given. Sulfur- and peroxide-crosslinked polymers are compared in terms of properties. Other curing systems such as oxides, resins and amines are briefly elaborated.

Rubber compounds can be degraded by a wide variety of environmental influences: oxygen, ozone, light, metal ions and heat. Therefore **antidegradants** are important to protect rubber against aerobic aging (oxygen) and ozone attack. The last sub-chapter is dedicated to these additives. The most important classes of antidegradants are discussed and their efficiencies are compared

After studying this module, the student has a good overview of the different types of polymers, fillers, curing agents, plasticizers and anti-degradants, their properties and application fields. He can make a choice of different compound ingredients depending on the final application of the material and the required property profile.

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CHAPTER 1   POLYMERS

In recent years, a great variety of synthetic elastomers have been developed besides Natural Rubber. In the first place, they were meant to replace Natural Rubber in tire applications. Later on, specialty elastomers were introduced for applications where Natural Rubber and its synthetic counterparts were found to be less suitable. The most important elastomers with their specific characteristics and applications are further detailed in the following sections.

1.1   Natural Rubber (NR)

Structure:
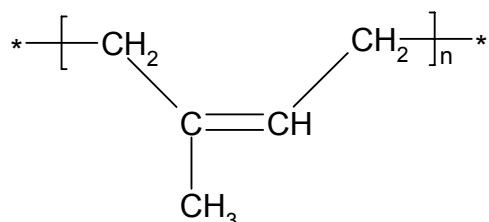
Figure 1-1: Structure of natural rubber (cis-polyisoprene).

It is obtained from the milky substance, latex, tapped from the "Rubber tree": Hevea Brasiliensis.
The latex contains 30 – 38 % solids, colloidally dispersed and stabilized by proteins.

There are other NR-producing plants and trees:
- Euphorbias, to which the Hevea Brasiliensis also belongs;
- Most of the Ficus-types;
- The Guayule shrub (cactus-like plant, which grows in New Mexico);
- The Russian dandelion.

The production of latex is a natural way of protection of the plant against damage, by formation of a dried skin layer on top of the wound.

Winning of NR:
- Hevea trees are multiplied via grafting. The first tapping can then be done 6 – 8 years after planting;
- Tapping occurs via a "half-helix" notch around the Hevea tree; every two days the notch is scratched open;
- The yield is around 2000 kg NR/ ha./year;
- The latex is diluted with water to 12 – 18% solids content;
- Next, the latex is coagulated with formic acid or acetic acid. The latex coagulates at pH 5.1 – 4.8;

- The coagulum immediately needs to be processed further, in order to protect it from bacterial attack.

- Processing to Smoked Sheet:
    o Aluminum partitioning plates are placed in the coagulum, which results in sheets of ca. 4 cm thickness;
    o The water is squeezed out via a consecutive series of rollers: sheets of 2 – 3 cm thickness;
    o These sheets are dried in "smoke"-houses by exposing the rubber to hot smoke from wood and nut shells;
    o This takes 2 – 3 days;
    o And gives light – dark brown rubber bales.

- Processing to Pale Creep:
    o In order to remove the acids and other organic pollutants, the coagulum is washed several times with water;
    o Water is squeezed out via a consecutive series of rollers;
    o Air-drying for 10 – 12 days;
    o This gives white to light brown rubber bales; the sheets can still be seen in the bales.

- NR is a natural product subject to seasonal and regional influences. It is therefore impossible to apply narrow quality specifications, apart for some basic requirements for purity. Standardization of the NR-types is done according to the SMR (Standard Malaysian Rubber) standard:
    o Prescribes delivery in bales, wrapped in plastic foil;
    o Gives maximum values for:
      Contaminants, ash content, volatile substances and copper, respectively manganese contents.

- Non-stabilized NR (the main part) degrades pretty fast under the formation of gel, caused by branching to a fully crosslinked material by a reaction between aldehyde-groups in the NR (present because of the smoking step) and the NH2 – groups from the proteins present. This requires a pretreatment of the NR called: mastication. During the mastication process the viscosity is decreased by breaking the crosslinks and branches mechanically by shear forces on a two-roll mill.

- Some stabilized types of NR are less sensitive towards gelation. Stabilizer: hydroxylamine salts.

Strain crystallization of Natural Rubber

Natural Rubber shows, contrary to other synthetic rubber, the special characteristic of reversible crystallization on stretching and releasing. This gives the natural rubber a huge reinforcement, which appears as a strong increase of the modulus on stretching. The resulting tensile strength may be a factor of 10 higher than the tensile strengths attainable with synthetic rubbers. Compare for instance NR and SBR; see Chapter 6.4.

In order to understand the origin of this strain crystallization, we go back to the network model, as introduced in Chapter 3. Consider a piece of rubber. If under isobaric conditions at a certain temperature Tm under stretched conditions, part of the rubber is crystalline and the other part is amorphous, the condition for phase equilibrium reads:

Figure 1-2: Tapping of NR-latex.

$$F_c(T_m) = F_a(\lambda, T_m)$$

(**1.1**)

With :
Fc(Tm)   = Helmholtz free energy of the crystalline phase at Tm;
Fa(λ,Tm)   = Free energy of the amorphous, non crystallized phase at Tm and relative strain λ.

If Tm0 is the melting temperature of the rubber under non-stretched conditions (λ=1), it holds:

$$F_c(T_m^{\,0}) = F_a(1, T_m^{\,0})$$

$$(\mathbf{1.2})$$

By subtracting Eq. (1.2) from Eq. (1.1) we obtain:

$$F_c(T_m) - F_c(T_m^{\ 0}) = F_a(\lambda, T_m) - F_a(1, T_m^{\ 0}) = [F_a(\lambda, T_m) - F_a(1, T_m)] + [F_a(1, T_m) - F_a(1, T_m^{\ 0})]$$

$$(\mathbf{1.3})$$

or:

$$\left[F_c(T_m) - F_a(1, T_m) \right] - [F_c(T_m^{\ 0}) - F_a(1, T_m^{\ 0})] = F_a(\lambda, T_m) - F_a(1, T_m)$$

$$(\mathbf{1.4})$$

The left hand side of Eq. (1.4) corresponds to the difference between the Helmholtz free energies of the crystalline and amorphous (non stretched) phases at Tm, minus the difference in free energy of the crystalline and amorphous (non-stretched) phases at Tm0. Because:

$$-S = (\partial F / \partial T)_{l,V}$$

$$(\mathbf{1.5})$$

The left hand side of Eq. (1.4) can be rewritten as:

$$[F_c(T_m) - F_a(1, T_m)] - [F_c(T_m^{\ 0}) - F_a(1, T_m^{\ 0})] = -\Delta S_m \cdot T_m + \Delta S_m \cdot T_m^{\ 0}$$

$$(\mathbf{1.6})$$

With:
ΔSm   = Difference in entropy between the crystalline and amorphous phase in non-stretched conditions.

If we assume that this ΔSm in first approximation does not depend on temperature, and with:

$$\Delta H_m = T_m \cdot \Delta S_m$$

$$(\mathbf{1.7})$$

With:
ΔHm   = Crystallization enthalpy.

It follows that:

$$\left[F_c(T_m)-F_a(1,T_m)\right]-\left[F_c(T_m^0)-F_a(1,T_m^0)\right]=-\left[(\Delta H_m/T_m)T_m+(\Delta H_m/T_m)T_m^0\right]=-\Delta H_m(T_m-T_m^0)/T_m$$

(1.8)

The right hand side of Eq. (1.4) corresponds to the increase of the free energy of the amorphous rubber with strain λ at temperature Tm. In its simplest form we know this part from the network model:

$$\Delta F_a(T_m)=T_m\Delta S_{strain}=-\tfrac{1}{2}\nu kT_m\left(\lambda^2+2\lambda^{-1}-3\right)$$

(1.9)

Combining Eq. (1.8) and Eq. (1.9) finally results in:

$$1/T_m=1/T_m^0-\frac{\tfrac{1}{2}\nu k}{\Delta H_m}\left(\lambda^2+2\lambda^{-1}-3\right)$$

(1.10)

At a certain value of strain or deformation the crystallization or melting temperature Tm increases. The amount of increase depends on the heat of crystallization or heat of melting of the polymer.

Table 1.1: Crystallization enthalpies and crystallization temperatures of some rubbers and thermoplastics.

Polymer	ΔHm [kJ/mol]	ΔHm [J/g]	Tm0[°C]
Natural rubber	4.5	66	ca. -14
Trans- polybutadiene	9.2	170	ca. 100
Trans - polychloroprene	8.4	82	ca. 115
Polyethylene	7.8	280	ca. 110

Natural rubber has a relatively small crystallization- or melt- enthalpy, combined with a crystallization temperature of only −14°C (non stretched). This is below room temperature, but not so much. As a result, the crystallization temperature can easily be raised to above room temperature upon stretching, which means that the natural rubber crystallizes. On releasing the natural rubber and returning to the undeformed state the crystallization disappears again.

Important properties of NR

Mooney Viscosity ML (1+4) 100°C: 50 – 90 (depends on the season).

This strain-crystallization gives extra strength upon mechanical loading, which also occurs in the vulcanized state. In combination with the great number of unsaturated double bonds, which gives a high vulcanization yield, NR-vulcanizates show exceptionally high tensile and tear strength. The high abrasion resistance (tires) can also be explained by these characteristics of NR.

Other characteristic properties are:

- High network density → good rebound properties;
- High network density → low damping/low hysteresis / low heat built-up at dynamic deformations (the tire does not heat up much!);
- High network density → very good set-properties (at room temperature);
- Poor ageing resistance / ozone resistance, because of the unsaturation in the backbone. NR is very sensitive towards chain scission;
- Poor oil resistance.

Table 1.2 Specifications for Standard Malaysian Rubber (SMR)

Standardized Malaysian Rubber (SMR)

SMR was the first, and today still is the most important NR grade belonging to the group of Technically Specified Rubbers (TSR). As already mentioned, TSR's, including SMR, are marketed as compressed bales. The first SMR scheme was introduced in 1965 [2.56], and revised in 1979 [2.58]. As shown in Table 2.1, it comprises latex grades SMR L and SMR WF, sheet material SMR 5, field grade material SMR 10, 20, and 50 [2.59], the viscosity-stabilized latex grades CV and LV [2.60], and the viscosity-stabilized general-purpose grade SMR GP [2.61], which is a blend of 60 parts of factory processed latex and 40 parts of field coagulum. Specifications and test procedures are summarized in reference [2.62], and the main producers are listed in [2.57].

SMR's are graded for dirt content (indices in grade designations indicate dirt as multiples of 0.1%), ash content, and nitrogen content, in addition to volatile matter, and the so-called plasticity retention index (PRI) [2.63–2.65]. To determine this index, the ratio in plasticity of rubber before and after it has been heated for 30 minutes at 140 °C is multiplied by a factor of 100. The higher the index, the less the rubber degrades, and the better the uniformity of the compound viscosity during mixing processes [2.66]. The index also gives some indication as to the aging resistance that can be expected of the rubber. Depending on their purity, the different SMR grades have PRI values of 30 to 60.

Table 2.1: Standard Malaysian Rubber Specifications Mandatory from 1 January 1979

Parameter[a]	SMR CV	SMR LV[b]	SMR L	SMR WF
	Latex			
	Viscosity stabilized			
Dirt retained on 44μ aperture (max., % wt)	0.03	0.03	0.03	0.03
Ash content (max., % wt)	0.50	0.50	0.50	0.50
Nitrogen content (max., % wt)	0.60	0.60	0.60	0.60
Volatile matter (max., % wt)	0.80	0.80	0.80	0.80
Wallace Rapid Plasticity-minimum initial value (P_0)	–	–	30	30
Plasticity Retention Index, PRI (min., %)	60	60	60	60
Colour limit (Lovibond Scale, max.)	–	–	6.0	–
Mooney viscosity ML+4, 100 °C	–[c]	–[d]	–	–
Cure	R[f]	R[f]	R[f]	R[f]
Colour coding marker[g]	Black	Black	Light green	Light green
Plastic wrap colour	Transparent	Transparent	Transparent	Transparent
Plastic strip colour	Orange	Magenta	Transparent	Opaque white

[a] Testing for compliance shall follow ISO test methods.
[b] Contains 4 p.h.r. light, non-staining mineral oil. Additional producer control parameter: acetone extract 6%–8% by weight.
[c] Three subgrades, viz. SMR CV50, CV60 and CV70 with producer viscosity limits at 45–55, 55–65 and 65–75, units respectively.
[d] One grade designated SMR LV50 with producer viscosity limits at 45–55 units.
[e] Producer viscosity limits are imposed at 58–72 units.
[f] Cure information is provided in the form of a rheograph (R).
[g] The colour of printing on the bale identification strip.

Table 2.1 (continued)

Parameter[a]	SMR 5	SMR GP	SMR 10	SMR 20	SMR 50
	Sheet material	Blend	Field Grade Material		
		Viscosity stabilized			
Dirt retained on 44μ aperture (max., % wt)	0.05	0.10	0.10	0.20	0.50
Ash content (max., % wt)	0.60	0.75	0.75	1.00	1.50
Nitrogen content (max., % wt)	0.60	0.60	0.60	0.60	0.60
Volatile matte (max., % wt)	0.80	0.80	0.80	0.80	0.80
Wallace Rapid Plasticity-minimum initial value (P_0)	30	–	30	30	30
Plasticity Retention Index, PRI (min., %)	60	50	50	40	30
Colour limit (Lovibond Scale, max.)	–	–	–	–	–
Mooney viscosity ML+4, 100 °C	–	–[c]	–	–	–
Cure	–	R[f]	–	–	–
Colour coding marker[g]	Light green	Blue	Brown	Red	Yellow
Plastic wrap colour	Transparent	Transparent	Transparent	Transparent	Transparent
Plastic strip colour	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white

1.2 Synthetic polyisoprene (IR)

This is the synthetic counterpart of NR. It is not consumed in such high amounts as NR because of the high cost prize of the raw isoprene. Only in Russia there is traditionally a high capacity for IR (900 kTon/year), because of their former difficulties in obtaining sufficient amounts of NR.

Different kinds of IR are available, depending on the way in which the isoprene-molecule is built into the polymer: 1,4-, 1,2-, and 3,4- addition, respectively cis- and trans- isomers are possible. Furthermore, there are different possibilities in the direction of addition: head-head, taild-tail addition. Depending on the sort of catalyst, these different possibilities occur in various relative amounts. See Table 1.2.

There are two kinds of polymerization technologies in use for IR:
- By Ziegler-Natta coordination catalysis (TiCl4 and Al(alkyl)3 in a 1:1 ratio) in dry pentane or hexane;
- By anionic polymerization with Li-alkyls (n-Butyl-Li or s-Bu-Li), also in low boiling aliphatic solvents.

Especially the Ti-catalyzed polymerization is sensitive towards impurities in the reaction medium. As a result, the composition of the product may vary. The Bu-Li catalyst is far less sensitive and better defined. A disadvantage of the Bu-Li catalyst is, that the resulting IR contains less cis-linkages and as a result the resulting IR resembles less NR.

Table 1.2: Molecular structure of polyisoprene.

IR-catalyst	Cis-1,4 [%]	Trans-1,4 [%]	3,4 [%]	1,2 [%]	Branching	Gel [%]	molar mass [106 g/mol]
NR	100	0	0	0	much	variable	
IR (Ti)	98	0	2	0	little	20-30	1- 1.5
IR (Li)	92	1	7	0	no	0	1.5- 2

Main properties of IR, compared to NR

The molecular differences between NR and IR may seem quite small, but the properties differ to a great extent. In NR there are a lot of all kinds of non-rubber substances present, whereas in IR this is not the case. This gives IR less tendency to hardening. Furthermore, the small deviations in the microstructure of Ti-IR accounts already for a 100% increase in half life time at –20°C for crystallization (5 hours), compared to NR. Li-IR does not crystallize spontaneously at all. Processing and vulcanization characteristics are accordingly different.

The lack of strain crystallization is seen in the stress-strain diagram (green strength) of pure, unvulcanized NR versus IR: the lack of an upturn in the stress-strain curve for IR compared to NR, see Figure 1-3. The lower strength of IR gives rise to a worse abrasion resistance, lower modulus and lower tack, which is required for the production of tires.

For a quick comparison between IR and NR, see Table 1.3. Most differences can be explained by the different stress-strain behavior.
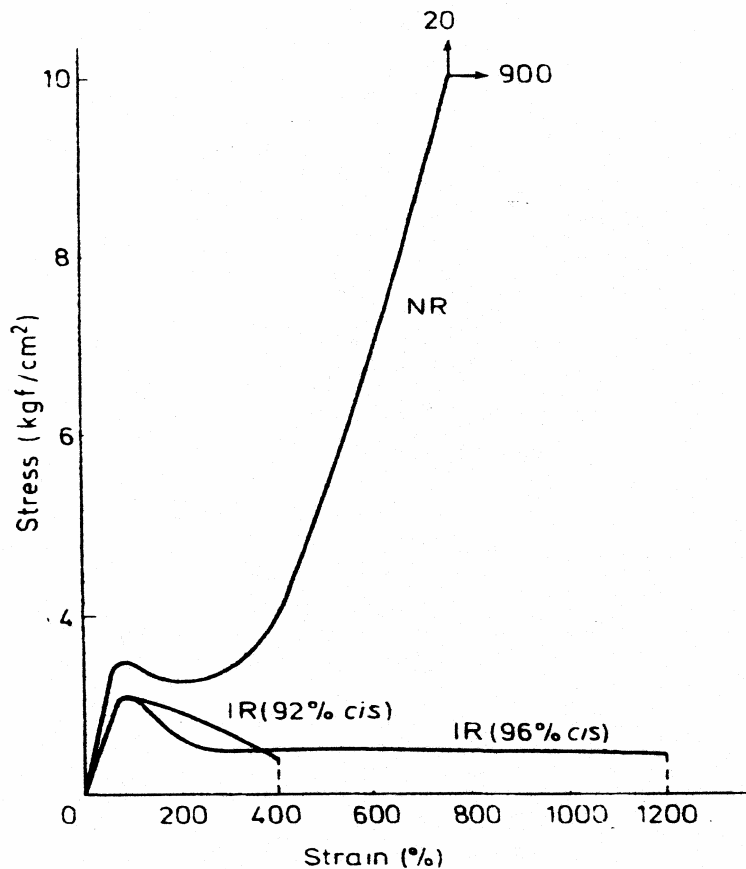
Figure 1-3: Green strength (tensile strength) of unvulcanized tire tread compounds based on NR and IR; strain speed: 10cm/min, temperature 25°C.

Table 1.3: Comparison of the most important properties of NR and IR.

	NR	IR
Processing:		
Mastication	-	+
Hardening on storage	-	+
Mixing time	-	+
Die swell	-	+
Tack	+	-
Green strength	+	-
Vulcanizate properties:		
Tensile strength	+	-
Tear strength	+	-
Abrasion resistance	+	-
Elasticity	=	=
Compression set	-	+

$+$ = Better; $-$ = worse.

1.3   Butadiene rubber (BR)

Structure:
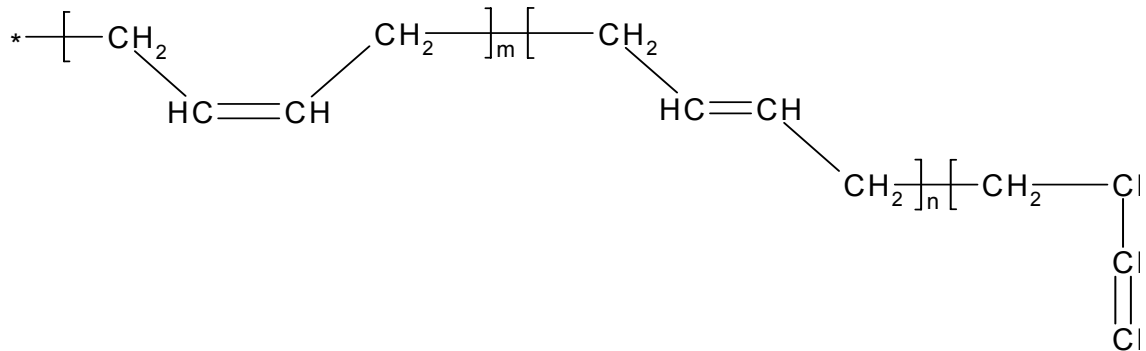
Figure 1-4: Structure of butadiene rubber with three different types of linkages: Cis-1,4 (m); Trans-1,4 (n); 1,2-Vinyl (o).

The ratio between the cis, trans and 1,2-vinyl structures depend on the catalyst system chosen. Normally, preference is for high cis contents (compare NR) for the best elastic properties.

Nowadays, BR is mainly produced with solution polymerization, with various catalyst systems.
A summery can be found in Table 1.4.

Ti – BR: via a Ziegler-Natta (coordination) catalyst: Ti I4/AlR3 or Ti I3 OEt/TiCl4 / AIR3 in benzene or toluene as solvent; temperature: 5 – 35°C.

Co – BR: same, with CoCl2 or Co-(octenate)2 with diethylaluminum-chloride or Et3Al2Cl3 in benzene or toluene as solvent; temperature 5 – 30°.

Ni – BR: same, with Ni(naphtenate)2/BF3 – etherate and aluminum-trialkyl in aliphatic or cycloaliphatic solvents; temperature: 50 – 60°C.

Nd – BR: same, with a carboxylate of Nd; a Lewis acid Et3Al2Cl3; an aluminum-alkyl like Et3Al, i-Bu3Al,
i-Bu2AlH; cycloaliphatic solvents; different temperatures between 0°C and 60°C. With increasing temperature the cis-content and the molecular weight decrease.

Li-BR: anionic polymerization with n-Bu-Li of s-Bu-Li as initiator. These polymerizations are 'living polymerizations' (polymerization takes a long time, the chains grow with an equal rate) which results in a very narrow molecular weight distribution. The cis-trans-vinyl content is strongly dependent on the polarity of the solvent: in general, cycloaliphatic solvents are used with the addition of well-defined amounts of THF or dimethoxyethane; temperature: 50 – 80°C.

Emulsion-BR: polymerized as latex in water, with a redox-system as activator. This way of production is hardly used anymore for vulcanized rubber applications. This type of BR is only used in its latex form as basis for the impact modification of polystyrene and ABS.

In general BR is characterized by a very narrow molecular weight distribution in comparison with NR or E-SBR (see later) and because of that, it shows a high degree of coldflow (flow of the bale during storage), especially the Li – BR and Ti – BR. In order to avoid this, a 'Mooney jump' is created after polymerization, for example by adding some traces of divinylbenzene to the Li – BR during the polymerization. This divinylbenzene contains two double bonds, which can act as a crosslinker. In this way, the molecular weight is slightly increased; the molecules are branched, respectively the molecular weight distribution is a bit broadened.

Table 1.4: Microstructure of different types of BR.

Catalyst used	cis [%]	trans [%]	vinyl [%]
Nickel	98	1	1
Neodymium	97	2	1
Cobalt	97	2	1
Titanium	92	4	4
Butyl-lithium	36	54	10
Emulsion pol.	9	72	18

Most important properties of BR

- Lowest Tg of all rubber polymers:
    o 100 % cis – 1,4 BR: Tg= -100°C;
    o 96 % cis – 1,4 BR: Tg= -90°C;
  Especially the vinyl content causes a higher Tg; pure 1,2 – vinyl BR is not rubbery but thermoplastic: Tg = -10°C; Tm = 126°C for the isotactic type and 156°C for the syndiotactic type.

- Very high network densities after sulfur vulcanization, because of the high degree of unsaturation. This gives high abrasion resistance, good elasticity, good tear strength at dynamic deformation, good elasticity at low temperatures, low heat build up (important for the tire application).

- However: low wet-traction or friction coefficient for tires on a wet road, low tensile strength (no strain crystallization).

BR is used in large amounts in tread recipes for trucks and cars, although never in its pure form. BR is always blended with SBR because of the low wet traction.

1.4   Styrene-butadiene rubber (SBR)

The most important counterpart of NR in tire applications is SBR. During the Second World War production was set up on a large scale in the US and in Germany.

Structure:

$$* \left[CH_2 - CH = CH - CH_2 \right]_n \left[CH_2 - CH \right]_m *$$
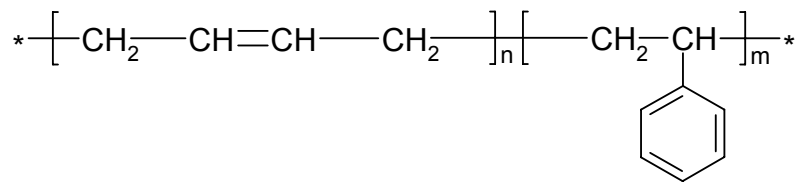
Figure 1-5: Structure of SBR.

It is by far the most important synthetic rubber. The butadiene gives the possibility to vulcanize with sulfur and accounts for rubber-elastic properties; the styrene does not contribute to the rubber elasticity, but accounts for the damping, needed for the skid resistance of tires. Depending on the ratio styrene/butadiene, SBR is a built-in compromise for optimum tire performance.

The butadiene and styrene are randomly distributed throughout the molecular chain. The styrene content lies between 23 – 40%, depending on the SBR type. Another important parameter is the way in which the butadiene monomer is built in: cis, trans or vinyl. The cis-type is the most flexible (see also NR and BR) one, the trans type is a bit less flexible and the vinyl configuration is the least flexible. The ratio in which the different configurations are built in, mainly depends on the catalyst used and the type of polymerization process.

1.4.1   Emulsion SBR (E-SBR)

This type of polymerization has always been the most important and cheapest process. It started in 1937 in Schkopau (former East Germany) as Buna S. The reaction was radically activated with potassium-persulfate, at 45°C; this required 30 hours for a 65% conversion: "Hot SBR". Later on, the reaction time was reduced by a redox-activated catalyst: 65% conversion in 3 hours at 40°C. The Hot SBR contains rather large quantities of gel (material crosslinked during the synthesis) and is hardly used anymore nowadays.

In 1940 and later, the so-called "Cold SBR" was developed in the US by redox activation at + 5°C.This product contains only small traces of gel. Nowadays about 97% of E-SBR is of the cold SBR-type.

Typical ingredients for an E-SBR process are:
- Emulsifiers: mixtures of Na-salts of fatty acids and rosin acids;
- Catalyst system: organic peroxides (oxidators) with sodium formaldehyde sulfoxylate, respectively $FeSO_4$ as reductor;
- Molecular weight controllers to prevent branch-formation: tertiary dodecyl mercaptane;
- Short stoppers: soluble dithiocarbamates and sodium-polysulfide;
- Stabilizers: phenolic (non staining) or p-phenylene-diamine type (staining);
- Coagulants for the flocculation of the emulsion: salts, acids, etcetera.

A disadvantage of the emulsion polymerization, besides the great variety of polymerization additives, is the limited possibility to control the polymerization structure. The only parameters, which can be adjusted, are the styrene/butadiene ratio and the molecular weight. As butadiene and styrene monomer show the same affinity towards the growing chain, one is in any way assured of a good statistically randomized order of the units in the polymer chain.

In Cold SBR the butadiene moiety occurs 9% in the cis, 76% in the trans and 15% in the 1,2-vinyl conformation. With a styrene content of 23% this results in a Tg of about −50°C.

Influence of the styrene/butadiene ratio:

With increasing styrene content:

- The polymerization time decreases;
- Less gel formation (gel formation occurs via the butadiene moiety);
- The Tg of the product rises;
- The wet skid-resistance of tires is improved (poorer network because of less butadiene);
- The ozone resistance improves (less unsaturation);
- The tensile strength and the abrasion resistance get worse (poorer network);
- The rolling resistance of the tires gets worse (poorer network).

Since long, the E–SBR types are standardized. A standard code, developed by The International Institute of Synthetic Rubber Producers (IISRP), is commonly used:

Series 1000: Hot E-SBR;
1500: Cold E-SBR;
1600: Cold E-SBR, masterbatches with 14 phr or less oil;
1700: Cold E-SBR, oil masterbatches;
1800: Cold E-SBR, oil-carbon black masterbatches with more than 14 phr oil;
1900: various other masterbatches.

Oil contents are normally 37,5 phr or 50 phr. Usually, highly aromatic oils are used, although sometimes also naphtenic oils are used. Because aromatic oils contain a

relatively high level of carcinogenic polycyclic aromatic compounds, there is a tendency in the tyre- and rubberindustry to replace those with low PNA-containing oils, which position themselves between aromatic and naphthenic. See also paragraph on oils. The SBR, which is mixed with the aromatic oils is usually delivered with staining p-phenylene diamine stabilizers; non-staining hindered phenolic stabilizers are usually used with light or colorless naphtenic oils. The staining stabilizers are in general better than the non-staining ones. And after all, staining cannot be seen in a black application!

Most important properties of E-SBR

- E-SBR can be delivered in all desired viscosities and no mastication like with NR, is needed;
- SBR does not show strain-crystallization like NR; in order to obtain good mechanical properties, reinforcement with highly reinforcing blacks or silica's is needed. Black-filled SBR compounds nevertheless show lower tensile strength, clearly lower tear strength and elasticity than NR;
- Skid resistance of tire treads is clearly better than with NR, because of the worse network;
- High heat built-up upon dynamic deformation (poorer network);
- Better fatigue and heat resistance than NR (less unsaturation in the main chain).

Applications of E-SBR, especially of the oil-extended types: tire treads of cars. Further a wide variety of technical rubber products like conveyor belts, sealings and profiles.

1.4.2   Solution SBR (SBR)

This SBR type is produced with lithium-alkyls as anionic catalyst in non-polar solvents (see BR). Under these circumstances the butadiene has a 300-fold higher tendency to attach to the growing chain than styrene. Without precautions, only a butadiene homopolymer would be produced out of a butadiene/styrene mixture of monomers. When the reaction mixture runs out of butadiene, styrene is slowly built in, more or less as a homopolymer. As a result a butadiene-styrene block copolymer is produced, see Figure 1-6. On addition of polar substances (ethers, amines) the copolymerization is directed towards a statistically randomized polymerization. Nevertheless, the structure of S-SBR shows more block formation than of E-SBR.

Figure 1-6: Styrene-butadiene block copolymer.

In Table 1.5 some important differences between E-SBR and S-SBR are shown. An important difference is, that (same as for BR) the solution polymerization of SBR provides for a narrower molecular weight distribution and additionally a remarkably higher cis-1,4 content of the butadiene. This gives better elastic properties of the networks of S-SBR, among others less dangling ends. Furthermore, the solution polymerization technique offers the manufacturer more possibilities to govern the desired polymer structure.

S-SBR is more expensive than E-SBR, which hindered the development of S-SBR for a long time. The recently introduced "Green Tire" produced by Michelin however, based on the use of highly reinforcing silica instead of carbon black, requires the use of S-SBR. E-SBR offers insufficient possibilities to control the structure-property relations of the polymer, required for this application.

Table 1.5: Comparison of some characteristic differences between E-SBR and S-SBR.

	S-SBR (random types)		E-SBR (1500 type)
Styrene content [%]	22	25	23.5
Cis-1,4 butadiene [%]	33	22	14
Trans-1,4 butadiene [%]	57	50	67
1,2-Vinyl butadiene [%]	10	28	19
Tg [°C]	-65	-47	-50
Ash content [% wt]	0.1		0.75
Organic acids [% wt]	0 – 0.5	6.25	
Mol. weight distribution	Narrow		Broad
Long chain branching	Little		Much
Color	White		Yellow to dark
Vulcanizate properties:			
Tensile strength [MPa]	21.4		25.5
Max. elongation [%]	315		405
Tear strength [kN/m]	39.4		61.3
Lüpke-rebound [%]	62		48

Numbering System Tables 3 & 4

1000 series Hot non-pigmented rubbers
1500 series Cold non-pigmented rubbers
1600 series Cold black masterbatch with 14 or less parts of oil per 100 parts SBR
1700 series Cold oil masterbatch
1800 series Cold oil back masterbatch with more than 14 parts of oil per 100 parts SBR
1900 series Emulsion resin rubber masterbatches

Various producers have been assigned ranges of code numbers for designating new semi-commercial dry rubbers or latices containing styrene-butadiene or only butadiene (emulsion polymerization). These code numbers are shown below:

Semi-Commercial
Numbers . . . . Company

3000-3499 . . . . American Synthetic Rubber Corporation
3500-3999 . . . . Copolymer Rubber & Chemical Corporation
4500-4999 . . . . Ameripol Synpol Co.
5000-5499 . . . . Goodyear Tire & Rubber Company
5500-5599 . . . . EniChem Elastomeri S.r.l.
5700-5799 . . . . Shell Chimie, S.A.
5800-5899 . . . . Shell Chemical International Chemical Company Ltd.
5900-5999 . . . . Hüls AG
6000-6499 . . . . Uniroyal Chemical Company Inc.
7000-7499 . . . . Polysar Elastomers
7500-7999 . . . . Shell Chemical International Chemical Company Ltd.
8000-8499 . . . . Ameripol Synpol Company
9000-9499 . . . . General Tire Inc.
9500-9599 . . . . Nippon Zeon Company, Ltd.
9600-9699 . . . . Japan Synthetic Rubber Co., Ltd.
9700-9799 . . . . Australian Synthetic Rubber Co., Ltd.
9800-9899 . . . . Petroflex-Industria e Comercio S.A.
9900-9999 . . . . PASA Petroquímica Argentina S.A.
10000-10499 . . . . Hules Méxicanos S.A.

Figure 1-7: Numbering system for SBR-types according to the IISRP.

1.4.3 Rolling resistance and wet skid resistance, or wet traction

Quite a few times, in these chapters the functional properties of tires have been mentioned in the considerations for the preceding rubbers: NR, BR, IR and SBR. For further understanding it is useful to broaden our scope and take a look at the functional properties in more detail.

The conditions for fuel saving in the car industry are mainly translated into demands for the tires. Of every 100 units of energy required to drive a car at a constant speed of 80 km/h, 6.6% is consumed by the tires.

Of all losses because of hysteresis (losses of energy because of the fact that deformations are not reversible for 100%) the tire tread takes about 60% on its account. That is why a reduction of the hysteresis in the tire treads can give us the biggest contribution in possible fuel saving. For car tires a reduction of the rolling resistance of 10% gives a fuel saving of 1.5 %, whereas for truck tires this corresponds to a reduction of the rolling resistance of only 5%!
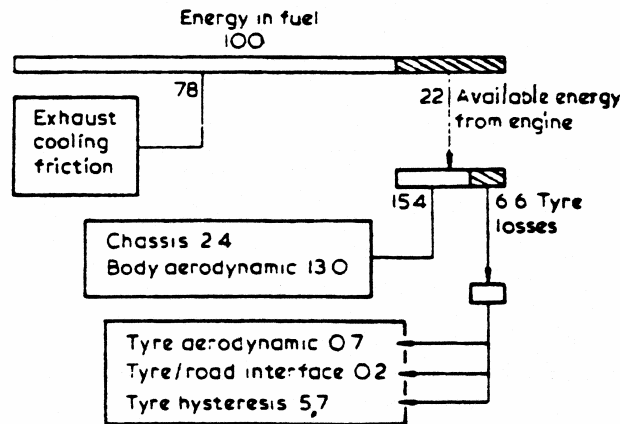

Figure 1-8: Contributions in energy losses in a passenger car tire.

Rolling resistance is the energy, which is converted into heat (H) for a rolling tire per unit of distance traveled (l):

$$F = \frac{dH}{dl}, \quad v = \frac{dl}{dt}, \quad F = \frac{1}{v} \cdot \frac{dH}{dt}$$

(**1.11**)

F has the dimension of J/m, which equals N (= force). However, F is a scalar and not a force, so rolling loss would be a better name. F depends on a lot of factors: construction of the tire, dimensions of the tire, rolling speed, load on the tire, tire pressure etcetera. At increasing pressure of the tire and decreasing loading of the tire, the rolling resistance decreases.

If one wants to decrease the hysteresis of the tire tread, this can be done by increasing the rubber content in the recipe. This can be explained by the fact, that the rubber contributes to the elastic component of the tire and thus gives the elasticity; the carbon black and oil do not contribute to the elastic component of the tire, but to the viscous component and thus give damping. The problem in optimizing the recipe for the tire tread is the apparent incompatibility of the wet skid resistance, which requires damping and the good hysteresis properties for the rolling resistance. Secondly, the abrasion resistance should also be optimized. A good quantity to evaluate the rolling resistance as well as the wet skid resistance is the ratio between the loss modulus and the storage modulus in a dynamic mechanical test, also called tan δ:

$$\tan\delta = G'' / G'$$

<div align="right">(1.12)</div>

In most cases a reduction in rolling resistance goes at the expense of the wet skid resistance. When looking in more detail into the subject, one will see that the conditions to be met by the tire tread can be separated with respect to the operating temperature. At 60°C, which is the normal operating temperature of the tire, the tan δ should be as low as possible to provide low hysteresis and a low rolling resistance.

At low temperature however, say 0°C, the tan δ should be as high as possible in order to improve the wet skid resistance. 0°C corresponds to a wet or an icy road in winter conditions. A high tan   gives high damping on the interface tire-road and as a result, the tire adheres to the road.

By mixing different types of NR, SBR and BR, the tire manufacturers are able to control the properties of the tire (wet skid resistance, rolling resistance and abrasion resistance). Meanwhile, numerous rubbers have been developed, which have more or less united this compromise in one product.
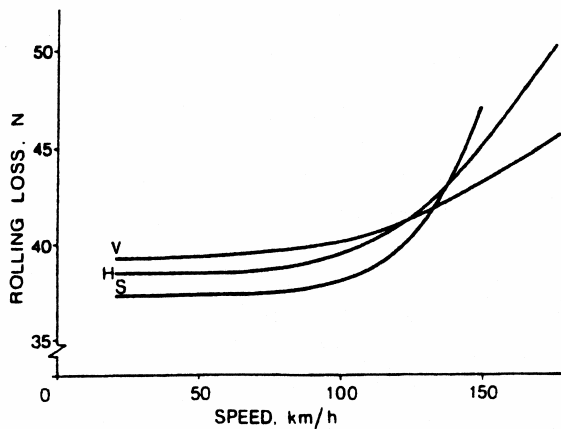

Figure 1-9: Rolling resistance of typical tires at different driving speeds: 3.3 kN loading and 200 kPa tire pressure.
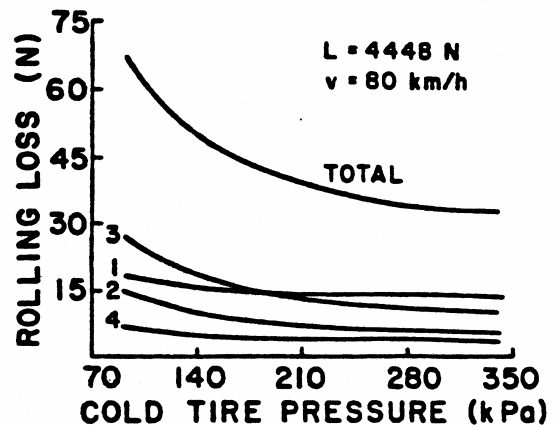
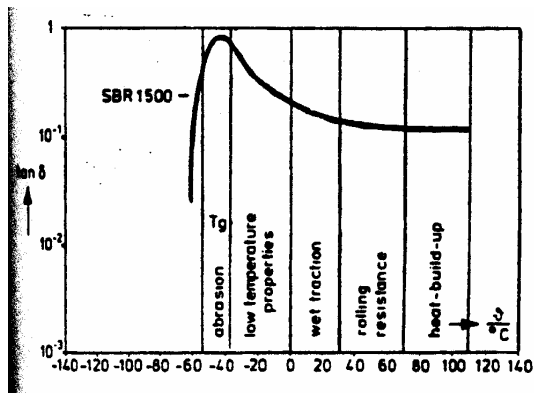*Figure 1-10: Rolling resistance at various tire pressures.*

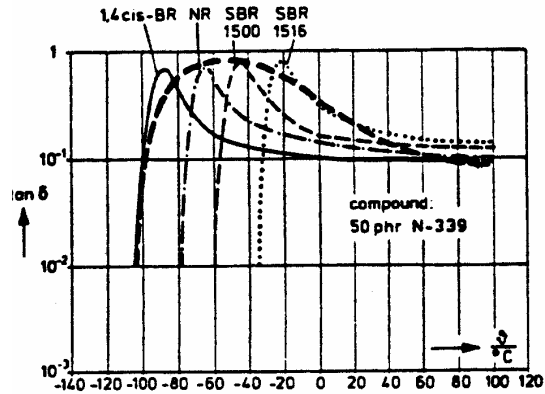*Figure 1-11: Dependence of tan delta on temperature.*

Figure 1-12: Damping curve of an ideal tire tread rubber.

Especially the anionically polymerized S-SBR's offer great opportunities to construct an ideal tire tread recipe, because of its wide possibilities to vary the micro and macro structure. It is important to keep an eye on the following aspects:

1. Few free chain ends, i.e. high molecular weights, narrow molecular weight distributions and little branch formation. This condition is restricted by the difficult processability at high viscosities.
2. Low Tg leads to low damping (tan δ): this can be influenced by the controlling the styrene content as well as the 1,2-vinyl content of the butadiene moiety.
3. Controlling the Tg by adjusting the 1,2 vinyl content may result in advantages with respect to the tan   , however, there may be disadvantages with respect to the tensile and tear strengths. Increasing the amount of styrene increases the tensile and tear strengths, but this leads also to block formation of the styrene, which leads to higher values of tan δ.

As one can see, finding a proper set of parameters requires experience and is typically work for a specialist!
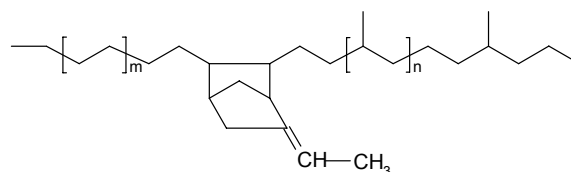
1.5 Ethylene-propylene (-diene) rubber (EPM and EPDM)

Figure 1-13: Structure of EPDM.

Copolymers of ethylene and propylene (EPM) are synthesized with the aid of Ziegler-Natta catalysts.
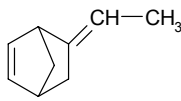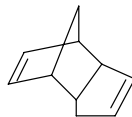
Both monomers are almost randomly built into the chain. Contrary to the homopolymers of ethylene and propylene, EPM behaves amorphous and rubbery.

The ratio ethylene / propylene in commercial products lies between 75/25 and 45/55 by weight. The high ethylene EPM's have a Tm of about + 25°C, which gives the product at room temperatures and lower the tendency to crystallize: these products are called crystalline types; low ethylene EPM's are called amorphous types.

EPM is fully saturated and that is why these polymers can only be vulcanized with peroxides. In order to be able to vulcanize with sulfur, a so-called third monomer has to be built in. This third monomer has to meet the following requirements:
- At most two double bonds; one for the polymerization and one for the crosslinking;
- The reactivity for polymerization should be comparable with that of ethylene and propylene, be it that the reactivity for incorporation of the second double bond should be clearly lower;
- The third monomer should be incorporated randomly;
- The reactivity of the free double bond of the third monomer should be high enough for sulfur vulcanization.

Extensive research on possibilities for third monomers has till now resulted in only three options which are used in practice:

1. 5-Ethylidene-2-norbornene (ENB):

2. Dicyclopentadiene (DCPD):

3. 1,4-Hexadiene (not used anymore since a few years)
$$CH_2{=}CH{-}CH_2{-}CH{=}CH{-}CH_3$$

Dicyclopentadiene does not fully meet the criteria given above. The double bonds in the molecule are symmetrical in the molecule, which results in an equal reactivity during polymerization. This may cause a double reaction of the diene during polymerization, leading to branch formation or in the worst-case gel formation. That is why the incorporation of DCPD is restricted to 4 %wt (1 mol%), whereas for ENB incorporation up to 12 %wt is successfully applied.
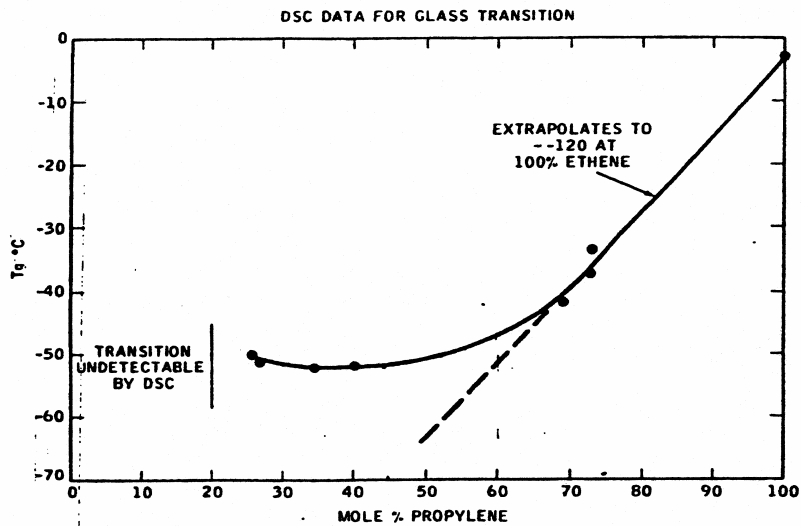
Figure 1-14: Tg of copolymers consisting of ethylene and propylene.

EPM and EPDM are synthesized in solution (hexane or special boiling point spirit) or in suspension (propene). Catalysts are Ziegler-Natta systems, mainly Vanadium containing substances: VCl4 or VOCl3 with alkyl-aluminumhalogenides, such as Et2AlCl or Et3Al2Cl3 as co-catalysts. It is supposed that in the active catalyst the Vanadium is present as V3+. Because of the fact that V3+ easily can be reduced to the inactive V2+, which can only produce polyethylene, the lifetime of this catalyst is rather short. By adding oxidizers like highly chlorinated organic substances like CCl4 or perchloro-acetic acid etc, called promoters, the vanadium is kept in its active form for a longer time.
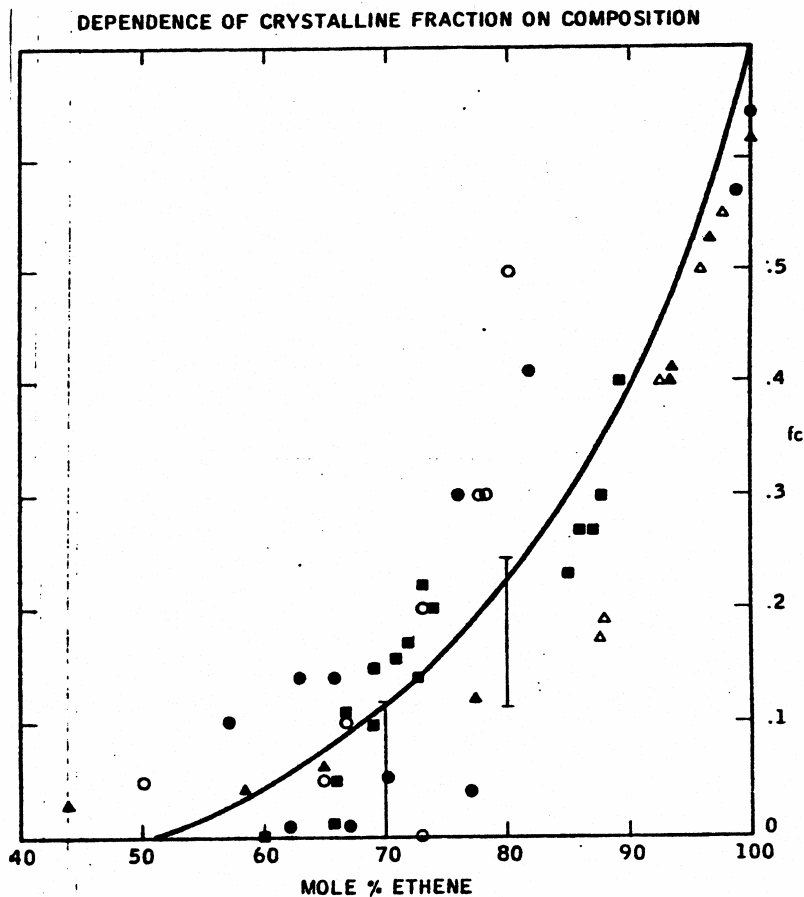
Figure 1-15: Crystalline fraction (X-ray) as a function of the ethylene content in ethylene-propylene copolymers; the variation comes from the different catalyst systems used.

Most important properties of EP(D)M

- Molecular weights Mn between 30000 and 150000 (liquid types have molecular weights as low as 1500);
- Molecular weight distribution Mw/Mn between 2.0 (theoretical minimum) and >5.0: from narrowly to broad distribution;
- Mooney viscosities ML(1+4) 125°C from 20 → 100 (liquid types <1);
- With and without paraffinic oil extension;
- Exceptional ozone and ageing resistance because of the saturated backbone;
- Can be highly filled with filler and oil, due to the high green strength obtained form the crystallization of high ethylene sequences (results in cheap mixtures);
- EPDM can be vulcanized with sulfur, but in comparison with NR or BR is it quite difficult. It requires a vulcanization temperature that is about 15 degrees

higher, a lot of (ultra-) accelerators and still a small amount of crosslinks are formed. After all, the amount of double bonds available for vulcanization is very small: 1- 3 mol% diene gives 4 – 15 double bonds per 1000 carbon atoms whereas, for instance, BR has 250 double bonds per 1000 carbon atoms. As a result, the network density which can be achieved is limited;

- ENB reacts about twice as fast with sulfur in comparison with DCPD. Hexadiene lies in between.
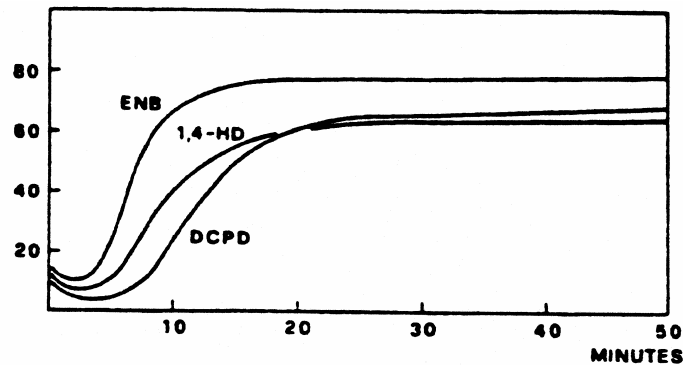
Figure 1-16: Reometer curves of EPDM with different diene monomers.

The application of EP(D)M is mainly in the field of non-dynamic applications where long lasting ozone resistance is important:
- Automotive profiles (solid and sponge);
- Construction profiles;
- Radiator, heating and brake hoses;
- Roofing, soil covers;
- All sorts of domestic sealings.

1.6 Butyl rubber (IIR)

Butyl rubber is the only specialty rubber of small commercial extent that is used in the tire industry, because of its low gas permeability: inner tubes.

Figure 1-17: Structure of IIR.

IIR is built of poly-isobutylene and 1-5 %wt isoprene. The isoprene is incorporated in the trans configuration. The abbreviation IIR stands for isobutylene-isoprene rubber.

Butyl rubber is one of the oldest synthetic rubbers. It is produced via cationic polymerization with AlCl3 as initiator and a small amount of nucleo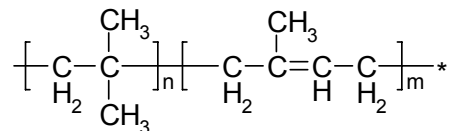philic substances like water of alkylhalogenides as co-catalysts. Methyl chloride is used as solvent, from which the polymer is precipitated. The reaction has to be done at very low temperature in order to prevent chain transfer and resulting low molecular weights. Because of the fact that isoprene poisons the polymerization reaction by chain transfer, at maximum 5 %wt can be incorporated; otherwise the resulting molecular weight would be insufficiently high.

Most important properties of IIR

The polymer structure (dimethyl substitution on every second carbon atom of the chain and low level of unsaturation) determine the main properties of butyl rubber:

- Low gas permeability;
- Reasonable resistance to ozone, oxygen and heat ageing;
- Good resistance to chemicals;
- What strikes is the low elasticity, although the glass transition temperature is relatively low at − 70°C. Butyl rubber is a rather 'dead' rubber; that is why it is used frequently as the base for chewing gum.

Most important applications for IIR are inner tubes for automobiles and bicycles, because of its low permeability. But also for lining for industrial vessels and vibration dampening elements (low elasticity).

Nowadays, an ever-increasing amount (more than 50 %) of halogenated (chlorated, CIIR, and brominated, BIIR) butyl rubber is used in industry, because it has more affinity with high-unsaturation rubbers. The halogen, which is incorporated in the methyl group, enhances the reactivity of the vulcanization site. In this way a vulcanization rate is obtained that happens at the same reaction temperature as tire rubbers. This is very important for the inner liners for passenger-cars. The halogen groups can also react with zinc oxide and in this way very temperature-stable networks are formed.

1.7   Nitrile rubber (NBR)

Butadiene-acrylonitrile copolymers distinguish themselves from NR and SBR in their good resistance against non-polar substances like gasoline, diesel fuel, oils and fats, good ageing resistance and good resistance to chemicals.
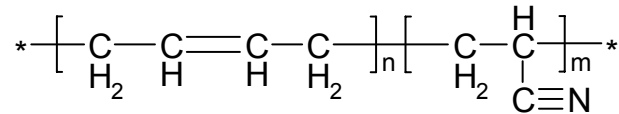
Figure 1-18: Structure of NBR.

NBR is produced in the same way, and partly in the same factories, as SBR. Butadiene and acrylonitrile are copolymerized in aqueous emulsion. The same sort of catalysts and polymerization additives are used: hot NBR (30-40°C) is activated by persulfate and cold NBR (5°C) by organic peroxides. The following structural and production parameters play an important role:
- Acrylonitrile (ACN) content of the copolymers: 18-48 %;
- Molecular weight;
- Microstructure of the polymers;
- Branching level and gel content;
- Possibly comonomers like (met)acrylic acid.

The polymerization is stopped at 70-80% conversion in order to prevent branching/gelation. Unstabilized NBR latex is very susceptible to oxidation. That is why a stabilizer is added to the latex prior to coagulation and drying. Subsequently the latex is treated in the same way as the SBR.

Most important properties of NBR

The physical and technological characteristics of NBR are closely related to the ACN-content. Because polyacrylonitrile (Tg = 90°C, thermoplastic!) and polybutadiene (Tg=-100, rubbery) differ in Tg and in polarity, the Tg and polarity of the copolymer increase with higher ACN content.

With increasing ACN-content:
- Vulcanizates have better resistance against swelling in gasoline, diesel fuel, oils, fats and organic solvents;
- The polymer is better miscible with polar plasticizer and polar solvents;
- The polymer is better miscible with polar synthetic materials, like PVC;
- The polymer is better miscible with compounding ingredients;
- The elasticity and cold-flexibility get worse.

The polymer structure is, beside the monomer composition, mainly dependent on the polymerization temperature. The polymer structure governs the processability of the raw polymers as well as the mechanical properties of the vulcanizates. Cold NBR is less branched and easier to process compared to hot NBR. The compression set however of hot NBR mixtures is better: the branches act as temporary entanglements. The polymerization temperature also governs the structure of the butadiene part: for instance in NBR, polymerized at 28 °C and with an ACN-content of 36%, the butadiene structure is as follows: 12% cis – 78% trans – 10% 1,2 vinyl.

Because ACN is built randomly into the chain, NBR is an amorphous rubber.

The most important properties of NBR are in the area where oil, gasoline and diesel fuel resistance are important. Examples are sealings, fuel hoses at fuel stations, hydraulic hoses, cable insulators and two roll mill linings.

PVC and NBR with a high amount of ACN are miscible at all ratios. In this way, one can combine the oil and solvent resistance and the elastic properties of NBR with the ageing and ozone resistance of PVC, at all ratios. In practice the ratio is most of the times between 30 and 55% PVC: fuel hoses in cars.

1.8   Polychloroprene (CR)

Polychloroprene is often called neoprene. This is abuse of the trade name, which has been given by DuPont to the first commercially produced polychloroprene (compare Nylon, for polyamides).
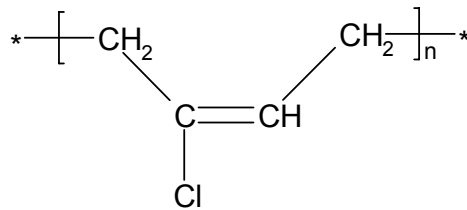
Figure 1-19: Structure of polychloroprene.

Nowadays, CR is produced exclusively via radical polymerization in aqueous emulsion at temperatures of $10 - 45°C$. Emulsifiers and other additives are comparable with other emulsion rubbers. The polymerization is stopped at 70 % conversion. Acetic acid is used to bring the pH of the latex to $5.5 - 6.5$. The latex is continuously coagulated at $-15°C$ as a thin film on a slow two-roll mill. Then the rubber film is continuously removed from the two-roll mill, warmed up till room temperature, washed and dried, and cut to chips.

Control of the microstructure of the CR is done via the polymerization temperature. At increasing temperature, mistakes in the structure increase. The trans -1,4 part of the chloroprene is favorable for spontaneous crystallization. The CR, which is used as basic material for contact adhesives, gets its strength in the linkage because of this crystallization. Therefore, a high amount of the trans- 1,4 configuration is required. For the real rubber applications, this crystallization leads to an undesired hardening of the product. That is why for rubber applications most of the times CR is used that is polymerized at a higher temperature. The higher polymerization temperature gives also

another advantage: it increases the 1,2 vinyl configuration in the CR, which is necessary for the vulcanization:

Table 1.6: Microstructure of polychloroprene.

Polym. Temp [°C]	Cis- 1,4 [%]	Trans- 1,4 [%]	1,2- part [%]	3,4- part [%]	Total double bonds [%]
-40 *)	5	94	0.9	0.3	100
+10	9	84	1.1	1.0	95
+40	10	81	1.6	1.0	94
+100	13	71	2.4	2.4	89

*) By addition of methanol to the water phase.

Contrary to the other diene rubbers, CR is vulcanized with metal oxides like MgO and ZnO, not with sulfur. This is done by elimination of HCl. Especially the chlorine-atom that is situated opposite to the 1,2-vinyl group can easily be abstracted, because it is attached to a tertiary carbon atom and, besides, it is in the an allylic position with respect to the double bond of the monomer. A certain amount of 1,2- vinyl configuration in the polymer is therefore needed for good vulcanization.

Most important properties of CR

- Medium oil resistance;
- Medium resistance against chemicals;
- Limited resistance against weathering, ageing and ozone;
- Good flame-resistance properties, because of the chlorine atom.

Typical applications of CR are profiles and hoses for trucks, seals, sealing rings and bellows for machineries and automobiles, bridge suspensions, rollers, conveyor belts and cable insulation.

1.9 Specialties

Nowadays, there are about forty commercially available rubbers, from which the most important ones as to sales and quantities have been discussed in the former paragraphs. The smaller ones with respect to quantity provide in the demand for rubber applications under extreme conditions: heat, cold, and oil-resistance, especially in the automobile industry.
This group of specialty rubbers has some common chemical characteristics:
- A saturated main chain, possibly with heteroatoms;
- They possess polar functional groups.

The first characteristic is required for a good resistance against oxidative ageing and ozone. The polar groups provide resistance against swelling by oils and gasoline. Increasing polarity means in the most cases a decrease in low temperature properties. Qualitatively the following order applies for the functional groups:

Oil resistance: F > CN > Cl > H
Heat resistance: F > H > CN > Cl
Low temperature behavior: H > F > Cl > CN

1.9.1   Fluororubber (FKM)

Fluororubbers are co- and terpolymers consisting of at least 75 % vinylidenefluoride with the following comonomers:

-   Hexafluoropropene;   CF2=CF-CF3
-   Tetrafluoroethene;   CF2=CF2
-   1,2,3,3,3- pentafluoropropene;   HCF=CF-CF3
-   Trifluoromethyl- trifluorovinylether. CF2=CF-O-CF3

These rubbers are produced in emulsion polymerization. Vulcanization is done with diamines in combination with basic metal oxides (MgO). The vulcanization is very slow and takes about 24 hours at a temperature of 200°C.

Fluororubbers allow the highest use temperatures, for instance up to 240°C. These products have a very good oil resistance. The mechanical properties, the elasticity and the cold flexibility of FKM are their weaker points, besides the high prize. The main applications are: all sorts of fuel and oil resistant o-rings, sealings etc.
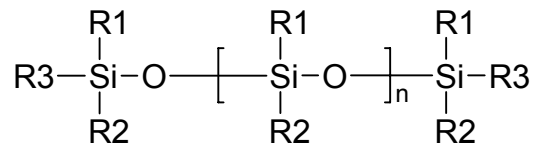

1.9.2   Silicone rubber (Q)

Figure 1-20: General structure of silicone rubber.

By varying the substituents in the general formula, the properties of the vulcanizates change as follows:

R1, R2 = methyl: bad cold flexibility;   [polydimethyl   siloxane (PDMS)]
R1, R2 = phenyl: improved cold flexibility;
R1 = methyl, R2 = vinyl: good compression set;
R1 = phenyl, R2 = vinyl: good compression set;
R1 = vinyl, R2 = trifluoropropyl: good oil resistance.

In general the silicone rubbers distinguish themselves by a:
   - Good high temperature, ozone and UV resistance;
   - Good cold flexibility;
   - Little temperature dependence of the mechanical properties;
   - Low Mooney viscosities at high molecular weights;
   - High gas permeability.

These properties can be explained from the molecular structure: the high temperature resistance follows from the stability of the Si-O bond (373 KJ/mol; C-C: 343 KJ/mol) and from the thermal and chemical stability of the organic substituents. Because of the fact that polysiloxane chains show little intermolecular and intramolecular interactions, silicone rubbers show large chain flexibility (Tg ≈ -120°C). This explains the high gas permeability, cold temperature properties (at non-crystalline derivates), low tensile strength and little temperature dependence of the mechanical properties.

The Si-O bond can be hydrolyzed by strong acids and bases. This sensitivity towards acids and bases has always been a constraint in the application of silicone rubber with respect to its high temperature resistance. For example: sealings in high yield heating boilers, in which acidic smoke gas condenses, and has to be drained away. On the other hand, the synthesis of diorgano-dichlorosilane-hydrolysates proceeds by acid catalyzed polycondensation or base catalyzed ring-opening polymerization of cyclic oligomers.

There are two types of silicone rubbers, depending on the vulcanization temperature: warm vulcanizing (HV-types) and room temperature vulcanizing (RTV). HV-silicones have high molecular weights (3-7*105 g/mol, while RTV silicones are liquid having acetate- and methoxy-functional end groups (104 - 105 g/mol).
In order to improve the strength of the vulcanizates, highly reinforcing filler is added, mostly pyrogenic silica.

Applications are: sealings, cable isolations, medical articles and sealing kits.

1.9.3   Acrylate rubber (ACM)

The commercial acrylate rubbers are (co-) polymers of ethylene or butylenes acrylate. They are produced via a solution or emulsion polymerization process. These rubbers distinguish themselves by a very good heat and oil resistance, especially polyethylene-acrylate. The cold flexibility is relatively bad (Tg = -21°C). Polybutylene-acrylate has a somewhat better cold flexibility (Tg= -49°C), but its heat and oil resistance is worse than that of polyethylene-acrylate. By copolymerizing the two monomers, one can get combination of the good properties. The newer ACM monomers contain other monomers as well, which can improve the combination of the cold flexibility and oil resistance.

In order to increase the vulcanization speed and the vulcanization yield, more reactive monomers are incorporated. The vulcanization system for these polymers is then fine-tuned for these monomers. Copolymerization of ethylene and acrylates also improves the cold flexibility (Vamac, of Dupont de Nemours).

Acrylate rubbers have a poor processability, because of their high viscosity.
Applications are: oil hoses, o-rings etc.

1.9.4   HNBR

Selectively hydrogenating the butadiene double bonds of NBR results in a product combining the oil resistance of NBR and the oxidation, ozone and ageing resistance of EPDM. HNBR is a relatively new product on the market and is still under development.
Especially the processing of HNBR is difficult, but it is getting improved. Completely hydrogenated types are cured with peroxides. For partly hydrogenated types sulfur vulcanization can still be used.

Application of HNBR: especially in the automobile industry for sealings, conveyor belts, timing belts, hoses, etc., but also in the mineral oil winning.

1.10 ASTM/ISO nomenclature for rubbers

In ASTM standard D-1418 and ISO standard 1629, regulations are given for the nomenclature of various rubbers on the basis of their chemical structure. This systematic code touches upon the last letter of the code, which tells something about the heat and ageing resistance of most of the rubbers. The following groups are defined:

M   Rubbers with a saturated carbon main chain of the polymethylene type;
N   Rubbers with carbon and nitrogen in the main chain (not existing yet);
O   Rubbers with carbon and oxygen in the main chain;
Q   Rubbers with silicium and oxygen in the main chain;
R   Rubbers with an unsaturated carbon main chain;

T   Rubbers with carbon, oxygen and sulfur in the main chain;
U   Rubbers with carbon, oxygen and nitrogen in the main chain;
Z   Rubbers with phosphor and nitrogen in the main chain.

Generally, rubbers with unsaturation in the main chain (R- rubbers) are more sensitive towards ozone and heat ageing than rubbers which are fully saturated, or which have the unsaturation in a side chain. For instance, EPDM has a better ozone and heat resistance than NR or SBR, because of the absence (EPDM) or presence (NR and SBR) of unsaturation in the main chain.

1.11 Classification of rubber types

In choosing the type of rubber for a certain application, the first two things that must be considered are the heat resistance (and in relation to that: the ozone resistance) and the resistance against oil. For the latter, one generally uses the amount of swelling of a vulcanizate in an ASTM standardized oil #3, which is held in stock in large quantities for common use. How the different elastomers compare with each other can be seen in Figure 1-21.

Bottom-left in the figure, we see the rubbers with poor oil resistance and low heat resistance. In the right upper part, on can find the oil resistant, high temperature resistant rubbers. Bottom left- rubbers are sometimes called 'commodity rubbers'; prizes are 1-2 Euro per kg. The right upper part consists of the specialty rubbers; prizes are up to 50 Euro per kg!
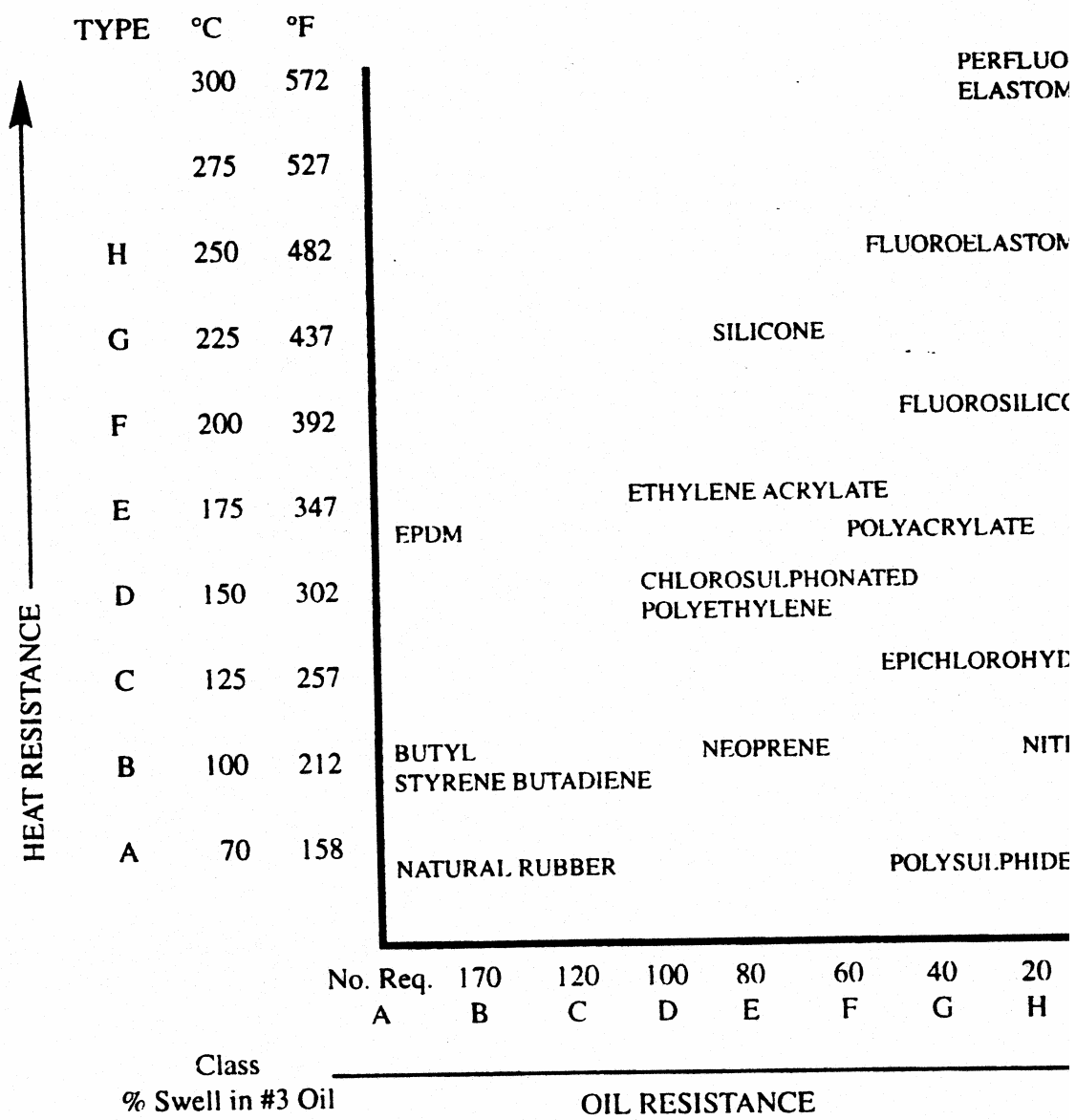
TYPE	°C	°F						
	300	572					PERFLUO ELASTOM	
	275	527						
H	250	482					FLUOROELASTON	
G	225	437		SILICONE				
F	200	392				FLUOROSILIC(		
E	175	347	EPDM	ETHYLENE ACRYLATE POLYACRYLATE				
D	150	302		CHLOROSULPHONATED POLYETHYLENE				
C	125	257				EPICHLOROHYC		
B	100	212	BUTYL STYRENE BUTADIENE		NEOPRENE		NITI	
A	70	158	NATURAL RUBBER			POLYSULPHIDE		

HEAT RESISTANCE

No. Req.	170	120	100	80	60	40	20
	A	B	C	D	E	F	G	H

Class
% Swell in #3 Oil   OIL RESISTANCE

Figure 1-21: Relative oil and heat resistance of the different elastomers.

INTERNATIONAL STANDARD

ISO 1629

Third edition
1995-11-15

Rubbers and latices — Nomenclature

Caoutchouc et latex — Nomenclature

Figure 1-22: International Standard ISO 1629.

Rubbers and latices — Nomenclature

1 Scope

1.1 This International Standard establishes a system of symbols for the basic rubbers in both dry and latex forms, based on the chemical composition of the polymer chain.

1.2 The purpose of this International Standard is to standardize the terms used in industry, commerce and government, and it is not intended to conflict with, but rather to act as a supplement to, existing trade names and trade marks.

NOTE 1 In technical papers or presentations, the name of the rubber should be used if possible. The symbols should follow the chemical name for use in later references.

2 Rubbers

Rubbers, in both dry and latex forms, are grouped and symbolized on the basis of the chemical composition of the polymer chain in the following manner:

M Rubbers having a saturated carbon chain of the polymethylene type

N Rubbers having carbon and nitrogen in the polymer chain

NOTE 2 No rubber has so far been symbolized in the "N" group.

O Rubbers having carbon and oxygen in the polymer chain

Q Rubbers having silicon and oxygen in the polymer chain

R Rubbers having an unsaturated carbon chain, e.g. natural rubber and synthetic rubbers derived at least partly from conjugated dienes

T Rubbers having carbon, oxygen and sulfur in the polymer chain

U Rubbers having carbon, oxygen and nitrogen in the polymer chain

Z Rubbers having phosphorus and nitrogen in the polymer chain

3 Symbol groups

3.1 The "M" group

The "M" group comprises rubbers having a saturated chain of the polymethylene type. The following symbols are used:

ACM Copolymer of ethyl acrylate (or other acrylates) and a small amount of a monomer which facilitates vulcanization. (Usually known as acrylic rubber)

AEM Copolymer of ethyl acrylate (or other acrylates) and ethylene

ANM Copolymer of ethyl acrylate (or other acrylates) and acrylonitrile

CM Chloropolyethylene[1)]

CSM Chlorosulfonylpolyethylene

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1) In ISO 1043-1[1], the abbreviation given for chloropolyethylene is PE-C.

1

EPDM Terpolymer of ethylene, propylene and a diene with the residual unsaturated portion of the polymerized diene in the side chain

EPM Ethylene-propylene copolymer

EVM Ethylene-vinyl acetate copolymer[2)]

FEPM Copolymer of tetrafluoroethylene and propylene

FFKM Perfluoro rubber in which all substituent groups on the polymer chain are fluoro, perfluoroalkyl or perfluoroalkoxy groups

FKM Fluoro rubber having substituent fluoro, perfluoroalkyl or perfluoroalkoxy groups on the polymer chain

IM Polyisobutene[3)]

NBM Fully hydrogenated acrylonitrile-butadiene copolymer (see 3.4.2)

3.2 The "O" group

The "O" group comprises rubbers having carbon and oxygen in the polymer chain. The following symbols are used:

CO Polychloromethyloxirane (usually known as epichlorohydrin rubber)

ECO Copolymer of ethylene oxide (oxirane) and chloromethyloxirane (also known as epichlorohydrin copolymer or rubber)

GECO Terpolymer of epichlorohydrin-ethylene oxide-allyl glycidyl ether

GPO Copolymer of propylene oxide and allyl glycidyl ether (also known as polypropylene oxide rubber)

3.3 The "Q" group

The "Q" group is defined by inserting the name of the substituent group on the polymer chain prior to the silicone designation. The following symbols are used:

FMQ Silicone rubber having both methyl and fluorine substituent groups on the polymer chain

FVMQ Silicone rubber having methyl, vinyl and fluorine substituent groups on the polymer chain

MQ Silicone rubber having only methyl substituent groups on the polymer chain, such as dimethyl polysiloxane

PMQ Silicone rubber having both methyl and phenyl substituent groups on the polymer chain

PVMQ Silicone rubber having methyl, vinyl and phenyl substituent groups on the polymer chain

VMQ Silicone rubber having both methyl and vinyl substituent groups on the polymer chain

The letter for substituent group(s) on the polymer chain is inserted to the left of the code letter for rubber with silicon and oxygen in the backbone (Q) in descending order of per cent present, i.e. largest nearest the Q.

NOTE 3 In ISO 1043-1[1], the symbol for silicone polymers is SI.

3.4 The "R" group

3.4.1 Description

The "R" group, in both dry and latex forms, is defined by inserting, before the word "rubber", the name of the monomer or monomers from which the rubber was prepared (except for natural rubber). The letter preceding the letter "R" signifies the conjugated diene from which the rubber was prepared (except for natural rubber). Any letter or letters preceding the diene letter signifies the comonomer or comonomers, substituent groups or chemical modifications. The designation may be prefixed by the letter E and a hyphen to signify an emulsion-polymerized rubber or the letter S and a hyphen to signify a solution-polymerized rubber.

For latices, the designated symbol is followed by the word latex, e.g. "SBR latex".

The symbols given in 3.4.2 to 3.4.4 are used.

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2) In ISO 1043-1[1], the abbreviation given for ethylene-vinyl acetate copolymer is E/VAC.

3) In ISO 1043-1[1], the abbreviation given for polyisobutene is PIB.

2

3.4.2 General

ABR   Acrylate-butadiene rubber

BR   Butadiene rubber

CR   Chloroprene rubber

ENR   Epoxidized natural rubber

HNBR   Hydrogenated NBR (some unsaturation remains, see 3.1)

IIR   Isobutene-isoprene rubber (usually known as butyl rubber)

IR   Isoprene rubber, synthetic

MSBR α-methylstyrene-butadiene rubber

NBR   Acrylonitrile-butadiene rubber (usually known as nitrile rubber)

NIR   Acrylonitrile-isoprene rubber

NR   Natural rubber

PBR   Vinylpyridine-butadiene rubber

PSBR   Vinylpyridine-styrene-butadiene rubber

SBR   Styrene-butadiene rubber

     E-SBR   Emulsion-polymerized SBR

     S-SBR   Solution-polymerized SBR

SIBR   Styrene-isoprene-butadiene rubber

3.4.3 Rubbers having substituent carboxylic acid groups (COOH) on the polymer chain

XBR   Carboxylic-butadiene rubber

XCR   Carboxylic-chloroprene rubber

XNBR   Carboxylic-acrylonitrile-butadiene rubber

XSBR   Carboxylic-styrene-butadiene rubber

3.4.4 Rubbers containing halogen on the polymer chain

BIIR   Bromo-isobutene-isoprene rubber (usually known as bromobutyl rubber)

CIIR   Chloro-isobutene-isoprene rubber (usually known as chlorobutyl rubber)

3.5 The "T" group

The "T" group comprises rubbers having carbon, oxygen and sulfur in the polymer chain. They are usually known as polysulfide rubbers. The following symbols are used:

OT   A rubber having either a

$$-CH_2-CH_2-O-CH_2-O-CH_2-CH_2-$$

group or occasionally an R group, where R is an aliphatic hydrocarbon, not usually $-CH_2-CH_2-$, between the polysulfide linkages in the polymer chain.

EOT   A rubber having a

$$-CH_2-CH_2-O-CH_2-O-CH_2-CH_2-$$

group and R groups which are usually $-CH_2-CH_2-$ but occasionally other aliphatic groups between the polysulfide linkages in the polymer chain.

3.6 The "U" group

The "U" group comprises rubbers having carbon, oxygen and nitrogen in the polymer chain. The following symbols are used:

AFMU   Terpolymer of tetrafluoroethylene, trifluoronitrosomethane and nitrosoperfluorobutyric acid

AU   Polyester urethane

EU   Polyether urethane

3.7 The "Z" group

The "Z" group comprises rubbers having phosphorus and nitrogen in the polymer chain. The following symbols are used:

FZ   A rubber having a $-P\equiv N-$ chain and having fluoroalkoxy groups attached to the phosphorus atoms in the chain

PZ   A rubber having a $-P\equiv N-$ chain and having aryloxy (phenoxy and substituted phenoxy) groups attached to the phosphorus atoms in the chain

CHAPTER 2   FILLERS

2.1 Reinforcing and non-reinforcing fillers

Originally, fillers were only added to the rubber in order to make product articles cheaper. Later on, it was found that the addition of fine particles of certain fillers could improve the properties of the rubber vulcanizates in a positive way. It was therefore thought, that the rubber and filler had an interaction, whatever this interaction may be. This interaction is even nowadays hardly understood in many cases.

There is a distinction between fillers, which have much and little interaction: active or reinforcing fillers, and non-active or non-reinforcing fillers. With activity or reinforcement, commonly all kinds of rubber/filler interactions are meant which express themselves in physical properties that can be measured. More specific, the term reinforcement is used for an increase in tensile strength and/or improvement of abrasive properties.

2.2 Reinforcing Effects

A condition for filler reinforcement is the interaction between the filler particles and the polymer. These interactions can be strong, for example in the case of covalent bonds between functional groups on the filler surface and the polymer, or weak as in the case of physical attractive forces. When carbon black is blended with a polymer, the level of physical interaction is high. In contrast to this, the interaction between silica particles and the polymer is very weak, and only by the use of a coupling agent a bond is formed between the filler and the polymer.

Besides the interaction between the polymer and the filler, an interaction between filler particles occurs, predominantly above a critical concentration threshold, the percolation threshold: The properties of the material change drastically, because a filler-filler network is established. This results for example in an overproportional increase of electrical conductivity of a carbon black filled compound. But even at lower concentrations, the filler-filler interactions influence the material characteristics, as expressed by the Payne effect. Figure 2-2 illustrates the strain-dependence of the Payne effect and the strain-independent contributions to the shear modulus for carbon black filled compounds and silica filled compounds.

The main contributions to the complex shear modulus are the hydrodynamic effect, the polymer network, the filler-polymer and the filler-filler interaction.
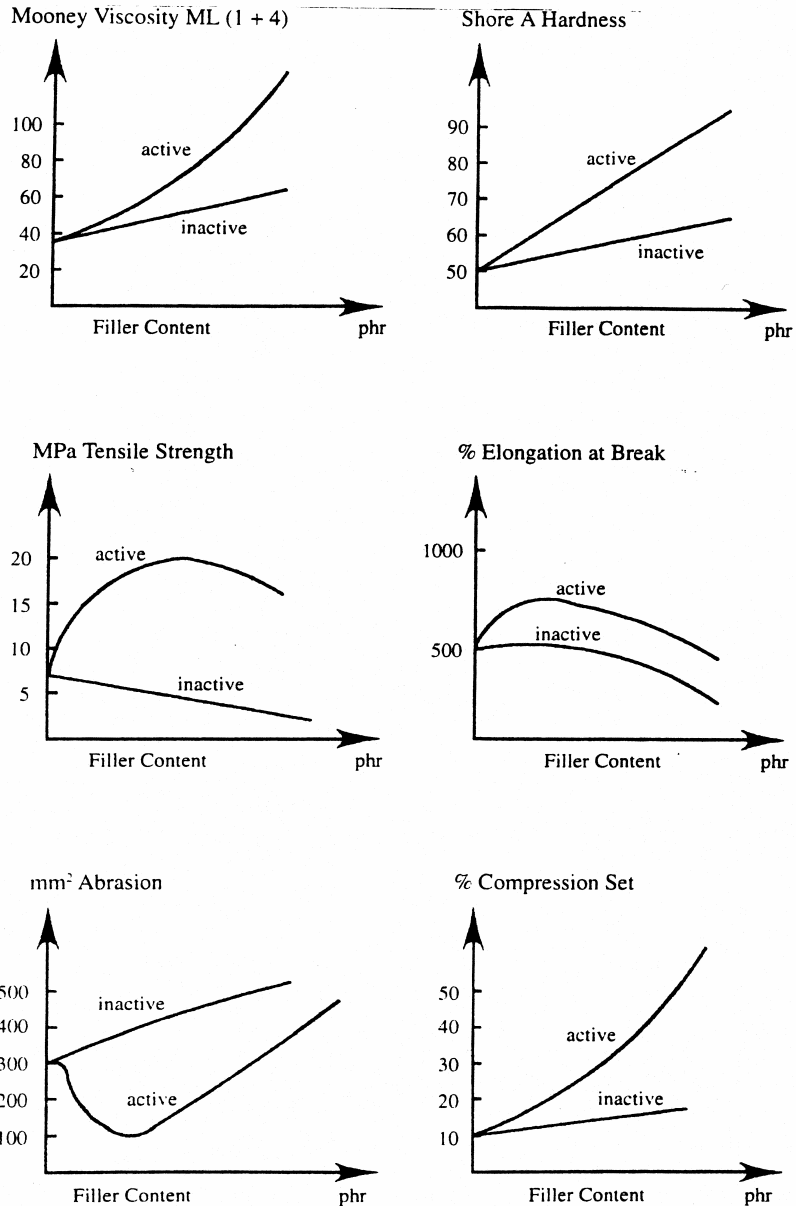
Figure 2-1: Influence of active and inactive fillers on vulcanizate properties.

a. Hydrodynamic effect

The addition of particles to a viscous fluid results in an increase of the viscosity of the fluid, commonly designated as the hydrodynamic effect. In a polymeric matrix this effect is also measured as an increase of the modulus. The phenomenon was modeled by Einstein almost a century ago, and he described the viscosity increase by rigid spherical particles dispersed in a liquid. Einstein made the following assumptions for his model:

- o Perfect wettability of the spheres
- o Uniform spherical particles
- o No interaction between the particles

Especially the last two requirements are rarely met in filler-polymer systems. This discrepancy between Einstein's theory and practical experience was taken into consideration by an additional term, introduced by Guth and Gold: a function of the filler volume fraction to the power of two, emphasizing the influence of the filler concentration.

The addition of the filler increases the shear modulus of the pure elastomer G0 and results in a shear modulus Gf for the filled compound. The same correlation holds for the Young's modulus E. A correction for the non-spherical shape of the filler particles, a shape factor fS, was added by Guth: The shape factor represents the ratio of the longest dimension to the shortest dimension of the particle.

b. Filler-polymer interaction
The filler-polymer related effects are determined by the special structure of the filler in the rubber matrix and its interaction with the polymer. The occluded rubber contributes to this effect: Polymer chains are trapped in the voids of the filler agglomerates and aggregates; they are immobilized and shielded from deformation. They do not contribute to the elastic behavior of the matrix, as their properties resemble the properties of the rigid filler particles rather than the properties of the elastic and flexible free polymer chains. Occluded rubber increases the effective filler loading and thus the strain independent contribution to the modulus. The filler-polymer interaction can be attributed to physical interactions, for example van der Waals forces, or chemical reactions as in the case of a silica-coupling agent system.

c. Polymer network contribution
The polymer network formed during vulcanization is the third strain-independent contribution to the modulus: The modulus is proportional to the concentration of elastically active network chains υ and the absolute temperature T, with the proportionality constant being the Boltzmann constant kB:

d. Filler-filler interaction: Payne effect
The strain-dependent contribution to the modulus is caused by filler-filler interactions. This effect was first brought into focus by Payne, and he interpreted the sigmoidal decrease of the storage modulus versus the double strain amplitude in logarithmic scale from a limiting zero-amplitude value to a high amplitude plateau as the result of the breakage of physical bonds between filler particles, for example van der Waals or London forces. This effect is largely reversible once the strain is released and is independent of the type of polymer, but is dependent on the type of filler. Figure 2-2 shows the key difference between carbon black and silica: The Payne-effect is stronger for silica, as a consequence of the strong interparticle forces between the filler particles.
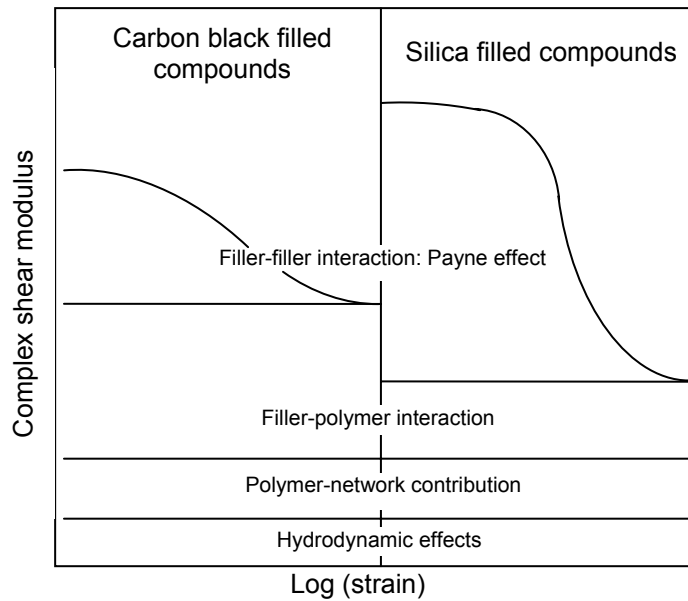
*Figure 2-2: Effects contributing to the complex shear modulus*

2.3 Mixing with fillers: dispersive mixing

Mixing of rubber is not just a process with the aim of a homogenous distribution of the compound additives in the polymer matrix, but includes processes such as plasticization, incorporation of solids and dispersion. During mixing all these processes take place, but depending on the mixing parameters and the degree of mixing the rate of the different processes changes.
On macroscopic scale the dispersion of a filler into a polymer matrix shows the following stages:

o The filler smears into striations following the deformation pattern of the polymer
o Agglomerates up to 10 to 100 micrometer in size appear
o Agglomerates are continuously broken and aggregates with an average size of 100 nanometers till 0.5 micrometers appear
o Smaller aggregates and primary particles appear on the expense of larger aggregates and agglomerates

Figure 2-3 illustrates the transition from large silica agglomerates into smaller aggregates and primary particles, and gives an indication of their dimensions.
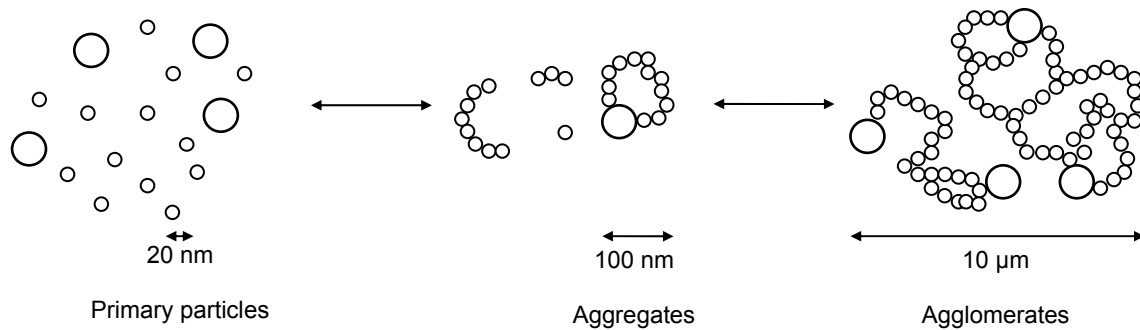
Figure 2-3: Filler aggregation and dispersion

Based on these phenomena, Yoshida described mixing as a three step process: transposition, insertion and breaking of the disperse system. During transposition the system is subjected to stretching deformation by shearing forces, which increases the interface between the disperse phase and the matrix, and results in a gradual insertion of the disperse phase into the matrix. The particles of the dispersed phase are disrupted by shearing forces, and the size of agglomerates and aggregates is reduced. The degree to which the filler finally has to be dispersed depends on the quality requirements of the compound: the higher the degree of dispersion, the better the properties. But there is a lower limit to the aggregate size as the properties deteriorate with very small aggregate sizes and an increasing amount of primary particles.

A more refined model of dispersive mixing separates the process into four different steps:

o   Incorporation
o   Plasticization
o   Dispersion
o   Distribution

In the initial stages of mixing before incorporation starts, two processes take place: The first process involves large deformations and subsequent relaxation of rubber domains, during which filler aggregates are sandwiched between rubber layers. The second mechanism is based on the disintegration of the rubber into small particles, which are blended with the filler agglomerates and finally seal them inside.

a. Incorporation
The incorporation of the filler is subdivided into two phases: formation of a rubber shell around the filler particles followed by filling up the voids within the filler agglomerates, in other words between the filler aggregates. It includes a subdivision step: breaking of large agglomerates into smaller entities.

b. Mastication and plasticization

Mastication and plasticization take place during the whole mixing process and result in a change of the rheological properties of the compound, especially a viscosity decrease of the polymer matrix by degradation of the elastomer chains. Figure 2-4: gives a schematic view of the viscosity changes during mixing and the contributions of temperature increase and polymer breakdown to the viscosity decreases.

c. Dispersion

At the end of the incorporation stage the majority of the filler is present as agglomerates. They act as large, rigid particles, whose effective volume is higher than that of the filler alone due to rubber trapped inside the filler voids and the rubber immobilized on the surface. The bound and occluded rubber increases the rate of dispersive mixing by increasing the effective radii of the filler particles: larger effective radii lead to higher stress during mixing. The filler agglomerates are successively broken to their ultimate size, mainly by shear stress. Parallel with the reduction of the agglomerate size the interface between the matrix and the filler is increased, and the filler particles are distributed homogenously throughout the rubber matrix. When the filler agglomerates decrease in size, the occluded rubber concentration is reduced. The viscosity of the compound decreases and finally reaches a plateau region. In general, the average particle size reaches a minimum value and a further energy input does not result in a reduction of the size of the filler aggregates any more, as the mixing and dispersion efficiency is decreasing with reduced viscosity of the compound.
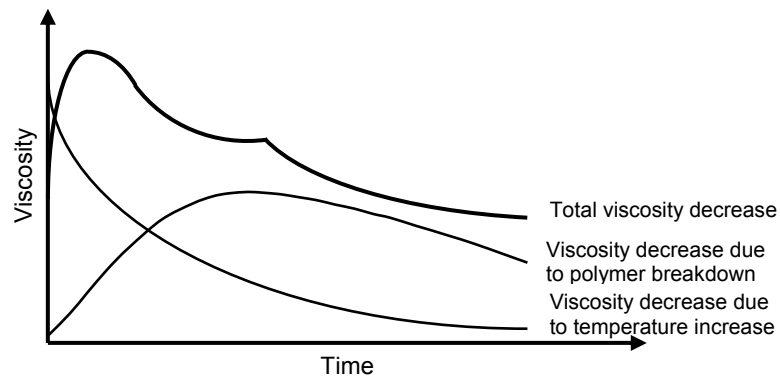
Figure 2-4: Contributions of polymer breakdown and temperature increase to the viscosity decrease

d. Distribution

In the distributive mixing step particles are spread homogenously throughout the polymer matrix without changing their size and physical appearance. The thermodynamic driving force for this process is the entropy increase of the blend.

Figure 2-5 illustrates the different mixing stages with respect to filler subdivision, incorporation, dispersion and distribution.
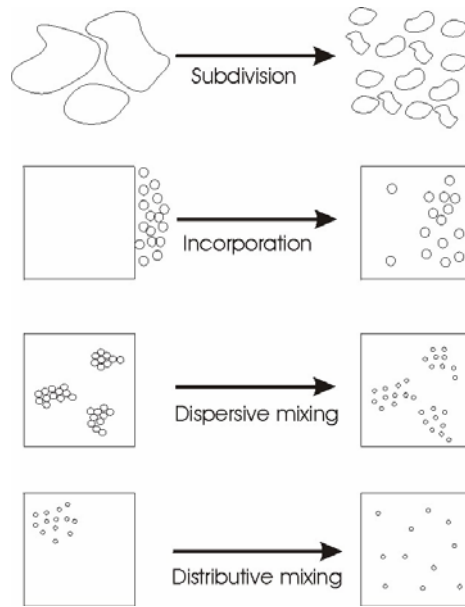
Figure 2-5: Illustration of the different mixing stages for filler-polymer systems

2.4 Carbon black

The most widely used active filler in the rubber industry is carbon black. Several types of carbon black are generally recognized:

- Furnace blacks;
- Channel blacks;
- Thermal blacks;
- Several other types of blacks, like conducting blacks, light blacks etc.

By far the most important category of blacks comprises the Furnace blacks. About 95% of applied blacks in rubber are produced with the furnace-method. Preheated oil with high contents of aromatic components and low content of sulfur (<3%) is sprayed by means of pressed air in a flame of gas and preheated air. Because of the high temperature (1300-1800°C) and because of the reductive atmosphere in the flame as a result of a low oxygen level, the oil is thermally cracked. In this way, the hydrocarbons are reduced to carbons. Spraying of water stops the reaction. The residence time in the furnace is only a few milliseconds. Carbon black and combustion gas are cooled by means of a heat exchanger and the carbon black is separated by a cyclone. Finally, the carbon black is pressed to granular size, whether dry or with water or with adhesives. Advantage of the Furnace process is that a great variety of black types can be produced (specific area and structure, see later). The primary particles have a diameter size of 10-80 nm.

The Channel blacks are hardly used anymore in the rubber industry. The raw material is natural gas (methane) sometimes with addition of oil. The raw material is burnt with shortage of oxygen by lots of small burners, against slowly moving iron channels. The carbon black deposited on the iron channels is scratched off, gathered and pelletized. This process has a very low efficiency (3-6%). Because of environmental and energetic considerations, it is therefore not used anymore. The primary carbon black particles of this process are very small: 10-30 nm.

The principle of the Thermal–black process is the decomposition of natural gas (methane) in carbon and hydrogen at around 1300°C in absence of air. The process consists of two furnaces, which work alternately: natural gas is passed through the first furnace, which is already heated by combustion of hydrogen. Carbon black and hydrogen are then formed. Carbon black is separated from the hydrogen and the hydrogen is subsequently used to heat up the other furnace. Cycle times of the furnaces are about 5 minutes. As well as the Channel process, this Thermal process has a disadvantage compared to the Furnace process because of environmental and energetic considerations. The primary carbon black particles are about 200-500 nm.
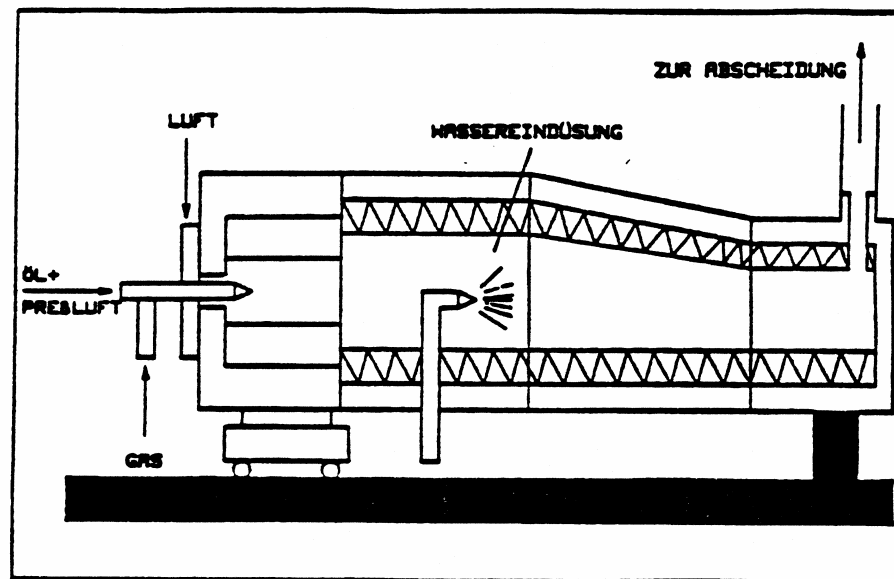

Figure 2-6: Furnace-black reactor.

2.4.1 Morphology of carbon black

In the morphology of carbon black, generally three different characteristic properties or dimensions are recognized:

- The primary particles, as they are formed in the different processes, with dimensions of 10-500 nm. Each primary particle consists of concentric, or according to some carbon black experts irregular, ordered carbon crystallites. The absorption-loci of carbon black are especially at the edges of the carbon crystallites, or on the transition from one to the other carbon crystallite.
- Carbon aggregates: the primary carbon particles appear to be clustered, tightly bonded to larger carbon black units. In practice, these aggregates are the smallest stable structural units from which carbon black is built up. By adequately mixing into rubber, the carbon black particles can only be broken up to the dimensions of these aggregates.
- Carbon black agglomerates: the clustered carbon black aggregates held together by the Van der Waals forces, which eventually form the powdery product of the production process. These agglomerates are finally compacted to carbon black pearls, in the way they are delivered to the rubber processing industry.
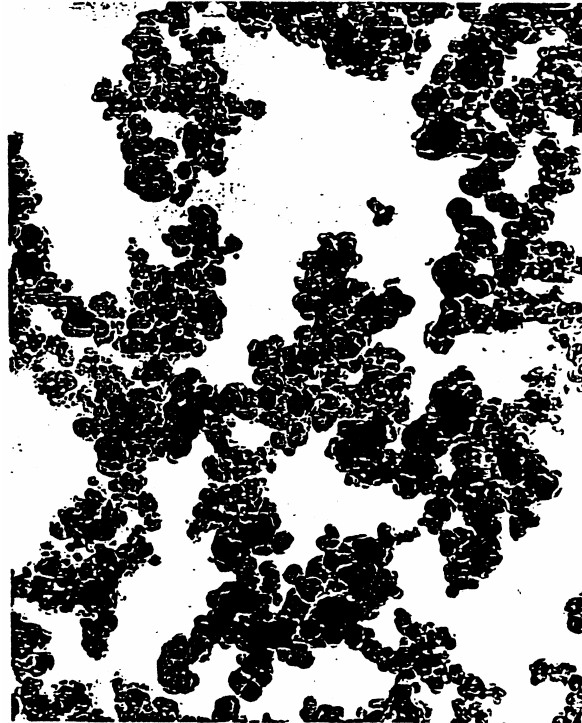

10 nm

10 nm

Macromolecular chains
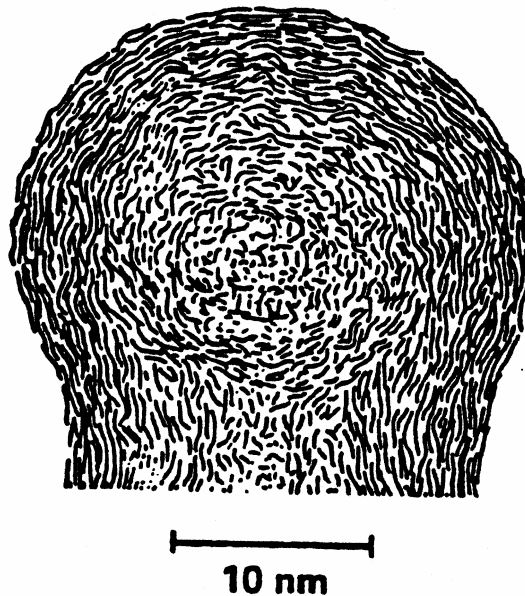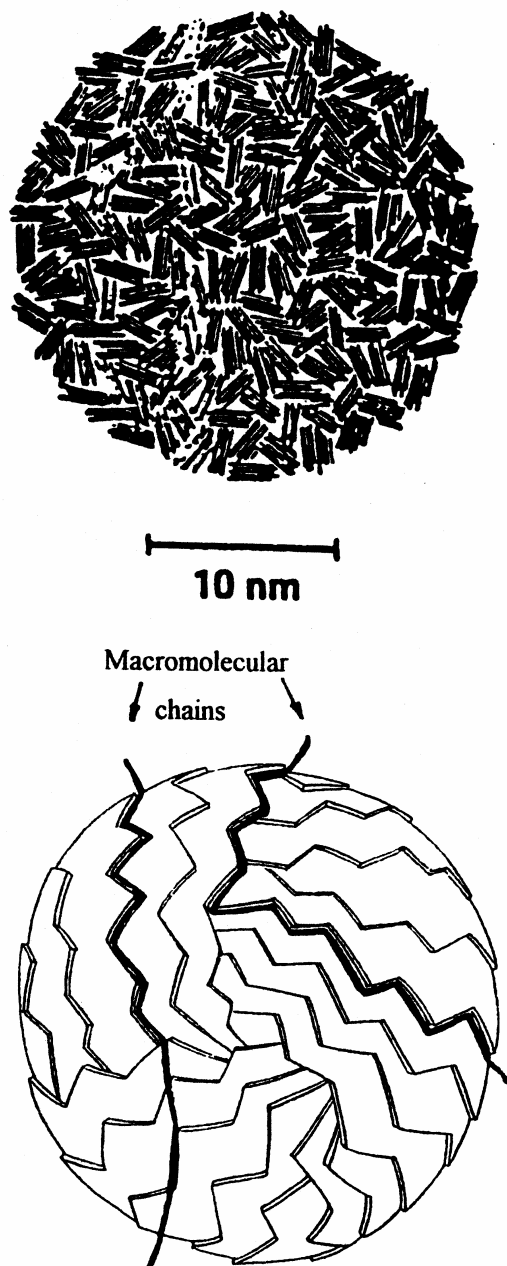
Figure 2-7: Concentric layer-model of the surface of a primary carbon black particle; respectively, model of irregularly ordered crystallites at the surface of a carbon black particle. Schematic representation of the conformation of rubber molecules on the surface of a primary carbon black particle.
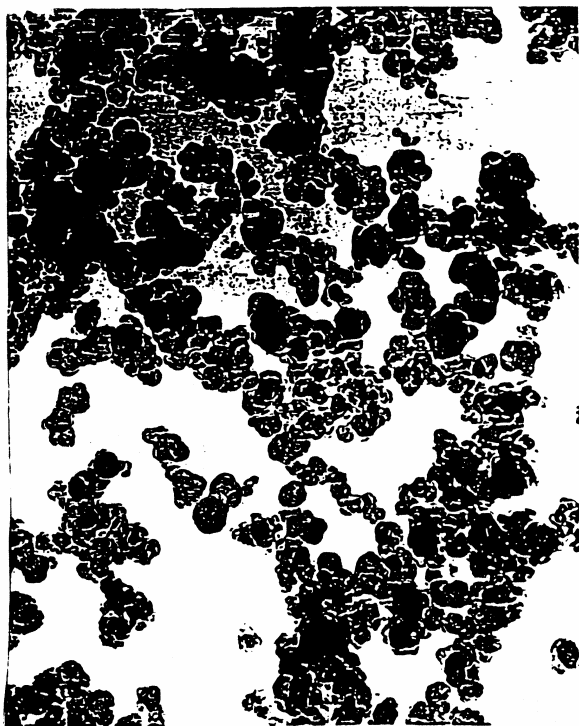
Elektronenmikroskopaufnah-
me von N 326 (niedrig strukturiert)

Elektronenmikroskopaufnah-
me von N 330 (normal strukturiert)

Figure 2-8: Aggregate-structure of carbon black N326 (low structure) and N330 (medium structure) and N339 (high structure).

2.4.2   Parameters influencing the reinforcing effect of a filler

A.   The specific surface area of the filler

An important quantity that determines the reinforcing effect of a filler the amount of surface area per gram filler. This quantity is mainly determined by the dimensions of the primary particles. These dimensions determine how much contact area is available for interaction between the filler and rubber. It can easily be seen that a filler with small primary particles possesses more specific surface area than a filler with bigger primary particles.

The specific surface area of fillers is normally determined by standard techniques, in which the adsorption of gas (N2: BET-method), Iodium or cetyl-trimethylammonium bromide (CTAB-method) is measured.

As an example, typical values for the specific surface area of different types of carbon black are appr. 6-160 m2/g black.

B.   The aggregate structure

Because during mixing, a reinforcing filler is mainly broken down to the dimensions of aggregates, the spatial shape of these aggregates is an important factor. In Figure 2-8 three different types of carbon black can be seen, having the same dimensions of the primary particles, but a different spatial shape of the aggregates.

Looking at the different spatial shapes, we can see shapes like 'strings of pearls', vs. more or less coagulated structures like "grape bundles" of primary particles. With the 'structure' of the filler, the degree of coagulation of primary particles is meant, that forms an aggregate. Low structure, respectively high structure refers to a low degree of coagulation vs. high degree of coagulation.

Determination of the structure

Non-spherical particles have a lower packing density than spherical particles (74.01%). This means that the empty volume comprises 25.99% of the space. This empty volume is used to determine the structure of the filler: the empty volume is filled with a liquid, i.c. dibutylphtalate. This is done in a Cabot-adsorptometer or a Brabender plastograph, a kind of small batch mixer: the machine is filled with a certain amount of e.g. carbon black and slowly, dibutyl-phtalate is added. The powdery carbon black gradually transforms to a coherent mass. At the moment that the empty volume is just filled with dibutyl-phtalate, a strong increase in torque is observed. The quantity of dibutyl-phtalate added till that moment is called ml DBP per 100 grams of carbon black.
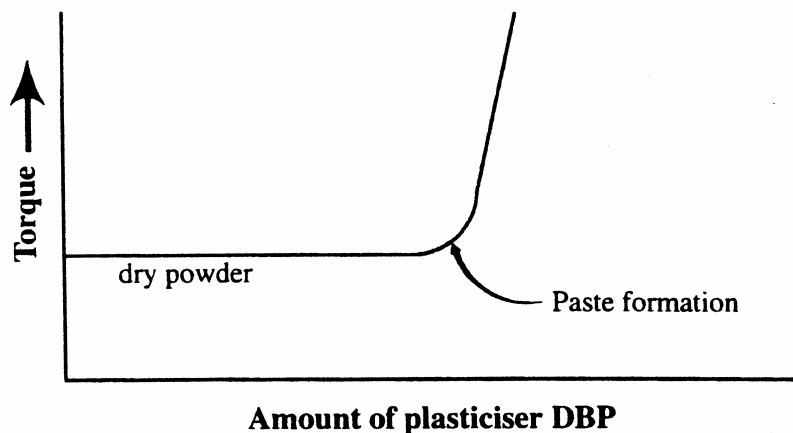
Figure 2-9: Determination of the DBP-adsorption in a Cabot-Adsorptometer.

The higher the structure of a filler, the higher is the DBP absorption. There is a relation between the DBP absorption and the reinforcing effect of the filler, as becomes visible in the 300% Modulus. With equal crosslink density, the 300% Modulus increases on increasing DBP-number if blacks with the same specific area are used. Thereby, it is thought that the carbon black aggregates enclose a certain amount of rubber inside their structure. Subsequently, the carbon black aggregates and the enclosed rubber act

together as one unit. The acting unit becomes bigger, as the structure of the black is higher. For the translation to mechanical properties of the rubber compounds, see Chapter 2.4.4.
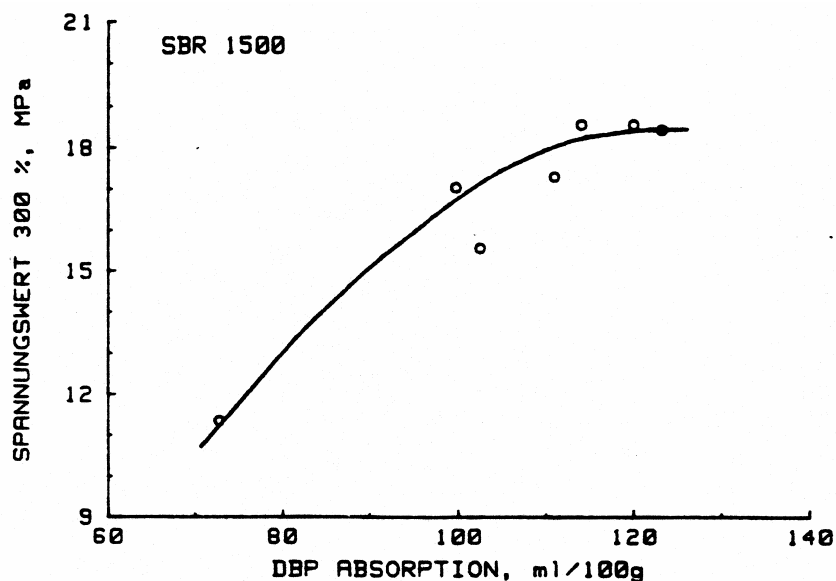

Figure 2-10: Modulus @ 300% strain of a SBR-compound as a function of the DBP-number (Nitrogen-surface area is almost equal).

C.   The specific surface activity

The type of linkage that is formed at the surface of the filler with the rubber, has been the subject of many studies, but has not been fully elucidated. Some researchers reason about chemical bonds between e.g. the carbon black and the rubber molecules, via several functional groups at the carbon black surface:

-H, -OH, =O, -COOH, -C=O and/or free radicals.

Others reason about physical absorption. Again others believe in a model, in which elastomer molecules stick behind the crystal-edges of the carbon black particle and in this way get attached to the black. An argument in favor of this model is that in measurements of the heat of absorption it has been shown that the absorptive activity of carbon black is irregularly distributed on the carbon black surface. The absorptive active surface comprises only 5% of the total available surface.

Sure is, that the heat of absorption of the filler surface is of outmost importance for the formation of reinforcement. This can also be seen for silica, as will be dealt with in the

next chapter. However, the formation of a covalent chemical bond is not an absolute necessity for reinforcement. Without covalent chemical bonds, reinforcement is also observed. Though, the presence of chemical bonds works in a positive way.

2.4.3 ASTM D1765 Carbon black classification

The great variety of blacks requires a classification, in order to realize a possible interchangeability between the different suppliers. In 1967, a consequent classification has been introduced by the ASTM (American Standards Association). A nomenclature was set up, consisting of a letter and three digits: N and S respectively, for Normal and Slow curing (Channel and post-oxidized black). The first of the three digits corresponds with the diameter of the primary particle size, ranging from 1 to 9. The following two digits were chosen randomly and do not have a specific meaning.

Generally, the 100-series blacks have the smallest primary particle sizes. Because of their large specific surface area, they are highly reinforcing. On the other hand, these blacks are quite difficult to incorporate in the rubber, because of the high shear forces needed for the dispersion. The 900-series blacks have very large primary particles: they are easy to disperse but do not show high reinforcement. The type of black that suits best to a particular rubber depends on the one hand on the application and on the other hand also on the intrinsic plasticity of the type of rubber. For instance: highly viscous/elastic NR for tire tread applications for which high abrasion resistance is required will/can be reinforced with 200- respectively 300-series blacks. In EPDM, which does not possess a high intrinsic plasticity, these types of black can hardly be incorporated and dispersed. Therefore, for EPDM 500- to 700-series blacks will/have to be used.

Before the ASTM nomenclature was introduced, people used to (and still do) designate blacks after their application type. Some commonly used names are:

        300-series: HAF   High Abrasion Furnace
        400-series: ISAF   Semi Abrasion Furnace
        500-series: SRF   Semi Reinforcing Furnace
        700-series: FEF   Fast Extrusion Furnace

See Table 2.1 for the ASTM classification of the most commonly used black types.

2.4.4 Reinforcement: dependence of the physical compound and vulcanizate properties on the filler level

Attempts to describe the properties of the rubber mixture and rubber vulcanizate quantitatively, have hardly been successful up till now for practical work. A few number of practical correlations are worthwhile mentioning though, because they offer some insight.

For a suspension of spherical particles in a medium of viscosity η0 an old relation holds. Einstein originally derived this relation, but later it was modified by Guth and Gold:

$$\eta = \eta_o \left(1 + 2,5\,\phi + 14,1\,\phi^2 \right)$$

(2.1)

$$\phi = \frac{V_F}{V_F + V_R}$$

(2.2)

With:

η   = Viscosity of the mixture;
VR   = Volume of the rubber part;
VF   = Volume of the filler part;
φ   = Volume fraction of filler in the mixture.

For small values of φ, the third term between brackets vanishes. The formula then transforms into the original form derived by Einstein. Note that in this equation, filler particle size does not play a role.

Glass beads and MT-black (900-series), a black with almost spherical dimensions, obey this relation pretty well. Blacks with larger surface area's and more structure deviate upwards compared to the theoretical prediction. Explanations for these findings are:

- The carbon black aggregates are not spherical;
- The carbon black aggregates cannot move feely through the rubber medium;
- The carbon black aggregates stick more or less behind each other and in this way they cause thixotropy;
- The rubber molecules which occupy the empty volumes within the filler aggregates and which form in this way rubber-filler aggregates, cannot move freely;
- The rubber molecules occupying the empty holes do not participate in deformations, thereby increasing the effective filler concentration;
- It appears that rubber molecules with higher molecular weight are preferentially absorbed by the filler particles. In this way, the remaining rubber has a lower molecular weight.

That is why neither the η0, nor the φ, represents the real situation.

Table 2.1: ASTM-classification of carbon black types.

ASTM designation	Target Values					
	Iodine Adsorption No.,d D 1510 g/kg	DBP No., D 2414 cm3/100 g	DBP No., Compressed Sample, D 3493. cm3/100 g	CTAB D 3765, m2/g	Nitrogen Adsorption D 3037 m2/g	Tint Strength D 3265
N110	145	113	98	126	143	124
N121	121	132	112	121	132	121
S212		85	82	119	117	115
N220	121	114	100	111	119	115
N231	121	92	86	108	117	117
N234	120	125	100	119	126	124
N242	121	124	106	111	125	116
N293	145	100	92	114	130	117
N299	108	124	105	104	108	113
S315		29	75	85	88	
N326	82	72	69	93	84	112
N330	82	102	88	93	83	103
N332	84	101	90			118
N339	90	120	101	95	96	110
N347	90	124	100	88	90	103
N351	68	120	97	74	73	100
N358	84	150	112	88	87	99
N375	90	114	97	98	100	115
N472	250	178	114	145	270	
N539	43	111	84	41	41	
N550	43	121	88	42	42	
N630	36	78	62	38	38	
N642	36	64	62	37	37	
N650	36	122	87	38	38	
N660	36	90	75	35	35	
N683	35	133		39	37	
N754	24	58	57	29		
N762	27	65	57	29	28	
N765	31	115	86	33	31	
N774	29	72	62	29	29	
N787	30	80	74	32	30	
N907		34			11	
N908		34				
N990		43	40	9	9	
N991		35	38	8	7	

| Note 1:	The Iodine adsorption number and DBP number values represent target values. A target value is defined as an agreed upon value on which producers center their production process and users center their specifications. All other properties shown are averages of typical values supplied by several manufacturers.
Note 2:	IRB data was obtained form tests performed during the certification of IRB No.6 carbon black
d	In general, Test Method D 1510 can be used to estimate the surface area of furnace blacks but no channel, oxidized and thermal blacks.
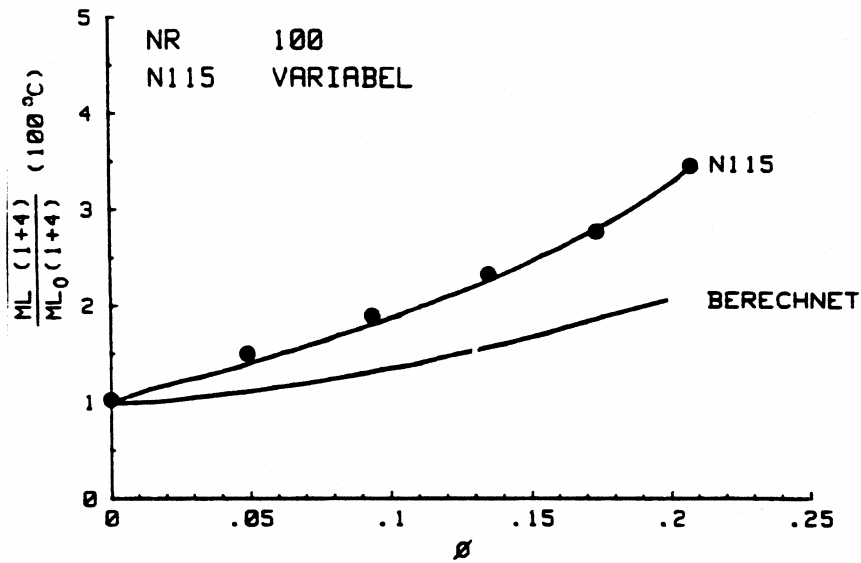
Figure 2-11: Deviation of the viscosity of the for a NR compound filled with 50 phr N115 black.

Reinforced networks behave viscoelastically; the elasticity modulus is next to the viscosity also a very important quantity. Smallwood showed that for elastic media filled with spherical particles an equation similar to (can be applied. The only thing that needs to be changed is that η should be replaced by the elasticity modulus E:

$$E = E_0 \left(1 + 2{,}5\,\phi + 14{,}1\,\phi^2 \right)$$

(**2.3**)

Similar to (, this relation only holds for spherical filler particles, like glass beads and MT-black and only for very low deformations. However, the relation does not hold for rubber fillers with structure, as is shown in Figure 2-12. A strong deviation can be seen for a peroxide-cured NR filled with carbon black N115.
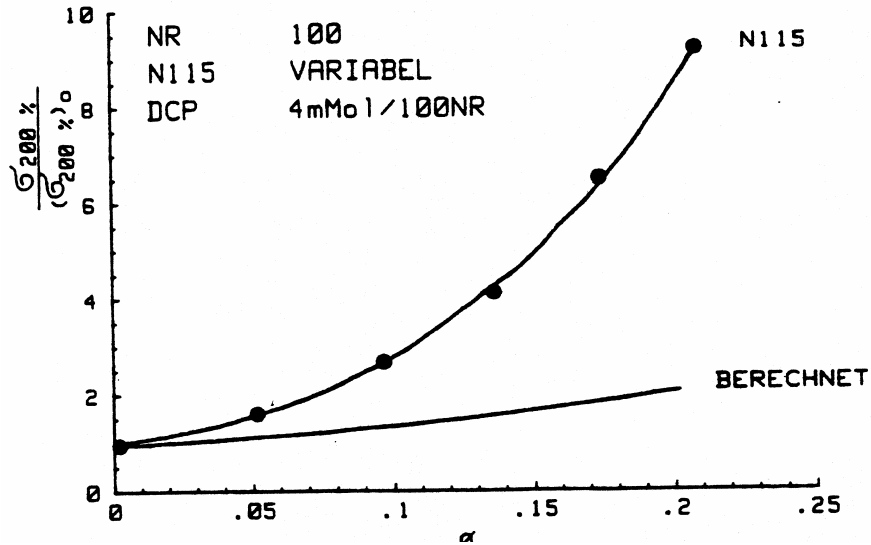
Figure 2-12: Deviation of the 200% Modulus from Eq.(2.3) for NR filled with N115 carbon black.

For high filler loadings, typically up to a volume fraction of φ ≈ 0.35. a Padé approximation of the series expansion in Eq. (, (2.2) and (2.3) up to the second order in the volume fraction leads to another suitable and theoretically founded expression:

$$E = E_0 \left(1 + 2.5\,\phi + 5\phi^2 + ... \right) \approx E_0 \left(\frac{1 + 2.5\phi}{1 - 2\phi} \right)$$

(2.4)

A recent approach to the reinforcement of fillers in rubbers makes use of the fractal description of percolating networks. The percolation point is defined as the volume fraction of filler φ*, at which filler aggregates touch to form an electrically conductive (percolating) path through the rubber compound. The fractal theory is based on the principle in nature, that above a certain length scale matter seems homogeneous, but below that length scale shows a certain morphological structure, which repeats itself at smaller and smaller length scales: fractal. Percolating filler networks are typically fractal: above a certain length scale the compound seems homogeneous, but below that length scale the filler network can be discerned, at smaller length scale the aggregate structure, etc.

It would take too much to go in full detail about the fractal theory in the present context. It suffices to state, that for volume fractions of filler larger than the percolation point:

$E \approx \phi^{3.5}$ *for* $\phi > \phi^*$

(**2.5**)

At these volume fractions the size of the primary particles, or specific surface area of the particular carbon black filler does not play a role.
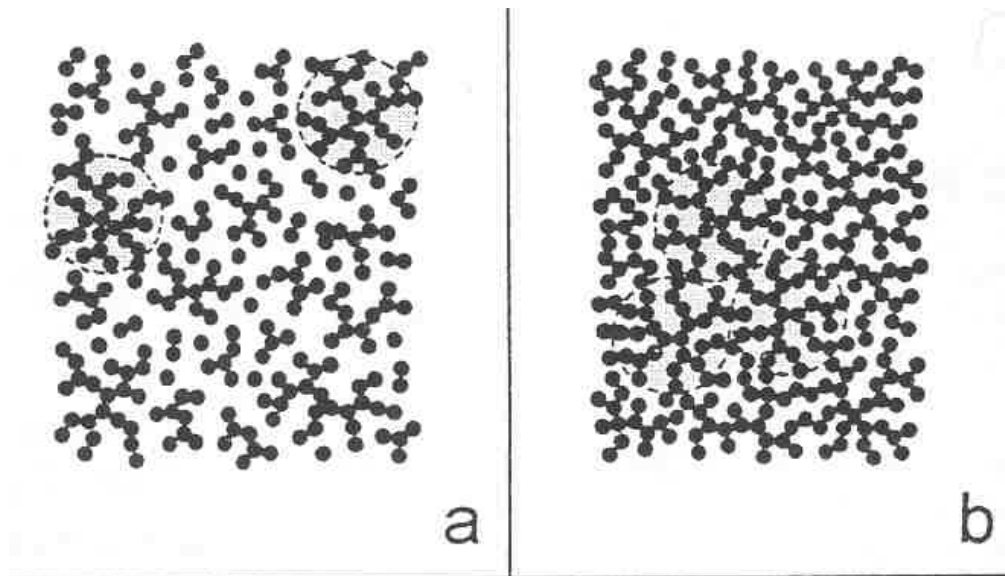

Figure 2-13: Filler aggregate configurations in rubbers: a) $\phi < \phi*$ *and b)* $\phi > \phi*$, *above the percolation point.*

Even though equations (and (2.3) have limited applicability, they give a first estimate of the influence of reinforcing filler on the viscosity and elasticity modulus of compounds and vulcanizates. Numerous refinements have been derived in the past, of which the 'stress-concentration'-variant is one of the most well known. Deforming a reinforced rubber compound causes differences between the microscopic and macroscopic deformation, because the filler particles do not participate in the deformation. The vulcanized rubber has to carry the entire load between filler particles and is thus more deformed than when no filler is present. The stress/forces in the individual rubber molecules in reinforced rubber are a factor higher, than when the rubber would not have been reinforced.

The observation that the tensile strength of a reinforced rubber increases relative to non-reinforced rubber, can be made clear as follows. The tensile strength of crosslinked, non-crystallizing rubbers is low, because the stress is not equally distributed over the whole mass. The crosslinks are randomly distributed causing differences in chain length between two crosslinks. During a tensile test, the shortest and therefore most stressed chain segments will fail first. If, however, the most stressed

chain segments have enough opportunity to slide along the reinforcing particle, the point of failure will be shifted towards higher stress. In this way, the stress is divided among a higher number of effectively loaded chain segments. The result is a higher tensile strength.

An illustration of this behavior is shown in Figure 2-14.
In the non-extended state, AA' represents the shortest and most stressed chain segment. If on straining the stress on AA' is increased, it can only be reduced by sliding of chain segments along the filler surface. At the same time, chain segment BB' is stretched. On further straining, the stress is divided by sliding of the rubber molecules absorbed on the filler particle. In this way, all chains between the filler particles get more or less the same stress. By releasing the stress, the rubber chains between the filler particles do not retain the same length so that the situations (a) and (d) are not identical.

This model for reinforcement also explains the so-called Mullins-effect. This Mullins-effect comprises the so-called stress softening of carbon black-reinforced rubbers on cyclic deformations.
See Figure 2-14.
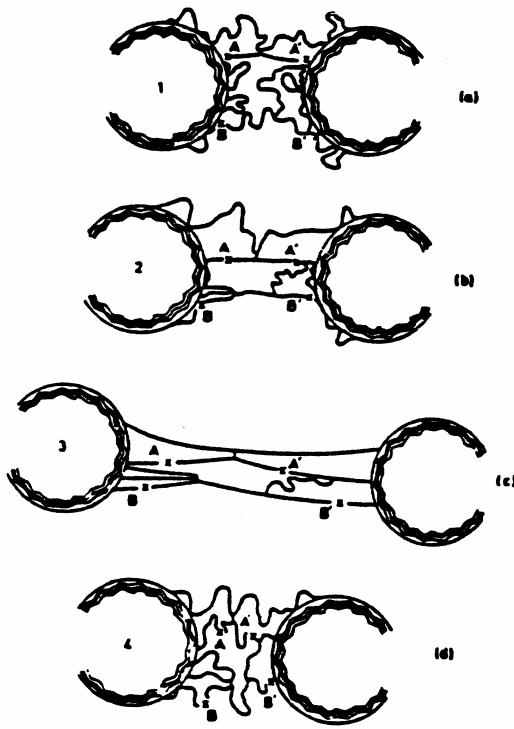
Figure 2-14: Molecular sliding model to explain the mechanism of reinforcement of rubber as well as the so-called Mullins-effect:

(a) *State at beginning of the experiment;*
(b) *On straining: shortest chain segment AA' is unloaded by sliding of A and A';*
(c) *All chains are fully strained and have the same length between the carbon black particles;*
(d) *After unloading, the chains remain the same length between the carbon black particles.*

Situation (a) differs from situation (d).

2.4.5 The Payne-effect

Another model that is often used is, that the filler forms a sort of own network inside the rubber network. On deformation, this filler network is easily disturbed, while the rubber network remains intact. An example of this is the so-called Payne-effect: the elasticity modulus of reinforced rubber depends on the magnitude of the deformation. On increasing strains, the E-modulus decreases. Especially at dynamic mechanical deformations (cyclic sinusoidal deformations), it is clear to see that E' and E" depend on the amplitude of the deformation (not to be confused with the Mullins-effect). See Figure 2-15.
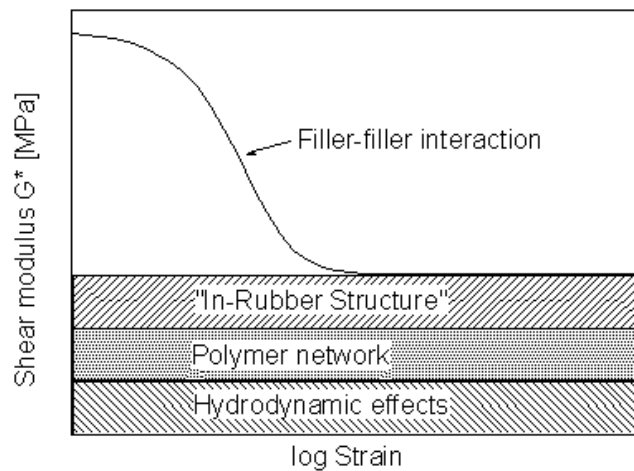
Figure 2-15: The Payne-effect.

The interpretation of Figure 2-15 is as follows:

- The vulcanized rubber network has an amplitude-independent contribution to the elasticity modulus.
- On top of this rubber network contribution, there is an, also amplitude-independent, hydrodynamic contribution as described by Eq.(2.3);
- On top of these two, there is an amplitude-dependent, or strain-dependent contribution to the elasticity modulus of the filler network.

With these three contributions, the modulus of the vulcanized rubber with filler is determined.

The model of a carbon black filler network has already been known for many years and it is generally accepted. But, although the model is capable of explaining many observations in an empirical way, a quantitative description of the reinforcement of carbon black filler of the rubber is practically impossible. See the preceding pages. It is

therefore not surprising that other models have been proposed to describe the rubber-filler interaction, in a more quantitative way.

One explanation of the Payne-effect deals with the destruction-reformation of the percolating filler network upon deformation of the rubber. This can as well involve polymer bound to the filler surface.

A very elegant model has been introduced some years ago, in which the interaction between the rubber matrix and the carbon black is modeled in a similar way as the so-called Langmuir-isotherm for adsorption of gas molecules on a solid substrate. This Langmuir-isotherm is based on a dynamic equilibrium between gas molecules being absorbed to and gas molecules being desorbed from the solid substrate. In equilibrium, there is a certain ratio between the occupied and vacant absorption sites on the substrate. This ratio is only determined by the partial vapor pressure of the gas molecules: the higher the partial vapor pressure, the higher the fraction of occupied absorption sites.

The fact that carbon black tends to absorb all kinds of chemical substances is not new. In synthetic organic chemistry, purification with activated carbon is a well-known process step. In analogy, we can imagine that rubber molecules are absorbed on carbon black particles. Though, in the present case not the whole rubber chain is attached to the contours of the carbon black particle. The chain molecule curls along the carbon black particle and, every now and then along the chain, a bond with the carbon particle is formed.
As this system is also subjected to thermal Brownian motion, sometimes bonds dissociate and on other places new bonds are formed. In this way, a dynamic equilibrium like the Langmuir-isotherm can be imagined. If the reinforced rubber is deformed, this equilibrium becomes disturbed: more contact points are released than there are formed, causing decrease of strength. On the other hand, if the rubber is released again, the equilibrium will settle again in the old way.

This model is capable in an excellent manner to describe the Payne-effect qualitatively. The future will tell us, whether this model will gain acceptance or not, compared to the filler-network model.

There remains the fact that, because of the Payne-effect, the mechanical properties of a reinforced rubber are dependent on the amount of deformation and also on the time span between two subsequent large deformations. This dependence on deformation and time differs for each singular rubber mixture and is very difficult to describe. Therefore, during the development of a rubber article, the mechanical properties are very hard to predict. This is pretty annoying. Omitting the filler reinforcement of the compound causes that the properties of the final product will go down with a factor of ten, which is also not desirable. See here a big problem waiting for a solution!

2.4.6 Bound rubber

This is a phenomenon that has drawn the attention of people working in rubber technology already for a long time, because till now, its character is not completely understood. But as a matter of fact, it proofs that there exists some kind of bond between the rubber and the carbon black particle: "bound rubber".

If an unvulcanized black-filled rubber is extracted with a good solvent, part of the rubber appears to be insoluble. This fraction remains as a hard, brittle gel bound to the carbon black and it is filtered off along with the carbon black. This fraction is called the bound rubber. This bond between the rubber and the carbon black depends on a lot of factors, among others:
- The type of black and the filler level;
- The kind of elastomer;
- The mixing technique: temperature and time;
- The time between the mixing and the actual extraction.

In short: only under strictly standardized conditions, values of bound rubber can be compared with each other.

Of course, bound rubber is caused by the interaction between the black particle and the rubber as a result of adsorption, various sorts of chemisorption, bonding between free rubber radicals, etcetera.
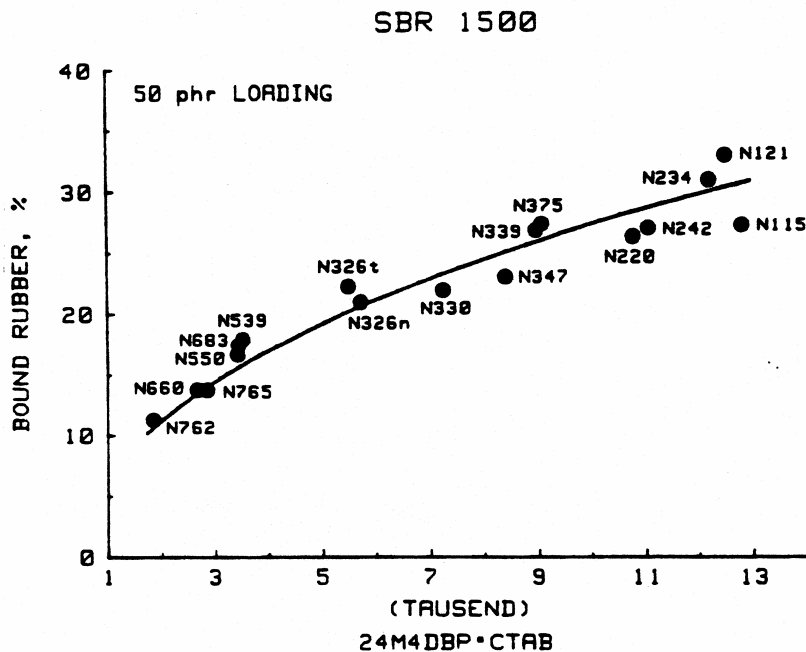

Figure 2-16: Variation of the bound rubber in a SBR 1500 compound, reinforced with 50 phr Furnace black under standardized conditions.

An essential part of the bound rubber consists of a layer of immobilized polymer around the primary filler particle. This immobilization is so strong, that at certain spots the polymer behaves like being in the glassy state. This glassy layer model also yields a physical understanding of the temperature dependence of the Payne-effect. It is generally known that the Payne-effect, the difference between the modulus at low strain relatively to large strain, decreases with increasing temperature. The low-strain modulus remains roughly constant. Hereby, two distinct mechanisms with different activation energies can be observed. The one at low temperature relates to the glass transition, confirmed by very large apparent activation energies. The one at high temperature, well above the glass transition temperature of the rubber polymer, gives activation energies of ≈ 10 KJ/mol, in the range of physical Van der Waals interactions.

The following Figure 2-17 gives a nice description of this effect. It demonstrates the structure of filler-filler bonds in a bulk rubber matrix. In the narrow gap size between neighboring filler particles the mobility of the confined bound rubber becomes so low, that the confined rubber behaves like a polymer glass.
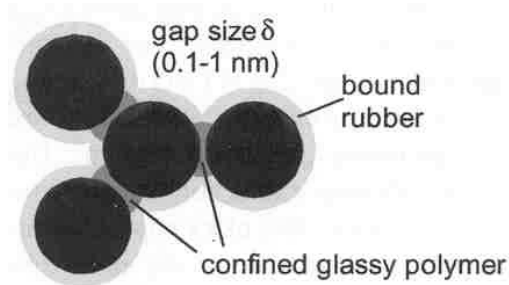
Figure 2-17: Schematic view of a small filler cluster in elastomers with stabilizing bound rubber and nanoscopic bridges of confined glassy polymers.

2.5 Silica

2.5.1 Types of silica

After dealing elaborately with carbon black reinforcement of elastomers, we can be shorter in our description of silicas and silicates. The mechanisms are quite comparable. The equivalence can already be seen by the fact that silicas, which are used in rubber reinforcement, have a comparable specific surface area of $25 - 250$ m2/g.

For the preparation of silica fillers nowadays, there are two processes in use:
-   The precipitation process;
-   The pyrogenic of thermal process.

In the rubber industry, mainly the cheaper precipitated silicas are used. Silicates were used in the past, but have now almost all been replaced by pure silica. The much more expensive pyrogenic silica, having much smaller particle sizes than the precipitated

silicas, are almost solely used in silicone rubber applications (and in thermoplastic elastomers).

2.5.2   Precipitated silicas

Raw materials for silicas are alkali-silicate solutions, preferably sodium silicate, from which the silica is isolated by the addition of an acid. The white precipitate consists, after filtration, washing and drying, of 86 –88 % SiO_2 and 10 –14 % water and chemically bonded residues of the salts formed at the conversion, respectively small traces of added metal oxides. Besides pure silicas, several metal silicates can be produced in the same way, when using metal salts instead of acids as the precipitation agent. In this way mainly Ca- and Al-silicates are formed.

The final properties of the product can be governed by process conditions like precipitation time, temperature, electrolyte concentration and pH. In this way, a whole range of products can be obtained, from silicas to silicates. The silicas and silicates that are used for rubber applications have surface areas from 25 – 250 m2/g (N2), as mentioned before.

After precipitation, a separation step by filtration in filter presses follows. In this step, the salts that were formed are also washed out. Then the filtered precipitates are dried in an oven. Finally, the dried precipitates are grinded to cut the large agglomerates and other hard, poorly mixable substances that were formed in the drying step.

2.5.3   Pyrogenic silicas

A homogeneous gas mixture containing $SiCl_4$, hydrogen and oxygen is combusted in a cooled reactor:

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$
$$SiCl_4 + 2\, H_2O \rightarrow SiO_2 + 4\, HCl$$
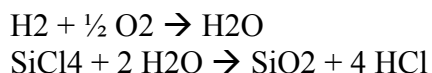
The concentration of $SiCl_4$, the temperature of the flame and the residence time of the SiO_2-nuclei determine the particle size, the surface area and the secondary coagulation.

The SiO_2 is flocculated and post-treated with humid hot air in order to remove HCl residues. The bulk density of these kinds of silicas is very low: circa 15 g/l! Before packaging, the product is compressed a little bit, but it remains a very light material.

2.5.4 Silica versus Carbon Black

Silica compared to carbon black is characterized by weaker filler-polymer interactions and stronger filler-filler interactions. This results in a higher compound viscosity, a higher modulus at low strain amplitudes, a lower modulus at high strain amplitudes and a lower bound rubber content. However, the combination of silica with a coupling agent has a higher reinforcing effect and different dynamic mechanical properties compared to carbon black. The main influence on the mechanical properties when replacing carbon black by silica combined with a coupling agent is found for:

o Tear, abrasion and heat resistance
o Flex stability
o Hardness, stiffness and modulus
o Tack
o Heat build up
o Resilience

The stronger reinforcing effect of silica compared to carbon black allows the reduction of the filler content without any negative influence on the property profile, but with an additional positive effect on elasticity due to the higher ratio of elastic component to damping filler. This results in an additional reduction of the rolling resistance.

The stability of the covalent silica-polymer network results in a lower rate of breaking and reformation of the silica-polymer bonds compared to the carbon black-polymer network during a deformation cycle, resulting in a decrease of the loss modulus. A low value of the loss modulus together with a high value of the storage modulus results in a low value of the phase angle. As both, loss modulus and storage modulus, depend on deformation, the phase angle is also influenced by the applied strain: It increases with increasing deformation.

2.5.5 Silica Properties and Surface Characteristics

The primary filler characteristics influencing elastomer reinforcement are:

o Surface chemistry, structure and relative surface area
o Particle size and particle size distribution
o Structure of the filler aggregates, agglomerates and primary particles

The rubber-filler interface formed during mixing is primarily responsible for the level of properties such as abrasion resistance, tensile strength and tear propagation. The structure of the filler network influences the viscoelastic properties like elasticity, loss modulus and hysteresis.

2.5.6 Surface chemistry

The surface of silica is covered by a layer of acidic silanol groups and different siloxane groups: geminal, vicinal, clustered and isolated groups. The functional groups are randomly distributed over the whole surface, in contrast to carbon black, where the functional groups are preferably located on the edges of the crystallites. The silanol groups on the surface of different silica particles interact with each other, resulting in strong agglomerates due to the hydrogen bonds between the silanol groups. The moieties on the silica surface also interact with basic accelerators, resulting in reduced curing rates and lower crosslink densities. They can react with other chemical compounds such as stearic acid, polyalcohols and amines. These compounds compete with the coupling agent for adsorption sites on the filler surface; reduce the concentration of free surface silanol groups and thus the silanization efficiency.

The silica surface has a tendency to adsorb moisture due to the hydrophilic character of the filler. This adversely influences the curing reaction and hence the properties of the final product. However, a certain moisture content is required for the silanization reaction, as hydrolysis of the ethoxy groups of the coupling agent is a precondition for the secondary reaction to take place.

The average size of silica aggregates in a rubber matrix depends on the surface concentration of the silanol groups: A higher number of silanol groups per unit surface area results in an increase of aggregate size, leading to a higher concentration of occluded rubber. The relative surface area has an ambivalent influence on processing and properties of a rubber compound: On one hand it has a negative influence on the processing behavior, as a larger surface area results in a higher compound viscosity, and compound additives like accelerators are inactivated on the filler surface to a higher degree. On the other hand, a higher surface area has a positive influence on filler dispersion.

2.5.7 Surface energy

The energy distribution of the silica surface is inhomogeneous due to the distribution of silanol and siloxane groups and impurities. The surface energy γ_s of fillers is comprised of a dispersive and a specific component, γ_{sd} and γ_{ssp} respectively:

$$\gamma_s = \gamma_s^d + \gamma_s^{sp}$$
(**2.6**)

The dispersive component, based for example on London forces, is responsible for the rubber-filler interaction. This component is rather low in the case of silica, thus resulting in a low reinforcing effect, expressed by very low concentrations of bound rubber and a low modulus at medium and large strain amplitudes. However, polymer chains are entrapped in voids of the silica agglomerates and aggregates: occluded

rubber. The dispersive component is influenced by the degree of hydration of the silica: Increasing water contents are reducing the dispersive component even further. The specific component characterizes the interaction between the filler particles, and examples of these forces are dipole-dipole forces, induced dipole forces or hydrogen bonds. The contribution of the specific forces to the surface energy is higher for silica compared to carbon black. The balance of the dispersive and specific surface forces results in the unfavorable situation, that the filler-filler interaction is high and the interaction with the polymer is low for silica, with the consequence, that viscosity as well as Payne effect are high. These effects can be reduced by using coupling agents, silanes for example, together with the silica filler.

The reaction of silica with a silane results in a decrease of the specific component of the surface energy, leading to a decrease of the interaction between the silica particles. This facilitates filler incorporation and dispersion and reduces filler agglomeration. However, it also reduces the filler-polymer interaction, resulting in a reduction of the reinforcing effect. Therefore, the coupling agent contains a rubber-reactive group, which allows the formation of covalent bonds between the polymer and the coupling agent, thus providing a chemical link between the silica particles and the polymer during curing of the compound.

2.5.8   The Silica-Polymer Interaction

One of the models for the adsorption of polymers on the surface of carbon black is based on the uncoiling of the polymeric chains and multiple adsorption of these chains onto the surface of the filler. The released adsorption enthalpy is partly changing the chain conformation entropy, enabling the chains to abandon their coiled conformation and to take the form of trains. With several contacts per polymer chain the bonding strength of a polymer molecule is in the range of a chemisorptive interaction.

The intensity of wetting of the filler by a polymer depends on the difference of the solubility parameters: The surface concentration of adsorbed trains is inversely proportional to the difference of the solubility-parameters between the polymer and the filler. For the silica-polymer system the difference of the solubility parameters is significant, with the effect that the two materials are difficult to blend. When a coupling agent is used, a hydrophobic shell is formed around the filler particle and the solubility parameter of the filler is reduced, the difference in the solubility parameters decreases and the compatibility of the two materials increases.

2.5.9   Silica-Silane Reaction

The formation of a hydrophobic shell around the silica particle by the silica-silane reaction prevents the formation of a filler-filler network due to the reduction of the specific surface energy. Prior to the chemical reaction of the silane with the silanol groups on the silica surface, the silane molecule has to make contact with the silica surface by adsorption. Then the chemical reaction of silica with an alkoxysilyl moiety

of the coupling agent takes place in a two-step, endothermic reaction. The primary step is the reaction of alkoxy-groups with silanol groups on the filler surface. Two possible mechanisms are reported: Direct reaction of the silanol groups with the alkoxy groups of the coupling-agent, and hydrolysis of the alkoxy-groups followed by a condensation reaction with the silanol-groups. The fact, that the rate of silanization is influenced by the moisture content, is an indication that a hydrolysis step is involved. The reaction follows a pseudo-first order kinetic law. Figure 2-19 shows the mechanism of the primary reaction.
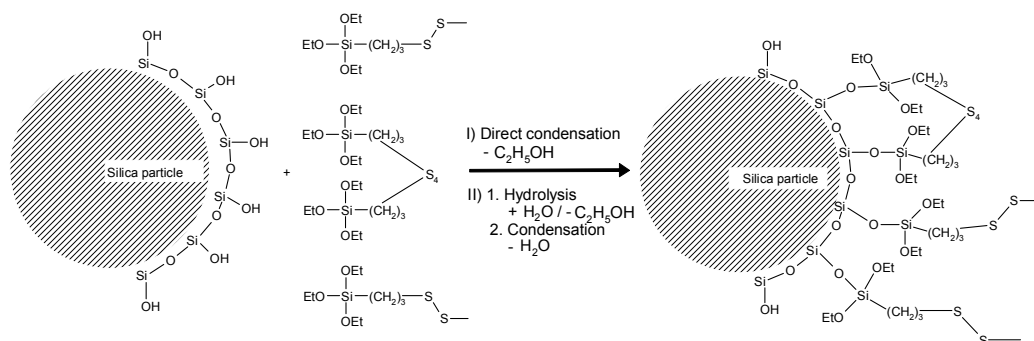
Figure 2-18: The primary reaction of silica with a silane

The secondary reaction (Figure 2-20) is a condensation reaction between adjacent molecules of the coupling agent on the filler surface or between alkoxy-groups of the coupling agent and silanol groups of the silica. It is generally accepted, that a hydrolysis step is involved in the reaction. In comparison to the primary reaction this step is slower with a factor of approximately 10. The energy of activation for both reactions, the primary and the secondary, is within the range of 30 to 50 kJ/mol. This value is rather low, indicating that the temperature dependence of the reaction rate is not very strong. The rates of both reactions are influenced by the acidity of the matrix, and the reaction is acid as well as alkaline catalyzed. The reaction rate is reduced by steric hindrance and an electron donating effect of the leaving group. Not all ethoxy groups react during the silanization reaction: The reaction results in two silane-silica bonds per silyl group, with one hydrolyzed ethoxy group remaining. But as the secondary reaction has only a slight influence on the properties of the compound, the incomplete reaction does not negatively influence the final quality of the material.
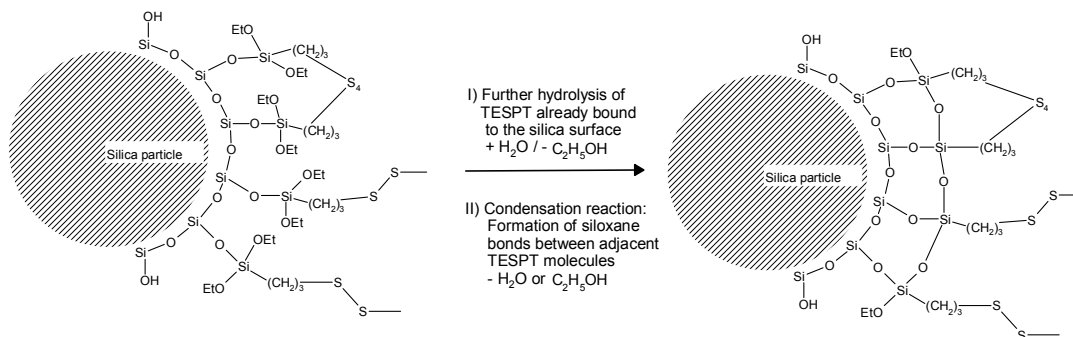
Figure 2-19: The secondary reaction of silica with a silane

The coupling agents need a moiety enabling them to react with the polymer during vulcanization in order to be reinforcing. This is shown in experiments with coupling agents, which can react with the filler but not with the polymer: The reinforcing effect is reduced, as the formation of bound rubber is impossible. In general, the moiety reacting with the polymer is a sulfur-group, either a poly- or disulfidic group or a blocked sulfur-group. Other functional groups used to link the coupling agents to the polymer are double bonds, which have to be activated by the addition of an active sulfur-compound or by the generation of a radical moiety in order to have a simultaneous crosslinking of the polymer and the coupling agent with comparable reaction rates during curing.

The polysulfidic moieties of the silanes are unstable, and the cleavage of the sulfur groups results in active sulfur moieties, very probably radicals, which react with the polymer under formation of a filler-silane-polymer bond. Figure 2-21 shows a general reaction scheme for the formation of the filler-polymer bond:
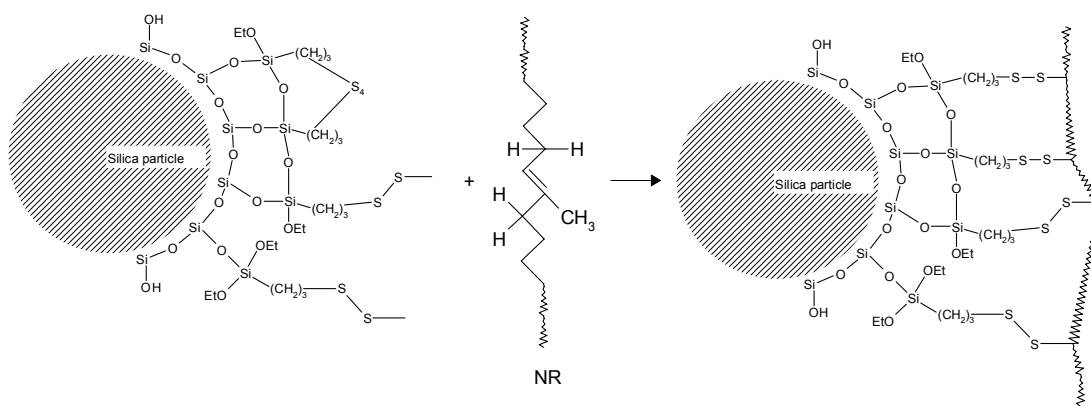

Figure 2-20: General scheme of the reaction of a polysulfidic silane with an unsaturated polymer

2.5.10 Main applications of silicas and silicates

The production capacity of silicas is about 12 – 15 % of the carbon black production. About 67% of the silicas is used in elastomers. The remaining 33% is used as carrier material for toothpaste, as improvement of transport properties and free flowing of pasting of food (e.g. castor sugar) and many others.

In the rubber industry, silica has its main application for 65% in shoe soles, 25% in tires (but this area shows a strong increase over the latest years) and about 10% in technical goods. In the shoe soles-application, silica has now almost completely replaced carbon black, because of the black stripes remaining on floor coverings. In technical goods, silica is used instead of carbon black as reinforcing filler in non-black applications. In the tire industry, silica is used in radial tires as an ingredient in the resorcinol/formaldehyde/latex dip in the cords that enhances the adhesion between the rubber and the cords (see later). Especially nowadays there is a strong increase in the use of silica in tires, because silica in combination with S-SBR offers the possibility to reduce the rolling resistance with 30%. This is achieved because of a lower hysteresis, while the wet skid resistance, wet traction and snow behavior remain at the same level. This results in fuel savings of about 5%: "The Green Tyre" (Michelin) and the winter tire of Vredestein.

2.5.11 Morphology and surface properties of silicas

From a number of silicas, electron microscopy images are shown below. These show complicatedly built up aggregates of primary silica particles, more or less with the same structure as with carbon black particles. The only difference is that silicas possess a much higher structure.

Table 2.2: Average diameter of primary particles, N2-adsorption area and DPB-numbers of silicas and silicates.

Type of silica / silicate	Particle diameter [nm]	N2-surface area [m2/g]	DBP-number [ml/100 g]
Ultrasil VN3	14	177	176
Ultrasil VN2	16.5	132	203
Durosil	38	56	168
Extrusil	45	40	141
Silteg AS7	28	65	155

Compared to furnace blacks, silicas have the same primary particle diameter and N2 - surface area. However, DBP-numbers are much higher for silicas than for highly structured blacks. This means that silica has a higher empty or void volume. The reason

for this is that, besides the van der Waals-forces, silica is bound together by silicon-hydrogen bonds between the particles.

At the surface of the silica particle, there are two types of bonds present: siloxane (-Si-O-Si-) and silanol (-Si-O-H). Besides that, precipitated silicas contain also water. The amounts of water present in these silicas may vary greatly, depending on temperature and relative humidity. This water also plays a role in the formation of hydrogen bonds between the primary particles.

2.5.12 Rubber reinforcement with silicas

The reinforcement of a SBR and a NR with 50 phr of carbon black and silica is compared in Table 2.3 by means of the Mooney Viscosity:

Table 2.3: Comparison of the viscosity of carbon black and silica, having the same N2 surface, 50 phr mixed into SBR 1500 and NR.

Type of filler		N2-surface area [m2/g]	DBP-number [ml/100g]	ML (1+4) SBR 1500	ML(1+4) NR
Corax N115	Black	143	113	104	52
Ultrasil VN2	Silica	130	231	201	93
Aerosil 130	Silica	130	266	237	92

Even though the primary particles have the same diameter (N2-surface), we find a much higher Mooney viscosity for silica compounds than for the carbon black compounds. This is the result of the much higher structure of silica compared to black. On top of that, silica is hydrophilic because of the siloxane and silanol groups, whereas most of the rubbers are hydrophobic. This results in a poor tendency to mix with rubber. Instead, silicas preferably remain clustered in large aggregates causing bad flow of the compounds, or tough compounds. As a result, the processability of highly filled silica compounds can be very poor.

But there is an even bigger disadvantage: silica has a negative influence on almost all vulcanization reactions. With normal sulfur-vulcanization, the scorch time is increased; the speed of vulcanization is decreased as well as the degree of crosslinking. Despite the intrinsically higher reinforcing effect of silica, silica compounds show relatively poor mechanical properties. Adding extra amounts of sulfur and accelerators has hardly any effect. The reason seems to be the blocking of the first step in the vulcanization-process, the formation of poly-sulfidic bonds by silanol groups. So, we have look for either accelerator combinations that directly form only mono-sulfidic or di-sulfidic bonds, or shield the silanol groups of the silica (see next paragraph). In peroxide vulcanizations, a similar problem occurs. In that case, silica tends to direct the peroxide to heterolytic scission, which does not lead to crosslinks: see later.

The most striking property of silica compared to (furnace) black, is the dynamic mechanical behavior of vulcanizates, in relation to the already mentioned "Green Tire technology". For blacks with increasing surface area, the loss angle increases. Silica has a smaller loss angle and even for high N2-areas, silicas are at the same level as low N2-area blacks. The complex dynamic modulus of silicas clearly increases with increasing N2-areas, whereas for furnace blacks there are hardly any influences of the surface area or the structure. Together, this results in a lower heat built-up for silica, which gives a lower rolling resistance in the case of tire applications.

In short: silicas have in general the same reinforcing capabilities as furnace blacks. But, because of sulfur- vulcanization problems, not the similarities are interesting, but the differences. Especially the dynamic properties for silica catch the eye. Combining silica and carbon black offers possibilities to tune the properties, which could not have been achieved with one of the components alone. The use of sulfur vulcanization causes problems in the case of silica reinforcement, but these can be overcome with the aid of silanes.

2.5.13 Silane-surface modification and formation of elastomer-filler interactions

The regular surface structure of the silica particle with silanol-groups, offers possibilities to coat the silica particles with other moieties that can shield the silanol-groups. In these reactions, Si-R (R= hydrocarbon-rest), Si-O-R, or (Si-O-Si)-R3 bonds are formed, which also modify the silica particle from a hydrophilic into a hydrophobic substance. As a result, the coated silica particles show a better tendency to mix with the (normally apolar) rubber and the adverse effect of the silanol groups for sulfur vulcanization is limited.

One would expect the reinforcing effect to be adversely affected, because of the reduced surface energy of the silica particle after coating. However, introducing a second functional group in the coating agent, which can react with the rubber, compensates this effect.
Two of the most commonly used silanes are:
- Bis-(triethoxysilyl-propyl)–tetrasulfide (TESPT) or –disulfide (TESPD);
- γ-Mercapto propyl triethoxy silane.

The objective is, that the trialkoxysilylgroups react with the silica surface. The sulfur containing groups are meant to participate in the sulfur vulcanization. Especially on this last assumption, there are many doubts: there are also indications that the participation in the sulfur vulcanization does not take place and that the role of the molecules is purely based on the fact that the silanol groups are shielded and that the silica particles are made hydrophobic. Whatever it may be, the application of silanes has enhanced the use of silica as reinforcing filler remarkably, without adverse effects on the sulfur vulcanization: the "Green-tire".
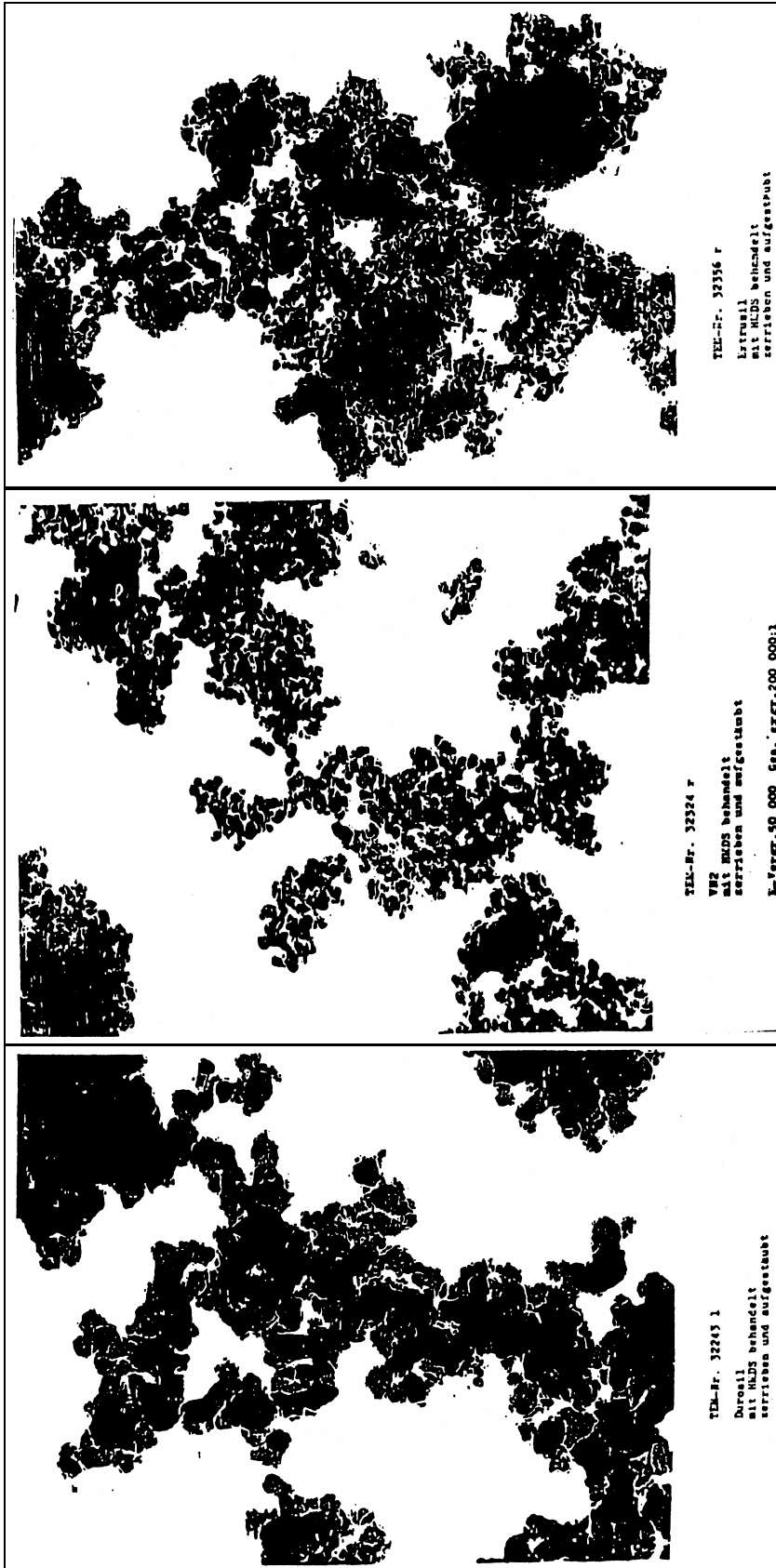
*Figure 2-21:
Images obtained by
electronmicroscopy
of different types of
silica from
Degussa:*

- *Top:
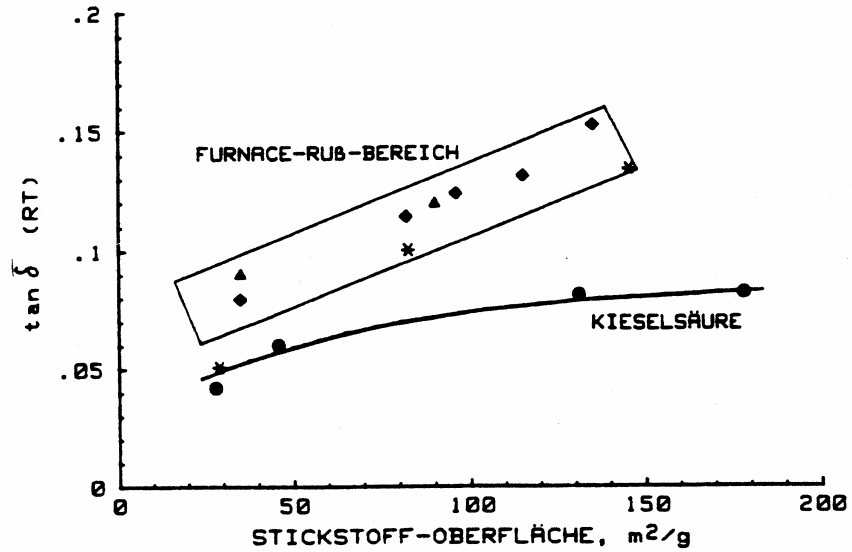 Extrusil;*

- *Middle:
  VN2;*

- *Bottom:
  Durosil.*

Figure 2-22: Dependence of the loss angle delta in peroxide-cured NR (constant crosslink density) on the surface area of silica. For comparison, Furnace black–properties are given as well.
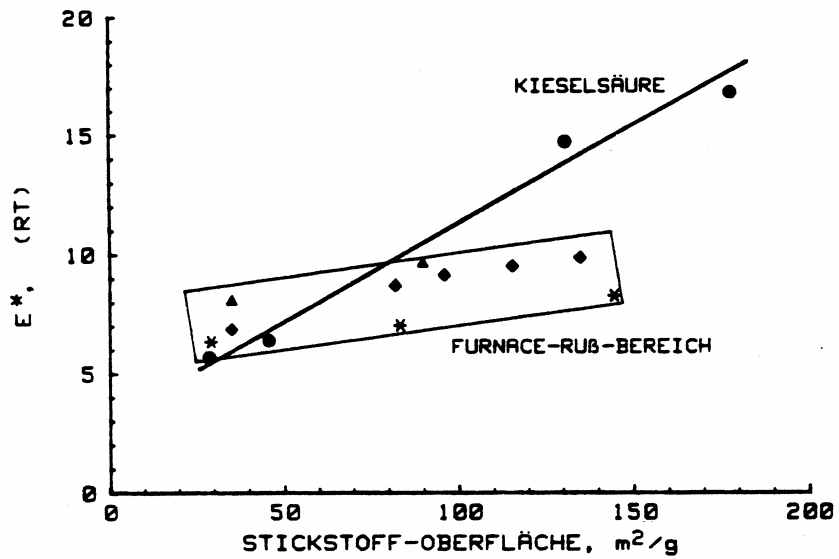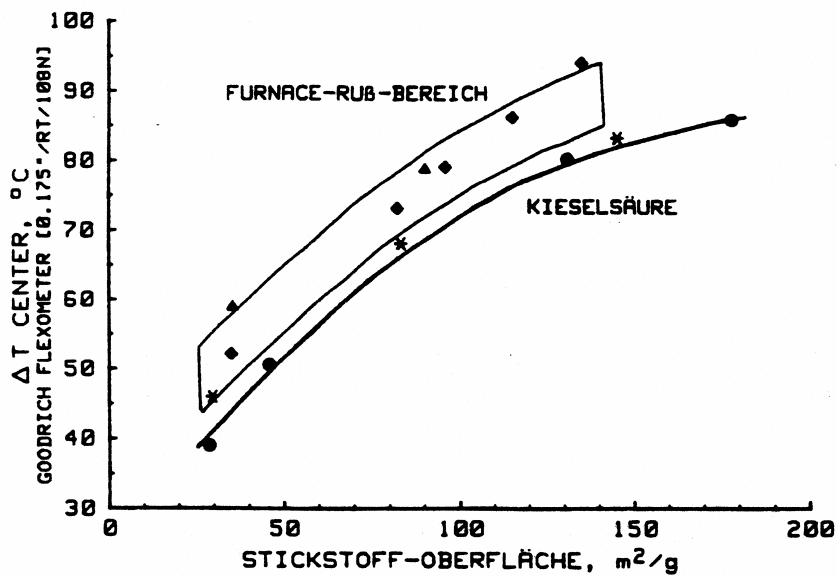

Figure 2-23: Dependence of the complex dynamic modulus (E*) in peroxide-cured NR (constant crosslink density) on the surface area of silica. For comparison, Furnace black–properties are given as well.

Figure 2-24: Dependence of heat build-up in peroxide-cured NR (constant crosslink density) on the surface area of silica. For comparison, Furnace black–properties are given as well.

The reaction of the tri-alkoxysilylgroups with the silanol groups can take place in three possible ways:

- The wet process: either the silane is added to an aqueous silica-suspension or the silane is precipitated onto the silica in an indifferent organic solvent at reaction temperatures of about 80°C;
- The dry process: silica and silane are mixed intensively. At about 120°C, the reaction takes place;
- In situ: the silane is added to the rubber mixture after incorporation of the silica. The reaction takes place during the mixing and/or vulcanization.

Silica fillers that require higher loadings are almost completely silanized via the in-situ process. The in-situ process is also very cheap, because it is part of the rubber mixing process. On the other hand, this has also its weaknesses. The high temperatures needed for the silanisation-reaction are not always reached and all the steps are not easy reproducible because of variations in the rubber mixing steps. The various types of rubber do not allow too high temperatures, without other reactions taking place. In short, this is also a field of rubber science in which a lot of improvements are still to be achieved.

2.5.14 Mineral fillers

Besides the reinforcing fillers, there is a wide range of non-reinforcing fillers, which all have a common main property: making black and non-black compounds cheaper.

- Whiting: milled, washed and precipitated. They differ somewhat in color and in their effect on the processability and vulcanization. It is possible to prepare calcium carbonate with very small particle diameter, which has a semi-reinforcing effect. Some of the whiting types have been treated with ca. 3 % stearate to increase miscibility and dispersibility;
- Kaolin, or clay. Soft clays or hard clays, calcined clays and treated clays. Some are pure fillers without further reinforcement; others have BET-surfaces of 20-50 m2/g and show a bit reinforcement;
- Aluminum-trihydrate: less used as filler as such, but more because of its capability of splitting off water at elevated temperatures and in this way to act as a flame retardant. However, such high loadings are needed in the recipe that many of the elastic properties are lost;
- Talc and micro-talc. A finely milled mineral, mainly built up of Mg- and Al-silicate. It is very inert filler and it is mainly used in heat-resistant compounds for sleeves, autoclave-sealings, etcetera. Talc is so inert, that it is used in large quantities as release agent. It prevents sticking of rubber surfaces onto each other, or other surfaces;
- TiO2: white coloring agent, somewhat reinforcing;
- Many others.

CHAPTER 3   PLASTICIZERS

3.1 Plasticizers and extender oils

This filler is normally added to the compound to increase the processability of the compound. As a result of the addition of the reinforcing fillers, the viscosity increases so much that the compound cannot be processed anymore. If, on the other hand, less filler is added to the compound, less reinforcement is obtained, or we have a very expensive compound. In most cases, the prizes of fillers are lower than those of the pure elastomers. The compounders will therefore always try to add a maximum of filler, and subsequently account for the processability-loss by adding the desired amounts of plasticizers and extender oils.

3.1.1   Mineral oils

Mineral oils, or oils directly obtained from crude oil refining, are by far the most widely used plasticizers. Depending on the character of the crude oil, various types of oil can be obtained. In the oil industry, the oils usually are classified according to their density (or specific gravity) and their viscosity. In this way, an unambiguous specification can be obtained: the so-called Viscosity Gravity Constant, or VGC:

$$VGC = \frac{D - 0,24 - 0,022 \log_{10} (V_t - 35,5)}{0,755}$$

$$(\textbf{3.1})$$

With :
D   = density of the oil at 60°F (15.6°C)/density of water at 60°F;
Vt   = the Saybolt-viscosity at 210°F (98.9°C).

Although the choice of this quantity is empirically determined and seems to be coincidental, the various types of oil can be distinguished very well with this characteristic, see Table 3.1.

The difference between 'paraffinic', 'naphtenic' and 'aromatic' can be deduced from the presence or ab-sence of paraffinic, naphtenic of aromatic groups in the oil. There are test methods in which these groups can be quantified. For instance, an oil having a VGC of 0.90 contains ca. 35% paraffinic, 40% naphtenic and 25% aromatic groups. From this, the compatibility of the oil with the various rubber types can be deduced by comparing this composition with the basic structure of the elastomer itself, seeTable 3.2.

Table 3.1: Relation between VGC and the content of mineral oils.

Type of oil	Range of VGC
Paraffinic	0.791 – 0.820
Relatively naphtenic	0.821 – 0.850
Naphtenic	0.851 – 0.900
Relatively aromatic	0.901 – 0.950
Aromatic	0.951 – 1.000
Strongly aromatic	1.001 – 1.050
Extremely aromatic	> 1.050

In general, one can state that the polar plasticizers/oils are compatible with polar rubbers and that non-polar plasticizers/oils are compatible with apolar rubbers. The amount of plasticizers in rubber varies from 5 –30 phr for natural rubber or SBR-compounds, till more than 100 phr for EPDM.

Table 3.2: Compatibility of mineral oils with the different types of rubber.

	NR	SBR	BR	NBR	CR	CSM	EPDM	IIR
Paraffinic	+	+	+	-	-	-	+	+
Relatively naphtenic	+	+	+	-	-	-	+	+
Naphtenic	+	+	+	0	0	0	+	0
Relatively aromatic	+	+	+	0	+	+	+	-
Aromatic	+	+	+	+	+	+	0	-
Strongly aromatic	+	+	+	+	+	+	0	-

3.1.2   Synthetic plasticizers

For the more polar rubbers NBR and CR it is difficult to find a compatible mineral oil. Therefore, one also applies synthetic plasticizers in these compounds, despite their high cost prize. Because of the great variety in composition and specific chemical functional groups, there is a large number of these plasticizers on the market. Most of them are meant to obtain specific properties in the vulcanizates. Here, some of them are described in more detail:

- Ester plasticizers, well known, also as plasticizers for PVC.
- Phtalic acid esters, mainly dibutyl- (DBP), dioctyl- (DOP), diisooctyl- (DIOP) and diisononyl-phtalate (DINP). Phtalic esters are especially suitable for NBR and CR compounds, to improve their elasticity and low-temperature flexibility. At higher molecular weights, low temperature properties are adversely affected. Amounts: 5 – 30 phr.
- Adipinic acid esters, for instance dioctyl adipate. These are more expensive than phtalic acid esters, but give better low temperature flexibility, especially for NBR.
- Phosphoric acid esters: chemicals like tricresyl- and diphenylcresyl-phosphate, sometimes mixed with trixylyl- or trioctyl-phosphate. The phosphoric acids are especially used because of their low flammability, especially in rubber which already has a low flammability, like CR. Additions of small amounts of mineral oil or non phosphoric acid ester plasticizer make that CR looses all its non-flammability. By using phosphoric acid esters, the low flammability more or less remains. Amounts used are 5 – 15 phr.
- Chlorinated carbohydrates: chlorinated paraffines are added in amounts of 20 phr to decrease the flammability of rubber vulcanizates. When bigger amounts are used, the properties of the vulcanizates decrease too much. In CR usually only 10 phr is added. Antimony-trioxide is usually applied as a synergistic flame-extinguisher. Besides the chlorinated paraffines, chlorinated or brominated diphenyls are used as well, or even chlorinated rubber itself.
- Polycondensated products: polyesters from adipinic or sebacinic acid and 1,2-propyleneglycol are used because of their high molecular weights and their still liquid behavior as a non-volatile, non-migrating plasticizer. They are specially used in NBR.
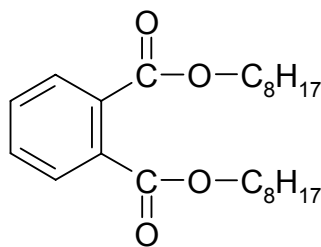
Figure 3-1: Structure of DOP.

Literature
- See common references;
- F.W. Barlow, "Rubber Compounding, Principles, Materials and Techniques", 2nd ed., New York – Basel – Hong Kong: Marcel Dekker, Inc. (1993).

CHAPTER 4   VULCANIZATION

4.1 Introduction

In order to create a rubber network, the separate rubber macromolecules have to be crosslinked with each other, which normally takes place at elevated temperatures: vulcanization. It is remarkable, that even after 160 years, sulfur is by far the most widely used vulcanization chemical for natural rubber and general-purpose synthetic rubber. Only in very few cases other vulcanization chemicals are used. Either because of the wish to obtain rubber products with specific properties, or because of the lack of double C=C bonds in the specific rubber, that are necessary for the crosslinking with sulfur. It is because of that reason, that most of the content of this chapter deals with sulfur vulcanization.

4.2 Sulfur-vulcanization

When a mixture of natural rubber and free sulfur is heated up, most probably free radicals are formed as a result of the ring opening of the eight-membered sulfur rings:

$$S_8 \longrightarrow S_x$$
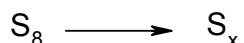
Which can react afterwards with the unsaturation of the natural rubber in this way:

$$S_x + 2R \longrightarrow R\text{-}S_x\text{-}R$$
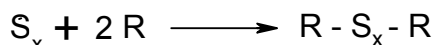
An extremely diverse mixture of inter- and intramolecular sulfur-bridges is formed. Some of these sulfur- bridges develop to real network crosslinks, while some of them are spoilt, because they become linked to the same polymer chain at both ends, see Figure 4-1.
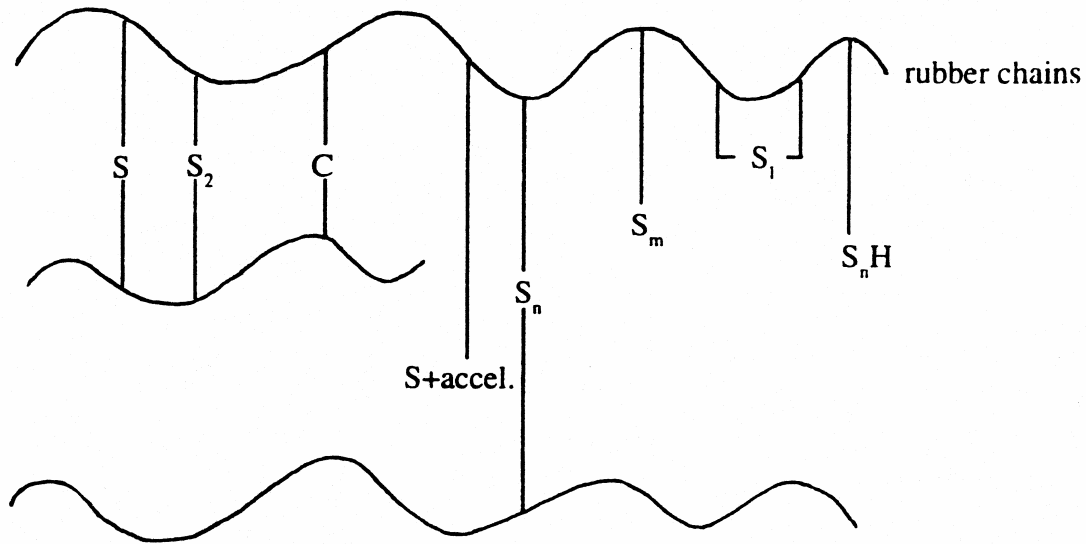
S	=	monosulphide		S_nH	=	thiol groups
S_2	=	disulphide		S + accel.	=	sulphur donor accelerator residues
S_n	=	polysulphide		C	=	carbon-carbon crosslinks
S_1	=	main chain bound sulphur chains		Sm	=	cyclic sulphur structures

Figure 4-1: Model of an 'accelerated' NR-sulfur network.

If this reaction is carried out, one will soon see that this reaction with sulfur only proceeds very slowly. For instance, a compound of NR with 6 phr sulfur needs 4 hours at 140 °C to crosslink to some extent. Soon, it was discovered that 2 – 5 phr of zinc oxide (ZnO) could speed-up the reaction remarkably. However, it works in particular if the ZnO is made soluble by adding small amounts of acids, especially fatty acids like stearic acid. It is thought that these fatty acids form Zn-salts which are soluble in rubber, and that these Zn-salts increase the reaction rate. As an alternative, people directly add these Zn-salts, like Zn-stearate.

In 1906, Oenslager discovered that some organic substances could increase the reaction rate even more. His first accelerator was aniline, but because this is a very toxic substance, people kept looking for alternatives. Nowadays, there is a whole range of accelerators available, which almost all contain sulfur as well as nitrogen. Their functionality ranges from 'normal' for NR, BR and SBR, to 'ultra'- accelerators for rubbers with low degrees of unsaturation such as EPDM. Besides the function of increasing the reaction rate, accelerators account also for a better network structure and furthermore they offer the possibility to govern to some extent the length of the sulfur-bridge: from polysulfidic –Sx –, via disulfidic –S2 –, to monosulfidic –S –, which has a positive influence on the ageing behavior of the vulcanizates.

4.2.1 Measuring vulcanization

Since vulcanization leads to crosslinks and the fact that the elasticity modulus is directly related to the crosslink density (see Ch.**), it is obvious to monitor the formation of crosslinks via this property. Almost all vulcameters, rheometers or curemeters have as the mechanism that cyclic movements of a rotor in a rubber-filled chamber are performed, and that the torque is measured as a function of time, that the vulcanizing rubber sample is subjected to the vulcanization temperature. As time proceeds, the rubber becomes more and more crosslinked, which reflects in an increasing value of the torque. The torque is in approximation directly proportional to the modulus of the compound.
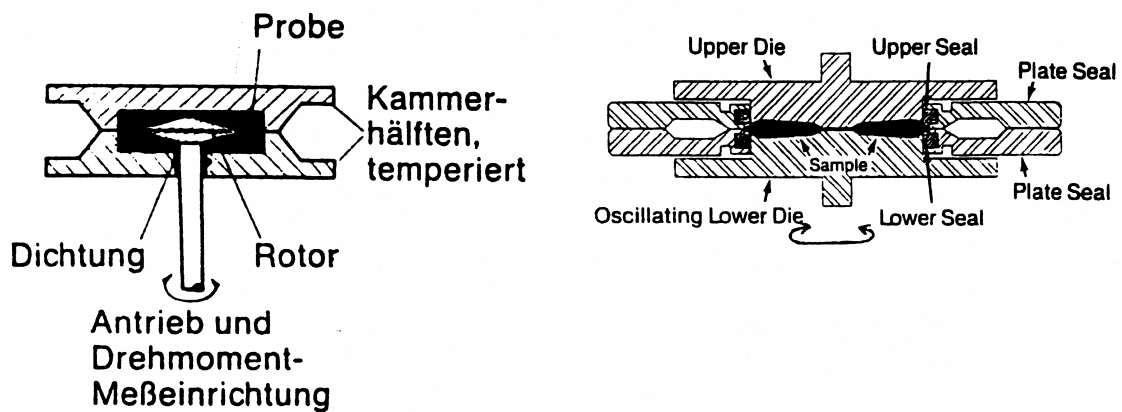
Figure 4-2: Vulcameters with and without a rotor.
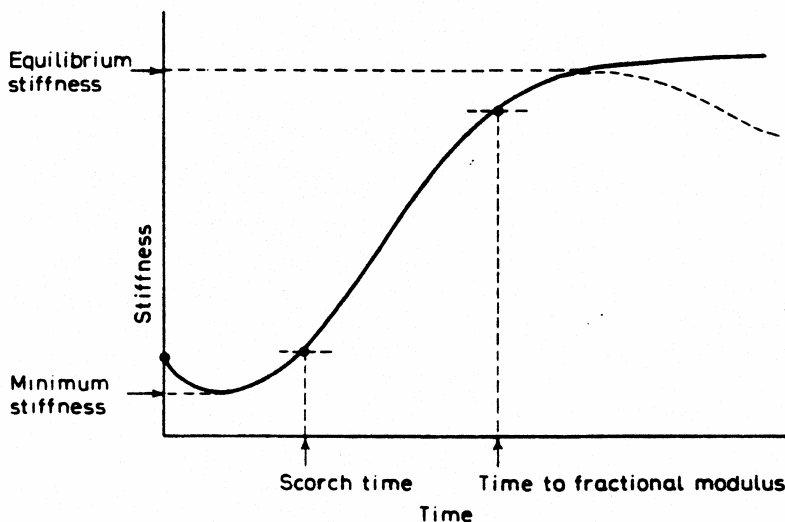
Figure 4-3: The different stadia of the vulcanization, as measured in a vulcameter.

In such a plot, also called a rheogram, several characteristic quantities are generally recognized:

- *tS2*: The scorch time: the time needed to increase the torque by two units above the minimum value. The vulcanization has just started at this time. Within the scorch time, the rubber compound is still processable;
- *ML*: Minimum torque: determined by the heating of the compound and the beginning of vulcanization;
- *MH*: Maximum torque: determined by the extent of crosslinking;
- *t50*: The time needed to bridge 50 % of the difference between minimum and maximum torque;
- *t90*: The time needed to bridge 90% of the difference between minimum and maximum torque. This time is generally used as a typical value for an optimal vulcanization time.

Another thing which is important, is the way the curve develops after full vulcanization:

- Steadily increasing: Marching Modulus;
- Levels off to reach an equilibrium plateau;
- Decrease of torque after the maximum: Reversion.

Reversion is encountered a lot with highly unsaturated rubbers. It is a nasty property, which is the result of preliminary degradation or oxidation of the newly formed sulfur bridges. Reversion partly undoes the effect of the vulcanization.

The recording of a vulcameter or rheometer-curve is always an important step in the preparation of a rubber compound. With the aid of this curve, it can be seen whether the vulcanization recipe is properly adjusted to the temperature profiles belonging to the process technique. At low temperatures, the compound has to remain processable for a long enough time, while at the vulcanization temperature a dense enough network has to be formed as quickly as possible.
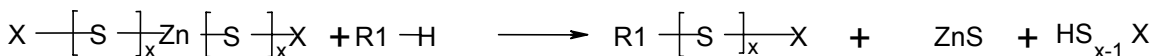
4.2.2   Sulfur accelerators

Before going deeper into detail about the several types of accelerator, first some words should be spent to the chemical mechanism of the function and properties of accelerators in general. However, it has to be said beforehand that up till present this mechanism is still rather unclear. On the one hand, this is due to the fact that many products are generated in the mixture of rubber, sulfur, zinc oxide and accelerators (the last two often in combinations). This makes chemical analysis very difficult, the more so because after vulcanization the rubber cannot be dissolved anymore (definition of rubber), which precludes the use of most chemical analytical techniques. On the other hand, not many people are well educated in the sulfur chemistry to feel at home in this business.

As it is known now, the first step in the vulcanization is the reaction of the accelerator (X) with ZnO in which the Zn-salt of the accelerator is formed. Subsequently, this reacts with sulfur to form a zinc perthio-salt, in which X stands for the accelerator fragment:

$$ZnO + X \longrightarrow ZnX$$

$$ZnX + S_8 \longrightarrow X-(S)_x Zn (S)_x X$$
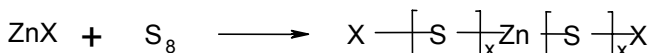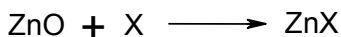
This salt reacts with the rubber hydrocarbon RH to a rubber-bound intermediate:

$$X-(S)_x Zn(S)_x X + R1-H \longrightarrow R1-(S)_x X + ZnS + HS_{x-1} X$$

The perthio-salt, yet with lower sulfur content, will form another active complex with ZnO, so every accelerator molecule remains active. The intermediate RSxX on its turn reacts with another rubber molecule to form the real crosslink:

$$R1-(S)_x X + R2-H \longrightarrow R1-(S)_{x-1} R2 + HSX$$
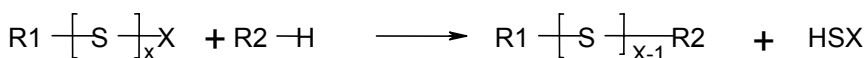
If one keeps on heating, the accelerator tends to react again with the crosslink, which leads then to a decrease in length of the sulfur bridge: from polysulfidic to disulfidic and eventually to monosulfidic.

It is generally thought that the reaction at the rubber hydrocarbon proceeds via abstraction of the hydrogen which has an allylic position relative to the double bond, for instance in NR:

$$\underset{(1)\quad(2)\quad\quad(3)\quad(4)}{-CH_2-\underset{\underset{(2)}{|}}{\overset{\overset{CH_3\quad(5)}{|}}{C}}=CH-CH_2-}$$
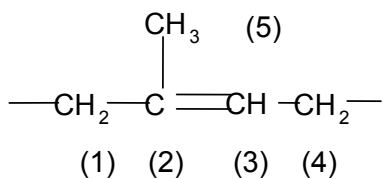
The hydrogens (1), (4) and (5) are the most labile in such a reaction. As a rule of thumb it holds that, as the elastomer possesses more allylic hydrogen on a molar base, the rubber is easier or faster to vulcanize with sulfur. Compare NR or SBR, vs. EPDM or IIR. In practice, larger quantities and more active accelerators are needed when the rubber has less allylic hydrogens, or higher vulcanization temperatures are needed to obtain a proper degree of vulcanization.

Further, accelerators react in a different way with various elastomers. Whereas a 50 phr carbon black-filled NR compound needs 2.25 phr sulfur and 0.5 phr sulfenamide to be vulcanized, a similar SBR compound needs 1.75 phr sulfur and 0.8 phr sulfenamide. EPDM and IIR require more sulfur than the available double bonds can handle. In order to yet obtain a proper degree of vulcanization, accelerators are added in amounts reaching the limits of solubility in rubber. Adding even more causes 'blooming', the appearance of a white powder on the surface. This can be avoided by adding more than one accelerator, at levels lower than the respective separate solubilities. The vulcanization recipes of EPDM contain in most cases three or more different accelerators, vs. NR normally one or at most two.

A.   Thiazoles

Besides the sulfenamides, thiazoles are by far the most well known category of accelerators. Thiazoles are widely used in the rubber industry because of their huge variation possibilities in scorch time and vulcanization speed. The most well known is 2-mercapto-benzothiazol (MBT) and its Zn-salt (MBTS):
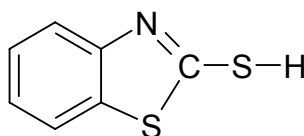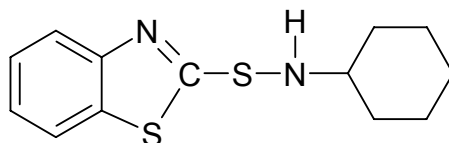

Figure 4-4: Chemical structure of MBT.

In most cases, MBT or MBTS is not used alone; this accelerator is a bit too slow then. Usually, a bit of TMTD or diphenylguanidine (DPG) is added. For guanidines, see below. For instance for a SBR compound: 1.5 phr MBTS + 0.15 phr TMTD + 2.80 phr S.

B.   Sulfenamides

Sulfenamides are the most widely applied category of accelerators: they are often called "delayed-action" accelerators, because of the long scorch time. The delayed action is caused by the fact, that the sulfenamide first has to split in thiazol and amine, before the thiazol can act as accelerator. One of the most well known representatives of this category is N-cyclohexyl-2-benzothiazolsulfenamide (CBS).

Figure 4-5: Chemical structure of CBS.

Amines function as activators (coagents) for accelerators. The sulfenamides contain built-in amines and indeed, increasing basicity of the incorporated amine results in shorter scorch times and shorter vulcanization times. For instance: N,N-diisopropyl 2-benzothiazolsulfenamide (DIBS) is the fastest sulfenamide, while N-cyclohexyl-2-benzothiazolsulfenamide is the slowest.

Sulfenamides are often applied in combination with secondary accelerators like tetramethyl-thiuramdisulfide (TMTD), see under E: Thiuram sulfides. For instance for a NR compound 0.7 phr CBS + 0.1 phr TMTD + 2.25 phr S can be used.

C.   Guanidines

These accelerators are hardly used as primary accelerators, but mostly as secondary accelerators in combination with sulfenamides or thiazoles. Most common are diphenylguanidine (DPG) and di-o-toluylguanidine (DOTG). Usually. 0.25 phr DPG is used in combination with 1 phr thiazole or sulfenamide.

Figure 4-6: Chemical structure of DPG and DOTG.

D.   Dithiocarbamates

Because of their very fast reaction, dithiocarbamates and their Zn-salts are known as ultra-accelerators. Well-known representatives are zinc-dimethyl-dithiocarbamate (ZDMC), zinc-diethyl-dithiocarbamate (ZEDC) and zinc-dibutyl-dithiocarbamate (ZDBC).
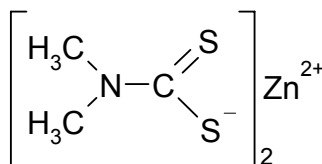

Figure 4-7: Chemical structure of ZDBC.

Dithiocarbamates belong to the most powerful accelerators and for that reason they are hardly used alone. They tend to start vulcanizing already at room temperature: preliminary scorch during storage of a compound, which makes it not processable anymore in later process-stages. Therefore, usually the dithiocarbamates are added to slower thiazoles or sulfenamides to speed up the vulcanization reaction.

An example for a SBR compound: 0.5 phr ZDMC + 0.75 phr MBT + 1.8 phr S. For NR: 0.5 phr ZMDC + 0.75 phr MBT and 2.0 phr S.

E.   Thiuram sulfides

Thiuram sulfides are similar to dithiocarbamates "ultra"-accelerators. Common representatives of this category are tetramethyl-thiurammonosulfide (TMTM), tetramethyl-thiuramdisulfide (TMTD), tetraethyl-thiuramdisulfide (TETD) and tetrabenzyl-thiuramdisulfide (TBzTD). As an example, the chemical structure of TMTD is shown below.
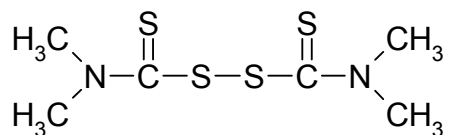
$$
\begin{array}{c}
H_3C \\
\diagdown \\
\end{array}
N-\underset{\underset{\displaystyle S}{\|}}{C}-S-S-\underset{\underset{\displaystyle S}{\|}}{C}-N
\begin{array}{c}
\diagup CH_3 \\
\diagdown CH_3 \\
\end{array}
$$

with H_3C on lower left.

Figure 4-8: Chemical structure of TMTD.

From the structure, it can be seen that thiuram-sulfides actually consist of two dithiocarbamate molecules. Therefore, the action of a thiuram-sulfide is that upon reaction with zinc, the molecule splits into two zinc-dithiocarbamate molecules. This zinc-dithiocarbamate is the actual accelerator.

Another striking phenomenon is, that the two sulfur atoms forming the bridge, can easily be increased to five or even six S-atoms: tetramethyl-thiurampentasulfide or -hexasulfide.

On the other hand, reduction of the sulfur bridge is also possible: one S-atom in tetramethyl-thiurammonosulfide. The thiurams can donate their incorporated (free) sulfur to the compound. In fact, the thiuram is a combination of free sulfur and dithiocarbamate.

For that reason thiurams are often used in low-sulfur or sulfur-free vulcanization systems. Only TMTM cannot donate free sulfur, because the bridge consists of only one S-atom. Therefore, TMTM cannot be used alone in the vulcanization process.

The low-sulfur vulcanization systems are often denoted as Semi Efficient Vulcanizing (SEV) systems and the sulfur-free vulcanization systems as Efficient Vulcanizing (EV) systems. This designation does not say anything about the efficiency of the vulcanization system; it rather tells something about the type of crosslinks that are formed. SEV-systems typically form disulfide crosslinks, while EV-systems form mono-sulfide crosslinks. These vulcanizates are often characterized by a better thermal stability than polysulfidic crosslinks.

TMTD is so active, that is causes preliminary scorch in NR. TMTM can be used in NR. Thiuram sulfides are mostly used in NR as a secondary accelerator for thiazoles or

sulfenamides. On the other hand, in systems that are not easy to vulcanize, like EPDM, TMTD is a widely used accelerator, sometimes in combination with thiazoles.

Table 4.1: Examples of conventional, SEV and EV-systems for EPDM.

Accelerator	Conventional	SEV	EV
TMTD	1.5	0.8	
MBT	1.25		
DPTH		0.8	0.8
DPTT			0.8
ZDMC		1.5	
CBS		1.5	1.5
S	1.5	1.5	0.2

F.   Dithiophosphates

The most important representative of this category is zinc-dibutyl-dithiophosphate. The structure is shown below:
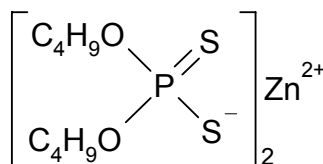
Figure 4-9: Chemical structure of ZDBP.

Dithiophosphates have structure similar to dithiocarbamates. Dithiocarbamates are just a little bit slower and, therefore, they are used as substitutes of dithiocarbamates. Especially in rubbers like EPDM, where high amounts of dithiocarbamates are needed, the maximum solubility may be exceeded. Partial substitution by dithiophosphates can offer a solution. Furthermore, dithiophosphates are non-nitrosamine forming, while dithiocarbamates are, see next paragraph.

4.2.3   Activators

In the beginning of this chapter, there were some remarks about the role of ZnO in the sulfur vulcanization. The ZnO was considered an activator; however, vulcanization in the absence of ZnO hardly works. Traditionally, 5 phr is added, but less ZnO works as well, especially because ZnO is considered as being ecotoxic, nowadays. Via abrasion of the tires or via leaching of rubber roofings, a lot of ZnO comes into the environment. On the other hand, ZnO enhances the thermal stability of rubber vulcanizates, even up to 10 phr.

Stearic acid is also classified as activator. Its role is to enhance the solubility of the ZnO in the rubber. Besides, it has a positive influence on the processability of the compounds. It prevents the compounds from excessive sticking on the two-roll mills and in mixers.

Furthermore, in general it can be stated that sulfur vulcanization takes place in a basic environment, and therefore it is activated by increase of the pH. For that reason, amines like mono-, di-, and tri-ethanolamine are added, as well as mono- and dibutylamine, dibenzylamine etc. In cases of sulfenamides, the amines are brought along with the accelerator itself.

4.2.4   Retarders

In cases, that scorch leaves no time for enough processing and that preliminary scorch is observed, vulcanization retarders may be added to the compound. The action of these additives lays in the fact that decrease of pH results in delay of the vulcanization reaction. Volatile organic acids or derivatives are often used. For instance: benzoic acid, phtalic anhydride, and salicylic acid. An example of a derived chemical, in which we can see a large similarity with CBS, is N-cyclohexyl-thiophtalimide.
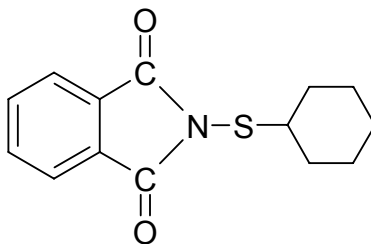

Figure 4-10: Chemical structure of N-cyclohexyl-thiophtalimide.

4.2.5   Anti-reversion chemicals

Reversion, as mentioned in paragraph 1.2.1, is a nasty property. With the vulcanization of very thick articles, like tunnel sealings, fenders, large tires etc. where the energy for the vulcanization is delivered from outside, very inhomogeneously vulcanized articles can be obtained. This is the result of the fact that during the vulcanization process, the outside of the article already starts to decrease in properties, while the inside of the material has not yet started to vulcanize.

There is not much you can do about it, except to vulcanize at very low temperatures for very long times. FLEXSYS (formerly AKZO NOBEL) introduced an anti-reversion chemical in the nineties, Perkalink 900 with the following structure:
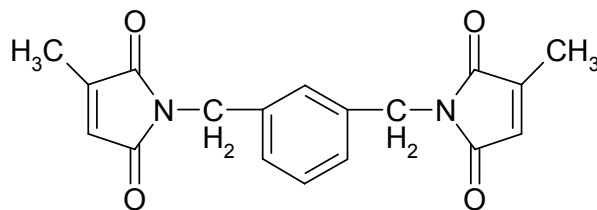
Figure 4-11: Chemical structure of Perkalink 900.

The mechanism of the anti-reversion is supposed to be that this chemical substance attaches to broken S-S linkages. In this way, broken crosslinks can be recovered. It seems that this works very well, as can be seen in the much better abrasion resistance of truck tires, to which Perkalink 900 has been added.

4.2.6   Reaction mechanism of the accelerator

Although vulcanization chemistry is already 160 years old, still the mechanism has only marginally been solved. The most important reason for this is the multiplicity of reactions occurring during vulcanization. Every accelerator, retarder and anti-reversion chemical has its own contribution to these reactions. Besides, the length of the sulfur bridge changes continuously during vulcanization. Overall, it can be stated that during vulcanization, there is a whole melting pot of reactants and reactions at work, which results finally in a vulcanized network. It is nearly impossible to chart every single reaction.

In a number of cases, in which one single accelerator is reacted with one type of rubber both with and without the presence of sulfur, some things have been cleared up. The following mechanism for instance, shows the reaction of a string of sulfur atoms, on both sides attached to MBT, with an unsaturated carbon-carbon double bond. The direction of the movement of the electrons is shown with the aid of arrows.
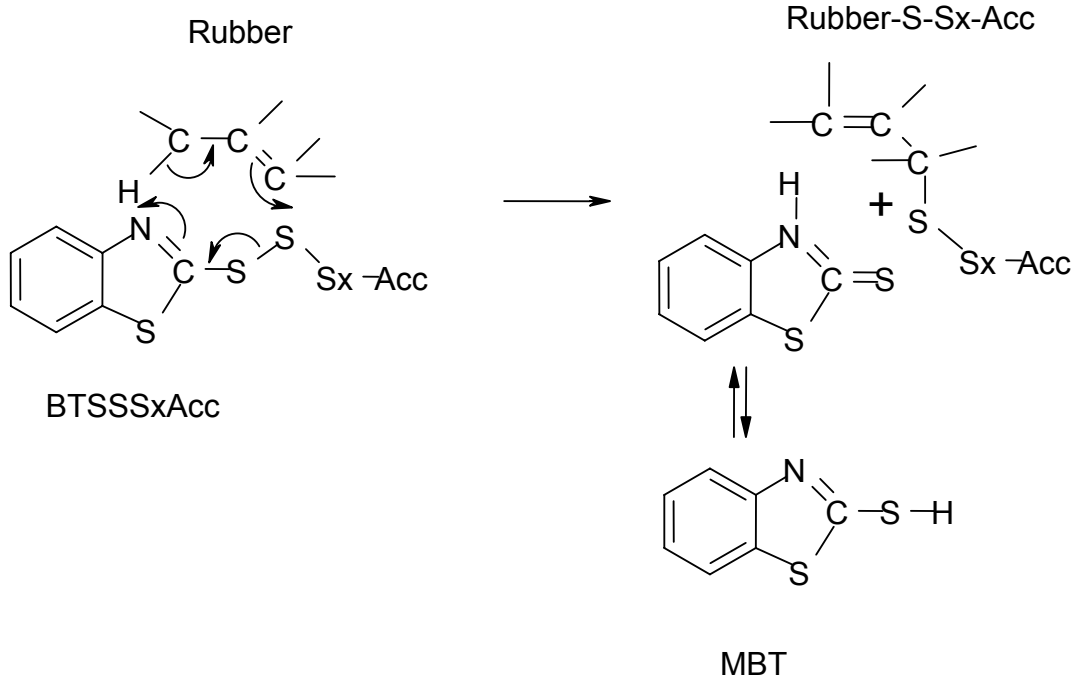
Figure 4-12: Example of a possible reaction path for MBT and a rubber.
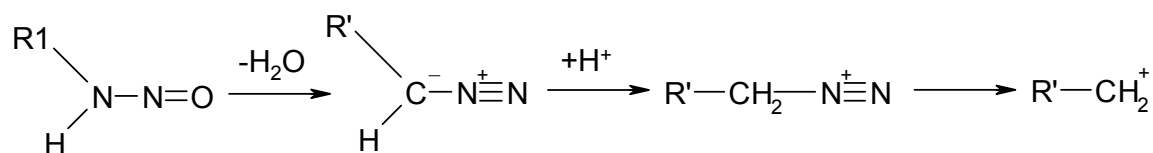
4.2.7 Sulfur accelerators and toxicity

For a long time already, the rubber industry has been under suspicion of the fact that the vapors generated during vulcanization are harmful to the people's health. The vapors and gasses consist to a large extent out of volatile components of the extender oils and reaction products of the accelerators. However, it has never been proven indisputably, that the suspicions are justified. Nevertheless, most rubber manufacturers take the necessary precautions to minimize the exposure to vulcanization gasses as much as possible.

Over the latest years, many concerns have risen about the toxicity of nitrosamines, especially in Germany. Nitrosamines be formed during vulcanization. After release of the vulcanizates from the press, they can come into the air. N-Nitrosamines have the following structure:
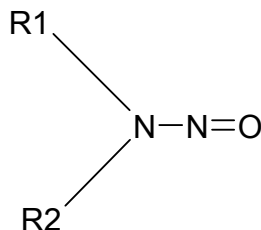
Depending on the number of hydrocarbon groups attached to the nitrogen, the nitrosamine is formed from a primary, secondary or tertiary amine. It has already been known for a long time that N-nitrosamines can form cancer in animals during laboratory tests and therefore they are considered carcinogenic. N-nitrosamines based on primary amines are so instable that they decompose before they can cause any harm. N-nitrosamines based on tertiary amines are stable. Especially the n-nitrosamines based on secondary amines can react in the human body according to the following mechanism, which may cause changes to the DNA:

$$R1 \overset{}{\underset{H}{N}}-N=O \xrightarrow{-H_2O} R' \overset{}{\underset{H}{C}}-\overset{+}{N}\equiv N \xrightarrow{+H^+} R'-CH_2-\overset{+}{N}\equiv N \longrightarrow R'-\overset{+}{C}H_2$$

N-nitrosamines can form rather spontaneously from secondary amines and NOx. It has to be mentioned that NOx is always available for reaction because it is present in the normal environment in high enough concentrations. The availability of secondary amines as decomposition products of accelerators is always the most important thing. Looking at the chemical structure of the various accelerator categories, it can readily be seen that the thiuram sulfides, the dithiocarbamates and some of the sulfenamides can form secondary amines. Examples of secondary amines coming from several accelerators are:

- Dimethylamine   from TMTD and/or dimethyl-dithiocarbamate
- Diethylamine   from TETD and/or diethyl-dithiocarbamate
- Dibutylamine   from TBTD and/or dibutyl-dithiocarbamate
- Diisopropylamine from DIBS

The severe conditions regarding the reduction of nitrosamines in Germany over the latest years have caused large decreases in the consumption of many of these ultra-accelerators. The problem for the rubber compounders is the search for suitable alternatives. Especially in the case of EPDM this is important, because EPDM-vulcanization is mainly dependent on ultra-accelerators.

A solution for this problem in the case of thiurams and dithiocarbamates is the use of tetrabenzyl thiuramdisulfide (TBzTD) or dibenzyl-dithiocarbamate. It seems that dibenzyl-nitrosamine is not carcinogenic, in contrast to its aliphatic counterpart. The vulcanization characteristics of TBzTD are very similar to those of TMTD in NR, SBR, NBR and EPDM. One has to keep in mind though, that correction is needed for the high molecular weight of TBzTD compared to TMTD (544: 240). In order to get on a molar basis the same amounts of accelerator in order to have a similar scorch time and to keep the same speed of vulcanization, about twice the amount of TBzTD has to be added on weight basis. As the prize of TBzTD per kilogram is much higher and

because higher amounts are needed, this substitution means a huge increase of cost for the rubber compounder.

4.3 Peroxide-vulcanization

Since the beginning of last century it is known that polymers can be vulcanized by means of peroxides. The possibilities to achieve crosslinking with peroxides are very divers. Almost all polymers, that do not tend to decompose under the influence of radicals, can be crosslinked with peroxides. Unsaturated bonds are not necessary for peroxide vulcanization. It is therefore a vulcanization technique that has gained importance since the introduction of fully saturated polymers like EVA (ethylene-vinylacetate), EPM, EPDM, CM (chlorinated polyethylene) and Q. For NR, SBR and NBR, peroxide vulcanization is only applied on small scale. This is due to the fact that these unsaturated polymers need to be stabilized by means of antiozonants and antioxidants. In general, these antidegradants are very strong radical scavengers. It will be clear that the application of these antidegradants conflicts with peroxide vulcanization, that proceeds according to a radical mechanism.

The common chemical formula for peroxides is shown below:

$$R - O - O - R$$
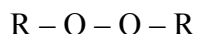
In this formula R stands for any aliphatic, aromatic or carboxylic group.

In the description of the various reactions taking place before two molecular chains are linked, an analogous terminology is used as for polymerization chemistry. The following three consecutive steps are recognized:

- Initiation or formation of the radical: the decomposition of the peroxide in radicals.
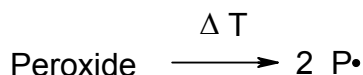
$$\text{Peroxide} \xrightarrow{\Delta T} 2 \text{ P} \cdot$$

In this reaction scheme P· stands for the peroxy radical.

- Propagation: proton abstraction by the peroxy radical from the polymer chain. This results in stable peroxide-decomposition products and a polymer radical.

$$\text{P} \cdot + \text{R} \longrightarrow \text{PH} + \text{R} \cdot$$
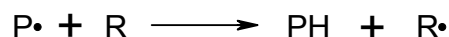
In this reaction scheme R stands for a rubber molecule.

- Termination: recombination of two polymer radicals, under formation of a crosslink.

R• + R• ⟶ R—R

The first step, the formation of the radical, is a slow first-order reaction. This is the rate-determining step. Therefore, the time necessary to achieve vulcanization is directly related to the speed of decomposition of the peroxide. The efficiency of the overall-vulcanization mainly depends on the types of radicals formed after decomposition of the peroxide and the various termination-reactions that can take place. It is thus the chemical structure of the peroxide that plays the decisive role in the vulcanization process.

The speed of decomposition of a peroxide at a certain temperature depends on the bond strength of the weakest bond in the molecule, which is the O − O bond. This bond strength is directly governed by the chemical structure of R, as can be seen in Table 4.2.

Table 4.2: Influence of the chemical structure of the hydrocarbon group on the decomposition of peroxides.

R-group	Bond energy O-O bond [kJ/mol]	Half-lifetime: $t_{1/2}$ @ 120°C	Temperature for having $t_{1/2}$ = 1 hr.
Tert.Butyl	157	5 hrs	136°C
Cumyl	144	125 mins	128°C
Benzoyl	130	4,5 min	92°C

The thermal stability of a peroxide is commonly indicated by the half-life time: the time necessary to decompose half of the peroxide at a certain temperature. In this way, an overview of all peroxides can be obtained as shown in Figure 4-13.

The efficiency of the crosslinking is the resultant of the three reaction steps mentioned before. The decomposition of the peroxides into radicals is very efficient under vulcanization conditions. However, during the propagation step all sorts of side reactions may take place, such as the formation of stable polymer-peroxide radical combinations. These side reactions have a negative influence on the overall crosslinking, of course.

Table 4.3 offers us some insight into the type of hydrogen that is abstracted during the vulcanization.

Table 4.3: Dissociation-energy of the various hydrogen atoms.

Type of polymer	Type of hydrogen	Dissociation energy [kJ/mol]
HDPE (linear)	Secondary	398
LDPE (branched)	Tertiary	381
EPM	Tertiary, opposed to a methyl	381
ENB-EPDM	Tertiary, allylic to ENB	339
ENB-EPDM	Secondary, allylic to ENB	362

From this, we can derive that in EPDM the allylic hydrogen is abstracted first. However, the excess of secondary and tertiary hydrogen atoms is so huge, that it is reasonable to assume that a lot of them are abstracted as well.

If finally the crosslink has been formed, it is illustrative to compare the dissociation energy of the C – C- crosslink with the various sulfur-crosslinks, as is shown in Table 4.4.

Table 4.4: Dissociation energy of the various crosslinks.

Type of bond	Dissociation energy {kJ/mol]
-C-C-	352
-C-S-C- monosulfidic	285
-C-S-S-C- disulfidic	268
-S-S-S-S- polysulfidic	<268

In this table the typical property of peroxide vulcanizates clearly shows: the high bond strength of the C – C-bond. This forms the basis for the much better thermal ageing stability of peroxide-vulcanizates compared to sulfur-vulcanizates.

Usually, peroxides are divided in two categories:
-   Peroxides with carboxy-groups, with diacetylperoxide as aliphatic example and dibenzoylperoxide as aromatic example;

Half-life time data of various crosslinking agents determined in chlorobenzene as solvent, using DTA technique.
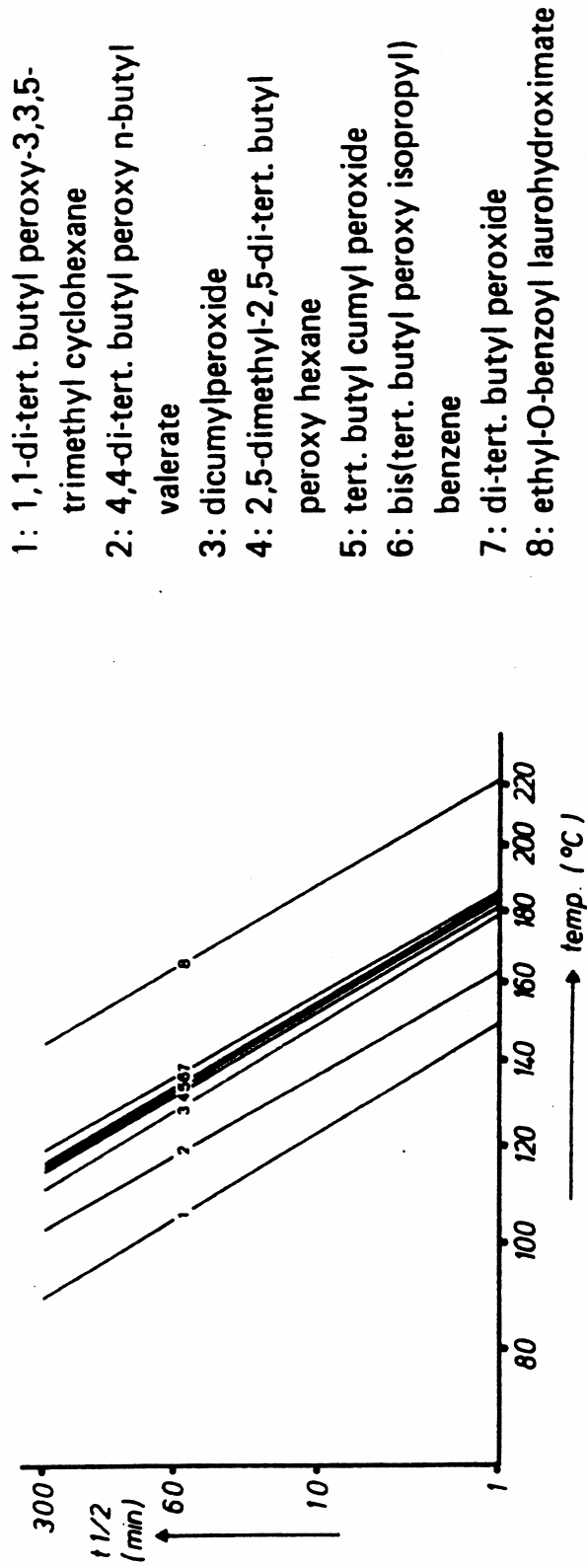
1: 1,1-di-tert. butyl peroxy-3,3,5-trimethyl cyclohexane
2: 4,4-di-tert. butyl peroxy n-butyl valerate
3: dicumylperoxide
4: 2,5-dimethyl-2,5-di-tert. butyl peroxy hexane
5: tert. butyl cumyl peroxide
6: bis(tert. butyl peroxy isopropyl) benzene
7: di-tert. butyl peroxide
8: ethyl-O-benzoyl laurohydroximate

Figure 4-13: Half-life time for various peroxides as a function of temperature.

$$H_3C - \underset{\underset{O}{\|}}{C} - O - O - \underset{\underset{O}{\|}}{C} - CH_3$$
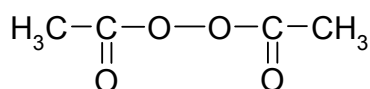
Figure 4-14: Structure of diacetylperoxide.
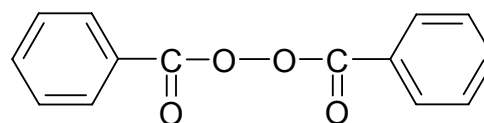
Figure 4-15: Structure of dibenzoylperoxide.

- Peroxides without carboxy-groups, with di-tert.butylperoxide as aliphatic example and dicumylperoxide as aromatic example.
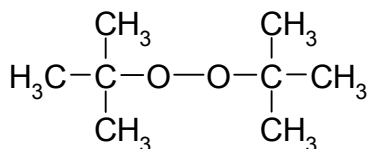
$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - O - O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

Figure 4-16: Structure of di-tert. Butylperoxide.
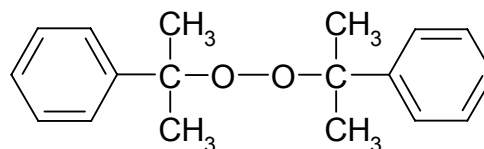
Figure 4-17: Structure of dicumylperoxide.

In general, carboxy-containing peroxides decompose at lower temperatures than the non-carboxy-peroxides.
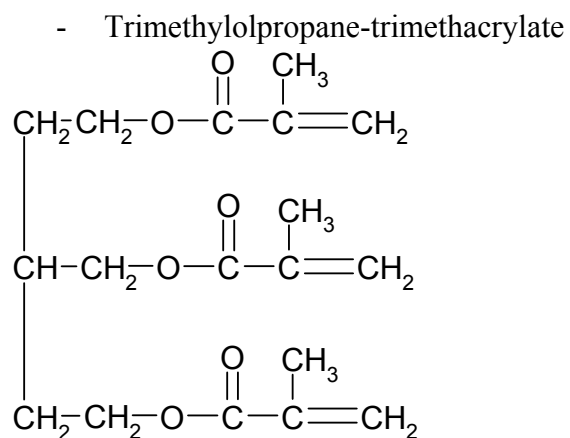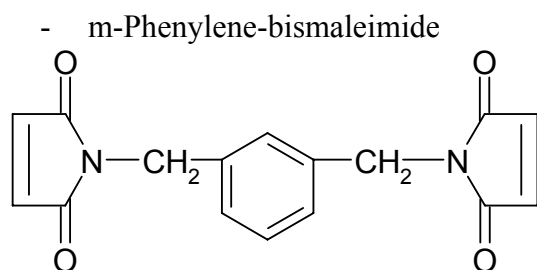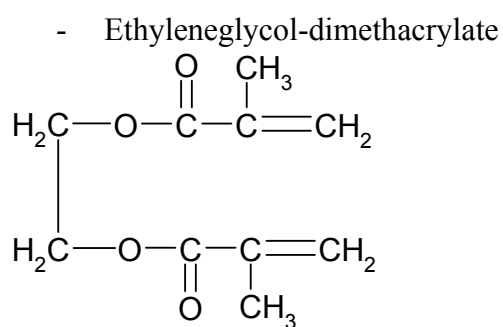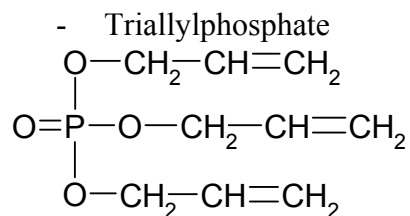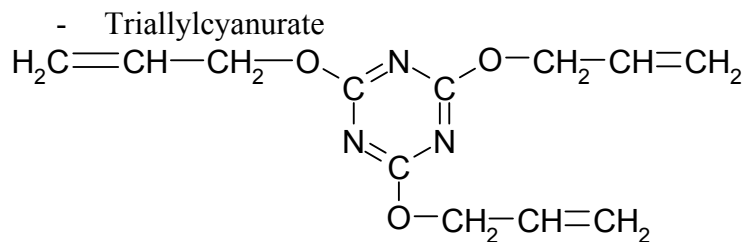
Besides symmetric peroxides, there are also combinations of different sorts of peroxides, asymmetric peroxides. An example of an asymmetric peroxide is t-butyl cumylperoxide. Symmetric peroxides have in general a higher efficiency than the asymmetric types.

Which peroxide suits best for which polymer and which vulcanization technique, is difficult to predict. In practice, it is useful to use the advices of the peroxide-suppliers.

4.3.1 Activators for peroxides

Accelerators like in sulfur-vulcanization are not known for peroxide-vulcanization. After all, the rate-determining step is the decomposition of the peroxide. However, we can have influence on the yield of crosslinks for a given peroxide.

The yield of crosslinks can be increased by so-called coagents. These are polyvalent substances that bring about several consecutive reactions at the peroxide decomposition. Examples of these coagents are di- or triallylic substances, maleimids or reactive acrylic-substances:

- Triallylcyanurate

H_2C=CH—CH_2—O ... N ... O—CH_2—CH=CH_2

(triazine ring with C, N atoms)

O—CH_2—CH=CH_2

- Triallylphosphate

O—CH_2—CH=CH_2

O=P—O—CH_2—CH=CH_2

O—CH_2—CH=CH_2

- Ethyleneglycol-dimethacrylate

H_2C—O—C—C=CH_2 (with O double bond and CH_3)

H_2C—O—C—C=CH_2 (with O double bond and CH_3)

- m-Phenylene-bismaleimide

(two maleimide rings connected by N—CH_2—phenylene—CH_2—N)

- Trimethylolpropane-trimethacrylate

$CH_2$$CH_2$—$O$—$C$—$C$=$CH_2$ (with O double bond and CH_3)

CH-CH_2—O—C—C=CH_2 (with O double bond and CH_3)

CH_2—CH_2—O—C—C=CH_2 (with O double bond and CH_3)

- Many others.

4.3.2 Influences on the efficiency of peroxides

The efficiency of a peroxide – the number of crosslinks per peroxide radical – depends on many factors: the type of polymer, the acidity of the compound – mainly determined by the type of filler – and the type of plasticizer.

Regarding the influence of the polymer, three examples are given below:

High efficiency

In a BR with high content of 1,2-vinyl-groups up to 10 crosslinks per radical are formed. When the radical-function transfers from the peroxide-radical to the 1,2-vinyl group, a relatively stable radical forms, because of mesomery of the free electron. This radical jumps from one to the other vinyl-group, leaving a trace of crosslinks behind. So, there is a snowball effect of crosslinks between the 1,2-vinyl-groups.

Low efficiency

In the disproportionation-reaction two polymer radicals react by transfer of the radical moiety from one chain to the other. This results in a saturated and an unsaturated chain.
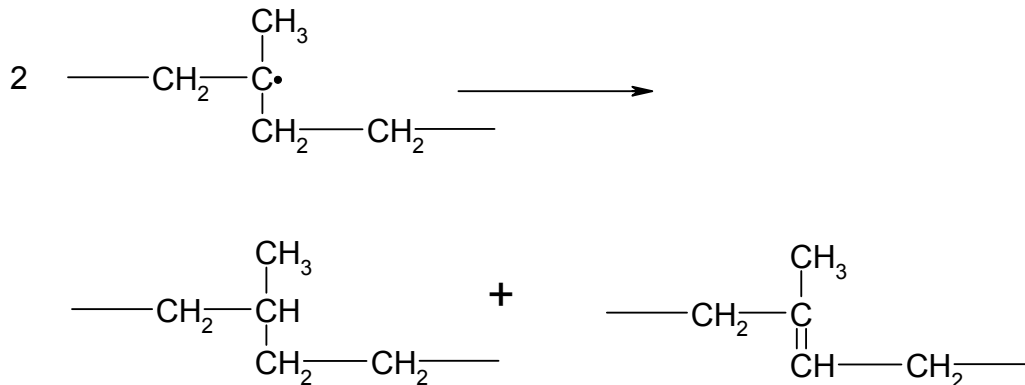

Figure 4-18: Schematic representation of the disproportionation reaction of two polymer- radicals.

In the case of chain-scission, the polymer-radical breaks and one chain with an unsaturated C=C bond at the end is formed, together with a chain having a radical at the end. This reaction can be expected, especially when two tertiary or quaternary carbon atoms in the main chain are separated by only one secondary carbon atom. This is the case in for instance polypropylene, butyl rubber and EPDM. This phenomenon is called β-scission.
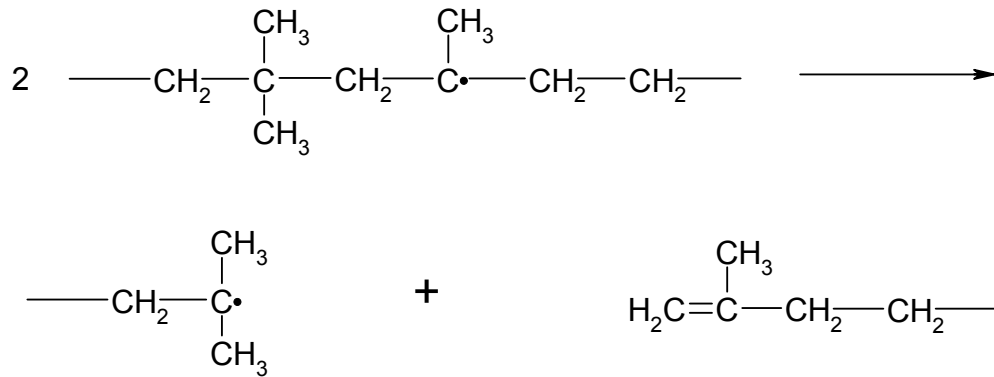
Figure 4-19: Schematic representation of the β-scission reaction.

Chain scission reduces the average molecular weight of the polymer. As a result, the properties of the final vulcanizates decrease. If chain-scission prevails, the rubber polymer degrades instead of crosslinking. This is the case for butyl rubber. Butyl rubber cannot be vulcanized by means of peroxides.

Which reactions take place and to which extent, differs strongly per type of rubber-polymer, and even within one type of rubber-polymer, depending on the composition. An example of this is EPDM. Depending on the propylene content, tertiary carbon atoms separated by only one secondary carbon atom occur more (high propylene) or less (low propylene). Especially the low-propylene EPDM-types show the highest efficiency in peroxide-vulcanization. In general for EPDM, the yield of crosslinks is lower than one crosslink per peroxide-radical.

Influence of filler

The type of filler also has a big influence on the efficiency. Fillers with an acidic surface – silica – cause heterolytic decomposition of the peroxide. This leads to fragments that are unable to initiate crosslinking and thus to a lower efficiency. An example of an acid-catalyzed non-radical decomposition of a peroxide is given below:
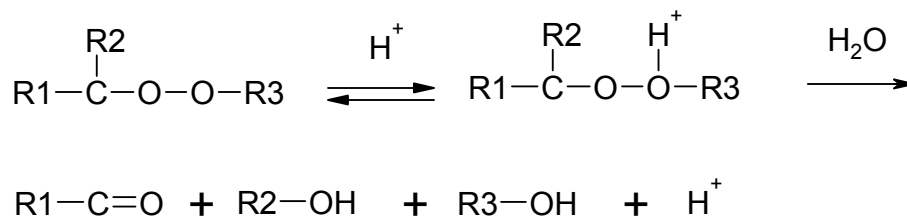

Figure 4-20: Schematic representation of an acid-catalyzed non-radical decomposition of a peroxide.

In neutral or basic environment, this reaction proceeds via the formation of radicals. But even then, not always the first-formed radical will eventually form the crosslink, as can be seen below in the case of dicumylperoxide.
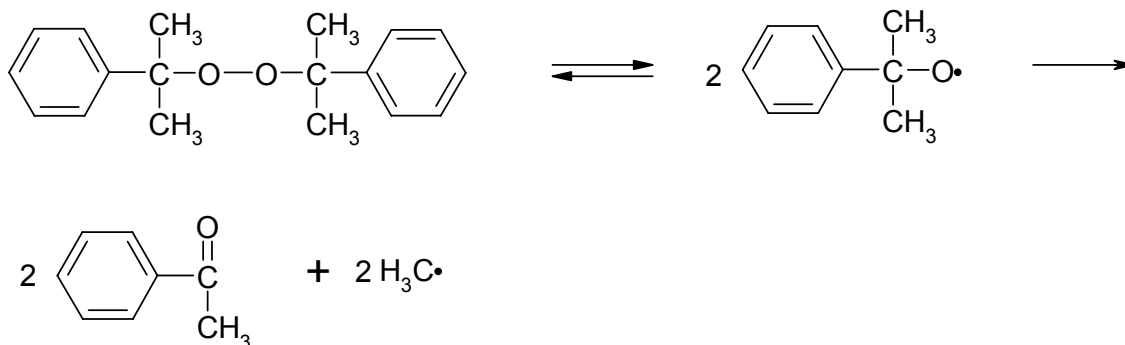

Figure 4-21: Decomposition-reaction for dicumylperoxide.

This reaction scheme shows us that during the decomposition of dicumylperoxide acetophenon is formed as a by-product. This migrates to the surface and it gives the vulcanizates a typical bad odor. Further, acetophenon crystallizes at the surface in small needles, that may cause an allergic reaction on the skin of certain people, if such articles are touched frequently.

Influence of plasticizers

Aromatic moieties in plasticizers have a strong deactivating effect on peroxides. So, use of aromatic oil in combination with peroxides hardly results in crosslinking. Peroxide vulcanization is only possible with paraffinic oil or synthetic plasticizers; see Chapter 3.1.

4.3.3   Properties of peroxide-vulcanizates compared to sulfur

Peroxide-vulcanizates are tougher than sulfur-vulcanizates, leading to lower tensile properties, lower elasticity and worse dynamic properties.

On the other hand, the heat resistance of peroxide-vulcanizates is remarkably better compared to sulfur-vulcanizates. This is due to the earlier-mentioned high dissociation energy of the C-C bond. Also the compression set is in general better for peroxide-vulcanizates than for sulfur-vulcanizates, even compared to SEV and EV-systems. Furthermore, the compression set remains constant over a wider temperature range, while the compression set of sulfur-vulcanizates may increase strongly on increasing temperature. Applications for which peroxide-vulcanizates are used are, for instance, window seals in the builiding industry. Temperatures may vary from –30°C up to 80°C,

and still a proper sealing is required. A constant value for the compression set for this whole temperature range is therefore of utmost importance.
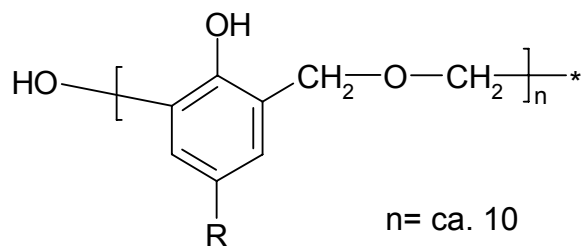
Table 4.5: Example of the influence of temperature on the compression set of a EPDM compound vulcanized with different systems.

Compression set	CV sulfur		EV sulfur	Peroxide
72 hrs @ 23°C	3	4	6	
22 hrs @ 70°C	5	6	6	
22 hrs @ 100°C	22	11	7	

4.4 Other vulcanization systems

With sulfur-vulcanization and peroxide-vulcanization, the greater part of the vulcanization-systems has been covered. However, there are some systems that are worth mentioning, especially because of their application with specialty elastomers:

- ZnO and/or MgO for CR: see Chapter 1.8 and for CIIR and BIIR: see Chapter 1.6;
- Polymethylol-phenol resin:

n= ca. 10

This polymethylol-phenol resin has become known for IIR and to a lesser extent for EPDM-vulcanization. The vulcanization requires quite a lot of resin: 5-12 phr, together with some parts SnCl2.2H2O as a Lewis-acid. The vulcanization proceeds rather slow, but good compression sets are obtained and very good thermal properties. Resin-vulcanization of IIR is especially applied in the manufacturing of bladders for the tire-vulcanization. The bladder is an inflatable inner-tire that pushes the tire against the vulcanization-mould. It has to withstand many vulcanization-cycles.

- Amines and polyamines: for the vulcanization of FKM and ACM.

4.5 Vulcanizate properties as a function of the degree of crosslinking

The term "optimal degree of vulcanization" is used quite often in the rubber industry, but it not always clear what exactly is meant. In most cases, people refer to the time derived from the rheogram to achieve 90% vulcanization. But quite differently, not all mechanical properties are pure monotone functions of the degree of vulcanization under the chosen time-temperature conditions. Some properties show a maximum, others a minimum, some increase slowly and some decrease slowly. In other words: when using the term optimal degree of vulcanization, one should relate this to the specific property that is meant.
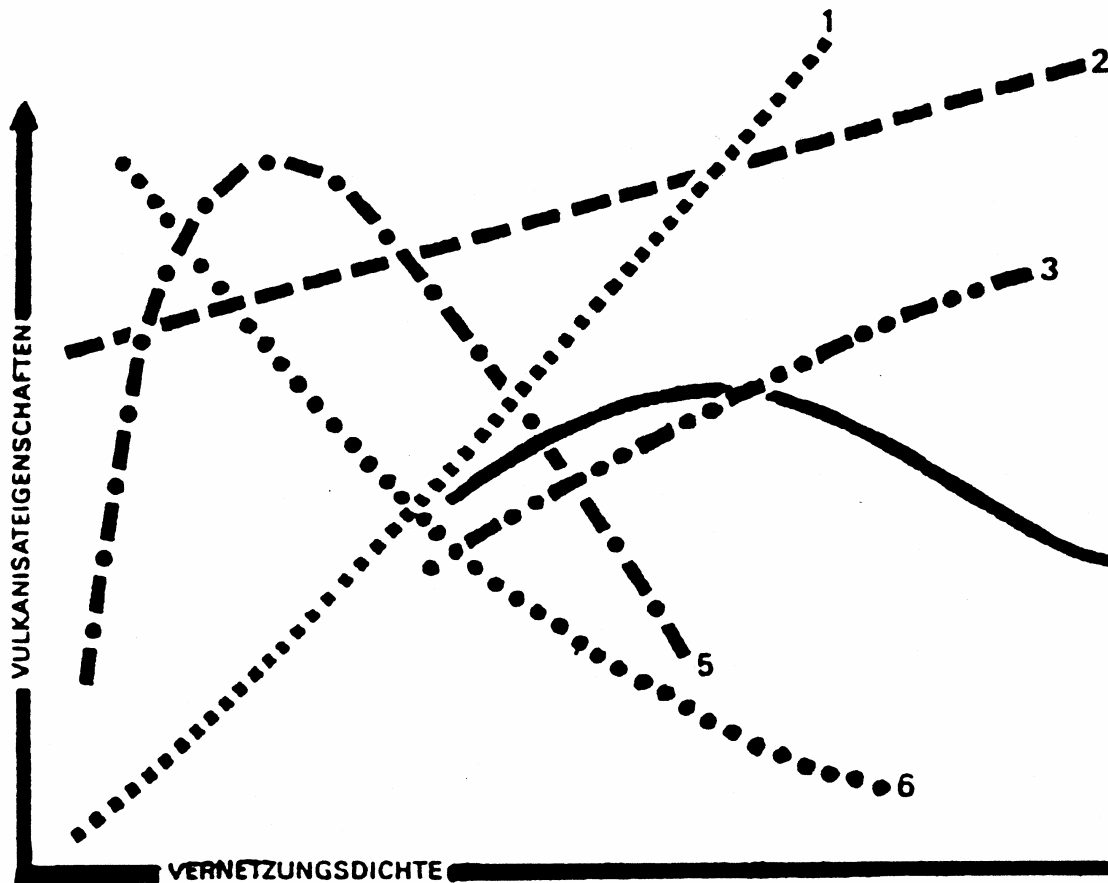

Figure 4-22: Vulcanizate properties as a function of the degree of crosslinking: 1: Static modulus and resistance to dynamic heat build-up; 2: Dynamic modulus at high velocities; 3: Hardness; 4: Tensile strength; 5: Notch-toughness, fatigue-resistance; 6: Hysteresis, compression set and tension set, elongation at break.

Literature

- W.Hofmann, "Rubber Technology Handbook", Hanser Publ.; New York: Oxford University Press (1989);
- J. van Alphen, Rubber Chemicals; Ed. C.M. van Turnhout PRRI-TNO; D. Reidel Publ. Comp., Dordrecht/Boston.

CHAPTER 5
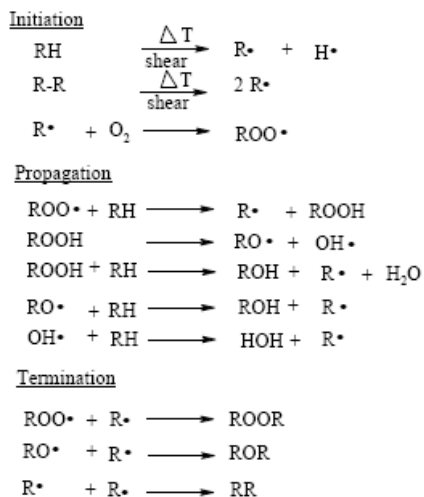# ANTIOXIDANTS, ANTIOZONANTS

5.1 Introduction

Rubber compounds can be degraded by reactions with oxygen, ozone, light, metal ions and heat. Antidegradants protect rubber against aerobic aging (oxygen) and ozone attack. They are of prime importance and play a vital role in rubber products to maintain the properties at service conditions.

Degradation by oxygen and ozone proceeds via different chemical mechanisms and results in different effects on physical properties of rubber:

- Ozone degradation: discoloration, cracking (primarily a surface phenomenon)
- Oxygen degradation: hardening or softening (depending on the base polymer) throughout the rubber article

For example, vulcanizates that are based on natural rubber (NR), polyisoprene rubber (IR) and butyl rubber (IIR) preferably undergo cleavage reactions during the oxidation process; they generally become softer. During progressive aging, a crosslinking mechanism starts to dominate again: completely oxidized NR is usually hard and brittle. On the other hand, vulcanizates obtained from styrene-butadiene-rubber (SBR), nitrile butadiene rubber (NBR), chloroprene rubber (CR), ethylene propylene diene rubber (EPDM), etc. undergo cyclization and crosslinking reactions that lead to hardening of the aged part. When completely oxidized, these vulcanizates are turned into hard and brittle products. Rubbers that do not contain C=C unsaturation, such as acrylic rubber (ACM), chlorinated polyethylene (CM), chlorosulfonated polyethylene (CSM), polychloromethyloxiran (CO), ethylene-ethyl acrylate copolymer (EAM), epichlorohydrin rubber (ECO), ethylene propylene rubber (EPM), ethylenevinylacetate copolymer (EVM), rubbers with fluoro and fluoralkyl or fluoralkoxy substituent groups on the polymer chain (FKM), silicone rubber (Q), and others are much less sensitive to oxidation than diene rubbers.

5.1 Oxidation

Oxidation chemistry

The oxidation of polymers is most commonly depicted in terms of the kinetic scheme as given in Figure 0-1. The key to the process is the initial formation of a free-radical species. At high temperatures and at large shear forces, it is likely that free radical formation takes place by cleavage of carbon-carbon and carbon-hydrogen bonds.

Initiation

$$RH \xrightarrow[shear]{\Delta T} R\bullet + H\bullet$$

$$R\text{-}R \xrightarrow[shear]{\Delta T} 2\,R\bullet$$

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

Propagation

$$ROO\bullet + RH \longrightarrow R\bullet + ROOH$$

$$ROOH \longrightarrow RO\bullet + OH\bullet$$

$$ROOH + RH \longrightarrow ROH + R\bullet + H_2O$$

$$RO\bullet + RH \longrightarrow ROH + R\bullet$$

$$OH\bullet + RH \longrightarrow HOH + R\bullet$$

Termination

$$ROO\bullet + R\bullet \longrightarrow ROOR$$

$$RO\bullet + R\bullet \longrightarrow ROR$$

$$R\bullet + R\bullet \longrightarrow RR$$

RH: rubber hydrocarbon

Figure 0-1: Oxidation mechanism

Oxidation of rubber is accelerated by ultraviolet light. Fillers like zinc oxide, titanium dioxide, whiting and specially carbon black, lower the rate of oxygen absorption with exposure to UV-light. This is attributed to the ability to make the compound opaque, thus limiting the penetration of UV-light. The presence of metal ions such as iron, copper, manganese and cobalt worsen oxidation by increasing the rate of peroxide decomposition. The efficiency of antioxidants to deactivate these rubber poisons depends at least partially on a complex formation (chelation) of the metal ion. In favor of this theory is the fact that simple chelating agents that have no aging protective activity, like ethylene diamine tetraacetic acid (EDTA), act as protectors.

Stabilization mechanism of antioxidants

Complete inhibition of oxidation is rarely obtained in elastomers by addition of antioxidants or stabilizers. What is usually observed is an extended period of retarded oxidation in the presence of the antioxidant. It has been demonstrated that during this period the rate of oxidation decreases with inhibitor concentration until the optimum concentration is reached and then increases again: using the optimal antidegradant concentration is crucial.

Five general modes of oxidation inhibition are commonly recognized:

1. Metal deactivators - Organic compounds capable of forming coordination complexes with metals are known to be useful in inhibiting metal-activated oxidation. These compounds have multiple coordination sites and are capable of forming cyclic structures, which "cage" the pro-oxidant metal ions. EDTA and its various salts are examples of this type of metal chelating compounds.

2. Light absorbers – These chemicals protect from photo-oxidation by absorbing the ultraviolet light energy, which would otherwise initiate oxidation, either by

decomposing a peroxide or by sensitizing the oxidizable material to oxygen attack. The absorbed energy must be disposed of by processes, which do not produce activated sites or free radicals. Fillers which impart opacity to the compound (e.g. carbon black, zinc oxide) tend to stabilize rubbers against UV catalyzed oxidation.

3. Peroxide decomposers – These function by reacting with the initiating peroxides to form nonradical products. Presumably mercaptans, thiophenols, and other organic sulfur compounds function in this way. It has been suggested that zinc dialkyldithiocarbamates function as peroxide decomposers, thus giving rubber
compounds good initial oxidative stability.

4. Free radical chain stoppers – These chemicals interact with chain propagating radicals to form inactive products.

5. Inhibitor regenerators -They react with intermediates or products formed in the chain-stopping reaction so as to regenerate the original inhibitor or form another product capable of functioning as an antioxidant.

Termination of propagating radicals during the oxidative chain reaction is believed to be the dominant mechanism by which amine and phenolic antioxidants operate. The mechanism proposed to account for this behavior is given in Figure 0-2:
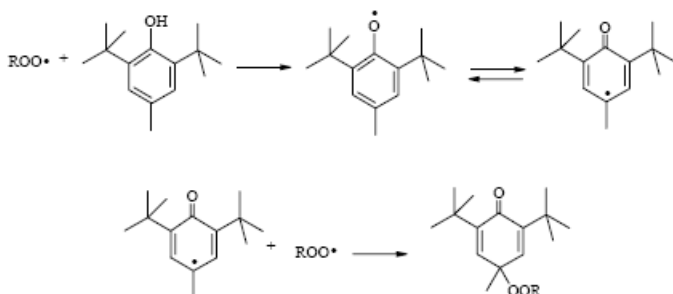

Figure 0-2: Primary stabilization via radical scavenging by hindered phenols

The peroxy radicals abstract a labile hydrogen from primary stabilizers like hindered phenols or secondary amines, resulting in less active hydroperoxides and preventing hydrogen abstraction from the polymer chain. The resulting antioxidant radical is more stable than the initial peroxy radical and terminates by reaction with another radical in the system. It has also been proposed that aromatic compounds such as phenols and aromatic amines can form π-electron complexes with peroxy radicals, which terminate to form stable products. It appears that direct hydrogen absorption, π -electron complex formation or both, describe the antioxidant action of most amine and phenolic antioxidants.
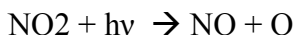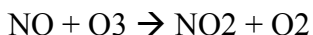
5.2 Ozone attack

Ozone Chemistry

Ozone in the atmosphere is formed by the chemical reaction of atomic and molecular oxygen:

$O_2 + O \rightarrow O_3$

Photolysis of nitrogen dioxide is the major source of oxygen atoms:

$NO_2 + h\nu \rightarrow NO + O$

The nitric oxide produced in this reaction reacts with ozone to regenerate oxygen and nitrogen dioxide:

$NO + O_3 \rightarrow NO_2 + O_2$

An equilibrium is established which gives rise to a so-called photostationary state relation, which depends on the relative rates of the above reactions:

$[O_3] = j\,[NO_2] / k\,[NO]$

j = reaction rate of the formation of O_3
k = reaction rate of the decomposition of O_3

Ozone attack on elastomers

Ozone cracking is an electrophilic reaction and starts with the attack of ozone at a location where the electron density is high. In this respect unsaturated organic compounds are highly reactive with ozone. The reaction of ozone is a bimolecular reaction where one molecule of ozone reacts with one double bond of the rubber, as can be seen in Figure 0-3:

The first step is a direct 1,3-dipolar addition of the ozone to the double bond to form a primary ozonide (I), or molozinide, which is only detectable at very low temperatures. At room temperature, these ozonides cleave as soon as they are formed to give an aldehyde or ketone and a zwitterion (carbonyl oxide). Cleavage occurs in the direction, which favors the formation of the most stable zwitterion (II). Thus, electron donating groups, such as the methyl group in natural rubber, are predominately attached to the zwitterion, while electron-withdrawing groups, such as the chlorine in chloroprene rubber, are found on the aldehyde.
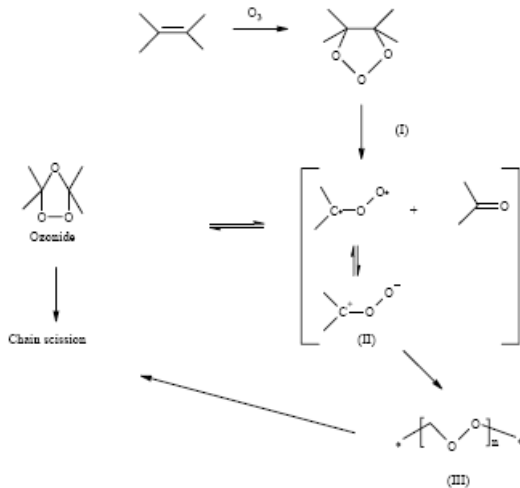
Figure 0-3: Reaction of ozone with double bonds of a polymer

Normally, in solution, the aldehyde and zwitterion fragments recombine to form an ozonide, but higher molecular weight polymeric peroxides (III) can also be formed by combination of zwitterions. The presence of water increases the rate of chain cleavage, which is probably related to the formation of hydroperoxides. Rubbers that contain only pendant double bonds such as EPDM, do not cleave since the double bond is not in the polymer backbone.

When rubber chains are cleaved, they retract in the direction of the stress under the formation of the characteristic ozone cracks. Unstretched rubber reacts with ozone until all of the surface double bonds are consumed, and then the reaction stops. The reaction is fast in the beginning, the rate progressively decreases while the available unsaturation is depleted and ultimately the reaction stops. During this reaction, a gray film, or frosting, forms on the surface of the rubber, but no cracks are noticed. Cracks are only observed when the rubber is stretched above a critical elongation. Two factors determine cracking under static conditions: the critical stress necessary for cracks to form and the rate of crack growth.

The rate of crack growth depends on the polymer and is directly proportional to the ozone concentration, but independent of the applied stress as long as it exceeds the critical value. It depends on the mobility of the underlying chain segments of rubber, which is necessary to untangle and position double bonds for further attack by ozone. Consequently, anything that will increase the mobility of the rubber chains will increase the rate of crack growth. For example, the slow crack growth rate in IIR becomes equal to that of NR and SBR when sufficient plasticizer is added or when the temperature is raised.

Stabilization mechanism of antiozonants

Rubbers can be protected against ozone by use of chemical antiozonants and via several physical methods. The chemical antiozonants protect rubber under both static and dynamic conditions, whereas the physical methods are more related towards protection under static conditions.

Protection against ozone under static conditions - There are several physical methods that can be used to protect rubber against ozone: wrapping, covering, or coating the rubber surface. This can be accomplished by adding waxes to the rubber and/or adding an ozone resistant polymer that increases the critical stress. Waxes are the most important in this respect. Two types of waxes are used to protect rubber against ozone: paraffinic and microcrystalline waxes.

- Paraffinic waxes are predominantly straight chain hydrocarbons of relatively low molecular weight of about 350 to 420. They are highly crystalline due to their linear structure and form large crystals having a melting range from 38 to 74°C.

- Microcrystalline waxes are obtained from higher molecular petroleum residuals and have higher molecular weights than the paraffinic waxes, ranging from 490 to 800.

In contrast to the paraffinic waxes, microcrystalline waxes are predominantly branched, and therefore form smaller, more irregular crystals that melt from about 57 to 100°C. Waxes exert their protection by blooming to the surface to form a film of hydrocarbons that is impermeable to ozone. Protection is only obtained when the film is thick enough to provide a barrier to the ozone. Thus the thicker the film, the better the protection. The obtained thickness of the bloom layer depends both on the solubility and the diffusion rate of the wax, which depend on the temperature. Bloom occurs whenever the solubility of the wax in the rubber is exceeded. Therefore, at temperatures lower than 40°C, the smaller and more soluble paraffinic waxes provide the best protection. Lowering the temperature reduces the solubility of the paraffinic waxes and increases the thickness of their bloom. Yet, their small size allows them to migrate rapidly to the surface, in spite of lower temperatures. Conversely, as the temperature increases, the high solubility of the paraffinic waxes becomes a disadvantage. They become too soluble in the rubber and do not form a thick enough protective bloom. Microcrystalline waxes perform better at higher temperatures, since higher temperatures increase their rate of migration to the surface and this allows more wax to be incorporated into the rubber. Therefore, blends of paraffinic and microcrystalline waxes are commonly used to guarantee protection over the widest possible temperature range. Combinations of waxes and chemical antiozonants show synergistic improvement in ozone resistance. Presence of the antiozonant results in a thicker bloom layer.

Another way to protect rubber against ozone is to add an ozone-resistant polymer (i.e. EPM, EPDM, halobutyl, polyethylene, polyvinyl acetate, etc.) to the rubber. Microscopic studies of these mixtures show that the added polymer exists as a separate, dispersed phase. Consequently, as a crack grows in the rubber, it encounters a domain

of the added polymer, which reduces the stress at the crack tip. This raises the critical stress required for cracking to occur, and crack growth ceases. Under dynamic conditions, where almost no critical stress is required, these polymer blends do not completely prevent cracking. In this case they function by reducing the segmental mobility of the rubber chains and this slows the rate of crack growth. This method is effective when the polymer is added at a level between 20 and 50%. Higher levels do not result in further improvement of the ozone resistance. At lower levels, propagating cracks circumvent the stress-relieving domains or will not reduce segmental mobility sufficiently. This method of protecting rubber against ozone is used on a limited basis, since vulcanizates of these blended rubbers frequently exhibit poorer properties. However, it is the only effective nondiscoloring method of protecting rubber under dynamic conditions.

Protection against ozone under dynamic conditions - Under dynamic conditions, i.e. under cyclic deformations (stretching and compression) the physical methods to protect against ozone are no longer valid. Chemical antiozonants have been developed to protect rubber against ozone under such dynamic conditions. Several mechanisms have been proposed to explain how chemical antiozonants protect rubber. The scavenging mechanism, the protective film mechanism or a combination of both are nowadays the most accepted mechanisms.
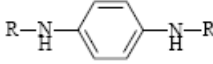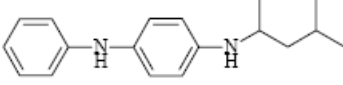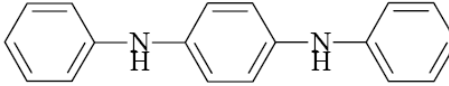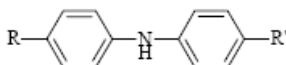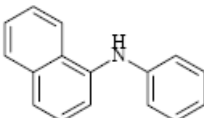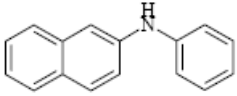
The scavenging mechanism states that antiozonants function by migrating towards the surface of the rubber and, due to their exceptional reactivity towards ozone, scavenge the ozone before it can react with the rubber. The scavenging mechanism is based on the facts that all antiozonants react much more rapidly with ozone than do the double bonds of the rubber molecules. A shortcoming of this mechanism is the rate of diffusion of antiozonants to the rubber surface, which is too slow to scavenge all the available ozone.

The protective film mechanism states that the rapid reaction of ozone with the antiozonant produces a film on the surface of the rubber, which prevents attack on the rubber, like waxes are doing.
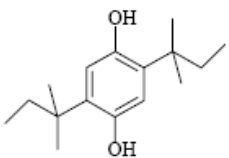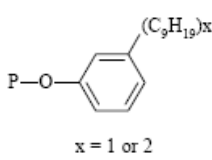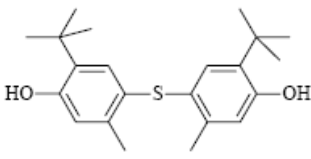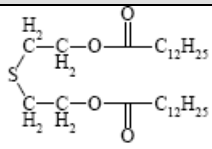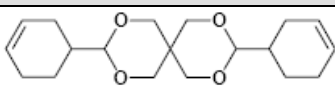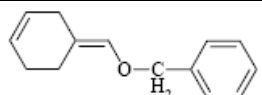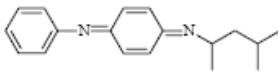
Currently, the most accepted mechanism of antiozonant action is a combination of the scavenging and the protective film formation.

The most effective antiozonants are substituted paraphenylene diamines, PPD's. Their mechanism of protection against ozone is based on the 'scavenger-protective film' mechanism. The reaction of ozone with the antiozonant is much faster than the reaction with the carbon-carbon double bonds of the rubber on the rubber surface. The rubber is protected from the ozone attack till the surface antiozonant is depleted. As the antiozonant is continuously consumed through its reaction with ozone at the rubber surface, diffusion of the antiozonant from the inner parts to the surface replenishes the surface concentration to provide the continuous protection against ozone. A thin flexible film developed from the antiozonant/ozone reaction products on the rubber surface also offers protection.

5.3   Classes of antidegradants

		Staining	Oxygen protection	Ozone protection	Fatigue protection	Remarks
	Paraphenylene diamines	✓	✓	✓	✓	
General formula	R—N̲H⟨⟩N̲H—R'					
N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)		✓	✓	✓	✓	Most effective antidegrandants for all general purpose rubbers
N,N'-Diphenyl-p-phenylenediamine (DPPD)		✓	✓	✓	✓	
N-Isopropyl-N'-phenyl-p-phenylenediamine (IPPD) N-N'-Bis-(1,4-dimethylpentyl)-p-phenylenediamine (77PD) N,N'Bis-(1-ethyl-3-methylpentyl)-p-phenylenediamine (DOPD) N,N'-Ditolyl-p-phenylenediamine (DTPD) N,N'-Di-ß-naphthyl-p-phenylenediamine (DNPD)		✓	✓	✓	✓	
	Diphenylamines	✓	✓	---	✓	
General formula	R⟨⟩N̲H⟨⟩R'					For all general purpose rubbers. Good heat protection, esp. in CR
Octylated diphenylamine (ODPA) Styrenated diphenylamine (SDPA) Acetone/diphenylamine condensation product (ADPA) 4,4'-Bis(a,a-dimethylbenzyl) diphenylamine 4,4-Dicumyl-diphenylamine		✓	✓	---	✓	
	Naphtylamines	✓	✓	---	✓	
Phenyl-a-naphthylamine (PAN)		✓	✓	---	✓	Higly effective antioxidants, but toxicological risk
Phenyl-ß-naphthylamine (PBN)		✓	✓	---	✓	

	Dihydroquinolines	✓	✓	---	---	
6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ETMQ)		✓	✓	---	---	
2,2,4-Trimethyl-1,2-dihydroquinoline, polymerized (TMQ)		✓	✓	---	---	
	Monophenols	---	✓	✓	✓	
Styrenated phenol (SPH)		---	✓	✓	✓	
2,6-Di-t-butyl hydroxy toluene (BHT)		---	✓	---	---	Volatile
2,6-Di-t-butyl-4-nonylphenol 3-(3,5-Di-t-butyl-4-hydroxyphenyl) propionic methyl ester 2,6-Di-t-butyl-4-ethyl phenol Octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate 4-Nonylphenol		---	---		---	
	Bisphenols	---	✓	---	---	
2,2'-Methylene-bis-(4-methyl-6-tert.butylphenol) (BPH)		---	✓	---	---	
2,2'-Methylene-bis-(4-methyl-6-cyclohexylphenol) 2,2'-Isobutylidene-bis-(4-methyl-6-tert.butylphenol) 2,2'-Dicyclopentyl-bis-(4-methyl-6-tert.butyl-phenol) Triethyleneglycol-bis(3-t-butyl-4-hydroxy-5-methylphenyl)-propionate		---	---		---	
	Benzimiazoles	---	✓	---	---	
2-Mercaptobenzimidazole (MBI)		---	✓	---	---	Synergistic effect with other antioxidants
ZMBI (Zinc-2-mercaptoimidazole MMBI (Methyl-2-mercaptobenzimidazole ZMMBI (Zinc-2-methylmercaptoimidazole ZMMBI)		---	✓	---	---	
	Hydroquinones	---	✓	---	---	

Name	Structure					Notes
2,5-Di(tert-amyl)hydroquinone (TAHQ)		---	✓	---	---	Stabilizer for uncured rubber
2,5-Di-t-butyl hydroquinone (TBHQ) Hydroquinone (HQ) p-Methoxy-phenol Toluhydroquinone (THQ)		---	✓	---	---	
Phosphites		---	✓	---	---	
Tris(mixed mono- and di-nonylphenyl)phosphate (TNPP)		---	✓	---	---	Only effective in uncured compounds (destroyed during curing)
Diphenyl isodecyl phosphite (DIDP) Diphenyl isooctyl phosphite (DIOP) Distearyl pentaerythritol diphosphite (DPDP)		---	✓	---	---	
Thio-bisphenols		---	✓	---	---	
4,4'-Thiobis-6-(t-butyl-m-cresol) (TBMC)		---	✓	---	---	Slight activation of sulfur curing
2,4-Bis[(octylthio)methyl]-o-cresol		---	✓	---	---	
Thioesters		---	✓	---	---	
Dilauryl thiodipropionate (DLTDP)		---	✓	---	---	
Dimystril thiodipropionate Distearyl dithiodipropionate Distearyl thiopropionate		---	✓	---	---	
Waxes		---	---	✓	---	
Unsaturated acetals		---	---	✓	---	
Bis-(1,2,3,6-tetrahydrobenzaldehyde)-pentaerythrityl acetal) (AFS)		---	---	✓	---	Mainly for EPDM and halobutyl
4-Benzyloxymethylene) cyclohexene (AFD)		---	✓	---	---	
Polymer bound anti-oxidants		---	✓	---	---	
Quinone diimines (QDI)		---	✓	---	---	20-60% of the anti-oxidant is bound to a polymer

Literature

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